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ABERDEEN UNIV (SCOTLAND) DEPT OF CHEMISTRY
NITRILE POLYMERISATION AND HETEROCYCLIC SYNTHESIS USING IMINYLS--ETC(U)
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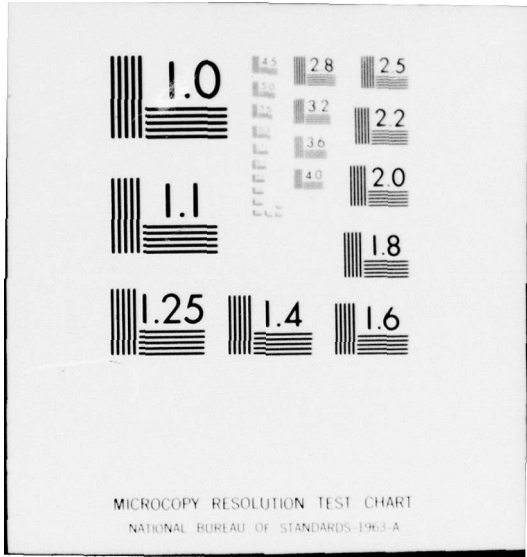
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Nitrile Polymerisation and Heterocyclic
Synthesis using Iminyls

Final Technical Report

By

Professor R. H. Thomson

31st March 1977

EUROPEAN RESEARCH OFFICE

United States Army

London, NW1 5TH, England

Contract Number DA-ERO-76-G-301

Professor R.H. Thomson,
Department of Chemistry,
University of Aberdeen,
Meston Walk,
Aberdeen, AB9 2UE, Scotland

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20 (U) ABSTRACT

Three types of iminyl radical bearing a -nitrile group have been investigated as models for the suggested radical-initiated polymerisation of the nitrile groups in polyacrylonitrile. The iminyls were generated by oxidation of the corresponding oxime-O-acetic acids with persulphate and it has been shown that the most appropriate model iminyls are those derived from keto-nitriles possessing a t-alkyl nitrile group, an unhindered carbonyl and some degree of molecular rigidity. Three important homolytic reactions are thought to occur during polymerisation of polyacrylonitrile, viz, intramolecular addition of iminyl to nitrile, intramolecular hydrogen abstraction by the iminyl, and formation of iminyl by intramolecular addition of alkyl radical to nitrile. The second of these has been shown to occur readily with some of the above models.

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Nitrile Polymerisation and Heterocyclic
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R.H. Thomson

Department of Chemistry, University of Aberdeen, Scotland

31st March 1977

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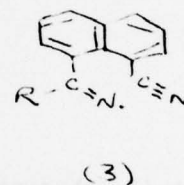
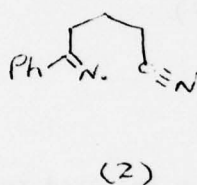
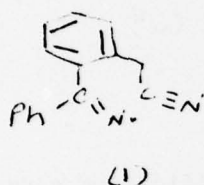
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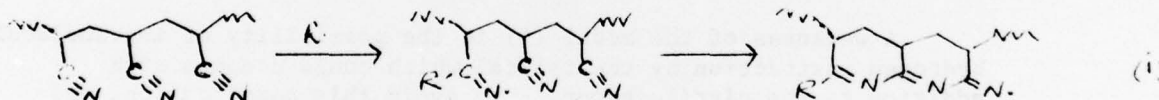
Abstract

Three types of iminyl radical bearing a γ -nitrile group have been investigated as models for the suggested radical-initiated polymerisation of the nitrile groups in polyacrylonitrile. The iminyls were generated by oxidation of the corresponding oxime-O-acetic acids with persulphate and it has been shown that the most appropriate model iminyls are those derived from keto-nitriles possessing a t-alkyl nitrile group, an unhindered carbonyl and some degree of molecular rigidity. Three important homolytic reactions are thought to occur during polymerisation of polyacrylonitrile, *viz*, intramolecular addition of iminyl to nitrile, intramolecular hydrogen abstraction by the iminyl, and formation of iminyl by intramolecular addition of alkyl radical to nitrile. The second of these has been shown to occur readily with some of the above models.

1. Following our statement of objectives in the Research Proposal we have concentrated on the preparation of precursors of iminyl radicals bearing γ -nitrile groups (1), (2) and (3), these being



models for the suggested radical-initiated polymerisation of the nitrile groups in polyacrylonitrile, (1).



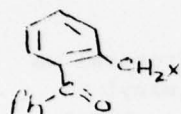
Oxidation of oximinoacetic acids is now an established method for iminyl production,^{1,2} and hence our synthetic work has been directed at the ketone precursors of the oximinoacetic acids.

Model (1)

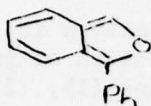
Bromination of the ketone (4; X=H) with *N*-bromosuccinimide (2 mol) in boiling carbon tetrachloride gave the benzylic bromide (4; X=Br) in 83% yield (by n.m.r.) but conversion to the nitrile (4; X=CN) by reaction with potassium cyanide in ethanol did not proceed smoothly. Although the crude product showed both carbonyl

¹ A.R. Forrester, M. Gill, J.S. Sadd, and R.H. Thomson, J. Chem. Soc. Chem. Comm., 1975, 291.

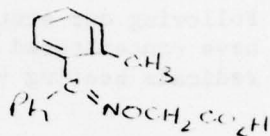
² A.R. Forrester, M. Gill, and R.H. Thomson, J. Chem. Soc. Chem. Comm., 1976, 677.



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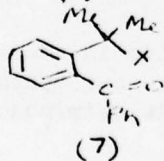
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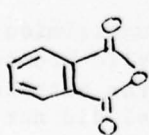
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and nitrile absorption in the infrared region purification gave mainly 1-phenylisobenzofuran (5). While this work was in progress the spontaneous cyclisation of the ketone (4; X=Br) to (5) was reported³ and it appears that the nitrile (4; X=CN) undergoes a similar change. Benzylic bromination of the oximinoacetic acid (6) was also efficient (93%) but the subsequent reaction with potassium cyanide gave a complex mixture of acidic material.

