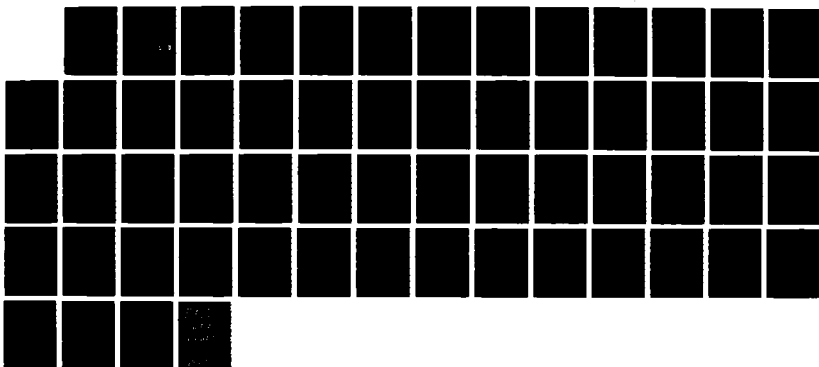


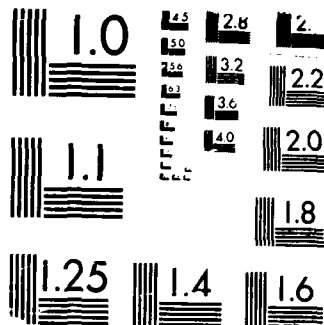
AD-A194 320 NITROLYSIS OF THE CN SINGLE BOND AND RELATED CHEMISTRY 1/1
OF NITRO AND NITROSO GROUPS(U) NEW ORLEANS UNIV LA
J H BOYER MAR 88 N00014-85-K-0096

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Azabicyclononanes. Nitrile oxides. Bicyclo HMX. Nitronates. Azo compounds. Nitrotetraazapentalenes. Triazoles. Nitrocyanamide. Nitrobimanes Furoxans. Isocyanates. Nitramines Nitrosamines		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number)		
A. Pentaazabicyclononanes were discovered. B. Trityl chloride and silver phenylcyanomethane nitronate gave trityl phenylcyanomethane nitronate, an unstable ester that rearranged and fragmented to a 1-triphenylmethoxy-4,5-diphenyl-1,2,3-triazole, carbon dioxide, α, α' -bis(triphenylmethaneazo)stilbene, benzonitrile-N-oxide, and trityl isocyanate.		

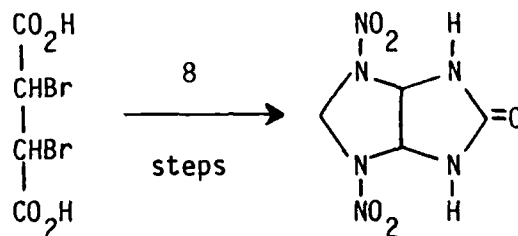
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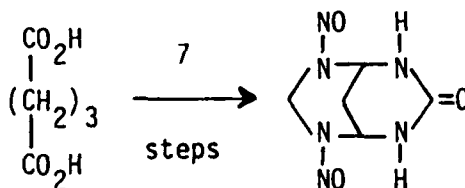
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20. Abstract, continued:

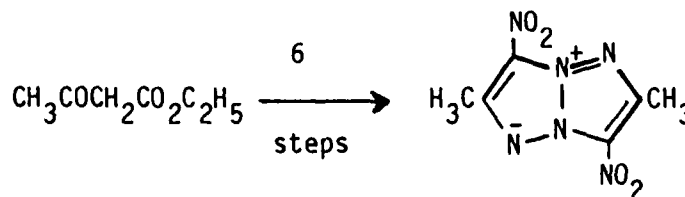
- C. Alkyl and aralkyl halides were converted to isocyanates (63% - 89%) by treatment with the silver salt of nitrocyanamide. This new reaction offers the first direct conversion of an organic halide to an isocyanate that is general, efficient, and facile.
- D. Olefins, aromatic compounds, amines, sulfides, and various anions abstracted both bromo substituents in nitrodibromoacetonitrile (NDBA) and in dinitrodibromomethane. Nitrocyanocarbene from NDBA was proposed.
- E. Photolysis of α -nitrohydrazones (from N,N-disubstituted hydrazines) gave nitrosamines. This afforded the first method for the oxidation of hydrazines (R_2NNH_2) to nitrosamines (R_2NNO).
- F. meso-Dibromosuccinic acid was converted in eight steps to the bicyclic dinitraminourea shown:



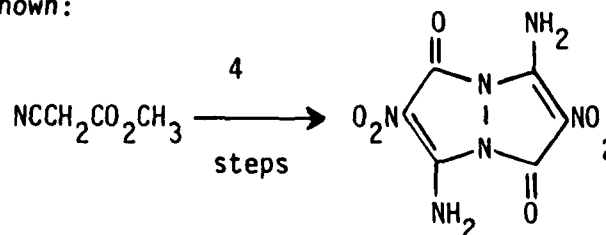
Glutaric acid in seven steps was converted to the bicyclic dinitrosamino-urea shown:



- G. Ethyl acetoacetate was converted in six steps to the known dinitrodimethyltetraazapentalene shown:



- H. Methyl cyanoacetate was converted in four steps to the known dinitrodiminobimane shown:



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A. PENTAAZABICYCLONONANES

HETEROCYCLES. Vol 26 No 1, 1987

Joseph H. Boyer* and Govindarajulu Kumar

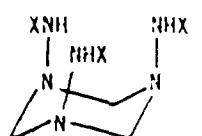
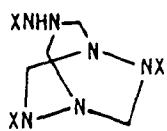
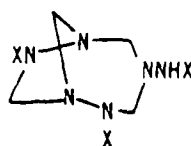
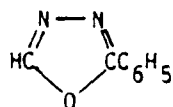
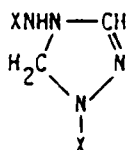
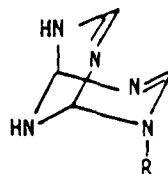
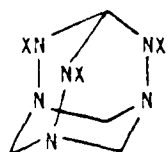
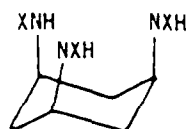
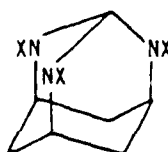
Department of Chemistry, University of New Orleans, New Orleans, LA 70148, U.S.A.

Abstract - The synthesis of 3-benzamido-6,8-dibenzoyl-1,3,5,6,8-pentaazabicyclo[3.2.2]-nonane 2 and 2,7-dibenzoyl-4-benzamido-1,2,4,6,7-pentaazabicyclo[4.2.1]nonane 3 provides the first examples of pentaazabicyclononanes.

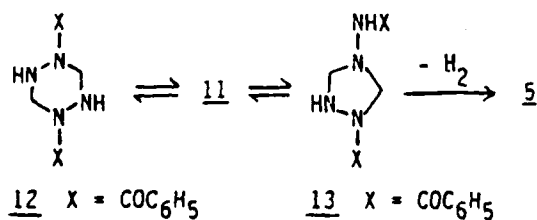
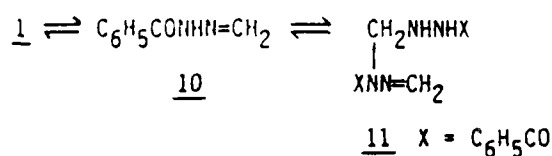
Treatment of 1,3,5-tribenzamidohexahydro-1,3,5-triazine 1 as the monohydrate^{1,2} with ethyl orthoformate and a few drops of concentrated sulfuric acid in toluene at 110°C for 0.5 h gave 3-benzamido-6,8-dibenzoyl-1,3,5,6,8-pentaazabicyclo[3.2.2]nonane 2. When sulfuric acid was not present in the mixture a different isomerization of the heterocycle 1 gave 2,7-dibenzoyl-4-benzamido-1,2,4,6,7-pentaazabicyclo[4.2.1]nonane 3, 2-phenyl-1,3,4-oxadiazole 4,³ and 1-benzoyl-4-benzamido- Δ^2 -1,2,4-triazoline 5. Structures 1-3 and 5, were determined by x-ray crystallographic analyses.² Compounds 2 and 3 introduced 1,3,5,6,8-pentaazabicyclo[3.2.2]nonane and 1,2,4,6,7-pentaazabicyclo[4.2.1]nonane as parent molecules of new ring systems. Except for compounds 2, 3, and examples claimed in a patent to be 2,4,6,8,9-pentaazabicyclo[3.3.1]nonadienes 6⁴ pentaazabicyclononanes remain unknown.

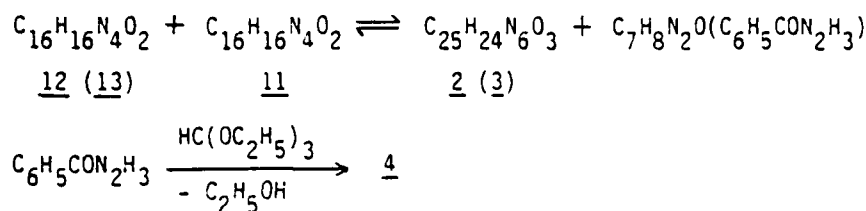
An anticipated interaction between the hexahydrotriazine 1 and ethyl orthoformate to give 2,8,9-tribenzoyl-2,3,5,7,8,9-hexaazatricyclo[3.3.1.1^{3,7}]decane 7 was patterned after a similar conversion of *cis-cis*-1,3,5-tris-benzylaminocyclohexane 8 to 2,4,10-tribenzyl-2,4,10-triazaadamantane 9.⁵ Formation of the hexaazatricyclodecane 7 was not detected.

When ethyl orthoformate was not included in the reaction mixture, the hexahydrotriazine 1 in toluene containing a catalytic amount of concentrated sulfuric acid, was recovered and gave the pentaazabicyclo[3.2.2]nonane 2 in a trace amount. Longer heating gave intractable mixtures. Similar treatment in the absence of both ethyl orthoformate and concentrated sulfuric acid had negligible effect on the hexahydrotriazine; again prolonged heating brought about degradation and the formation of many products.

1 X = C₆H₅CO2 X = C₆H₅CO3 X = C₆H₅CO4 X = C₆H₅CO5 X = C₆H₅CO67 X = C₆H₅CO8 X = CH₂C₆H₅9 X = CH₂C₆H₅

A rationale for the formation of products 2 - 5 depended on the presence of the hydrazone 10 derived from the hexahydrotriazine 1 by depolymerization.^{6,7} The hydrazone 10 afforded 1,4-dibenzoyl-hexahydro-5-tetrazine 12 and 1-benzoyl-4-benzamidotetrahydro-1,2,4-triazole 13 by ring-closures from the dimer 11.⁸ A reaction between the reduced tetrazine 12 and the dimer 11 then afforded the pentaazabicyclo[3.2.2]nonane 2 with the formal ejection of benzhydrazide. From the isomeric dimer 13 a reaction with the dimer 11 afforded the pentaazabicyclo[4.2.1]nonane 3. A critical role for ethyl orthoformate, beyond the known reaction with benzhydrazide to form the oxadiazole 4³ which thereby favorably shifted the equilibrium 1 $\rightleftharpoons$ 2 (3), has not been ascertained. Dehydrogenation of the triazolidine 13 to the triazoline 5 was assumed.





EXPERIMENTAL

Instruments included Pye-Unicam SP-200 IR, Varian A-60 and T-60 NMR Spectrometers. Elemental analyses were provided by Micro-Tech Laboratories, Inc., Skokie, Illinois.

3-Benzamido-6,8-dibenzoyl-1,3,5,6,8-pentaazabicyclo[3.2.2]nonane 2. To a suspension of the monohydrate of 1,3,5-trisbenzamido-hexahydrotriazine 1^{1,9} (0.9 g, 0.002 mol) in toluene (25 ml) triethylorthoformate (0.30 g, 0.002 mol) and a drop of concentrated sulfuric acid were added. The mixture was heated at 110°C for 30 min. Toluene was removed and the residue was separated chromatographically (silica gel, chloroform) to give a colorless solid (0.31 g, 34%), mp 238-240°C (decomp.) after recrystallization from toluene; ir (KBr): 3200-3500 (broad, NH) 1620-1660 cm⁻¹ (C=O); nmr (CDCl₃): δ 4.5 (broad s, 4H, N-CH₂-N) 5.0 (broad s, 4H, N-CH₂-N), 7.2-7.8 (m, 15H, aromatic) and 8.8 (broad s, 1H, NH); anal. calcd. for C₂₅H₂₄N₆O₃: C, 65.79; H, 5.26; N, 18.42; found: C, 65.70; H, 5.29; N, 18.26.

2,7 Dibenzoyl-4-benzamido-1,2,4,6,7-pentaazabicyclo[4.2.1]nonane 3. A suspension of 1,3,5-trisbenzamido-hexahydrotriazine 1^{1,9} (0.9 g, 0.002 mol) in toluene (25 ml) was mixed with triethylorthoformate (0.30 g, 0.002 mol) and heated at 110°C for 30 min. Toluene was removed and the residue was separated chromatographically (silica gel, chloroform) to give 2-phenyl-1,3,4-oxadiazole 4 as a colorless liquid (0.075 g, 8%); ir (neat): 3110, 1605, 1550, 1480, 1100, 1060, 700, and 680 cm⁻¹; nmr (CDCl₃): δ 8.50 (s, 1H, H-5), 7.33-7.76 (m, 3H, phenyl), 7.83-8.26 (m, 2H, phenyl).¹⁰ Further elution gave the bicyclononane 3 (0.26 g, 28%) as a colorless solid, mp 217-219°C after recrystallization from toluene; ir (KBr): 3250 (NH) and 1650 cm⁻¹ (CO); nmr (CDCl₃): δ 3.6-5.5 (m, 8H, CH₂), 7.3-7.8 (m, 15H, aromatic) 9.2 (s, 1H, NH); anal. calcd. for C₂₅H₂₄N₆O₃: C, 65.79; H, 5.26; N, 18.42; found: C, 65.74; H, 5.50; N, 18.43. The recrystallization of product 3 for x-ray crystallographic analysis also gave a few crystals of the triazoline 5, a structure confirmed by x-ray crystallographic analysis but not characterized further.

ACKNOWLEDGMENT

Financial support was received from ONR.

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2. We are indebted to R. Gilardi, C. George, and J. L. Flippen-Anderson of the Naval Research

Laboratory, Washington, D. C., for the x-ray analyses of compounds 1 (the three benzamido groups are all on the same side of the hexahydrotriazine ring), 2, 3, and 5. The data will be published elsewhere.

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4. a. Neth. Appl. 6,500,521; Chem. Abstr., 1966, 64, 2116. b. J. C. Hinshaw, Report 1983, Order No. AD-A128309, Avail. NTIS; from Gov. Rep. Announce. Index (U.S.), 1983, 83, 4502; Chem. Abstr. 1984, 100, 6470h.
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8. S. R. Johns, J. A. Lamberton, and E. R. Nelson, Austr. J. Chem., 1973, 26, 1297; 1971, 24, 1859. Reversibly formed dimers 12, 13 (X = Ar) of formaldehyde arylhydrazones were isolated as derivatives from further condensation with formaldehyde.
9. The monohydrate $C_{24}H_{24}N_6O_3 \cdot H_2O$, mp 160-163°C (dec) gave satisfactory elemental analysis;¹ we obtained values for an anhydrous analytic sample, mp 160-163°C (dec): calcd for $C_{24}H_{24}N_6O_3$: C, 64.85; H, 5.44; N, 18.91; found: C, 64.43; H, 5.51; N, 19.00.
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Received, 25th August, 1986

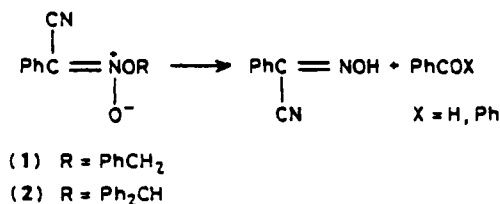
B. Triphenylmethyl Phenylcyanomethylenenitronate: Formation and Thermolysis

J. CHEM. SOC. PERKIN TRANS. I 1987

Joseph H. Boyer*, Thankiavelu Manimaran, and Vayalakkavoor T. Ramakrishnan
Chemistry Department, University of New Orleans, New Orleans, LA 70148

The previously reported formation of carbon dioxide, α,α' -bis(trityl)stilbene (4), benzonitrile *N*-oxide (5), trityl isocyanate (6), and $C_{33}H_{25}N_3O$ (11) from a mixture of trityl chloride and silver phenylcyanomethylenenitronate in toluene is now attributed to the initial formation at -20°C of trityl phenylcyanomethylenenitronate (3) and its dissociations at 5°C . The ester (3) was characterized by conversion into bromonitrophenylacetonitrile (7) by treatment with bromine, to *p*-nitrobenzoyl cyanide (8) by treatment with dinitrogen tetroxide, to trityl alcohol by hydrolysis, and to a mixture of trityl alcohol and trityl peroxide by exposure to the atmosphere. The bisazostilbene (4) (18%) and $C_{33}H_{25}N_3O$, identified by X-ray crystallographic analysis to be 4,5-diphenyl-1-triphenylmethoxy-1,2,3-triazole (11) (24%), were obtained from the nitronate ester (3) in toluene at 5°C ; the nitrile oxide (5) and the isocyanate (6) were obtained in low yields from the ester (3) in dimethyl sulphoxide at 25°C . Hydrolysis converted the triazole (11) into 1-hydroxy-4,5-diphenyl-1,2,3-triazole (12) and trityl alcohol. Silver *p*-bromophenylcyanomethylenenitronate and trityl chloride afforded α,α' -bis(tritylazo)-*p,p'*-dibromostilbene and its thermolysis product, *p,p'*-dibromodiphenylacetylene. Fragmentation of the ester (3) in the presence of added phenyl isocyanate gave the bisazo compound (4) and 3,4-diphenyl-1,2,4-oxadiazol-5-one (18). A similar mixture stored at -20°C gave the triazole (11) and the oxadiazolone (18). Aroyl nitrile oxides as well as phenyl isocyanate suppressed the formation of the red bisazostilbene (4). The intermediacy of the *N*-trityl imine (14) of 4*H*-3-phenyl-1,2-oxazet-4-one 2-oxide in the thermolysis of the nitronate (3) was discussed.

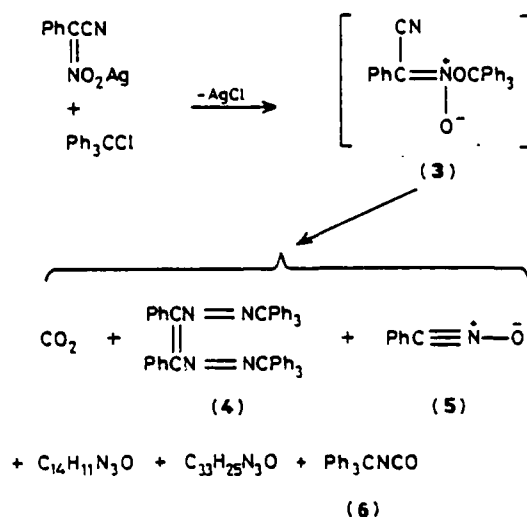
Phenylcyanomethylene nitronates and esters of other nitronic acids tend to be thermally unstable. Methyl phenylcyanomethylenenitronate had a half-life of several hours (25°C).¹ Neither the benzyl (1) nor the benzhydryl ester (2) was isolated and each fragmented to the oxime of benzoyl cyanide and an appropriate carbonyl derivative (Scheme 1).² The formation of



Scheme 1.

trityl phenylcyanomethylenenitronate (3) from a mixture of trityl chloride and silver phenylcyanomethylenenitronate in toluene was not previously detected.³⁻⁵ (An α -oxo triphenylmethylenenitronate was obtained from trityl chloride and the sodium salt of α -nitrocamphor.⁶) Instead, products whose formations were not explained included carbon dioxide, α,α' -bis(tritylazo)stilbene (4), benzonitrile *N*-oxide (5), trityl isocyanate (6), and two unidentified compounds $C_{33}H_{25}N_3O$ and $C_{14}H_{11}N_3O$ (Scheme 2).

