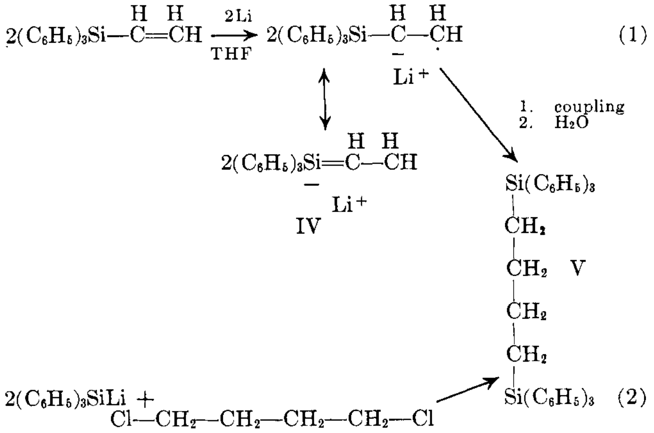
ambiguous synthesis from the known reaction[10] of 1,4-dichlorobutane with triphenylsilyllithium (equation 2). Consequently, the formation of V from triphenylvinylsilane and lithium metal can be formulated most reasonably as a reductive coupling proceeding by way of transitory 1:1 lithium–vinylsilane adducts (radical-anion IV, equation 1). The similarity to the behavior of 1,1-diphenylethylene is most striking.



Added assurance that V was not known compound 1,2-bis(triphenylsilyl)ethane (VI) (possibly arising by the cleavage of triphenylvinylsilane to produce triphenylsilyllithium and the addition of the latter to unchanged triphenylvinylsilane) was obtained by comparing V with an authentic sample of VI. Infrared spectral and mixture melting point comparison showed V and VI to be different.

The generality of this reductive coupling reaction is reflected in the ability of alkylvinylsilanes, such as triethylvinylsilane and dimethyldivinylsilane, also to react readily with alkali metals in tetrahydrofuran.[9] In these cases a styrene-like polymerization under agency of the alkali metal also appears to occur. The large number of vinyl derivatives available of both metals and metalloids offers the opportunity of extending the foregoing observations to the dimerization and polymerization of many related systems. This aspect is being actively considered in this laboratory.

Experimental

Starting Materials and General Procedures.—Reactions involving metals or organometallic reagents were conducted under an atmosphere of dry, oxygen-free nitrogen. The tetrahydrofuran employed in such reactions was purified by successive treatments with sodium hydroxide pellets, sodium metal slices, and lithium aluminum hydride. The purified tetrahydrofuran was distilled finally from the lithium aluminum hydride directly into the reaction vessel.

The lithium metal ribbon (carefully scraped free of oxide and nitride while under dry benzene) contained 0.6% of sodium metal. The triphenylvinylsilane was prepared from trichlorovinylsilane and phenylmagnesium bromide in tetrahydrofuran by following a recent procedure.[6] The authentic 1,4-bis(triphenylsilyl)butane was prepared from 1,4-dichlorobutane and triphenylsilyllithium, m.p. 214–215° (lit.[10] m.p. 215–216°).

All melting points are uncorrected. The infrared spectral data were obtained from samples recorded in mineral oil mulls on a Perkin-Elmer infrared spectrophotometer, Model 21.

Reaction of Triphenylvinylsilane with Lithium Metal in Tetrahydrofuran.—A 500-ml., three-necked, round-bottomed flask, equipped with a low-temperature thermometer and a sealed polytetrafluoroethylene paddle stirrer was charged with 250 ml. of pure, dry tetrahydrofuran and 14.3 g. (0.050 mole) of triphenylvinylsilane. The reaction system was purged with dry nitrogen gas. Through the third neck of the flask, 0.12 g. of finely cut lithium metal ribbon pieces was introduced. The flask was restoppered and the stirrer was started. A yellow coating soon formed on the surface of the lithium pieces and eventually the whole solution developed a light orange color. The triphenylvinylsilane solution was thereupon cooled to $-70°$ to $-75°$ with a Dry Ice–acetone bath. After 80 min. of vigorous stirring at this temperature the second 0.12-g. portion of lithium pieces was introduced into the reaction mixture. The system gradually became a light yellow fluid paste. (Some of the material which had splashed up into the warmer parts of the flask turned brown.) After an additional 100 min. of reaction the third and last 0.12-g. portion of lithium pieces was added [total, 0.36 g. (0.052 g.-atom) of lithium]. The reaction system was stirred for another hour (total reaction time, 4 hr.) and then diluted with 175 ml. of pure tetrahydrofuran. The suspension was allowed to stir for three more hours and then it was cautiously treated with 200 ml. of *N* sulfuric acid at $-75°$. After the mixture was allowed to come to room temperature, 200 ml. of ether was added. The separated organic layer was washed successively with water, aqueous sodium bicarbonate solution and, finally, again with water. After drying over anhydrous magnesium sulfate the organic extract was freed of solvent to give 13.8 g. of crude organic product, whose infrared spectrum showed no absorption bands characteristic of triphenylsilane (Si–H, 2270), triphenylsilanol (Si–OH, 3300), hexaphenyldisiloxane (Si–O–Si, 1095), or 1,2-bis(triphenylsilyl)ethane (1140 cm.$^{-1}$).

