

AD-A144 690

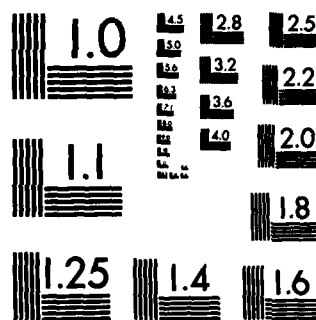
SYNTHESIS OF MONOMERS FOR THE PREPARATION OF
REGIOSPECIFICALLY SUBSTITUTE. (U) ARMY MATERIALS AND
MECHANICS RESEARCH CENTER WATERTOWN MA
S E WENTWORTH ET AL. JUN 84 AMMRC-TR-84-23 F/G 7/3

1/1

UNCLASSIFIED

NL

END



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

AMMRC TR 84-23

AD

**SYNTHESIS OF MONOMERS FOR
THE PREPARATION OF REGIOSPECIFICALLY
SUBSTITUTED POLY(PHENYLACETYLENES)
AS POTENTIAL CHEMICAL DETECTORS**

STANLEY E. WENTWORTH, JENNIE B. LIBBY and
PAUL R. BERGQUIST
POLYMER RESEARCH DIVISION

June 1984

Approved for public release; distribution unlimited.

ARMY MATERIALS AND MECHANICS RESEARCH CENTER
Watertown, Massachusetts 02172

84 08 24 076

AD-A144 690

DTIC FILE COPY

DTIC
ESTD
AUG 27 1984

S D E

The findings in this report are not to be construed as an official Department of the Army position, unless so designated by other authorized documents.

Mention of any trade names or manufacturers in this report shall not be construed as advertising nor as an official endorsement or approval of such products or companies by the United States Government.

DISPOSITION INSTRUCTIONS

Destroy this report when it is no longer needed.
Do not return it to the originator.

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

Block No. 20

ABSTRACT

A number of substituted phenylacetylenes have been prepared as precursors to poly(phenylacetylenes) having regiospecific substitution. These latter were required for a study attempting to correlate structure with electronic properties, especially conductivity. The following phenylacetylenes were prepared: o-, m-, and p-nitrophenylacetylene, p-trifluoromethylphenylacetylene, o- and p-aminophenylacetylene (m-commercially available), o-, m-, and p-acetamido, and m- and p-trifluoroacetamidophenylacetylene. Starting materials were the appropriate nitro or trifluoromethyl cinnamic acids. Bromination followed by dehydrobromination and decarboxylation gave the corresponding phenylacetylenes. The amino compounds were obtained by $\text{Zn}/\text{NH}_4\text{OH}$ reduction of the o- and p-nitrophenylacetylenes. Acylations were accomplished with acetic or trifluoroacetic anhydride.

Accession For	
NTIS GRA&I	☒
DTIC TAB	☐
Unannounced	☐
Justification	
By	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A-1	

2210
COPY
INSPECTED
2

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

INTRODUCTION

In the mid-sixties, NASA-funded work directed toward the development of space cabin atmosphere contaminant detectors lead to the preparation of a series of mono-substituted poly(phenylacetylenes).¹ Follow-up work at MIT incorporated some of these materials into a solid-state device with potential as an early warning fire alarm.² Subsequent studies under Navy sponsorship lead to refinement of the device, now designated the charge-flow transistor (CFT), and a preliminary understanding of the mechanism by which it operates.³

Our interest in this area was engendered by the Army's need for a sensitive, specific means of detecting chemical agents. It was envisioned that the CFT in conjunction with an "appropriately modified" poly(phenylacetylene) could fill this need.

In order to determine just what constitutes an appropriate modification of the poly(phenylacetylene), it is necessary to understand the structure/property relationship of the interaction of these materials with the CFT. Of particular interest is the effect on conductivity of varying the electronic parameters and location of the substituent. Unfortunately, this information is not available from published reports because of structural ambiguities in the polymers studied arising from their method of synthesis, the key feature of which involves the nitration of poly(phenylacetylene) with mixed acid¹ to yield, it is claimed, poly(p-nitrophenylacetylene). While the p-isomer, no doubt, predominates, it is highly likely that at least some of the o- and m-isomer is produced as well. In addition, given the delocalized nature of the polymer backbone, nitration here is possible as well. Di- or poly-nitration is also a possibility. All in all, the detailed structure of material so prepared must be regarded as uncertain.

In view of this, we determined to prepare a series of substituted poly(phenylacetylenes) in which both the nature and location of the substituents is known with certainty. The approach we have taken involves the preparation of specifically substituted monomeric phenylacetylenes. These are then polymerized into the desired polymers by a variety of techniques. A description of the procedures used for the preparation of these monomers comprises the balance of this report.

DISCUSSION

Our basic strategy for the preparation of specifically substituted phenylacetylenes as outlined in scheme 1 (Figure 1) begins with an appropriately substituted cinnamic acid. Bromination followed by base-catalyzed double dehydrobromination and decarboxylation yields the corresponding phenylacetylene on which further transformation of X can be performed as needed.

