To conclude, it is worth noting that although the results presented here are mainly qualitative, the technique employed allows (1) the detection of the presence of different conformers of a molecule in the gas phase and the estimation of their energy differences and (2) the detection of molecular complexes and the study of their polarity, which gives insight into their structure and symmetry.

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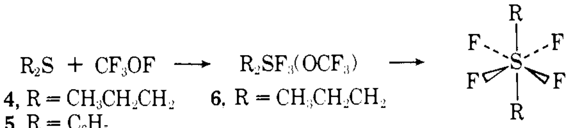
## Dialkyl- and Diaryltetrafluoropersulfuranes[1]

*Sir:*

Recently it was reported that dialkyl and diaryl sulfides react with trifluoromethyl hypofluorite (**1**) to yield dialkyl- and diaryldifluorosulfuranes (**2**).[2] At

$$\underset{\mathbf{1}}{CF_3OF} + R_2S \longrightarrow \underset{\mathbf{2}}{R_2SF_2} \xrightarrow{CF_3OF} \underset{\mathbf{3}}{R_2SF_4}$$

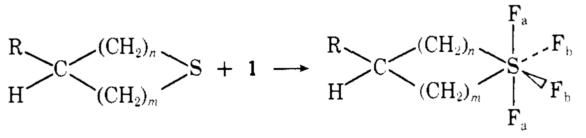
that time it was noted that di-*n*-propyl sulfide appeared to react further with **1** to give di-*n*-propyltetrafluoropersulfurane. This observation prompted an investigation of the reactions of compounds **2** with excess **1**. Treatment of di-*n*-propyl sulfide (**4**) with excess **1** at −80° gave a solution whose $^{19}F$ nmr spectrum showed three absorptions at δ −47.1, −40.9, and +50.3 in the ratio 1:1:3. These are assigned to the compound **6**.[3] On warming gas was evolved and the $^{19}F$ nmr spectrum changed to a quintet at δ −60.6, $J_{FSCH}$ = 8.4 Hz. The $^1H$ nmr spectrum at −70° showed a triplet at δ 0.88, $J_{HCCH}$ = 7.5 Hz, which is assigned to the absorption of the hydrogens of the methyl group. There was a multiplet at δ 1.67–2.15 and an apparent quintet of triplets at δ 3.69. The latter absorption is assigned to the hydrogens of the methylene group which is bonded to sulfur. A solution prepared as outlined above was treated with aqueous sodium bicarbonate at −78°. The mixture was allowed to warm to room temperature, and di-*n*-propyl sulfone was found, 61%, by infrared, nmr, and glpc. The above data strongly support the contention that **7** has been formed and that it has the structure shown with the propyl groups trans to each other.



**4**, $R = CH_3CH_2CH_2$
**5**, $R = C_6H_5$
**6**, $R = CH_3CH_2CH_2$
**7**, $R = CH_3CH_2CH_2$
**8**, $R = C_6H_5$

Treatment of diphenyl sulfide with **1** at −78° gave a material whose $^{19}F$ nmr spectrum had a single absorption at δ −64.5. It is believed that this is due to the presence of **8**. It was noted that conversion of the difluorodiphenylsulfurane was quite slow and a large excess of **1** was required.

The cyclic sulfides, **9–12**, have been allowed to react with excess **1** at −78° and in all cases persulfuranes, **13–16**, were formed. The persulfurane from **9** showed two kinds of fluorines in the $^{19}F$ nmr spectrum. There was a well-defined triplet at δ −84, $J_{F_aSF_b}$ = 96.5 Hz, and a less well-defined triplet with considerable fine structure at δ −63, $J_{F_aSF_b}$ = 97 Hz. The $^1H$ nmr spectrum showed two groups of multiplets at δ 2.0–2.35 and 4.4–5.0 in the ratio 2:3.9. Clearly two different fluorine environments are present in **13**, and thus the spectral data are in accord with the assigned structure.



