base peak at m/e 199 ($C_7F_6H^+$). The H^1 nmr spectrum (CCl_4) showed a triplet ($J = 7$ Hz) at τ 8.70 ($-CH_3$) and a quartet at 5.71 (CO_2CH_2-) superimposed on a multiplet for the methyne proton. The F^{19} nmr spectrum showed three multiplets of equal area (in CCl_4 from external fluorotrichloromethane). The following assignments were made using F–F and F–H spin–spin decoupling: $J_{HF_{AA'}} = 22.5$ Hz; δ_A 110 ppm, δ_B 149 ppm, and δ_C 155 ppm. When the BB′CC′ portion of the spectrum (A decoupled) was assigned $J_{BB'} = 19$, $J_{BC} = J_{B'C'} = 3.5$, $J_{B'C} = J_{BC'} = 26.5$, and $J_{CC'} = 1$ or 2 Hz, reasonable (but not exact) fits were obtained when observed, and computer-calculated spectra were compared. The spectrum remained essentially unchanged to −99° (in $CFCl_3$ solvent).

Anal. Calcd for $C_{10}H_6F_6O_2$: C, 44.13; H, 2.22. Found: C, 44.17; H, 2.77.

Registry No.—Ia, 16021-14-0; II, 16021-15-1; III, 16021-16-2; hexafluorobenzene, 392-56-3.

The Addition of Cyclopentadienylidene to Hexafluorobenzene[1]

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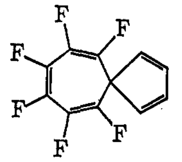
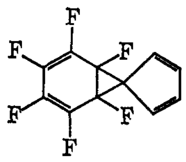
In the course of our investigations of reactions of carbenes in hexafluorobenzene we chanced to observe that, whereas fluorenylidene[3] does not react with hexafluorobenzene, the more reactive cyclopentadienylidene[4] does. The caveat of Gale[5] should therefore certainly be heeded: hexafluorobenzene is by no means always inert toward divalent carbon.

Irradiation of a solution of diazocyclopentadiene in hexafluorobenzene with a medium-pressure Hanovia mercury arc gave, after removal of the hexafluorobenzene and bulb-to-bulb distillation, a yellow oil in *ca.* 30% yield. The high resolution mass spectrum establishes the composition as $C_{11}F_6H_4$. The infrared spectrum shows evidence of carbon–fluorine bonds by several strong bands in the 1000–1400-cm^{-1} region and of fluorinated double bonds by a strong band at 1682 cm^{-1}.[6] The pmr spectrum shows a single symmetrical signal centered at τ 3.59; the ^{19}F nmr[7] spectrum shows three multiplets of equal intensity centered at 110, 145, and 151 ppm upfield from internal fluorotrichloromethane. The ultraviolet spectrum exhibits maxima at 221 and 266 mμ (ε 7300 and 3600).

In considering the structure of the adduct, attention is inevitably focused on I and II. While the products of additions of carbenes to benzenes are usually (but not always[8]) tropilidenes, it might be expected that the notorious[9,10] preference of fluorine for saturated over unsaturated carbon would lead to the norcaradiene being favored. Two facts argue strongly against structure II. First, one would not expect a symmetrical pmr pattern for II, and, second, there appears to be no signal in the ^{19}F nmr spectrum at high enough field to be reconcilable with a tertiary cyclopropyl fluorine.[11–13a] Accordingly we prefer structure I. The question arises as to why the tropilidene is favored over the norcaradiene which has two fewer fluorines on double bonds. Conceivably the aversion of fluorine for double bonds is an effect of hybridization[14] and fluorine feels little difference between a carbon–carbon double bond and a cyclopropane ring. This would also explain why the fluorine in fluorobullvalene prefers the triallylic rather than cyclopropyl position.[10] Other structures which fit the nmr data and which contain exocyclic double bonds can be constructed, but these suffer a variety of deficiencies including the lack of an appropriate infrared stretching frequency and extreme mechanistic improbability.



I



II

On heating, either in a flow system or on incautious gas chromatography, I rearranges cleanly to III. The infrared spectrum is qualitatively similar to that of I, but the ultraviolet spectrum shows a maximum at 250 mμ (ε6 040) and a shoulder at 290 mμ (ε 2200) and the pmr spectrum has undergone a striking change. There are now two signals of equal area at τ 3.25 (symmetrical multiplet) and 6.54 (multiplet). These are thought to correspond to two vinyl protons and to two protons adjacent to an extensively conjugated system. Indene is a good model and shows, in addition to peaks for aromatic protons, a symmetrical multiplet at τ 3.35 and

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[1] We thank the National Science Foundation for support of this work in the form of GP-5257. Grants GP-6803 and GP-5200 to Princeton University for the purchase of high resolution mass and nuclear magnetic resonance spectrometers are also gratefully acknowledged. We further thank the Lilly Research Laboratories for a generous unrestricted grant.

[2] Alfred P. Sloan Research Fellow, 1967–1968.

