Table I. g Values and Line Widths for the TMB Cation Radical

Oxidation system[a]	g value[b,c]	g shift × 10^5 [d]	Line width, G
Br_2–CH_3NO_2	2.00401	5	0.07
Br_2–CH_3CN	2.00399	3	0.09
Br_2–CH_2Cl_2	2.00440	44	0.27
Br_2–$CHCl_3$	2.00472	76	0.34
$AlCl_3$–CH_3NO_2	2.00396	0	0.04
$AlCl_3$–CH_2Cl_2	2.00406	10	0.06
$AlCl_3$–$CHCl_3$	2.00403	7	0.08

[a] All measurements are for a temperature of −20°. [b] g values were measured in dual sample cavity relative to the perylene radical anion whose g value is taken to be 2.00267. [c] All measured values are ±0.00001. [d] g shift relative to the g value of the $AlCl_3$–CH_3NO_2 system.

counteranions are not observed.[6] This is most easily rationalized in terms of the mechanisms leading to the hyperfine splitting, for halide anions electron transfer would place unpaired spin density in the p orbital which must in turn spin polarize the s electrons before hyperfine splitting is observed. For alkali metal cations direct electron transfer into the s orbital is, however, possible. One might expect that hyperfine splittings are much more likely for alkali metal cations than for halide anions.

The sign and magnitude of the observed g shifts can be compared with shifts observed for the alkali metal naphthalenide systems.[7] The largest g shift observed is for cesium–naphthalene which has a shift of -17×10^{-5}. Simple considerations of g tensors allow us to explain the positive g shift of halide ion pairs as opposed to the negative g shift of alkali metal ion pairs.[8] The much larger magnitude of the g shift of $Br^-TMB\cdot^+$ is undoubtedly due to the larger spin–orbit coupling constant of bromine as compared to cesium (*i.e.*, 2400 and 369 cm^{-1}, respectively).

Additional experiments have indicated that the observed g shifts are temperature dependent. For $TMB\cdot^+$ in Br_2–$CHCl_3$ the g shift changes from 80×10^{-5} at +20° to 73×10^{-5} at −60°. This is probably due to an increase in solvation as the temperature is decreased.

Another compound which is readily oxidized by bromine is 1,4-diethoxy-2,5-diethylthiobenzene. This compound is found to give g shifts similar to TMB. For example, in Br_2–CH_3NO_2, $g = 2.00696$; in Br_2–$CHCl_3$, $g = 2.00767$, a shift of $+71 \times 10^{-5}$.

From the above results it is concluded that for the first time direct esr evidence has been obtained for the formation of ion pairs in solutions of simple organic cation radicals. These results open up the possibility of further study of ion pairs of cation radicals which, in view of the many interesting results found for ion pairs of anion radicals, is certainly an area worthy of further investigation.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund administrated by the American Chemical Society and to the Research Corporation for partial support of this research.

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Received August 2, 1972

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[6] Additional splittings have been observed in dilute solutions of $TMB\cdot^+$ in Br_2–CH_2Cl_2. The origin of these splittings is presently in doubt and they may be due to secondary radicals.

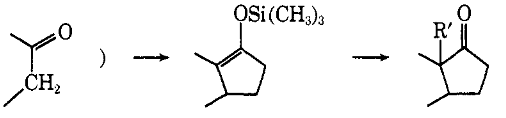
[7] W. G. Williams, R. J. Pritchett, and G. K. Frankel, *J. Chem. Phys.*, 52, 5584 (1970).

[8] A. Carrington and A. D. McLachlan, "Introduction to Magnetic Resonance," Harper and Row, New York, N. Y., 1967, p 138.

New Synthetic Reactions. Cyclopentane Annelation

Sir:

The discovery of many important natural products containing five-membered rings such as the prostaglandins,[1] several sesquiterpene antibiotics,[2] and various flavor and fragrance principles[3] requires new methods for cyclopentane synthesis. We wish to report a method of annealing a cyclopentane ring onto a carbonyl compound possessing an adjacent methyl or methylene unit with the further ability to introduce additional alkyl groups regiospecifically as illustrated in eq 1.



(1)

Condensation of diphenylsulfonium cyclopropylide[4] with carbonyl groups generates oxaspiropentanes in isolated yields of approximately 90% in most cases (see Scheme I).[5,6] For example, use of 1.0 equiv of sulfonium salt per 1.0 equiv of cyclopentanone with a reaction time of 3 hr produced the corresponding oxaspiropentane in 94% yield. Treatment of this compound with lithium diethylamide in hexane at room temperature effected ring opening with formation of 1-cyclopentenyl-1′-cyclopropanol.[7,8] Work-up of the

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[1] For some recent synthetic efforts see T. K. Schaaf and E. J. Corey, *J. Org. Chem.*, 37, 2921 (1972), and references therein; M. P. L. Caton, E. C. J. Coffee, and G. L. Watkins, *Tetrahedron Lett.*, 773 (1972); E. J. Corey and T. Ravindranathan, *ibid.*, 4753 (1971); C. J. Sih, R. G. Salomon, P. Price, R. Sood, and G. Peruzzotti, *ibid.*, 2435 (1972), and references therein; H. L. Slates, Z. S. Zelawski, D. Taub, and N. L. Wendler, *Chem. Commun.*, 304 (1972); J. Fried, C. H. Lin, J. C. Sih, P. Dalven, and G. F. Cooper, *J. Amer. Chem. Soc.*, 94, 4342 (1972); J. Fried, J. C. Sih, C. H. Lin, and P. Dalven, *ibid.*, 94, 4343 (1972), and references therein; P. Crabbe, A. Cervantes, and A. Guzman, *Tetrahedron Lett.*, 1123 (1972).

