Polycyano Radicals

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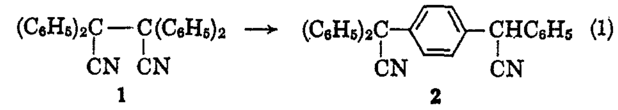
The α,α-dicyanobenzyl radical generated from phenylmalononitrile and *t*-butyl peroxide or from *sym*-diphenyltetracyanoethane dimerized to give *p*-(α,α-dicyanobenzyl)phenylmalononitrile. The dicyanobenzyl radical was unreactive toward oxygen, but was trapped with nitrogen dioxide, nitric oxide, bromine, and 2,2-diphenylpicrylhydrazyl. The dicyanobenzyl radical abstracted hydrogen from tetrahydrofuran, but did not initiate the polymerization of styrene. Radicals were produced from 1,2-bis(4-nitrophenyl)-1,1,2,2-tetracyanoethane, *sym*-dicyanotetraphenylethane, and hexacyanoethane in solution at room temperature. 9-Cyano-9-tricyanomethylfluorene underwent a much slower homolytic dissociation. The attempted preparation of 1,1,1-tricyano-2,2,2-triphenylethane led to the formation of the stable ketenimine 1,1,1,5,5,5-hexaphenyl-4-cyano-2-aza-2,3-pentadiene.

Several observations have been made which suggest that free radicals bearing a plurality of cyano substituents are relatively unreactive organic radicals. In general, their chemistry appears to be that of radical–radical reactions such as disproportionation and dimerization rather than reactions with nonradicals such as hydrogen abstraction and olefin addition. The reactions of azobisisobutyronitrile with tetracyanoethylene (TCNE)[1] and with tetracyanoquinodimethan (TCNQ)[2] as well as the reaction of TCNQ with dinitrogen tetroxide[3] are examples of radical–radical reactions of the type that is shown below.

$$\mathrm{RC(CN)_2\cdot + R\cdot \longrightarrow RC(CN)_2R}$$

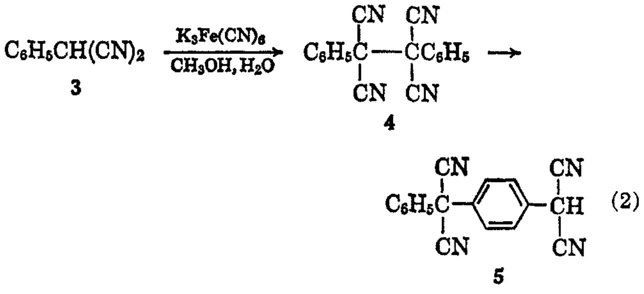
The formation of TCNE from dibromomalononitrile[4] may involve the dimerization of the bromodicyanomethyl radicals. Bromodicyanomethyl radicals are reactive enough, however, to add to terminal olefins.[5] We have found that protonation of TCNE anion radical causes disproportionation to give TCNE and tetracyanoethane. The instability in solution of compounds such as hexacyanoethane[6] and 1,2-diphenyl-1,1,2,2-tetracyanoethane suggested to us the possibility of homolytic dissociation of this type of compound. It has already been shown[7] that the reaction 1 → 2 occurs at elevated temperatures and a radical dissociation–recombination mechanism (eq 1) has been suggested.



This paper reports our results of an investigation of the instability of some polycyano compounds in solution.

Results

1,2-Diphenyl-1,1,2,2-tetracyanoethane (4) was prepared in nearly quantitative yield by the oxidation of phenylmalononitrile with potassium ferricyanide. The product precipitates from solution as it is formed and cannot be purified by recrystallization. Pure material has only been obtained by using pure phenylmalononitrile and by extensive water washing of the product. The infrared spectrum of **4** shows only aromatic hydrogen and monosubstituted aromatic absorptions. The nitrile absorption is weak and unconjugated (4.42 μ). The nmr spectrum of **4** in deuteriochloroform shows a broad resonance of aromatic protons centered at τ 2.3. The assigned structure **4** is based on these data.



The nmr spectrum of a solution of **4** is completely changed when rerun after 18 hr. Two fairly sharp resonances of aromatic hydrogens are seen at τ 2.17 and 2.33 along with another resonance at τ 4.75 which is approximately one-ninth as intense as the combined aromatics. The new material has been shown to be the isomeric **5**. The isomerization **4** → **5** occurred when solutions of **4** in chlorobenzene or chloroform stood overnight. The isolated yields of **5** were only 40 and 12%, respectively. The only other product, which was isolated in small amounts was a high-melting solid (260°) which could not be purified. The isomerization **4** → **5** was unaffected by the presence of oxygen. Compound **4** was dissolved in methylene chloride and oxygen was passed through the solution for 18 hr. The crude reaction product was analyzed and found to contain no oxygen. Styrene was also a good solvent for the isomerization of **4** to **5**.