Several factors influenced the selection of X. Firstly, it was desired to include the substituents studied by Byrd¹ and Senturia.² Secondly, we wished to examine substituents having widely different electronic effects and finally, we wanted to study an electron withdrawing substituent which operated by means of

1. BYRD, N. R. *Space Cabin Atmosphere Contaminant Detection Techniques*. NASA CR-86047, July 1968.
2. SENTURIA, S. D. *Fabrication and Evaluation of Polymeric Early-Warning Fire-Alarm Devices*. NASA CR-134764, 1975.
3. SENTURIA, S. D. *Studies of Conduction Mechanisms in Gas-Sensitive Polymer Films*. Final Report ONR Contract N00014-77-C-0361, NTIS Accession No. AD-A100995, February 1981.

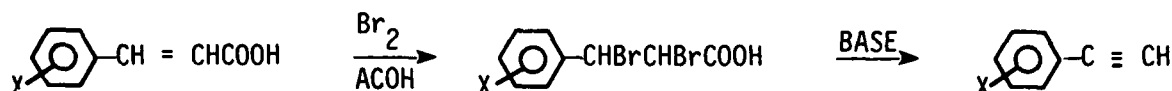


Figure 1. Scheme 1.

induction with no significant resonance contribution. It was also desired to examine the o-, m-, and p-isomers of each substituent wherever possible. In view of these considerations, phenylacetylenes bearing the substituents shown in Table 1 were selected for synthesis.

The nitrophenylacetylenes were, as indicated, prepared from the corresponding commercially available nitrocinnamic acids essentially according to published procedures. Initial conversion to the dibromo derivative was accomplished according to the procedure of Grob and Pfaendler.⁴ For the m- and p-isomers, a two-stage dehydrohalogenation, proceeding through the β -bromostyrene according to Reich and Chang⁵ and Cristol et al.⁶ was found acceptable. In the case of the o-isomer, a one-step double dehydrohalogenation to the propiolic acid followed by decarboxylation as described by Schofield and Simpson⁷ was employed.

The o- and p-amino phenylacetylenes were prepared by reduction of the corresponding nitro compounds with zinc dust in ammonium hydroxide using Grob and Pfaendler's⁴ procedure. The m-isomer, as indicated in Table 1, is commercially available.

Acetamido- and trifluoroacetamido-derivatives of the various amino compounds were prepared by direct reaction with the appropriate anhydride. Except for the trifluoroacetylation of the o-amino compound where the situation was apparently complicated by ring closure to the indole nucleus (see Experimental), these preparations were entirely straightforward. Although these derivatives were initially

Table 1. SUBSTITUTED PHENYLACETYLENES
SELECTED FOR SYNTHESIS

Substituent	o	m	p
NO ₂	X	X	X
NH ₂	X	*	X
$\begin{array}{c} \text{O} \\ \parallel \\ \text{NHCCCH}_3 \end{array}$	X	X	X
$\begin{array}{c} \text{O} \\ \parallel \\ \text{NHCCCF}_3 \end{array}$	X	X	X
CF ₃	—	—	X

*Commercially available

4. GROB, C. A., and PFAENDLER, H. R. *Solvolysis of β -Bromo-p-aminostyrene*. *Helvetica Chimica Acta*, v. 54, 1971, p. 2060.
5. REICH, S., and CHANG, N. Y. *Sur Les Acides o- et p-Nitro- α -bromocinnamiques*. *Helvetica Chimica Acta*, v. 3, 1920, p. 235.
6. CRISTOL, S. J., BEGOON, A., NORRIS, W. P., and RAMEY, P. S. *Mechanisms of Elimination Reactions. XII. The Reaction of Cis- and Trans-p-nitro- β -bromostyrene with Ethanolic Alkali*. *Journal of the American Chemical Society*, v. 76, 1954, p. 4558.
7. SCHOFIELD, K., and SIMPSON, J. C. E. *Cinnolines. Part III. The Richter Reaction*. *Journal of the Chemical Society*, 1945, p. 512.

prepared to prevent complexation and thus deactivation of Lewis acid type polymerization catalysts by the free amino groups, it was also appreciated that they provided the basis for two other series of polymers whose electronic properties could contribute to the establishment of structure-property relationships. Subsequent hydrolysis would, of course, yield the desired free-amino polymer.

The synthesis of p-trifluoromethylphenylacetylene began with the preparation of p-trifluoromethyl cinnamic acid which, in this case, was not commercially available. This was accomplished via a classic Knoevenagel reaction between p-trifluoromethylbenzaldehyde and malonic acid according to the procedure of Rapoport⁸ as reported by Trachtenberg.⁹ The balance of the synthesis exactly paralleled that used for the m- and p-nitrophenylacetylenes.

RESULTS

In general, the yields for the individual steps in the various syntheses ranged from fair to good. This, of course, resulted in only fair to poor overall yields of the desired monomers. Nevertheless, a sufficient quantity of each was obtained to permit us to go on to a study of their polymerization and an investigation of the electrical properties of the resultant polymers. These efforts are being reported elsewhere.*

EXPERIMENTAL

General: Melting points and boiling points are uncorrected. The o-, m-, and p-nitrocinnamic acids (predominantly trans) were obtained from Aldrich Chemical Company and used as received. The m-aminophenylacetylene was obtained from Eastman Kodak and distilled before use. The p-trifluoromethylbenzaldehyde was obtained from PCR Research Chemicals and distilled before use. All other reagents and solvents were commercially available and used as received unless otherwise noted. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tennessee.