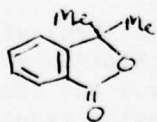
A weakness of the model (1) is the possibility of intramolecular hydrogen abstraction by the radical which could compete with addition to the nitrile group. To avoid this complication, and to impede spontaneous cyclisation of the intermediate bromo- or cyano-ketone to an isobenzofuran, we attempted to synthesise the homologous keto-nitrile (7; X=CN) via the "known"⁴ alcohol (10b)



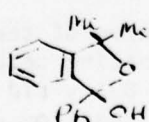
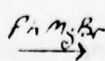
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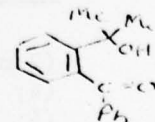
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(10a)



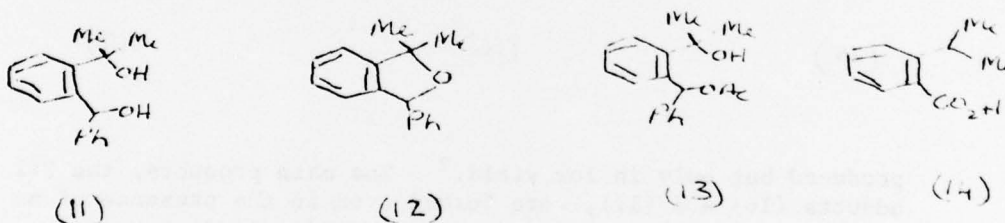
(10b)

³ R. Faragher and T.L. Gilchrist, J. Chem. Soc. Perkin Trans. I, 1976, 336.

⁴ E. De. Barnett, J.W. Cook, and I.G. Nixon, J. Chem. Soc., 1927, 504.

by the reaction sequence (8 → 9 → 10). The structure of the product (10a or 10b), which had not previously been established,⁴ was easily shown to be the ring tautomer (10a) (ν_{OH} 3578 cm^{-1} , no ν_{CO} band). However this tautomer did not react to give ring-opened products. No reaction occurred with hydroxylamine, sodium cyanide, acetic anhydride or *p*-toluenesulphonyl chloride, and with methoxyamine in acidic ethanol solution the corresponding ethyl acetal was formed.

In an alternative approach to the keto-nitrile (7; X=CN) the lactone (9) was reduced with sodium amalgam to the diol (11) (cf. ref. 5) but subsequent oxidation with manganese dioxide again gave the ring tautomer (10a). Attempts to protect the tertiary hydroxyl group by reaction with *p*-toluenesulphonyl chloride or acetic anhydride resulted in formation of the cyclic ether (12) and monoacetate (13), respectively.



Hydrogenation of the lactone (9) over Raney nickel yielded the acid⁶ (14) which was converted into the *o*-isopropyl ketone (7; X=H) by known procedures.⁶ Photolytic bromination gave the bromide (7; X=Br) in good yield but this cyclised readily, especially in aqueous-ethanolic solvents, forming the hemiacetal (10a) or its ethyl acetal. In non-aqueous solvents (DMF, TEF) nucleophilic substitution did not occur but cyclisation ensued, as before, during the aqueous work-up. Spontaneous cyclisation was prevented by conversion of the ketone into the oxime methyl ether but bromination of this ether was a poor reaction and the oximino-ether, although usable, is a less desirable substrate for oxidation

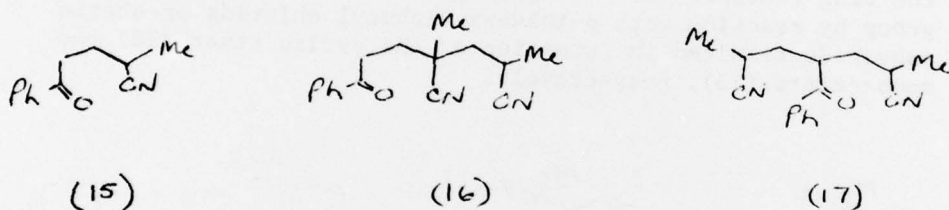
⁵ F. Seidel, *Ber.*, 1928, 61, 2267.

⁶ J.G. Smith, *Canad. J. Chem.*, 1968, 46, 2273.

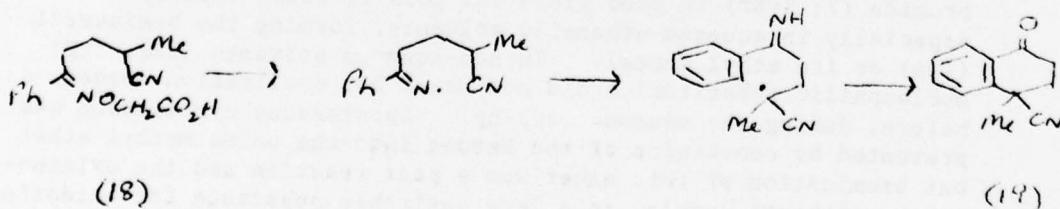
than the oximinoacetic acid. Because of this, and the ease with which intermediate compounds cyclise in this series we discontinued work on this model.

Model 2

The simplest approach to the ketone precursor of model (2) is by Michael addition of the appropriate ketone to an α,β -unsaturated nitrile. In this way the keto-nitrile (15) was

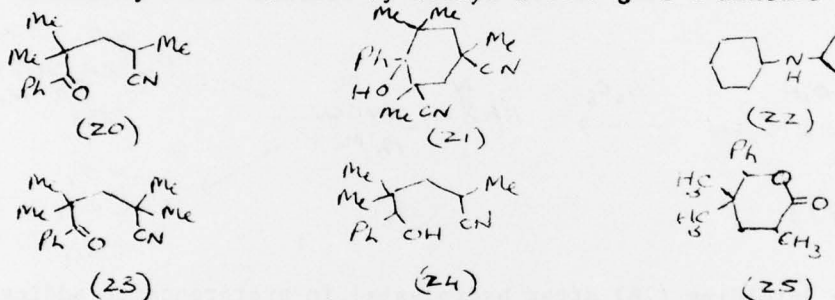


produced but only in low yield.⁷ The main products, the 2:1 adducts (16) and (17), were formed even in the presence of a large excess of ketone and were very difficult to separate. Oxidation of the oximinoacetic acid (18), derived from (17), with persulphate gave mainly (19). This product does not arise by addition of iminyl to nitrile but by intramolecular hydrogen



⁷ A.D. Campbell, C.I. Curtis, and S.N. Slater, J. Chem. Soc., 1948, 1741.

abstraction by the iminyl, followed by intramolecular cyclisation of the ensuing alkyl radical, as indicated. This reaction is the iminyl equivalent of the Barton, Hofmann-Löffler-Freytag, and Yang reactions, and other examples have recently been reported² from this laboratory. Although the abstractable γ -hydrogen of the ketone (15) [and the acid (18)] could have been replaced by alkylation, simultaneous alkylation of the methylene group α - to the carbonyl is also possible. Hence, we considered it simpler to alkylate the keto-nitrile (20) from isobutyrophenone and methacrylonitrile. Treatment of (20) with sodium hydride followed by methyl iodide gave a mixture of products,

