trap. Pure pinacolyl chloride (**8**, 9.2 g, 49% yield) distilled next at 30–35 °C (oil bath) (20 Torr): ir (neat)[28] 2975 (s), 2860 (m), 1455 (m), 1375 (m), 1360 (s), 1270 (m), 1190 (m), 1070 (s), 860 (m), 725 (m), and 664 cm^{-1} (s); NMR ($CDCl_3$, 4 M) δ 1.08 (s, 9, 3 CH_3), 1.51 (d, 3, CH_3CH, $J = 7.0$ Hz), 3.83 (q, 1, methyne, $J = 7.0$ Hz); mass spectrum *m/e* (rel intensity) 107, 105 ($M^+ - 15$) (2, 6), 69 (22), 57 (100).

Acknowledgments. The author is grateful to Mr. Horacio Aragona and Mr. Ignacio Martín for technical assistance.

Registry No.—**7b**, 25966-61-4; **8**, 5750-00-5; lithium chloride, 7447-41-8.

References and Notes

(1) F. C. Whitmore and H. S. Rothrock, *J. Am. Chem. Soc.*, **55**, 1106 (1933); F. C. Whitmore and F. Johnston, *ibid.*, **55**, 5020 (1933).
(2) G. G. Ecke, N. C. Cook, and F. C. Whitmore, *J. Am. Chem. Soc.*, **72**, 1511 (1950).
(3) H. Bilke, G. Collin, C. Duschek, W. Hoebold, R. Hoehn, W. Pritzkow, H. Schmidt, and D. Schnurpfeil, *J. Prakt. Chem.*, **311**, 1037 (1969).
(4) 2,3-Dimethyl-2-chlorobutane, bp 112 °C (749 Torr); see D. Pawlow, *Justus Liebigs Ann. Chem.*, **196**, 124 (1879). 3,3-Dimethyl-2-chlorobutane, bp 109 °C (734 Torr); see ref 5.
(5) F. C. Whitmore, H. I. Bernstein, and L. W. Mixon, *J. Am. Chem. Soc.*, **60**, 2539 (1938).
(6) J. E. Anderson and H. Pearson, *J. Chem. Soc., Chem. Commun.*, 908 (1972), and references cited therein.
(7) F. C. Whitmore and F. A. Karnatz, *J. Am. Chem. Soc.*, **60**, 2536 (1938).
(8) Previously treated with triphenyl phosphite.
(9) J. Cason and J. S. Correia, *J. Org. Chem.*, **26**, 3645 (1961).
(10) H. N. Rydon, *J. Chem. Soc.*, 2224 (1953).
(11) G. J. Karabatsos, C. E. Orzech, Jr., and S. Meyerson, *J. Am. Chem. Soc.*, **86**, 1994 (1964); R. E. Ireland, C. J. Kowalsky, J. W. Tilley, and D. M. Walba, *J. Org. Chem.*, **40**, 992 (1975).
(12) H. R. Hudson, *J. Chem. Soc. B*, 664 (1968).
(13) G. A. Wiley, B. M. Rein, R. L. Hershkowitz, and B. C. Chung, *J. Am. Chem. Soc.*, **86**, 964 (1964); G. A. Wiley, B. M. Rein, and R. L. Hershkowitz, *Tetrahedron Lett.* 2509 (1964).
(14) P. C. Crofts and I. M. Downie, *J. Chem. Soc.*, 2559 (1963); I. M. Downie, J. B. Holmes, and J. B. Lee, *Chem. Ind. (London)*, 900 (1966).
(15) E. T. Snyder, *J. Org. Chem.*, **37**, 1466 (1972).
(16) At the time of this writing the use of solid phase phosphorus reagents for the conversion of alcohols to alkyl halides has been reported. Its behavior with compounds amenable to rearrangement remains to be explored. See S. L. Regen and D. P. Lee, *J. Org. Chem.*, **40**, 1669 (1975).
(17) After 14 h of reaction at ca. 42 °C a 90% yield of material composed of 9% olefins and 91% chlorides **8** and **10** in a 2:3 ratio was obtained.
(18) R. S. Tipson, M. A. Clapp, and L. H. Cretcher, *J. Org. Chem.*, **12**, 133 (1947); R. T. Blikenstaff and F. C. Cheng, *J. Am. Chem. Soc.*, **80**, 2726 (1958), and references cited therein.
(19) G. L. Jenkins and J. C. Kellett, Jr., *J. Org. Chem.*, **27**, 624 (1962).
(20) A. Wyschnegradsky, *Justus Liebigs Ann. Chem.*, **190**, 357 (1878).
(21) J. E. Nordlander, R. R. Gruetzmacher, and F. Miller, *Tetrahedron Lett.*, 927 (1973).
(22) Dimethylformamide is known to promote hydrogen halide elimination in alkyl halides at moderately high temperatures. See N. Kornblum and R. K. Blackwood, *J. Am. Chem. Soc.*, **78**, 4037 (1956).
(23) Lithium halides in combination with HMPA has been used in lithium salt catalyzed ring opening of glycidic esters. See B. C. Hartman and B. Rickborn, *J. Org. Chem.*, **37**, 2060 (1972).
(24) J. F. Normant and H. Deshayes, *Bull. Soc. Chim. Fr.*, 2455 (1967); H. Normant, *ibid.*, 801 (1968).
(25) 3-Methylbutan-2-ol and 3,3-dimethylbutan-2-ol were purchased from Aldrich Chemical Co. Infrared spectra were measured on a Perkin-Elmer 337 spectrophotometer. NMR spectra were obtained from a Varian Associates A-60 spectrometer using a mixture of tetramethylsilane, acetone, methylene chloride, and chloroform as internal standards. VPC analyses were performed in a Varian Aerograph series 1400 gas chromatograph using a 5% diisodecyl phthalate on Chromosorb G column treated with dimethylchlorosilane. Mass spectra were obtained from a Varian MAT 111 instrument at 20 eV. The experimental conditions described furnish a maximum yield of compound **8**.
(26) Compounds **8** and **10** have essentially the same retention time in a variety of columns.
(27) Distillation of pinacolyl chloride at atmospheric pressure was precluded by its decomposition into hydrogen chloride and olefins at temperatures above 70 °C.
(28) J. J. Shipman, V. L. Folt, and S. Krim, *Spectrochim. Acta*, **18**, 1603 (1962).

