polymerizes rapidly in the condensed phase. 7,7,8,8-Tetrafluoroquinodimethan would seem to be the most logical polymer precursor. Attempts to isolate and characterize 7,7,8,8-tetrafluoroquinodimethan by gas chromatography of the pyrolysate followed by mass spectrographic analysis of the fractions failed to give evidence of the quinodimethan. Interestingly, the most abundant mass peak of III is 176 corresponding to $F_2CC_6H_4CF_2^+$. The instability of tetrafluoroquinodimethan is in marked contrast to the high order of stability of 7,7,8,8-tetracyanoquinodimethan and may be attributed at least in part to the lack of conjugation between fluorine and the quinodimethan nucleus.

Experimental

1,4-Dibromo-1,4-bis(trifluoromethyl)cyclohexane (I).—1,4-Dibromo-1,4-cyclohexanedicarboxlic acid (48.6 g., 0.147 mole) and 96 g. of sulfur tetrafluoride were heated in a shaker tube at 100° under autogenous pressure for 10 hr. The crude product was dissolved in ether and washed with dilute aqueous sodium bicarbonate. Distillation of the ether solution through a 2- t. spinning-band column gave 24.6 g. (44%) of 1,4-dibromo-1,4-bis-(trifluoromethyl)cyclohexane as a solid, b.p. 99–102° (27 mm)., m.p. 59–61°.

Anal. Calcd. for $C_8H_8F_6Br_2$: C, 25.4; H, 2.13; Br, 42.3. Found: C, 25.6; H, 2.16; Br, 42.4.

1,4-Bis(difluoromethylene)cyclohexane (II).—To a stirred, refluxing slurry of 484 g. of zinc dust, 500 ml. of water, and 200 ml. of ethanol was added a solution of 474.6 g. of I in 1000 ml. of ethanol at such a rate that the mixture refluxed without external heating. After the addition was complete, refluxing was continued for 1 hr. using external heating. The reaction mixture was filtered with a Filter-aid, and the filtrate was extracted with 1000 ml. of pentane. The pentane layer was washed three times with water and distilled through a 2-ft. spinning-band column to give 185 g. (82%) of 1,4-bis(difluoromethylene)cyclohexane, b.p. 77.5–78° (147 mm.), $n^{24}D$ 1.4059.

Anal. Calcd. for $C_8H_8F_4$: C, 53.3; H, 4.47; F, 42.2. Found: C, 53.7; H, 4.78; F, 43.1.

The infrared spectrum of the product showed intense absorption at 1770 cm.$^{-1}$, characteristic of $F_2C{=}C$ with no evidence of olefinic hydrogen.

Reaction of 1,4-Bis(difluoromethylene)cyclohexane with N-Bromosuccinimide.—A mixture of 235 g. (1.14 moles) of N-bromosuccinimide, 800 ml. of acetonitrile, and 0.2 g. of azobisisobutyronitrile was heated with stirring. When the temperature reached 60°, addition of 60 g. (0.33 mole) of 1,4-bis(difluoromethylene)cyclohexane was begun. The addition was carried out over 15 min. while heating to reflux was continued. Refluxing was continued for an additional 4.5 hr., and the red solution was then cooled and diluted with water. The bromine color was discharged by the addition of sodium bisulfite and the resulting solution was extracted with 1:1 pentane–ether. The extract was washed twice with water, dried over sodium sulfate, and distilled through a 2-ft. spinning-band column to give 38 g. (34%) of 1,4-bis(bromodifluoromethyl)benzene (III), b.p. 79–79.5° (6 mm.), $n^{24}D$ 1.4971–1.4965. Further purification was achieved by preparative gas chromatography on tetrafluoroalkylpyromellitate on Chromosorb.

Anal. Calcd. for $C_8H_4F_4Br_2$: C, 28.6; H, 1.20; Br, 47.6; F, 22.6. Found: C, 29.5; H, 1.44; Br, 47.0; F, 22.9.