**9, 13**, $n = m = 1$; $R = H$
**10, 14**, $n = m = 1$; $R = CH_3$
**11, 15**, $n = 1$; $m = 2$; $R = H$
**12, 16**, $n = 2$; $m = 2$; $R = H$

Preparation of **14** allows assignment of the $F_a$ and $F_b$ resonances of **13**. The $^{19}F$ nmr spectrum of **14** had a three-line pattern at δ −85, a triplet of broad peaks at δ −72.8, and another triplet of multiplets at δ −60.6. These absorptions were in the ratio 1.95:1.0:1.0. The absorption at −85 is due therefore to the $F_b$ fluorines, and, thus, in **13** the $F_b$ fluorines are found at δ −84 and the $F_a$ fluorines at δ −63. The $^1H$ nmr spectrum of **14** had a doublet at δ 1.3, $J_{HCCH}$ = 7.0 Hz, which is assigned to the absorptions of the hydrogens of the methyl group. Three other complex absorptions were found at δ 2.4–3.0, 3.9–4.5, and 4.5–4.9.

Preparation of **15** proceeded smoothly to give a material whose $^{19}F$ nmr spectrum showed a sharp triplet at δ −98.2, $J_{F_aSF_b}$ = 92.4 Hz, a triplet which was further split at δ −57.7, $J_{F_aSF_b}$ = 92.4 Hz. By analogy to **13** and **14** the $F_b$ fluorines can be tentatively assigned to those absorbing at δ −98.2. The $^1H$ nmr spectrum showed two complicated absorptions at δ 1.72–2.12 and 2.73–3.30. Similarly, **16** showed one sharp triplet at δ −118, $J_{F_aSF_b}$ = 101 Hz; another triplet with slightly broader peaks was found at δ −49.1, $J_{F_aSF_b}$ = 101 Hz. The $^1H$ nmr spectrum had three complex multiplets at δ 1.56–1.79, 2.03–2.23, and 3.50–3.69.

The above data all support the contention that **1** has reacted to give persulfuranes. In general warming solutions of these materials to room temperature leads to extensive decomposition to unidentified products. If trimethyl-*N*,*N*-diethylaminosilane[4] is added, decomposition is inhibited and solutions of the persulfuranes are stable for several weeks.

Previous preparations of persulfuranes have been limited to monoalkyl- and -arylpentafluoropersulfuranes and perfluorodialkylpersulfuranes,[5] and, thus, this report represents the first indication that the molecules of this report can be prepared and studied.

In most cases evidence was obtained for the formation of an intermediate, $R_2SF_3OCF_3$, which subse-

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[1] This research has been supported by the National Science Foundation and by Public Health Service Research Grant No. CA-10737 from the National Cancer Institute.

[2] D. B. Denney, D. Z. Denney, and Y. F. Hsu, *J. Amer. Chem. Soc.*, **95**, 4064 (1973).

[3] There are three structures which can be written for **6**; at the moment it is not possible to distinguish between them.

[4] D. G. Ibbott and A. F. Janzen, *Can. J. Chem.*, **50**, 2428 (1972).

[5] (a) R. D. Dresdner and T. R. Hooper, "Fluorine Chemistry Reviews," Vol. 4, P. Tarrant, Ed., Marcel Dekker, New York, N. Y., 1969; (b) H. L. Roberts, "Inorganic Sulphur Chemistry," G. Nickless, Ed., Elsevier, New York, N. Y., 1968, Chapter 12.

quently decomposed to the persulfurane. Such a finding is not completely unexpected; it has been noted that **1** and sulfur tetrafluoride react to give $CF_3OSF_5$.[6] Further work on these compounds and related materials is in progress and details will be reported in a subsequent publication.

(6) G. Pass and H. L. Roberts, *Inorg. Chem.*, **2**, 1016 (1962).

