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.

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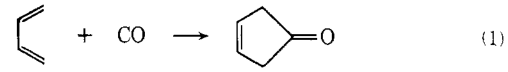
Reaction of 1,3-Dithienium Fluoroborate with 1,3-Dienes. A Synthesis of Δ^3-Cyclopentenones

Sir:

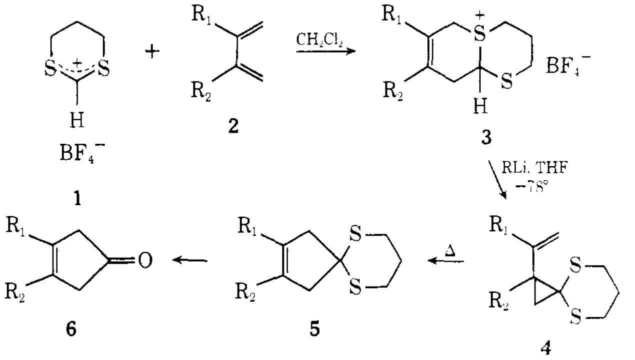
The object of the research which is outlined herein has been the development of a synthetic method for the conversion of 1,3-dienes to Δ^3-cyclopentenones, *i.e.*, to find a process which in a formal sense provides the equivalent of 1,4 addition of carbon monoxide to a diene.[1]



(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.

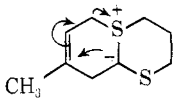
[5] Satisfactory (a) infrared and pmr spectra and (b) mass spectral data or elemental analysis have been obtained for a purified sample of this intermediate.

[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.

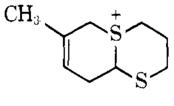
[7] This solvent mixture may be dried very conveniently and rigorously by preliminary use of molecular sieve (Linde type 4A) and finally brief treatment (15 min) with a little phosphorus pentoxide at *ca.* 20°. The dried solvent is removed either by decantation or syringe.

advantages for work on larger scale or for dienes which are not very soluble in methylene chloride.

Treatment of the isoprene adduct **3a** ($R_1 = H$; $R_2 = CH_3$) in stirred suspension in tetrahydrofuran under argon with 1 equiv of *n*-butyllithium in pentane at −78° for 20 min and at −78 to 25° over 25 min afforded after evaporative distillation at 80–82° (0.65 mm) the cyclopropyl derivative **4a** ($R_1 = H$; $R_2 = CH_3$)[5] as a colorless oil in 96% yield. The pmr spectrum of this product was especially important in structural assignment, since it clearly indicated the presence of methyl at quaternary carbon, cyclopropylmethylene, and C_3-$CCH{=}CH_2$ and trimethylene thioketal units. The conversion of **3a** ($R_1 = H$; $R_2 = CH_3$) to **4a** ($R_1 = H$; $R_2 = CH_3$) is readily understood in mechanistic terms as proceeding from the ylide **7**. The formation of the rearrangement product **4a** ($R_1 = H$; $R_2 = CH_3$) also argues emphatically against structure **8** for the isoprene adduct.[8] In a similar way the adducts **3** from 2,3-dimethylbutadiene and butadiene have been converted, respectively, to **4b** ($R_1 = R_2 = CH_3$),[5] colorless oil, distilled at 110–115° (bath (0.75 mm), 93% yield), and **4c** ($R_1 = R_2 = H$),[5] colorless oil, distilled at 72–74° (bath (0.65 mm), 87% yield). The rearrangement $3 \rightarrow 4$ thus represents a novel and highly effective way of using the Diels–Alder reaction for the synthesis of vinylcyclopropane derivatives.



7



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As expected, the vinylcyclopropane derivatives **4** upon heating to 200° undergo rearrangement to cyclopentenes of structure **5**.[9] The reaction proceeds very cleanly in benzene solution[10] (200°) to afford, starting with the corresponding cyclopropane **4**, the cyclopentenone thioketals (as colorless liquids) **5a** ($R_1 = H$; $R_2 = CH_3$)[5] (4 hr heating, 97% yield, bp 85–90° (0.5 mm)), **5b** ($R_1 = R_2 = CH_3$)[5] (5 hr heating, 95% yield, bp 125–130° (0.7 mm)), and **5c** ($R_1 = R_2 = H$)[5] (16 hr heating, 97% yield, bp 90–95° (0.6 mm)).