The infrared spectrum of **5** showed the presence of saturated as well as aromatic hydrogen. The absorptions of unconjugated nitrile (4.45 μ), *para*-substituted aromatic (12.0 μ), and monosubstituted aromatic (13.2 and 14.45 μ) were present. The spectral data are in accord with that expected for structure **5**. Compound **5** reacted with a sodium hydride dispersion in mineral oil to release hydrogen. Compound **5**

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(1) W. J. Middleton, R. E. Heckert, E. L. Little, and C. G. Krespan, *J. Am. Chem. Soc.*, **80**, 2783 (1958).

(2) D. S. Acker and W. R. Hertler, *ibid.*, **84**, 3370 (1962).

(3) W. R. Hertler, H. D. Hartzler, D. S. Acker, and R. E. Benson, *ibid.*, **84**, 3387 (1962).

(4) T. L. Cairns, *et al.*, *ibid.*, **80**, 2775 (1958).

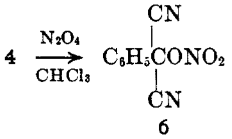
(5) K. Torssell and K. Dahlqvist, *Acta Chem. Scand.*, **16**, 346 (1962); J. R. Roland, E. L. Little, Jr., and H. E. Winberg, *J. Org. Chem.*, **28**, 2809 (1963).

(6) S. Trofimenko and B. C. McKusick, *J. Am. Chem. Soc.*, **84**, 3677 (1962).

(7) G. Wittig and W. Hopf, *Ber.*, **65**, 760 (1932); G. Wittig and H. Petri, *Ann.*, **513**, 26 (1934).

was also obtained in 22% yield when a mixture of phenylmalononitrile, *t*-butyl peroxide, and chlorobenzene was heated at 135°.

Although **4** could not be recovered from any solution, the isomerization of **4** to **5** did not occur when bromine, nitric oxide, or dinitrogen tetroxide were added to solutions of **4**. Only in the latter reaction, however, was a pure product isolated. A 36% yield of the nitrate **6** along with a trace of *p*-nitrobenzoic acid was formed.



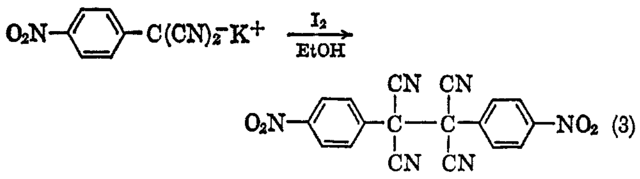
$$4 \xrightarrow[CHCl_3]{N_2O_4} C_6H_5\underset{CN}{\overset{CN}{C}}ONO_2$$

6

Compound **6** showed absorptions in the infrared of aromatic CH, monosubstituted aromatic, unconjugated nitrile (4.47 μ), nitro (6.50 and 7.42 μ), and carbon–oxygen (9.0 μ). If **6** was ground with potassium bromide the spectrum was changed. Compound **6** was unstable to storage even at −80°. Structure **6** is consistent with all of the data and is a likely oxidation product of an initially formed nitrite.

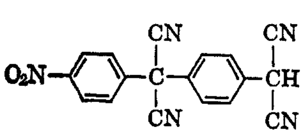
When **4** was dissolved in tetrahydrofuran, an 8% yield of phenylmalononitrile was obtained. The other products were not purified. Compound **4** also reacted with diphenylpicrylhydrazyl (DPPH) in acetonitrile solution. A product was isolated whose analysis was close to that calculated for one dicyanobenzyl unit and one DPPH.

Bis-1,2-*p*-nitrophenyl-1,1,2,2-tetracyanoethane (**7**) was prepared in 61% yield by the oxidation of the potassium salt of *p*-nitrophenylmalononitrile[8] with iodine (eq 3). Oxidation of *p*-nitrophenylmalononitrile with potassium ferricyanide gave only a 34% yield of **7**. Compound **7** is much more stable in solution than **4**. Compound **7** was destroyed, however, when heated in chlorobenzene solution at 135° for 12 hr. The reaction products could not be purified. Compound **7** did react with DPPH at room temperature in acetonitrile solution to give a material which analyzed for a 1:1 product of dicyano-*p*-nitrobenzyl and DPPH. When a solution of **7** in chloroform was allowed to stand for 8 days, a 53% yield of *p*-nitrophenylmalononitrile was obtained.



7

When a chloroform solution of equimolar amounts of **4** and **7** was allowed to stand for 8 days, no crossed product **8** was obtained. The reaction did give *p*-nitrophenylmalononitrile in 38% yield and **5** in 40% yield.

