tropic carbon migration with antarafacial allylic participation. Further experimentation will be needed to dissect the rate constant $k_\alpha = 2[k(2a \rightarrow 2b) + k(2a \rightarrow 2d)]$ into its two components. If racemization should occur only through the process $2a \rightarrow 2b$, then the entire methylenecyclobutane automerization could occur with antarafacial allylic participation, $2a \rightarrow 2c$.

(18) National Science Foundation Trainee, 1968–1971.

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### Cyclooctatriene–Bicyclooctadiene Equilibria. Effects of Additional Ring Fusions and Metal Binding

Sir:

The question of the relative stabilities of the mono- and bicyclic tautomers of C_8H_{10}, **1a** and **1b**, was first in-

$1, X = X' = CH_2$
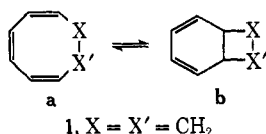
vestigated in these laboratories more than 20 years ago by Cope, *et al.*[1] The free energy difference was found to be small and the rate of interconversion slow at room temperature. More recently, Huisgen, *et al.*,[2] have examined the influence of variations in the X–X' group on the position of equilibrium. This varies from a **b/a** ratio of ~ 0 for X–X' = HC=CH, through 1/8 for H_2C-CH_2 to ≥ 100 for several cases. They examined two possible, simple explanations for the observed variation and found one (nonbonded repulsions) untenable and the other (hybridization effects) doubtful. The problem remains unsolved.

While we are not able to offer a general solution, we wish to report some new observations which are interesting and may be significant. Our first concern is with the effects of fusing saturated rings of different sizes across the C(7)–C(8) bond on the position of equilibrium. We have also employed the $Fe(CO)_3$ and $Mo(CO)_3$ groups (diene and triene seekers, respectively) to shift the equilibria and allow isolation of complexes of the isomeric olefins. The three systems **2a,b**, **3a,b**, and **4a,b** have been prepared (by reaction of $Li_2C_8H_8$ with $Br(CH_2)_nBr$, $n = 2, 3, 4$) and studied.[3,4] The size of

(1) A. C. Cope, A. C. Haven, F. L. Ramp, and E. R. Trumbull, *J. Amer. Chem. Soc.*, 74, 4867 (1952).
(2) R. Huisgen, G. Boche, A. Dahmen, and W. Hechtl, *Tetrahedron Lett.*, 5215 (1968).
(3) All compounds discussed here have been characterized by satisfactory elemental analyses and spectra.
(4) The general preparative reaction is based on that reported for *cis*-bicyclo[6.4.0]deca-2,4,6-triene by S. W. Staley and T. J. Henry, *J. Amer. Chem. Soc.*, 92, 7612 (1970).

the appended ring has been found to influence the position of the **a** $\rightleftharpoons$ **b** equilibrium for **2**, **3**, and **4**.

$2, n = 2; 3, n = 3; 4, n = 4$
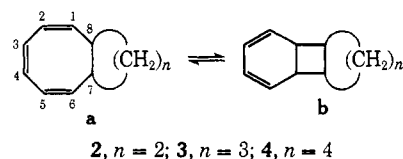
Not surprisingly, for **2** ($n = 2$) the **b** (tricyclo) isomer is destabilized to the extent that it cannot be detected in the products of the preparative reaction. Pure **2a** is isolated from the preparative reaction. For **3** the situation is reversed. From the preparative reaction, mixtures of **3a** and **3b**, in comparable molar quantities, are obtained by distillation at 25° (0.01 mm). The rate and equilibrium of the reaction **3a** $\rightarrow$ **3b** have been studied[5] at 34 and 58°. Assuming a frequency factor of 10^{13}, the Arrhenius activation energy is 24 ± 1 kcal/mol, and the rate constants are 3.4×10^{-3} (58°), 4.2×10^{-5} (34°), and 1.6×10^{-5} sec^{-1} (20°, by extrapolation). The equilibrium ratio **3b/3a** at 58° is ~ 32 and $\Delta G°$ for the reaction is thus ~ -2.0 kcal/mol. These values are comparable to those for several systems studied by Huisgen, *et al.*; for the C_8H_{10} system itself, **1** (X = X' = CH_2), they found k_1 (20°) = 5.3×10^{-7} sec^{-1}, and both $\Delta G^{\ddagger}$ and $\Delta G°$ more positive by ~ 3 kcal/mol. While we cannot yet attempt to account quantitatively for the stabilizing influence of the fused five-membered ring on the tricyclodiene tautomer, the effect is qualitatively understandable. The most stable conformation of a cyclopentane ring causes C–H bonds from two adjacent carbon atoms to be coplanar. Presumably the cyclohexadiene ring in any bicyclo structure of type **b** imposes planarity upon the 4 ring. Thus any additional factor which also favors planarity of the 4 ring will enhance the relative stability of the **b** tautomer.

