triplet at δ 4.32 (J = 7 Hz), and a triplet at δ 2.44 (J = 7 Hz). These are assigned to $H_{2,5}$, $H_{3,4}$, $H_{1,6}$, and H_7, respectively, from low-temperature double-resonance experiments. Thus, irradiation of the low-field multiplet centered at δ 6.05 leads to collapse of the signal at δ 5.20 to a singlet and of the signal at δ 4.32 to a doublet ($J \sim 7$ Hz). This requires that the latter two absorptions be assigned to $H_{3,4}$ and $H_{1,6}$ respectively, or less likely that this assignment be reversed. The latter alternative is excluded by irradiation of the signal at δ 4.32, which results in the collapse of the H_7 triplet to a broad singlet and of the multiplet at δ 6.05 to a broad doublet. In further conformity with these assignments, irradiation of the signal at δ 5.20 results in the collapse of only the signal at δ 6.05 to a doublet ($J \sim 7$ Hz).

The mechanism of proton averaging in **1** is being investigated.

Acknowledgment. We are indebted to Dr. G. Dudek of Harvard University for assistance in carrying out the double-resonance experiments and to Dr. E. Grunwald of this department for helpful discussions. This research was supported by a grant from the National Science Foundation (GP-8714) which is gratefully acknowledged.

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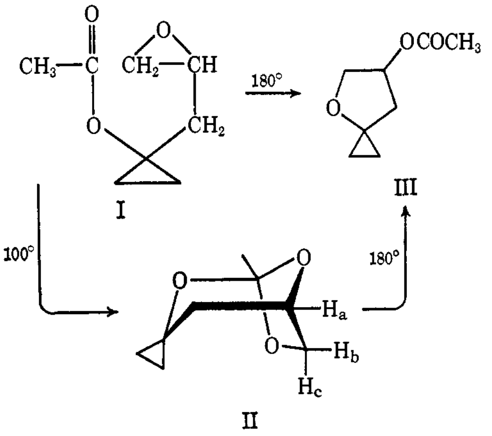
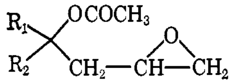
Carbonyl Epoxide Rearrangements. Synthesis of Brevicomin and Related [3.2.1] Bicyclic Systems

Sir:

During studies on the reactions of 1-alkenylcyclopropanols formed from cyclopropanone[1] we have observed that the epoxide of 1-allylcyclopropyl acetate (I) undergoes a novel thermal rearrangement (75% at 180°) to yield 2,2-dimethylene-4-acetoxytetrahydrofuran (III):[2] $\nu_{max}^{CCl_4}$ 3000, 1745 cm^{-1}; τ (CCl_4)[3] 4.85 (m, 1 H), 6.25 (m, 2 H), 7.96 (m, 2 H), 8.00 (s, 3 H), and 9.1–9.72 (m, 4 H). The intermediate in this transformation appears to be the orthoester II, since II may be formed from I at somewhat lower temperatures (80% at 100°). The trioxabicyclo[3.2.1]octane (II) shows no ir carbonyl absorption, a strong ether peak at 1125 cm^{-1}, and nmr absorption[4] at τ 5.4 (m, H_a), 5.88 (d, H_c), 6.2 (a doublet of doublets, H_b), 7.5 (d, 1 H), 8.53 (s, 3 H), 8.9–9.7 (m, 5 H). When heated to 180°, II is readily converted to III (85%).[5]



We have also found that pyrolysis of similarly constituted epoxy acetates such as IVa–c yields products analogous to II and III, along with unsaturated glycol monoacetates.[6] However, if the reaction is applied to



IVa, $R_1 = R_2 = CH_3$
b, $R_1 = CH_3$; $R_2 = H$
c, $R_1, R_2 = (CH_2)_5$

the epoxides of δ,ε-unsaturated ketones, conversion to the [3.2.1] bicyclic system takes place exclusively and, as will be shown below, with a high degree of stereoselectivity.[7] Thus, 6,7-epoxy-2-heptanone (VIa)[8] may be transformed on heating at 210° to 1-methyl-7,8-dioxabicyclo[3.2.1]octane (VIIa) (75%).[9] The ketal VIIa shows no hydroxyl or carbonyl absorption in the ir and has the expected peaks in the nmr at τ (CCl_4) 5.63 (m,

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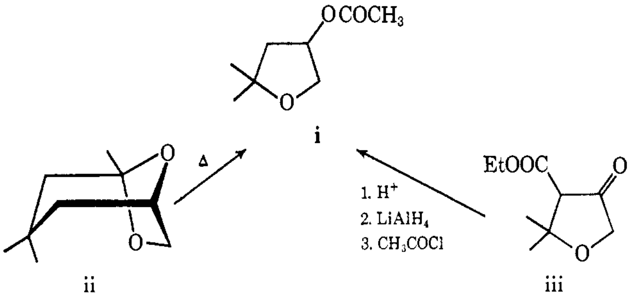
[1] H. H. Wasserman, R. E. Cochoy, and M. S. Baird, *J. Amer. Chem. Soc.*, **91**, 2375 (1969).

