These conformational effects are by no means restricted to cyclohexyl derivatives. We have found that the relative orientation of hydroxyl groups in bicyclic systems is reflected by the chemical shift of the carbinol carbon. The results for borneol and isoborneol show that the carbon bearing an *endo*-OH (borneol) is shielded by *ca.* 4 ppm relative to that in the *exo* epimer and a similar difference is found for the *exo*- and *endo*-norborneols. Comparable differences can be expected in pyranose ring systems and an investigation of the ^{13}C shieldings of some monosaccharides is in hand to establish the utility of this technique for problems in carbohydrate chemistry. To overcome the limited precision inherent in the method[10] employed to obtain the results reported in this communication, it would be desirable to use the greater sensitivity and resolution of the absorption mode conditions as described by Paul and Grant[11] in future work with natural abundance materials. If ^{13}C-enriched material were used, normal high-resolution techniques could be employed to study concentration effects at very low dilutions.

At present, however, it is clear that ^{13}C spectroscopy constitutes an alternative approach to the study of molecular conformations and gains new strength as a tool for stereochemical elucidations. A wide variety of potential applications of this technique remains to be investigated.

Acknowledgments. We are grateful for the support of this research by the Ontario Research Foundation, the National Research Council of Canada, and the Petroleum Research Fund, administered by the American Chemical Society.

(10) The precision of these chemical shift measurements is estimated to be ±0.3 ppm.[8]

(11) E. G. Paul and D. M. Grant, *J. Am. Chem. Soc.*, **86**, 2977 (1964).

(12) Holder of an Ontario Graduate Fellowship, 1965–1966.

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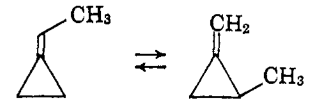
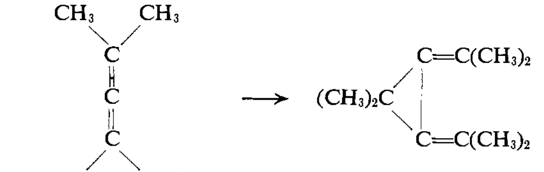
The Pyrolysis of Alkenylidenecyclopropanes. A Convenient Synthesis of Dimethylenecyclopropanes

Sir:

We wish to record a simple and efficient new synthetic method for the preparation of dimethylenecyclopropanes that makes this interesting class of highly unsaturated small-ring compounds readily available for the first time.[1,2] Consideration of the thermal rearrangements common to methylenecyclopropanes,[3] as illustrated below for a simple example (**1** ⇄ **2**), suggested that a similar rearrangement might obtain in the case of alkenylidenecyclopropanes. In that event, pyrolysis of the fully methylated derivative **3**[4] in a flow system at 360° and 0.25 mm resulted in an almost quantitative conversion to **4**. The structure of **4** is deduced from its spectroscopic properties which agree in every detail with those reported by Bleiholder and Shechter[1] for this same compound obtained in another manner. A similar efficient conversion of **5** is instructive in that the three isomeric dimethylenecyclopropanes **6**, **7**, and **8** are produced. The ratio of these products varies with temperature, being about 10:2:3 at 360° and 2:3:6 at 410°. Furthermore, pyrolysis of pure samples of either **6** or **7** at 380° yields a mixture of the three isomeric compounds whereas **8** is recovered essentially unchanged from this treatment. Raising the temperature to 460°, however, causes a transformation of **8** to **6** and **7**.[5] Gas chromatographic separation provided pure samples for spectroscopic examination. Compound **6** exhibits infrared absorption at 5.56 and 6.06 μ and ultraviolet absorption (hexane) at 245 mμ (ϵ 20,000) and 253 mμ (ϵ 17,500), and its nmr spectrum shows a six-proton singlet at τ 8.84, singlets at τ 8.19 and 8.09 overlapping a doublet in the same region (nine protons), and a one-proton quartet at τ 4.60 (J = 7 cps). Compound **7** has infrared absorption at 5.56 and 6.03 μ, ultraviolet maxima (hexane) at 244 mμ (ϵ 18,700) and 254 mμ (ϵ 15,700), and resonances at τ 8.78 (six-proton singlet), 8.2 (nine-proton multiplet), and 4.42 (a one-proton quartet, J = 7 cps). Compound **8** is uniquely defined by its absorption in the infrared at 5.53 and 6.05 μ, in the ultraviolet (hexane) at 251 mμ (ϵ 19,700) and 262 mμ (ϵ 18,560), and in the nmr at τ 8.89 (three-proton distorted doublet, J ~ 6 cps) and ~8.1 (a thirteen-proton grouping). A rigorous distinction between **6** and **7** is not easy to make but the assignments given are based on the expectation that the olefinic proton in **7** should absorb at lower fields than the corresponding proton in **6** due to its position in the deshielding zone of the other double bond.[6] Each of the compounds gives a strong molecular ion at m/e 136 in its mass spectrum,[7] and an accurate mass determination on **8** confirmed its molecular formula (calcd for $C_{10}H_{16}$, 136.125; found, 136.123).[8]