The 3-cyclopentenone thioketals **5** upon gentle hydrolysis could be smoothly converted to the corresponding ketones **6**. For example, treatment of the thioketal **5a** ($R_1 = H$; $R_2 = CH_3$), in acetone–water (*ca.* 8:1) with excess mercuric chloride–calcium carbonate for 16 hr at 25° with stirring, afforded 3-methyl-3-cyclopentenone (**6**) ($R_1 = CH_3$; $R_2 = H$), in 94% yield by vapor phase chromatographic (vpc) analysis which also revealed the absence of detectable amounts of the isomer 3-methyl-2-cyclopentenone. Filtration of solids, removal of acetone at reduced pressue, extraction with ether, and distillation yielded pure 3-methyl-3-cyclopentenone[5] (infrared max at 5.69 μ in CCl_4 due to carbonyl) uncontaminated by the conjugated isomer (vpc analysis).

The sequence 1,3-diene (**2**) to Δ^3-cyclopentenone (**6**) which is described above extends the Diels–Alder reaction to five-membered carbocycles in a way which is novel and potentially of considerable utility.[11] The process has also been applied successfully to the cyclic substrate 1,3-cyclohexadiene. We hope to report at a later time on the scope of this process and on other methods for the synthesis of Δ^3-cyclopentenones.[12] We are also studying the reactions of **1** with a variety of other substrates including monoolefins.

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[8] The rearrangement $3 \rightarrow 4$ by way of **7** is a bicyclic analog of the familiar allylsulfonium ylide rearrangement; see, for example, E. Hunt and B. Lythgoe, *J. Chem. Soc., Chem. Commun.*, 757 (1972). The formulation of the isoprene adduct as **8** would also violate expectations based on the Markovnikov mode of addition of electrophilic carbon of **1** to isoprene.

[9] See C. D. Gutsche and D. Redmore, "Carbocyclic Ring Expansion Reactions," Academic Press, New York, N. Y., 1968, Chapter IX.

[10] We have not investigated thermolysis in the gas phase, but we have no reason to believe that this would not be an equally smooth process.

[11] The synthesis of cyclopentanones from 1,3-dienes by cyclohydroboration [H. C. Brown and E. Negishi, *J. Amer. Chem. Soc.*, **94**, 3567 (1972)] followed by carbonylation [H. C. Brown, *Accounts Chem. Res.*, **2**, 65 (1969)] deserves mention in connection with the method described here.

[12] This investigation was assisted financially by the National Institutes of Health and the National Science Foundation.

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Pentafluorosulfur Hydroperoxide

Sir:

The fluorinated hydroperoxide, CF_3OOH, has been used in the synthesis of new fluorinated peroxides and is prepared by the hydrolysis of $F_3COOC(O)F$.[1–5] The appropriate equation is

$$CF_3OOC(O)F + H_2O \longrightarrow CF_3OOH + CO_2 + HF$$

This communication describes the preparation of F_5SOOH by an analogous reaction

$$F_5SOOC(O)F + H_2O \longrightarrow F_5SOOH + CO_2 + HF$$

and suggests the use of F_5SOOH as a convenient source of the F_5SOO group in synthesis.

The hydrolysis of $F_5SOOC(O)F$ with a stoichiometric amount of H_2O at 0° gives a nearly quantitative yield of F_5SOOH. An excess of water at 0° gives a hydrate of F_5SOOH which makes purification of the product very difficult. An excess of water at 22° leads to the formation of SO_2F_2, O_2, HF, and CO_2.

Pentafluorosulfur hydroperoxide is a stable colorless liquid up to 30° [bp 0° (150 mm)]; it freezes to a colorless solid at −55.6°. The vapor at less than 50 mm of pressure is monomeric (obsd mol wt, 160.1; calcd for monomer, 160.6). When the compound is heated to 85° in a Monel reactor, rapid decomposition as indicated by the following equation occurs

$$0.20F_5SOOH \longrightarrow 0.20OSF_4 + 0.10O_2 + 0.20HF^{6}$$

The decomposition is analogous to that of F_3COOH which forms COF_2, O_2, and HF on heating.

The infrared shows major absorptions (cm^{-1}) at 3560 (m, OH), 1385 (s, δ OOH), 920 and 880 (vs, SF_5O), 725

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[1] R. L. Talbott, *J. Org. Chem.*, **33**, 2095 (1967).

[2] Peter A. Bernstein, F. A. Hohorst, and D. D. DesMarteau, *J. Amer. Chem. Soc.*, **93**, 3882 (1971).

[3] D. D. DesMarteau, *Inorg. Chem.*, **11**, 193 (1972).

[4] P. A. Bernstein and D. D. DesMarteau, *J. Fluorine Chem.*, **2**, 315 (1972–1973).

[5] C. T. Ratcliffe, C. V. Hardin, L. R. Anerson, and W. B. Fox, *J. Amer. Chem. Soc.*, **93**, 3886 (1971).

[6] The experimental value of HF was 0.18. It was estimated by difference.