Charge-Transfer Polymers Containing 7,7,8,8-Tetracyanoquinodimethan and Tetrathiafulvalene

W. R. Hertler

Contribution No. 2314 from the Central Research and Development Department,
E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898

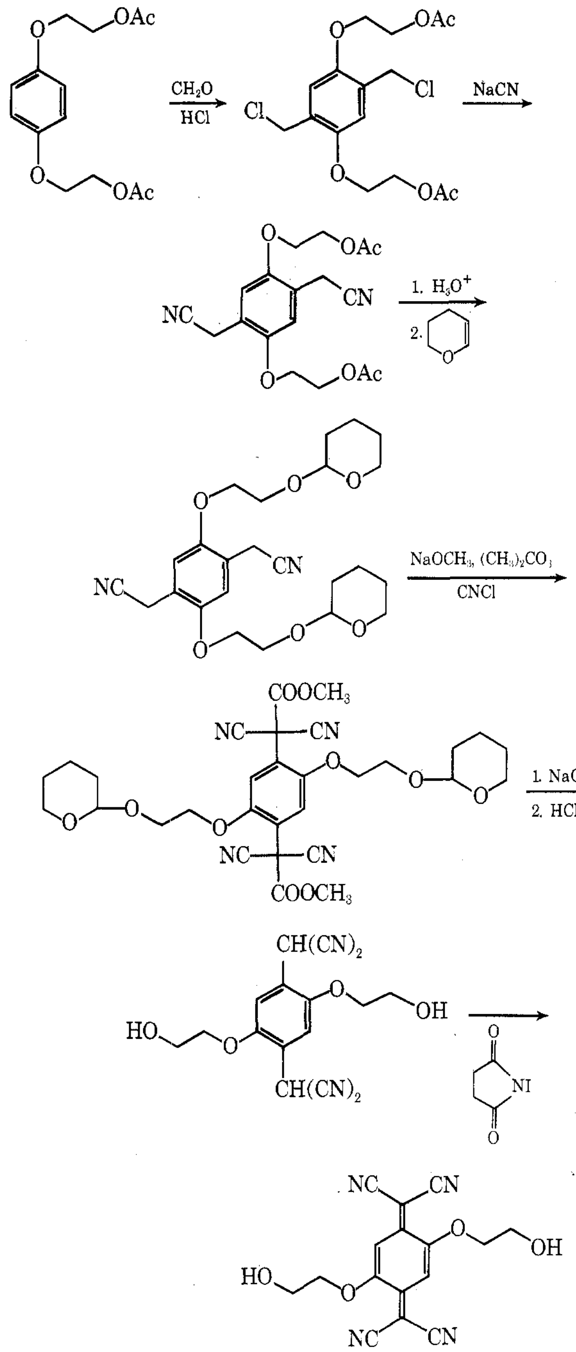
Received October 10, 1975

Semiconducting charge-transfer polyurethanes were prepared by condensation of 2,5-bis(2-hydroxyethoxy)-7,7,8,8-tetracyanoquinodimethan with 1,1′-diisocyanatoferrocene or 4,4′-diisocyanatotetrathiafulvalene. Powder compactions of the black polymers have electrical conductivities of 3×10^{-3} and 1.66×10^{-7} ohm^{-1} cm^{-1}, respectively. Condensation of 4,4′-bis(hydroxymethyl)tetrathiafulvalene with 4,4′-diisocyanatotetrathiafulvalene gave a polyurethane which was converted to its iodide. The iodide has an electrical conductivity of 2×10^{-6} ohm^{-1} cm^{-1}. The syntheses of monomers are described.

Although many semiconducting organic polymers have been synthesized, the goal of an organic polymer having metallic conductivity has remained elusive. The recent demonstration of metallic conductivity in the charge-transfer complex of 7,7,8,8-tetracyanoquinodimethan (TCNQ) and tetrathiafulvalene (TTF)[1,2] suggested that polymers containing these materials might display metallic conductivity if properly oriented. The literature contains many examples of electrically conductive polymers in which $TCNQ\cdot^-$ is present as a counterion in a polymeric quaternary ammonium ion.[3] To prepare a polymer containing covalently bound TCNQ, it was necessary to synthesize a TCNQ derivative containing suitable reactive functional groups on the ring. The sequence of reactions used to synthesize 2,5-bis(2-hydroxyethoxy)-7,7,8,8-tetracyanoquinodimethan (**1**) is shown in eq 1.

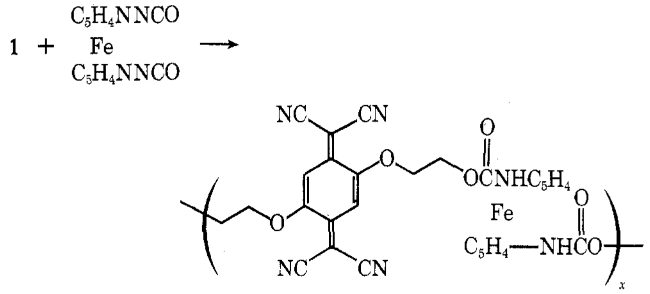
2,5-Bis(2-hydroxyethoxy)-7,7,8,8-tetracyanoquinodimethan (**1**) is a stable red compound with mp 228–232 °C. A charge-transfer polymer was prepared by reaction of **1** with 1,1′-diisocyanatoferrocene[4] to give a black polyurethane, **2**, containing electron-acceptor TCNQ units alternating with electron-donating ferrocene units. Inasmuch as the polymer is insoluble in organic solvents, electrical conductivity measurements were performed on a compacted powder. The value obtained was 3×10^{-3} ohm^{-1} cm^{-1}, which is similar to that reported for a TCNQ complex of poly(3-vinylbisfulvalenediiron).[5]