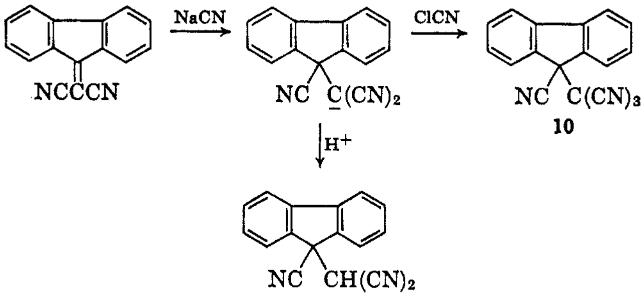


8

Hexacyanoethane and tetraphenylsuccinonitrile also reacted with DPPH at room temperature in acetonitrile solution. Under comparable conditions there was no reaction with *meso*-diphenylsuccinonitrile and DPPH.

9-Cyano-9-tricyanomethylfluorene (**10**) was prepared from 9-dicyanomethylenefluorene (Scheme I). Addition of cyanide gave the anion of 9-cyanofluoroenylmalononitrile, from which the free acid **9** was obtained in 95% yield. Reaction of the anion with cyanogen chloride gave **10** in 50% yield. The tetracyanoethane **10** did not react with DPPH at room temperature. Reaction did occur slowly at 80°.

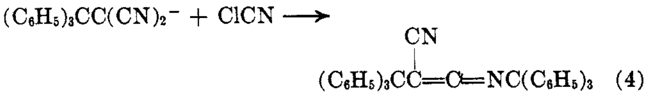
SCHEME I



10

9

The preparation of tritylcyanoform was attempted by treating cyanogen chloride with the anion of tritylmalononitrile. The product obtained was the stable ketenimine **11** (eq 4). As is discussed below, tritylcyanoform is thought to be an intermediate in the formation of **11**.

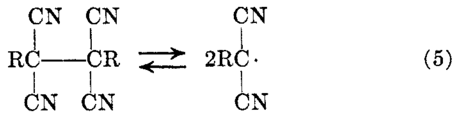


$$(C_6H_5)_3CC(CN)_2^- + ClCN \longrightarrow (C_6H_5)_3C\overset{CN}{\overset{|}{C}}=C=NC(C_6H_5)_3 \qquad (4)$$

11

Discussion

The reactions of the polycyanoethanes are best explained by assuming a facile, reversible homolytic dissociation (eq 5). Many of the reactions of the polycyanoethanes are typical radical reactions such as the hydrogen-abstraction reactions of the dicyanobenzyl radicals and the reactions with DPPH. The dicyanobenzyl radical when generated by hydrogen abstraction from phenylmalononitrile yielded the same product **5** as was obtained from the diphenyltetracyanoethane **4** (Scheme II). The dissociations are thought to be reversible because there is no appreciable concentration of radicals in solution.



$$R\underset{CN}{\overset{CN}{C}}-\underset{CN}{\overset{CN}{C}}R \rightleftarrows 2R\underset{CN}{\overset{CN}{C}}\cdot \qquad (5)$$

It is possible that the dicyanobenzyl radicals could recombine to give a ketenimine isomeric with **4**. If such an isomerization occurs, the ketenimine must readily undergo dissociation too, for it does not build up in solution as judged by the nmr spectrum of the reacting mixture. Attempts to obtain electron spin resonance signals were for the most part unsuccessful. A weak esr signal was seen when a solution of **7** in

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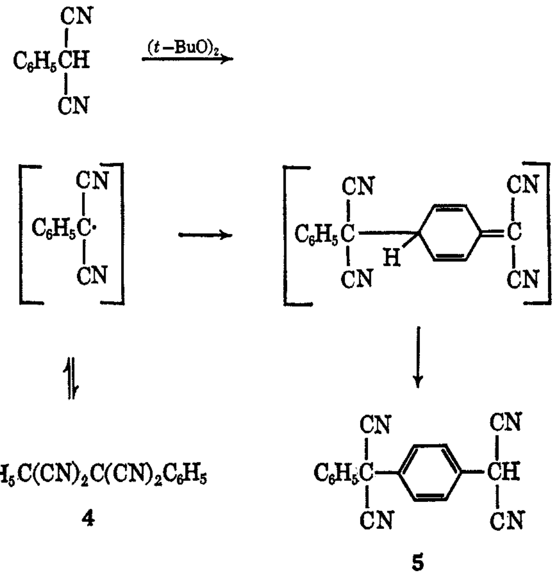
[8] H. D. Hartzler, *J. Am. Chem. Soc.*, **86**, 2174 (1964).

acetonitrile was heated at 70°. No hyperfine structure could be resolved; so no assignment of structure of the radical can be made. Therefore, the radical concentration in these reactions is never greater than 10^{-6} M. While the isomerization reaction **4** → **5** is slow, reactions of **4** with dinitrogen tetroxide, bromine, and DPPH are rapid even at room temperature. Since the dicyanobenzyl radical can be formed rapidly from **4**, disappears only slowly to give **5**, and never builds up in concentration, it must also return to **4**.