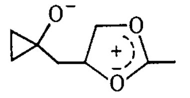
[2] The structures of all intermediates and products are consistent with their infrared and nmr spectra. Satisfactory elemental analyses were obtained for all new compounds.

[3] The nmr spectrum is in complete accord with the spectra of authentic tetrahydrofurans such as i. The latter, isolated from the pyrolysis of ii (28%), was prepared independently from iii by the method of M. A. Gianturco, P. Friedel, and A. S. Giammarino, *Tetrahedron*, 20, 1763 (1964).



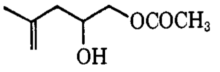
[4] This spectrum corresponds very well to the nmr spectrum of 2,7,8-trioxabicyclo[3.2.1]octane reported by G. Krank and F. W. Eastwood, *Australian J. Chem.*, 17, 1385 (1964).

[5] Conversion of II to III appears to take place by heterolytic C–O cleavage with formation of the intermediate iv.

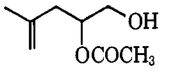


iv

[6] From IVa, and also from ii,[3] for example, v and vi (42%) are obtained at 168°, in addition to i (28%).



v

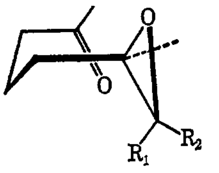


vi

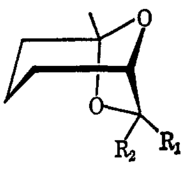
[7] Very recently, Y. Ganoni [*J. Chem. Soc., C*, 2925 (1968); 2934 (1968)] has reported the isolation of 2,7-dioxabicyclo[2.2.1]heptanes from the *m*-chloroperbenzoic acid oxidation of γ,δ-unsaturated ketones. Further peracid oxidation of the 2,7-dioxabicyclo[2.2.1]heptanes yielded 2,7,8-trioxabicyclo[3.2.1]octanes.

[8] The epoxy ketone VIa was prepared by condensation of 4-bromo-1-butene with acetoacetic ester followed by hydrolysis, decarboxylation, and epoxidation with *m*-chloroperbenzoic acid.

[9] At 210° in the absence of acid catalysis, 50% cyclization of VIa–c to VIIa–c took place in *ca.* 12 hr. For complete conversion, heating for a period of time up to 40 hr was necessary. Use of acid catalysts such as $SnCl_4$ or H_2SO_4 caused almost instant cyclization to VIIa–c but also resulted in substantial polymerization.



VI



VII

a, $R_1 = R_2 = H$
b, $R_1 = C_2H_5$; $R_2 = H$
c, $R_1 = H$; $R_2 = C_2H_5$

1 H), 6.25 (m, ABX, 2 H), 8.1–8.6 (m, 6 H), and 8.7 (s, 3 H).

We have further applied the above thermal rearrangement of δ,ϵ-epoxy ketones to a useful synthesis of brevicomin, the principal sex attractant of the western pine beetle *Dentroctonus brevicomis*.[10,11] When *cis*-6,7-epoxynonan-2-one (VIb) (prepared by alkylation of acetoacetic ester with *cis*-1-bromo-3-hexene, saponification, and decarboxylation, followed by epoxidation with *m*-chloroperbenzoic acid) was heated to 210° in a base-washed sealed tube, nearly complete (95%) conversion took place to yield a mixture of *exo*-6-ethyl-1-methyl-7,-8-dioxabicyclo[3.2.1]octane (VIIb) (90%) and the corresponding *endo* isomer VIIc (10%). The *exo* isomer VIIb was identical (ir, nmr, glpc retention time) with brevicomin,[11] the structure of which was recently established by Silverstein, based on nmr data and an alternate independent synthesis.[12]

In like manner, *trans*-6,7-epoxynonan-2-one[13] could be transformed under the above conditions to yield, nearly quantitatively, *endo*-6-ethyl-1-methyl-7,8-dioxabicyclo[3.2.1]octane (VIIc) (epibrevicomin)[14] (91%) and the *exo* isomer, brevicomin (VIIb) (9%).

While the mechanistic details of this carbonyl epoxide rearrangement remain to be explored,[15] it seems clear from the above results that during thermolysis of the δ,ϵ-epoxy ketones, the epoxide ring undergoes opening predominantly with inversion of configuration.

Acknowledgments. This work was supported by Grant GM-07874 from the National Institutes of Health.

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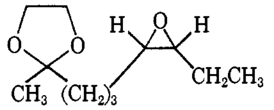
[10] R. M. Silverstein, R. G. Brownlee, and T. E. Bellas, *Science*, **159**, 889 (1968); *Tetrahedron*, in press.