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## Why a Cyclopropyl Group Is Good at Stabilizing a Cation but Poor at Transmitting Substituent Effects

*Sir:*

The cyclopropane ring is the most effective unsubstituted hydrocarbon neighboring group for stabilizing a primary carbocationic center—a property which has labeled it the saturated analog of a carbon–carbon double bond. However, cyclopropyl is remarkably ineffective at transmitting resonance effects, in contrast to good $\pi$-stabilizing groups. These seemingly disparate conclusions have been drawn from both experiment[1,2] and theory.[3,4] This communication presents some new theoretical results pertaining directly to this problem and provides a simple interpretation that we hope will untangle these contradictory observations.

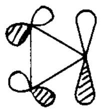
The first three columns of Table I present representative experimental data related to the relative stability of the parent cyclopropylcarbinyl cation along with our CNDO/2[5,6] results. The degree of agreement provides support for using simple quantum mechanical models to probe the question raised above.

**Table I.** Carbocation Stabilization by Some Hydrocarbon Groups

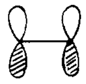
| R | Appearance potential of $RCH_2^+$, eV | Log $k_{rel}$ for solvolysis[a] | Methyl cation stabilization, energy, eV[b] | 2-Cyclopropylcarbinyl substituent effect, eV[c] |
|---|---|---|---|---|
| H | 14.4[d] | 0 | 0 | 0 |
| $CH_3$ | 12.9[d] | 4.7 | 3.061 | 0.283 |
| CH=CH | 12.1[e] | 6.7 | 3.499 | 0.280 |
| $C_6H_5$ | 12.0[d] | 8.4 | 4.253 | 0.431 |
| c-$C_3H_5$ | 11.85[f] | 9.5[g] | 4.340 | 0.461 |

[a] Solvolysis of tertiary derivatives; H. C. Brown and M. H. Rei, *J. Amer. Chem. Soc.*, **86**, 5008 (1964); A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill, New York, N. Y., 1963. [b] Calculated (CNDO/2) energy for the reaction: $RCH_2^+ + CH_4 \rightarrow RCH_3 + CH_3^+$. [c] Calculated (CNDO/2) energy for the reaction of 2-R-cyclopropylcarbinyl cation with cyclopropylmethane as in footnote *b*. [d] R. W. Taft, R. H. Martin, and F. W. Lampe, *J. Amer. Chem. Soc.*, **87**, 2491 (1965). [e] J. L. Franklin, *et al.*, *Nat. Stand. Ref. Data Ser., Nat. Bur. Stand.*, **No. 26**, 43 (1969). [f] R. H. Martin, Ph.D. Thesis, Pennsylvania State University, 1965; cited in ref 1a. [g] Extrapolated from the value of C. D. Poulter and S. Winstein, *J. Amer. Chem. Soc.*, **91**, 3650 (1965).

A qualitative answer to why the cyclopropyl group is a more effective stabilizer than $\pi$ substituents is easily obtained using the Walsh model for the bonding in cyclopropane[8] and simple perturbation theory considerations.[9,10] Despite the greater energy difference between the interacting levels in the cyclopropyl (ionization potential[10] = 10.9 eV) system the interaction is greater than the interaction of vinyl (ionization potential[10] = 10.5 eV) with an empty p orbital. This is because of the larger coefficient in the Walsh orbital, **1**, of



1



2

cyclopropyl carbon adjacent to the p orbital [$\sqrt{2/3}$] compared to the coefficient of the corresponding AO in the HOMO, **2**, of vinyl [$\sqrt{1/2}$]. In other words the increase in $H_{ij}$ overcomes the increase in $\Delta E$ in the perturbation expression[9]

$$E = E^\circ + (H_{ij}^2/\Delta E) \qquad (1)$$

A similar analysis is applicable to benzyl cation where the HOMO energy is relatively high (9.2 eV[11]), but the relevant coefficient is only $\sqrt{1/3}$.