A nonpolymeric model charge-transfer complex of 2,5-bis(2-hydroxyethoxy)-7,7,8,8-tetracyanoquinodimethan and 1,1′-bis(methoxycarbonylamino)ferrocene[4] (**3**), was prepared to compare its properties with those of the charge-transfer polymer **2**. The donor and acceptor compo-

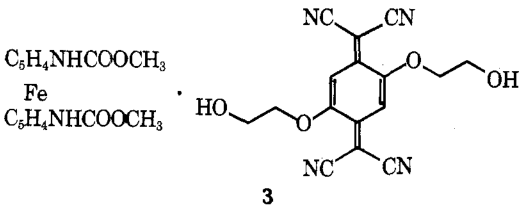


(1)

1



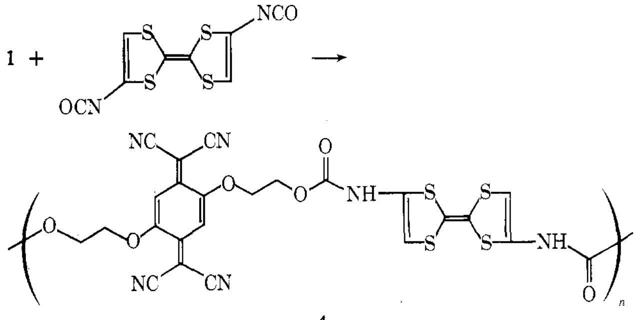
2



3

nents in each case should have similar redox potentials. The black charge-transfer complex **3** has an electrical conductivity of 2.4 × 10^{-1} ohm^{-1} cm^{-1}. The ultraviolet spectrum of **3** in acetonitrile solution shows mostly free 2,5-bis-(2-hydroxyethoxy)-7,7,8,8-tetracyanoquinodimethan with only 1.5–2% of the corresponding anion radical. As is generally the case, the nonpolymeric charge-transfer complex showed substantially higher electrical conductivity than the polymeric charge-transfer complex.

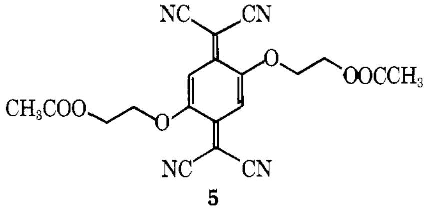
A second charge-transfer polymer was prepared by reaction (eq 2) of the diol **1** with 4,4′-diisocyanatotetrathiafulvalene which was obtained from 4,4′-tetrathiafulvalenedicarboxylic acid[6] by the Curtius reaction. The resulting black polyurethane, **4**, was found to be amorphous by x-ray analysis. The polymer **4** has an electrical conductivity of 1.66 × 10^{-7} ohm^{-1} cm^{-1} and is, thus, substantially less conductive than the ferrocene-containing polymer, **2**. If the diisocyanatotetrathiafulvalene is a mixture of cis and trans (4,4′ and 4,5′) isomers, this would introduce disorder into the polymer perhaps accounting for the absence of crystallinity.



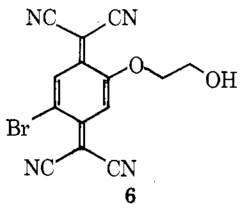
4

(2)

Polarographic reduction of **1** in acetonitrile solution showed two one-electron reduction waves with half-wave potentials of +0.16 and −0.40 V (vs. SCE). The difference of 0.56 V between the two waves is anomalously large. It is, in fact, the largest difference observed for any substituted TCNQ. The structurally similar 2,5-bis(2-acetoxyethoxy)-7,7,8,8-tetracyanoquinodimethan (**5**) showed half-wave potentials of +0.03 and −0.42 V. The difference in half-wave potentials of 0.45 V is more characteristic of other substituted TCNQ's. A possible explanation is that intramolecular hydrogen bonding occurs to stabilize the anion radical of **1**. However, the anomalous spread between half-wave potentials is not observed with 2-bromo-5-(2-hydroxyethoxy)-7,7,8,8-tetracyanoquinodimethan (**6**), which has half-wave potentials of +0.24 and −0.21 V.

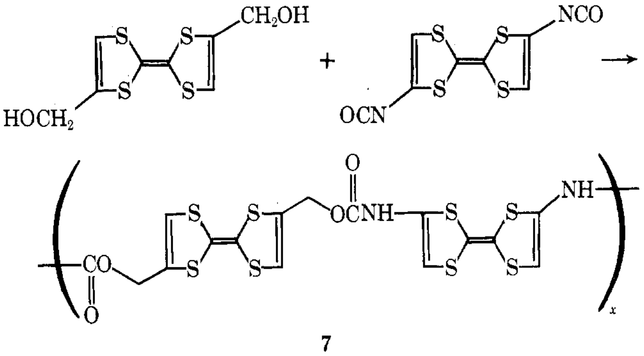


5



6

To synthesize a polymer containing TTF units, 4,4′-bis(hydroxymethyl)tetrathiafulvalene was synthesized by the reduction of 4,4′-tetrathiafulvalenedicarbonyl chloride using lithium tri-*tert*-butoxyaluminum hydride. The resulting diol was then combined with 4,4′-diisocyanatotetrathiafulvalene to give the polyurethane **7**.



7

The TTF polyurethane, **7**, is a brown polymer for which a solvent could not be found. Even in the absence of an added π acid, this polymer has a remarkably high electrical conductivity, 2×10^{-8} ohm^{-1} cm.$^{-1}$ When the polymer was suspended in an acetonitrile solution of iodine, a black polymeric complex was obtained containing about one iodine atom per TTF unit. The poly-TTF iodide has a conductivity of 2×10^{-6} ohm^{-1} cm^{-1}, two orders of magnitude greater than the uncomplexed polymer.

Ueno, Masuyama, and Okawara[7] have recently reported the synthesis of polymeric tetrathiafulvalenes by coupling of 4,4′-polymethylenebis(1,3-dithiole-2-ylium perchlorates). The polymers prepared by the Japanese workers, although insoluble, were converted to charge transfer complexes with TCNQ and DDQ.

The failure of the polymers in this study to show the very high electrical conductivities characteristic of several nonpolymeric charge-transfer complexes is probably a result of geometric constraints. The polymer is probably unable to achieve the high degree of orientation required to enable the donor units and acceptor units in the polymer backbone to form the face-to-face stacks[8–10] which play an important role in the conductivity of, for example, TTF–TCNQ.