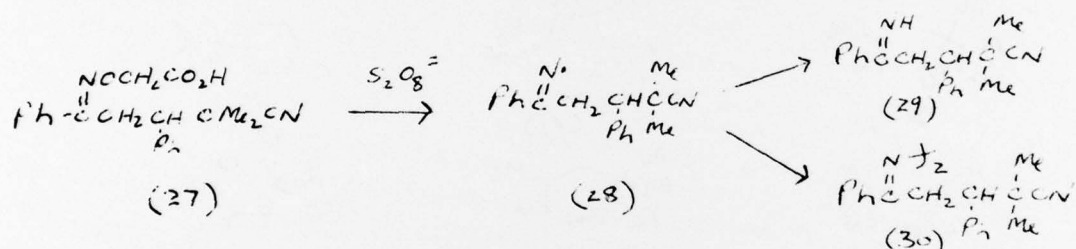
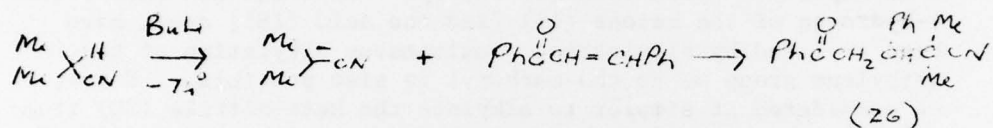


the principal component of which showed nitrile and hydroxyl but no carbonyl i.r. absorption. Its n.m.r. spectrum showed four separate singlets but no $>$ CHO resonance. We assign structure (21) to this product. Using the anion of the hindered base (22) and methyl iodide at -74° the ketone (23) was obtained in moderate yield together with (24) and (25).

Oximation of aryl *t*-alkyl ketones is difficult, and the keto-nitriles (20) and (23) had to be heated under reflux in aqueous alcohol with hydroxylamine and sodium acetate for 5 h before significant reaction occurred. The crude products showed nitrile absorption in the i.r. but treatment with bromoacetic acid gave crystalline acids which did not. Full identification of these acids was not made but we surmise that the nitriles in the crude oxime reaction mixtures are merely unreacted keto-nitriles and that amidoxime formation (followed by cyclisation?) competes with oximation of the hindered carbonyl group.

Therefore the required keto-nitrile precursor of the iminyl-model must possess a *t*-alkyl nitrile group and an unhindered carbonyl. Synthesis of such a model (26) was achieved by the Michael addition

shown and the carbonyl group was transformed into the iminoxy-acetic acid function in the usual way. Oxidation of this acid (27) with persulphate gave no cyclised product. Product analysis indicated that the iminyl (28) dimerises to (30) and abstracts

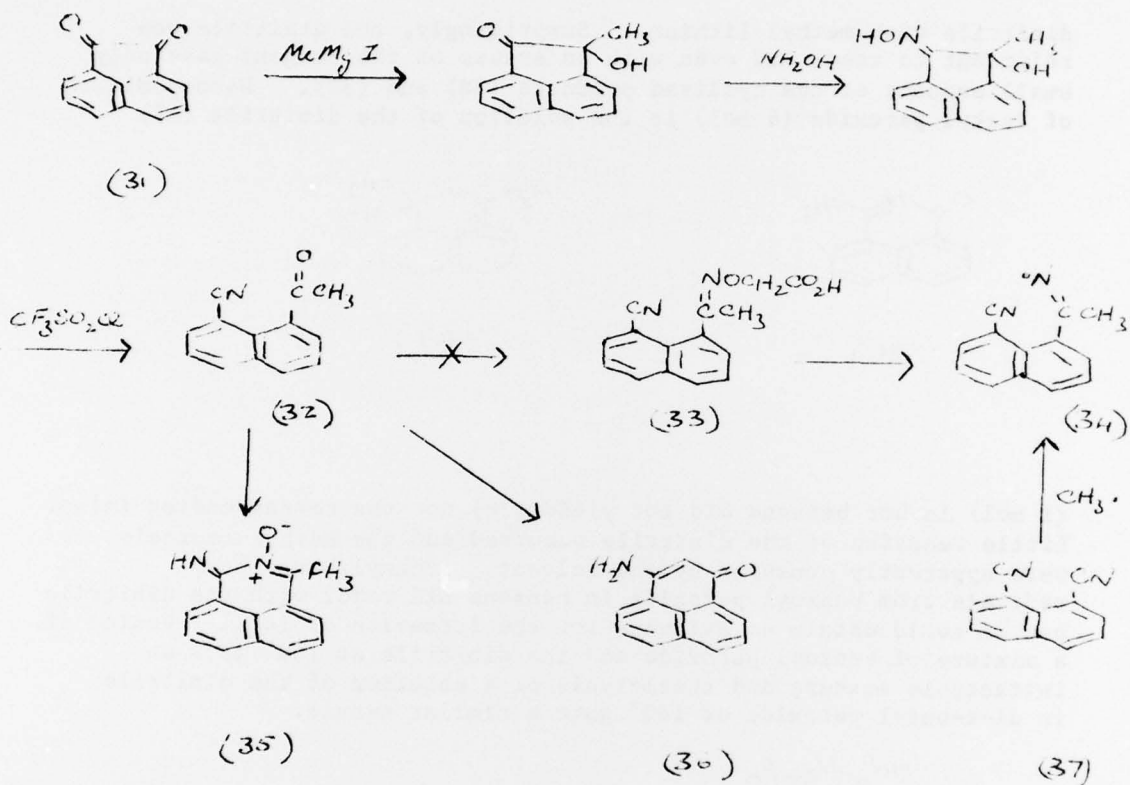


hydrogen [yielding (26) after hydrolysis] in preference to adding to the nitrile group. We attribute this disappointing result to the flexibility of the chain in (28) the radical centre reacting in other ways before it can adopt the geometrical and conformational arrangement necessary for intramolecular addition to occur. Thus, some degree of molecular rigidity (almost certainly a feature of polyacrylonitrile) appears to be a further requirement for the model.

Model 3

Accordingly, we have turned our attention to the keto-nitrile precursor (32) of the iminyl (34). Synthesis of this keto-nitrile from acenaphthoquinone (31) was achieved by adaption of a recently described⁸ preparation of aliphatic keto-nitriles and is shown below. However, treatment of the keto-nitrile (32) with hydroxylamine-sodium

⁸ T. Wakamatsu, M. Fukui, and Y. Ban, Synthesis, 1976, 341.