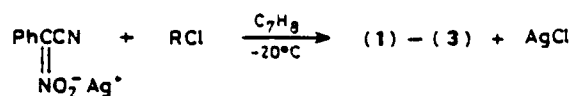
A re-investigation of this reaction was undertaken to determine structures for the unidentified products and to explain the formation of all products.⁷ The formation of carbon dioxide was unique and of particular interest since the reaction, carried out in the absence of air, required the facile transfer of both oxygen atoms in the nitronate group to a carbon atom. This phenomenon is pertinent to detonations that produce carbon dioxide from organic nitro compounds.



Scheme 2.

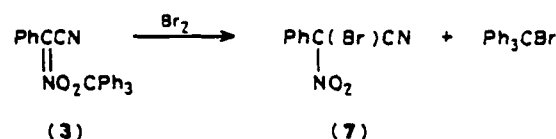
Results and Discussion

The formation of benzyl (1), benzhydryl (2), and trityl phenylcyanomethylenenitronate (3) by *O*-alkylation of the corresponding silver nitronate in toluene at -20°C (Scheme 3), was established by similarities throughout the i.r. spectra (-20°C) for the three esters. In particular, the intense azomethine absorption at 1590 (1), 1580 (2), and 1585 cm^{-1} (3)^{1b} and the absence of dual absorption near 1550 and 1350 cm^{-1} , characteristic of the nitro group,^{1c} eliminated the presence of significant amounts of the isomeric products from *C*- and *N*-tritylation.



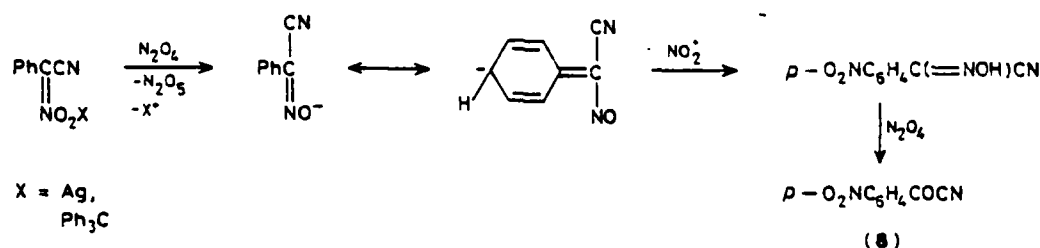
Scheme 3.

Just as bromination of sodium phenylcyanomethylenenitronate gave bromonitrophenylacetonitrile (7),^{8a,b} the trityl nitronate (3) gave bromonitrophenylacetonitrile (7) (53%) and trityl bromide (69%) on treatment with bromine (Scheme 4).



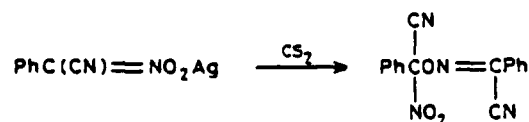
Scheme 4.

Conversion into *p*-nitrobenzoyl cyanide (8) (23%) was brought about by treatment with dinitrogen tetroxide (Scheme 5). These reactions were compatible with the ester structure (3) but not with the isomeric *C*- and/or *N*-trityl structures. Silver phenylcyanomethylenenitronate and dinitrogen tetroxide also gave the cyanide (8) (43%) (Scheme 5). It was proposed that both the nitronate salt and the nitronate ester (3) were converted initially into the oxime anion of benzoyl cyanide as dinitrogen tetroxide was oxidized to dinitrogen pentaoxide. A facile nitration of the intermediate oxime anion followed by an independently established reaction between the oxime of *p*-nitrobenzoyl cyanide and dinitrogen tetroxide completed the conversion into the cyanide (8) (Scheme 5).⁹



Scheme 5.

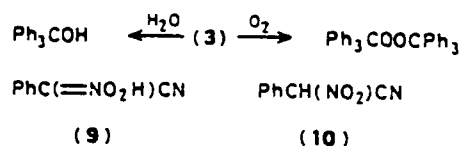
The reaction (Scheme 5) is reminiscent of the conversion of silver phenylcyanomethylenenitronate in carbon disulphide at 40 °C into the *O*-nitrocyano benzyl derivative of the oxime of benzoyl cyanide (Scheme 6), for which radical intermediates were proposed.¹⁰



Scheme 6.

Hydrolysis of the ester (3) at -20 °C was partially successful (Scheme 7). Water containing a few drops of hydrochloric acid converted the ester (3) into trityl alcohol (48%) but neither

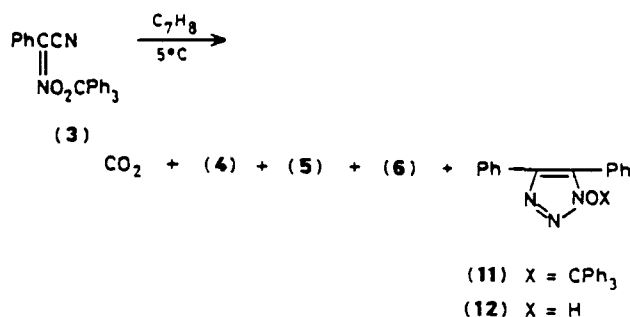
phenylcyanomethylenenitronic acid (9) nor nitro(phenyl)acetonitrile (10) were detected. (Hydrolysis of nitronate esters are competitive with the Nef reaction, the formation of hydroxamic acids, and auto-oxidation-reduction.¹¹) Exposure to moist air at -20 °C converted the ester (3) into trityl alcohol (38%) and trityl peroxide (3%) (Scheme 7). Formation of the peroxide



Scheme 7.

required attack by oxygen on the ester or an equivalent intermediate, insofar as neither trityl alcohol nor the corresponding chloride under similar conditions gave the peroxide.

The ester (3) fragmented (Scheme 8), when its toluene

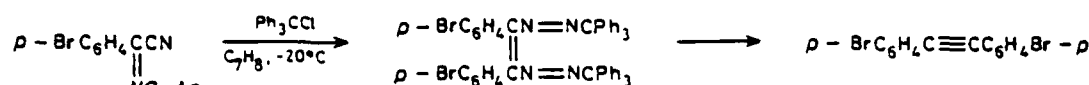


Scheme 8.

solution was warmed to 5 °C and stored for 15 h. X-Ray crystallographic analysis* showed the product, C₃₃H₂₅N₃O, to be 4,5-diphenyl-1-triphenylmethoxy-1,2,3-triazole (11). It was hydrolysed by hydrochloric acid to trityl alcohol and 1-hydroxy-4,5-diphenyl-1,2,3-triazole (12) (C₁₄H₁₁N₃O). Contact with atmospheric moisture slowly brought about the same conversion (11) → (12) (Scheme 8).⁴ The fragmentation was not noticeably affected by the added presence of either di-*t*-butyl nitroxide (a radical scavenger) or benzoyl peroxide (a radical source).

A partial extension of the overall conversion was realized in the production of *α,α'*-bis(tritylazo)-*p,p'*-dibromostilbene (2%) and *p,p'*-dibromodiphenylacetylene (28%) from silver *p*-bromo-

* We are indebted to Dr. E. D. Stevens and Dr. C. Stevens for the X-ray analysis. The data will be published elsewhere.

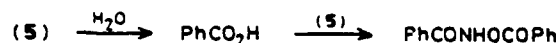


Scheme 9.

phenylcyanomethylenenitronate and trityl chloride (Scheme 9). Just as thermolysis of the bisazostilbene (4) in benzene at 80°C in the presence of air gave diphenylacetylene (86%) and trityl peroxide (75%),⁴ the bisazo-*p,p'*-dibromostilbene afforded *p,p'*-dibromodiphenylacetylene. In the absence of air trityl peroxide was not a co-product.

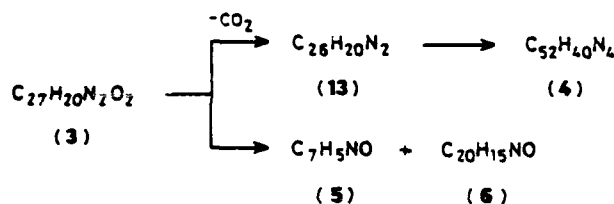
Attempts to bring about a reaction between triphenylsilyl chloride and silver phenylcyanomethylenenitronate under comparable conditions were unsuccessful and afforded recovery (95%) of the silyl chloride. Attempts to alkylate sodium phenylcyanomethylenenitronate with trityl chloride were also unsuccessful.

In dimethyl sulphoxide at 25°C under nitrogen, silver phenylcyanomethylenenitronate and trityl chloride gave trityl isocyanate (6) (10%) and *O*-benzoylbenzhydroxamic acid (29%) after the mixture was treated with water. It was assumed that benzonitrile *N*-oxide (5) (an initial product) and benzoic acid (by hydrolysis) combined to form the hydroxamic acid (Scheme 10).¹²



Scheme 10.

The deep-seated changes in the spontaneous reaction (Scheme 8) required the cleavage of at least five and the formation of at least seven bonds. Product analysis revealed two pathways for fragmentation of the ester (3) ($\text{C}_{27}\text{H}_{20}\text{N}_2\text{O}_2$): one afforded carbon dioxide and $\text{C}_{26}\text{H}_{20}\text{N}_2$, the other gave benzonitrile *N*-oxide (5) ($\text{C}_7\text{H}_5\text{NO}$) and trityl isocyanate (6) ($\text{C}_{20}\text{H}_{15}\text{NO}$) (Scheme 11). The intermediate $\text{C}_{26}\text{H}_{20}\text{N}_2$ was

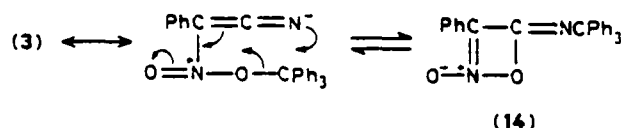


Scheme 11.

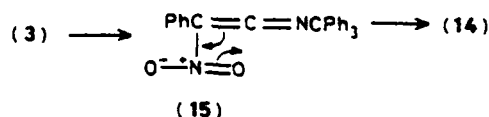
assigned the structure of benzonitrile-trityl imine (13) to provide for the formation of the bisazostilbene (4) ($\text{C}_{52}\text{H}_{40}\text{N}_4$) by dimerization and the triazole (11) by a migration of the trityl group from a nitrogen to an oxygen atom after a dipolar addition with benzonitrile *N*-oxide (5) (or an equivalent dipolarophile) gave 4,5-diphenyl-2-trityl-1,2,3-triazole 1-oxide (Schemes 11 and 12). [The nitrile imine (13) was previously abandoned as a precursor to the bisazostilbene (4) when benzonitrile *N*-oxide (5) and trityl isocyanate (6) failed to give an adduct that would

ostensibly afford the nitrilimine (13) and carbon dioxide by fragmentation.⁵]

The intermediacy of the *N*-trityl imine (14) of 4*H*-3-phenyl-1,2-oxazet-4-one 2-oxide was proposed to accommodate the fragmentation. Availability of the imine (14) depended on isomerization of the ester (3) for which both a direct pathway (Scheme 13) and an indirect pathway via *N*-trityl phenyl-nitroketene imine (15) (Scheme 14) were envisaged but not



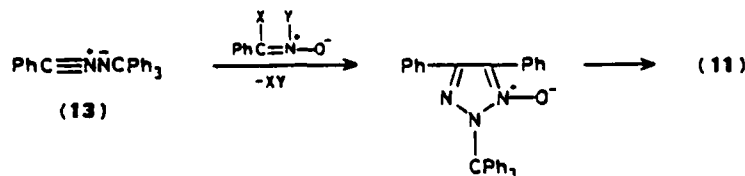
Scheme 13.



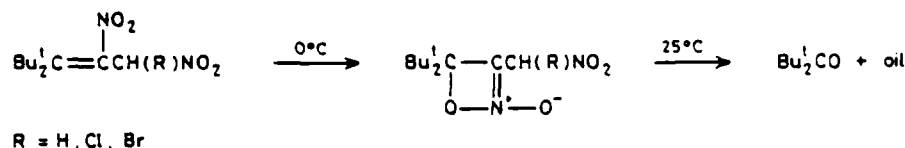
Scheme 14.

differentiated. Generation of the keteneimine (15) constituted a formal change from *O*- to *N*-tritylation of the phenylcyanomethylenenitronate anion. [Attempts to prepare the keteneimine (15) by a reaction between trityl isocyanide and the sodium salt of chloro(nitro)phenylmethane were unsuccessful.⁵] Although *C*-nitroketene imines are virtually unknown, the *N*-*t*-butylimine of dinitroketene, $(\text{O}_2\text{N})_2\text{C}=\text{C}=\text{NBu}^t$, was produced from the anion of dinitrocyanoethane and *t*-butyl bromide. It was not isolated and was instead immediately converted into *N*-*t*-butyldinitroacetamide, $(\text{O}_2\text{N})_2\text{CHCONHCBu}^t$.¹³ Ring closure of the nitroketeneimine (15) to the intermediate oxazete (14) was reminiscent of the facile ring closure to 3-methyl-4,4-di-*t*-butyl-4*H*-1,2-oxazete 2-oxide from 3-*t*-butyl-4,4-dimethyl-2-nitropent-2-ene with time at 25°C . This was the first recognized example of an isomerization of an α,β -unsaturated nitro compound to a four-membered heterocycle. It underwent facile dissociation to give di-*t*-butyl ketone and an oil (Scheme 15).¹⁴

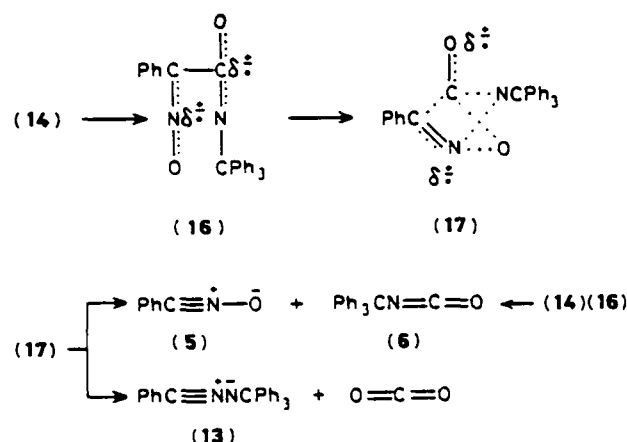
The known facile dissociation of trialkyloxazetes¹⁴ was extended to a cleavage of the oxazete (14) to account for a formation of benzonitrile *N*-oxide (5) and trityl isocyanate (6) (Scheme 16). A bond reorganization was required to account for fragmentation to benzonitrile-*N*-trityl imine and carbon dioxide. Ring-opening by cleavage of the oxazete *N*-*O* bond to afford an intermediate model in which new CO and NN bonding developed as CC, CN, and NO bonding deteriorated was proposed (Scheme 17). [A rearrangement of an $\text{O}-\text{N}-\text{O}-\text{C}=\text{N}'$ system, to an $\text{N}'-\text{N}-\text{O}-\text{C}=\text{O}$ system, prior to, or with dissociation, $(14) \rightarrow (13) + \text{CO}_2$, is involved. A related



Scheme 12.

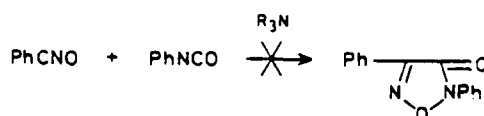


Scheme 15.

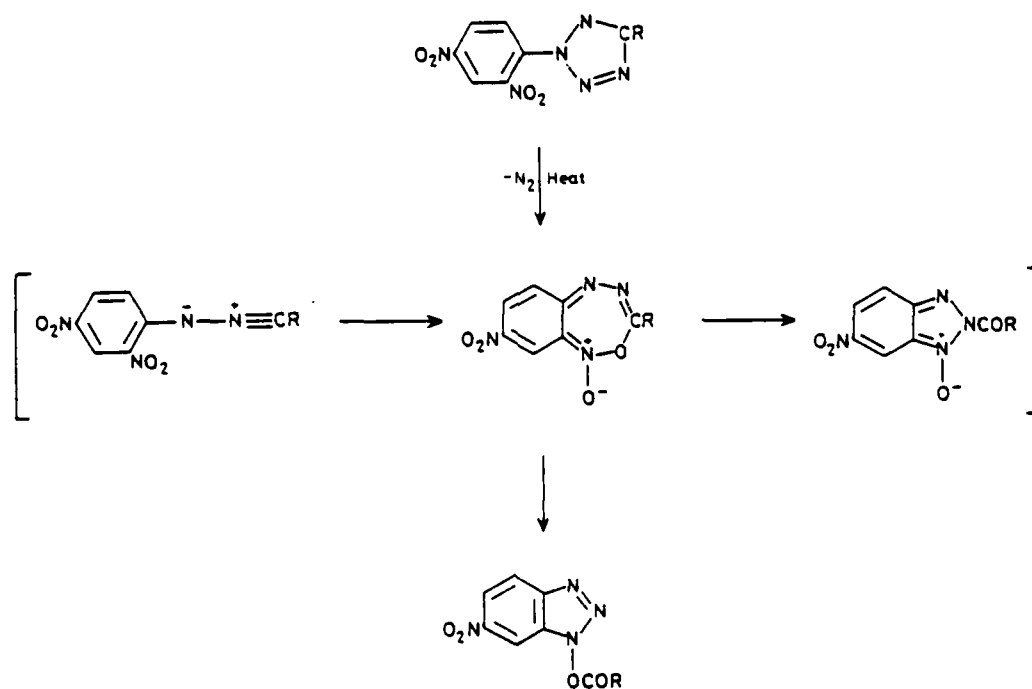


Scheme 16.

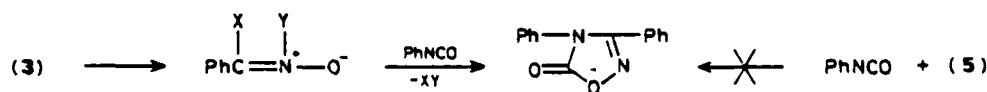
fragmentation reaction mixture at 5°C afforded 3,4-diphenyl-1,2,4-oxadiazol-5-one (18) (8%) (Scheme 18) and the bisazostilbene (4). Since independent investigations revealed that phenyl isocyanate did not combine with benzonitrile *N*-oxide (5) under comparable conditions to give a dipolar adduct, it was assumed that the isocyanate captured the oxazete (14), or an equivalent intermediate dipolarophile, in an addition-elimination reaction to give the oxadiazolone (18) (Scheme 18). [The formation of 2,4-diphenyl-1,2,5-oxadiazol-3-one from a reaction between benzonitrile *N*-oxide (5) and phenyl isocyanate in the presence of triethylamine or sodium hydroxide has been reported (Scheme 19).^{16,17} Our attempts to reproduce this



Scheme 19.