Experimental Section

2,5-Bis(2-acetoxyethoxy)-*p*-xylylene Dichloride. In a 3-l. flask equipped with a mechanical stirrer, thermometer, reflux condenser, and gas inlet tube was placed 372 g (1.315 mol) of 1,4-bis(acetoxyethoxy)benzene (prepared from the reaction of acetyl chloride with 2,2′-*p*-phenylenedioxydiethanol at reflux), 99 g of paraformaldehyde, 220 ml of acetic acid, and 440 ml of concentrated hydrochloric acid. The mixture was stirred while bubbling in a stream of gaseous hydrogen chloride while maintaining the temperature at 50–55 °C. After 2 h, the mixture was cooled and filtered. The filter cake was washed with water and recrystallized from methylene chloride to give 120 g of 2,5-bis(2-acetoxyethoxy)-*p*-xylylene dichloride, mp 130.5–133 °C.

Anal. Calcd for $C_{16}H_{20}Cl_2O_6$: C, 50.67; H, 5.32. Found: C, 50.58; H, 5.70.

2,5-Bis(2-acetoxyethoxy)-*p*-xylylene Dicyanide. In a three-neck, 2-l. flask equipped with a mechanical stirrer, thermometer, and reflux condenser under a nitrogen atmosphere were placed 336 ml of anhydrous dimethyl sulfoxide and 58.5 g of sodium cyanide. Then 190.7 g of 2,5-bis(2-acetoxyethoxy)-*p*-xylylene dichloride was added portionwise at a rate such that the temperature rose to 50 °C and remained near 50 °C during the addition. When the addition was complete, stirring was continued at 50 °C for 1 h, and the mixture was then heated to 85 °C, cooled, diluted with a large volume of water, and filtered. The filter cake was washed with water and with ether. Recrystallization from dioxane gave 105 g of 2,5-bis(2-acetoxyethoxy)-*p*-xylylene dicyanide, mp 168–169.5 °C.

Anal. Calcd for $C_{18}H_{20}N_2O_6$: C, 59.99; H, 5.59; H, 7.77. Found: C, 59.97, 59.98; H, 5.89, 5.79; N, 7.41, 7.52.

2,5-Bis(2-hydroxyethoxy)-*p*-xylylene Dicyanide. A mixture of 20.8 g of 2,5-bis(acetoxyethoxy)-*p*-xylylene dicyanide, 200 ml of acetonitrile, and 200 ml of dioxane was warmed with stirring until solution was complete. Then 80 ml of 10% hydrochloric acid was added, and the solution was stirred at room temperature for 3 days at which time a precipitate was observed. In subsequent preparations an improved yield was obtained by allowing the hydrolysis to proceed for 6 or 7 days. The mixture was filtered, and the filter cake was washed with water, dioxane, and ether and dried to give 12.8 g of 2,5-bis(2-hydroxyethoxy)-*p*-xylylene dicyanide, mp 179–180.5 °C.

Anal. Calcd for $C_{14}H_{16}N_2O_4$: C, 60.86; H, 5.84; N, 10.14. Found: C, 60.84; H, 5.83; N, 9.91.

The infrared spectrum of the product shows no absorption attributable to carbonyl.

2,5-Bis[2-(tetrahydro-2-pyranyloxy)ethoxy]-*p*-xylylene Dicyanide. A mixture of 45 g of 2,5-bis(2-hydroxyethoxy)-*p*-xylylene dicyanide, 250 ml of tetrahydrofuran, 150 ml of dihydropyran (Aldrich Chemical Co.), and 330 mg of *p*-toluenesulfonic acid monohydrate was stirred at reflux for 1.5 h after a homogeneous solution was obtained. The solution was evaporated in vacuo, and the residue was stirred with cold water and dried in vacuo to give 78.5 g of solid. The crude product was dissolved in benzene and passed through a 3-in. column of basic alumina. The eluate was boiled while adding heptane. On cooling and adding additional heptane, there was obtained 49 g of 2,5-bis[2-(tetrahydro-2-pyranyloxy)ethoxy]-*p*-xylylene dicyanide as an isomeric mixture. An analytical sample (mp 90–93 °C) was obtained by recrystallization from cyclohexane.

Anal. Calcd for $C_{24}H_{32}N_2O_6$: C, 64.85; H, 7.26; N, 6.30. Found: C, 65.19, 65.27; H, 7.30, 7.13; N, 5.91, 5.97.

2,5-Bis(2-hydroxyethoxy)-7,7,8,8-tetracyanoquinodimethan. A stirred mixture of 87.4 g of the 2,5-bis[2-(tetrahydro-2-pyranyloxy)ethoxy]-*p*-xylylene dicyanide, 25.6 g of sodium methoxide, and 400 ml of dimethyl carbonate was distilled over a period of 2.5 h until the temperature of the distillate reached 85 °C. An additional 200 ml of dimethyl carbonate was added, the mixture was cooled in an ice bath to 5–10 °C, and 31.5 ml of cyanogen chloride was slowly distilled into the reaction flask while stirring. After stirring for 2 h at 5 °C, the mixture was slowly warmed to 50 °C and then evaporated in vacuo. The gummy, dark residue was treated with 500 ml of warm 10% aqueous sodium hydroxide and Darco, and filtered. The filtrate was cooled and acidified with dilute hydrochloric acid. The dark gum which precipitated was extracted with methylene chloride, treated with Darco, dried, and evaporated to 11 g of red oil. The red oil was dissolved in acetonitrile and treated with a solution of 10.3 g of *N*-iodosuccinimide in acetonitrile. The solution was evaporated in vacuo, and the dark, gummy residue was washed well with water and hexane. The residue was treated with methanol, diluted with water, and filtered. The filter cake, which was free of iodine, was boiled with 350 ml of methanol and filtered hot to give 3.1 g of orange solid. Two recrystallizations from acetonitrile gave 2.3 g of dark purple-red needles of 2,5-bis(2-hydroxyethoxy)-7,7,8,8-tetracyanoquinodimethan, mp 228–232 °C. From a second extraction of the dark, gummy residue with 500 ml boiling 10% aqueous sodium hydroxide was obtained an additional 1.2 g of 2,5-bis(2-hydroxyethoxy)-7,7,8,8-tetracyanoquinodimethan, mp 225–230 °C.