SCHEME II



The formation of **5** must be a radical dimerization, for the dicyanobenzyl radical does not attack aromatics such as benzene or chlorobenzene. It would not be expected to attack phenylmalononitrile or **4**.

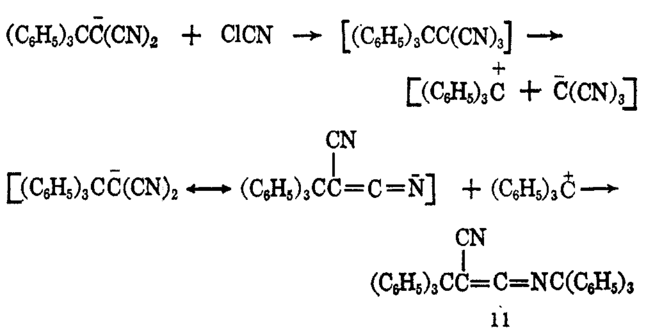
Although **7** appears to be much more stable in solution than **4**, the two compounds react with DPPH at comparable rates. Because of the *p*-nitro group, **7** cannot undergo an isomerization analogous to that of **4**. The *p*-nitro-α,α-dicyanobenzyl radicals did not dimerize by attack at the *ortho* position, presumably because of the steric hindrance of the dicyanomethylene group. In the absence of the dimerization reaction, the *p*-nitro-α,α-dicyanobenzyl radical does undergo hydrogen abstraction with solvent.

The reaction of **4** and **7** in chloroform solution gave **5** and *p*-nitrophenylmalononitrile, but the expected cross product **8** was not isolated. The material balance for the reaction was not good; so some **8** could have been present and been undetected. A more likely explanation is that the reaction of *p*-nitro-α,α-dicyanobenzyl radicals with chloroform proceeds at a different rate than does the isomerization of **4**. This could be true even though the rates of reaction of **4** and **7** with DPPH are roughly comparable.

Several attempts were made to generate the tricyanomethyl radical. Hexacyanoethane reacted with DPPH at room temperature more slowly than did **4** or **7**. Because of the difficulties in obtaining pure hexacyanoethane,[6] other sources of the tricyanomethyl radical were investigated. Bromocyanoform underwent extremely facile additions to olefins to give polymeric materials, but these reactions appeared to be ionic rather than radical. 9-Cyano-9-tricyanomethylfluorene (**10**) was easily made and purified, but it dissociated into radicals much less readily than the preceding compounds. At 80°, **10** reacted slowly with DPPH. A competing reaction under these conditions was the formation of dicyanomethylenefluorene (and presumably cyanogen) from **10**. This reaction apparently occurred from adventitious nucleophiles in solution and has previously been observed with hexacyanoethane.[6] The DPPH reaction was a reaction of **10**, for dicyanomethylenefluorene did not consume DPPH under these conditions.

The formation of **11** from tritylmalononitrile anion and cyanogen chloride was probably the result of the sequence shown in Scheme III.

SCHEME III



The relative ease of homolytic dissociation (as judged by rates of reaction with DPPH) of the ethanes investigated are summarized by the sequence: $(C_6H_5)_3CC(C_6H_5)_3 \gg C_6H_5C(CN)_2C(CN)_2C_6H_5 \sim p\text{-}O_2NC_6H_4C(CN)_2C(CN)_2C_6H_4NO_2\text{-}p > (C_6H_5)_2CCNCCN(C_6H_5)_2 > (NC)_3CC(CN)_3 \gg$ **10**. The equating of reaction rates with DPPH with dissociation rates assumes that there is no reaction of the substrates with DPPH. This assumption would appear to be reasonable for compounds such as phenyl malononitrile, *p*-nitrophenylmalononitrile, and *meso*-diphenylsuccinonitrile gave no evidence of reaction with DPPH. The order is not a clear one and renders difficult any assessment of aromatic and cyano substituents in stabilization of free radicals. It is well known that triphenylmethyl radicals are not planar,[9] and it seems reasonable that the diphenylcyanomethyl radicals would not be planar. The aryldicyanomethyl radicals, however, probably are planar and enjoy stabilization by conjugation with all three substituents. The relative inertness of **10** toward homolysis was surprising, especially in view of the recent demonstration[10] of the greater stability of the 9-phenylfluorenyl radical *vs.* the triphenylmethyl radical.