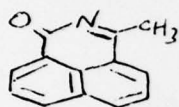


acetate in aqueous ethanol did not give the corresponding oxime. Instead, the cyclic imino-nitrone (35) ($\nu_{\text{max}} 3170$; no $\nu_{\text{C}\equiv\text{N}}$) was formed. Further attempts to produce the oxime in alkaline solution yielded the amino-ketone (36) [$\nu_{\text{max}} 3350, 3250, 1635$ and 1570 cm^{-1} ; no $\nu_{\text{C}\equiv\text{N}}$; $\delta=5.95(1\text{H})$] and in acid solution no reaction occurred. Formation of the iminoxyacetic acid (33) directly from the keto-nitrile (32) by reaction with aminoxyacetic acid was also unsuccessful.

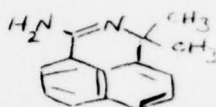
To overcome these difficulties we attempted to generate the iminyl in situ from the known⁹ dinitrile (37) by reaction with methyl radicals. An authentic specimen of the expected product from such a reaction was considered desirable and hence we first treated the

⁹ A.J. Boulton and S.S. Mathur, *J. Org. Chem.*, 1973, **38**, 1054.

dinitrile with methyl-lithium. Surprisingly, the dinitrile was reluctant to react and even with an excess of the reagent gave only small amounts of the cyclised products (38) and (39). Decomposition of acetyl peroxide (4 mol) in the solution of the dinitrile (37)

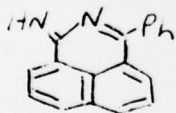


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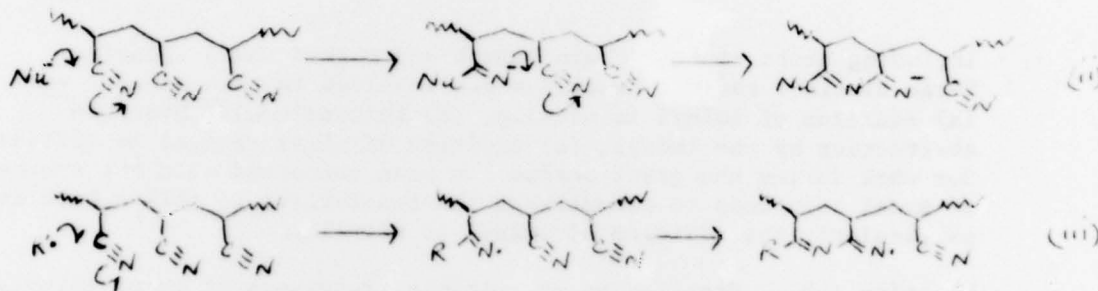
(1 mol) in hot benzene did not yield (38) nor the corresponding imine. Little reaction of the dinitrile occurred and the methyl radicals were apparently consumed by the solvent. Phenyl/benzoyloxy radicals from benzoyl peroxide in benzene did react with the dinitrile but we could obtain no evidence for the formation of (40). Fusion of a mixture of benzoyl peroxide and the dinitrile at 160° gave an intractable mixture and thermolysis of a solution of the dinitrile in di-t-butyl peroxide at 140° gave a similar result.



(40)

Discussion

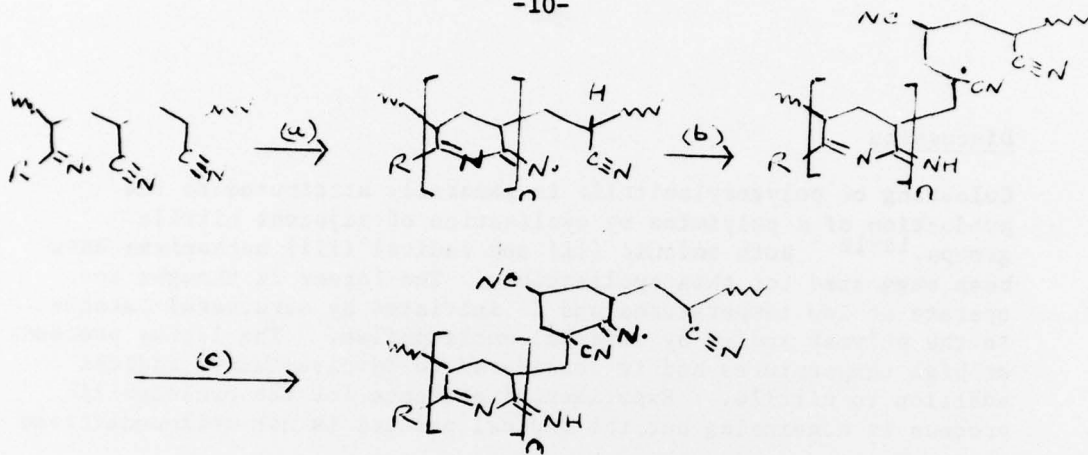
Colouring of polyacrylonitrile is generally attributed to the production of a polyimine by cyclisation of adjacent nitrile groups.¹⁰⁻¹² Both anionic (ii) and radical (iii) mechanisms have been suggested for this cyclisation. The former is thought to operate at low temperatures and is initiated by structural defects in the polymer and/or by external nucleophiles. The latter proceeds at high temperatures and is considered to involve iminyl radical addition to nitrile. Experimental evidence for the nucleophilic process is convincing but the radical process is not well-understood



although it is the more important commercially since it is implicated in carbon fibre production.

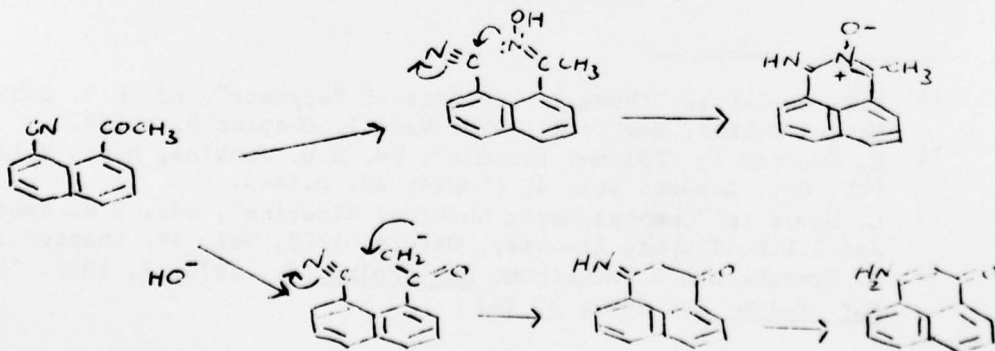
In a recent and particularly careful study by Grassie and McGuchan¹³ using thermogravimetric and differential thermal analysis techniques the following radical mechanism (iv) was proposed. This satisfies most of the experimental observations of the thermal process,

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- ¹⁰ R.T. Conley in "Thermal Stability of Polymers", ed. R.T. Conley, Marcel Dekker, New York, 1970, Vol. 1, Chapter 8, p.223.
 - ¹¹ N. Grassie in "Polymer Science", ed. A.D. Jenkins, North Holland Pub. Co., London, Vol. 2, Chapter 22, p.1443.
 - ¹² C. David in "Comprehensive Chemical Kinetics", eds. C.H. Bamford and C.F.H. Tipper, Elsevier, Oxford, 1975, Vol. 14, Chapter 1, p.1.
 - ¹³ N. Grassie and R. McGuchan, Eur. Polym. J., 1971, 7, 1357, 1503; Eur. Polym. J., 1972, 8, 243.