[2] For example, hirsutic acid [F. W. Comer, F. McCapra, I. H. Oureshi, and A. I. Scott, *Tetrahedron*, 23, 4761 (1967); F. W. Comer and J. Trotter, *J. Chem. Soc. B*, 11 (1966)] and pentalenolactone [D. G. Martin, G. Slomp, S. Mizsak, D. J. Duchamp, and C. G. Chidester, *Tetrahedron Lett.*, 4901 (1970); S. Takeuchi, Y. Ogawa, and H. Yonehara, *ibid.*, 2737 (1969)]. For recent efforts toward hirsutic acid, see P. T. Lansbury, N. Y. Wang, and J. E. Rhodes, *Tetrahedron Lett.*, 2053 (1972); F. Sakan, H. Hashimoto, and A. Ichihara, *ibid.*, 3703 (1971).

[3] For some recent synthetic efforts see J. A. Marshall, W. F. Huffman, and J. A. Ruth, *J. Amer. Chem. Soc.*, 94, 4691 (1972); J. A. Marshall and A. E. Greene, *J. Org. Chem.*, 37, 982 (1972); J. E. McMurry and T. E. Glass, *Tetrahedron Lett.*, 2575 (1971); G. Büchi and B. Egger, *J. Org. Chem.*, 36, 2021 (1971); J. E. McMurry and J. Melton, *J. Amer. Chem. Soc.*, 93, 5309 (1971).

[4] B. M. Trost and M. J. Bogdanowicz, *ibid.*, 93, 3773 (1971).

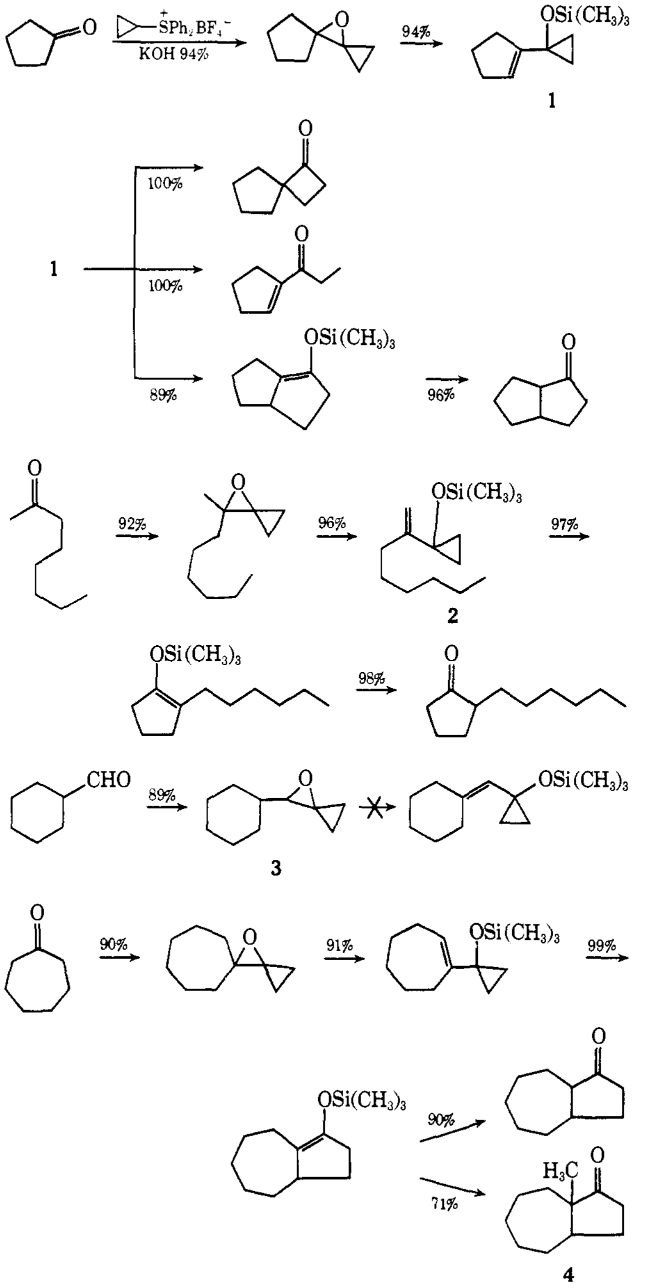
[5] M. J. Bogdanowicz and B. M. Trost, *Tetrahedron Lett.*, 887 (1972).