Anal. Calcd for $C_{16}H_{12}N_4O_4$: C, 59.3; H, 3.73; N, 17.3. Found: C, 59.5; H, 3.73; N, 17.6.

Uv (acetonitrile) ϵ_{342} 44 700, ϵ_{412} 43 100.

Polymerization of 1,1′-Diisocyanatoferrocene with 2,5-Bis(2-hydroxyethoxy)-7,7,8,8-tetracyanoquinodimethan. To a stirred solution of 324.3 mg (1 mmol) of **1** and 268.0 mg (1 mmol) of 1,1′-diisocyanatoferrocene[4] (freshly recrystallized from hexane) in 8 ml of dimethylformamide under an argon atmosphere was added 0.015 ml of dibutyltin dilaurate. The solution, which was initially red in color, turned green and polymer precipitated. After stirring for 20 h, 4 ml of methanol was added, and the mixture was filtered. The filter cake was washed with dimethylformamide and then with methanol to give 185 mg of black, insoluble polymer.

Anal. Calcd for $(C_{28}H_{20}N_6O_6Fe)n$: C, 56.8; H, 3.40; N, 14.2. Found: C, 55.3, 55.5; H, 3.50, 3.51; N, 13.6, 13.6.

The resistivity of a compaction of the black polymer is 3×10^3 ohm cm. The x-ray powder pattern of the black polymer shows both crystalline and amorphous components.

Dilution of the filtrate with methanol gave additional precipitate. Filtration gave 362 mg of green-brown polymer.

Anal. Found: C, 54.2, 54.1; H, 3.65, 3.66; N, 13.1, 13.0.

The electrical resistivity of the green-brown polymer is 10^7 ohm cm. The infrared spectra of the black and green-brown polymers differed greatly.

Nonpolymeric Model for Copolymer of 1 and 1,1′-Diisocyanatoferrocene. To a warm solution of 162.1 mg of 1 in 15 ml of acetonitrile was added 166.1 mg of 1,1′-bis(methoxycarbonylamino)ferrocene.[4] Upon concentrating the warm, deep-red solution under a stream of nitrogen, a mixture of black crystals and crystals of 1 separated. The crystals were redissolved, and the solution was treated with 100 mg of additional 1,1′-bis(methoxycarbonylamino)ferrocene. The warm solution was concentrated under a stream of nitrogen to a volume of about 10 ml. The solution was allowed to cool to room temperature, and black crystals separated. Filtration followed by rinsing with acetonitrile gave 268 mg of black 1:1 complex.

Anal. Calcd for $C_{30}H_{28}N_6O_8Fe$: C, 54.89; H, 4.30; N, 12.80. Found: C, 54.76; H, 4.38; N, 12.89.

The resistivity of a compaction of the product is 24 ohm cm. The ultraviolet spectrum of the complex in acetonitrile shows absorption characteristic of 1 and only 1.5–2% of the anion radical of 1, indicating a high degree of dissociation of the complex in solution.

4,4′-Tetrathiafulvalene Dicarbonyl Chloride. A mixture of 1.2 g of 4,4′-tetrathiafulvalenedicarboxylic acid,[6] 20 ml of methylene chloride, 1 drop of pyridine, and 1.7 ml of oxalyl chloride was stirred overnight at room temperature and 3 days at reflux. The mixture was cooled to room temperature and filtered to give 1.04 g of 4,4′-tetrathiofulvalene dicarbonyl chloride as a purple solid, mp 240–245 °C, ir 1700 cm^{-1} (COCl).

Anal. Calcd for $C_8H_2O_2S_4Cl_2$: C, 29.18; H, 0.61. Found: C, 29.29; H, 0.76.

4,4′-Diisocyanatotetrathiafulvalene. A mixture of 5.5 g of 4,4′-tetrathiafulvalene dicarbonyl chloride, 100 ml of anhydrous acetonitrile, and 2.2 g of activated sodium azide was stirred at room temperature for 15 min, at reflux for 2 h, and at room temperature overnight. Then 400 ml of toluene was added, and the acetonitrile was removed by distillation. The mixture was then stirred at 104 °C for 1.5 h and filtered hot. The filtrate was evaporated in vacuo nearly to dryness, treated with hexane, cooled, and filtered. The red filter cake was recrystallized from benzene–heptane to give 2.82 g of 4,4′-diisocyanatotetrathiafulvalene as red crystals, mp 156 °C dec; ir 2250 cm^{-1} (NCO).

Anal. Calcd for $C_8H_2N_2S_4O_2$: C, 33.57; H, 0.70; N, 9.79. Found: C, 33.87; H, 1.16; N, 9.96.

Polymerization of Diisocyanatotetrathiafulvalene with 2,5-Bis(2-hydroxyethoxy)-7,7,8,8-tetracyanoquinodimethan. To a stirred solution of 324.3 mg (1 mmol) of 2,5-bis(2-hydroxyethoxy)-7,7,8,8-tetracyanoquinodimethan and 298.4 mg of 4,4′-diisocyanatotetrathiafulvalene in 8 ml of dimethylformamide under an argon atmosphere was added 0.015 ml of dibutyltin dilaurate. The solution gradually became viscous and gelled over a period of a few hours. After 24 h, a few drops of methanol were added. After 15 min, excess benzene and methanol were added. The black polymer (591 mg) was collected by filtration and dried at 65 °C (0.1 mm).

Anal. Calcd for $(C_{24}H_{14}N_6O_6S_4)x$: C, 47.2; H, 2.30; N, 11.62; S, 21.00. Found: C, 46.70, 46.20, 45.66; H, 3.17, 3.25, 3.24; N, 11.62, 11.20, 10.75; S, 20.98.

No solvent was found for the polymer.