1 **2**



3 **4**

The mechanistic details of these thermal interconversions are very likely analogous to those of methylenecyclopropanes themselves. The rearrangements of the

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(1) R. F. Bleiholder and H. Shechter, *J. Am. Chem. Soc.*, **86**, 5032 (1964).

(2) Trimethylenecyclopropanes have also been reported recently. See E. A. Dorko, *ibid.*, **87**, 5518 (1965); P. A. Waitkus L. I. Peterson, and G. W. Griffin *ibid.*, **88**, 181 (1966); G. Kobrich and H. Heinemann, *Angew. Chem. Intern. Ed. Engl.*, **4**, 594 (1965).

(3) J. P. Chesick, *J. Am. Chem. Soc.*, **85**, 2720 (1963); E. F. Ullman, *ibid.*, **81**, 5386 (1959); **82**, 505 (1960); E. F. Ullman and W. S. Fanshaw, *ibid.*, **83**, 2379 (1961).

(4) H. D. Hartzler, *ibid.*, **83**, 4990 (1961).

(5) A small-scale pyrolysis of **8** showed major amounts of an additional product by gas chromatography. However, repeated attempts to duplicate this result on a preparative scale gave only minor amounts of a fourth component having the same retention time as **5**.

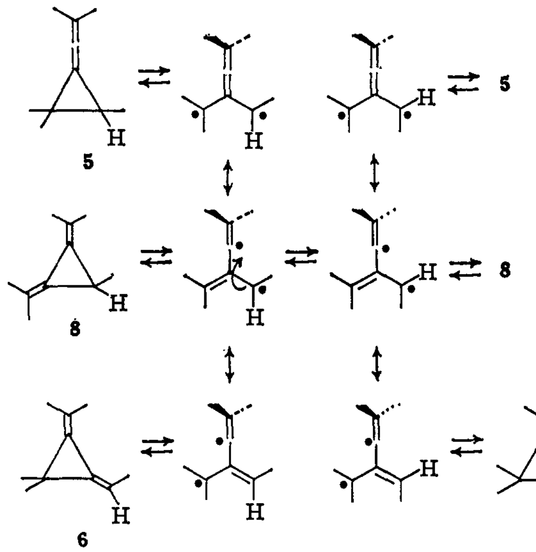
(6) N. S. Bhacca and D. H. Williams, "Applications of NMR Spectroscopy in Organic Chemistry," Holden-Day, Inc., San Francisco, Calif., 1964, pp 88–89.

(7) Mass spectra were obtained using an AEI MS-9 spectrometer.

(8) The carbon and hydrogen microanalytical values for **6**, **7**, and **8** consistently totaled less than 100% in a nonreproducible fashion, possibly due to reaction of these dienes with atmospheric oxygen. However, the carbon-to-hydrogen ratios were proper and there were no peaks other than isotopic ones at m/e greater than 136.

latter system are thought to proceed by way of planar, delocalized trimethylenemethane intermediates.[3] Very recently experimental evidence concerning the existence and nature of this interesting species has been presented.[9] A similar intermediate can be invoked to describe the rearrangements observed above. This differs from trimethylenemethane in that one of the peripheral carbons is sp hybridized. According to simple molecular orbital theory[10] the planar form of this intermediate should also enjoy substantial stabilization. Chart I depicts a rational scheme accounting for the data concerning the pyrolysis of **5** in terms of such an intermediate, denoted here in valence bond terminology. There are two isomeric, trimethylenemethane-type intermediates possible, and it is likely that interconversion by rotation about the designated radial carbon–carbon bond is relatively facile at pyrolysis temperatures. Each of the products can, in theory, be reconverted to the pair of trimethylenemethane intermediates by reversal of its formative process and thus be repartitioned among the three original products. Compounds **6** and **7** undergo this redistribution easily but more drastic conditions are required for **8**. This suggests that bond cleavage to a *nonplanar* diradical precedes formation of the delocalized species. Accordingly **8**, with a single stabilizing methyl on the incipient saturated radical center, requires a greater activation energy to generate the trimethylenemethane intermediates than **6** or **7**, which can form tertiary radicals at this site.

