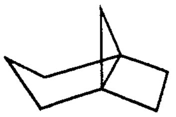
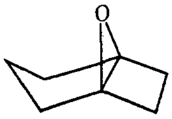
Communications to the Editor

Tricyclo[3.2.1.0^{1,5}]octane and 8-Oxatricyclo[3.2.1.0^{1,5}]octane. Heat of Formation, Strain Energy, and Reactivity[1]

Sir:

We have recently reported the syntheses of tricyclo[3.2.1.0^{1,5}]octane (I)[2] and 8-oxatricyclo[3.2.1.0^{1,5}]octane (II).[3] With these compounds, a quantity of particular interest is the strain energy. The heat of combustion of I could not easily be obtained because of its reactivity toward oxygen (see below). Thus, we have studied II and obtained ΔH_c (25°, l) = -997.67 ± 0.23 kcal/mole or ΔH_f (25°, l) -2.28 kcal/mole.[4] ΔH_v (=8.7 kcal/mole) may be estimated using the method of Miles,[5] giving ΔH_f (25°, g) = $+6.4$ kcal/mole. The heat of formation of an unstrained model was estimated using Franklin's group equivalents[6] and a group equivalent for –O– derived from di-*n*-propyl and di-*n*-butyl ethers[7] giving ΔH_f (calcd, g) = -53.2 kcal/mole. The difference between observed and calculated values gives a strain energy of 60 kcal/mole. The strain energy is a minimum value since alkyl substitution α to an ether oxygen appears to provide more stabilization for the ether than similar substitution stabilizes the corresponding hydrocarbon.[8] Since II has completely substituted α positions, the calculated heat of formation from group equivalents is perhaps as much as 4 kcal/mole too high.

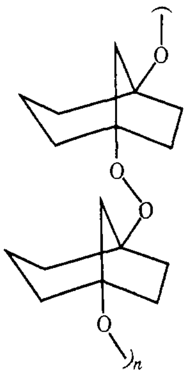

I


II

Since the strain energies of cyclopropane and ethylene oxide are essentially the same,[9] it is clear that I has a minimum strain energy of 60 kcal/mole. The most strained structural component of I, bicyclo[2.1.0]pentane, has a strain energy of 53 kcal/mole.[10] The addition of the cyclopentane ring should increase the strain by 3 kcal/mole[11] plus the strain associated with the distortion of the bridgehead positions of bicyclopentane. Thus, the distortion is responsible for an increase in strain of at least 4 kcal/mole and possibly as high as 10 kcal/mole.[12]

The bridgehead carbons and the three atoms attached to them (other than the other bridgehead atom) should lie approximately in a plane. An ideal hybridization would be sp^2, leaving a p orbital to form the central bond. The resulting bond should be relatively weak. This is not reflected in a large increase in strain energy, but is seen in the reactivity of I. The hydrocarbon reacts with oxygen rapidly and spontaneously at room temperature to give a polymer (mol wt (average) 1700). The polymer has a ratio of O_2:I of 0.9:1, has no olefinic protons (nmr), and has an nmr spectrum similar to that of I except for the loss of the cyclopropyl hydrogens.

The high-resolution mass spectrum of the polymer was not reproducible, being dependent on the probe temperature. The highest peaks in the spectrum were at *m/e* 281.17412, corresponding to two molecules of I, four oxygen atoms, and a hydrogen, and *m/e* 280.16547, derived from the other by the loss of a hydrogen. These data strongly suggest structure A


A

Similarly, I reacts with acetylenedicarboxylate at room temperature, whereas bicyclo[2.1.0]pentane reacts only at 100° in 5 days.[13] The reactivity toward acetic acid has already been described.[2]

These reactions stand in marked contrast to the thermal stability of I ($t_{1/2}$ ~20 hr at 190°).[2] As indicated previously, this probably arises from the lack of a good reaction path.[2] The thermal stability of I suggests that tricyclo[2.2.1.0^{1,4}]heptane (III) may be isolable. Indeed, III may have been formed as an intermediate in the reaction of 1,4-dichloronorbornane with lithium–sodium alloy, for Wilcox and Leung[14] found that carbonation of the reaction product gave 1,4-norbornanedicarboxylic acid, but no 4-chloro-

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(1) This investigation was supported by the U. S. Army Research Office.

(2) K. B. Wiberg and G. J. Burgmaier, *Tetrahedron Letters*, 317 (1969).