Experimental Section[11]

1,2-Diphenyl-1,1,2,2-tetracyanoethane (4).[12]—A solution of 17 g of potassium ferricyanide in 150 ml of water was added to

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(9) M. Szwarc, *Discussions Faraday Soc.*, **2**, 139 (1947).

(10) S. G. Cohen, F. Cohen, and C. H. Wang, *J. Org. Chem.*, **28**, 1479 (1963).

(11) Melting points are corrected. Infrared spectra were obtained on a Perkin-Elmer Model 21, ultraviolet and visible spectra on a Cary Model 14, and nmr spectra on a Varian A-60 spectrometer.

(12) This preparation was initially made by Dr. J. K. Williams of this laboratory.

a solution of 7.1 g of phenylmalononitrile in 250 ml of methanol. The precipitated solid was collected by filtration and washed thoroughly with water. After drying *in vacuo* at 100°, the solid weighed 4.12 g (58%). The decomposition point of **4** was approximately 120°, depending upon the rate of heating.

Anal. Calcd for $C_{18}H_{10}N_4$: C, 76.6; H, 3.57; N, 19.9. Found: C, 76.6; H, 3.65; N, 20.3.

The infrared spectrum of **4** showed absorption at 3.25 (aromatic CH), 4.42 (nonconjugated nitrile), 6.26 and 6.69 (aromatic unsaturation), and 13.55 and 14.45 μ (monosubstituted aromatic). The nmr spectrum of **4** in deuteriochloroform showed only absorption of aromatic protons at τ 2.3.

Rearrangement of 4 to *p*-(α,α-Dicyanobenzyl)phenylmalononitrile (**5**). **A. At 135°.**—A solution of 0.53 g of **4** in 10 ml of chlorobenzene was heated at 135° for 7 hr. The mixture was cooled and filtered. The filtrate was evaporated to dryness. The residue was crystallized from benzene–hexane (2:1) to give 0.21 g (40%) of **5**, mp 156–158°.

Anal. Calcd for $C_{18}H_{10}N_4$: C, 76.6; H, 3.57; N, 19.8: mol wt, 282. Found: C, 76.8; H, 3.60; N, 19.7; mol wt, 291 (vapor phase osmometer, ethyl acetate).

The infrared spectrum of **5** showed absorption at 3.28 (unsaturated CH), 3.50 (saturated CH), 4.45 (unconjugated nitrile), 12.0 (*para*-substituted aromatic), and 13.2 and 14.45 μ (monosubstituted aromatic). The nmr spectrum of **5** showed aromatic hydrogen at τ 2.17 and 2.33 as well as a singlet at τ 4.75 which had one-ninth the area of the aromatic hydrogens.

B. At 25°.—A solution of 1.77 g of **4** in 40 ml of chloroform stood at 25° for 16 hr. After removal of the solvent an oil remained. The oil was stirred with 25 ml of ether and filtered to give 0.68 g of crude **5**. Recrystallization from benzene–hexane gave 0.21 g (12%) of **5**, mp 157–160°.

C. At 25° with Oxygen.—Oxygen was bubbled through a solution of 2.1 g of **4** in 50 ml of methylene chloride. After 18 hr the solvent was removed *in vacuo* and the crude residue, mp 120–160° dec, was analyzed. No oxygen was incorporated.

Anal. Calcd for $(C_9H_5N_2)_n$: C, 76.6; H, 3.57; N, 19.9. Found: C, 77.5; H, 3.60; N, 19.6.

Phenylmalononitrile and *t*-Butyl Peroxide.—A solution of 6.48 g (0.046 mole) of phenylmalononitrile and 3.36 g (0.023 mole) of *t*-butyl peroxide (Shell, redistilled, n^{24}_{D} 1.3880) in 25 ml of chlorobenzene was heated at reflux for 12 hr under a short distillation head. Acetone and *t*-butyl alcohol distilled from the reaction mixture. The mixture was cooled and filtered to remove a small amount of solid, and the filtrate was concentrated *in vacuo*. The residue was triturated with hot hexane from which was recovered 0.62 g (10%) of unreacted phenylmalononitrile. The hexane-insoluble material was recrystallized from 2:1 benzene–hexane to give 1.45 g (22%) of **5**, mp 157–160° dec.

α,α-Dicyanobenzyl Nitrate.—A solution of 3.53 g of **4** in 100 ml of chloroform containing 2.8 g of dinitrogen tetroxide (dried by passage through phosphorus pentoxide) was stirred overnight under nitrogen at room temperature. The solution was concentrated to a volume of approximately 30 ml. A white crystalline solid separated and was collected by filtration. The unstable nitrate (1.8 g, 36%) melted at 83–85° with decomposition.