Substituents in the 2 position of the ring in the cyclopropylcarbinyl system have provided puzzling results for over a decade.[2] Sneen[2a,12] showed that a *trans*-2-phenyl substituent provides an acceleration of only a factor of 2.2 over the unsubstituted (cyclopropylcarbinyl) $\beta$-naphthalene sulfonate in solvolysis. Recently Traylor[2e] has found evidence for a remarkably small effect of a 2-methoxy substituent during a study of

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(1) The unique stability of the cyclopropylcarbinyl cation has been amply and elegantly demonstrated by a generation of physical organic chemists. See: (a) N. C. Deno, *et al.*, *J. Amer. Chem. Soc.*, **87**, 4533 (1965), and references cited therein; (b) H. G. Richey in "Carbonium Ions," Vol. III, G. A. Olah and P. v. R. Schleyer, Ed., Wiley Interscience, New York, N. Y., 1972, p 1295; K. B. Wiberg and A. J. Ashe, *ibid.*, p 1201; (c) G. A. Olah and G. Liang, *J. Amer. Chem. Soc.*, **95**, 3792 (1973).

(2) The absence of good through conjugation by cyclopropane is exemplified by: (a) R. A. Sneen, *et al.*, *J. Amer. Chem. Soc.*, **83**, 4843 (1961); (b) P. v. R. Schleyer and G. W. Van Dine, *J. Amer. Chem. Soc.*, **88**, 2321 (1966); (c) R. Fuchs and J. J. Bloomfield, *J. Org. Chem.*, **28**, 910 (1963); (d) R. G. Pews and N. D. Ojha, *J. Amer. Chem. Soc.*, **91**, 5769 (1969), and references cited therein; (e) R. S. Brown and T. G. Traylor, manuscript submitted for publication (we thank Professor Traylor for communicating his results prior to publication); (f) C. F. Wilcox, Jr., and J. N. Hsu, *J. Amer. Chem. Soc.*, **94**, 8232 (1972) (the second author was given erroneously as H. D. Banks in the journal).

(3) The charge distribution, rotational barriers, and geometry of cyclopropylcarbinyl cation have been theoretically investigated by many workers. Among these are: (a) R. Hoffmann, *J. Chem. Phys.*, **40**, 2480 (1964); (b) R. Hoffmann, *Tetrahedron Lett.*, **43**, 3819 (1965); (c) K. B. Wiberg, *Tetrahedron*, **24**, 1083 (1968); (d) L. Radom, J. A. Pople, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **94**, 5935 (1972); (e) W. J. Hehre and P. C. Hiberty, *J. Amer. Chem. Soc.*, **94**, 5917 (1972); (f) R. Hoffmann, "Special Lectures at the XXIIIrd International Congress of Pure and Applied Chemistry," Vol. 2, Butterworths, London, 1971, p 233.

(4) L. D. Kispert, C. Engelman, C. Dyas, and C. U. Pittman, Jr. (*J. Amer. Chem. Soc.*, **93**, 6948 (1971)) found small changes in bond orders, charge distributions, and rotational barriers in vinylcyclopropanes substituted with groups of varying electron deficiencies.

(5) CNDO/2[6] calculations were performed using Wiberg's parameterization[7] with the following geometries: C—C single bonds, 1.51 Å; C=C bonds, 1.34 Å; C=C aromatic bonds, 1.40 Å; $C—C^+$ bonds, 1.45 Å; C—H bonds to tetragonal carbons, 1.09 Å; C—H bonds to trigonal carbons, 1.05 Å; conformations were chosen so as to maximize conjugative overlaps and minimize steric repulsions.

(6) J. A. Pople and D. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N. Y., 1970.

(7) K. B. Wiberg, *J. Amer. Chem. Soc.*, 90, 59 (1958).

(8) A. D. Walsh, *Trans. Faraday Soc.*, **45**, 179 (1949).

(9) (a) R. Hoffmann, *Accounts Chem. Res.*, **4**, 1 (1971); (b) M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y., 1969.

(10) P. Bischof, R. Gleiter, E. Heilbronner, V. Hornung, and G. Schröder, *Helv. Chim. Acta*, **53**, 1645 (1970).

(11) See footnote *e* in Table I.

(12) See also: T. Shono, I. Nishiguchi, and R. Oda, *J. Org. Chem.*, **35**, 42 (1970).