[3] M. Jones, Jr., and K. R. Rettig, *J. Amer. Chem. Soc.*, **87**, 4013, 4015 (1965).

[4] R. A. Moss, *J. Org. Chem.*, **31**, 3296 (1966).

[5] D. M. Gale, *ibid.*, **33**, 2536 (1968). We thank Dr. Gale for advising us of his work and for graciously suggesting simultaneous publication.

[6] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1958, pp 42 and 329.

[7] We are most grateful to Drs. B. Stewart of the Allied Chemical Co., Morristown, N. J., and L. A. Wilson of Varian Associates, Linden, N. J. for measuring the fluorine nmr spectra.

[8] E. Ciganek, *J. Amer. Chem. Soc.*, **89**, 1454 (1967).

[9] E. W. Schlag and W. B. Peatman, *ibid.*, **86**, 1676 (1964).

[10] G. Schröder and J. F. M. Oth, *Angew. Chem. Intern. Ed. Engl.*, **6**, 414 (1967).

[11] This is not an easy assignment to make. If one takes 142 ppm as the shift of geminate cyclopropyl fluorines,[12] then the usual shift to higher field of *ca.* 50–60 ppm in going to the tertiary system leads to an estimate of 190–200 ppm. Addition of a double bond, thus making the fluorine allylic, should lead to a downfield shift of 7–15 ppm.[12,13] The final estimate of 180–190 ppm for structure II seems significantly higher than any signal in the spectrum. A similar treatment for cyclobutenyl fluorine leads to a prediction of 175 ppm in good agreement with the shifts of 178 and 180 ppm observed by Gale.[5]

[12] R. A. Mitsch, *J. Amer. Chem. Soc.*, **87**, 758 (1965).

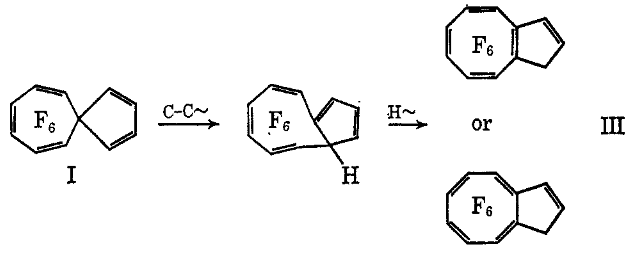
[13] J. W. Emsley, J. Feeney, and L. M. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Pergamon Press Ltd., London, 1966, Chapter 11.

[13a] NOTE ADDED IN PROOF.—1,2,3,4,5,6-Hexafluorotropilidene has recently been synthesized. Here the distinction between tropilidene and norcaradiene is easy. The ^{19}F nmr of this compound (signals at 113, 146, and 156 ppm upfield of fluorotrichloromethane) is very similar to that of I. Accordingly the assignment of structure I seems secure: L. S. Kobrina, G. G. Yakobson, and N. N. Vorozhtsov, *Zh. Vses. Khim. Obshchest.*, **12**, 597 (1967).

[14] D. Peters, *J. Chem. Phys.*, **38**, 561 (1963).

a triplet at τ 6.67.[15] The fluorine nmr spectrum of III shows peaks for six different fluorines grouped roughly in pairs at 107, 113, 120, 122, 131, and 133 ppm upfield from internal fluorotrichloromethane.

These chemical shifts seem inconsistent with any structure containing the valence–tautomeric bicyclo[4.2.0] system[11] and III is preferred, although the structure cannot be regarded as unequivocably proved.



A mechanism for the conversion of I into III can be constructed and involves a carbon–carbon bond shift (possibly in the norcaradiene form II) followed by a hydrogen shift. These steps have rather good analogy, albeit in much more simple systems.[16–18]

Experimental Section

Spiro[4.6]-6,7,8,9,10,11-hexafluoroundeca-1,3,6,8,10-pentaene (I).—A solution of 1 ml of diazocyclopentadiene[19,20] in 122 g of hexafluorobenzene was irradiated through a Pyrex filter with a 450-W Hanovia medium-pressure mercury arc for 14 hr. The hexafluorobenzene was removed by distillation at 0.1 mm leaving a dark brown, thick oil. This was distilled in a bulb-to-bulb apparatus at room temperature and 0.025 mm to yield 500 mg of a yellow oil. Spectral analysis revealed this to be I contaminated with traces of dicyclopentadiene.

Anal.[21] Calcd for $C_{11}H_4F_6$: C, 52.82; H, 1.61. Found: C, 53.01; H, 1.72.

Pyrolysis of I. A. Flow System.—A solution of 10 mg of I in 0.5 ml of cyclohexane was dropped slowly into a 12-in. Pyrex tube packed with glass helices under nitrogen at 220°. Residence time was *ca.* 1 sec. Under these conditions I is converted into a mixture of 40% I and 60% III with *ca.* 90% recovery. Increasing the temperature to 255° resulted in 90–95% conversion into III with somewhat reduced recovery.