Scheme 17.



Scheme 18.

rearrangement was previously encountered in an explanation of the thermolysis of a 5-aryl-2-(2,4-dinitrophenyl)tetrazole to 1-aryloxy-6-nitrobenzotriazole (Scheme 17).^{13]}

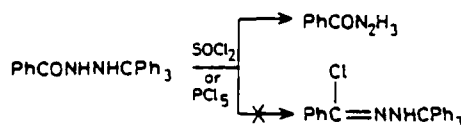
Addition of an equimolar amount of phenyl isocyanate to the

result were unsuccessful. Phenyl isocyanate has a low order of dipolarophilic activity. It gave 4-mesityl-3-phenyl-1,2,4-oxadiazol-5-one (76%) in a reaction with mesitonitrile *N*-oxide at 25°C that required 15 months.^{17]} When the fragmentation

reaction mixture was treated with phenyl isocyanate and stored at -20°C the products isolated were the triazole (11) and the oxadiazolone (18). Formation of the red bisazostilbene (4) was suppressed.

Formation of the red azostilbene (4) was also suppressed by addition of an extra amount of benzonitrile *N*-oxide (5) or of phenylacetylene to the reaction mixture (Scheme 8). [The addition of radioactive benzonitrile *N*-oxide (5) showed not only that it was not a precursor but also that in sufficient amount it could be an inhibitor for the formation of the stilbene (4).⁵ This inhibition is compatible with the competitive formation of compounds (4) and (11) (Schemes 11 and 12). Added phenylacetylene diminished the formation of the stilbene (4).⁴ The probability that phenylacetylene and benzonitrile-*N*-triphenylmethyl imine (13) can form an adduct has not been established.] A similar suppression has been brought about by the addition of either *p*-chloro- or *p*-methyl-benzonitrile *N*-oxide. The possibility that interaction between a nitrile oxide and the stilbene (4) accounted for the diminished yield of the latter was shown to be invalid when independent experiments established that no reaction occurred between compound (4) (recovered 88%, 80%) and (5) or its *p*-chloro derivative. Dimerization of the nitrile oxides gave the expected diarylfuroxanes (66%, 60%).

Attempts to produce the *N*-trityl imine (13) independently were abandoned when (a) tritylhydrazine and benzaldehyde failed to undergo conversion to the expected hydrazone desired for dehydrogenation to compound (13) and (b) β -*N*-tritylbenzohydrazide gave benzohydrazide (43%, 60%) in an unexpected replacement of the trityl group with hydrogen upon treatment with either thionyl chloride or phosphorus pentachloride: *N*-tritylbenzhydrazidoyl chloride desired for dehydrochlorination to compound (13) was not detected (Scheme 20). Attempts to



Scheme 20.

prepare the oxime (20) of the monotritylhydrazone (19) of benzil were unsuccessful. The oxime (20) was desired for an oxidative cyclization to 4,5-diphenyl-2-trityl-1,2,3-triazole 1-oxide, an intermediate in Scheme 12. (A similar oxidation of the monoxime monophenylhydrazone of benzil to 2,4,5-triphenyl-1,2,3-triazole 1-oxide has been reported.¹⁸)

The thermal stability of 3-phenyl-4-trityl-1,2,4-oxadiazol-5-one (21) ($\text{C}_{17}\text{H}_{10}\text{N}_2\text{O}_2$), decomp. $>250^{\circ}\text{C}$, precluded the heterocycle as an intermediate in the fragmentation reaction (Scheme 8) and as a precursor to carbon dioxide and the nitrile imine (13) (Scheme 11).⁵ [Benzonitrile *N*-oxide (5) failed to give



Scheme 21.

an adduct with either trityl isocyanate (6)⁵ or phenyl isocyanate. A more reactive dipolarophilic intermediate, e.g. the oxazete (14), combined with phenyl isocyanate to give the adduct (18) but failed to combine with trityl isocyanate (14) + (6) $\rightarrow$ (21) + (6).]

Experimental

M.p.s were determined on a Thomas-Hoover capillary melting point apparatus. I.r. spectra were obtained with a Pye-Unicam SP 200 spectrophotometer. N.m.r. spectra were recorded on a Varian A-60 spectrometer from tetramethylsilane as the internal standard. Mass spectra were obtained from an AEI Scientific Apparatus Limited MS 30 mass spectrometer. Elemental analyses were provided by Micro-Tech Laboratories, Skokie, IL. Toluene was stored over anhydrous potassium carbonate.

Reaction of Silver Phenylcyanomethylene nitronate and Trityl Chloride.—Trityl chloride (13.9 g, 0.05 mol) in toluene (100 ml) was added slowly to a stirred suspension of silver phenylcyanomethylenenitronate (13.3 g, 0.05 mol) in toluene (50 ml) at -20°C under a nitrogen atmosphere. The mixture was stirred for 3 h at -20°C . Silver chloride (6.58 g, 92%) was removed by cold filtration to leave trityl phenylcyanomethylenenitronate (3) in toluene. On storage at 5°C the bisazoethylenes (4) was precipitated and was isolated after washing with benzene as a red crystalline solid (3.3 g, 18%), m.p. 144–145 $^{\circ}\text{C}$ (decomp.) [lit.⁴ m.p. 145 $^{\circ}\text{C}$ (decomp.)], ν_{max} (KBr) 3 090, 3 060, 3 030, 1 600, 1 495, 1 450, 1 040, 910, 760, 700, and 650 cm^{-1} .

The filtrate was concentrated and treated with benzene to precipitate 1-triphenylmethoxy-4,5-diphenyl-1,2,3-triazole (11) as a colourless solid (2.85 g, 24%), m.p. 217–219 $^{\circ}\text{C}$ (lit.⁴ m.p. 216–219 $^{\circ}\text{C}$) after recrystallization from benzene; ν_{max} (KBr) 3 070, 1 605, 1 490, 1 450, 880, 760, and 700 cm^{-1} ; δ (CDCl_3) 7.0–7.7 (Found: C, 82.55; H, 5.55; N, 8.5. Calc. for $\text{C}_{33}\text{H}_{23}\text{N}_3\text{O}$: C, 82.65; H, 5.25; N, 8.76). In a further run the cold filtrate, after separation from silver chloride, was stirred for 1 h at 0°C with water (50 ml) containing a few drops of concentrated hydrochloric acid. The reaction mixture was kept at 5°C for 16 h, treated with benzene to give trityl alcohol, m.p. 161–162 $^{\circ}\text{C}$ ¹⁹ (3.1 g, 48%). No other product was isolated from the intractable mixture.

In a further experiment air was bubbled through the cold filtrate after removal of silver chloride for 2 h at -20°C and the solution was stored at 5°C for 16 h. The clear yellow solution was concentrated under reduced pressure. The residue was treated with benzene (25 ml) and the solid was filtered off and washed with a little benzene to give trityl alcohol, m.p. 161–162 $^{\circ}\text{C}$ (2.50 g, 38%). The mother liquor was left at room temperature for a few days; a small amount of trityl peroxide (0.10 g, 3%) was isolated, m.p. 183–185 $^{\circ}\text{C}$ (lit.²⁰ m.p. 187 $^{\circ}\text{C}$). [Modification in work-up determined the isolation of carbon dioxide,^{3,4} and trityl isocyanate (5).³] Benzonitrile *N*-oxide (5) was trapped in a dipolar addition reaction as 3,5-diphenylisoxazole (DPI) by the added presence of phenylacetylene.⁴ The formation of DPI by the dipolar addition of phenylacetylene to the nitrile oxide (5) has not been differentiated from a dipolar addition-elimination reaction with the oxazete (14) [(14) + $\text{PhC}\equiv\text{CH} \rightarrow \text{DPI} + (6)$].^{3,4}

Bromine and the Nitronate (3).—Trityl chloride (6.95 g, mmol) in benzene (50 ml) was slowly added to a suspension of the silver salt of nitro(phenyl)acetonitrile (6.65 g, 25 mmol) in benzene (50 ml) at 0 – 5°C under nitrogen. After the mixture had been stirred for 2 h at 0 – 5°C , silver chloride was filtered off and a slight excess of bromine (2.4 g 30 mmol) was slowly added with stirring to the filtrate at 0 – 5°C . The reaction mixture was kept at 5°C for 16 h. T.l.c. of this mixture showed only two spots identical with those for bromonitro(phenyl)acetonitrile and trityl bromide. Solvent was removed from the reaction mixture to give trityl bromide (5.56 g, 69%), m.p. and mixed m.p. with an authentic sample was 153–154 $^{\circ}\text{C}$,²¹ isolated by filtration. The filtrate was found to be bromonitro(phenyl)acetonitrile (3.2 g, 53%) by comparison (t.l.c. and i.r.) with an authentic sample prepared by a reported procedure.²²

Dinitrogen Tetraoxide and the Nitronate (3).—After removal of silver chloride the filtrate in toluene (-20°C) (above) was treated with an excess of dinitrogen tetraoxide, stirred at -20°C for 3 h, stored at 5°C for 40 h, concentrated, and combined with anhydrous ether (50 ml) to give *p*-nitrobenzoyl cyanide (1.0 g, 23%), as colourless crystals, m.p. $114\text{--}115^{\circ}\text{C}$ (lit.²³ m.p. 116°C). Trityl alcohol (2.8 g, 43%), m.p. $161\text{--}162^{\circ}\text{C}$ was obtained from the mother liquor on concentration.

Phenyl Isocyanate and the Nitronate (3).—(a) After removal of silver chloride the filtrate (above) in toluene was treated at -20°C with phenyl isocyanate (3.0 g, 25 mmol), stored at 5°C for 16 h, and filtered to remove the bisazo compound (4) as a red solid (1.80 g, 20%). From the filtrate stored at 25°C for a few days 3,4-diphenyl-1,2,4-oxadiazol-5-one (18) (0.48 g, 8%) separated as a colourless crystalline solid, m.p. $166\text{--}167^{\circ}\text{C}$ (lit.²⁴ m.p. 167°C).

(b) After removal of silver chloride the filtrate (above) was treated at -20°C with phenyl isocyanate (3.0 g, 25 mmol) and stored at -20°C for 2 days. The clear yellow solution was warmed to 25°C as it turned red-orange. After storage at 25°C for a day the yellow colour of the solution was restored. The solvent was removed and the residue was treated with ether (50 ml) to give the triazole (11) as a colourless solid (0.85 g, 14%), m.p. $215\text{--}217^{\circ}\text{C}$. The filtrate was stored at room temperature to bring about the precipitation of the oxadiazolone (18) isolated as a colourless solid (0.65 g, 11%), m.p. $165\text{--}167^{\circ}\text{C}$.

Benzonitrile Oxide and Phenyl Isocyanate.—Benzhydroxamic acid chloride [PhC(=NOH)Cl] (3.88 g, 25 mmol) and phenyl isocyanate (3.00 g, 25 mmol) in toluene (50 ml) were stirred at -20°C under nitrogen. Triethylamine (2.6 g, 25 mmol) in toluene (30 ml) was added dropwise and stirring was continued for 2 h. The reaction mixture was filtered to remove triethylamine hydrochloride (2.82 g, 82%) and the filtrate was left at room temperature overnight. Filtration gave diphenylurea (1.20 g, 45%), m.p. $238\text{--}239^{\circ}\text{C}$ (lit.²⁵ m.p. 235°C). The filtrate was concentrated and the residue was recrystallized from methylene dichloride–hexane to give 3,4-diphenylfuroxane (1.7 g, 58%), m.p. $113\text{--}114^{\circ}\text{C}$ (lit.²⁶ m.p. 114°C).

Dimethyl Sulphoxide as Solvent.—Silver phenylcyanomethylenenitronate (13.3 g, 50 mmol) dissolved in dimethyl sulphoxide (45 ml) was treated with a solution of trityl chloride (13.9 g, 50 mmol) in dimethyl sulphoxide (45 ml) added slowly at room temperature under nitrogen. The mixture was stirred for 1 h and added to cold water (400 ml) layered with benzene (200 ml). After three extractions (3×100 ml) with benzene, the combined benzene extracts were washed with water, dried (MgSO_4), and concentrated under reduced pressure. The residue, a waxy solid, was treated with benzene (20 ml) to give *O*-benzoyl-benzhydroxamic acid as a colourless solid (1.72 g, 29%), m.p. $164\text{--}165^{\circ}\text{C}$ (lit.²⁷ m.p. 166°C) after washing with benzene and filtration. The mother liquor was concentrated to give trityl isocyanate (6) (1.45 g, 10%), m.p. $92\text{--}93^{\circ}\text{C}$ (lit.²⁸ m.p. 93°C).

***p*-Nitrobenzoyl Cyanide Oxime with Dinitrogen Tetraoxide.**—An excess of dinitrogen tetraoxide was added to a solution of *p*-nitrobenzoyl cyanide oxime (0.191 g, 1 mmol) in benzene (20 ml) and stirred at room temperature for 6 h. The solvent was removed under reduced pressure and the residue was recrystallized from methylene dichloride–hexane to give *p*-nitrobenzoyl cyanide (0.140 g, 80%), m.p. and mixture m.p. with an authentic sample m.p. $114\text{--}115^{\circ}\text{C}$.

Silver *p*-Bromophenylcyanomethylenenitronate and Trityl Chloride.—To a suspension of silver *p*-bromophenylcyanomethylenenitronate (7.0 g, 20 mmol) in benzene (25 ml), a solution of trityl chloride (5.6 g, 20 mmol) in benzene (50 ml) was

added dropwise with stirring at $0\text{--}5^{\circ}\text{C}$ under a nitrogen atmosphere. The mixture was stirred at $0\text{--}5^{\circ}\text{C}$ for 4 h and filtered to remove silver chloride. The clear filtrate was left at room temperature for a day. *z,z'*-Bis(tritylazo)*p*-bromostilbene was precipitated as a red solid, (0.15 g, 2%), m.p. $143\text{--}144^{\circ}\text{C}$ (decomp.); ν_{max} (KBr) 1600, 1495, 1455, 1020, 810, and 705 cm^{-1} ; (Found: C, 70.65; H, 4.55; N, 6.4. Calc. for $\text{C}_{22}\text{H}_{18}\text{Br}_2\text{N}_4$: C, 71.07; H, 4.33; N, 6.38).

From the filtrate, di-*p*-bromophenylacetylene was isolated by concentration (0.95 g, 28%), m.p. $181\text{--}182^{\circ}\text{C}$ (lit.²⁹ m.p. 183°C).

3-Phenyl-4-trityl-1,2,4-oxadiazol-5-one (21).—To a solution of 3-phenyl-1,2,4-oxadiazol-5-one³⁰ (1.62 g, 10 mol) in a mixture of benzene and dimethylformamide, sodium hydride (slight molar excess) was added with stirring. Within a few minutes the sodium salt of the heterocycle was precipitated. Trityl chloride (2.78 g, 10 mmol) was added and the reaction mixture refluxed for 110 h. The unchanged sodium salt was filtered off and gave, on acidification, recovery of the oxadiazolone (65%). The organic layer was concentrated, dissolved in ethyl acetate, and the solution washed with water, and dried (MgSO_4). Removal of the solvent left a residue (2.7 g) chromatographically separated from a silica gel column to give trityl alcohol (800 mg), recovered starting oxadiazolone (300 mg, 20%), and 3-phenyl-4-trityl-1,2,4-oxadiazol-5-one (21) (400 mg, 65% yield based on recovered starting oxadiazolone), m.p. $188\text{--}189^{\circ}\text{C}$ (chloroform–hexane); ν_{max} (CHCl_3) 1770 cm^{-1} ; δ (CDCl_3) 7.0–7.4 (m); m/z (70 eV) 404 (100%, *M*), 360 (40), 359 (19), 301 (36), 284 (26), 283 (56), 257 (17), 256 (12), 243 (28), 180 (16), 167 (25), 166 (45), 165 (90), 152 (19), 141 (13), 103 (14), 77 (14), and 44 (50) (Found: C, 80.0; H, 4.9; N, 6.9. Calc. for $\text{C}_{21}\text{H}_{12}\text{N}_4\text{O}$: C, 80.18; H, 4.98; N, 6.93%). [The assignment (21) was made in accordance with a similar methylation of 3-phenyl-1,2,4-oxadiazol-5-one to give the 4-methyl derivative, differentiated from the alternative *N*- and *O*-methyl derivatives by direct examination of the three compounds.³¹]

4,5-Diphenyl-1,2,3-triazol-1-ol (12).—The triazole (11) (1 g, 2.1 mmol) was dissolved in chloroform (10 ml) and stirred with 5*M* hydrochloric acid (10 ml) for 20 h. More chloroform (50 ml) was added after which the chloroform layer was washed with water and dried. The solvent was removed and the residue was treated with ether (20 ml), and the mixture was filtered to give the hydroxytriazole (12) as a colourless solid (0.13 g, 26%), m.p. $178\text{--}180^{\circ}\text{C}$ (lit.³ m.p. 182°C). From the filtrate, trityl alcohol (0.29 g, 53%), m.p. $160\text{--}162^{\circ}\text{C}$ was isolated.

Benzil Monotriylhydrazone (19).—Benzil monohydrazone³² (11.2 g, 50 mmol), trityl chloride (16.8 g, 60 mmol) and magnesium sulphate (3 g, 25 mmol) in absolute ether (200 ml) were stirred under a nitrogen atmosphere. Dry pyridine (5 ml, 60 mmol) was added dropwise and the mixture was gently refluxed for 10 h. The mixture was cooled to 5°C . The insoluble material was filtered off and washed several times with water to give recovery of unchanged benzil monohydrazone (2.8 g). The ethereal filtrate was washed with dilute hydrochloric acid, aqueous sodium hydrogen carbonate, and water and then dried (MgSO_4). The solution was concentrated to precipitate benzil monotriyl hydrazone (19) (11.8 g, 67%), m.p. $151\text{--}152^{\circ}\text{C}$; ν_{max} (KBr) 3320 (NH), 1635 (C=O), 1600, 1540, 1495, 1450, 1340, 1240, 1185, 1030, 880, and 700 cm^{-1} ; δ (CDCl_3) 6.9–7.8 (m, ArH) (Found: C, 85.0; H, 5.55; N, 6.1. Calc. for $\text{C}_{33}\text{H}_{26}\text{N}_2\text{O}$: C, 84.55; H, 5.77; N, 6.16). Attempts to prepare the oxime (20) of benzil monotriylhydrazone were unsuccessful.

Acknowledgements

Financial support was received from O.N.R.

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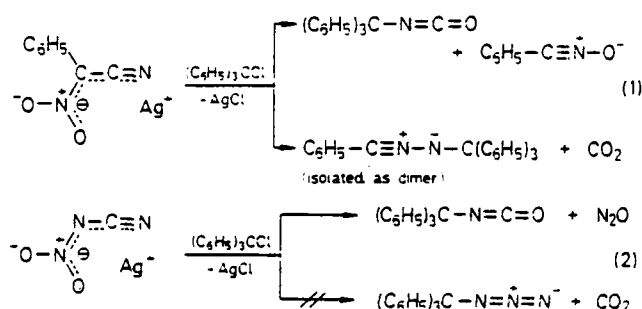
Synthesis October 1987

Joseph H. Boyer,* Thanikavelu Manimaran

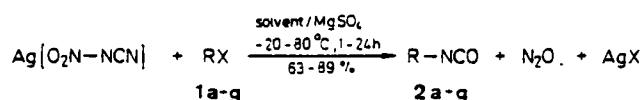
Department of Chemistry, University of New Orleans, New Orleans, LA 70148, U.S.A.