3-(o-Nitrophenyl)-2,3-dibromopropionic Acid: Using the procedure of Grob and Pfaendler,⁴ a stirred suspension of 25.0 g (0.129 mol) of o-nitrocinnamic acid in 125 ml of glacial acetic acid was heated to 90°C. To this was added dropwise over 3-1/2 hours a solution of 21.2 g (0.133 mol) of bromine in 50 ml of glacial acetic acid. The temperature was then raised to 110°C and maintained there for an additional 3 hours. After cooling and standing overnight at room temperature, the solution was chilled to 0°C by means of an ice bath. The resultant crystals were removed by vacuum filtration. Treatment of the filtrate with water produced a second crop which was combined with the first crop and recrystallized from acetic acid to yield 35.3 g (77%) of material melting 182°C to 184°C (184°C to 185°C)¹⁰.

*WENTWORTH, S. E., and BERGQUIST, P. R. *Regiospecifically Substituted Poly(phenylacetylenes) as Potential Chemical Detectors*. To be submitted for publication.

8. RAPORPORT, H., WILLIAMS, A. R., LOWE, O. G., and SPOONER, W. W. *The Hydrolysis of Some Cyanocinnamic Acids*. Journal of the American Chemical Society, v. 75, 1953, p. 1125.
9. WITTSTRUCK, T. A., and TRACHTENBERG, E. N. *A Nuclear Magnetic Resonance Study of Transmission of Electronic Effects. Ethylbenzenes, Dihydrocinnamic Acids and Cis- and Trans- Cinnamic Acids*. Journal of the American Chemical Society, v. 89, 1967, p. 3803.
10. BUCKLES, R. E., HAUSMAN, E. A., and WHEELER, N. G. *The Action of Bromine Vapor on Solid Aromatic Compounds*. Journal of the American Chemical Society, v. 72, 1950, p. 2494.

o-Nitrophenylpropionic Acid: Using the procedure of Schofield and Simpson,⁷ 18.9 g (0.054 mol) of 3-(o-nitrophenyl)-2,3-dibromopropionic acid were dissolved in 114 ml of 10% aqueous NaOH by stirring overnight. Cautious addition of 180 ml of 2N HNO₃ produced a heavy yellowish precipitate which was removed by vacuum filtration and air-dried overnight, yielding 9.9 g (96%) of material melting 161°C to 162°C (166°C to 167°C⁷).

o-Nitrophenylacetylene: Using the procedure of Schofield and Simpson,⁷ 5.5 g (0.029 mol) of o-nitrophenylpropionic acid were refluxed with 800 ml of distilled water for a total of 16 hours over 2 successive days. The resultant steam volatile product collected in the condenser from which it was frequently washed with ether (in practice, two condensers were alternated, thereby eliminating loss during the ether wash). The pooled washings were evaporated to dryness and the resultant residue recrystallized from ethanol to yield 3.2 g (74%) of the desired material melting 81°C to 82°C (81°C to 82°C⁷).

o-Aminophenylacetylene: Using the procedure of Grob and Pfaendler,⁴ a suspension of 12.5 g (0.085 mol) of o-nitrophenylacetylene in 45.5 ml of water and 56.8 ml of concentrated NH₄OH was cooled to 0°C in an ice bath. Added to this in small portions over 1 hour under a nitrogen blanket was 41.5 g (0.635 g atom) of recently purchased Zn dust. Vigorous shaking was maintained between additions. After an additional 1 hour of shaking while warming to room temperature, the flask was attached to a mechanical shaker and shaken an additional 16 hours. Added to this was 100 ml of degassed distilled water and the liquid phase removed by decantation. This was extracted with several portions of ether. The residual Zn dust was triturated with several portions of ether which were added to the ether extracts. After drying over Na₂CO₃, the ether was removed on a rotary evaporator resulting in a greenish-blue liquid which was vacuum distilled at 3 mm to yield 7.5 g (75%) of product boiling at 78°C to 80°C (b₁₂ 98°C to 100°C¹¹).

o-Acetamidophenylacetylene: Freshly distilled acetic anhydride, 0.95 g (0.009 mol), was added dropwise to 1.05 g (0.009 mol) of o-aminophenylacetylene in a small round bottom flask suspended in a water bath. The mixture was then heated at 60°C for 1 hour and cooled to room temperature. The resultant solid was recrystallized from water to yield 0.55 g (38%) of product melting at 73°C to 74.5°C (84°C¹¹; 75°C¹²).

o-Trifluoroacetamidophenylacetylene: Using the procedure of Pailer and Hübsch,¹³ 1.02 g (0.009 mol) of o-aminophenylacetylene were dissolved in 15 ml of anhydrous ether and the solution chilled to 0°C by means of an ice bath. To this was added, dropwise with stirring, 1.8 g (0.009 mole) of trifluoroacetic anhydride. The reaction mixture was allowed to come to room temperature and stand for 1 hour after which an additional 50 ml of ether were added to it. The resulting solution was washed successively with three 50 ml portions of water, 50 ml of aqueous Na₂CO₃ solution, and a final 50 ml of water after which it was dried over anhydrous MgSO₄. After filtering, the ether was removed by means of a rotary evaporator. The resultant white solid was recrystallized from 85% heptane -15% acetone to yield material melting at 65.5°C to 66.5°C. Due to mechanical loss, no yield figure is available.