B. Gas Chromatography.—Compound I is easily converted into III in the injector or detector–collector of a gas chromatograph. The peak corresponding to I is simply collected and reinjected. Injection on a 5-ft SE 30 silicone oil column operated at 95° (injector, 130°, and detector, 210°) with a flow rate of 100 cc of helium/min results, as revealed by reinjection, in *ca.* 25% I (retention time 22 min) and 75% III (retention time 42 min, mp 50–52°).

Anal. Found: C, 52.71; H, 1.66.

Registry No.—I, 16033-88-8; III, 16021-17-3; diazocyclopentadiene, 1192-27-4; hexafluorobenzene, 392-56-3.

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[15] N. S. Bhacca, L. F. Johnson, and J. N. Shoolery, "Varian NMR Spectra Catalog," Varian Associates, Palo Alto, Calif., 1962, No. 227.

[16] J. W. De Haan and H. Kloosterziel, *Rec. Trav. Chim. Pays-Bas*, **84**, 1594 (1965), and references therein.

[17] W. R. Roth, *Tetrahedron Lett.*, 1009 (1964).

[18] S. McLean and R. Haynes, *ibid.*, 2385 (1964).

[19] W. von E. Doering and C. H. DePuy, *J. Amer. Chem. Soc.*, **75**, 5955 (1953).

[20] T. Weil, *J. Org. Chem.*, **28**, 2472 (1963).

[21] Although acceptable carbon and hydrogen analyses could be obtained on I, fluorine analysis was poor. We do not know the precise cause of this but can point out that I is most unstable. Exposure to air results in rapid darkening and eventual deposition of a brown-black solid.

Electron-Transfer Polymers. XXXIII. Compounds Related to Tocopherol

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Redox polymers[1a] have been prepared by polycondensation of 2,5-disubstituted benzoquinones.[1b] In the resulting linear polymers the redox group is part of the chain. In this paper we report the preparation of redox monomer from a quinonyl glycol. In this polymer the redox groups are pendant from the chain.[2] In the course of preparing this monomer several interesting new compounds, analogs of tocopherol derivatives, were prepared, and new behaviors were observed.

Trimethylhydroquinone (1,3,4-trimethyl-2,5-dihydroxybenzene) was converted into 3-hydroxy-6-methoxy-2,4,5-trimethylbenzyl chloride (I).[3] Treatment with sodioethyl malonate produced ethyl(3-hydroxy-6-methoxy-2,4,5-trimethylbenzyl)malonate (II). Reduction of II with lithium aluminum hydride yielded 2-(3′-hydroxy-6′-methoxy-2′,4′-5′-trimethylbenzyl)propane-1,3-diol (III). (See Chart I.) Oxidative cleavage of the methoxy group in III with lead tetraacetate suspended in 50% aqueous tetrahydrofuran (THF) produces the desired monomer, 2-(duroquinonyl)propane-1,3-diol (V), as yellow crystalline material. If, however, III is oxidized with lead tetraacetate suspended in dry THF there is produced a white, crystalline material with a carbonyl band at 1683 cm^{-1}, and no hydroxyl band in the ir spectrum and λ_{max} at 244 mμ (ϵ 1.09 × 10^4) in the uv spectrum. The uv spectrum closely resembles that of 9-substituted α-tocopherol.[4] This new substance appeared to be 8a,3-epoxymethano-5,7,8-trimethyl-6H,8aH-dihydrochroman-6-one (IV). Then IV, shaken with cation exchange resin in the acid form in 50% aqueous THF, gives V in good yield. Reduction of IV in the presence of palladium charcoal yields 3-hydroxymethyl-5,7,8-trimethylchroman-6-ol (VII) quantitatively. Reoxidation of VII produces IV by using ceric ammonium nitrate or silver oxide in dry THF quantitatively. When yellow V is reduced in an attempt to obtain 2-(durohydroquinyl)propane-1,3-diol (VI), a white crystalline material could be isolated but in air it quickly oxidizes to red (quinhydrone!) then yellow quinone V. If the reduction is carried out in acid, there is obtained stable VII, presumably *via* VI. When the methoxy group of III is cleaved with HCl, there is formed VII, presumably *via* the VI pathway (Chart I). These behaviors bear strong analogy to those of the tocopherols. Structure VII differs from α-tocopherol only in the substituents on the oxygen ring. When the corresponding ring is opened there is

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[1] (a) H. G. Cassidy and K. A. Kun, "Oxidation–Reduction Polymers," Interscience Publishers, Inc., New York, N. Y., 1965; (b) G. Wegner, N. Nakabayashi, and H. G. Cassidy, *J. Org. Chem.*, **32**, 3155 (1967).

[2] Syntheses and properties of the polymers will be published elsewhere.

[3] W. John and F. H. Rathmann, *Ber.*, **74**, 890 (1941).

[4] W. H. Harrison, J. E. Gander, E. R. Blakley, and P. D. Boyer, *Biochim. Biophys. Acta*, **21**, 150 (1956).