[11] We thank Dr. R. M. Silverstein for providing us with an authentic sample of brevicomin and for spectral data on epibrevicomin. Our product (VIIb) has been assayed by Dr. Silverstein and found to be active.

[12] Brevicomin was synthesized[10] by a somewhat longer process involving acid-catalyzed hydrolysis of the epoxy ketal vii followed by cyclization of the intermediate (unisolated) keto diol.

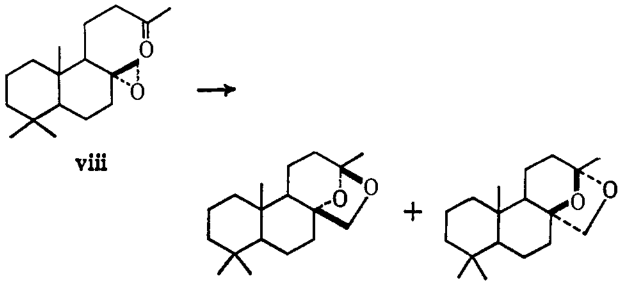


vii

[13] Prepared by epoxidation (*m*-chloroperbenzoic acid) of *trans*-6-nonen-2-one.

[14] Epibrevicomin was identified by comparison of nmr and ir spectra with the corresponding spectra provided by Dr. Silverstein.

[15] Related acid-catalyzed cyclizations of δ,ϵ-epoxy ketones have recently been reported by E. Demole and H. Wuest, *Helv. Chim. Acta*, **50**, 1314 (1967); U. Scheidegger, K. Schaffner, and O. Jeger, *ibid.*, **45**, 400 (1962). Thus, viii is converted to a 1:9 mixture of ix and x in the presence of *p*-toluenesulfonic acid, while with silicic acid, ix and x are formed in the ratio of 3:1.



viii

ix

x

[16] National Institutes of Health Predoctoral Fellow, 1965–1969.

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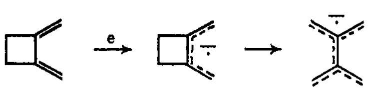
The Tetramethyleneethane (2,2′-Diallyl) Anion Radical

Sir:

Recently a number of conjugated dienes have been reduced electrolytically and the esr spectra of their anion radicals obtained in liquid ammonia[1] and in tetrahydrofuran.[2] We wish to report here the formation of the previously unknown anion radical of tetramethyleneethane (2,2′-diallyl) by reduction of 1,2-dimethylenecyclobutane (**1**),[3] followed by spontaneous electrocyclic isomerization of the anion radical **2** of the latter diene.



1 **2** **3**

Electrolysis of a 5 × 10^{-3} *M* solution of **1** in THF at −90° (tetrabutylammonium perchlorate electrolyte) gives a nine-line esr spectrum.[4] From the line intensities and line spacings it is clear that the nine lines originate from eight equivalent protons, $a_H = 7.65 \pm 0.05$ G. The spectrum is inconsistent with **2**, but can be nicely interpreted in term of structure **3**. HMO calculations predict an odd electron density, $\rho_i = 0.25$, at the four terminal carbons. Comparing this with the results for the allyl radical, which has $\rho_i = 0.5$ and an average terminal methylene coupling of 14.35,[5] the hyperfine splitting of $a_H = {}^1/_2(14.35) = 7.17$ is predicted for **3**. This is in excellent agreement with experiment. That the *exo* and *endo* protons of **3** are not distinguished as to coupling constants is reasonable in terms of the relatively small expected differences (0.9 G for the *exo* and *endo* protons of the allyl radical) and the large line width observed for **3** (1.9 G).

The broad hyperfine lines of **3** are reminiscent of the cyclooctatetraene anion radical (which coincidentally also has nine lines, but a much smaller a_H) where exchange between the anion radical and dianion broadens the lines.[6,7] Exchange with neutral COT is unimportant because of the latter's different geometry (nonplanarity). The tetramethyleneethane system, like COT, has two nonbonding MO's (Chart I). Thus it too

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[1] D. H. Levy and R. J. Myers, *J. Chem. Phys.*, **44**, 4177 (1966).

[2] W. M. Tolles and D. W. Moore, *ibid.*, **46**, 2102 (1967).

[3] A. T. Blomquist and J. A. Verdol, *J. Am. Chem. Soc.*, 77, 1806 (1955).

[4] The esr spectra were recorded on the X band of a Varian V-4520-15 spectrometer.

[5] J. K. Kochi and P. J. Krusic, *J. Am. Chem. Soc.*, **90**, 7157 (1968).

[6] T. J. Katz, *ibid.*, **82**, 3784, 3785 (1960).

[7] F. J. Smentowski and G. R. Stevenson, *ibid.*, **89**, 5120 (1967).