11. SCHOFIELD, K., and SWAIN, T. *Cinnolines. Part XXI. Further Observations on the Richter Synthesis.* Journal of the Chemical Society, 1949, p. 2393.
12. BAEYER, A., and LANDSBERG, L. *Synthesis by Means of Phenylacetylenes and Their Derivatives.* Berichte Der Deutsche Chemischen Gesellschaft, v. 15, 1882, p. 57.
13. PAILER, M., and HUBSCH, W. J. *Determination of Primary and Secondary Amines as Amides by Means of Gas Chromatography on Packed and Capillary Columns.* Monatshefte Fur Chemie, v. 97, 1966, p. 1541.

Anal. Calcd. for $C_{10}H_6F_3NO$: C, 56.35; H, 2.84; F, 26.74; N, 6.57
Found: C, 56.08; H, 3.36; F, 26.42; N, 6.39

While these results are entirely consistent with the expected trifluoroacetamide, mass spectrometry failed to confirm the structure, giving, instead, a molecular ion of $m/e = 215$ rather than the required $m/e = 213$. This indicates the incorporation of two hydrogens giving rise to a material whose empirical formula is $C_{10}H_8F_3NO$ and having the following composition: C, 55.82; H, 3.75; F, 26.49; and N, 6.51. The experimental values are also in excellent agreement with this formula. Further investigation by NMR spectrometry indicates the material to be the product of a reductive cyclization to yield a trifluoroacetyl indole derivative, but does not distinguish between two isomeric possibilities. This sort of transformation is not without precedent in the indole series.^{14,15} Further elaboration of the structure was deemed to be outside the scope of this present study. In view of these complications, efforts to obtain this trifluoroacetamide were abandoned.

3-(m-Nitrophenyl)-2,3-dibromopropionic Acid: Using the procedure described above for the o-nitro isomer, 49.75 g (0.258 mol) of m-nitrocinnamic acid were treated with 42.50 g (0.266 mol) of bromine in acetic acid. When chilling of the reaction mixture failed to induce crystallization of the product, it was poured with stirring into 3.0 liters of water to produce a white precipitate which was removed by vacuum filtration. After thorough washing with 3:1 (V/V) water/acetic acid, the material was vacuum dried at 60°C to yield 82.5 g (91%) of product melting at 173°C to 174°C (176°C¹⁰).

β -Bromo-m-nitrostyrene: Using the procedure of Reich and Chang,⁵ a stirred suspension of 82.5 g (0.234 mol) of 3-(m-nitrophenyl)-2,3-dibromopropionic acid and 95.6 g (1.17 mol) of anhydrous sodium acetate in 600 ml of anhydrous ethanol was refluxed for 4 hours. After cooling, most of the ethanol was removed by means of a rotary evaporator. The resulting solid was taken up in water and extracted with four 100-ml portions of ether. The combined ether extracts were dried over $MgSO_4$. After filtration, the ether was removed by means of a rotary evaporator to yield 48.3 g of crude product in the form of a dark red liquid. This was used without purification in the next step.

m-Nitrophenylacetylene: Using essentially the procedure of Cristol et al.,⁶ 48.3 g (0.212 mol) of the crude β -bromo-m-nitrostyrene prepared above were dissolved in 80 ml of ethanol and added rapidly with stirring to a solution of 100 g (2.50 mol) of sodium hydroxide in 1.0 l of ethanol. After stirring at room temperature for 45 minutes, sufficient acetic acid was added to bring the pH to approximately 7. The ethanol was then removed by means of a rotary evaporator and the resulting solid taken up in water. This solution was extracted with several portions of ether which were combined and dried over $MgSO_4$. After filtration, the ether was removed by means of a rotary evaporator to yield a dark red liquid. Vacuum distillation gave 12.9 g (40%) of product b.p. 81°C to 92°C, (b.p. 80°C¹⁶).

m-Acetamidophenylacetylene: Using a modification of the procedure of Grob and Pfaendler,⁴ 2.0 g (0.009 mol) of m-aminophenylacetylene in a flask suspended in a water bath were treated dropwise with 1.8 g (0.018 mol) of freshly distilled acetic

14. SHIGEKI, H. *Indole and Its Derivatives. IV. The Mechanism of Indole Formation*. Nippon Kagaku Zasshi, v. 79, 1958, p. 227.

15. FERRIS, J. P., and ANTONUCCI, F. R. *Photochemistry of Ortho-Substituted Benzene Derivatives and Related Heterocycles*. Journal of the American Chemical Society, v. 96, 1974, p. 2010.