Alkyl and aralkyl halides were converted to isocyanates (63%–89%) by treatment with the silver salt of nitrocyanamide. This new reaction offers the first direct conversion of an organic halide to an isocyanate that is general, efficient, and facile.

In an elucidation of a complex reaction between trityl chloride and silver phenylcyanomethanenitronate, a branched reaction pathway accounted for the formation of trityl isocyanate and benzonitrile *N*-oxide by one route and benzonitrile-*N*-triphenylmethyylimine and carbon dioxide by the other (eq. 1).^{1,2} Our prediction that a similar tritylation of silver nitrocyanamide would give trityl isocyanate and or trityl azide was based on these results (eq. 2). The experiment showed that trityl isocyanate was obtained nearly quantitatively with no trace of trityl azide.



Further experiments with a variety of halides revealed that treatment with silver nitrocyanimide produced the expected isocyanate in excellent yields (Table).^{3,4} This new reaction is recommended for the direct conversion of halides to isocyanates. It is more reliable than the replacement of halogen by an isocyanate group in the reaction between organic halides and metal cyanates, which has given very erratic results.^{5,6}



Each halide was obtained from Aldrich Chemical Co. GC data was obtained using an HP-5790 instrument with a HP-3390A integrator (column: 3% OV-17 on 80/100 Gas Chrom Q stainless steel 6 ft X 1/8 in; carrier gas nitrogen; column temp. between 50° and 200°C. with FID).

Sodium nitrocyanimide was obtained from *N*-methyl-*N*-nitroso-*N'*-nitroguanidine by treatment with sodium hydroxide in water. *Caution: It is recommended that the operation be carried out in a well-ventilated hood to eliminate the possible accumulation of diazomethane, the by-product.* The sodium salt was converted to silver nitrocyanimide by treatment with silver nitrate in water. *Silver nitrocyanimide has been described as a dangerous, sensitive explosive; handling with caution is advised.*

Conversion of Halides to Isocyanates: General Procedure:

Silver nitrocyanaide (10.00 g, 0.052 mol) and anhydrous MgSO_4 (1.00 g) are suspended in anhydrous benzene (30 mL) and stirred under nitrogen. A solution of benzyl bromide (8.55 g, 0.050 mol) in anhydrous benzene (20 mL) is added in drops, and the mixture is stirred at room temperature for 24 h. The exclusive formation of benzyl isocyanate can be seen by the presence of a single peak in the GC analysis of the liquid phase. Inorganic salts are filtered and the solvent is removed under reduced pressure to give the crude product (5.90 g, 90%); distillation (65 °C/4 Torr) afforded 5.19 g (78%) of pure benzyl isocyanate, identified by direct comparison with an authentic sample.³ Similar treatment converted other alkyl and aralkyl halides to isocyanates (Table).

Financial assistance was received from O.N.R.

Received: 30 January 1987

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- (4) The possible intermediacy of an alkyl nitrocyanamide, and/or an alkyl isonitramine $[RON(O)=NCN]$, and/or an *N*-alkyl-*N*-nitrocarbodiimide $(RN=C=NNO_2)$ for the formation of an isocyanate and dinitrogen oxide will be discussed in a longer report.
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Table. Isocyanates 2 from Halides and Silver Nitrocyvanamide.

Halide I		Solvent	Temp. (°C)	Time (h)	RNCO	Yield % ^a , (%) ^b	m.p. (°C) or b.p. (°C/Torr)	Lit. m.p. or b.p. (°C or °C/Torr)
R	X							
(C ₆ H ₅) ₃ C	Cl	toluene	-20	4	2a	96 (84)	91	85-87 ⁹
(C ₆ H ₅) ₃ C	Cl	CH ₂ Cl ₂	0	1	2a	94 (84)		
(C ₆ H ₅) ₂ CH	Br	benzene	25	15	2b	92 (74)	148/4	148/4 ¹⁰
C ₆ H ₅ CH ₂	Br	benzene	25	24	2c	90 (78)	65/4	137/30 ⁸
(CH ₃) ₃ C	Br	ether	25	4	2d	81 (63)	67/760	67/760 ¹¹
CH ₃ (CH ₂) ₇	I	benzene	80	20	2e	90 (75)	60/3.5	95/18 ¹²
c-C ₆ H ₁₁	Br	benzene	25	24	2f	95 (70)	58/8	65/18 ¹³
1-adamantyl	Br	benzene	25	4	2g	96 (89)	147	144-145 ¹⁴

* Yield refers to the crude product obtained after removing the solvent.

^b Yield of the product isolated by recrystallization or distillation.

D. Alkylation of Nitrocyanamide. A New Synthesis of Isocyanates.

Joseph H. Boyer, Thanikavelu Manimaran and Lionel T. Wolford

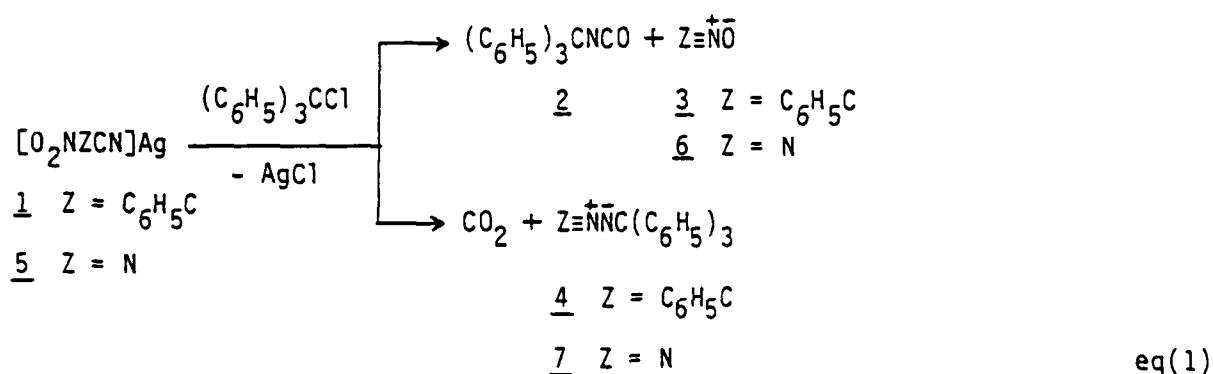
Department of Chemistry, University of New Orleans, New Orleans, LA 70148

Abstract. Thirteen alkyl halides (primary, secondary, and tertiary aliphatic including alicyclic, aralkyl, and heteroalkyl systems) and certain nonvicinal dihalides on treatment with silver nitrocyanamide were converted to corresponding isocyanates (63% - 95%). Intermediate alkyl nitrocyanamides, spectroscopically detected, thermolyzed (-20°C to 80°C) to the expected isocyanates. In certain examples silver nitrocyanamide was generated in situ from sodium nitrocyanamide and silver nitrate. Silver nitrocyanamide did not react with cyclopropyl bromide, acetyl chloride, *p*-toluenesulfonyl chloride, phenacyl bromide and 2-bromomethyldioxolane 27, and the ethylene ketal 28 of 4-iodo-1-bromopentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonan-9-one. Silver nitrocyanamide reacted with syn-9,10-dioxo-(bromomethyl,methyl)bimane 26, to give an intractable mixture. Vicinal dihalides gave erratic results without the detectable formation of vicinal diisocyanates: unisolated 2-bromoethyl isocyanate (tentative assignment) was detected in a product mixture from ethylene dibromide; a not unexpected rearrangement during the reaction with 1,2-dibromocyclobutane brought about the formation of 4-bromobuten-3-yl isocyanate isolated as ethyl 4-bromobuten-3-yl carbamate in low yield; and 1,2-dibromocyclohexane gave 2-bromocyclohexyl isocyanate isolated as ethyl N-2-bromocyclohexyl carbamate in low yield.

Introduction. A direct conversion of an alkyl halide offers an attractive, but rarely encountered, synthesis of an isocyanate. A trimerization of an isocyanate precluded its isolation when produced from an organic halide and an alkali cyanate in an aprotic solvent, e.g., dimethylformamide; however,

methoxymethyl, allyl, and 2-butenyl isocyanates and methylene diisocyanate were similarly obtained and isolated.^{1a} In a mathematical description of the reaction a maximum conversion (87.02%) of benzyl chloride when treated with potassium cyanate was achieved at 175°C in N,N-dimethylacetamide with a copper powder catalyst.^{1b}

Recognition that trityl chloride and silver phenylcyanomethane nitronate 1 gave trityl isocyanate 2 and benzonitrile-N-oxide 3 by one pathway and carbon dioxide and benzonitril-N-triphenylmethylimine 4 by a competitive pathway^{2,3} permitted the prediction that a similar tritylation of silver nitrocy-
anamide 5 would give trityl isocyanate 2 along with nitrous oxide 6 and/or trityl azide 7 along with carbon dioxide, eq (1). The prediction was partially fulfilled when the isocyanate 2 was obtained nearly quantitatively from the salt 5; the formation of trityl azide 7, nitrous oxide, and carbon dioxide was not detected.^{4,5} The present report describes extensions of this new reaction to provide preparations of isocyanates of various structures and gives some limits on its applicability.



Results. Primary Alkyl Systems. Silver nitrocy-
anamide efficiently converted the appropriate primary halide to benzyl, n-octyl, methoxymethyl, and N-phthalimidomethyl isocyanates 8 - 11 ($X = \text{NCO}$), and o-, m-, and p-xylylene- α,α' -diisocyanates 12 - 14 (Table). Previously unknown isocyanates 11 $X = \text{NCO}$ and

12 gave expected derivatives: syn-di-(N-phthalimidomethyl)urea 15, 2,3,4,5-tetrahydro-1H-2,4-benzodiazepin-3-one 16 and diethyl o-xylylene- α,α' -dicarbamate 17. Unidentified, presumably oligomeric material formed from the xylylene diisocyanates after standing for a few hours. A diisocyanate was not obtained from 1,2-dibromoethane; instead treatment with silver nitrocyamide brought about a very slow but efficient conversion to 2-bromoethyl isocyanate 18 (tentative identification).

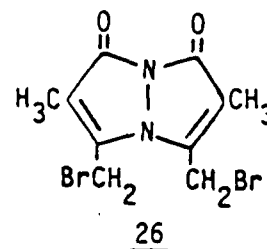
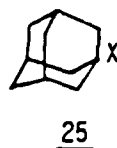
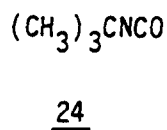
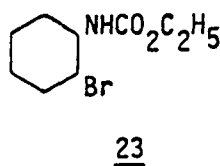
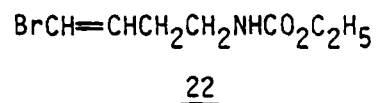
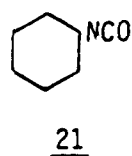
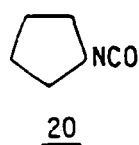
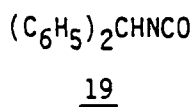
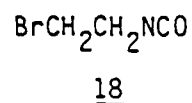
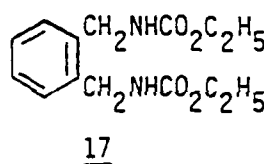
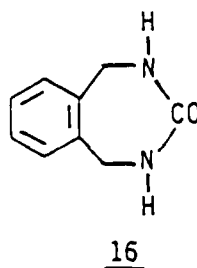
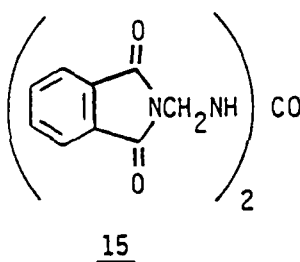
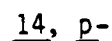
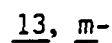
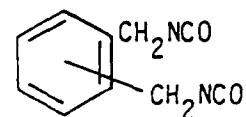
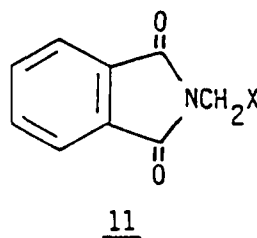
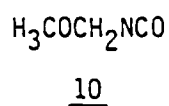
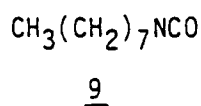
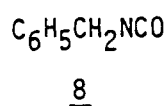
Primary and Secondary Alkyl Systems. Secondary halides afforded benzhydryl, cyclopentyl, and cyclohexyl isocyanates 19 - 21 (Table). Explosions obtained on heating samples of crude cyclopentyl isocyanate 20 from repeated preparations were attributed to presumed trace quantities (undetected by IR and NMR) of the intermediate cyclopentyl nitrocyamide. The isocyanate 20 was isolated by non-preparative gas chromatography.

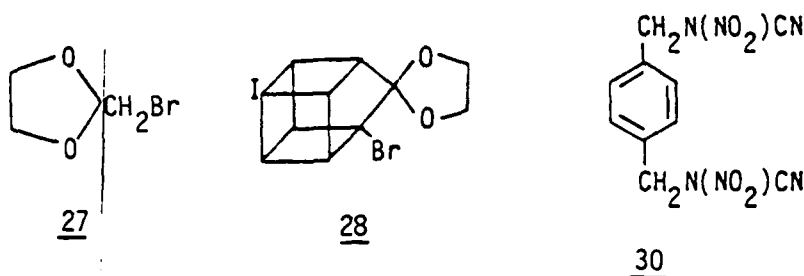
A carbon skeleton rearrangement was encountered in the inefficient conversion of 1,2-dibromocyclobutane to 4-bromobuten-3-yl isocyanate, subsequently converted to ethyl 4-bromobuten-3-yl carbamate 22 for structure confirmation. Related rearrangements from cyclobutyl and cyclopropylmethyl systems have been reported.⁶ In contrast 1,2-dibromocyclohexane and silver nitrocyamide gave a mixture that contained a moderate yield of 2-bromocyclohexyl isocyanate. The latter was converted to ethyl N-2-bromocyclohexylcarbamate 23.

Tertiary Alkyl Systems. Tertiary halides afforded trityl, tert-butyl, and 1-adamantyl isocyanates 2, 24, and 25, X = NCO (Table).

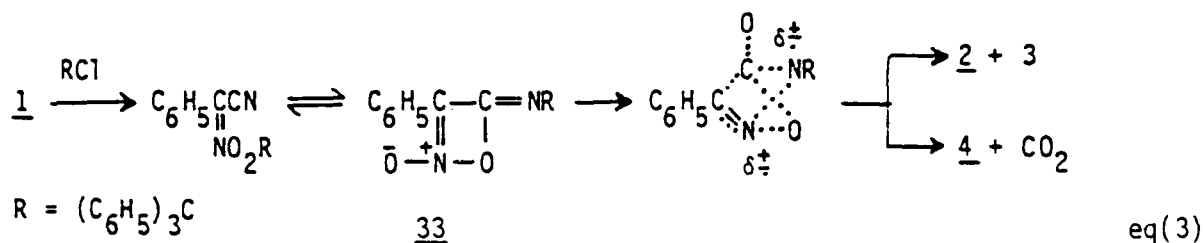
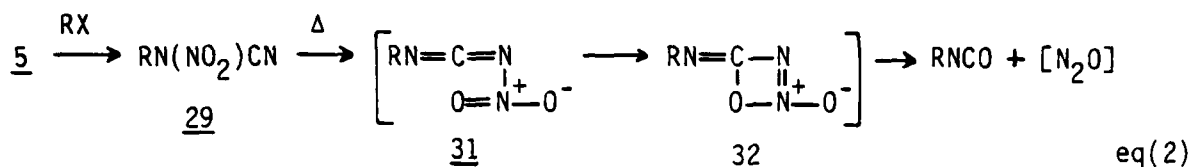
Halides that did not give Isocyanates. An intractable mixture was obtained from syn-9,10-dioxa-(bromomethyl,methyl)bimane 26⁷ and silver nitrocyamide. Cyclopropyl bromide, acetyl chloride, p-toluenesulfonyl chloride, phenacyl bromide, 2-bromomethyldioxolane 27 and the ethylene ketal 28 (we thank

Professor R. M. Moriarty for a generous sample) of 4-iodo-1-bromopentacyclo-[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonane-9-one failed to react with silver nitrocyanamide at 80° for 20 h. To understand the scope of the reaction more completely further investigations are underway.





Discussion. It was shown that the conversion, eq(1) $Z = \text{N}$, proceeded via an intermediate alkylnitrocyanamide 29, eq(3), by stopping a reaction after a short time to detect ir absorption at $2200\text{ (C}\equiv\text{N)}$ and $1270\text{ cm}^{-1}\text{ (N-NO}_2\text{)}$. As the reaction proceeded these peaks disappeared and intense absorption at $2260\text{ cm}^{-1}\text{ (NCO)}$ developed. Benzylnitrocyanamide 29 ($\text{R} = \text{C}_6\text{H}_5\text{CH}_2$) and p-xylylene-bis-nitrocyanamide 30 were each isolated in high yield and were readily thermolysed quantitatively to benzyl isocyanate 8⁸ and p-xylylenediisocyanate 14. Thermolysis of acyl and sulfonyl nitrocyanamides to acyl and sulfonyl isocyanates was recently reported.⁹ A structure assignment in favor of benzylnitrocyanamide 29 ($\text{R} = \text{C}_6\text{H}_5\text{CH}_2$) rather than the isomeric carbodiimide 31 ($\text{R} = \text{C}_6\text{H}_5\text{CH}_2$) was determined by the ^{13}C chemical shift signal at 104.38 ppm in the center of the range $100\text{--}110\text{ ppm}$ attributed to the $\text{NC}\equiv\text{N}$ group and outside the range $120\text{ to }130\text{ ppm}$ assigned to the -N=C=N- group.¹⁰ The assumption that each alkyl nitrocyanamide underwent thermal isomerization to an undetected N-alkyl-N'-nitrocarbodiimide 31 followed by ring closure and dissociation provided a straightforward explanation for the formation of the isocyanate, eq(2). A similar sequence was proposed to account for the thermal conversion of triphenylmethyl phenylcyanomethane nitronate,²⁻⁴ eq(3). At this time a rationale for bond switching in the intermediate 33 (implicated to account for product formation) and its suppression in intermediate 32 cannot be offered.



Acknowledgment: Financial support was received from ONR.

Experimental

Instruments included a Pye-Unicam SP 200 ir spectrophotometer, a Varian A-60 spectrometer, and an AEI Scientific Apparatus Limited MS30 mass spectrometer. GC data was obtained from and HP-5790 instrument with an HP-3390A integrator (column: 3% OVB-17 on 80/100 Gas Chrom Q stainless steel 6 ft X 1/8 in; carrier gas nitrogen; column temp. between 50° and 200°C, with FID). Elemental analyses were obtained from Micro-Tech. Laboratories, Skokie, IL. The organic halides listed in the Table, acetyl chloride, tosyl chloride, phenacyl bromide, 1,2-dibromoethane, 1,2-dibromocyclohexane, 2-bromomethyldioxalane and cyclopropyl bromide were obtained from the Aldrich Chemical Company, Inc. syn-9,10-Dioxa-(bromomethyl, methyl)bimane 26,⁷ the ethylene ketal 28¹¹ of 4-iodo-1-bromopentacyclo-[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonane-9-one and 1,2-dibromocyclobutane¹² were obtained according to methods in the literature cited. Sodium nitrocyuanamide was obtained from N-methyl-N-nitroso-N'-nitro-guanidine by treatment with sodium hydroxide in alcohol.¹³ It is recommended that the operation be carried out in a well-ventilated hood to eliminate the possible accumulation of diazomethane, a by-product. The sodium salt was

converted to silver nitrocyuanamide by treatment with silver nitrate in water. To avoid handling neat silver nitrocyuanamide (explosive) the salt was kept moist with solvent.¹³ Silver nitrocyuanamide prepared in situ from an equimolar mixture of sodium nitrocyuanamide (non-explosive)¹³ and silver nitrate was successfully used in one example.