For **4**, the preparative procedure yields an approximately 7:3 mixture of **a** and **b**. Only at temperatures above 100° could significant changes in the relative amounts of the two be observed as a function of time; the equilibrium ratio **4a/4b** at 114° is approximately 1.0. Thus the fused cyclohexane ring is much less effective in stabilizing the **b** tautomer, presumably because fusion to a planar 4 ring forces the cyclohexane ring to adopt a half-chair conformation (or, less likely, a tub conformation).

In the three systems, **2**, **3**, and **4**, the electronegativity and inductive effects must be substantially constant; steric and strain effects must be decisive. In order to examine these influences in detail later, accurate structural data will be required. Through the agency of metal carbonyl moieties which have particular affinities for 1,3-diene and 1,3,5-triene groups, it has been possible to sequester selectively the triene and diene tautomers as complexes of $Mo(CO)_3$, $Fe_2(CO)_6$, and $Fe(CO)_3$ moieties. The various complexes isolated,[6] all in the form of crystals suitable for X-ray study, are shown as **5–13**. All of these complexes have been

(5) These measurements were made by maintaining samples in an nmr tube in a constant temperature bath and periodically monitoring the concentrations by nmr.
(6) The metal carbonyl derivatives were all prepared by thermal reactions of the olefins with $Fe_2(CO)_9$ or $Mo(CO)_3(CH_3CN)$ and purified by sublimation or recrystallization.
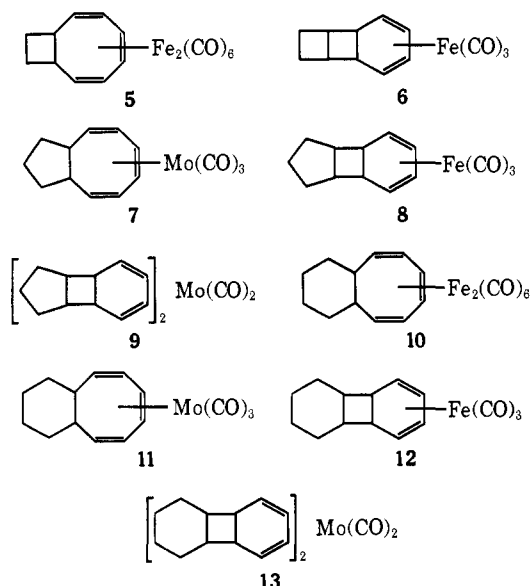
characterized as to gross structure (connexity of bonds) by solution nmr.[7,7a]

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## Mechanisms of Ozonolysis. Isolation of the Dioxetane Intermediate

Sir:

We earlier reported[1] that certain aldehydes and ketones, when used as solvents, intercept and reduce a labile intermediate in the ozonolysis of olefins to the extent that no peroxidic products are isolable; however, the double bond is cleaved and the normal carbonyl products are obtained in high yield. This phenomenon is observed in solvents which will readily undergo Baeyer–Villiger oxidation; such solvents are henceforth termed "Baeyer–Villiger" solvents. On the basis of this observation we proposed that the intermediate so reduced in this sequence is most likely the Staudinger molozonide (2).[2] Reduction of the molozonide 2 in this way generates the corresponding dioxetane 3.