Anal. Calcd for $C_9H_5N_3O_3$: C, 53.2; H, 2.48; N, 20.7. Found: C, 53.4; H, 2.71; N, 20.4.

Additional amounts of the product could be obtained from the original filtrate. These were not obtained pure, however, and no satisfactory recrystallization procedure was found. The compound could not be stored.

The infrared spectrum of the nitrate showed absorption at 4.47 (unconjugated nitrile), 6.50 and 7.42 (nitro group), and 9.0 μ (CO).

4 with Tetrahydrofuran.—A solution of 4.9 g of **4** in 125 ml of purified tetrahydrofuran stood at 25° for 2 days. The solvent was removed leaving a yellow oil. The oil was rinsed several times with hexane. Phenylmalononitrile, mp 67–68° (0.35 g, 8%), was obtained from the hexane extracts. No pure material was isolated from the hexane-insoluble portion.

Bis-1,2-*p*-Nitrophenyl-1,1,2,2-tetracyanoethane (**7**).—A slurry of 4.50 g (0.02 mole) of the potassium salt of *p*-nitrophenylmalononitrile[8] in 150 ml of ethanol was stirred while iodine (2.56 g) was added. The mixture was stirred for 3 hr and poured into 600 ml of ice–water. Filtration gave crude **7** (3.58 g), mp 149–150°. Recrystallization from ethylene chloride gave 2.28 g (61%) of **7**, mp 164–166°.

Anal. Calcd for $C_{18}H_8N_6O_4$: C, 58.1; H, 2.17; N, 22.6; mol wt, 372. Found: C, 57.7; H, 2.19; N, 22.6; mol wt, 358 (vapor phase osmometer, ethyl acetate).

The infrared spectrum of **7** showed absorption at 3.20 (unsaturated CH), 4.40 (unconjugated nitrile), 6.19 and 6.67 (nitro group), and 13.5 and 14.26 μ (monosubstituted aromatic).

7 was also prepared in 34% yield by a procedure analogous to the preparation of **4**.

7 with Diphenylpicrylhydrazyl.—Solutions of 0.39 g of **7** in 25 ml of acetonitrile and of 0.75 g of DPPH in 40 ml of acetonitrile were mixed at room temperature. After 15 min the color of DPPH had nearly completely disappeared. The solvent was removed under nitrogen. The residue was stirred with methanol and filtered to give 0.98 g of crystalline solid, mp ~120° dec. Recrystallization from ethanol gave red-brown solid, mp 125–127° dec.

Anal. Calcd for $C_{27}H_{16}N_8O_8$: C, 55.9; H, 2.78; N, 19.3. Found: C, 55.7; H, 2.98; N, 18.9.

7 with Chloroform.—A solution of 0.70 g of **7** in 200 ml of chloroform was stirred for 2 days. The mixture was filtered to remove a small amount of insoluble material. The filtrate was stirred with 10% aqueous sodium bicarbonate solution. A purple solid separated and was collected by filtration. The purple salt was added to dilute aqueous hydrochloric acid to give 0.38 g (53%) of *p*-nitrophenylmalononitrile,[8] mp 107–109°.

Tetraphenylsuccinonitrile and DPPH.—A solution of 0.96 g of tetraphenylsuccinonitrile[13] and 1.97 g of DPPH in 100 ml of acetonitrile was stirred at room temperature under nitrogen for 20 hr. The solvent was removed under nitrogen. The residue was taken up in 50 ml of ether and filtered to remove a small amount of insoluble material. Evaporation of the ether left 2.75 g of solid, mp 124–132°. Recrystallization from ethanol gave material which melted at 132–134° dec.

Anal. Calcd for $C_{32}H_{22}N_6O_6$: C, 65.5; H, 3.78; N, 14.3. Found: C, 65.1; H, 4.02; N, 14.1.

9-Dicyanomethylenefluorene.—A mixture of 98.7 g of 9-fluorenone, 40 g of malononitrile, and 1 g of β-alanine in 20 ml of acetic acid and 500 ml of benzene was heated at reflux under a water separator for 16 hr. The mixture was cooled and filtered to give 118 g (92%) of 9-dicyanomethylenefluorene as red-orange crystals, mp 230–232°. Recrystallization from ethylene chloride raised the melting point to 237.6–238.6°, lit.[14] 213°.

9-Cyano-9-dicyanomethylfluorene (**9**).—A slurry of 2.3 g of 9-dicyanomethylenefluorene, 0.50 g of sodium cyanide, 10 ml of water, and 20 ml of ethanol was stirred at room temperature. The system slowly became homogeneous. The yellow solution was cooled in ice and acidified with cold, dilute hydrochloric acid. Filtration gave 2.41 g of solid, mp 142–147°. Rapid recrystallization from ethanol gave 2.20 g (90%) of **9**, mp 151.5–153°.