Conversion of Halides to Isocyanates, General Procedure: Silver nitrocyuanamide (10.0 g, 0.05 mol) and anhydrous magnesium sulfate (1.0 g) were suspended in anhydrous benzene (30 ml) and stirred under nitrogen. A solution of benzyl bromide (8.5 g, 0.05 mol) in anhydrous benzene (20 ml) was added in drops and the mixture was stirred at room temperature for 24 h. The exclusive formation of benzyl isocyanate was shown by a single peak in the GC analysis of the liquid phase. Inorganic salts and the solvent were removed to give the crude product (5.9 g, 90%); distillation (65°C, 4 torr) afforded 5.2 g (78%) of pure benzyl isocyanate, identified spectroscopically (ir and nmr) by direct comparison with data from an authentic sample.⁸ Similar treatment converted other alkyl and aralkyl halides to isocyanates (Table). When silver nitrocyuanamide was prepared in situ from sodium nitrocyuanamide and equimolar silver nitrate and the reaction time with N-phthalimidomethyl bromide was arbitrarily increased to 3 hours, the yield of the isocyanate 11 X = NCO, isolated as the urea 15, was 80%. This result was nearly identical with the efficiency obtained in the reaction with isolated silver nitrocyuanamide (Table).

Phthalimido-N-methyl isocyanate 11 X = NCO treated with aqueous acetone gave the urea 15 m.p. 244-245°C; IR (KBr): 3320 (NH), 1770 and 1700 cm⁻¹ (C=O); NMR (DMSO-d₆): δ 7.86 (s, 4, aromatic), 6.97 (t, 1, NH, J = 6 Hz) and 4.90 (d, 2, CH₂, J = 6 Hz); anal. calcd. for C₁₉H₁₄N₄O₅: C, 60.31; H, 3.70; N, 14.81; found: C, 60.17; H, 3.63; N, 12.46. Similar treatment of o-xylylene diisocyanate with aqueous acetone afforded the cyclic urea 16 m.p. >280°C-

(lit.¹⁴ m.p. 300°C) IR (KBr): 3320 and 3240 (NH) and 1660 cm^{-1} (C=O); NMR ($\text{CF}_3\text{CO}_2\text{H}$); δ 7.27 (d, 4, aromatic) and 4.53 (s, 4, CH_2).

Diethyl o-xylylene- α,α' -dicarbamate 17. o-Xylylene- α,α' -diisocyanate (1.0 g, 5.3 mmol) was treated with 4 ml of absolute ethanol and 1 drop of pyridine at 65°C for 0.5 hour. Removal of unreacted ethanol gave diethyl o-xylylene- α,α' -dicarbamate 17 (1.30 g, 87%) as colorless crystals, m.p. 117-118°C after recrystallization from ethanol; ir (KBr): 3300 (NH), 1680 (CO); ^1H NMR (CDCl_3): δ 7.15 - 7.45 (m, 4, aromatic), 5.50 (s, 2, NH), 3.80 - 4.57 (m, 8, CH_2), 0.87 - 1.77 (m, 6, CH_3); anal. calcd. for $\text{C}_{14}\text{H}_{20}\text{N}_2\text{O}_4$: C, 59.98; H, 7.19; N, 9.99; found: C, 59.81; H, 7.23; N, 9.87.

Reaction of 1,2-dibromoethane with silver nitrocyana-
mide (10.0 g, 52 mmol), anhydrous magnesium sulfate (1.0 g) and 1,2-dibromoethane (4.7 g, 25 mmol) were stirred under nitrogen and heated in an oil bath at 85-90°C for 4 days. Anhydrous ether (50 ml) was added and the mixture was filtered. Ether was removed to leave an unresolved mixture that contained a detectable amount of an isocyanate. IR (neat): 2260 cm^{-1} (NCO); ^1H NMR (CDCl_3): δ 3.70 (s, $\text{BrCH}_2\text{CH}_2\text{Br}$) 3.60 (t, 2, CH_2Br , $J = 6 \text{ Hz}$) and 3.57 (t, 2, CH_2NCO , $J = 6 \text{ Hz}$); m/z (70 ev): 186, 188, 190 (M^+ for $\text{BrCH}_2\text{CH}_2\text{Br}$); 149 and 151 (M^+ for $\text{BrCH}_2\text{CH}_2\text{NCO}$).

Reaction of 1,2-dibromocyclobutane and silver nitrocyana-
mide (5.1 g, 26 mmol) and anhydrous magnesium sulfate (1.0 g) were suspended in anhydrous benzene (20 ml) and stirred under nitrogen. 1,2-Dibromocyclobutane (2.8 g, 12.5 mmol) was added and the mixture was heated at 80°C for 120 h. The removal of inorganic salts and the solvent left an impure isocyanate (1.4 g) as a yellow oil; IR (neat): 2260 (NCO) cm^{-1} . Absolute ethanol (2 ml) with 4 drops of anhydrous pyridine at 65°C for 0.5 h gave a new oil,

1.3 g, which did not contain an isocyanate; IR (neat): 3340 (NH), 1700 (CO) cm^{-1} . Purification by column chromatography (silica gel, elution by a 1:1 mixture of dichloromethane and hexane) gave ethyl 4-bromobuten-3-yl carbamate 22 as a pale yellow liquid, 0.52 g (19%); IR (Neat): 3300 (NH) and 1680 (CO) cm^{-1} ; ^1H NMR (CDCl_3): δ 1.03-1.23 (t, 3, CH_3), 2.10-2.57 (m, 2, CH_2), 3.00-3.36 (m, 2, CH_2), 3.86-4.23 (m, 2, OCH_2), 4.83 (s, 1, NH), 6.00-6.17 (m, 2, $\text{CH}=\text{CH}$); ^{13}C NMR (CDCl_3): δ 156.60 (CO), 134.42, 131.24 ($=\text{CHBr}$), 109.91, 106.39 ($=\text{CH}$), 60.68 (OCH_2), 39.54, 39.21 (CH_2N), 33.37, 30.31 (CH_2), and 14.44 (CH_3); m/z (70 ev): 221, 223 (M^+); anal. calc'd for $\text{C}_7\text{H}_{12}\text{BrNO}_2$: C, 37.86; H, 5.44; N, 6.31; Br 35.98; found: C, 37.82; H, 5.40; N, 7.09; Br, 35.84.

Reaction of 1,2-dibromocyclohexane with silver nitrocyanamide. Silver nitrocyanamide (5.1 g, 26 mmol) and anhydrous magnesium sulfate (1.0 g) were suspended in anhydrous benzene (20 ml) and stirred under nitrogen. trans-1,2-Dibromocyclohexane (6.0 g, 24 mmol) was added and the mixture heated at 80°C for 48 hours. The removal of inorganic salts and solvent left a yellow liquid (4.4 g); IR (neat): 2250 (NCO), 2200 (CN) cm^{-1} . Treatment with absolute ethanol (4 ml) and pyridine (2 drops) at 65°C for 0.5 hour gave an oil, 4.5 g [IR (neat): 3290 (NH), 2200 (CN), and 1680 (CO) cm^{-1}] that afforded two products by flash chromatography. Elution with a mixture (1:1) of dichloromethane and hexane afforded an unidentified material as colorless prisms (2.0 g, 32%), m.p. $65-66^\circ\text{C}$; IR (KBr): 2200 cm^{-1} (CN); ^1H NMR(CDCl_3): δ 1.07-2.67 (m, 8, CH_2), 3.80-4.27 (m, 1, CHBr), 5.20 (br, 1, CHN or CHO); anal. calcd. for $\text{C}_7\text{H}_{10}\text{N}_3\text{O}_2\text{Br}$: C, 33.89; H, 4.06; N, 16.94; Br, 32.21; found: C, 34.51; H, 4.16; N, 15.89; Br, 32.20. Further elution with methanol afforded ethyl N-2-bromocyclohexyl carbamate 23 as a yellow crystalline solid (1.3 g, 22%), m.p. $107-109^\circ\text{C}$.¹⁵ IR (KBr): 3285 (NH) and 1680 (CO) cm^{-1} . ^1H NMR(CDCl_3): δ 1.00-1.53 (t, 3, CH_3); 2.00-2.63 (m, 8, CH_2); 3.43-4.00 (m, 2, CHBr and CHN); 3.87-4.27

(q, 2, OCH₂); 5.27 (s, 1, NH). ¹³C NMR(CDCl₃): δ 155.82 (CO); 60.55 (OCH₂); 56.26, 55.61 (CHBr and CHN); 36.62, 32.98, 25.95, and 24.07 (CH₂); 14.38 (CH₃). M/z (70 ev): 249, 251 (M⁺).

Reaction of silver nitrocyanoamide (26 mmol) and trans-1,2-dibromocyclohexane (12 mmol) also gave a mixture that contained the unidentified solid, C₇H₁₀N₃O₂Br, m.p. 65-66°C and 2-bromocyclohexyl isocyanate (identified as ethyl N-2-bromocyclohexyl carbamate).

Preparation of alkyl nitrocyanoamides: Benzyl bromide (3.4 g, 20 mmol) was added in drops to a solution of silver nitrocyanoamide (4.0 g, 21 mmol) in acetonitrile (15 ml) at 0°C under nitrogen. Immediate precipitation of silver bromide was observed. The mixture was stirred for an hour and filtered. The solvent was removed under vacuum without heating. The residue was triturated in chloroform (50 ml). Unreacted silver nitrocyanoamide was removed by filtration and the clear chloroform solution was concentrated to give 3.2 g (91%) of benzyl nitrocyanoamide 29 (R = C₆H₅CH₂), m.p. 47-48°C; IR (KBr): 2220(C≡N), 1600 and 1270 cm⁻¹ (N-NO₂); ¹H NMR (CDCl₃): δ 7.43 (s, 5, aromatic) and 5.03 (s, 2, CH₂); ¹³C NMR (CDCl₃): δ 130.46, 129.81, 129.15, 128.83 (aromatic), 104.38 (C≡N) and 55.74 (CH₂); m/z = 177 (M⁺); anal calcd. for C₈H₇N₃O₂: C, 54.24; H, 3.95; N, 23.73; found: C, 54.55; H, 3.45; N, 23.85.

p-Xylylene-α,α'-dibromide (2.6 g, 10 mmol) was treated with a solution of sodium nitrocyanoamide (2.2 g, 20 mmol) and silver nitrate (3.4 g, 20 mmol) in acetonitrile (15 ml) for 4 hours to give the bisnitrocyanoamide 30 (2.48 g, 90%), m.p. 88-89°C; IR (KBr): 2220 (C≡N), 1600 and 1270 cm⁻¹ (N-NO₂); ¹H NMR (CDCl₃): δ 7.50 (s, 4 aromatic) and 5.10 (s, 4, CH₂); ¹³C NMR (CDCl₃): δ 132.60, 129.94 (aromatic), 104.38 (NCN) and 55.21 (CH₂); m/z (70 ev) = 276 (M⁺); anal. calcd. for C₁₀H₈N₆O₄: C, 43.48; H, 2.90; N, 30.43; found: C, 43.35; H, 3.01; N, 29.18.

Conversion of alkyl nitrocyanamides to isocyanates: Benzyl nitrocyanamide (1.0 g, 6 mmol) was dissolved in dry benzene (10 ml) and refluxed for 10 hours. Removal of benzene afforded 0.7 g (93%) of benzyl isocyanate. Similarly, refluxing a benzene solution of *p*-xylylene- α,α' -bisnitrocyanamide (1.0 g, 4 mmol) for 2 hours gave *p*-xylylene- α,α' -diisocyanate (0.65 g, 96%); m.p. 43-44°C (lit.¹⁶ m.p. 46°C).

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Table
Isocyanates from Halides and Silver Nitrocyanamide

Halide	Solvent	Temp. °C	Time h	Isocyanate ^a	Yield %	mp, °C or bp, °C (torr) ^b
C ₆ H ₅ CH ₂ Br	C ₆ H ₆	25	24	<u>8</u>	78	65(4) ^c
<u>n</u> -C ₈ H ₁₇ I ^d	C ₆ H ₆	80	20	<u>9</u>	75	60(3.5) ^e
H ₃ COCH ₂ Br	(C ₂ H ₅) ₂ O	35	4	<u>10</u>	84	90(760) ^f
<u>11</u> , X = Br	C ₆ H ₆	80	1	<u>11</u> , X = NCO	81	— ^g
<u>o</u> -C ₆ H ₄ (CH ₂ Br) ₂	C ₆ H ₆	80	3	<u>12</u>	90	— ^h
<u>m</u> -C ₆ H ₄ (CH ₂ Br) ₂	C ₆ H ₆	80	3	<u>13</u>	94	— ⁱ
<u>p</u> -C ₆ H ₄ (CH ₂ Br) ₂	C ₆ H ₆	80	3	<u>14</u>	82	44 ^j
(C ₆ H ₅) ₂ CHBr	C ₆ H ₆	25	15	<u>19</u>	74	148(4) ^k
cyclo-C ₅ H ₉ Br	(C ₂ H ₅) ₂ O	35	4	<u>20</u> ^m	95	— ⁿ
cyclo-C ₆ H ₁₁ Br	C ₆ H ₆	25	24	<u>21</u>	70	58(8) ^p
(C ₆ H ₅) ₃ CCl	C ₆ H ₅ CH ₃	-20	4	<u>2</u> ^q	84	91 ^r
(CH ₃) ₃ CBr	(C ₂ H ₅) ₂ O	25	4	<u>24</u>	63	67(760) ^s
<u>25</u> , X = Br	C ₆ H ₆	25	4	<u>25</u> , X = NCO	89	147 ^t

^a Each isocyanate showed ir absorption near 2260 cm⁻¹(NCO) and was in complete agreement with the structure required by its ¹H NMR data. ^b Values shown were in agreement with literature data cited. ^c Ref. 8. ^d n-Octyl bromide gave comparable results. ^e H. J. Niclas and D. Martin, *Tetrahedron*, 1978, 34, 703. ^f W. J. Kauffman, *J. Org. Chem.*, 1974, 39, 2472. ^g Isolated as the urea 15. See Experimental. ^h Isolated as the cyclic urea 16 and as the urethan 17. See Experimental. ⁱ On isolation from the product mixture the isocyanate as an oil showed IR (neat) at 2260 cm⁻¹ (NCO), NMR (CDCl₃): δ 7.23 (s, 4,

aromatic) and 4.30 (s, 4, CH₂); and m/z (70 eV) at 188 (M⁺). Attempted distillation was unsuccessful [bp 159-162°C (12 torr) reported in Ref. 16]. ^j Mp 46.5°C (Ref.16). ^k J. J. Donleavy and J. English, J. Amer. Chem. Soc., 1940, 62, 218. ^m The isocyanate 20 was isolated by gas chromatography. Attempted purification by distillation resulted in explosions. ⁿ A bp of 145-146°C was reported by D. F. Hayman, V. Petrow, and O. Stephenson, J. Pharm. Pharmacol., 1964, 16, 538. ^p N. Bortnick, L. S. Luskin, M. D. Hurwitz, and A. W. Rytina, J. Amer. Chem. Soc., 1956, 78, 4358. ^q A comparable conversion was carried out in methylene chloride at 0°C for 1 hour. ^r L. W. Jones and C. D. Hurd, J. Amer. Chem. Soc., 1921, 43, 2422. ^s A. Danopoulos, M. Avowin, and S. Peraskewas, Synthesis, 1985, 682. ^t H. Stetter and C. Wulff, Chem. Ber., 1962, 95, 2302.

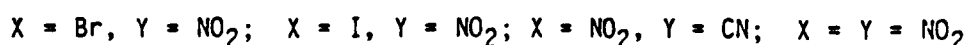
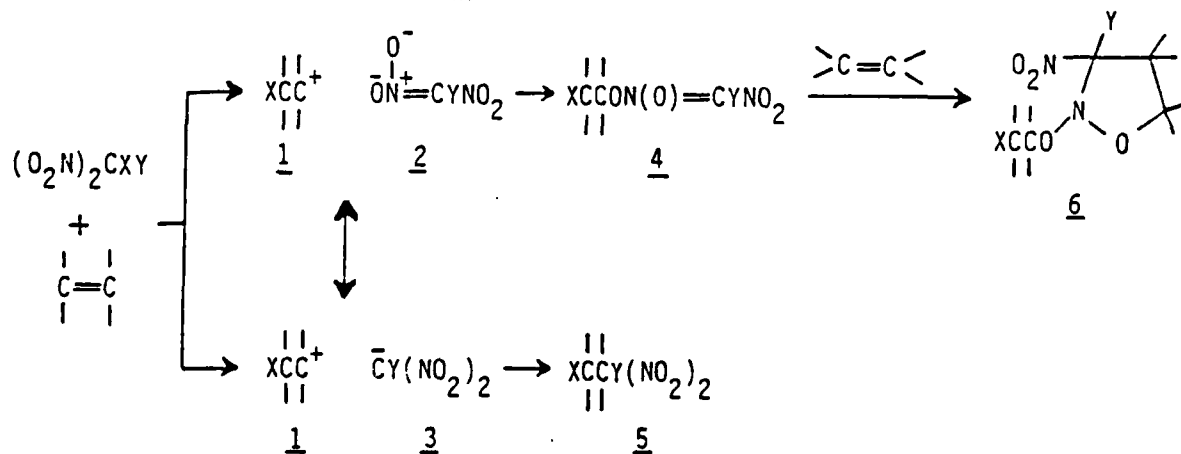
D. Nitrodibromoacetonitrile and Dibromodinitromethane
in Reactions with Nucleophiles

Joseph H. Boyer,* Thanikavelu Manimaran and Robert T. Patterson,
Department of Chemistry, University of New Orleans, New Orleans, LA 70148

Abstract. In dichloromethane nitrodibromoacetonitrile (NDBA) converted (a) tetramethylethylene to 2,3-dibromo-2,3-dimethylbutane (42%) and 3-cyano-4,4,5,5-tetramethylisoxazol-2-in-2-oxide (45%); (b) dimethyl sulfide to dimethylsulfonium cyanonitromethylide (80%); (c) tetrahydrothiophene to tetramethylenesulfonium cyanonitromethylide (54%); (d) anthracene to 9,10-dibromoanthracene (65%); and (e) phenol to 4-bromophenol (46%). NDBA converted (a) triethylamine in carbon tetrachloride to triethylamine hydrobromide (45%) and triethylammonium cyanonitromethylide (5%); (b) cyclohexene (solvent) to di-(2-bromocyclohexyl)nitroacetonitrile (9%); (c) cupric acetylacetonate in acetone to cupric bromoacetylacetonate (56%); and (d) benzene (solvent) in the presence of copper powder to benzoyl cyanide (28%), also obtained (97%) under similar conditions from phenylnitroacetonitrile. In dichloromethane dibromodinitromethane (DBDNM) and tetramethylethylene gave 2,3-dibromo-2,3-dimethylbutane (40%) but norbornene gave 2-bromo-3-nitrosonorbornane isolated as the dimer (25%). Treatment with DBDNM in acetonitrile followed by hydrolysis transformed tetramethylethylene to 3-aza-5-bromo-1,1-dinitro-2,4,4,5-tetramethylhexene (low yield); (d) norbornene to 3-bromo-3a,4,5,6,7,7a-hexahydro-4,7-methano-1,2-benzisoxazole-2-oxide (25%) (tentative assignment); (e) norbornadiene to 3-bromo-3a,4,7,7a-tetrahydro-4,7-methano-1,2-benzisoxazole-2-oxide (29%) (tentative assignment); (f) 2-methylthiophene to 2-bromo-5-methylthiophene (67%); and (g) 2,5-dimethylthiophene to 3-bromo-2,5-dimethylthiophene (78%). DBDNM with (a) potassium hydroxide gave potassium bromo-

nitromethanenitronate (76%) and (b) sodium sulfite in aqueous sodium carbonate gave sodium nitromethanenitronate (89%). Nitrocyanocarbene was a proposed intermediate in the reactions of NDBA with tetramethylethylene and with benzene.

