norbornane-1-carboxylic acid was found. It is not unreasonable that the initial monolithium derivative lost lithium chloride giving III, and that the latter with estimated strain of ~85 kcal/mole may have reacted with lithium to give the 1,4-dilithium compound. This possibility is under investigation.

Acknowledgment. We wish to thank Mr. James Minor, Jr., and the other members of the Thermochemistry Section of the National Bureau of Standards for their advice on the construction and standardization of our calorimeter. We also wish to thank Dr. Walter McMurry for the high-resolution mass spectra and the Du Pont Film Department for a generous gift of Mylar film.

(15) NASA Trainee, 1965–1968; Proctor and Gamble Fellow, 1968–1969.

(16) National Institutes of Health Predoctoral Fellow, 1968–1969.

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Valence Isomers of (CCF$_3$)$_6$

Sir:

The recent report of Haszeldine and his coworkers[1] on the photoisomerization of hexakis(trifluoromethyl)-benzene (in solution at >200 nm) prompts us to recount our related observations obtained under different conditions.[2]

In a typical experiment, several grams of the benzene[3] was introduced into a 2-l. Vycor flask connected to a cold trap; the system was then evacuated and closed. With the trap maintained at −78°, the flask was irradiated at 254 nm[4] until all of the solid had sublimed. Much unchanged hexakis (trifluoromethyl)benzene was recoverable from the cool region above the photolysis zone, but the remainder was accounted for by a colorless liquid in the cold trap. This mixture comprised three highly volatile components in the proportions 3:54:43 (in order of increasing glpc retention time on 20% dioctyl phthalate–HMDS-treated Chromosorb W). Irradiation in the 300-nm region[5] under the conditions described above yielded only the last two components, in the ratio 10:90.[6]

The most abundant photoproduct at 254 nm proved to be the Dewar benzene, hexakis(trifluoromethyl)-bicyclo[2.2.0]hexadiene (1). Although this mobile liquid had $\nu_{\max}^{\text{neat}}$ 1701 cm^{-1} (ν(C=C)), in reasonable agreement with the literature value, its ultraviolet spectrum differed significantly from that reported: $\lambda_{\max}^{\text{isooctane}}$ 203 nm (ϵ 1670), $\lambda_{\max}^{\text{vapor}}$ 202.5 nm (lit.[1] $\lambda_{\max}$ 210–211 nm (ϵ 620)). The ^{19}F nmr spectrum (Freon 113) comprised two broad signals at 12.29 and 12.82 ppm[7] (relative areas 1:2), corresponding to the bridgehead and vinyl CF$_3$ groups, respectively.

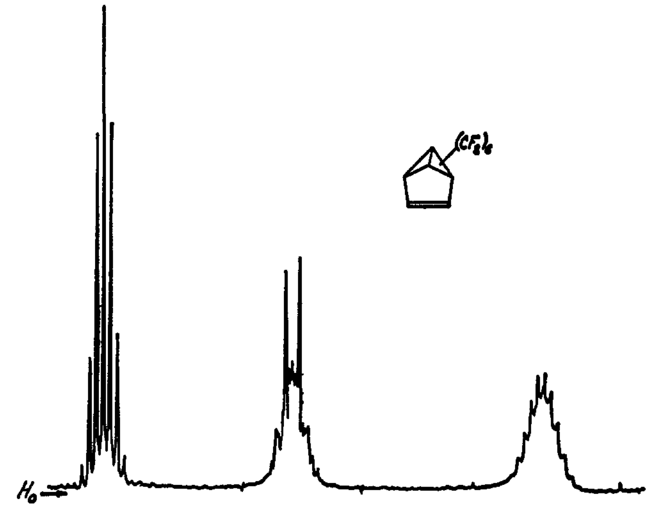
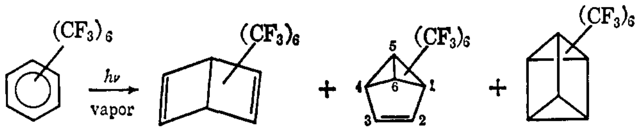


Figure 1. ^{19}F nmr spectrum of hexakis(trifluoromethyl)benzvalene (neat).



1 2 3

The product of longest glpc retention time was hexakis(trifluoromethyl)benzvalene (2), a liquid displaying $\nu_{\max}^{\text{neat}}$ 1655 cm^{-1} (ν(C=C)) and $\lambda_{\max}^{\text{isooctane}}$ 221 nm (ϵ 2260). Its ^{19}F nmr spectrum (neat, Figure 1) consists of three multiplets of equal intensity centered (in Freon 113) at 15.76, 19.70, and 22.55 ppm.[7] The septet at lowest field is assignable to the CF$_3$ groups at C5 and C6, the only magnetically equivalent pair, and the remaining multiplets arise from the vinyl and allylic CF$_3$'s, respectively.

