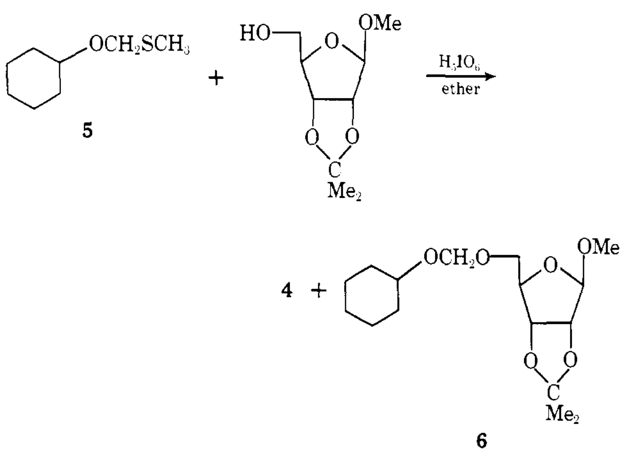
Scheme II



products in this experiment,[13] one can presume that in those cases where the sulfoxide **2** is one of the intermediates in the reaction of an alcohol with DMSO and NBS, it could also be the precursor of the acetal.[14] If the highly reactive oxonium compounds such as **3** are indeed formed during the acid-catalyzed decomposition of α-alkoxy sulfoxides, then a wide variety of synthetic transformations are possible with this little explored class of sulfoxides. Efforts in this direction are in progress in this laboratory.

Acknowledgment. The authors thank the National Research Council of Canada for financial support and Professor C. R. Johnson for helpful discussions.

[13] Based on the nature of the products, the formation of formaldehyde in significant amounts can be ruled out in these reactions.

[14] The formation of cyclic methylene acetals from *cis*-diols can also be explained by invoking α-alkoxy sulfoxide and oxonium intermediates. The situation is somewhat more complicated in the case of the trioxepan derivative arising from *trans*-cyclohexane-1,2-diol, and a definitive mechanism must await further studies.

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Protonated Cyclopropanes. VII. Evidence for Edge Protonation

Sir:

According to the steady-state treatment of Collins,[1] in reactions with 1-propyl-*1*-^{14}C systems, in which secondary isotope effects should be negligible, the 1-propyl product *can* show more isotopic scrambling to C-3 than C-2 if the mechanism were to involve equilibrating edge-protonated cyclopropane intermediates. On the other hand, processes involving corner-protonated species *can never* give more scrambling to C-3 than C-2. Most of our previous studies on such systems gave 1-propyl products showing about equal amounts of rearrangement of the ^{14}C label from C-1 to C-2 and to C-3.[2] In the treatment of 1-chloropropane-*1*-^{14}C with AlCl$_3$,[3] more scrambling to C-3 than C-2 was observed in the recovered 1-chloropropane, but in this case, reversible isomerization between 1- and 2-chloropropanes rendered these results inapplicable to the conclusions of Collins. We now report that the trifluoroacetolysis of 1-propyl-*1*-^{14}C-mercuric perchlorate (**1**-HgClO$_4$-*1*-^{14}C) indeed gave a 1-propyl product with more scrambling to C-3 than C-2.

A solution of **1**-HgClO$_4$-*1*-^{14}C[2c] (about 0.5 *M*) in F$_3$CCOOH was heated under reflux for 8 hr. The products, analyzed by vpc, consisted of 7 and 93%, respectively, of the 1- and 2-propyl trifluoroacetates (**1**-OAcF$_3$-^{14}C and **2**-OAcF$_3$-^{14}C) (total yield was 92–95% as measured by isotope dilution). Degradation[2c] of the vpc purified **1**-OH-^{14}C derived from the **1**-OAcF$_3$-^{14}C gave the results summarized in Table I.

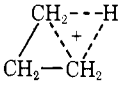
Table I. Isotopic Scrambling Data from Degradation of 1-Propanol-^{14}C Derived from 1-Propyl-^{14}C Trifluoroacetate

	Specific activity, cpm/mmol			^{14}C distribution, %		
Expt	CH$_3$CH$_2$-CH$_2$OH[a]	CH$_3$-COOH[b]	CH$_3$NH$_2$[c]	C-1	C-2	C-3
1	97,400	24,500	14,500	74.8	10.3	14.9
2	83,100	21,000	12,300	74.7	10.5	14.8
3	108,000	28,200	15,500	73.9	11.7	14.4
4	107,000	26,100	15,600	75.6	9.8	14.6

[a] Assayed as the α-naphthylurethane. [b] Assayed as the *p*-toluidide. [c] Assayed as the *p*-toluenesulfonamide.