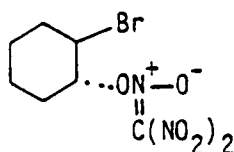
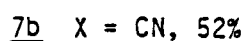
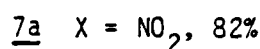
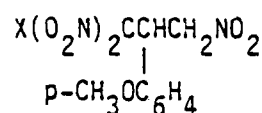
Introduction. Nucleophilic abstraction of a "positive" substituent from bromotrinitromethane (BTM),¹ iodotrinitromethane (ITM),² trinitroacetonitrile (TNA),³ and tetranitromethane (TNM)⁴ by an alkene led to the formation at ambient temperature of nitronate esters 4 and/or polynitro compounds 5.⁵ To avoid thermolysis on formation each nitronate ester 4 was converted to an isoxazolidine derivative 6 by a dipolar addition with the alkene present in excess.^{4,5} The isomers 4 and 5 were recognized as products from the collapse of a proposed ion pair intermediate 1, $2 \leftrightarrow 1$, 3. Charge localization in a carbonium ion 1 correlated with O-alkylation to give nitronates and delocalization correlated with C-alkylation to give polynitro compounds.⁴ These reactions were believed to proceed without radical intermediates since there was no effect on product formation in the presence of radical initiators and a dependence on solvents of high polarity was observed in certain examples.^{1,4} The cage pathway leading to polynitroalkanes 5 does not necessarily detract from the generalization that C-alkylation of a discrete α -nitrocarbanion proceeded by a radical chain ($S_{RN}1$)^{6a-d} or non-chain^{6e} mechanism.



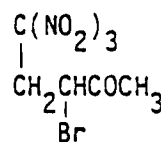
eq(1)

TNM and TNA gave C-alkylation adducts 7a and 7b with *p*-methoxystyrene. The nonplanar trinitromethide anion 3 ($Y = \text{NO}_2$) was more efficient than the planar dinitrocyanomethide anion 3 ($Y = \text{CN}$).^{3b,4e} It was also shown that addition of the more nucleophilic trinitromethide anion to methyl acrylate occurred under conditions whereby the dinitrocyanomethide anion failed to react with the unsaturated ester. Diminished nucleophilicity in the latter anion was attributed to more extensive *p*-electron delocalization than was characteristic of the non-planar trinitromethide anion.⁷

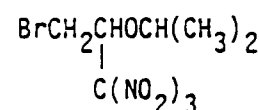
BTM with cyclohexene gave *trans*-2-bromocyclohexyldinitromethanenitronate 8 (84%)¹ via an O-alkylation pathway but methylvinylketone gave 3-bromo-5,5,5-trinitropentan-2-one 9 and isopropylvinyl ether gave isopropyl α -trinitromethyl- β -bromoethyl ether 10 via C-alkylations.⁸ ITM and an alkene reacted only by an O-alkylation pathway.²



8



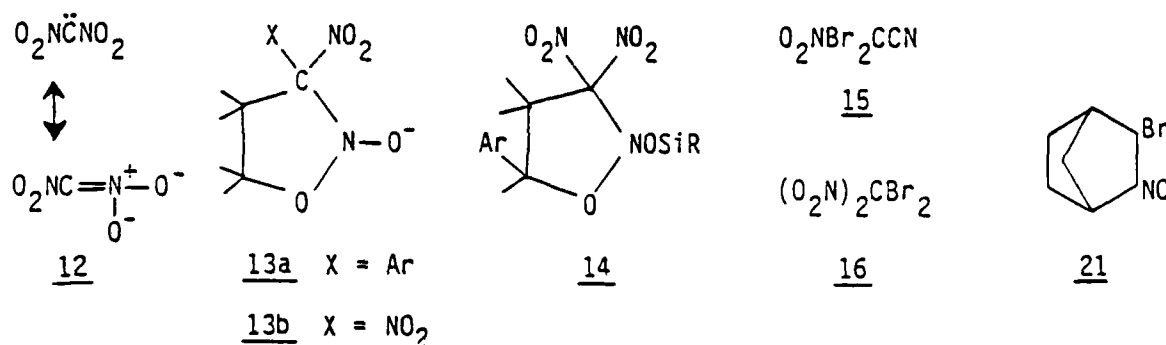
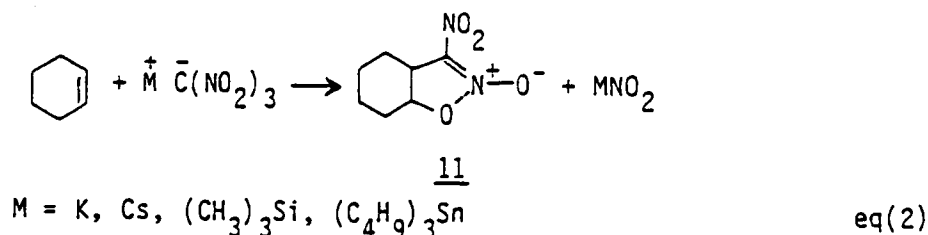
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10

Certain metal trinitromethide salts treated with alkyl and aryl alkenes in aprotic solvents at 20-50°C gave nitroisoxazoline-N-oxides in low yields, *e.g.*, cyclohexene afforded 3-nitro-4,5-tetramethyleneisoxazol-2-in-2-oxide 11, eq(2).^{5,9} Other polynitromethide salts gave similar reactions.^{5,10} The intermediacy of dinitrocarbene 12 was considered;⁹ however, it was not established that ejection of the elements of the metal nitrite occurred prior to the formation of the heterocycle. Isoxazolidine-N-oxy anions 13a were proposed intermediates from the addition of aryl nitromethanenitronate anions to alkenes^{10a} and a similar anion 13b was a proposed intermediate from an alka-

line hydrolysis of a silyl ether 14.^{10b} Each anion 13a,b with sodium, or potassium, or other "hard" counterions thermolysed preferentially to an isoxazoline along with a metal nitrate and none or trace amounts of the isoxazoline-N-oxide along with a metal nitrite, the preferred product pair when the counterion was silver, a "soft" cation.^{10a} That it is unlikely for an anion 13b to be a precursor to products in eq(2) and related reactions between alkenes and "hard" metal dinitromethanenitronates strengthens the case for the intermediacy of a dinitrocarbene 12. The generality of the formation of isoxazoline-N-oxides from "hard" metal dinitromethanenitronates and alkenes under ambient conditions tends to preclude the intervention of the anion 2 as a discreet intermediate in reactions between an alkene and covalent derivatives of polynitromethane, eq(1), where the formation of isoxazoline-N-oxides have so far not been detected.

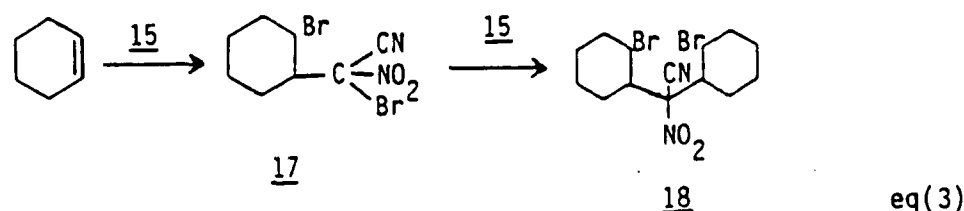


The present investigation was undertaken to (a) find an example of an isoxazoline-N-oxide from an alkene and a dihalo derivative of a covalent

nitromethane, (b) to investigate reactions between dihalonitromethanes and nucleophiles, and (c) to defend the intermediacy of nitrocarbenes in certain reactions.

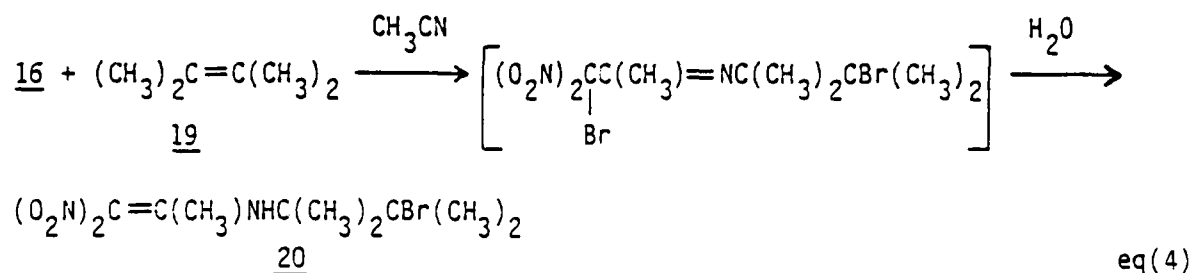
Results and Discussion.¹¹ One or both bromo groups were abstracted from nitrodibromoacetone nitrile 15 (NDBA) and dibromodinitromethane 16 (DBDNM) by a variety of nucleophilic reagents in this survey of olefins, aromatic compounds, amines, sulfides, nitroacetone nitrile, and various inorganic anions.

A simple adduct (1:1) between an alkene and either NDBA 15 (from the ammonium salt of nitroacetone nitrile and bromine)¹² or DBDNM 16 (from 2,4,6-tribromoaniline and nitric acid)^{13,14} was not found; however, such an adduct 17 was assumed for the ultimate formation of the adduct (2:1), di-(2-bromocyclohexyl)nitroacetone nitrile 18 (9%) (stereochemistry unknown), from cyclohexene and NDBA by a C-alkylation pathway, eq(3). The proposed structure 18 was compatible with its elemental analysis, molecular weight determination and ν_{as} 1550 and ν_s 1390 cm^{-1} (NO_2). Thermolysis of a nitronate ester produced by a competitive O-alkylation was assumed to account in part for the intractable portion of the product mixture. A resistance to a dipolar addition of this nitronate ester to cyclohexene to form a stable N-alkoxyisoxazolidine, 6, was comparable to an inefficient addition (18%) of cyclohexene to the nitronate ester that was obtained from the olefin and TNM.^{4a,b}



C-Alkylation led to a unique adduct (1:1:1) in low yield from the combination of DBDNM 16, tetramethylethylene 19, and acetonitrile (solvent). It was isolated as 3-aza-5-bromo-1,1-dinitro-2,4,4,5-tetramethylhex-1-ene 20

after adventitious hydrolytic replacement of a "positive" bromine with a hydrogen atom, eq(4). The structure of the azahexene 20 was confirmed by an X-ray crystallographic analysis.* Further investigation is needed to determine the reaction parameters.



The formation of the bromonitroso derivative 21, isolated as a known dimer,¹⁵ from DBDNM and norbornene in dichloromethane represented a reaction not detected from other alkenes similarly tested with DBDNM. A proposed isomerization of DBDNM to a nitrite ester, $\text{Br}_2\text{C}(\text{NO}_2)\text{ONO}$, would afford nitrosyl bromide (by a 1,2-elimination) needed for reaction with the olefin in the usual manner. Nitrosations by bromotrinitromethane¹ and tetranitromethane⁴ (see below) can be rationalized by a similar isomerization and dissociation to a nitrosyl derivative.

The assumption that an isoxazoline-N-oxide could be produced in a reaction between an olefin and a halonitromethane, presumably via an onium nitromethide salt was dependent on a nitromethide anion with severely limited ability to undergo C- and/or O-alkylation by the counterion and consequently an opportunity to combine with the olefin (electron rich) to give the heterocycle along with an ejection of an inorganic anion. Nitrodibromoacetonitrile (NDBA) 15 was chosen for investigation since the corresponding cyanonitrobromomethide anion 3 ($\text{Y} = \text{CN}$) was assumed to be planar and weakly nucleophilic as

* We are indebted to Dr. E. D. Stevens and Dr. C. Stevens for the X-ray analysis. The data will be published elsewhere.

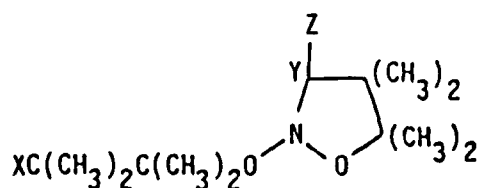
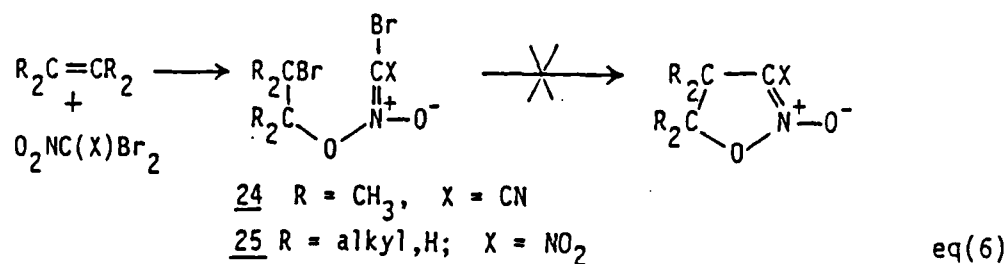
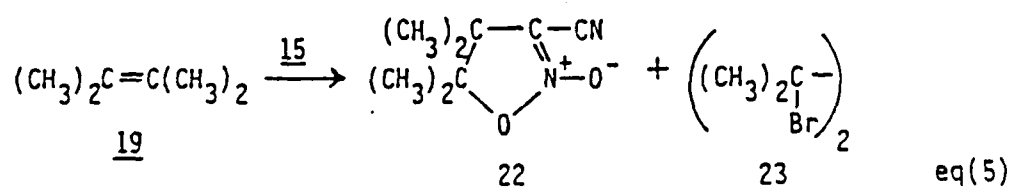
a consequence of the replacement of a nitro group in the cyanodinitromethide anion (planar and weakly nucleophilic)⁷ with the stereo-comparable bromo group. A consideration of electron rich symmetrically substituted alkenes capable of abstracting not only the "positive" bromine from NDBA but also subsequently accepting an ejected bromide anion led to the successful choice of tetramethylethylene.

Tetramethylethylene 19 (2 moles) and NDBA 15 in dichloromethane at 25°C gave 3-cyano-4,4,5,5-tetramethylisoxazol-2-in-2-oxide 22 (45%) and 2,3-dibromo-2,3-dimethylbutane 23 (42%), eq(5). The structure of the new heterocyclic compound 22 was confirmed by an x-ray crystallographic analysis.[#] An explanation for the formation of the heterocycle 22 by cyclization from a nitronate ester 24, a hypothetical adduct from NDBA and the olefin 19, was considered unlikely since similar cyclizations from β -bromoalkylnitronates 25, known adducts from trinitrobrromomethane and olefins,¹ were not observed, eq(6), e.g., 8 $\rightarrow$ 11. Support for the intermediacy of the nitronate ester 24 in eq(5) was further diminished by the failure to detect the formation of an isoxazolidine derivative 26a, the dipolar adduct from the alkene 19 and the ester 24. A comparable adduct 26b, was obtained^{4b} from the olefin 19 and the ester $\text{O}_2\text{NC}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{ON}(\text{O})=\text{C}(\text{NO}_2)_2$.

That the formation of neither the heterocycle 22 nor the dibromide 23 proceeded from a radical precursor was shown by a lack of inhibition in product formation by the added presence of either di-tert-butylnitroxide or tetracyanoethylene (radical scavengers), an observation supported by an absence of a CIDNP signal for the reaction, eq(5). It is proposed that the re-

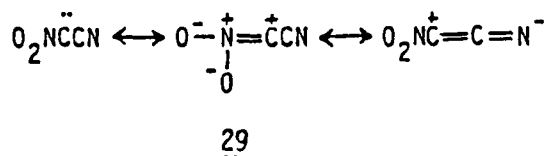
[#] We are indebted to Dr. R. Gilardi and Dr. C. George, Naval Research Laboratory, Washington, D.C. for the X-ray analysis. The data will be published elsewhere.

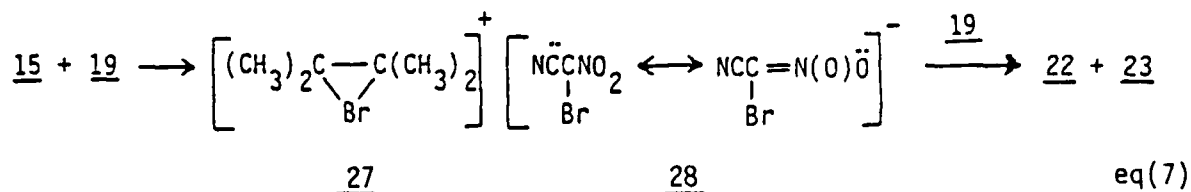
action proceeded through the formation of a bromonium methide 27/28 as an ion pair. The formation of the heterocycle 22 and the dibromide 23 was attributed to a straightforward interaction between the intermediate and the olefin 19, eq(7), without differentiation between concerted and stepwise pathways that required additional intermediates. In a preferred explanation the intermediate 27/28 produced the dibromide 23 and nitrocyanocarbene 29; the latter, either on formation or subsequently, added to the olefin 19 to produce the heterocycle 22, eq(8). It is anticipated that the isoxazoline-N-oxide 22 will also be produced by a reaction between tetramethylethylene and bromodinitroacetonitrile, $(\text{O}_2\text{N})_2\text{C}(\text{Br})\text{CN}$; ¹⁶ an investigation is planned.



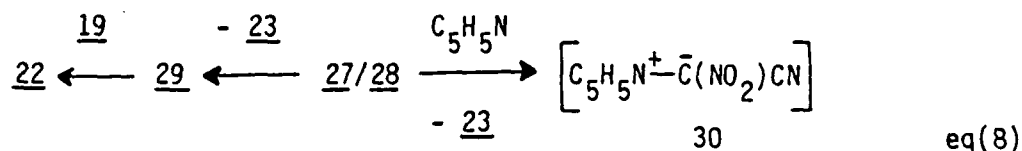
26a X = Y = Br, Z = CN

26b X = Y = Z = NO₂

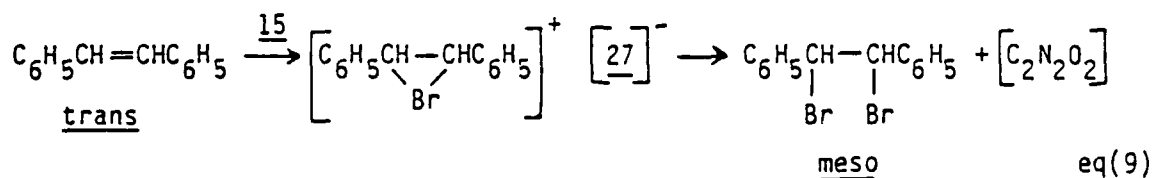




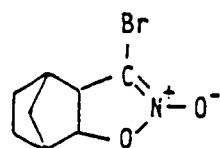
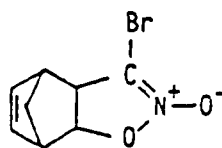
Support for the proposed intermediate 27/28 was found in the complete suppression of the formation of the heterocycle 22 and no effect on the formation of the dibromide 23 by the added presence of pyridine in the reaction mixture. It was assumed that pyridine converted the intermediate to the dibromide 23 and pyridinium nitrocyanomethylide 30, however the latter was not detected in the complex product mixture, eq(8).