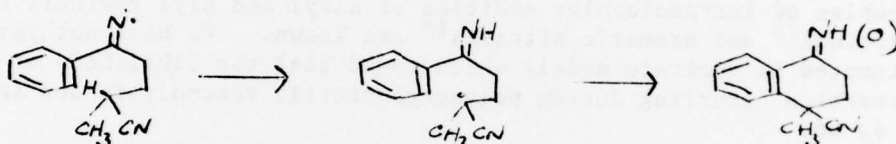
including short kinetic chain length and marked chain transfer. Three distinct radical reactions are involved in this scheme, *viz.* (a) addition of iminyl to nitrile, (b) intramolecular hydrogen abstraction by the iminyl, (c) addition of alkyl radical to nitrile. Our work during the grant period has been concerned with the synthesis of model compounds to demonstrate the feasibility of this scheme and particularly the addition of iminyl to nitrile.

Reaction (a). Preparation of suitable precursors of model iminyls has been more difficult than was envisaged at the outset and we cannot yet claim to have obtained a satisfactory model which illustrates the iminyl addition to a nitrile. All of our proposed iminyls have been derived from keto-iminoxyacetic acids which are formed from keto-nitriles by nucleophilic addition. A competing intramolecular addition to nitrile has been the main complicating factor, exemplified particularly well by the reactions of the keto-nitrile (32) with hydroxylamine and alkali. Significantly these reactions provide supporting evidence for the low temperature cyclisation of nitriles



under the influence of an added nucleophile.

Reaction (b). Our work has clearly established the feasibility of this reaction. The example given below, and others reported from

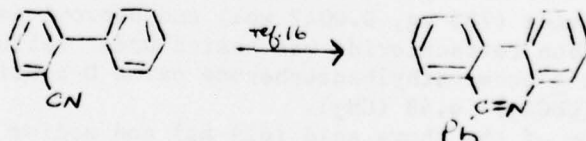


this laboratory,¹⁴ indicate that such reactions are likely events in the degradation of polyacrylonitrile at high temperature.

Reaction (c). Intermolecular addition of alkyl and aryl radicals to nitriles is rare and only a few examples are known.¹⁵ We have observed only one reaction of this type in the present work and this



proceeded in low yield.¹⁶ Hence our inability to find conditions under which methyl and phenyl would add to 1,8-dicyanonaphthalene is



¹⁴ A.R. Forrester, M. Gill and R.H. Thomson, Chem. Comm., 1976, 677.

¹⁵ D.D. Tanner, N.J. Bunce, JACS, 1969, 91, 3028; W.E. Hanby and W.A. Waters, J. Chem. Soc., 1939, 1792.

¹⁶ R.H. Thomson, 2nd Quarterly Status Report 1974 - Contract No. DAJA37-74-C-1531.

not surprising. Indeed, the reverse process, fragmentation of iminyis to nitriles is more frequently encountered.¹⁷

However, intramolecular addition of alkyl radicals to nitriles, given favourable geometry, appears to proceed more easily and examples of intramolecular addition of alkyl and aryl radicals to steroidal¹⁸ and aromatic nitriles¹⁹ are known. We have not yet attempted to generate models which would test the likelihood of such a reaction occurring during polyacrylonitrile thermolysis but intend to do so.

Experimental

Model (1) Experiments

Attempted preparation of o-(cyanomethyl)benzophenone oxime-O-acetic acid

(i) A solution of crude o-(bromomethyl)benzophenone³ (1.045 g, 0.0038 mol) and sodium cyanide (1.0 g, 0.019 mol) in dioxan (30 ml) and water (6 ml) was heated under reflux for 2 h and then diluted with water. Extraction of the reaction mixture with ether followed by evaporation of the solvent and chromatography (t.l.c.) of the residue on silica with chloroform-petrol (1:1) gave (a) o-methylbenzophenone (24%) (b) 1-phenylisobenzofuran³ (5) and (c) o-(cyanomethyl)benzophenone, ν_{\max} 2250 and 1669 cm^{-1} , δ (CDCl_3) 3.95 (CH_2). Product (c) gave (b) on standing.

(ii) A solution of benzophenone oxime O-acetic acid (538 mg, 0.002 mol), N-bromosuccinimide (783 mg, 0.0042 mol) and benzoyl peroxide (catalytic amount) in carbon tetrachloride was heated under reflux for 15 h. The acidic product o-bromomethylbenzophenone oxime O-acetic acid had M^+ 347 and δ (CDCl_3) 4.48 (CH_2).

A solution of the above acid (624 mg) and sodium cyanide (441 mg) in dioxan-water (10:1) (110 ml) was heated under reflux for 1 h. The acidic product was a dark yellow oil (300 mg), ν_{\max} 2250 and 1673 cm^{-1} .

¹⁷ M.L. Poutsma and P.A. Ibarbia, *J. Org. Chem.*, 1969, 34, 2848.

¹⁸ K. Heusler and J. Kalvoda, *Angew. Chem.*, 1964, 3, 525.

¹⁹ P.M. Brown, J. Russell, R.H. Thomson, and A.G. Wylie, *J. Chem. Soc.*, 1968, 842.

Attempted preparation of o-(cyanoisopropyl)benzophenone oxime-O-acetic acid

(i) 1-Hydroxy-3,3-dimethyl-1-phenylphthalan (1.5 g) in ethanol (100 ml) was stirred with sodium amalgam [from sodium (3.4 g) and mercury (114 g)] under reflux for 38 h. The reaction mixture was poured into water and the solid which precipitated, collected. Extraction of the filtrate with ether and evaporation of the extracts gave o-(hydroxyisopropyl)benzhydrylic alcohol (11) (1.66 g, 100%) as an oil (Found: M^+ -18 = 224.1201. Calc. for $C_{16}H_{18}O_2$ requires M -18, 224.1201), ν 3390 cm^{-1} , δ ($CDCl_3$) 1.66 (6H, s, 2Me), 3.05-3.20 (2H, s, 2OH), δ 6:58 (1H, s, CHO), and 7.15-7.35 (9H, m, ArH), m/e M^+ -18 (63%), 209(100), 194(25), 165(16).

