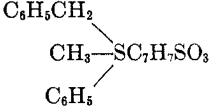
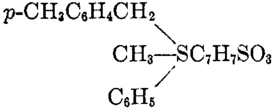
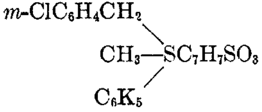
TABLE IV

PROPERTIES OF TRIMETHYLSULFONIUM SALTS AND BENZYLMETHYLPHENYLSULFONIUM TOSYLATES

Formula	Registry no.	Mp, °C (cor)	Calcd, % C	Calcd, % H	Calcd, % S	Found, % C	Found, % H	Found, % S
$(CH_3)_3SClO_4$		295 dec[a]						
$(CH_3)_3SC_6H_5SO_3$		166.5–168.5[b]						
$(CH_3)_3S$-*p*-$CH_3C_6H_4SO_3$	3084-73-9	173.5–175	48.55	6.49		48.53	6.37	
$(CH_3)_3S$-*p*-$BrC_6H_4SO_3$	16317-16-1	170–172	34.51	4.18		34.62	3.94	
$(CH_3)_3S$-*p*-$NO_2C_6H_4SO_3$	16317-12-7	195–196.5	38.70	4.69		38.33	4.55	
$(CH_3)_3SC_{10}H_7SO_3$	14343-63-6	187–188.5	54.90	5.67		55.22	5.81	
$(CH_3)_3SC_6H_2N_3O_7$		198–199[c]						
 $(C_6H_5CH_2)(CH_3)(C_6H_5)SC_7H_7SO_3$	16317-13-8	104.5–105.5	65.25	5.74	16.59	65.43	5.87	16.56
 $(p\text{-}CH_3C_6H_4CH_2)(CH_3)(C_6H_5)SC_7H_7SO_3$	16317-14-9	107–108	65.97	6.04	16.01	65.43	5.95	15.72
 $(m\text{-}ClC_6H_4CH_2)(CH_3)(C_6K_5)SC_7H_7SO_3$	16317-15-0	129–131	59.92	5.03	15.23	60.56	5.48	14.92

[a] K. Lohmann (Ph.D. Thesis, Massachusetts Institute of Technology, Cambridge, Mass., Jan 1959, p 67) reports mp 292°. [b] D. Vorlander [*Ber.*, **64B**, 1736 (1931)] reports mp 164–166°. [c] T. R. Lewis and S. Archer [*J. Amer. Chem. Soc.*, **73**, 2109 (1951)] report mp 164–166°.

Kinetics of Hydrolysis of Trimethylsulfonium Salts.—Solutions were prepared quantitatively under nitrogen atmosphere using carbonate-free water, and 7-ml samples were sealed in Pyrex ampoules. Measurements were begun after the ampoules had been in the constant temperature bath for about 30 min, and reactions were followed through two half-lives. Accurate 5-ml aliquots were titrated with 0.01 *M* sodium hydroxide to the bromthymol blue end point. Because the acid generated in the reaction was consumed by the Pyrex ampoules over long periods (up to 5% consumed after 8 days at 158°), "infinite time" points were calculated, not measured. Rate constants were evaluated by conventional first-order plots.

Kinetics of Trimethylsulfonium Hydroxide Decomposition.—Solutions containing added sodium perchlorate were prepared quantitatively under nitrogen from trimethylsulfonium perchlorate, sodium perchlorate, 0.1 *M* sodium hydroxide, and carbonate-free water. Solutions containing only sulfonium hydroxide were prepared by agitating a solution of trimethylsulfonium iodide and fresh silver oxide, filtered under nitrogen pressure, and diluted to volume. Measurements were begun after the ampoules had been in the bath for about 10 min, and the reactions were followed to 80% completion. Accurate 5-ml aliquots were treated with barium chloride and titrated with 0.01 *M* hydrochloric acid to the bromthymol blue end point. Rate constants were evaluated by conventional second-order plots.