[6] Complete spectral characterization and elemental composition confirm the structural assignment. Copies of spectra are available upon request from the authors.

[7] B. Rickborn and R. P. Thummel, *J. Org. Chem.*, 34, 3583 (1969); R. P. Thummel and B. Rickborn, *J. Amer. Chem. Soc.*, 92, 2064 (1970); R. P. Thummel and B. Rockborn, *J. Org. Chem.*, 36, 1365 (1971); C. L. Kissel and B. Rickborn, *ibid.*, 37, 2060 (1972).

[8] For other methods of preparation of 1-vinylcyclopropanols see H. H. Wasserman, R. E. Cochoy, and M. S. Baird, *J. Amer. Chem. Soc.*, 91, 2375 (1969); H. H. Wasserman, H. W. Adickes, and O. Espejo de Ochoa, *ibid.*, 93, 5586 (1971); J. R. Conia and J. M. Conia, *Tetrahedron Lett.*, 2849 (1972).

Scheme I. Cyclopentane Annelation[a]



[a] All yields represent isolated yields.

reaction with trimethylchlorosilane and 1–2 equiv of 1,2-dimethoxyethane followed by filtration (to remove precipitated salts), evaporation of solvent, and distillation under reduced pressure generated the silyl ether derivative **1** directly.[6] Purification could also be achieved by chromatography on silica gel. Further characterization was provided by its reactions with acid and base. Thus, treatment with a few drops of 6 *N* aqueous hydrochloric acid in tetrahydrofuran led to rearrangement to the previously characterized spirocyclobutanone and treatment with 1 drop of a 9 *N* aqueous sodium hydroxide solution in methanol led to 1-propionylcyclopentene.[6]

Passage of a hexane solution through a conditioned[9] hot tube packed with glass helices at 330° with a contact time of 4 sec led to smooth quantitative rearrangement to the enol silyl ethers. The much milder conditions required for the vinylcyclopropane rearrangement may be associated with stabilization of the transition state by the siloxy group. Hydrolysis unmasked the carbonyl group to give bicyclo[3.3.0]octan-2-one.[6,10]

To examine the orientational selectivity with an unsymmetrical ketone, the case of 2-octanone was explored. Utilizing the sequence outlined above produced a single vinylcyclopropanol silyl ether identified as **2**[6] and rearrangement generated exclusively 1-trimethylsiloxy-2-*n*-hexylcyclopentene.[6] Attempts to extend the reaction to include oxaspiropentane ring opening to a tertiary center, *i.e.*, **3**, failed. Thus, in agreement with Rickborn's results for the epoxide ring opening methyl reacts in preference to methylene and methine is inert.[7]

Utilizing the method of Stork[11] and House,[12] the initial products of rearrangement may be alkylated. Thus, treatment of the pyrolysate from the cycloheptanone case with methyllithium in 1,2-dimethoxyethane followed by methyl iodide produced the perhydroazulenone derivative **4** with the methyl group only at the bridgehead carbon as an approximately equimolar mixture of trans and cis isomers.[6] The assignment of configuration was based on the downfield shift of the methyl group observed for the cis isomer (δ 1.17) compared to that of the trans isomer (δ 1.13).[13]

It should be emphasized that the overall yield from starting carbonyl compound to annelated cyclopentanone is excellent, 73–83%. Combined with its regiospecificity and the ability to introduce further alkyl groups regiospecifically, this method is one of the most versatile cyclopentanone syntheses available.

Acknowledgment. We wish to thank the National Science Foundation and the National Institutes of Health for their generous support of our programs.

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[9] The hot column was washed with saturated aqueous sodium bicarbonate solution, followed by water, acetone, and hexane in that order. Further surface inactivation was achieved by either passing *O,N*-bistrimethylsilylacetamide or trimethylchlorosilane followed by diethylamine through the hot column.

[10] A. C. Cope and W. R. Schmitz, *J. Amer. Chem. Soc.*, 72, 3056 (1950).

[11] G. Stork and P. F. Hudrlik, *ibid.*, 90, 4462, 4464 (1968).

[12] H. O. House, L. J. Czuba, M. Gall, and H. D. Olmstead, *J. Org. Chem.*, 34, 2324 (1969); H. O. House, M. Gall, and H. D. Olmstead, *ibid.*, 36, 2361 (1971).

[13] H. O. House and B. M. Trost, *ibid.*, 30, 2502 (1965).

[14] Camille and Henry Dreyfus Teacher–Scholar Grant Recipient.

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Received October 3, 1972

The Possible Role of 1,4-Cyclohexylene Intermediates in Cope Rearrangements

Sir:

It has been generally assumed that the Cope rearrangement is a typical pericyclic process, that of 1,5-hexadiene (**1**), for example, involving the cyclic transition state **2**. Recently, however, Doering, *et al.*,[1] have drawn attention to the possibility of an alternate two-step mechanism, formation of the new C–C bond preceding rupture of the old one so that the reaction involves a biradical intermediate. In the case of **1**,

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[1] W. von E. Doering, V. G. Toscano, and G. H. Beasley, *Tetrahedron*, 27, 5299 (1971).