Reactions of o-(1-hydroxyisopropyl)benzhydrylic alcohol

(a) With manganese dioxide. Treatment of the alcohol in ether at room temperature with an excess of manganese dioxide gave 1-hydroxy-3,3-dimethyl-1-phenylphthalan (10a) (100%).

(b) With p-toluenesulphonyl chloride. The alcohol (181 mg) and p-toluenesulphonyl chloride (186 mg) in pyridine (2 ml) was left for 2 weeks and then poured into water. The reaction mixture was worked up in the usual way to give 3,3-dimethyl-1-phenylphthalan²⁰ δ ($CDCl_3$) 1.56 (3H, s, Me), 1.69 (3H, s, Me), 6.15 (1H, s, CH), 7.0-7.4 (9H, m, ArH).

(c) With acetic anhydride. The alcohol (150 mg) and acetic anhydride (1 ml) in pyridine (0.5 ml) was left at room temperature for 16 h. Work up gave o-(1-hydroxyisopropyl)benzhydrylic acetate (120 mg, 68%), ν 3460, 1710 cm^{-1} , δ ($CDCl_3$) 1.54 (3H, s, Me), 1.70 (3H, s, Me), 2.08^{max} (3H, s, COMe), 2.67 (1H, s, OH), 7.2-7.6 (9H, m, ArH) and 7.98 (1H, s, CHPh OAc).

(ii) A solution of o-isopropylbenzophenone (672 mg) in carbon tetrachloride (30 ml) was heated under reflux and irradiated with a 250 w sun-lamp while bromine (720 mg) in carbon tetrachloride (50 ml) was added during 15 min. The solution was allowed to cool and the o-(1-bromoisopropyl)benzophenone separated as a red oil. The crude product (700 mg, 98%) showed δ ($CDCl_3$) 2.12 (6H, s, 2Me), and 7.88-8.90 (9H, m, ArH).

²⁰ A. Fabrycy, Chem. Abs., 1959, 33, 1307.

In separate experiments o-(1-bromoisopropyl)benzophenone was treated with (a) sodium cyanide in ethanol-water, (b) potassium cyanide in THF and (c) aqueous sodium bicarbonate-chloroform. In each case the main product was 1-ethoxy-3,3-dimethyl-1-phenylphthalan (a, 25%), (b, 30%), (c, 100%), δ (CDCl₃) 1.2 (3H, t, J 8Hz, OCH₂CH₃), 1.67-1.70 (6H, d, 2Me), 3.42 and 3.61 (2H, each 1H, q J 8Hz, OCH₂CH₃), 7.20-7.77 (9H, m, ArH).

Model (2) Experiments

3-Benzoyl-1-methylbutyronitrile (15). To a stirred mixture of acetophenone (120 g, 1 mol) and potassium methoxide [from potassium (1.17 g) and methanol (25 ml)] methacrylonitrile (67.0 g, 1 mol) in dry benzene (100 ml) containing quinol (100 mg) was added dropwise with stirring. The reaction mixture was heated for 30 min and then left at room temperature overnight. Hydrochloric acid was added and the neutralised solution was extracted with ether. The ethereal extracts were evaporated and the residual oil distilled to give acetophenone (44 g, 33%), b.p. 40-48°/0.35 mm Hg and a yellow oil (85 g), b.p. 176-184°/0.35 mm Hg. The latter was redistilled to give two fractions 160-167°/0.25 mm Hg (8.5 g) and 167-180°/0.25 mm Hg (72 g). The lower boiling fraction was chromatographed (column) on silica using petrol-chloroform as irrigant to give (a) 3-benzoyl-1-methylbutyronitrile (2.5 g, 1.3%), m.p. 48° (from chloroform-benzene) (Found: C, 77.3; H, 7.2; N, 7.7. C₁₂H₁₃NO requires C, 77.0; H, 7.0; N, 7.5%), ν 2240 and 1685 cm⁻¹, δ (CDCl₃) 1.39 (3H, d, J 7.0Hz; CH₂CH₃), 1.89^{max}-2.21 (2H, m, CH₂), 2.56-3.02 (1H, m, CH), 3.22 (2H, t J 8.0Hz, CHCH₃), 7.48-7.59 (3H, m, ArH), 7.92-8.10 (2H, m, ArH), and (b) an oil from which 3-benzoyl-1,5-dimethylpimelonitrile (17) crystallised, m.p. 35-40°, ν 2215 (C≡N) and 1640 cm⁻¹, δ (CDCl₃) 1.32 (3H, d, J 7Hz, Me), 1.35^{max} (3H, d, J 7.0Hz, Me), 1.60-2.84 (6H, m, 2CH₂CH), 3.16-4.18 (1H, m, CH), 7.54-7.60 (3H, m, ArH), 8.01-8.12 (2H, m, ArH).

3-Benzoyl-1,3-dimethylvaleronitrile (20). Methacrylonitrile (14.40 g, 0.216 mol) was added dropwise with stirring to a solution of isobutyrophenone (25.0 g, 0.17 mol) in dioxan (100 ml) and 30% methanolic-potassium hydroxide (10 ml). The reaction mixture was heated at 70° for 5 h and then stirred at room temperature for 16 h. It was then poured into water and the oil which separated was extracted into

chloroform. Evaporation of solvent and distillation of the residue gave starting material (12.0 g) and a fraction of b.p. 120-130°/0.35 mm Hg which was crystallised from chloroform-petrol to give the lactam of 4-amino-4-hydroxy-4-methylamine-1,3,3-trimethylpentanoic acid (1.0 g, 24%), m.p. 165° (Found: C, 72.8; H, 8.8; N, 6.0. $C_{15}H_{21}NO_2$ requires C, 72.5; H, 8.5; N, 5.7%), ν 3200, 1670 cm^{-1} , δ (CDCl₃) 0.78 (3H, s, Me), 0.95 (3H, s, Me), 1.29^{max} (3H, d, J 6Hz, CHCH₃), 1.28-2.71 (3H, m, CH₂CH), 3.1 (3H, s, NMe), 6.42 (1H, s, OH), 7.4 (5H, s, ArH), m/e 247(2)(M).

Evaporation of the mother liquor and distillation of the residue gave 3-benzoyl-1,3-dimethylvaleronitrile (11.0 g, 30%) as an oil, b.p. 126-128°/0.35 mm Hg (Found: C, 78.0; H, 8.0; N, 6.8. $C_{14}H_{17}NO$ requires C, 78.1; H, 7.9; N, 6.5%), ν 2220, 1672 cm^{-1} , δ (CDCl₃) 1.32 (3H, d, J 7Hz, CHCH₃), 1.42 (3H, s, Me), 1.46 (3H, s, Me), 1.99-2.12 (2H, m, CH), 2.36-2.83 (1H, m, CH), 7.37-7.73 (5H, m, ArH), m/e 215(M).