The data in Table I were obtained from two sets of duplicate experiments carried out by different workers at different times. Hence the finding of more scrambling to C-3 than C-2 has in effect been independently verified. Under the conditions of the experiments, **2**-OAcF$_3$ did not give any **1**-OAcF$_3$ according to nmr analysis, thus also eliminating any complication from reversible 1,2-hydride shifts. These results, therefore, constitute evidence in support of equilibrating edge-protonated cyclopropane intermediates as the mechanism for the isotopic scrambling in the **1**-OAcF$_3$-^{14}C obtained from the trifluoracetolysis of **1**-HgClO$_4$-*1*-^{14}C.

Recently, however, Radom, *et al.*,[4] have carried out *ab initio* calculations with optimization of geometry on the C$_3$H$_7$$^+$ ions and have obtained results indicating that edge-protonated cyclopropane **3** is less stable than the corner-protonated species **4** by about 10 kcal/mol. It was also concluded that besides the 2-propyl cation, the only stable intermediate may be the methyl-eclipsed 1-propyl cation or distorted corner-protonated cyclopropane **5**, with **3** and **4** as transition states for the 1,3-hydride and 1,2-methyl shifts, respectively. These calculations predict that there should be more isotopic scrambling from C-1 to C-2 than to C-3 for reactions *via* protonated cyclopropanes from C-1 labeled 1-propyl substrates. It was suggested[4] that discrepancies between this prediction and data obtained from reactions in solution might be the result of a solvent assistance for the 1,3-hydride shift, or a specific hydrogen bonding of the edge proton in transition state **3** for the 1,3 shift.



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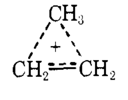

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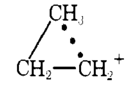

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[1] C. J. Collins, *Chem. Rev.*, **69**, 543 (1969).

[2] (a) C. C. Lee and K. M. Wan, *J. Amer. Chem. Soc.*, **91**, 6416 (1969); (b) C. C. Lee and W. K. Y. Chwang, *Can. J. Chem.*, **48**, 1025 (1970); (c) C. C. Lee and J. Law, *ibid.*, **49**, 2746 (1971).

[3] C. C. Lee and D. J. Woodcock, *J. Amer. Chem. Soc.*, **92**, 5992 (1970).

[4] L. Radom, J. A. Pople, V. Buss, and P. v. R. Schleyer, *ibid.*, **94**, 311 (1972).

Since F_3CCOOH is a solvent of extremely low nucleophilicity,[5,6] it is unlikely that F_3CCOOH would be capable of providing sufficient solvent assistance or specific H bonding to explain the scrambling data in Table I. Interestingly, still more recent calculations of Dewar, *et al.*,[7] using a modified version of the MINDO/2 method, have led to the entirely different finding that **3** is more stable than **4** or the 1-propyl cation, and that edge-protonated **3** is the only stable species besides the 2-propyl cation in the $C_3H_7^+$ potential surface. These conclusions are more in accord with our present results.

Professor P. v. R. Schleyer (private communications and as a referee) has pointed out to us that theoretical calculations are probably not yet capable of giving a definitive answer to the differentiation between edge- and corner-protonated cyclopropanes. Semiempirical calculations including the MINDO/2 type[7] tend to give too great a stability to structures containing small rings, while in *ab initio* calculations at the 4-31G level,[4] small rings tend to come out too unstable. It was indicated that very recent modifications by Pople to correct for the latter defect by the inclusion of polarization functions still led to the conclusion that corner-protonated cyclopropane is more stable than the edge-protonated species by about 5 kcal/mol, and that data to be published by M. Saunders on the scrambling of deuterium and ^{13}C labels in the 2-propyl cation in superacid also led to a similar conclusion. The apparent discrepancy in the conclusions arrived at from the present experimental results and from those of Saunders will require clarification. Schleyer suggests that in structures involving bridging protons, the possibility exists for the specific solvation of the small, highly charged bridging atom. Although trifluoroacetic acid is very low in nucleophilicity, when compared with superacid as a standard, perhaps even trifluoroacetic acid is sufficiently nucleophilic to exert the effects of specific solvation of the bridging proton.

Acknowledgment. We wish to extend our thanks to the National Research Council of Canada for financial support and to Professor P. v. R. Schleyer for valuable comments.

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(5) P. E. Peterson and F. J. Waller, *J. Amer. Chem. Soc.*, **94**, 991 (1972).

(6) T. W. Bentley, F. L. Schadt, and P. v. R. Schleyer, *ibid.*, **94**, 992 (1972).

(7) N. Bodor, M. J. S. Dewar, and D. H. Lo, *ibid.*, **94**, 5303 (1972).

