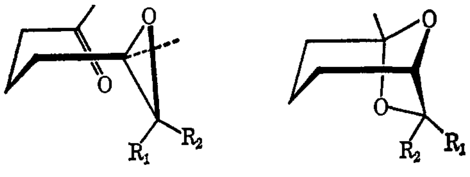


VI VII

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.

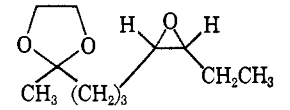
Acknowledgments. This work was supported by Grant GM-07874 from the National Institutes of Health.

---

[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.

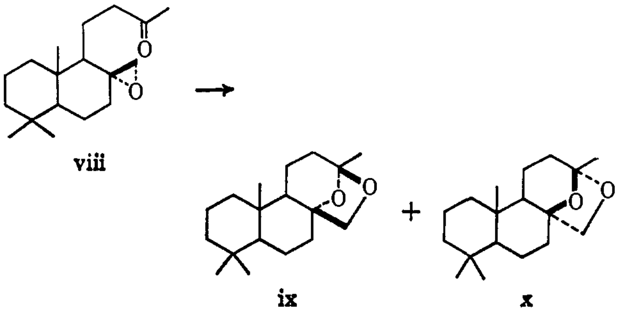


vii

[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



viii ix x

presence of *p*-toluenesulfonic acid, while with silicic acid, ix and x are formed in the ratio of 3:1.

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

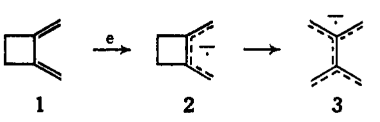
Harry H. Wasserman, Elliot H. Barber[16]
Department of Chemistry, Yale University
New Haven, Connecticut 06520

Received February 27, 1969

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 ρ_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

---

[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).

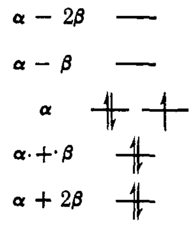
[4] The esr spectra were recorded on the X band of a Varian V-4520-15 spectrometer.

[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).

Chart I. Energy Level Diagram for **3**



could form a dianion relatively readily since a very low energy MO is available. Further, the neutral substrate possesses a different geometry from that of the anionic species. In accord with these speculations, excess **1** does not broaden the hyperfine lines of **3** appreciably. These facts and arguments constitute evidence for the dianion of **3**.

The 1,3-dienic MO of **1**, which must initially accept the reducing electron, has an HMO energy of $\alpha - 0.62\beta$. As Chart I indicates, the odd electron can occupy a nonbonding MO in **3**, thus making the electrocyclic reaction of the anion radical much more facile than that of the neutral molecule. In fact, since the presence of **2** was not observed, it would appear that the rearrangement is exothermic.[8,9]

The rotatory properties of the reaction **2** → **3** have not yet been ascertained, but are under investigation.

Acknowledgment. The Welch, Sloan, and National Science Foundations supported this work. The National Science Foundation provided funds for the esr spectrometer.

[8] Professor Glen Russell and his group at Iowa State have found an interesting example of an anion radical valence isomerization where the ring-*closed* anion radical is favored over the opened form (personal communication).[9]

[9] G. A. Russell and P. R. Whittle, *J. Am. Chem. Soc.*, **91**, 2813 (1969).

[10] Alfred P. Sloan Foundation Fellow, 1966–1968.

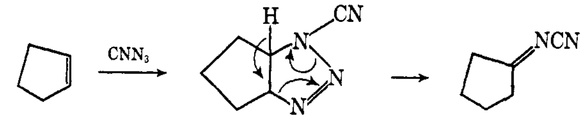
Nathan L. Bauld,[10] *Gerald R. Stevenson*
Department of Chemistry, The University of Texas
Austin, Texas 78712
Received April 1, 1969

A New Ring-Enlargement Reaction

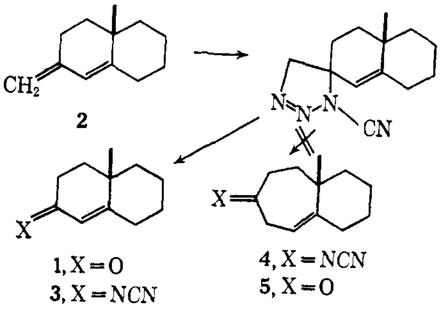
Sir:

In connection with our efforts in sesquiterpene synthesis, we have been interested in ring-enlargement reactions. Our primary goal has been the transformation of cyclohexenones into cycloheptenones, a reaction which is difficult to perform by literature methods.[1] We now wish to present a preliminary report of a new method we have developed for accomplishing this goal.