The crude product was digested with 200 ml. of hot benzene and the resulting suspension allowed to cool to room temperature. The colorless precipitate, upon collection and drying at 100°, weighed 8.92 g. (62%) and melted at 209–212°. Recrystallization from cyclohexane yielded fine needles melting consistently at 214–215°. Comparison of this product with an authentic sample of 1,4-bis(triphenylsilyl)butane by means of mixture melting point and infrared spectra established the identity of the two samples. Moreover, admixture of the product from triphenylvinylsilane and lithium metal with authentic 1,2-bis(triphenylsilyl)ethane[11] (m.p. 210–212°) caused a definite melting point depression.

The evaporation of the mother liquor from the benzene extraction of the crude product yielded a viscous, straw-colored oil, whose infrared spectrum showed no indication of Si–H, Si–O–H, or Si–O–Si linkages. The spectral absorptions suggested the presence only of triphenylvinylsilane and 1,4-bis(triphenylsilyl)butane.

---

(9) J. J. Eisch and L. L. Libit, unpublished studies.

(10) W. K. Johnson and K. A. Pollart, *J. Org. Chem.*, **26**, 4092 (1961).

(11) The authors are indebted to Professor Henry Gilman, Department of Chemistry, Iowa State University, Ames, Iowa, for providing them with an authentic sample of this compound.

Substituted Quinodimethans. VI. 7,7,8,8-Tetrafluoroquinodimethan Polymer

W. R. Hertler

Contribution No. 847 from the Central Research Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware

Received February 25, 1963

Recent work in these laboratories has led to the synthesis of several stable quinodimethans, including 7,7,8,8-tetracyanoquinodimethan,[1a] 7,7,8,8-tetrakis(methoxycarbonyl)quinodimethan,[1a] 7,7,8,8-tetrakis(ethylsulfonyl)quinodimethan,[1b] and 11,11,12,12-tetracyanonaphtho-2,6-quinodimethan.[1c] The stability of these quinodimethans may be attributed to the presence of electron-withdrawing substituents which permit

---

(1) (a) D. S. Acker and W. R. Hertler, *J. Am. Chem. Soc.*, **84**, 3370 (1962); (b) W. R. Hertler and R. E. Benson, *ibid.*, **84**, 3474 (1962); (c) J. Diekmann, W. R. Hertler, and R. E. Benson, *J. Org. Chem.*, **28**, 2719 (1963).

delocalization of electrons from the highly reactive quinodimethan nucleus. The powerful inductive electron-withdrawing ability of fluorine is well known. On the other hand, resonance delocalization of electrons in an olefinic system by fluorine should be negligible. In order to assess the relative importance of inductive and mesomeric electron withdrawal in stabilization of quinodimethans, the synthesis of 7,7,8,8-tetrafluoro-*p*-quinodimethan was undertaken.

A survey of the literature reveals that a stable 7,7,8,8-tetrahalo-*p*-quinodimethan has not been prepared, although in 1904 Thiele and Balhorn[2] obtained a polymeric material from the reaction of mercury and 1,4-bis(tribromomethyl)benzene. The polymer may have resulted from polymerization of an unstable tetrabromoquinodimethan.

The route selected for the synthesis of 7,7,8,8-tetrafluoroquinodimethan is based on the debromination of 1,4-bis(bromodifluoromethyl)benzene (III), which was prepared as outlined in Chart A.

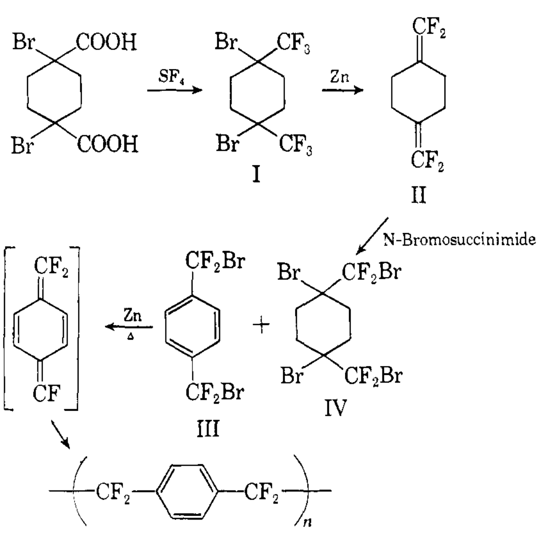


CHART A

1,4-Dibromo-1,4-cyclohexanedicarboxylic acid was fluorinated with sulfur tetrafluoride[3] to give 1,4-dibromo-1,4-bis(trifluoromethyl)cyclohexane (I) from which no attempt was made to isolate the pure isomers. Fluorination of the corresponding dimethyl ester with sulfur tetrafluoride led to an uncontrollable reaction; it was a less satisfactory method for preparation of I.