The electrical resistivity of the compacted polymer is 6×10^{10} ohm cm. The powder pattern of the polymer shows it to be amorphous. Differential scanning calorimetry shows a glass transition at −32 °C, a small, broad endotherm at 88 °C, and a major exotherm at 270 °C.

2,5-Bis(2-acetoxyethoxy)-7,7,8,8-tetracyanoquinodimethan. A mixture of 500 mg of 2,5-bis(2-hydroxyethoxy)-7,7,8,8-tetracyanoquinodimethan, 40 ml of acetic anhydride, and 60 ml of acetonitrile was stirred at reflux for 1.5 h and evaporated in vacuo. The residue was recrystallized from cyclohexane–benzene and then from 1-chlorobutane to give 326 mg of maroon plates, mp 144–175 °C dec.

Anal. Calcd for $C_{20}H_{16}H_4O_6$: C, 58.88; H, 3.95; N, 13.72. Found: C, 58.87; H, 4.14; N, 13.88.

Uv (acetonitrile) 430 nm (ϵ 48 100), 410 (45 600).

2-(2-Acetoxyethoxy)-*α*,*α*′,5-tribromo-*p*-xylene. A mixture of 20.8 g of 2-(2-acetoxyethoxy)-*p*-xylene, prepared by acetylation of 2-(2-hydroxyethoxy)-*p*-xylene (prepared in turn by the reaction of 2,5-dimethylphenol with ethylene carbonate at 180 °C in the presence of powdered potassium hydroxide), 300 ml of 1,2-dichloroethane, 59 g of *N*-bromosuccinimide, and 0.6 g of benzoyl peroxide was stirred at reflux under a nitrogen atmosphere for 18 h. The mixture was cooled, filtered, washed with 10% aqueous sodium bisulfite, washed three times with water, dried, and evaporated. The residue was suspended in ether and filtered to give 17.8 g of 2-(2-acetoxyethoxy)-*α*,*α*′,5-tribromo-*p*-xylene, mp 112.5–115.5 °C. Recrystallization from cyclohexane raised the melting point to 114–117 °C.

Anal. Calcd for $C_{12}H_{13}Br_3O_3$: C, 32.39; H, 2.95; Br, 53.97. Found: C, 32.63; H, 3.00; Br, 53.21.

NMR ($CDCl_3$) δ 7.5 (s, aromatic, 1 H), 6.95 (s, aromatic, 1 H), 4.54 (s, CH_2Br), 4.45 (s, CH_2Br), 4.04–4.5 (m, OCH_2CH_2O, total intensity of 4.54–4.05, 8.5 H), 2.1 ppm (s, CH_3CO, 3 H).

2-(2-Acetoxyethoxy)-5-bromo-1-bromomethyl-4-dibromomethylbenzene. A mixture of 191 g of 2-(2-acetoxyethoxy)-*p*-xylene, 550 g of *N*-bromosuccinimide, 2.8 l. of 1,2-dichloroethane, and 5.5 g of benzoyl peroxide was stirred at reflux overnight, filtered, washed with dilute sodium bisulfite solution and water (three times), dried, and evaporated in vacuo. The residue, which slowly crystallized, was twice suspended in 200 ml of ether and filtered to give 183.4 g of solid, mp 94–109 °C. The product was crystallized from cyclohexane and then from butyl chloride to give 85.7 g of 2-(2-acetoxyethoxy)-*α*,*α*′,5-tribromo-*p*-xylene, mp 113–114 °C. The second crop (21.3 g), mp 90–94.5 °C, was recrystallized twice from butyl chloride–ether to give crystals of 2-(2-acetoxyethoxy)-5-bromo-1-bromomethyl-4-dibromomethylbenzene, mp 95.5–96.5 °C.

Anal. Calcd for $C_{12}H_{12}Br_4O_3$: C, 27.6; H, 2.31; Br, 61.0. Found: C, 27.9; H, 2.32; Br, 61.28.

NMR ($CDCl_3$) δ 8.0 (s, aromatic, 1 H), 7.0 (s, $CHBr_2$, 1 H), 6.95 (s, aromatic, 1 H), 4.52 (s, CH_2Br, 2 H), 4.15–4.56 (m, $-CH_2CH_2-$, 4 H), 2.1 ppm (s, CH_2CO, 3 H).

2-(2-Acetoxyethoxy)-5-bromo-*p*-xylylene Dicyanide. To an ice-cooled, stirred slurry of 3 g of sodium cyanide and 25 ml of anhydrous dimethylformamide was added 1.5 ml of trifluoroacetic acid at a rate such that the temperature did not exceed 10 °C. Then 4.45 g (0.01 mol) of 2-(2-acetoxyethoxy)-*α*,*α*′,5-tribromo-*p*-xylene was added portionwise at a rate such that the temperature ramained below 10 °C. After stirring overnight at ambient temperature (in subsequent experiments, 80 min at 10 °C was found to be sufficient reaction time), the mixture was poured into ice and water and filtered to give 3.03 g of solid. Recrystallization from butyl chloride–heptane gave 1.89 g of 2-(2-acetoxyethoxy)-5-bromo-*p*-xylene dicyanide, mp 121–124.5 °C. Recrystallization from dioxane–heptane raised the melting point to 125–126 °C.

Anal. Calcd for $C_{14}H_{13}N_2BrO_3$: C, 49.9; H, 3.88; N, 8.31; Br, 23.7. Found: C, 49.8; H, 4.01; N, 8.07; Br, 23.7.

NMR ($CDCl_3$) δ 7.54 (s, aromatic, 1 H), 7.01 (s, aromatic, 1 H), 4.12–4.59 (m, $-CH_2CH_2-$, 4 H), 3.82 (s, CH_2CN, 2 H), 3.66 (s, CH_2CN, 2 H), 2.10 ppm (s, CH_3CO, 3 H).

2-(2-Hydroxyethoxy)-5-bromo-*p*-xylylene Dicyanide. A solution of 3.37 g of 2-(2-acetoxyethoxy)-5-bromo-*p*-xylylene dicyanide in 20 ml of acetonitrile, 20 ml of dioxane, and 8 ml of 10% aqueous hydrochloric acid was stirred at 35 °C for 18 h and then poured into ice and water. Filtration gave 2.54 g of 2-(2-hydroxyethoxy)-5-bromo-*p*-xylylene dicyanide, mp 137.5–140.5 °C. Recrystallization from methanol raised the melting point to 142–144 °C.