Although alkylation was not detected in the conversion of *trans*-stilbene to *meso*-1,2-dibromo-1,2-diphenylethane¹⁷ (10%) by treatment with NDBA, a rationale for the reaction was based on the intermediacy of a bromonium nitrocyanomethylide salt. A dissociation of the intermediate anion 28 would provide a bromide anion required to combine with the bromonium cation for product formation; however, the remainder of the intermediate methide anion was not accounted for, eq(9). Previously reported formations of 1-nitro-2-nitroso-1,2-diphenylethane (85%) from a neat mixture of stilbene and TNM and 1-nitro-2-nitrosocyclohexane (3%) from cyclohexene and TNM probably proceeded from similar intermediates.^{4,5} NDBA was unreactive to both *diphenyl-* and *dimethylacetylene* but reacted with *bis*-triethylsilylacetylene to give an intractable mixture.

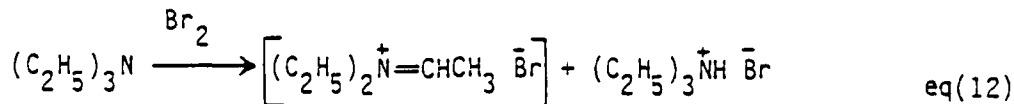
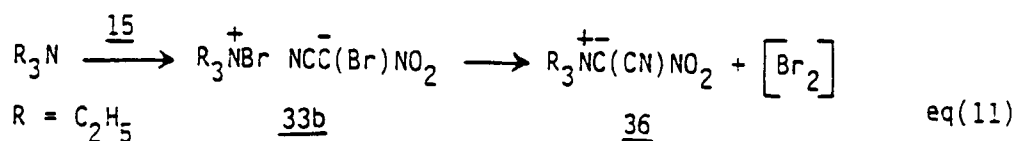
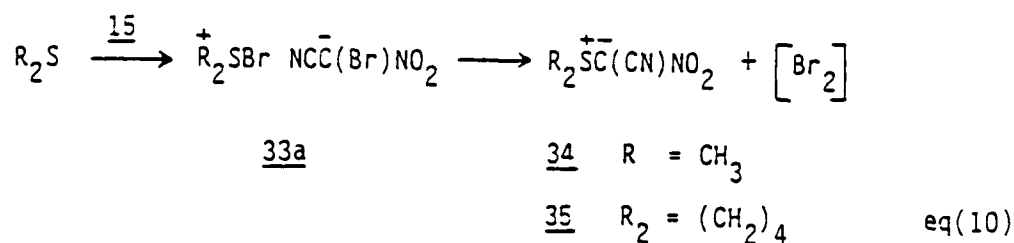


An amorphous solid product $\text{C}_8\text{H}_{10}\text{NO}_2\text{Br}$ was obtained from norbornene and DBDNM 16 in acetonitrile and a similar product $\text{C}_8\text{H}_8\text{NO}_2\text{Br}$ was obtained from norbornadiene and DBDNM in dichloromethane. The products were tentatively assigned the structures of bromoisoxazoline-N-oxides 31 and 32 on the basis of spectroscopic and analytical data. Further investigation of an unexpected preference for the loss of a nitro and a bromo substituent rather than two bromo substituents from DBDNM is needed since halodinitro anions at 0 - 5°C lost halide anions in preference to nitrite anions.^{5,18} No other products in the complex reaction mixtures were isolated. In dichloromethane the olefin 19 was converted by DBDNM to the dibromide 23 but other alkenes with DBDNM gave intractable mixtures.

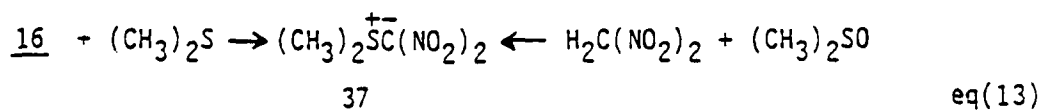
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A variety of nucleophiles reacted with NDBA and DBDNM. Dimethyl sulfide (2 equivalents) and NDBA 15 in methylene chloride at 0°C for 30 minutes gave a high yield of dimethylsulfonium nitrocyanomethylide 34, previously obtained from nitroacetonitrile and dimethyl sulfoxide.¹⁹ Tetrahydrothiophene gave tetramethylenesulfonium nitrocyanomethylide 35 by similar treatment eq(10). An excess of triethyl amine in benzene or carbon tetrachloride reacted with NDBA 15 to give triethylammonium nitrocyanomethylide 36

in low yield and triethylammonium bromide, eq(11,12). It is proposed that these reactions proceeded from intermediate onium methides 33a,b, eq(10,11). The formation of triethylammonium bromide from triethylamine and bromine, eq(12) was previously reported.²⁰ Attempts to liberate and capture nitro-cyanocarbene 12 from its adduct 34 by treatment with dimethoxy disulfide²¹ were unsuccessful.

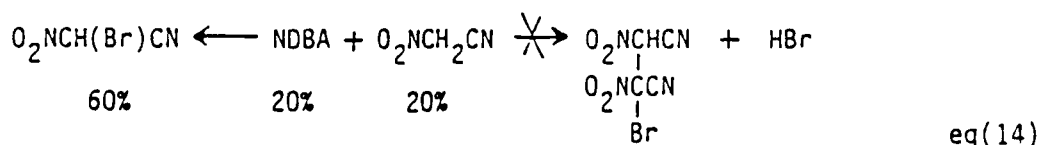


DBDNM 16 and dimethyl sulfide in dichloromethane gave dimethylsulfoniumdinitromethylide 37, a product previously obtained from dinitromethane and dimethylsulfoxide, eq(13).¹⁹

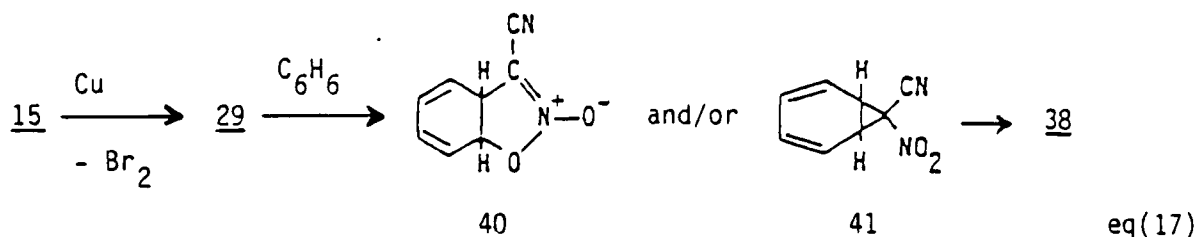
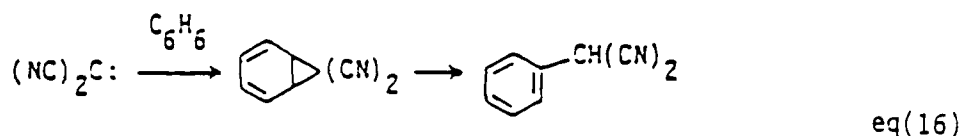
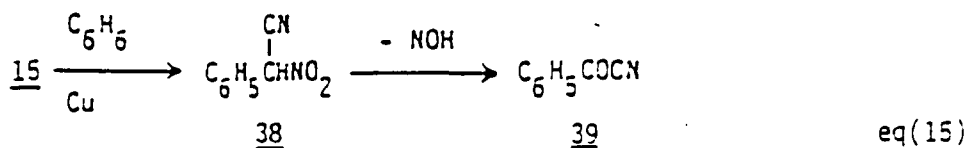


A mixture (3:1:1 shown by silica-gel gc) of bromonitroacetonitrile (δ 6.66), nitroacetonitrile¹² (δ 5.54), and NDBA was obtained on mixing equimolar portions of the latter two compounds in dichloromethane at 25°C, eq(14). Insofar as the formation of a dinitrodicyanobromoethane by C-alkylation failed to occur the reaction was assumed to be ionic rather than radical in nature.^{3,6} This reaction was seen as an extension of the bromination of polynitroalkanes

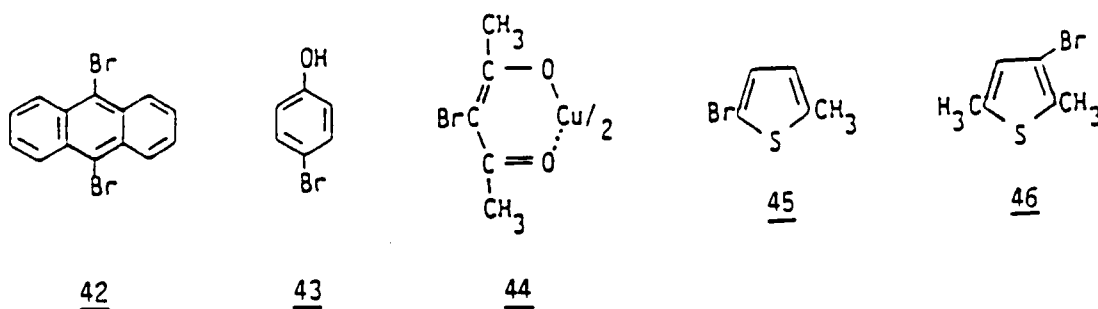
(RC(NO₂)₂H) by various bromodi- and trinitromethane derivatives including DBDNM.¹⁴



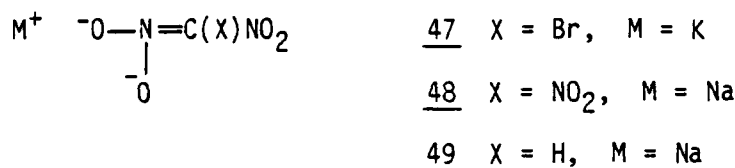
Aromatic compounds also reacted with the dibromides 15 and 16. Although a trace of benzoyl cyanide 39²² was detected in the reaction mixture, NDBA 15 tended to be unreactive to benzene at 80°C for 20 hours and was recovered (80%). A more efficient formation of the cyanide 39 was brought about by the added presence of copper, eq(15). The proposed intermediacy of phenyl-nitrocyanomethane 38 was supported by an independent quantitative conversion of compound 38 under similar conditions to the acyl cyanide 39. The conversion 38 → 39 is reminiscent of the facile thermolysis of an aryl bromonitroacetone nitrile, ArC(NO₂)BrCN, to the acyl cyanide, ArCOCN.²³ It was suggested that these α-nitronitriles underwent initial isomerization to a nitrite ester, ArC(ONO)XCN (X = H, Br) and that the cyanide 39 was produced by an elimination of nitroxyl, eq(15), whereas an elimination of nitrosyl bromide from ArC(ONO)-BrCN occurred. The isomerizations of α-nitronitriles to nitrite esters were described as radical processes.^{24,25} Copper promoted debromination of the dibromide 15 afforded an interaction with benzene to produce a formal adduct from cyanonitrocarbene. Since dicyanocarbene (from dibromodicyanomethane and copper) reacted with benzene by addition to an unsaturated bond rather than by direct insertion into a CH bond, eq(16),²⁶ it is proposed that nitrocyanocarbene and benzene gave a dihydrocyanobenzisoxazole oxide 40 and/or the isomeric norcaradiene 41 initially; however, the formation of intermediate 38 by an isomerization of adducts 40 and/or 41 has not been differentiated from formation by direct insertion of the carbene into a benzene CH bond, eq(17).



Anthracene and phenol underwent typical aromatic brominations at ambient temperatures to give 9,10-dibromoanthracene 42²⁷ and 4-bromophenol 43²⁸ on treatment with NDBA 15. In a similar reaction NDBA converted cupric acetylacetonate to its bromo derivative 44. Bromination of 2-methyl- and 2,5-dimethylthiophene by treatment with DBDNM 16 in acetonitrile gave the 5-bromo-45^{29,30} and the 3-bromo-46^{31,32} derivatives. The mild conditions required for aromatic bromination (assumed to be ionic) by NDBA and DBDNM are reminiscent of those required for tetranitromethane to form charge transfer complexes with electron rich olefins and certain aromatic compounds.¹ Only upon irradiation did the latter give nitroaromatic derivatives.³³



Alcoholic potassium hydroxide converted DBDNM 16 to the potassium salt 47 of bromodinitromethane^{34,35} in a reaction related to the conversion of tetranitromethane in sodium hydroxide to the sodium salt 48 of nitroform.³⁶ These results suggest that "positive" bromine was abstracted by the hydroxide anion in preference to a "positive" nitro group. In a related reaction sodium sulfite in a mixture of dichloromethane and water converted DBDNM 16 to the sodium salt 49 of dinitromethane.^{37,38}



Experimental

Instruments included Pye-Unicam SP 200 IR, Varian A-60 and JEOL FX 90 Q NMR, and Hatachi R MU-6 mass spectrometers. Elemental analyses were obtained from Micro-Tech Laboratories, Skokie, Il. NDBA,¹² DBDNM,¹³ and phenyl-nitroacetonitrile³⁹ were obtained by reported methods. Freshly precipitated copper powder⁴⁰ was used. The following starting materials were commercially available: anthracene; cupric acetylacetonate; cyclohexene; dimethyl sulfide; 2,5-dimethylthiophene; indene; 2-methylthiophene; norbornadiene; norbornene; phenol; tetrahydrothiophene; tetramethylethylene; and triethylamine.

Di-(2-bromocyclohexyl)nitroacetonitrile 18. A solution of NDBA 15 (12.2 g, 50 mmol) in an excess of cyclohexene (50 ml) was stirred overnight at 25°C. The mixture was concentrated to give the adduct 18 (1.9 g, 9%) as a colorless solid, mp 198-99°C (dec), IR (KBr): 1550, and 1390 cm⁻¹ (NO₂); ¹H NMR (CDCl₃): δ 1.3-2.5 (m, 18 H) 4.3 (m, 1 H) and 4.8 (m, 1 H); m/e (70 eV): 408 (M⁺); anal. calcd. for C₁₄H₂₀N₂O₂Br₂: C, 41.21; H, 4.90; N, 6.87; Br, 39.17; found: C, 41.00; H, 5.06; N, 6.90; Br, 39.25.

3-Aza-5-bromo-1,1-dinitro-2,4,4,5-tetramethylhex-1-ene 20. A solution from DBDNM 16 (1.7 g, 6.4 mmol) in acetonitrile (3 ml) added to tetramethylethylene 19 (1.6 g, 19.0 mmol) in acetonitrile (7 ml) was stored 2.5 h. The solvent was removed to leave a yellow solid (0.22 g) after trituration with cyclohexane/-benzene (1/1). Chromatography of the mother liquor through silica gel (15 g) gave an additional yellow solid (0.1 g). Recrystallization of the combined solids from cyclohexane/benzene/dichloromethane (3/2/6) gave the olefin 20 as a yellow crystalline solid, 0.35 g, mp 140-141°C (dec); ¹H NMR (CDCl₃): δ 1.68 (s, 2 CH₃), 1.93 (s, 2 CH₃), 2.4 (s, 1 CH₃); ¹³C NMR: δ 16.78, 24.98, 29.92, 66.47, 75.83, 144.89, 154.52; IR (KBr): 1520 and 1350 cm⁻¹ (NO₂); m/e, 70 eV (%): 311(3) and 309(3) for (C₉H₁₆N₃O₄Br)⁺, 230(10) (C₉H₁₆N₃O₄)⁺ 188(100), 165(25) and 163(26) for (C₆H₁₂Br)⁺, 142(68), 125(49), 100(26), 84(50), 83(74): anal calcd for C₉H₁₆N₃O₄Br: C, 34.85; H, 5.21; N, 13.55; O, 20.63; found: C, 34.63; H, 5.11; N, 13.38; O, 20.44.

2-Bromo-3-nitrosobicyclo[2.2.1]heptane 21. To a solution of norbornene (1.5 g, 16.0 mmol) in dichloromethane (7 ml) at 10°C was added DBDNM 16 (1.0 g, 3.8 mmol) and dichloromethane (3 ml). After 22 hr at room temperature, the solvent was removed and a solid (0.4 g) precipitated on tritulating the residue with benzene. Recrystallization from a mixture of dichloromethane and ethanol (2/3) gave the dimer of the nitroso compound 21 (0.2 g, 25%); mp 143-144°C (lit.¹⁵ mp 138-139°C); ¹H NMR (CDCl₃): δ 1.18 - 2.2 (m, 6 H), 2.5 (bs, 1 H), 2.76 (bs, 1 H), 4.4 (m, 1 H), 4.87 (m, 1 H); ¹³C NMR (CDCl₃): δ 26.5, 27.1, 35.8, 39.7, 46.1, 54.0, 73.6; m/e, 70 eV (%): 206 (4) and 204 (4) for (C₇H₁₀NOBr)⁺, 175 (53) and 173 (55) for (C₇H₁₀Br)⁺, 121 (8) and 119 (9) for (C₃H₄Br)⁺, 66 (100) for (C₅H₆)⁺.

3-Cyano-4,4,5,5-tetramethylisoxazol-2-in-2-oxide 22 and 2,3-dibromo-2,3-dimethylbutane 23. To a stirred solution of NDBA 15 (4.9 g, 20 mmol) in methyl-ene chloride (20 ml) at 25°C a solution of 2,3-dimethylbut-2-ene 19 (3.4 g, 40 mmol) in dichloromethane (30 ml) was added dropwise. Stirring was continued for 30 minutes, solvent was removed, and the residue was chromatographed over neutral alumina. Hexane (3 X 100 ml) eluted 2,3-dibromo-2,3-dimethylbutane 23, 2.1 g (42%), mp 168-169°C (dec)²⁰ after recrystallization from hexane. The same solvent (4 X 100 ml) then eluted 3-cyano-4,4,5,5-tetramethylisoxazol-2-in-2-oxide 22, 1.5 g (45%), mp 68-69°C after recrystallization from hexane; IR (KBr): 2220 (C≡N), 1605, and 1350 cm⁻¹; ¹H NMR (CDCl₃): δ 1.31 (s, CH₃) and 1.44 (s, CH₃); ¹³C NMR (CDCl₃): δ 109.69 (C-3), 103.53 (CN), 90.84 (C-5), 48.79 (C-4), 21.08 (CH₃ at C-5), 20.72 (CH₃ at C-4); m/e (70 eV)(%): 168 (M⁺, 36); anal. calcd. for C₈H₁₂N₂O₂: C, 57.14; H, 7.14; N, 16.67; found: C, 56.62; H, 7.29; N, 16.54. There was no change in the reaction when methylene chloride as solvent was replaced by benzene or cyclohexane. 2,3-Dibromo-2,3-dimethylbutane 23 was obtained from a solution of 2,3-dimethyl-2-butene 19 (1.6 g, 19.0 mmol) in dichloromethane when treated with DBDNM 16 (1.7 g, 6.4 mmol) in dichloromethane (3 ml). After 142 hr at room temperature solvent was removed to give an oil, 2.1 g, eluted by benzene from a column of silica gel (35 g) to give 2,3-dibromo-2,3-dimethylbutane 23, 0.63 g (40%).