Kinetics of Hydrolysis of Benzylmethylphenylsulfonium Tosylates.—Sufficient salt to prepare a 0.1 *M* solution (0.07 *M* in the case of the *m*-chloro derivative) was dissolved in carbonate-free water, and samples were sealed in Pyrex ampoules. Because of the limited solubility of the *p*-methyl and *m*-chloro derivatives it was necessary to maintain the solution at 60° while preparing samples. Ampoules were withdrawn periodically from the constant temperature bath, and accurate 3- or 4-ml aliquots were titrated with standard 0.1 *M* sodium hydroxide to the phenolphthalein or bromocresol green–methyl red end point. Reactions were followed through at least two half-lives. The first-order rate constants for these hydrolyses were evaluated by a computer program.[13]

Kinetics of Benzylmethylphenylsulfonium Hydroxide Decomposition.—Solutions 0.1 *M* in sulfonium salt and 0.2 *M* in sodium hydroxide in carbonate-free water were prepared under nitrogen, and samples were sealed in Pyrex ampoules. At intervals the tubes were removed from the constant temperature bath, and 3-ml aliquots were added to excess standard 0.1 *M* hydrochloric acid and back titrated with standard 0.1 *M* sodium hydroxide to the phenolphthalein end point. With the *p*-methyl and *m*-chloro derivatives the reaction was rapid enough that sealed ampoules were not used. Sufficient salt to prepare 50 ml of a solution 0.1 *M* in the methyl derivative or 0.07 *M* in the chloro derivative was dissolved in carbonate-free water at 60°. Enough aqueous sodium hydroxide to make the final solution 0.2 *M* in base was quickly added, and the entire flask was immersed in the constant temperature bath. At intervals 3-ml aliquots were withdrawn and treated as above.

All reactions were followed to at least 70% completion, and "infinite time" points were measured after at least ten half-lives. Rate constants were evaluated by means of a conventional second-order plot. Because hydrolysis of the *p*-methyl compound was a significant side reaction, a special graphic method was devised to calculate the second-order rate constant for that reaction.[2]

Products of Benzylmethylphenylsulfonium Hydroxide Decomposition.—Solutions prepared as above for the kinetic runs and allowed to stand ten half-lives at 60° were neutralized with hydrochloric acid and treated with a molarity of anisole equal to the calculated benzyl alcohol or thioanisole present. A solution for comparison, prepared by combining in aqueous sodium hydroxide the precise quantities of benzyl alcohol or *m*-chlorobenzyl alcohol and thioanisole predicted to be present in the reaction mixture, was treated in the same manner with hydrochloric acid and anisole. The dried, concentrated ether extracts of the mixtures were analyzed by glpc, using 12-ft columns of Carbowax on Chromosorb P for benzyl alcohol and silicone rubber on Chromosorb P for *m*-chlorobenzyl alcohol. The ratios of peak areas were identical with ±3% for both extracts and, after correction for relative peak sensitivity, the molar ratio of anisole/thioanisole/benzyl alcohol or *m*-chlorobenzyl alcohol was 1.0:1.0:1.0. No additional products were detected.

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[13] The program used was developed by K. G. Harbison from a general onlinear least squares curve fitting Fortran subroutine, ID code OR-NLLS, by Dr. P. D. Wood, Oak Ridge National Laboratory, Tenn. All computations were performed on an IBM 7090 electronic digital computer at the MIT Computation Center.

Reaction of Carbenes with Hexafluorobenzene

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Contribution No. 1399 from the Central Research Department, Experimetal Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898

Received November 6, 1967

The addition of carbenes to aromatics has been well documented.[1] However, it has been suggested that

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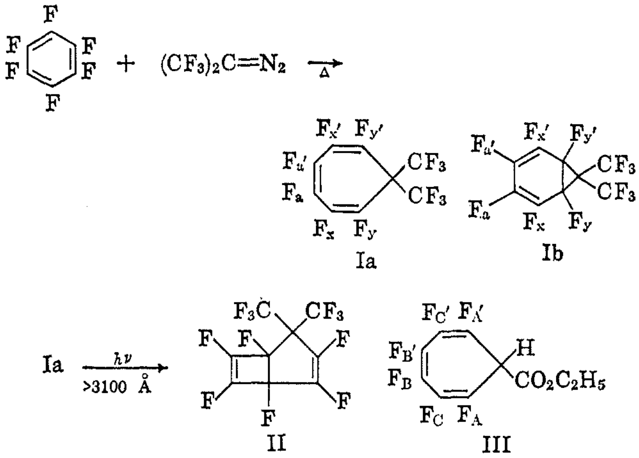
[1] See, *e.g.*, J. Hine, "Divalent Carbon," The Ronald Press Co., New York, N. Y., 1964.

hexafluorobenzene may serve as an inert solvent for the singlet–triplet interconversion of fluorenylidene.[2] We wish to report that certain carbenes generated from diazo compounds react with hexafluorobenzene; therefore, the latter should not generally be used as an inert solvent for carbene reactions.