Chart I



The pyrolytic conversion of alkenylidenecyclopropanes appears to be a general synthetic method for preparing dimethylenecyclopropanes, subject only to stability limitations of the compounds involved. The adaptability of the simple reaction procedure to vacuum-line work should allow its use in preparing even thermally labile and oxygen-sensitive materials. We are currently engaged in exploring further aspects of these pyrolysis reactions and examining the chemistry of dimethylenecyclopropanes.

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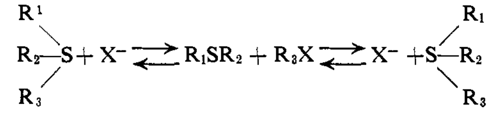
[9] P. Dowd, *J. Am. Chem. Soc.*, **88**, 2587 (1966); R. J. Crawford and D. M. Cameron, *ibid.*, **88**, 2589 (1966).

[10] A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, pp 43–44.

The Racemization of *t*-Butylethylmethylsulfonium Perchlorate[1]

Sir:

Optically active tertiary sulfonium salts have been known for many years.[2–4] The racemization of *l*-phenacylethylmethylsulfonium salts was studied by Balfe, *et al.*[4] They concluded that racemization involved a nucleophilic displacement on carbon by halide ion to produce inactive alkyl halide and sulfide followed by formation of the racemic sulfonium salt.



$$\overset{R^1}{\underset{R_3}{R_2{-}S}}{}^+ + X^- \rightleftarrows R_1SR_2 + R_3X \rightleftarrows X^- + {}^+\overset{R_1}{\underset{R_3}{S{-}R_2}}$$

We have studied the racemization of *t*-butylethylmethylsulfonium perchlorate[5] (I) and wish to present evidence that racemization of this system involves a different mechanism.

The optically active salt, I, mp 148.6° dec, $[\alpha]^{25}D - 34.6°$ (*c* 1.5, methanol), was obtained by resolution of the corresponding (−)-dibenzoylhydrogentartrate followed by replacement of the dibenzoylhydrogentartrate anion by perchlorate. Compound I racemizes faster than it solvolyzes in a variety of solvents. At 50° the racemization is *ca.* 15 times faster than solvolysis. Some typical rate constants are presented in Table I.

Table I. The Solvolysis of *t*-Butylethylmethylsulfonium Perchlorate in Various Solvents at 50.0°

Isomer	[I], *M*	Solvent	μ	$10^6k_{t'}$,[a] sec^{-1}	$10^6k_{\alpha'}$,[b] sec^{-1}
dl	0.01184	EtOH	0.015	44.9 ± 1.2	
(−)	0.01187	EtOH	0.015	45.1 ± 0.6	471 ± 15
dl	0.01462	HOAc	0.042[c]	36.2 ± 1.0	
(−)	0.01429	HOAc	0.042[c]		413 ± 17
dl	0.02990	H_2O	0.030	16.6	
(−)	0.02999	H_2O	0.030		283 ± 18
dl	0.02370	$(CH_3)_2CO$	0.030[d]	55.9 ± 1.1	
(−)	0.02373	$(CH_3)_2CO$	0.030[d]		460 ± 13

[a] Titrimetric rate constant. [b] Polarimetric rate constant. [c] NaOAc (0.0293 *M*) added. [d] 2,6-Lutidine (0.0510 *M*) added.

The racemization of I cannot involve a reversible nucleophilic displacement on carbon since the only anion present in the solutions is the nonnucleophilic perchlorate ion. Nucleophilic displacement by the solvent or its lyate ion would not be reversible.

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[1] Presented in part before the Division of Organic Chemistry at the 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966.

[2] W. J. Pope and S. J. Peachey, *J. Chem. Soc.*, 77, 1072 (1900).

[3] S. Smiles, *ibid.*, 77, 1074 (1900).

[4] M. P. Balfe, J. Kenyon, and H. Phillips, *ibid.*, 2554 (1930).

[5] All new compounds gave satisfactory analyses.