Anal. Calcd for $C_{17}H_9N_3$: C, 80.0; H, 3.55; N, 16.5. Found: C, 79.8; H, 3.57; N, 16.6.

The infrared spectrum of **9** showed absorption at 3.30 (unsaturated CH), 3.47 (saturated CH), and 4.50 μ (unconjugated nitrile). The chemical shift of the aliphatic hydrogen was τ 5.50.

9-Cyano-9-tricyanomethylfluorene (**10**).—Finely powdered sodium cyanide (1.55 g) was added to a stirred mixture of 7.1 g of 9-dicyanomethylenefluorene in 100 ml of acetonitrile. After 2 hr the red color had disappeared, and cyanogen chloride (3.9 g) was added. Stirring was continued for another 4.5 hr. The mixture was filtered to remove the sodium chloride. The filtrate was concentrated to a volume of about 10 ml and refiltered to give 4.93 g of crude **10**, mp 154–156°. Recrystallization from ethanol gave 3.78 g (44%) of **10**, mp 166–167°.

Anal. Calcd for $C_{18}H_8N_4$: C, 77.1; H, 2.88; N, 20.0. Found: C, 76.9; H, 3.01; N, 20.2.

The infrared spectrum of **10** showed no absorption of saturated CH. Nitrile absorptions were at 4.41 and 4.50 μ.

2-Aza-4-cyano-1,1,1,5,5,5-hexaphenylpenta-2,3-diene (**11**).—A slurry of 0.92 g of sodium hydride dispersion in mineral oil in 25 ml of tetrahydrofuran was stirred under nitrogen at −5°. Tritylmalononitrile[15] (6.2 g) in 25 ml of tetrahydrofuran was

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(13) V. Meyer and K. Auwers, *Ber.*, **22**, 1227 (1889).

(14) R. von Schenk and H. F. Finken, *Ann.*, **462**, 272 (1928).

(15) S. Patai and S. Dayagi, *J. Chem. Soc.*, 716 (1962).

added. Cyanogen chloride (5.2 g) was added in one portion and the mixture was stirred for 40 min. The mixture was filtered to remove the sodium chloride. The filtrate was evaporated to dryness. The residue was stirred with 20 ml of benzene and filtered to give 4.67 g of crude 11, mp 181–185°. Two recrystallizations from ethyl acetate gave 2-aza-4-cyano-1,1,1,5,5,5-hexaphenylpenta-2,3-diene (11), mp 200–202°.

Anal. Calcd for $C_{41}H_{30}N_2$: C, 89.4; H, 5.50; N, 5.08; mol wt, 551. Found: C, 89.4; H, 5.51; N, 5.00; mol wt, (ebullition in benzene), 563, 550.

The infrared spectrum of 11 showed absorption at 3.27 (unsaturated CH), 4.54 (conjugated nitrile), and 4.88 μ (cumulative unsaturation). The ultraviolet spectrum of 11 in acetonitrile showed λ_{max} 305 mμ (ϵ 782) and 250 mμ (ϵ 14,900).

The Reaction of Sulfonylureas and Sulfonamides with Carbonyl Chloride. A New Synthesis of Isocyanates[1]

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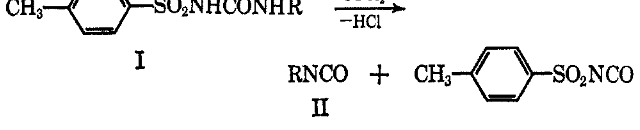
Several hitherto inaccessible mono- and diisocyanates were afforded from the reaction of carbonyl chloride with 1-arylsulfonyl-3-alkylureas and with alkylenebis(arylsulfonylureas) and -(sulfanilylureas), respectively. The conversion of arylsulfonamides to the corresponding arylsulfonyl isocyanates was readily accomplished by an isocyanate-catalyzed phosgenation reaction.

We recently reported that the reaction of 1,3-dialkylureas with carbonyl chloride affords a mixture of the N,N′-dialkylchloroformamidine hydrochlorides and the 2,4-dialkylallophanoyl chlorides,[2] the latter compounds being successfully dehydrochlorinated to alkyl isocyanates and alkylene diisocyanates.[3] In the case of the 1-arylsulfonyl-3-alkylureas, where the presence of the sulfonyl grouping can render the adjacent NH grouping less reactive to carbonyl chloride, one would expect both the arylsulfonyl and the alkyl isocyanates to be formed in good yield.