(3) K. B. Wiberg, J. E. Hiatt, and G. J. Burgmaier, *ibid.*, 5855 (1968).

(4) (a) The heat of combustion was determined using a Parr double valve bomb, and the values are based on carbon dioxide formed. Liquid samples were contained in Mylar bags. Benzoic acid was used as the primary standard and succinic acid (ΔH_c (25°, s) = -356.45 ± 0.08 kcal/mole (obsd); -356.38 kcal/mole corrected for the newer value of the joule)[4b] and *n*-nonane (ΔH_c (25°, l) = -1464.47 ± 0.23 kcal/mole (obsd); -1463.80 kcal/mole[4c]) were used as secondary standards. The error limits are twice the standard deviations. (b) H. M. Huffman, *J. Am. Chem. Soc.*, 60, 1171 (1938). (c) "Selective Values of Properties of Hydrocarbons," American Petroleum Institute Project 44, Carnegie Press, Pittsburgh, Pa., 1965.

(5) F. T. Miles, *Ind. Eng. Chem.*, 35, 1052 (1943).

(6) J. L. Franklin, *ibid.*, 41, 1070 (1949).

(7) G. Pilcher, H. A. Skinner, A. S. Pell, and A. E. Pope. *Trans. Faraday Soc.*, 59, 316 (1963); G. Pilcher, A. S. Pell, and D. J. Coleman, *ibid.*, 60, 499 (1964), and references therein.

(8) Reference 7 and data from ref 4d.

(9) G. Pilcher and A. S. Pell, *Trans. Faraday Soc.*, **60**, 73 (1964).

(10) R. B. Turner, P. Goebel, B. J. Mallon, W. von E. Doering, J. F. Coburn, Jr., and M. Pomerantz, *J. Am. Chem. Soc.*, **90**, 4315 (1969).

(11) The strain energy of cyclopentane is 6 kcal/mole, but the principal torsional interaction in cyclopentane is already present in the ring to which it is being added. Thus, the additional strain should be 6 kcal/mole less one torsional interaction (~3 kcal/mole).

(12) Correcting for the effects of alkyl substitution α to an ether oxygen and for the stabilization of cyclopropane by alkyl substitution (unpublished results, K. B. Wiberg and E. C. Lupton Jr.) could raise the value to 10 kcal/mole.

(13) P. G. Gassman and K. Mansfield, *Chem. Commun.*, 16, 391 (1965).

(14) C. F. Wilcox, Jr., and C. Leung, *J. Org. Chem.*, 33, 877 (1968).

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.

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(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.

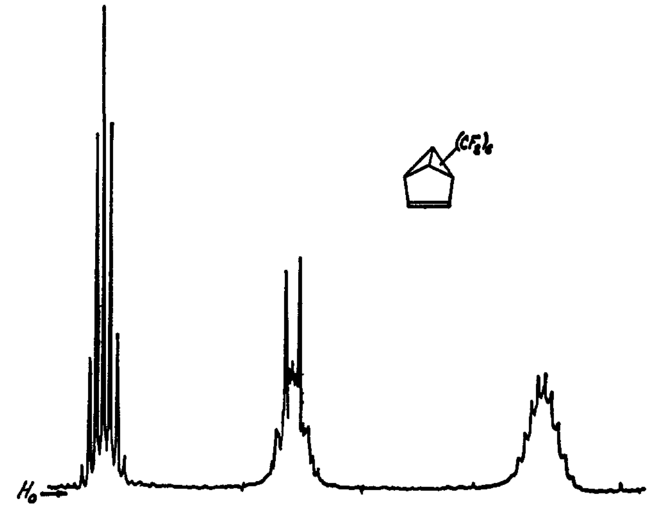
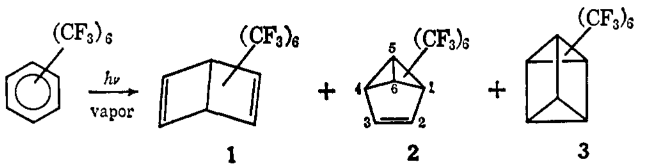


Figure 1. ^{19}F nmr spectrum of hexakis(trifluoromethyl)benzvalene (neat).



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).

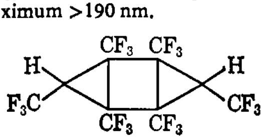
[2] Most of our work was reported at the First Northeast Regional Meeting of the American Chemical Society, Boston, Mass., Oct 13–15, 1968, Abstract 45.

[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.