Thermolysis of bis(trifluoromethyl) diazomethane[3] in excess hexafluorobenzene gave perfluoro-7,7 dimethyl-1,3,5-cycloheptatriene (Ia) in 20% yield. The tropylidene[4] constitution of the product was suggested by spectral data. The ultraviolet spectrum of Ia [$\lambda_{max}^{ethanol}$ 262 mμ (ε 6000) and 222 mμ (ε 7700)] excludes perfluoro-7,7-dimethylbicyclo[2.2.1]hepta-2,5-diene as a possible alternate structure, and is consistent with a cycloheptatriene chromophore. Another alternate structure, perfluoro-7,7-dimethylnorcaradiene (Ib), is more difficult to exclude. The tropylidene formulation is preferred, however, for the following reasons. (1) The trifluoromethyl groups are equivalent in the F^{19} nmr spectrum (triplet at +65.4 ppm from internal $FCCl_3$, $J = 17$ Hz; each line split further into triplets, $J \cong 1.5$ Hz; coupling constants assigned to CF_3–$F_{yy'}$ and CF_3–$F_{xx'}$, respectively) at room temperature to −99°.[5] (2) By analogy with 7,7-bis(trifluoromethyl)-1,3,5-cycloheptatriene for which the geminal trifluoromethyl groups show no tendency to force the ring into a norcaradiene form and, in fact, are believed to cause the triene ring to be more planar than usual.[3a] (3) Photoisomerization of Ia to bicyclic diene II in high yield parallels the behavior of 7,7-bis(trifluoromethyl)-1,3,5-cycloheptatriene[3a] and not that of 7,7-dicyanonorcaradiene.[6] (4) Fluorine atoms y and y' do not appear at high enough field to be on a cyclopropane ring.[7]

Cycloheptatriene III was prepared in fair yield by the photolytic decomposition of ethyl diazoacetate in excess hexafluorobenzene. The tropylidene formulation is preferred over that of the isomeric norcaradiene because (1) a close correlation of vinylfluorine chemical shifts (see Experimental Section) with those of Ia was observed, (2) only one isomer was found (there are two norcaradienes), (3) neither the 7-carbethoxy group[8] nor ring fluorine atoms (see above) are known to cause the norcaradiene form to be stabilized, and (4) the methyne proton (τ 5.7) seems at too low a field to be on a cyclopropane ring.[9]

Experimental Section

Perfluoro-7,7-dimethyl-1,3,5-cycloheptatriene (I).—A 7-g sample of bis(trifluoromethyl)diazomethane and 18 g of hexafluorobenzene (excess) were heated at 150° for 8 hr in an autoclave. Distillation (spinning band) afforded 3.9 g of product, bp 98–100° (not refluxing). Gas chromatographic analysis at 75° on a diglyceride column revealed at least 36 compounds in this fraction; a major product (68.8% of the area, 20% yield), however, was clearly present. The major "peak" was collected and shown to be perfluoro-7,7-dimethyl-1,3,5-cycloheptatriene on the basis of spectral data. Repetition of the experiment on a larger scale showed the product to have bp ~125°.

The F^{19} nmr spectrum (in CCl_4 with internal $CFCl_3$) showed a triplet (area 6) at +65.4 ppm ($J = 17$ Hz; split further into triplets of $J \cong 1.5$ Hz) assigned to the equivalent trifluoromethyl groups and a symmetrical "septet" (area 2) at +126 ppm ($J = 17$ Hz; split further) assigned to the yy' fluorine atoms. The remaining absorption (area 4) was a "weak–strong–strong–weak" pattern (with the weak and strong lines nearly equal in intensity, however) with "weak–strong" and "strong–weak" halves (considerable further splitting) centered at +143.5 and +149.5 ppm, assigned to the aa' and xx' fluorines, respectively, on the basis of complexity of the splitting and their chemical shift. The spectrum was essentially unchanged at −99° (in $CFCl_3$ solvent). The infrared spectrum showed >C=C< bands at 1700 and 1650 cm^{-1}. The mass spectrum[10] showed a parent ion at *m/e* 336, a base peak at *m/e* 267 (P − CF_3), and a large fragment at *m/e* 217 ($C_7F_7^+$).