The infrared spectrum of the product showed strong absorption in the 800–850-cm.$^{-1}$ region, characteristic of *para*-substituted benzenes. The ultraviolet spectrum in isooctane showed absorption at 232 (8650), 269 (1145), and 277 mμ (sh, ε 920).

The residue from the distillation was recrystallized twice from methanol to give 10.2 g. (6%) of 1,4-dibromo-1,4-bis(bromodifluoromethyl)cyclohexane (IV), m.p. 104–106°, which was identical with the sample described subsequently as determined by mixture melting points and comparison of infrared spectra.

Reaction of 1,4-Bis(difluoromethylene)cyclohexane with Bromine.—Bromine was added dropwise to a mixture of 28 g. of 1,4-bis(difluoromethylene)cyclohexane and 1 ml. of acetonitrile cooled in an ice bath until a permanent color remained. The resulting mixture was stirred with 20 ml. of acetonitrile and poured into cold water to give 66.6 g. of gummy solid which on crystallization from methanol gave 35.8 g. (22%) of white needles of 1,4-dibromo-1,4-bis(bromodifluoromethyl)cyclohexane (IV), m.p. 102–107°. Recrystallization from heptane gave colorless rods, m.p. 106–108°.

Anal. Calcd. for $C_8H_8F_4Br_4$: C, 19.2; H, 1.61; Br, 64.0; F, 15.2. Found: C, 19.6; H, 1.86; Br, 62.8; F, 15.3.

Debromination of 1,4-Bis(bromodifluoromethyl)benzene.—Into a vertical pyrolysis tube packed with 20-mesh zinc shot heated at 330° (0.025 mm.) and connected to a −78° trap, was dropped 3 g. of 1,4-bis(bromodifluoromethyl)benzene (III) over a period of 45 min. From the cold trap there was obtained 2.76 g. of unchanged III and 20 mg. of a white polymeric film which was insoluble in ether or methanol. The yield of polymer was improved slightly when zinc–copper couple was used in place of zinc. The polymer obtained from several runs was purified by extraction with ethanol in a Soxhlet apparatus for 7 hr. The polymer remained completely undissolved.

Anal. Calcd. for $(C_8H_4F_4)_x$: C, 54.6; H, 2.29; F, 43.2; Br, O. Found: C, 54.3; H, 2.84; F, 41.2; Br, 3.14.

The polymer began to soften and decompose at 380°. The infrared spectrum of the polymer is fairly simple and has absorption bands at 793 (1,4-disubstituted benzene), 900, 920, 1005, 1090, 1150, 1263, 1415, and 1760 (very weak) cm.$^{-1}$. The X-ray powder pattern is amorphous.

Photoaddition of Tetrahydrofuran to 7,7,8,8-Tetracyanoquinodimethan and Tetracyanoethylene

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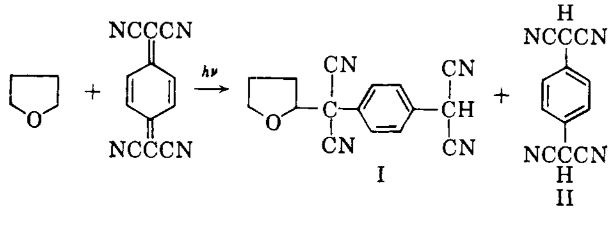
The free radical-initiated addition of ethers to olefins has recently received attention.[1] The initiator customarily consists of a peroxide which is decomposed by heat or irradiation. We have found an addition of tetrahydrofuran to 7,7,8,8-tetracyanoquinodimethan (TCNQ) and tetracyanoethylene (TCNE), where the unsaturated component can act as its own initiator on irradiation with sunlight or a GE sunlamp. Since the addition can also be initiated by the thermal decomposition of a catalytic amount of di-*t*-butyl peroxide, a free radical chain mechanism for the photo-initiated reaction is proposed.

Two TCNQ derivatives were isolated upon irradiation of TCNQ in tetrahydrofuran.