Further interest was provided by the sluggish reactions and poor yields reported for the reaction of sulfonamides with carbonyl chloride[4] and by the hope for obtaining alkylene diisocyanates and alkoxyethyl isocyanates from the 1-arylsulfonyl-3-alkylureas and alkylenebis(arylsulfonylureas), respectively—compounds obtainable only from the laborious Curtius degradation.[5]

The model compound, 1-*p*-toluenesulfonyl-3-*n*-butylurea (Ia), on reaction with carbonyl chloride in chlorobenzene at temperatures above 80°, did afford *n*-butyl isocyanate (IIa) and *p*-toluenesulfonyl isocyanate in the excellent yields of 85.2 and 88.5%, respectively. The reaction would not take place at room temperature. Similarly, 1-*p*-toluenesulfonyl-3-(2-ethoxyethyl)urea (Ib) gave the novel 2-ethoxyethyl isocyanate (IIb) in 76% yield. That no ether cleavage accompanied the reaction was well evidenced by both vapor phase chromatographic and H[1] nmr spectroscopic data.



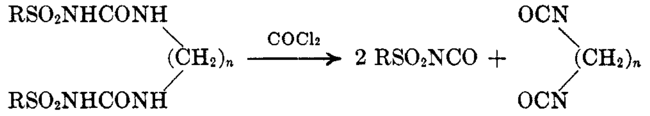
I

II

Ia, R = n-C_4H_9– IIa, R = n-C_4H_9–
b, R = $C_2H_5OCH_2CH_2$– b, R = $C_2H_5OCH_2CH_2$–

The several isocyanates prepared from 1-arylsulfonyl-3-alkylureas, along with their reaction conditions, are listed in Table I.

Bis(*p*-tolylsulfonylcarbamoyl)alkylenediamines (III), compounds readily available from the reaction of alkylenediamines with *p*-toluenesulfonyl isocyanate,[6] were also phosgenated, giving rise to the desirable alkylene diisocyanates listed in Table II.

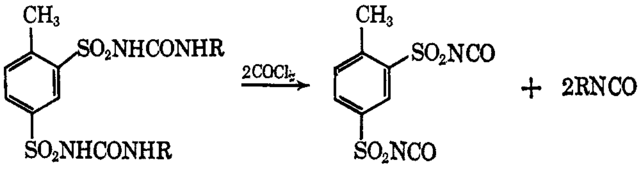


$$\begin{matrix}RSO_2NHCONH\\ \qquad (CH_2)_n\\ RSO_2NHCONH\end{matrix} \xrightarrow{COCl_2} 2\,RSO_2NCO + \begin{matrix}OCN\\ \qquad (CH_2)_n\\ OCN\end{matrix}$$

III

$R = p\text{-}CH_3C_6H$

Similarly, the arylbis(sulfonylalkylureas) were phosgenated to aryldisulfonyl diisocyanates. N,N′-Bis-(*n*-butylcarbamoyl)toluene-2,4-disulfonamide (IV), for example, was converted to toluene-2,4-disulfonyl diisocyanate (V, 38.3%).



IV V

R = *n*-butyl–

The success experienced with the carbonyl chloride-sulfonylurea reaction gave impetus to similar thoughts about the sulfanilylureas. Although the conversion of sulfanilamide to *p*-isocyanatobenzenesulfonamide was reported,[7,8] no syntheses for the isocyanatobenzenesulfonyl isocyanates appeared in the literature.[9] The large difference in reactivity of the isocyanato groupings renders these diisocyanates exceedingly useful in prepolymer systems.

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[1] Presented in part at the 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965.

[2] H. Ulrich, J. N. Tilley, and A. A. R. Sayigh, *J. Org. Chem.*, **29**, 2401 (1964).

[3] A. A. R. Sayigh, J. N. Tilley, and H. Ulrich, *ibid.*, **29**, 3344 (1964).

[4] H. Krzikalla, German Patent 817,602 (Oct. 18, 1951); *Chem. Abstr.*, **47**, 2206 (1953); C. King, *J. Org. Chem.*, **25**, 352 (1960); F. Effenberger and R. Gleiter, *Chem. Ber.*, **97**, 1576 (1964).

[5] W. Siefken, *Ann.*, **562**, 75 (1949).

[6] E. Habicht, U. S. Patent 2,962,530 (June 23, 1960); *Chem. Abstr.*, **55**, 17509 (1961).

[7] F. C. Meyer, U. S. Patent 2,827,470 (March 18, 1958); *Chem. Abstr.*, **52**, 12910 (1958); See also Houben-Weyl, "Methoden der Organischen Chemie IV," Vol. 8, Georg Thieme Verlag, Stuttgart, Germany, 1952, p 128.

[8] J. Smith, Jr., T. K. Brotherton, and J. W. Lynn, *J. Org. Chem.*, **30**, 1260 (1965).

[9] After completion of our work, Smith, Brotherton, and Lynn[8] reported the synthesis of one member of this class of compounds.