16. BOSCHAN, R. H. *Process for Making Nitroarylacetylenes and Nitroarylaldehydes*. United States Patent 4,125,563, Nov. 14, 1978.

anhydride. After heating at 60°C for 1 hour and cooling to room temperature, a white solid formed. Recrystallization from water afforded 2.04 g (75%) of product melting at 93.5°C to 94.5°C (94°C to 96°C¹⁷).

m-Trifluoroacetamidophenylacetylene: According to the procedure of Pailer and Hübsch,¹³ 2.2 g (0.019 mol) of m-aminophenylacetylene in 12.0 ml of ether contained in a flask suspended in an ice bath were treated dropwise with stirring with 4.0 g (0.019 mol) of trifluoroacetic anhydride over a 15-minute period. After warming to room temperature, the reaction mixture was allowed to stand for 1 hour. After dilution with an additional 50 ml of ether, the reaction mixture was washed with three 50-ml portions of water. The ether solution was then dried over MgSO₄. After filtration, the ether was removed by means of a rotary evaporator. The resulting white solid was recrystallized from 85:15 (V/V) heptane/acetone to yield 2.03 g (51%) of product melting at 97.5°C to 98°C.

Anal. Calcd. for C₁₀H₆F₃NO: C, 56.35; H, 2.84; F, 26.74; N, 6.57

Found: C, 56.12; H, 2.73; F, 26.60; N, 6.49

Mass Spectrum: M⁺ requires 213; Found, 213

3-(p-Nitrophenyl)-2,3-dibromopropionic Acid: Using the procedure described above for the o- and m-nitro isomers, 43.0 g (0.222 mol) of p-nitrocinnamic acid were treated with 36.6 g (0.228 mol) of bromine in acetic acid. Upon cooling to room temperature overnight, pale yellow crystals formed which were removed by suction filtration and washed with 3:1 (V/V) water/acetic acid. Addition of water to the filtrate produced a second crop which was isolated in the same manner and combined with the first to yield 73.4 g (93%) of product melting at 214.5°C to 215.5°C (217°C to 218°C¹⁸).

8-Bromo-p-nitrostyrene: Using the procedure described above for the m-nitro isomer, 50.0 g (0.142 mol) of 3-(p-nitrophenyl)-2,3-dibromopropionic acid were treated with 58.3 g (0.711 mol) of anhydrous sodium acetate in refluxing ethanol. After cooling to room temperature, the ethanol was removed by means of a rotary evaporator. The resulting pink solid was triturated with four 100-ml portions of ether, after which the residual solid was dissolved in water. The resulting solution was extracted with a further 200-ml portion of ether. This extract was combined with the previous ether triturations and dried over MgSO₄. After filtration, the ether was removed by means of a rotary evaporator to yield 30.0 g of crude oily yellow solid product which were used without further purification in the next step.

p-Nitrophenylacetylene: Using the procedure of Cristol et al.,⁶ a solution of 31.7 g (0.139 mol) of crude 8-bromo-p-nitrostyrene (prepared as above) in 250 ml of ethanol were added in one portion with stirring to a solution of 60.0 g (1.50 mol) of sodium hydroxide in 690 ml of ethanol. After stirring for one-half hour at room temperature, the pH of the reaction mixture was brought to about pH 7 using approximately 70 ml of glacial acetic acid. This caused the formation of a voluminous tan precipitate. After removal of the ethanol by means of a rotary evaporator, the resulting tan solid was triturated with three 100-ml portions of cold water. The residual crude product, after drying, melted at 144°C to 150°C and weighed 10.1 g (43%). Recrystallization from ethanol afforded material melting at 147.5°C to 148.5°C (149°C¹⁹).

17. ARNOLD, F. E., REINHARDT, B. A., and HEDBERG, F. L. *Aromatic Enyne Compounds and Their Synthesis*. United States Patent 4,162,265, July 24, 1979.

18. DREWSSEN, V. B. *Concerning Derivatives of Paranitrocinnamic Acid*. Justus Liebigs Annalen Der Chemie, v. 212, 1882, p.150.

19. MULLER, C. L. *Concerning Some Derivatives of Para- and Ortho-Nitrocinnamic Acid*. Justus Liebigs Annalen Der Chemie, v. 212, 1882, p. 122.

p-Aminophenylacetylene: Using essentially the procedure described above for the o-amino isomer, 7.25 g (0.049 mol) of p-nitrophenylacetylene were treated under N₂ with 22.4 g (0.343 g atom) of zinc dust in aqueous ammonium hydroxide. Isolation according to the above procedure afforded 5.6 g of crude product. Recrystallization from heptane gave 3.9 g (68%) of material melting at 97.5°C to 100°C (99°C to 100°C²⁰).

p-Acetamidophenylacetylene: Freshly distilled acetic anhydride, 1.26 g (0.012 mol), was added dropwise with stirring to a chilled (ice bath) ether solution of 1.40 g (0.012 mol) of p-aminophenylacetylene. After coming to room temperature and standing for 1 hour, the ether was removed by raising the temperature to 60°C (water bath) and holding for an additional hour. After cooling, the residue was recrystallized from water to yield 1.1 g (58%) of product melting at 122.5°C to 123.5°C (122°C to 123°C⁴).

p-Trifluoroacetamidophenylacetylene: Using the procedure described above for the o- and m-trifluoroacetamido-isomers, 2.2 g (0.019 mol) of p-aminophenylacetylene were treated with 4.0 g (0.019 mol) of trifluoroacetic anhydride in ether. Isolation, as above, yielded 2.32 g (57%) of crude product. Recrystallization from acetone/heptane gave material melting at 121.5°C to 123°C.