Anal. Calcd for $C_{12}H_{11}N_2BrO_2$: C, 48.95; H, 3.76; N, 9.50; Br, 27.1. Found: C, 48.46, 48.33, 48.57; H, 3.72, 3.62, 4.12; N, 8.82, 8.89, 9.80; Br, 26.9.

2-(2-Hydroxyethoxy)-5-bromo-*p*-phenylenedimalononitrile. A stirred mixture of 19.9 g of 2-(2-hydroxyethoxy)-5-bromo-*p*-xylylene dicyanide (0.0674 mol), 7.38 g of sodium methoxide (0.137 mol), and 160 ml of methyl carbonate was slowly distilled until the head temperature reached 90 °C and all of the methanol had been removed azeotropically. A gum had formed but solidified on cooling. The solid was broken up manually and stirred at 5 °C while 20 ml (at 0 °C) of cyanogen chloride was slowly added through a gas inlet tube. The mixture was stirred overnight at ambient temperature after addition of methyl carbonate to facilitate mixing. The mixture was filtered, and the filtrate evaporated to 31.2 g of a pale yellow oil. After washing several times with heptane, the oil was boiled with 170 ml of 10% sodium hydroxide solution, and the resulting red solution was poured gradually into 240 ml of cold 10% hydrochloric acid. The gummy precipitate, on standing overnight in the acidic medium, solidified. The mixture was blended in a Waring blender and filtered to give 13.1 g of solid, mp 126–143 °C. Recrystallization from methylene chloride–heptane containing a little dioxane followed by crystallization from aqueous acetic acid gave 3.7 g of 2-(2-hydroxyethoxy)-5-bromo-*p*-phenylenedimalononitrile, mp 150.5–153 °C.

Anal. Calcd for $C_{14}H_9N_4BrO_2$: C, 48.71; H, 2.63; N, 16.23. Found: C, 49.04; H, 2.87; N, 15.99.

NMR (CD_3CN) δ 7.82 (s, aromatic, 1 H), 7.43 (s, aromatic, 1 H), 5.69 [s, $CH(CN)_2$, 1 H], 5.63 [s, $CH(CN)_2$, 1 H], 3.75–4.37 (m, $-CH_2CH_2$, 5 H), 3.1 ppm (s, broad, OH, 1 H).

2-(2-Hydroxyethoxy)-5-bromo-7,7,8,8-tetracyanoquinodimethan. A mixture of 500 mg of 2-(2-hydroxyethoxy)-5-bromo-*p*-phenylenedimalononitrile and 50 ml of bromine water was stirred for 30 min and filtered. The filter cake was recrystallized from benzene to give 236 mg of red crystals of 2-(2-hydroxyethoxy)-5-bromo-7,7,8,8-tetracyanoquinodimethan, mp 213–217 °C dec.

Anal. Calcd for $C_{14}H_7N_4BrO_2$: C, 49.00; H, 2.06; N, 16.33. Found: C, 48.86; H, 2.25; N, 16.23.

Uv (CH_3CN) 485 nm (ε 4461), 413 (41 521), 390 (sh, 39 805), 280 (3157).

4,4′-Bis(hydroxymethyl)tetrathiafulvalene. To a stirred slurry of 6.5 g (0.0256 mol) of lithium tri-*tert*-butoxyaluminum hydride and 30 ml of tetrahydrofuran under nitrogen cooled to −78 °C was added 1.81 g (0.00555 mol) of tetrathiafulvalenedicarbonyl chloride. The mixture was stirred for 1 h at −78 °C and then allowed to slowly warm to room temperature during which time the purple solid became amber. After 3 h, the solvent was removed in a stream of nitrogen and water was added to the residue under nitrogen. The mixture was filtered under nitrogen, and the filter cake was stirred under argon with 10% sodium hydroxide solution for 1 h and refiltered. The filter cake was extracted with methanol, and the extract was diluted with aqueous sodium hydroxide and concentrated somewhat in vacuo causing separation of rust-colored crystals which were collected by filtration and washed with water to give 368 mg of 4,4′-bis(hydroxymethyl)tetrathiafulvalene which begins to decompose at 160 °C.

Anal. Calcd for $C_8H_8S_4O_2$: C, 36.34; H, 3.05. Found: C, 36.67; H, 3.29.

NMR (Me_2SO-d_6) 6.41 (s, 2 ring H), 5.39 (t, J = 5.5 Hz, OH, 2 H), 4.15 (d, J = 5.5 Hz, $-CH_2O$, 4 H), 3.27 ppm (s, H_2O, 1 H). Addition of D_2O causes disappearance of the 5.39 and 3.27 ppm peaks and a new exchange singlet appears at 3.78 ppm while the 4.15 ppm CH_2 peak collapses to a singlet.

Tetrathiafulvalene Polyurethane (7). To a stirred, refluxing mixture of 108.9 mg of 4,4′-bis(hydroxymethyl)tetrathiafulvalene, 118 mg of 4,4′-diisocyanatotetrathiafulvalene, and 15 ml of acetonitrile under argon was added 0.1 μl of dibutyltin dilaurate catalyst. After 2 h, the mixture was filtered under argon, and the filter cake was twice mixed with acetonitrile and centrifuged to give 167 mg of brown polymer. The infrared spectrum shows carbonyl absorption at 1730 cm^{-1} and NH absorption at 3400 cm^{-1}.

Anal. Calcd for $(C_{16}H_{10}N_2S_8O_4)x$: C, 34.89; H, 1.83; N, 5.09. Found: C, 33.52, 33.47; H, 2.17, 2.16; N, 5.35, 5.30.

Reaction of Tetrathiafulvalene Polyurethane with Iodine. A mixture of 30 mg of **7**, 10 ml of acetonitrile, and 14 mg of iodine was stirred under argon for 3 h and filtered in a nitrogen atmosphere to give 35.5 mg of black polymer.