2,4-Dicyano-2,4,6,6-tetramethyl-1-phenylcyclohexanol (21). 3-Benzoyl-1,3-dimethylvaleronitrile (1.0 g) in DMF (5 ml) was added dropwise to a stirred solution of sodium hydride (720 mg, in mineral oil) in DMF (3 ml) and benzene (2 ml) under nitrogen. After 15 min, methyl iodide (2.0 g) was added slowly and the reaction mixture was warmed to 40° for 3 h. It was then poured into water and worked up in the usual way to give 2,4-dicyano-2,4,6,6-tetramethyl-1-phenylcyclohexanol (130 mg, 13%), m.p. 243-250° (from chloroform-petrol), ν 3520, 2240 cm^{-1} , δ (CDCl₃) 0.76 (3H, s, Me), 1.19 (3H, s, Me), 1.49^{max} (3H, s, Me), 1.68 (3H, s, Me), 1.86 and 2.14 (each 1H, d J 4Hz, CH₂), 2.09 (1H, s, OH), 7.36 (5H, m, ArH), m/e 282(M)(2%).

3-Benzoyl-1,1,3-trimethylvaleronitrile (23). A stirred solution of N-cyclohexylisopropylamine (5.7 g, 0.0394 mol) in THF (10 ml) was treated with n-butyl-lithium (0.040 mol; 40 ml), in hexane at -74° under nitrogen. After 20 min, 3-benzoyl-1,3-dimethylvaleronitrile (7.5 g, 0.0386 mol) in THF (12 ml) was added dropwise and the reaction mixture was stirred for 20 min after which methyl iodide (7.95 g, 0.0562 mol) in THF (6 ml) was added. Stirring was continued for 1 h at -74° and a further 3 h at room temperature before the mixture was poured into water. Work up gave a neutral oil which was distilled and the fraction of b.p. 142-151° 0.7 mm Hg was chromatographed on silica (column) with chloroform-petrol to give (a) 3-benzoyl-1,1,3-trimethylvaleronitrile (Found: C, 76.8; H, 8.0; N, 5.9. $C_{15}H_{19}NO$ requires C, 78.6; H, 8.3; N, 6.1%), ν 2240, 1675 cm^{-1} , δ (CDCl₃) 1.33 (6H, s, 2Me), 1.48 (6H, s, 2Me), 2.15^{max} (2H, s, CH₂), 7.23-7.68 (5H, m, ArH); (b) the lactone of 4-hydroxy-4-phenyl-1,3,3-trimethyl-

pentanoic acid (25) (30 mg, 0.4%), m.p. 138-139° (from chloroform-petrol) (Found: C, 77.0; H, 8.2; $C_{16}H_{18}O_2$ requires C, 77.0; H, 8.3%), ν 1740 cm^{-1} , δ ($CDCl_3$) 0.88 (3H, s, Me), 0.9 (3H, s, Me), 1.35 (3H, max d J 6Hz, $CHCH_3$), 1.65-1.98 (2H, m, CH_2), 2.65-2.92 (1H, m, CH_2CHCH_3), 5.08 (1H, s, OCH), 7.3 (5H, s, ArH), m/e 219(3%), 218(22)(M) and (c) 4-hydroxy-4-phenyl-1,3-dimethylvaleronitrile (24) as a viscous oil (1.12 g, 15%) (Found: C, 77.1; H, 8.7; N, 6.6. $C_{14}H_{19}NO$ requires C, 77.38; H, 8.81; N, 6.45%), ν max 3470, 2240 cm^{-1} , δ ($CDCl_3$) 0.97 (3H, s, Me), 1.0 (3H, s, Me), 1.35 (3H, max d J 8Hz, $CHCH_3$), 1.3-1.75 (2H, m, CH), 2.08 (1H, s, OH), 2.52-3.00 (1H, m, $CHCN$), 4.48 (1H, s, $PhCHOH$), 7.31 (5H, s, ArH).

3-Benzoyl-1,1-dimethyl-2-phenylbutyronitrile (26). n-Butyl-lithium (0.032 mol, 35.45 ml) in hexane was added to a stirred solution of isobutyronitrile (2.42 g, 0.035 mol) in THF (12 ml) at -74° under nitrogen. The temperature was allowed to rise to 0° and then recooled to -74° before 2-benzoylstyrene (6.24, 0.03 mol) in THF (12 ml) was added and the temperature allowed to rise to room temperature. The reaction mixture was poured into water and the oil which separated was chromatographed on silica (column) using petrol-chloroform (1:1) as irrigant to give the starting ketone (1.8 g, 29%) and 3-benzoyl-1,1-dimethyl-2-phenylbutyronitrile (950 mg, 17%), m.p. 109-110° (from petrol-chloroform) (Found: C, 82.5; H, 6.9; N, 5.0. $C_{19}H_{19}NO$ requires C, 82.3; H, 6.9; N, 5.1%), ν (KBr) 2251, 1688 cm^{-1} , δ 1.19 (3H, s, Me), 1.46 (3H, s, Me), 3.4-3.7 (3H, m, $CHCH_2$), 7.31-7.50 (8H, m, ArH), 7.83-8.00 (2H, m, ArH).

Preparation of oxime O-acetic acids

3-Benzoyl-1-methylbutyronitrile oxime O-acetic acid. A solution of 3-benzoyl-1-methylbutyronitrile (374 mg, 0.002 mol), hydroxylamine hydrochloride (160 mg, 0.0024 mol) and sodium acetate (200 mg) in aqueous-alcohol was heated under reflux for 30 min. The product mixture was separated by chromatography to give the oxime (240 mg, 59%) as a viscous oil (Found: C, 71.6; H, 7.1; and N, 13.7%; M^+ , 202.1102. $C_{12}H_{14}N_2O$ requires C, 71.3; H, 6.9; N, 13.9%. M , 202.1106), ν max 3370, 2220 cm^{-1} .

The oxime (404 mg), bromoacetic acid (556 mg) and sodium hydroxide (300 mg) in aqueous-ethanol was heated, under reflux for 1 h. Work-up gave 3-benzoyl-1-methylbutyronitrile oxime-O-acetic acid (400 mg, 77%) as an oil (Found: C, 64.4; H, 6.2; N, 10.7. $C_{14}H_{16}N_2O_3$ requires C, 64.6; H, 6.2; N, 10.8%), ν max 3450-3150, 2220, and 1760-1720 cm^{-1} , δ ($CDCl_3$) 1.33 (3H, d, J 7.0Hz, Me), 1.72-2.08 (2H, m, CH_2CH), 2.56-3.16 (3H, m, CH and CH_2), 4.78 (2H, s, OCH_2), 7.28-7.76 (5H, m, ArH), 9.18 (1H, s, OH).