Anal. Calcd for C_9F_{12}: C, 32.16; F, 67.84. Found: C, 32.50; F, 68.51.

Perfluoro-2,2-dimethylbicyclo[3.2.0]hepta-3,6-diene (II).—A 1.5-g sample of the perfluorocycloheptatriene Ia was sealed in a Pyrex tube and irradiated for 2 weeks with a G. E. H85A3 lamp. The reaction was followed by nmr and uv analysis; the conversion was about 99%. The nmr spectrum (neat) clearly showed the product to be diene II ($n^{25}{}_D$ 1.3332): $C(CF_3)_2$ as an A_3B_3 pattern split further, centered at +68.5; >CF− at +178 and +180; vinyl-F at +120 (a quartet, $J = 10$ Hz; split further), +126, +143, and +148 (chemical shifts given in parts per million from external $FCCl_3$). The ultraviolet spectrum showed end absorption. The infrared spectrum showed double bonds at 1776 and 1745 cm^{-1}. The mass spectrum[10] showed a parent ion at *m/e* 336, a base peak at *m/e* 267 (P − CF_3), and a large fragment at *m/e* 217 ($C_7F_7^+$).

Anal. Calcd for C_9F_{12}: C, 32.16; F, 67.84. Found: C, 32.48; F, 67.70.

Ethyl 2,3,4,5,6,7-Hexafluoro-2,4,6-cycloheptatrienecarboxylate (III).—A 2-g sample of ethyl diazoacetate (Aldrich Chem. Co.) dissolved in 200 g of hexafluorobenzene was irradiated for 96 hr with a sun lamp through Pyrex. Copper powder (0.5 g) was added and the suspension was stirred and refluxed for 6 hr. (In another experiment, the copper powder and refluxing were omitted and a comparable result was obtained.) The copper powder was filtered off, most of the hexafluorobenzene was removed at 40° (100 mm), and the remaining material was distilled through a spinning-band column. The product, bp 55° (2.5 mm), 0.5 g (16%), was shown to be fluorinated cycloheptatriene III. The mass spectrum showed the parent ion at *m/e* 272, peaks at *m/e* 244 (P − ethylene) and *m/e* 227 (P − OCH_2CH_3), and a

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

(3) (a) D. M. Gale, W. J. Middleton, and C. G. Krespan, *ibid.*, **88**, 3617 (1966). (b) We are indebted to Dr. M. L. Ernsberger for suggesting this investigation.

(4) For a review of the norcaradiene–tropylidene problem, see G. Maier, *Angew. Chem. Intern. Ed. Engl.*, **6**, 402 (1967).

(5) If the norcaradiene formulation (Ib) were correct, the CF_3 groups would be expected to have different chemical shifts because of their markedly different environments, and thereby lead to a more complicated spectrum. The possibility of a rapid equilibrium between Ia and Ib, causing the CF_3 groups to become equivalent to the nmr time scale, is not excluded. Attempts to "freeze out" Ib at low temperatures were unsuccessful.

(6) E. Ciganek, *J. Amer. Chem. Soc.*, **89**, 1458 (1967). A problem with this argument is that the multiplicity of the excited state for each reaction may not be the same.

(7) P. B. Sargent, to be submitted. This argument is weakened by a lack of closely analogous model compounds.

(8) E. Ciganek, *J. Amer. Chem. Soc.*, **87**, 1149 (1965).

(9) The reaction of a carbene with hexafluorobenzene was discovered independently by Professor M. Jones, Jr. We are indebted to Professor Jones for informing us of this work prior to publication.

(10) Partly fluorinated analogs show a similar cracking pattern: D. M. Gale, *Tetrahedron*, **24**, 1811 (1968).

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: $J_{HFAA'} = 22.5$ 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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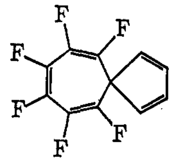
Received November 20, 1967

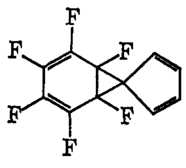
In the course of our investigations of reactions of carbenes in hexafluorobenzene we chanced to observe that, whereas fluorenylidene[3] does not react with hexafluorobenzene, the more reactive cyclopentadienylidene[4] does. The caveat of Gale[5] should therefore certainly be heeded: hexafluorobenzene 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

[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).