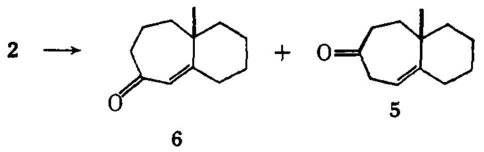
It is known that when cyclopentene is treated with cyanogen azide and the product hydrolyzed, cyclopentanone is produced.[2] The transformation presumably comes about[2] *via* 1,3 dipolar addition to the olefin, followed by rearrangement of the cyanotriazoline with hydride migration and loss of nitrogen.



We felt that, if a diene such as **2**[3] were treated with 1 equiv of cyanogen azide, dipolar addition should occur at the more accessible exocyclic double bond in the orientation indicated.[4] The cyanotriazoline intermediate should then rearrange with migration of the vinyl moiety, and, after hydrolysis, the desired cycloheptenone, **5**, would result.



When the reaction was carried out by allowing the diene **2** in acetonitrile to be in contact with 1 equiv of cyanogen azide[5] for 48 hr in the dark, followed by hydrolysis of the crude product with aqueous methanolic HCl, the sole product isolated (50%) was the starting enone, **1**. Presumably, the desired intermediate triazoline did in fact form, but decomposed with cleavage of the allylic bond and resultant loss of diazomethane to give **3**—an unexpected but not illogical occurrence. After much experimentation, conditions were found where ring enlargement did occur. Thus when diene **2** was treated with cyanogen axide in the presence of a proton source in a highly ionic medium (2.5 *M* LiClO$_4$ in 1:1 CH$_3$OH–CH$_3$CN)[6] for 48 hr at room temperature followed by acid hydrolysis, two ring-expanded products were formed.



Enone **6** [ir (neat) 1650, 1620 cm^{-1}; uv $\lambda_{\max}^{\mathrm{EtOH}}$ 240 mμ (ϵ 8000); nmr (CDCl$_3$) τ 4.26 (s, 1 H), 8.88 (s, 3 H); mass spectrum (80 eV), *m/e* (relative intensity) 178 (M$^+$, 100), 163 (44), 150 (49), 136 (32), 135 (62), 122 (64), 121 (60)], in which C$_8$-alkyl migration had taken place, was formed in 15% yield. Enone **5** [ir (neat) 1705 cm^{-1};

---

[1] For a recent review, see C. D. Gutsche and D. Redmore, "Carbocyclic Ring Expansion Reactions," Academic Press, New York, N. Y., 1968. For specific examples, see (a) E. J. Corey, M. Ohno, R. B. Mitra, and P. A. Vatakencherry, *J. Am. Chem Soc.*, **86**, 478 (1964); (b) W. S. Johnson, M. Neeman, S. P. Birkeland, and N. A. Fedoruk, *ibid.*, **84**, 989 (1962); (c) E. Muller, H. Kessler, and B. Zeeh, *Fortschr. Chem. Forsch.*, 7, 128 (1966); (d) G. Stork M. Nussim, and B. August, *Tetrahedron Suppl.*, **8**, Part 1, 105 (1966).

[2] F. D. Marsh and M. E. Hermes, *J. Am. Chem. Soc.*, **86**, 4506 (1964).

[3] Prepared in high yield by Wittig reaction on the corresponding enone according to the general procedure of R. Greenwald, M. Chaykovsky, and E. J. Corey, *J. Org. Chem.*, **28**, 1128 (1963).

[4] For a discussion of orientation in dipolar addition reactions, see R. Huisgen, *Angew. Chem. Intern. Ed. Engl.*, **2**, 633 (1963).

[5] Prepared by stirring a solution of cyanogen bromide in dry acetonitrile with powdered NaN$_3$ for 2 hr. The cyanogen azide containing supernatant is then removed from precipitated NaBr *via* syringe. A word of caution is in order: although we have conducted well over 100 experiments with cyanogen azide *solutions* without experiencing the slightest difficulty, the Du Pont workers[2] warn that "the *pure* azide detonates with great violence when subjected to mild mechanical or thermal shock."

[6] Detailed reasoning for the choice of these conditions will be presented in the full paper.