The structure of this material was indicated by mass spectroscopy wherein the required molecular ion, m⁺=213 was observed and confirmed by NMR spectroscopy which gave the anticipated spectrum.

p-Trifluoromethylcinnamic Acid: Using the procedure of Rapoport et al.,⁸ 13.8 g (0.079 mol) of freshly distilled p-trifluoromethylbenzaldehyde and 12.2 g (0.117 mol) of malonic acid in 60 ml of dry pyridine containing 1.2 ml of piperidine were heated to 80°C for one-half hour and an additional 2-1/2 hours at 100°C to 105°C. After cooling to room temperature, the solution was poured with stirring over a 20-minute period into 500 ml of 3N HCl. The resulting precipitate was removed by vacuum filtration, washed with water and oven-dried at 45°C to yield 15.7 g (91%) of product melting at 229°C to 230°C (229.5°C to 230°C⁹).

3-(p-Trifluoromethylphenyl)-2,3-dibromopropionic Acid: Using the procedure detailed above for the three nitro analogs, 15.7 g (0.073 mol) of p-trifluoromethyl cinnamic acid were treated with 13.2 g (0.082 mol) of bromine in acetic acid. After cooling to room temperature, the solution was poured with stirring into 1.5 liters of water. The resulting precipitate was removed by vacuum filtration and air-dried to yield 25.7 g (94%) of product melting at 203.5°C to 204°C.

Anal. Calcd. for C₁₀H₇Br₂F₃O₂: C, 31.94; H, 1.88; Br, 42.51; F, 15.16
Found: C, 31.88; H, 1.82; Br, 42.65; F, 15.24

β-Bromo-p-trifluoromethylstyrene: Using the procedure detailed above for the m- and p-nitro isomers, 25.7 g (0.068 mol) of 3-(p-trifluoromethylphenyl)-2,3-dibromopropionic acid were treated with 29.8 g (0.363 mol) of anhydrous sodium acetate in refluxing ethanol. After cooling to room temperature, the reaction mixture was worked up according to the procedure utilized for the p-nitro isomer. This resulted in 18.8 g of impure product in the form of a pale yellow oil, which were used without further purification in the next step.

20. BURAWOY, A., and CRITCHLEY, J. P. *Electronic Spectra of Organic Molecules and Their Interpretation*. Tetrahedron, v. 5, 1959, p. 340.

p-Trifluoromethylphenylacetylene: A solution of 29.0 g (0.725 mol) of sodium hydroxide in 300 ml of ethanol was placed into a flask containing 18.8 g (0.075 mol) of the crude β -bromo-p-trifluoromethylstyrene prepared above. After stirring at room temperature for 45 minutes, the mixture was poured with stirring into 1.5 liters of water. The resulting solution was extracted with several portions of ether which were combined and dried over MgSO_4 . After filtration, the ether was removed by means of a rotary evaporator to yield 5.0 g of impure liquid product. Vacuum distillation at 170 mm produced 2.0 g (after loss during distillation) of material boiling at 48°C . The structure of this material was indicated by infrared spectroscopy and confirmed by mass spectrometry which gave the requisite molecular ion, $m^+=170$.

ACKNOWLEDGMENT

The authors are grateful to Mr. Alfred J. Deome of these laboratories for the mass spectral analyses herein reported.

DISTRIBUTION LIST

No. of Copies	To
1	Office of the Under Secretary of Defense for Research and Engineering, The Pentagon, Washington, DC 20301
12	Commander, Defense Technical Information Center, Cameron Station, Building 5, 5010 Duke Street, Alexandria, VA 22314
1	Metals and Ceramics Information Center, Battelle Columbus Laboratories, 505 King Avenue, Columbus, OH 43201
1	Commander, Army Research Office, P.O. Box 12211, Research Triangle Park, NC 27709 ATTN: Information Processing Office
1	Commander, U.S. Army Materiel Development and Readiness Command, 5001 Eisenhower Avenue, Alexandria, VA 22333 ATTN: DRCLDC
1	Commander, U.S. Army Materiel Systems Analysis Activity, Aberdeen Proving Ground, MD 21005 ATTN: DRXSY-MP, H. Cohen
1	Commander, U.S. Army Electronics Research and Development Command, Fort Monmouth, NJ 07703 ATTN: DELSD-L
1	DELS-D-E
1	Commander, U.S. Army Missile Command, Redstone Arsenal, AL 35898 ATTN: DRSMI-RKP, J. Wright, Bldg. 7574
4	DRSMI-TB, Redstone Scientific Information Center
1	DRSMI-RLM
1	Technical Library
2	Commander, U.S. Army Armament, Munitions and Chemical Command, Dover, NJ 07801 ATTN: Technical Library
1	DRDAR-SCM, J. D. Corrie
1	DRDAR-QAC-E
1	DRDAR-LCA, Mr. Harry E. Pebly, Jr., PLASTEC, Director
1	Commander, U.S. Army Natick Research and Development Laboratories Natick, MA 01760 ATTN: Technical Library
1	Commander, U.S. Army Satellite Communications Agency, Fort Monmouth, NJ 07703 ATTN: Technical Document Center
1	Commander, U.S. Army Tank-Automotive Command, Warren, MI 48090 ATTN: DRSTA-ZSK
2	DRSTA-UL, Technical Library