Anal. Calcd for $C_{16}H_{10}O_4S_8N_2I_2$: C, 23.88; H, 1.25; N, 3.48. Found: C, 23.94, 23.97; H, 1.56, 1.54; N, 4.16, 4.29.

Electrical resistivity of compaction 2 × 10^6 ohm cm.

Registry No.—**1**, 58268-29-4; **2**, 58312-83-7; **3**, 58312,84-8; **4**, 58268-60-3; **5**, 58268-30-7; **6**, 58268-31-8; **7**, 58268-59-0; 2,5-bis(2-acetoxyethoxy)-*p*-xylylene dichloride, 58268-32-9; 1,4-bis(acetoxyethoxy)benzene, 47096-64-0; 2,5-bis(2-acetoxyethoxy)-*p*-xylylene dicyanide, 58268-33-0; 2,5-bis(2-hydroxyethoxy)-*p*-xylene dicyanide, 58268-34-1; 2,5-bis[2-(tetrahydro-2-pyranyloxy)ethoxy]-*p*-xylylene dicyanide isomer 1, 58268-35-2; 2,5-bis[2-(tetrahydro-2-pyranyloxy)ethoxy]-*p*-xylene dicyanide isomer 2, 58268-36-3; *N*-iodosuccimide, 516-12-1; 1,1′-diisocyanatoferrocene, 12288-75-4; 1,1′-bis(methoxycarbonylamino)ferrocene, 12277-09-7; 4,4′-tetrathiafulvalenedicarbonyl chloride, 58268-37-4; 4,4′-tetrathiafulvalenedicarboxylic acid, 51751-19-0; methylene chloride, 75-19-2; 4,4′-diisocyanatotetrathiafulvalene, 58268-38-5; 2-(2-acetoxyethoxy-α,α′,5-tribromo-*p*-xylene, 58268-39-6; 2-(2-acetoxyethoxy)-*p*-xylene, 58268-40-9; 2-(2-acetoxyethoxy)-5-bromo-1-bromomethyl-4-dibromomethylbenzene, 58268-41-0; *N*-bromosuccinimide, 128-08-5; 2-(2-acetoxyethoxy)-5-bromo-*p*-xylene dicyanide, 58268-42-1; 2-(2-hydroxyethoxy)-5-bromo-*p*-xylylene dicyanide, 58268-43-2; 2-(2-hydroxyethoxy)-5-bromo-*p*-phenylenedimalononitrile, 58268-44-3; 4,4′-bis(hydroxymethyl)tetrathiafulvalene, 58268-45-4; 4,4′-diisocyanatotetrathiafulvalene polymer, 58268-58-9; 2,5-bis(hydroxyethoxy)-7,7,8,8-tetracyanoquinodimethan 1,1′-diisocyanatoferrocene polymer, 58298-32-1; 2,5-bis(hydroxyethoxy)-7,7,8,8-tetracyanoquinodimethan 4,4′-diisocyanatotetrathiafulvalene polymer, 58268-57-8.

References and Notes

(1) J. Ferraris, D. O. Cowan, V. Walatka, Jr., and J. H. Perlstein, *J. Am. Chem. Soc.*, **95**, 948 (1973).

(2) L. B. Coleman, M. J. Cohen, D. J. Sandman, F. G. Yamagishi, A. F. Garito, and A. J. Heeger, *Solid State Commun.*, **12**, 1125 (1973).

(3) See, for example, K. Sanada, A. Iwasawa, E. Tsuchida, and I. Shinohara, *Nippon Kagaka Kaishi*, 955, 961 (1974).

(4) R. L. Schaaf and C. T. Lenk, *J. Chem. Eng. Data*, **9**, 103 (1964).

(5) C. U. Pittman, Jr., and B. Surynarayanan, *J. Am. Chem. Soc.*, **96**, 7916 (1974).

(6) L. R. Melby, H. D. Hartzler, and W. A. Sheppard, *J. Org. Chem.*, **39**, 2456 (1974).

(7) Y. Ueno, Y. Masuyama, and M. Okawara, *Chem. Lett.*, 603 (1975).

(8) M. J. Cohen, L. B. Coleman, A. F. Garito, and A. J. Heeger, *Phys. Rev., Sect. B*, **10**, 1298 (1974).

(9) S. K. Khanna, A. F. Garito, A. J. Heeger, and R. C. Taklevic, *Solid State Commun.*, **16**, 667 (1975).

(10) R. P. Groff, A. Suna, and R. E. Merrifield, *Phys. Rev. Lett.*, **33**, 418 (1974).

Synthesis of Halogen Substituted Bicyclo[2.1.1]hexan-2-ones

F. Thomas Bond,* Chih-Yung Ho, and Oliver McConnell

Department of Chemistry, University of California, San Diego, La Jolla, California 92093

Received October 21, 1975

Photochemical irradiation of chlorine substituted 1,5-hexadien-3-ones has led to the synthesis of 1-chloro-, *exo*-5-chloro-, and *endo*-5-chlorobicyclo[2.1.1]hexan-2-one. The nature and utility of the photocycloaddition is discussed. Bromination of bicyclo[2.1.1]hexan-2-one has been carried out using lithium dialkylamide to form the enolate.

Strained bicyclic and polycyclic compounds continue to play an important role in the understanding of many aspects of organic chemistry,[1] including theoretical studies,[2] solvolytic reactivity,[3] thermal rearrangements,[4] and reactivity of strained σ bonds.[5] For this reason, synthetic efforts in this area have been extensive. For some time now, we and others have been interested in the chemistry of bicyclo[2.1.1]hexanes, an area far less studied than that of the homologous bicyclo[2.2.1]heptanes, owing to the ready availability of the latter. In this paper we report extension of our previously noted synthesis of bicyclo[2.1.1]hexan-2-one[6] to the preparation of functionally activated bicyclo[2.1.1]hexan-2-ones, needed for various studies, some of which are reported in the accompanying paper.[7]

Most synthetic routes to the bicyclo[2.1.1]hexane nucleus have involved either ring contractions from bicyclo[2.2.1]heptanes[1a,8] or bicyclo[3.1.1]heptanes[8g,h,9] or photochemical cycloaddition of acyclic precursors.[6,10] Other