First-eluted and least abundant of the photolysis products was hexakis(trifluoromethyl)prismane (3), a beautifully crystalline solid, mp 36.7–38.1°. Its infrared spectrum, simpler than those of its congeners, revealed prominent maxima at 1458, 1368, 1248, 1218, and 1115 cm^{-1} (vapor phase). The 18 fluorines of the prismane appeared in the ^{19}F nmr spectrum (Freon 113) as a single sharp signal at 15.02 ppm.[7]

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(1) M. G. Barlow, R. N. Haszeldine, and R. Hubbard, *Chem. Commun.*, 202 (1969).

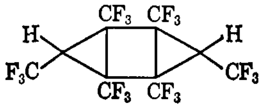
(2) Most of our work was reported at the First Northeast Regional Meeting of the American Chemical Society, Boston, Mass., Oct 13–15, 1968, Abstract 45.

(3) Prepared by a modification of the method of H. C. Brown, H. L. Gewanter, D. M. White, and W. G. Woods, *J. Org. Chem.*, 25, 634 (1960).

(4) Srinivasan-Griffin Rayonet photochemical reactor, Southern New England Ultraviolet Co., Middletown, Conn. 06457.

(5) The unfiltered emission from RPR 3000 Å lamps,[4] which contains a substantial component at 254 nm, was used in these experiments.

(6) Like the English group, we found that ultraviolet irradiation of the benzene in inert solvents led to the same three substances. Hydrogen abstraction occurred with ether as solvent, however, leading to a dihydro derivative, mp 45.0–45.5°. It is probably a stereoisomer of the tricyclohexane i, though a 1,4-dihydrobenzene structure is not rigorously excluded; ^{19}F nmr (ether): broad signals at 16.93 and 17.42 ppm,[7] relative areas 1:2; mol wt (mass spectroscopy) 488. The compound shows only very weak (if real) absorption in the 1700 cm^{-1} region and no ultraviolet maximum >190 nm.



i

(7) Nmr chemical shifts are presented in parts per million downfield from external trifluoroacetic acid.

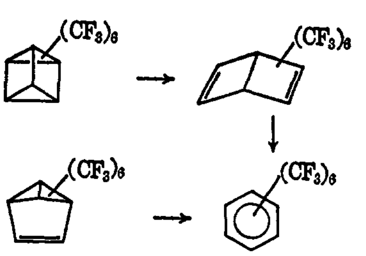


Figure 2. Thermal interconversions of the $(CCF_3)_6$ system.

Mass spectra (70 eV) of the four fluorocarbons are strikingly similar. In every case three peaks dominate the spectrum: m/e 467 (loss of F), 417 (loss of CF_3), and 69 (CF_3^+). Though the base peak varies, the other two are always >50% as intense. The parent peak increases in intensity from the prismane (4% of base) to the benzene (16% of base).

Highly strained fluorocarbons **1**–**3** appear to be the stablest (thermally) Dewar benzene,[8] benzvalene, and prismane[9] known at the present time. Steric effects are doubtless responsible in large measure for their impressive resistance to isomerization.[1] The Dewar benzene and benzvalene have half-lives at 234° of ~55 and ~9 min, respectively. It is interesting that their relative stability is opposite that found for the single other benzvalene–Dewar benzene pair which has been compared.[10] Haszeldine's group has reported that the prismane aromatizes at 170° at a rate intermediate between those of **1** and **2**, but in our hands the major product from **3** was the Dewar isomer **1** ($t_{1/2}$ ~ 7 min at 234°).[11] All, or nearly all, of the benzene found could be accounted for by decomposition of **1** under the reaction conditions (see Figure 2).

Hexakis(trifluoromethyl)benzene is the first aromatic whose Dewar, benzvalene, and prismane isomers have all been obtained in pure form.[14] Thus these compounds provide a unique opportunity for studying the interrelationships of valence isomers of benzenes.

Acknowledgments. We wish to express our gratitude to Professor P. R. Shafer for valuable advice and for assistance with the ¹⁹F nmr work. Mr. David Cane of Harvard University kindly determined our mass spectra, and the National Science Foundation, the Petroleum Research Fund of the American Chemical Society, and the U. S. Army Research Office (Durham) provided generous financial support.

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(8) The locked "Dewar" anthracene prepared by D. E. Applequist and R. Searle is excluded from consideration since its geometry prevents aromatization (*J. Amer. Chem. Soc.*, **86**, 1389 (1964)).

(9) Hexakis(pentafluoroethyl)prismane, comparable in stability to **3**, is a possible exception.[1]

(10) H. G. Viehe, *Angew. Chem. Intern. Ed. Engl.*, **4**, 746 (1965).