No. of
Copies

To

Commander, White Sands Missile Range, NM 88002
1 ATTN: STEWS-WS-VT

Director, U.S. Army Ballistic Research Laboratory, Aberdeen Proving Ground,
MD 21005
1 ATTN: DRDAR-TSB-S (STINFO)

Commander, Dugway Proving Ground, Dugway, UT 84022
1 ATTN: Technical Library, Technical Information Division

Commander, Harry Diamond Laboratories, 2800 Powder Mill Road, Adelphi, MD 20783
1 ATTN: Technical Information Office

Commander, Watervliet Arsenal, Watervliet, NY 12189
1 ATTN: DRSMC-LCB-TL, Mr. P. Casey

Commander, U.S. Army Foreign Science and Technology Center, 220 7th Street, N.E.,
Charlottesville, VA 22901
1 ATTN: Military Tech, Mr. Marley

Director, Eustis Directorate, U.S. Army Air Mobility Research and Development
Laboratory, Fort Eustis, VA 23604
1 ATTN: Mr. J. Robinson, DAVDL-E-MOS (AVRADCOM)

U.S. Army Aviation Training Library, Fort Rucker, AL 36360
1 ATTN: Building 5906-5907

Commander, U.S. Army Agency for Aviation Safety, Fort Rucker, AL 36362
1 ATTN: Technical Library

Commander, USACDC Air Defense Agency, Fort Bliss, TX 79916
1 ATTN: Technical Library

Commander, U.S. Army Engineer School, Fort Belvoir, VA 22060
1 ATTN: Library

Commander, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS 39180
1 ATTN: Research Center Library

Commander, U.S. Army Environmental Hygiene Agency, Edgewood Arsenal, MD 21010
1 ATTN: Chief, Library Branch

Commandant, U.S. Army Quartermaster School, Fort Lee, VA 23801
1 ATTN: Quartermaster School Library

Commander, U.S. Army Radio Propagation Agency, Fort Bragg, NC 28307
1 ATTN: SCCR-2

Naval Research Laboratory, Washington, DC 20375
1 ATTN: Dr. C. I. Chang - Code 5830
2 Dr. G. R. Yoder - Code 6384
1 Dr. H. J. Wohltjen

No. of
Copies

To

1 Chief of Naval Research, Arlington, VA 22217
1 ATTN: Code 471

Commander, U.S. Air Force Wright Aeronautical Laboratories,
Wright-Patterson Air Force Base, OH 45433

2 ATTN: AFWAL/MLTE, E. Morrissey
1 AFWAL/MLC
1 AFWAL/MLLP, M. Forney Jr.
1 AFWAL/MLBC, Mr. Stanley Schulman

National Aeronautics and Space Administration, Washington, DC 20546

1 ATTN: Mr. G. C. Deutsch - Code RW

National Aeronautics and Space Administration, Marshall Space Flight Center,
Huntsville, AL 35812

1 ATTN: R. J. Schwinghammer, EH01, Dir, M&P Lab
1 Mr. W. A. Wilson, EH41, Bldg. 4612

1 Ship Research Committee, Maritime Transportation Research Board, National Research
Council, 2101 Constitution Ave., N. W., Washington, DC 20418

1 Librarian, Materials Sciences Corporation, Guynedd Plaza 11, Bethlehem Pike,
Spring House, PA 19477

1 Mechanical Properties Data Center, Belfour Stulen Inc., 13917 W. Bay Shore Drive,
Traverse City, MI 49684

1 Dr. Peter Cukor, GTE Laboratories, 40 Sylvan Road, Waltham, MA 02254

1 Prof. H. DuPont Durst, Department of Chemistry, University of Puerto Rico,
Rio Piedras, Puerto Rico 00931

1 Prof. Bruce Foxman, Department of Chemistry, Brandeis University,
Waltham, MA 02254

1 Dr. Raimond Liepens, Los Alamos National Laboratory, P.O. Box 1663,
Los Alamos, NM 87545

1 Dr. E. J. Poziomek, Research Division, Chemical Systems Laboratory, Aberdeen
Proving Ground, MD 21010

1 Prof. S. D. Senturia, Department of Electrical Engineering and Computing
Science, Massachusetts Institute of Technology, Cambridge, MA 02139

Director, Army Materials and Mechanics Research Center, Watertown, MA 02172

2 ATTN: DRXMR-PL
3 Authors

Army Materials and Mechanics Research Center,
Watertown, Massachusetts 02172

AD UNCLASSIFIED
SYNTHESIS OF MONOMERS FOR THE PREPARATION OF
REGIOSPECIFICALLY SUBSTITUTED POLY(PHENYLACETYLENES)
AS POTENTIAL CHEMICAL DETECTORS -
Stanley E. Wentworth, Jennie B. Libby, and
Paul R. Bergquist

Key Words

Synthesis (chemistry)
Polymers
Electrical conductivity

Technical Report AMMRC TR 84-23, June 1984, 10 pp -
illus-table, D/A Project 11162105AH84