Accordingly, we wrote a unified concept for the ozonolysis reaction in which the key intermediate was the Staudinger molozonide 2 and the particular products of any given ozonolysis reaction were determined largely by competition among several possible reaction paths (B–E) involving this intermediate, 2. Using
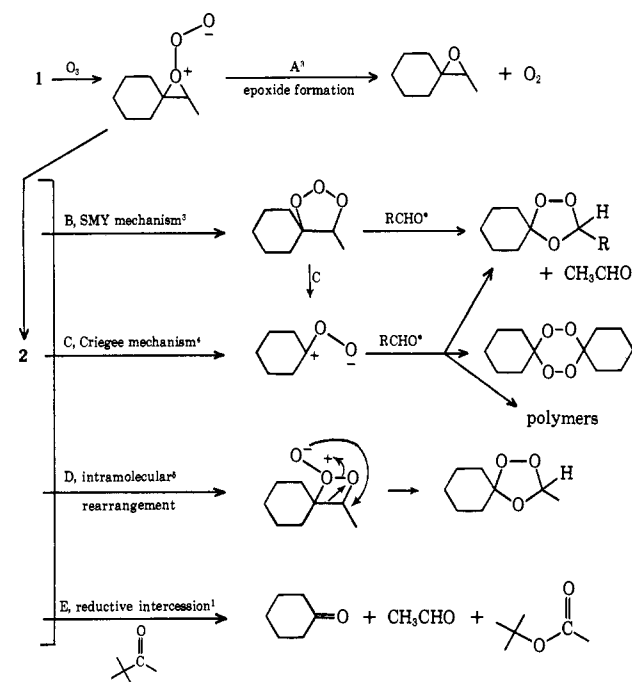
(1) P. R. Story, J. A. Alford, J. R. Burgess, and W. C. Ray, J. Amer. Chem. Soc., 93, 3042 (1971).

(2) P. R. Story, J. A. Alford, W. C. Ray, and J. R. Burgess, ibid., 93, 3044 (1971).
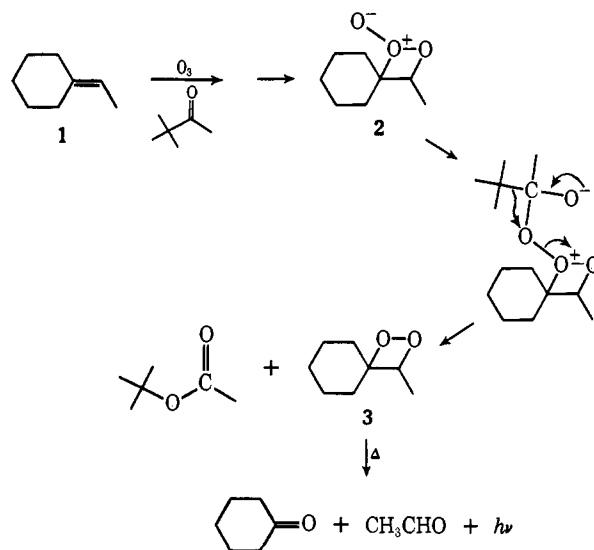
ethylidenecyclohexane (1) as a model, the overall scheme is illustrated here (Scheme I).

Scheme I[a]

[a] The asterisk indicates added foreign aldehyde or acetaldehyde produced in path C.

We can now report that we have isolated the dioxetane intermediate from the ozonolysis of several different olefins and it appears that this will be a general phenomenon for ozonolysis reactions. For ex-

(3) P. R. Story, R. W. Murray, and R. D. Youssefyeh, ibid., 88, 3144 (1966); P. R. Story, C. E. Bishop, J. R. Burgess, R. W. Murray, and R. D. Youssefyeh, ibid., 90, 1907 (1968).

(4) R. Criegee, Rec. Chem. Progr., 18, 111 (1957); R. Criegee in "Peroxide Reaction Mechanisms," J. O. Edwards, Ed., Interscience, New York, N. Y., 1962, p 29.

(5) P. R. Story and W. C. Ray, unpublished results.