I

II

The structure proof for the photoaddition product I rests on its elemental composition and unambiguous spectral data. The infrared and ultraviolet spectra clearly show the absence of the bands characteristic of the quinonoid TCNQ system and confirm the presence of a *p*-disubstituted benzene group. The n.m.r.

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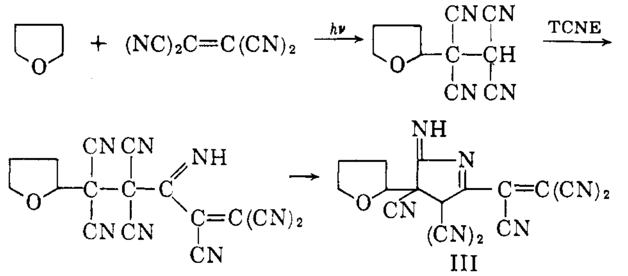
[1] (a) T. J. Wallace and R. J. Gritter, *J. Org. Chem.*, **27**, 3067 (1962); (b) T. M. Patrick, Jr., U. S. Patent 2,628,238 (1953); 2,684,373 (1954); 2,716,660 (1955).

spectrum of I in deuterated acetone has single peaks at 2.11 and 3.95 τ and multiple peaks centered at 5.41, 6.11, and 7.93 τ in a ratio 4.2:0.99:1.0:2.0:4.2 which supports the proposed structure. Furthermore, the 7- and 8-positions of TCNQ have been shown previously to be the sites of attack by free radicals.[2] The identity of the photo-reduced product II was established by comparison with a known sample.[2]

A solution of tetracyanoethylene (TCNE) in tetrahydrofuran also underwent a facile reaction when irradiated with a GE sunlamp. The colorless, crystalline product III had the composition of two moles of TCNE to one mole of tetrahydrofuran. An n.m.r. spectrum of the product in deuterated acetone showed a broad peak centered at 0.85 τ, and multiple peaks at 3.95, 5.95, and 7.9 τ in a ratio of 0.87:0.98:2.0:4.2. On standing, the peak at 0.85 τ gradually disappeared, and the broad peak at 7.9 τ increased in intensity by one proton due to exchange with the solvent, giving rise to the C–H peak of acetone.

Since the n.m.r. spectrum of III shows the presence of a mono-α-substituted tetrahydrofuran group, apparently the primary 1:1 photoaddition product underwent subsequent fast ionic addition to a neutral molecule of TCNE. The following over-all process is considered as one possibility.



III

The proposed conjugated cyclic imidine structure for III is in accord with its extensive ultraviolet absorption, its infrared spectrum, and its n.m.r. spectrum which showed the presence of a readily exchangeable proton. The primary photoaddition step across the ethylenic double bond rather than across a nitrile group is postulated in analogy to other free-radical additions to TCNE[3] and in analogy to the addition of tetrahydrofuran to TCNQ as previously discussed. The subsequent ionic addition to the nitrile group of another TCNE molecule explains the extensive ultraviolet absorption of III. Because of the present lack of suitable ultraviolet model compounds, any structure assignment concerning the bonding of the cyanocarbon moiety can only be tentative. In the n.m.r. spectrum, the shift of the tertiary α-hydrogen atom by 2.4 p.p.m. from that of tetrahydrofuran itself demonstrates an extremely strong field effect by the substituent group.

Experimental

Preparation of I by Irradiation.—A solution of 3.5 g. of TCNQ in 500 ml. of tetrahydrofuran was irradiated with a GE sunlamp for 8 hr. The solvent was then removed under reduced pressure. The residual brown oil solidified on rubbing with a benzene–petroleum ether mixture. On extraction with hot toluene and subsequent cooling, there was obtained 2.5 g. (55%) of round, off-white crystals, m.p. 136–139°. Recrystallization from a large volume of a benzene–cyclohexane mixture gave I as white rods, m.p. 138–140°.

Anal. Calcd. for $C_{16}H_{12}N_4O$: C, 69.6; H, 4.4; N, 20.3. Found: C, 69.8; H, 4.4; N, 20.3.