A number of substituted phenylacetylenes have been prepared as precursors to poly-(phenylacetylenes) having regiospecific substitution. These latter were required for a study attempting to correlate structure with electronic properties, especially conductivity. The following phenylacetylenes were prepared: o-, m-, and p-nitrophenylacetylene, p-trifluoromethylphenylacetylene, o- and p-aminophenylacetylene (m-commercially available), o-, m-, and p-acetamido, and m- and p-trifluoroacetamidophenylacetylene. Starting materials were the appropriate nitro or trifluoromethyl cinnamic acids. Bromination followed dehydrobromination and decarboxylation gave the corresponding phenylacetylenes. The amino compounds were obtained by Zn/NH₄OH reduction of the o- and p-nitrophenylacetylenes. Acylations were accomplished with acetic or trifluoroacetic anhydride.

Army Materials and Mechanics Research Center,
Watertown, Massachusetts 02172

AD UNCLASSIFIED
SYNTHESIS OF MONOMERS FOR THE PREPARATION OF
REGIOSPECIFICALLY SUBSTITUTED POLY(PHENYLACETYLENES)
AS POTENTIAL CHEMICAL DETECTORS -
Stanley E. Wentworth, Jennie B. Libby, and
Paul R. Bergquist

Key Words

Synthesis (chemistry)
Polymers
Electrical conductivity

Technical Report AMMRC TR 84-23, June 1984, 10 pp -
illus-table, D/A Project 11162105AH84

A number of substituted phenylacetylenes have been prepared as precursors to poly-(phenylacetylenes) having regiospecific substitution. These latter were required for a study attempting to correlate structure with electronic properties, especially conductivity. The following phenylacetylenes were prepared: o-, m-, and p-nitrophenylacetylene, p-trifluoromethylphenylacetylene, o- and p-aminophenylacetylene (m-commercially available), o-, m-, and p-acetamido, and m- and p-trifluoroacetamidophenylacetylene. Starting materials were the appropriate nitro or trifluoromethyl cinnamic acids. Bromination followed dehydrobromination and decarboxylation gave the corresponding phenylacetylenes. The amino compounds were obtained by Zn/NH₄OH reduction of the o- and p-nitrophenylacetylenes. Acylations were accomplished with acetic or trifluoroacetic anhydride.

Army Materials and Mechanics Research Center,
Watertown, Massachusetts 02172

AD UNCLASSIFIED
SYNTHESIS OF MONOMERS FOR THE PREPARATION OF
REGIOSPECIFICALLY SUBSTITUTED POLY(PHENYLACETYLENES)
AS POTENTIAL CHEMICAL DETECTORS -
Stanley E. Wentworth, Jennie B. Libby, and
Paul R. Bergquist

Key Words

Synthesis (chemistry)
Polymers
Electrical conductivity

Technical Report AMMRC TR 84-23, June 1984, 10 pp -
illus-table, D/A Project 11162105AH84

A number of substituted phenylacetylenes have been prepared as precursors to poly-(phenylacetylenes) having regiospecific substitution. These latter were required for a study attempting to correlate structure with electronic properties, especially conductivity. The following phenylacetylenes were prepared: o-, m-, and p-nitrophenylacetylene, p-trifluoromethylphenylacetylene, o- and p-aminophenylacetylene (m-commercially available), o-, m-, and p-acetamido, and m- and p-trifluoroacetamidophenylacetylene. Starting materials were the appropriate nitro or trifluoromethyl cinnamic acids. Bromination followed dehydrobromination and decarboxylation gave the corresponding phenylacetylenes. The amino compounds were obtained by Zn/NH₄OH reduction of the o- and p-nitrophenylacetylenes. Acylations were accomplished with acetic or trifluoroacetic anhydride.

Army Materials and Mechanics Research Center,
Watertown, Massachusetts 02172

AD UNCLASSIFIED
SYNTHESIS OF MONOMERS FOR THE PREPARATION OF
REGIOSPECIFICALLY SUBSTITUTED POLY(PHENYLACETYLENES)
AS POTENTIAL CHEMICAL DETECTORS -
Stanley E. Wentworth, Jennie B. Libby, and
Paul R. Bergquist

Key Words

Synthesis (chemistry)
Polymers
Electrical conductivity

Technical Report AMMRC TR 84-23, June 1984, 10 pp -
illus-table, D/A Project 11162105AH84

A number of substituted phenylacetylenes have been prepared as precursors to poly-(phenylacetylenes) having regiospecific substitution. These latter were required for a study attempting to correlate structure with electronic properties, especially conductivity. The following phenylacetylenes were prepared: o-, m-, and p-nitrophenylacetylene, p-trifluoromethylphenylacetylene, o- and p-aminophenylacetylene (m-commercially available), o-, m-, and p-acetamido, and m- and p-trifluoroacetamidophenylacetylene. Starting materials were the appropriate nitro or trifluoromethyl cinnamic acids. Bromination followed dehydrobromination and decarboxylation gave the corresponding phenylacetylenes. The amino compounds were obtained by Zn/NH₄OH reduction of the o- and p-nitrophenylacetylenes. Acylations were accomplished with acetic or trifluoroacetic anhydride.

END

FILMED

DTIC