(11) The other three prismanes whose thermal decomposition products have been reported give Dewar isomers,[12] exclusively in one case.[13]

(12) (a) K. E. Wilzbach and L. Kaplan, *J. Amer. Chem. Soc.*, **87**, 4004 (1965); D. M. Lemal and J. P. Lokensgard, *ibid.*, **88**, 5934 (1966); (b) W. Schäfer, R. Criegee, R. Askani, and H. Grüner, *Angew. Chem. Intern. Ed. Engl.*, **6**, 78 (1967).

(13) R. Criegee and R. Askani, *ibid.*, **5**, 519 (1966).

(14) In the tri-*t*-butyl and hexamethyl series all three ring systems have been found, but the prismane has not been obtained pure in the former nor the benzvalene in the latter series.[12a]

(15) Alfred P. Sloan Foundation Research Fellow, 1968–1970.

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The Absolute Configuration of the (−)-*cis*-Dichlorobis(ethylenediamine)ruthenium(III) Cation

Sir:

No ruthenium(III) complex has yet been assigned an absolute configuration. As a consequence of the resolutions[1] of both *cis*-$RuCl_2(en)_2^+$ and *cis*-$CoCl_2(en)_2^+$ with $Co(C_2O_4)_2en^-$ we now show that the diastereoisomers (−)-$RuCl_2(en)_2$-(−)-$Co(C_2O_4)_2en \cdot H_2O$ and (+) $CoCl_2(en)_2$-(−)-$Co(C_2O_4)_2en \cdot H_2O$ are isomorphous. (The signs refer to rotations in the sodium D line.) Making use of Jaeger's rule[2] relating configurations, as recently modified by Garbutt and Gillard,[3] the same absolute configuration can be assigned to both (−)-$RuCl_2(en)_2^+$ and (+)-$CoCl_2(en)_2^+$. The configuration[4] of (+)-$CoCl_2(en)_2^+$ has been related to the absolute D* configuration of (+)$Co(en)_3^{3+}$ so that (−)-*cis*-$RuCl_2(en)_2^+$ is here given an absolute D* configuration.

The diastereoisomer (−)-$RuCl_2(en)_2$-(−)-$Co(C_2O_4)_2en \cdot H_2O$ has already been described, but the mono- rather than the hemihydrate found previously was obtained.[1] The procedure for the Co(III) analog was as follows. Racemic $Na[Co(C_2O_4)_2en]$ was prepared and resolved by known methods.[5] (−)-$Na[Co(C_2O_4)_2en] \cdot H_2O$ (0.21 g) in water (2 ml) was added to 0.37 g of (±)-*cis*-$[CoCl_2(en)_2]Cl$ in water (8 ml) to give the purple diastereoisomer which was collected and washed with 50% ethanol. *Anal.* Calcd for $C_{10}H_{26}Cl_2N_6O_9Co_2$: C, 21.3; H, 4.6; N, 14.9. Found: C, 21.2; H, 4.5; N, 14.6. This diastereoisomer could be converted to (+)-$[CoCl_2(en)_2]I$ which had a molecular rotation of +2320 in the D line in good agreement with published values.[6] X-Ray data were obtained with Ni-filtered Cu Kα radiation. Bragg angles (θ) are given in Table I and confirm that the diastereoisomers are isomorphous.

Table I. Bragg angle Values for Ru(III) and Co(III) Diastereoisomers[a]

(+)-$CoCl_2(en)_2$-(−)-$Co(C_2O_4)_2en \cdot H_2O$		(−)-$RuCl_2(en)_2$-(−)-$Co(C_2O_4)_2en \cdot H_2O$	
6.80 s	11.53 m	6.80 m	11.45 m
7.20 w	12.39 w	7.18 m	12.35 m
7.70 vs	13.00 w	7.68 vs	12.90 w
8.30 m	13.90 s	8.28 m	13.80 m
8.84 m	14.60 w	8.90 m	14.60 m
9.15 m	18.00 w	9.10 w	17.92 w
9.60 m	18.60 w	9.64 m	18.50 w
10.60 s		10.60 s	

[a] s = strong, m = medium, w = weak.

Acknowledgment. A C.S.I.R.O. studentship to L. K. M. is gratefully acknowledged.

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(1) J. A. Broomhead and L. A. P. Kane-Maguire, *J. Chem. Soc., A*, 546 (1967).

(2) F. M. Jaeger, *Bull. Soc. Chim. France*, 4, 1201 (1937).

(3) K. Garbutt and R. Gillard, *J. Chem. Soc., A*, 802 (1966).

(4) R. D. Gillard and G. Wilkinson, *ibid.*, 1368 (1964).

(5) F. P. Dwyer, F. L. Garvan, and A. Shulman, *J. Amer. Chem. Soc.*, **81**, 290 (1959).

(6) J. P. Mathieu, *Compt. Rend.*, **199**, 278 (1934); **201**, 1183 (1935).

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