3-Bromo-3a,4,5,6,7,7a-hexahydro-4,7-methano-1,2-benzisoxazole-2-oxide 31. A solution of norbornene (1.5 g, 16.0 mmol) in acetonitrile (5 ml) was cooled to 14°C and DBDNM 16 (1.0 g, 3.8 mmol) was added over 2 minutes followed by more acetonitrile (5 ml). After storage for 3 hr at 14°C the solvent was removed and the oil was eluted by benzene (150 ml) and ethyl acetate/benzene (1:3) (200 ml) from a column of silica gel (30 g) to give the heterocycle 31 as a colorless solid, 0.22 g, (25%), mp 140-141°C; ¹H NMR (CDCl₃): δ 1.2 - 1.7 (m,

6 H), 2.5 - 2.7 (m, 2 H), 3.3 (m, 1 H), 4.70 (m, 2 H); ^{13}C NMR (CDCl_3): δ 22.6, 26.4, 32.1, 39.5, 41.9, 55.5, 81.4, 98.0; m/e, 70 eV (%): 233(8) and 231(9) for $(\text{C}_8\text{H}_{10}\text{NO}_2\text{Br})^+$, 67(100) $(\text{C}_5\text{H}_7)^+$; anal. calcd. for $\text{C}_8\text{H}_{10}\text{NO}_2\text{Br}$: C, 41.40; H, 4.35; N, 6.04; Br, 34.43; found: C, 41.40; H, 4.37; N 5.97; Br, 34.86.

3-Bromo-3a,4,7,7a-tetrahydro-4,7-methano-1,2-benzisoxazole-2-oxide 32. To a solution of norbornadiene (2.0 g, 22 mmol) in dry acetonitrile (10 ml) at 10°C DBDNM 16 (1.0 g, 3.8 mmol) in dry acetonitrile (5 ml) was added over 3 minutes. After one hr solvent was removed to give an oily residue (1.9 g). Flash chromatography on silica gel (30 g) with benzene/ethyl acetate (70/30) gave a yellow oil (0.8 g) that gave a solid (0.5 g), m p $65-67^\circ\text{C}$, after another chromatographic separation with benzene/diethyl ether (95/5). Recrystallization from dichloromethane/heptane (1:1) gave the heterocycle 32 as a colorless solid, 0.25 g, (29%), mp $75-76^\circ\text{C}$; ^1H NMR (CDCl_3): δ 6.1 (m, 2 H), 4.6 (d, 1 H.), 3.2 (m, 3 H), 1.7 (m, 2 H); ^{13}C NMR (CDCl_3): δ 42.5, 45.3, 48.5, 53.2, 79.7, 98.2, 133.9, 139.2; m/e, 70 eV (%): 231 (3) and 229 (3) for $(\text{C}_8\text{H}_8\text{NO}_2\text{Br})^+$, 214 (4) and 212 (4) for $(\text{C}_7\text{H}_3\text{NO}_2\text{Br})^+$, 202 (8) and 200 (8) for $(\text{C}_6\text{H}_3\text{NO}_2\text{Br})^+$, 133 (5), 123 (7) and 121 (5) for $(\text{C}_2\text{H}_2\text{OBr})^+$, 105 (15), 104 (17), 91 (24), 66 (100) for $(\text{C}_5\text{H}_6)^+$; anal-calcd for $\text{C}_8\text{H}_8\text{NO}_2\text{Br}$: C, 41.76; H, 3.51; N, 6.09; Br 34.73; found: C, 41.72; H, 3.62; N, 6.07; Br, 34.90.

E-1,2-Dibromoindane. To a solution (50°C) of freshly distilled indene (1.5 g, 12.9 mmol) in acetonitrile (10 ml) was added DBDNM 16 (1.7 g, 6.4 mmol) in acetonitrile (2 ml). After 48 hr the solvent was removed to give an oil, 3.2 g, extracted (4 X 15 ml) with cyclohexane/benzene (9:1). The combined extracts were filtered through silica gel (10 g) washed with additional solvent (100 ml) to give an oil mixture (0.5 g). Further elution by cyclohexane from

silica gel (70 g) gave an oil, 0.44 g (25%); ^1H NMR (CDCl_3): δ 3.16 (d, 1 H, $J = 17$), 3.76 (dd, 6 H, $J = 17$), 4.82 (d, 1 H, $J = 5$), 5.59 (bs, 1 H), 7.26 (m, 4 H); ^{13}C NMR (CDCl_3): δ 41.36, 54.37, 57.69, 125.32, 125.64, 127.85, 129.61, 140.47; m/e , 70 eV (%): 197(16) and 195(17) for $(\text{C}_9\text{H}_8\text{Br})^+$, 116(100) $(\text{C}_9\text{H}_8)^+$. The product is assumed to be 1,2-dibromoindane.

Dimethylsulfonium cyanonitromethylide 34. To a stirred solution of dimethyl sulfide (2.5 g, 40 mmol) in methylene chloride (20 ml) at 0-5°C a solution of NDBA 15 (4.9 g, 20 mmol) in methylene chloride (50 ml) was added dropwise. Stirring at 0-5°C was continued for 30 minutes. Precipitated dimethylsulfonium cyanonitromethylide 34, 2.7 g (80%) recrystallized from hot water as a colorless solid, mp 213-214°C (dec),¹⁹ IR (KBr): 2200 ($\text{C}\equiv\text{N}$), 1400, and 1295 cm^{-1} (NO_2).

A similar reaction with tetrahydrothiophene gave tetramethylenesulfonium cyanonitromethylide 35 (54%), mp 166-167°C (dec) after recrystallization from hot water; IR (KBr): 2200 ($\text{C}\equiv\text{N}$), 1395, and 1300 cm^{-1} (NO_2); ^1H NMR (CDCl_3): δ 2.1-2.7 (m) and 3.4-3.8 (m); anal. calcd. for $\text{C}_6\text{H}_8\text{N}_2\text{O}_2\text{S}$: C, 41.86; H, 4.65; N, 16.28; S, 18.60; found: C, 41.32; H, 4.78; N, 16.34; S, 18.64.

Triethylammonium cyanonitromethylide 36. A solution of triethylamine (4.0 g, 40 mmol) in carbon tetrachloride (25 ml) was added dropwise to a stirred solution of NDBA 15 (2.4 g, 10 mmol) in carbon tetrachloride at 25°C. The solvent was removed and the residue was triturated with acetone (20 ml), separated by filtration, and triturated with methylene chloride (25 ml) to give the methylide 36 as a colorless solid (90 mg, 5%), mp 154-155°C (dec); IR (KBr): 2200 ($\text{C}\equiv\text{N}$), 1420 (NO_2), 1330 cm^{-1} (NO_2); ^1H NMR: δ 1.50 (t, 9, CH_3), 3.17 (q, 6, CH_2); anal. calcd. for $\text{C}_8\text{H}_{15}\text{N}_3\text{O}_2$: C, 51.88; H, 8.16; N, 22.69; found: C, 51.20; H, 8.10; N, 22.96. The combined filtrates were concentrated to give

triethylammonium bromide as a colorless solid (1.7 g, 45%), mp 248-249°C (dec).²⁰ Similar results were obtained when benzene replaced carbon tetrachloride as solvent.

Dimethylsulfonium dinitromethylide 37. To a solution of dimethylsulfide (1.0 g, 16.1 mmol) in dichloromethane (15 ml) at 4°C a solution of DBDNM 16 (2.0 g, 7.6 mmol) in dichloromethane (5 ml) was added over 5 minutes. After stirring for an additional 0.5 hr at 4°C, the reaction mixture was placed in a freezer (0°C) overnight. The precipitated solids were isolated and washed with chloroform and with water (5 ml) and air dried for 2 hr to give the ylide 37 as a yellow solid 0.68 g (54%), mp 215-218°C (dec.), lit.¹⁹ mp 224-226°C (dec.); IR (KBr): 1595 and 1355 cm⁻¹(NO₂); ¹³C NMR (DMSO-d₆): δ 26.75; m/e, 70 eV (%): 166 (90) (M⁺), 62 (100) (C₂H₆S)⁺.

Benzoyl cyanide 39. The dibromide 15 (12.2 g, 50 mmol) and copper powder (6.4 g, 100 mmol) in dry benzene (100 ml) were heated at 80°C for 15 h. After insoluble inorganic material and the solvent were removed the residue was distilled in a Kugelrohr apparatus (130°C, 0.1 torr) to give benzoyl cyanide 39 (1.85 g, 28%), mp 30-32°C, lit.³⁴ mp 32°C. Phenylnitroacetonitrile 38 (4.05 g, 25 mmol) and copper powder (3.2 g, 50 mmol) in dry benzene (50 ml) were heated at 80°C for 10 hours to give benzoyl cyanide 39 (3.2 g, 97%).

Brominations. Anthracene (1.8 g, 10 mmol) in dichloromethane (30 ml) was treated with the dibromo compound 15 (4.9 g, 20 mmol) in dichloromethane (20 ml). The mixture was stirred for 3 h and concentrated to give 9,10-dibromoanthracene 42 (2.2 g, 65%) as yellow needles mp 218-220°C, lit.²⁷ mp 220°C.

A solution of the dibromide 15 (2.4 g, 10 mmol) in methylene chloride (25 ml) was added to a solution of phenol (0.5 g, 5 mmol) in methylene chloride (25 ml) and stirred for 4 h. The solvent was removed and the residue

was placed on a neutral alumina chromatography column. Elution with ethyl acetate afforded 4-bromophenol 43 (0.4 g, 46%), mp 63-64°C, lit.²⁸ mp 63°C.

To a solution of cupric acetylacetonate (2.6 g, 10 mmol) in acetone (50 ml) the dibromide 15 (4.9 g, 20 mmol) was added dropwise and the mixture was stirred for an hour to give cupric bromoacetylacetonate 44 that separated as dark green needles (1.9 g, 56%), mp 226-227°C (dec), lit.⁴¹ mp 220°C (dec); anal. calcd. for $C_{10}H_{12}Br_2O_4Cu$: C, 28.60; H, 2.86; found: C, 28.62; H, 2.76.

A solution of DBDNM 16 (1.7 g, 6.4 mmol) in acetonitrile (3 ml) and 2-methylthiophene (0.6 g, 6.4 mmol) in acetonitrile (7 ml) was kept 16 h at room temperature, and then added to a stirred aqueous solution of sodium hydroxide (0.5 g) (40 ml). The mixture was extracted with dichloromethane (3 X 20 ml) and the collected organic phases dried over calcium sulfate. The solvent was removed to give a crude oil (0.8 g.). Kugelrohr distillation gave 2-bromo-5-methylthiophene 45, 0.8 g (67%), bp 85°C/20 mm, lit.^{29,30} bp 85°C/45 mm, 29°C/1.8 mm; 1H NMR ($CDCl_3$): δ 8.24 (3 H), 6.50 (m, 1 H), 6.81 (d); ^{13}C NMR ($CDCl_3$): δ 15.47, 108.86, 126.88, 130.97, 142.94; m/e, 70 eV (%): 178(77) and 176(77) for $(C_5H_5SBr)^+$, 177(44) and 175(40) for $(C_5H_4SBr)^+$, 97(100) $(C_5H_5S)^+$, 65(48) $(C_5H_5)^+$.

A solution of DBDNM 16 (3.4 g, 12.9 mmol) in acetonitrile (5 ml) added at 4°C to 2,5-dimethylthiophene (1.4 g, 12.9 mmol) in acetonitrile (15 ml) was held at 4-10°C for 3 hr and added to a dilute solution of sodium hydroxide (1.1 g, 27 mmol) in water (90 ml). The aqueous mixture was extracted with dichloromethane (4 X 20 ml). After drying over calcium sulfate the solvent was removed to give a crude product, 2.1 g, that gave 3-bromo-2,5-dimethylthiophene 46, 1.9 g (78%) on distillation (Kugelrohr), bp 110-120°C/125 mm, lit.^{31,32} bp 68°C/8 mm; 1H NMR ($CDCl_3$): δ 2.35 (s, 3 H), 2.4 (s, 3 H), 6.55 (bs, 1 H); ^{13}C NMR ($CDCl_3$): δ 14.44, 15.22, 107.89, 127.46, 131.43, 136.70.

Potassium bromodinitromethanenitronate 47. A solution containing potassium hydroxide (0.5 g, 8.3 mmol) (85% purity) in absolute ethanol (8 ml) was treated with DBDNM 16 (2.0 g, 7.6 mmol) and stored for an hour at room temperature. Potassium bromodinitromethane 1.3 g (76.4%) mp 155-156°C (dec), lit.^{34,35} mp 152-154, 165°C (dec), separated as a yellow solid; IR (KBr): 1435, 1350, 1210, 1120, 1075, 815, 715 cm^{-1} ; λ_{max} (water) = 385 nm (ϵ 1.23 $\times 10^4$).⁴²

Sodium nitromethanenitronate 49. A solution of DBDNM 16 (1.0 g, 3.8 mmol) in dichloromethane (5 ml) added to sodium sulfite (1.0 g, 7.9 mmol) and sodium carbonate (0.8 g, 7.5 mmol) in water (10 ml) gave a mildly exothermic reaction. After 2 hr the pH had decreased to about 7.5. Sodium hydroxide (0.16 g, 4.0 mmol) was added to raise the pH to 10.75. The bright yellow solution had λ_{max} = 364 nm (ϵ 2.0 $\times 10^4$)^{37,38} that showed an 89% yield of sodium dinitromethane 49 by calculation.

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F. Nitrosamines from N,N-Disubstituted Hydrazines

Joseph H. Boyer* and Ashwin M. Krishnan

Dept. of Chemistry, University of New Orleans, New Orleans, LA 70148

Summary. Photolysis of α -nitrohydrazones (from N,N-disubstituted hydrazines and tetranitromethane) gave nitrosamines.

A preparation of nitrosamines 4 was discovered in the photolysis of α -nitrohydrazones 2. This step completed the first general "oxidation" of a hydrazine to a nitrosamine since each hydrazone 2 was obtained from the corresponding hydrazine and tetranitromethane.¹ In a typical example the dimethylhydrazone 2a in acetone was irradiated at 350 nm under argon for 72 hours. Dimethylnitrosamine 4a was isolated from an ether extract of the reaction residue. Other nitrosamines were prepared by similar procedures (Table).²

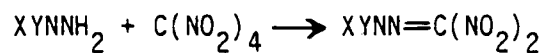
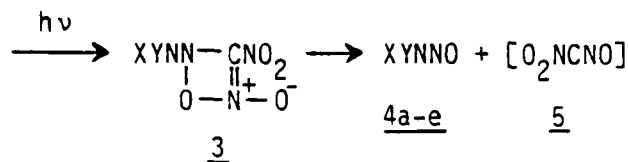
A proposed initial cyclization of each nitrohydrazone 2 to a 4-amino-3-nitro-1,2,4-oxadiazete-2-oxide 3 followed by ring cleavage accommodated the formation of the nitrosamine (comparable ring closure of a nitroolefin to an oxazetone, sometimes isolated, followed by cleavage to a carbonyl compound is known).^{3,4} The undetected nitro-nitriloxide 5 was presumably a coproduct; it may have dissociated to carbon dioxide and dinitrogen oxide.

Heretofore an "oxidation" of a hydrazine to a nitrosamine was limited to the detection of diphenylnitrosamine and N-nitroso-N-methyl-*p*-toluenesulfonamide from an appropriate hydrazone and singlet oxygen.⁵ Similar treatment of other hydrazones failed to produce nitrosamines.

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1a-e2a-e

a X = Y = CH₃; b X, Y = (CH₂)₅; c X = CH₃, Y = C₆H₅; d X = Y = C₆H₅; e X, Y = (CH₂)₂O(CH₂)₂

Table

Nitrosamines 4 from Hydrazines 1 via α -Nitrohydrazones 2.

	XYNNH ₂ ^a <u>1</u>		XYNN=C(NO ₂) ₂ ^{b,c}		XYNNO ^d <u>4</u>	
	X	Y	<u>2</u>	Yield %	Yield %	Reference
<u>a</u>	CH ₃	CH ₃		61	33	<u>e</u>
<u>b</u>		(CH ₂) ₅		74	61	<u>f, g</u>
<u>c</u>	CH ₃	C ₆ H ₅		84	42	<u>h</u>
<u>d</u>	C ₆ H ₅	C ₆ H ₅		43	23	<u>i</u>
<u>e</u>	(CH ₂) ₂ O	(CH ₂) ₂		52	26	<u>j</u>

^a The hydrazines were commercially available. ^b Sn. Shwartz, M. M. Krayushkhim, V.V. Sevostyonova and V. N. Yaravenko, Akad. Nauk. Ser. 1979, 4, 813-816; Eng. Trans. p 755. ^c New compound, 2e mp 107°-108°, gave IR, ¹HNMR(60 MHz), mass spectra and elemental analysis consistent with the assigned structure. ^d Each nitrosamine was isolated by flash

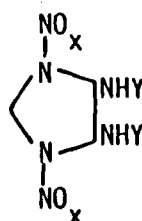
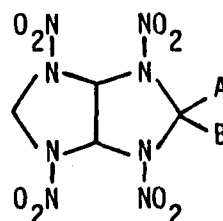
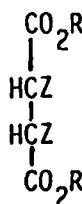
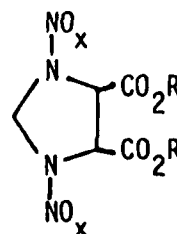
chromotography (silica gel, Merck grade 60,60A, mixture (1:1) of dichloromethane and hexane) or by distillation and identified by gc and ir data in comparison with authentic values. ^e H. H. Hatt, Organic Synthesis II, p 211. ^f Benzene was the solvent for photolysis. ^g W. D. Edmons, K. S. McCallum and J. P. Freeman, J. Org. Chem., 1954, 19, 1472. ^h W. W. Hartman and L. J. Roll, Organic Synthesis II, p 464. ⁱ B. Wexam, Farm Chilena, 1946, 20, 299; Chem Abstr. 1945, 405d. ^j G. Olah, L. Noszku, S. kuhn and M. Szelka, Chem. Ber., 1956, **89**, 2374.

F. Bicyclo-HMX

J. H. Boyer and G. Kumar

Chemistry Department, University of New Orleans, New Orleans, LA 70148

α -Functionalized nitrosamines and nitramines are not often encountered. Methods for their synthesis had to be discovered and developed to afford new approaches to gem-bisnitrosamines and gem-bisnitramines from other α -functional nitrosamines and nitramines. A portion of this program was directed to the preparation of previously unknown 1,3-dinitroso-4,5-diaminoimidazolidine 1 needed for a proposed conversion to bicyclo-HMX 2 and its oxo-derivative 3. Ethyl meso-diaminosuccinate 5 (obtained from meso-dibromosuccinic acid 4 in three steps) was converted to ethyl 1,3-dinitrosoimidazolidine-4,5-dicarboxylate 6 in two steps and was readily oxidized to the corresponding dinitramine 7. The conversion of the dinitrosamine 6 to the desired diamine 1 (isolated as an amide derivative 8) was recently successful. Investigations on the further conversion to the targets 2 and 3 were presented.

1 $x = 1, Y = H$ 8 $x = 1,2; Y = COR$ 2, $A = B = H$ 3, $AB = O$ 4 $R = H, Z = Br$ 5 $R = C_2H_5, Z = NH_2$ 6 $x = 1, R = C_2H_5$ 7 $x = 2, R = C_2H_5$

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