The structure assigned to I is confirmed by the F^{19} magnetic resonance spectrum which shows two unsplit peaks at +6.5[4] and +10.5 p.p.m. with relative integrated intensities of one and three, respectively. The values of δ are consistent with $-CF_3$ groups, and the absence of splitting confirms the presence of the bromine atoms at positions 1 and 4. The intensity ratio of 1:3 indicates a 1:1 mixture of *cis* and *trans* isomers. The H^1 magnetic resonance spectrum[4] shows a multiplet centered near 7.67 τ (in carbon tetrachloride) consistent with a methylene group adjacent to a halogenated carbon. Debromofluorination of I occurred readily with zinc in aqueous ethanol to give 1,4-bis(difluoromethylene)cyclohexane (II). The structural assignment of II is confirmed by the F^{19} magnetic resonance spectrum which shows a single peak at +30.4 p.p.m. (in carbon tetrachloride) in accord with a $C{=}CF_2$ group. The H^1 n.m.r. spectrum shows only a multiplet centered at 7.8 τ. The absence of resonance below 7.8 τ shows that no olefinic hydrogen is present. By analogy with the synthesis of 7,7,8,8-tetracyanoquinodimethan from 1,4-bis(dicyanomethylene)cyclohexane[1a] it might be expected that treatment of II with a brominating agent and pyridine would give tetrafluoroquinodimethan directly. Such was not the case, however. Reaction of II with N-bromosuccinimide gave two products, one was a distillable liquid, 1,4-bis(bromodifluoromethyl)benzene (III), and the other was a solid, presumably 1,4-dibromo-1,4-bis(bromodifluoromethyl)-cyclohexane (IV). The latter product could also be prepared from the reaction of bromine with II. The structure of III is confirmed by the F^{19} magnetic resonance spectrum which shows a single sharp peak at -22.3 p.p.m. consistent with a $-CF_2Br$ group. The H^1 magnetic resonance spectrum shows an unsplit peak at 2.50 τ (neat) characteristic of aromatic hydrogen. *para* Substitution is further confirmed by the presence of a quadruplet due to hydrogen split by C^{13} (J = 166.5 c.p.s.) and by ortho-hydrogen (J = 9.5 c.p.s.). Additional evidence for the structure of IV is provided by the F^{19} magnetic resonance spectrum which shows a single sharp peak at -14.6 p.p.m. (in chloroform) consistent with a $-CF_2Br$ group. The presence of only one peak indicates that only the *trans* isomer is present, and the absence of splitting precludes the presence of hydrogen on the carbon atoms adjacent to the $-CF_2Br$ groups. The H^1 spectrum of IV (in carbon tetrachloride) shows a multiplet centered near 7.57 τ. The absence of resonance at lower field shows that no olefinic hydrogen is present.

It is not known whether III arose from 1,6-bromination of an intermediate tetrafluoroquinodimethan or from a series of allylic brominations, dehydrobrominations, and allylic rearrangements not involving an intermediate quinodimethan. When the reaction occurred in the presence of a base, such as pyridine or sodium acetate, formation of III was suppressed, and only IV was isolated. Curiously when pyridine was used, a small amount of 3,5-dibromopyridine was isolated.

When III was passed through a heated pyrolysis tube filled with zinc or zinc–copper couple at reduced pressure and the exit vapor was led through a $-78°$ trap, a white polymeric film formed at the first cold area of the trap. Large amounts of unchanged III were also recovered in the trap. Elemental analysis of the polymer, which is highly insoluble in all solvents examined, shows it to be largely a polymer of tetrafluoroquinodimethan. However, the presence of a small percentage of bromine may be due to a little debromofluorination of III resulting in formation of a small amount of bromotrifluoroquinodimethan. The conversion of III to polymer was only 8% with a yield of 16%. Since there was no detectable polymer formation in the pyrolysis train until the exit gases reached the cooled portion of the trap, it seems very likely that the polymer did, indeed, result from a substance which is stable in the gas phase at low pressure but which

---

(2) J. Thiele and H. Balhorn, *Ber.*, **37**, 1463 (1904).

(3) W. C. Smith, C. W. Tullock, E. L. Muetterties, W. R. Hasek, F. S. Fawcett, V. A. Engelhardt, and D. D. Coffman, *J. Am. Chem. Soc.*, **81**, 3165 (1959).

(4) All F^{19} magnetic resonance spectra were determined at 56.4 Mc. using external 1,2-difluorotetrachloroethane as a reference. All H^1 magnetic resonance spectra were determined with a Varian A-60 spectrometer.

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-ft. 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, 0. 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

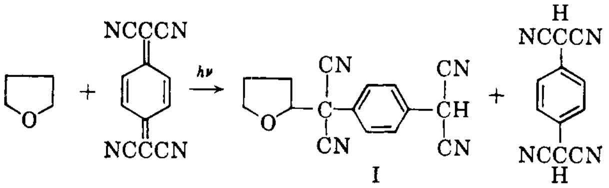
J. DIEKMANN AND C. J. PEDERSEN

Contribution No. 855 from the Central Research and Elastomer Chemicals Departments, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware

Received April 4, 1963

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.

---

[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).