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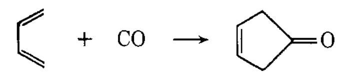
Reaction of 1,3-Dithienium Fluoroborate with 1,3-Dienes. A Synthesis of Δ^3-Cyclopentenones

Sir:

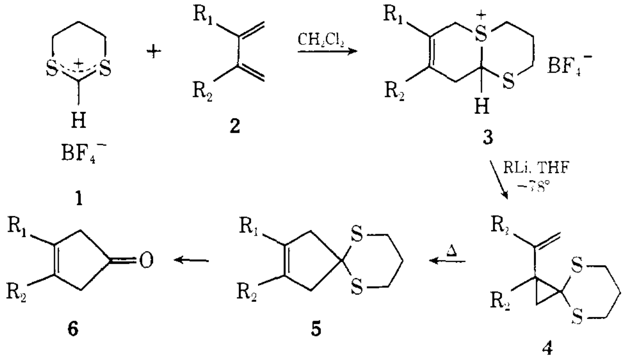
The object of the research which is outlined herein has been the development of a synthetic method for the conversion of 1,3-dienes to Δ^3-cyclopentenones, *i.e.*, to find a process which in a formal sense provides the equivalent of 1,4 addition of carbon monoxide to a diene.[1]



(1)

The new process which has resulted from our studies is outlined in Scheme I.

Scheme I



1,3-Dithienium fluoroborate (**1**), a yellow crystalline solid, mp 188–190° dec, is readily prepared from the reaction of 1,3-dithiane[2] with trityl fluoroborate[3] in dry methylene chloride as solvent (heating at reflux for 30 min, evaporation of solvent under reduced pressure, trituration with cold ether, and drying *in vacuo*, yield 92%).[4] The addition of the dithienium cation to 1,3-butadiene, isoprene, and 2,3-dimethyl-1,3-butadiene occurs smoothly in the Diels–Alder sense at 0–25° to afford adducts of type **3** in excellent yield. For example, addition of isoprene to a stirred suspension of dithienium salt **1** in dry methylene chloride (*ca.* 10 ml/g of **1**) at 0°, removal of the cooling bath, and stirring for an additional 35 min gave a solution of the adduct **3a** (R_1 = H; R_2 = CH_3), which could be obtained as colorless crystals (from acetone–ether), mp 131–132°, in 95% yield.[5] Similarly obtained were the adducts **3b** (R_1 = R_2 = CH_3),[5] mp 85–86°, from 2,3-dimethylbutadiene (96% yield), and **3c** (R_1 = R_2 = H),[5] mp 118–119° (85% yield), from butadiene.[6]

The reaction of dienes with the dithienium salt **1** can also be conducted under homogeneous conditions using a dry mixture of methylene chloride–nitromethane (2:1) as solvent[7] at +10°. This procedure has obvious

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[1] The direct addition of carbon monoxide to dienes according to eq 1 has not been clearly demonstrated as a feasible synthetic method, although mention of such a process has appeared in the patent literature; see M. S. Raasch and C. W. Theobald, British Patent 595,161 (1947) [*Chem. Abstr.*, **42**, 2988*a* (1948)]. Using standard thermochemical calculations and data [*e.g.*, see G. J. Janz, "Thermodynamic Properties of Organic Compounds," Academic Press, New York, N. Y., 1967], we calculate a favorable overall free-energy change for eq 1 [$\Delta G = 9 \pm 3$ kcal/mol]. In addition, the process should be allowed according to orbital symmetry considerations [*cf.* D. M. Lemal and S. D. McGregor, *J. Amer. Chem. Soc.*, **88**, 1335 (1966).

[2] E. J. Corey and D. Seebach, *Org. Syn.*, **50**, 72 (1970).

[3] H. J. Dauben, L. R. Honnen, and K. M. Harmon, *J. Org. Chem.*, **25**, 1442 (1960).

[4] The reagent **1** may be stored with exclusion of moisture in a freezer at −20° for several months without appreciable decomposition. The pmr spectrum (in CD_3NO_2) shows peaks at 11.10 (s), 3.6–3.8 (m), and 2.4–2.8 (m) ppm in a ratio of 1:4:2. This reagent was first prepared by S. W. W. at Pennsylvania State University in collaboration with Professor R. A. Olofson.

[5] Satisfactory (a) infrared and pmr spectra and (b) mass spectral data or elemental analysis have been obtained for a purified sample of this intermediate.

[6] In the case of butadiene the reaction was slower than that for the 2-methyl or 2,3-dimethyl derivatives and was conducted at *ca.* 0° for 15 hr.

[7] This solvent mixture may be dried very conveniently and rigorously by preliminary use of molecular sieve (Linde type 4A) and finally brief treatment (15 min) with a little phosphorus pentoxide at *ca.* 20°. The dried solvent is removed either by decantation or syringe.