The insoluble residue, 0.3 g. (8.5%), m.p. 242–245°, proved to be *p*-phenylenedimalononitrile (II)[2] by comparison of its infrared spectrum with that of an authentic sample. Admixture with an authentic sample did not lower its melting point.

A 10^{-3} molar solution of TCNQ in tetrahydrofuran upon a 20-min. exposure to sunlight no longer showed any absorption due to TCNQ (395 mμ, ϵ 63,600). No reaction took place in the dark.

Preparation of I by Initiation with Di-*t*-butyl Peroxide.—A solution of 1.5 g. (0.0075 mole) of TCNQ and 0.07 g. (0.0005 mole) of di-*t*-butyl peroxide in 250 ml. of tetrahydrofuran was heated in a shaker tube for 4 hr. at 150°. The solvent was then removed under reduced pressure. The residual oil dissolved to a large extent in hot benzene. On filtration and cooling, there was obtained 0.65 g. (33%) of I, m.p. 138–140°, mixture melting point with sample of I prepared by irradiation, 138–140°.

The undissolved residue, 0.15 g. (10%), proved to be *p*-phenylenedimalononitrile.

Preparation of III.—A solution of 50 g. of TCNE in 350 ml. of tetrahydrofuran was irradiated for 4 days with a GE sunlamp. The solution was clear and had a dark red-brown color. The solvent was then removed under reduced pressure, leaving 54 g. of dark residue. Extraction of the residue with 800 ml. of hot benzene afforded 24 g. (37%) of purple solid on cooling. A portion of this solid was recrystallized from a mixture of 400 ml. of benzene and 5 ml. of acetonitrile to give shiny, white crystals of III, m.p. 172° dec.

Anal. Calcd. for $C_{16}H_8N_8O$: C, 58.5; H, 2.4; N, 34.2; mol. wt., 328. Found: C, 58.7; H, 2.6; N, 34.1; mol. wt., 326 (b.p. in acetone).

The infrared spectrum of III shows bands at 3.10 (NH), 4.45 (conjugated CN), 6.08 (attributed to $\mathrm{N{-}\overset{|}{C}{=}N{-}}$), and at 6.45 μ (conjugated C=C); $\lambda_{\max}^{CH_3CN}$ 218 (22,800), 227 (21,600), 257 (5680), and 271 mμ (5960). TCNE, for comparison, absorbs at 256 (8100), 263 (9360), and 272 mμ (10,000).

The product III shows only very limited stability. On standing in the solid state, it slowly turns red. This process is accelerated in polar solvents.

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[2] D. S. Acker and W. R. Hertler, *J. Am. Chem. Soc.*, **84**, 3370 (1962).

[3] W. J. Middleton, R. E. Heckert, E. L. Little, and C. G. Krespan, *ibid.* **80**, 2783 (1958).

Trimethyl Trichlorohemimellitate from an Unusual Fragmentation Reaction

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A convenient path to bicycloheptadienes lies in the Diels–Alder reaction of cyclopentadienes with suitable acetylenes. Thermolysis of the resulting adduct leads to benzene derivatives in favorable circumstances. Thus, tetraphenylcyclopentadienone and diphenylacetylene on heating react to form hexaphenylbenzene and carbon monoxide.[1] Similarly, the reaction of phenylacetylene with 5,5-dimethoxytetrachlorocyclopentadiene affords 2,3,4,5-tetrachlorobiphenyl in low yield,[2] while the reaction of 5,5-dimethoxytetrachlorocyclopentadiene with 2-butynediol diacetate has been reported to give tetrachloro-1,2-diacetoxybenzene.[3]

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[1] W. Dilthey and G. Hurtig, *Ber.*, **67**, 2004 (1934).

[2] E. T. McBee, *et al.*, *J. Am. Chem. Soc.*, ,**77** 385 (1955).

[3] H. Feichtinger and H. Linden, German Patent 1,105,862 (1961).