3-Benzoyl-1,1-dimethyl-2-phenylbutyronitrile oxime-O-acetic acid was similarly prepared as a viscous oil (Found: M^+ , 350.1628. $C_{21}H_{22}N_2O_3$ requires M, 350.1630), ν 3200, 2237, 1730 cm^{-1} , δ ($CDCl_3$) 1.16 (3H, s, Me), 1.50 (3H, s^{max} , Me), 2.98-3.00 (3H, m, CH_2CH), 4.70 (2H, s, OCH_2), 7.16-7.38 (10H- m, ArH), 8.26 (1H, s, OH).

Oxidations with Persulphate. These were carried out by thermolysis as described previously.²¹

3-Benzoyl-1-methylbutyronitrile oxime-O-acetic acid gave 4-cyano-4-methyltetralone (19) (145 mg, 66%), m.p. 63° (Found: C, 77.5; H, 5.9; N, 7.4. $C_{12}H_{14}NO$ requires C, 77.8; H, 5.9; N, 7.6%), ν 2219, 1690 cm^{-1} , δ ($CDCl_3$) 1.85 (3H, s, Me), 2.28-2.60 (2H, m, CH_2^{max}); 2.78-2.99 (2H, m, CH_2CO), 7.38-7.68 (3H, m, ArH), 8.02-8.13 (1H, d, J 7Hz, ArH), m/e 185(32)(M), 157(100), 129(10).

3-Benzoyl-1,1-dimethyl-2-phenylbutyronitrile oxime-O-acetic acid gave the keto nitrile (26) (31%) and the azine of 3-benzoyl-1,1-dimethyl-2-phenylbutyronitrile (30) (7%), yellow needles, m.p. 185-188° (from petrol-chloroform) (Found: M^+2 , 496.3129. $C_{38}H_{40}N_4$ requires M^+2 , 496.3129), ν 2240 cm^{-1} , δ ($CDCl_3$) 1.08 (6H, s, 2Me), 1.36 (6H, bs, 2Me), 2.97-3.44 (6H, m, 2 CH_2CH), 7.08-7.51 (20H, m, ArH).

Model (3) Experiments

2-Hydroxy-2-methylacenaphthene-1-one. A solution of methyl magnesium iodide [prepared from methyl iodide (10.4 g) and magnesium (1.5 g) in ether (100 ml)] was added dropwise to a stirred solution of acenaphthene-1,2-dione (7.28 g, 0.04 mol) in THF (600 ml) at 4°. The reaction mixture was heated under reflux for 30 min and then allowed to cool to room temperature during 3 h before it was hydrolysed with aqueous ammonium chloride solution. After removal of THF the solution was extracted with ether and the ethereal extracts were concentrated. The starting material (1.2 g) which precipitated was collected and the filtrate gave 2-hydroxy-2-methylacenaphthene-1-one (2.45 g, 31%), m.p. 120-125° (from petrol-ethyl acetate) (Found: M^+ , 198.0680. $C_{13}H_{10}O_2$ require M, 198.0680), δ ($CDCl_3$) 1.67 (3H, s, Me), 3.11 (1H, s, OH), 7.6-8.11 (6H, m, ArH).

²¹ Final Technical Report October 1972

1-Acetyl-8-cyanonaphthalene (cf. ref. 8). A solution of the oxime of 2-hydroxy-2-methylacenaphthen-1-one (210 mg, 0.96 mmol) (prepared in the usual way from the corresponding ketone but not purified) and methane sulphonyl chloride (120 mg, 1.05 mmol) in pyridine was heated under reflux for 1 h. Water and 2M hydrochloric acid were added and the resultant solution was extracted with chloroform. Evaporation of solvent gave a dark red oil crystallisation of which from petrol-benzene gave 1-acetyl-8-cyanonaphthalene (100 mg, 53%), m.p. 98-100° (Found: M^+ , 195.0686. $C_{13}H_9NO$ require M, 195.0684), ν_{max} 2220, 1680 cm^{-1} , δ (CDCl₃) 2.81 (3H, s, Me), 7.48-7.64 (3H, m, 2,4,5-ArH), 7.95-8.15 (3H, m, 3,6,7-ArH), m/e 195(20%)(M).

Treatment of this ketone (100 mg, 0.47 mmol) with hydroxylamine hydrochloride (40 mg, 0.56 mmol) and sodium acetate (100 mg) gave 3-methyl-1H-benz[de]isoquinoline-N-oxide (28 mg, 25%) as green crystals, m.p. 165-169° (from chloroform-petrol) (Found: M^+ , 210.0791. $C_{13}H_{10}N_2O$ requires M, 210.0793), ν_{max} 1585, 1575 and 1525 cm^{-1} , δ (CDCl₃) 2.66 (3H, s, Me), 7.46-7.94 (6H, m, NH,ArH) 8.36 (1H, d, J 8Hz, ArH), m/e 210(45%)(M).

In aqueous-ethanol 2M sodium hydroxide solution the ketonitrile gave 3-aminophenalen-1-one, as orange crystals, m.p. 131-134° (Found: M^+ , 195.0686. $C_{13}H_{10}NO$ requires M, 195.0684), ν_{max} 3320, 3170, 1632 cm^{-1} , δ (CDCl₃) 5.94 (1H, s, 2-H), 7.66-7.76 (2H, m, ArH), 8.10-8.46 (4H, m, ArH), m/e 195(100%)(M+).

Reactions of 1,8-Dicyanonaphthalene

(i) 1,8-Dicyanonaphthalene (60 mg, 0.36 mmol) and methyl-lithium (1 mmol) in THF at room temperature gave (a) starting material (40%) (b) 3-methyl-1H-benz[de]isoquinol-1-one (1 mg), m/e 195(M) and (c) 3-amino-1,1-dimethyl-1H-benz[de]isoquinoline (12 mg) 2.70 (6H, s, 2Me) m/e 210(M). With methyl magnesium bromide starting material (30%) was recovered.

(ii) Treatment of 1,8-dicyanonaphthalene (1 mol) with (a) an excess of acetylperoxide in hot benzene (b) an excess of benzoyl peroxide in benzene under reflux, (c) solid benzoylperoxide (2 mol) at 200° for 5 min and (d) di-t-butyl peroxide (30 mol) at 126° for 20 h, gave either starting material (a) and (b) or starting material and intractable gums (c) and (d).