The basic procedure seems to be quite general and any reducing agent (chemical or electrical) with a higher potential than the metal salt will work. We have also prepared a number of other activated metals by this procedure and find that they too have unusual reactivity. We will be reporting on these metals and further reactions of the activated magnesium in the near future.

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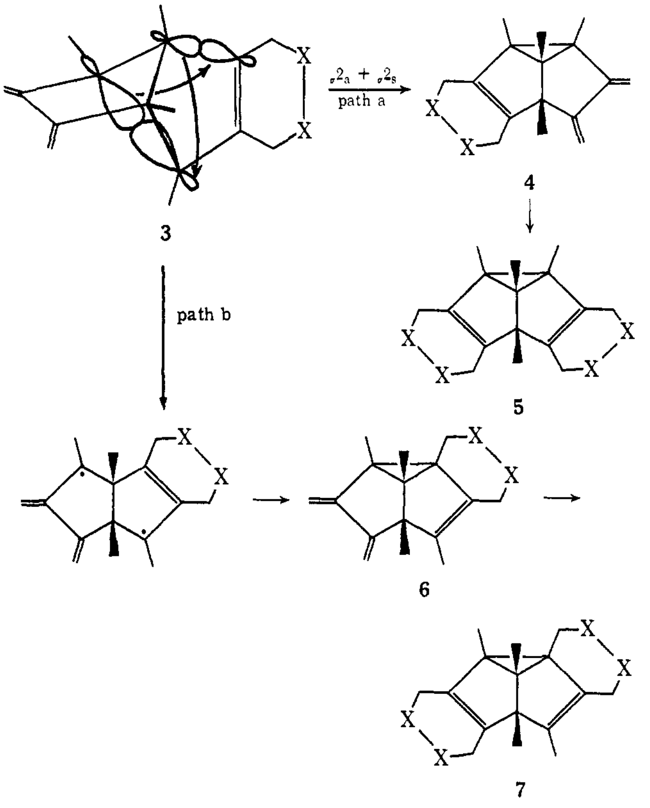
The Mechanism of Rearrangement of Molecules Containing Cyclobutane Rings 1,3 Bridged by Ethylene

Sir:

Although kinetic[1] and stereochemical[2] studies of the rearrangement of cyclobutanes 1,3 bridged by ethylene have been interpreted in terms of energetically proximate concerted ${}_{\sigma}2_{a} + {}_{\pi}2_{s}$[3] and biradical[4] pathways, the extraordinary facility of the rearrangement of tricyclo[3.3.0.0^{2,6}]octadiene (**1**) to semibullvalene[5,6] has prompted the suggestion[7,8] that this and similar[7] molecules may rearrange by a symmetry-allowed[3] but rarely observed[9,10] ${}_{\sigma}2_{a} + {}_{\sigma}2_{s}$ mechanism. In this communication we present experimental evidence that rules out a ${}_{\sigma}2_{a} + {}_{\sigma}2_{s}$ pathway in the extremely rapid rearrangement of an ethylene-bridged cyclobutane but which is wholly consistent with the biradical[4] mechanism originally proposed for the rearrangement of **1**.[5,6]

Recently, we reported that 1,2,5,6-tetramethyl-3,4,7,8-tetramethylenetricyclo[3.3.0.0^{2,6}]octane (**2**) undergoes Diels–Alder reaction with 2 mol of tetracyanoethylene (TCNE) in refluxing THF to give a bisadduct for which we suggested the structure **7a**.[11] The fact that when only 1 equiv of TCNE is used a mixture consisting of equal amounts of bisadduct and starting material **2** is obtained indicates that the second Diels–Alder reaction must be much faster than the first. The lack of Diels–Alder reactivity shown by molecules containing a cyclobutane ring 1,3 bridged by butadiene[12] suggests that the initial monoadduct **3a** rearranges more rapidly than it reacts with another mole of TCNE and that the rearrangement product then undergoes the rapid Diels–Alder reaction expected of a normal diene. This reaction scheme is illustrated below for both a ${}_{\sigma}2_{a} + {}_{\sigma}2_{s}$ (path a) and biradical[4] (path b) mechanism for the rearrangement of **3a**.



a, X–X = (NC)$_2$C–C(CN)$_2$ b, X–X = $\overline{\text{NCON(Ph)CON}}$

The bisadducts **5a** and **7a** expected from the two different mechanisms for the rearrangement differ in that the former possesses a plane of symmetry while the latter has an effective C$_2$ axis on the nmr time scale.[13] Thus, only two types of methyl groups should appear in the nmr spectrum of **7a**, while three different methyl resonances might be anticipated in the nmr of **5a**. We previously reported that the methyl groups in the nmr spectrum of the bisadduct appear as two sharp singlets at 100 MHz in acetone-d_6.[11] We have now obtained 220-MHz spectra of this compound in both acetone-d_6 and pyridine-d_5.[14] Despite the fact that the broad singlet from four of the methylene protons[11] is now resolved into an AB quartet, the methyl resonances remain sharp singlets.

Although the nmr spectra provide evidence against the structure **5a**, they cannot be considered as unequivocal proof of the correctness of structure **7a** for the product. Moreover, the nmr data from further bisadducts of **2** can increase the likelihood that **4** is the correct structure but never demand it. Experimentally, **2** proves so reluctant to undergo Diels–Alder cycloaddition that, despite our attempts with such reactive dienophiles as

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(1) H. M. Frey and R. G. Hopkins, *J. Chem. Soc. B*, 1410 (1970).

(2) W. R. Roth and A. Friedrich, *Tetrahedron Lett.*, 2607 (1969).

(3) R. B. Woodward and R. Hoffmann, *Angew Chem., Int. Ed. Engl.*, **8**, 781 (1969).

(4) J. A. Berson and L. Salem, *J. Amer. Chem. Soc.*, submitted for publication, have suggested that subjacent orbital effects could, in principle, favor a "forbidden" concerted ${}_{\sigma}2_{s} + {}_{\pi}2_{s}$ over a biradical pathway in 1,3-sigmatropic shifts.

(5) J. Meinwald, D. Schmidt, and H. Tsruta, *ibid.*, **91**, 5877 (1969).

(6) H. E. Zimmerman, J. D. Robbins, and J. Schantl, *ibid.*, **91**, 5878 (1969).

(7) J. E. Baldwin and A. H. Andrist, *ibid.*, **93**, 3289 (1971).

(8) M. J. Goldstein and R. Hoffmann, *ibid.*, **93**, 6193 (1971).

(9) J. E. Baldwin and A. H. Andrist, *Chem. Commun.*, 1561 (1970); J. E. Baldwin and G. D. Andrews, *J. Amer. Chem. Soc.*, **94**, 1775 (1972).

(10) S. McLean, D. M. Findlay, and G. I. Dmitrienko, *ibid.*, **94**, 1380 (1972).

(11) W. T. Borden and A. Gold, *ibid.*, **93**, 3830 (1971).

(12) We find that whereas the reaction of 1,2-dimethylenecyclobutane with tetracyanoethylene in THF is instantaneous at room temperature, that of 2 requires several hours at reflux for completion.

(13) Semibullvalene derivatives are rapidly fluxional at all but very low temperatures: H. E. Zimmerman and G. L. Grunwald, *J. Amer. Chem. Soc.*, **88**, 183 (1966); F. A. L. Anet and G. E. Schenck, *Tetrahedron Lett.*, 4237 (1970).

(14) These spectra were obtained on a Varian HR 220 instrument at the Central Research Laboratories of the E. I. DuPont de Nemours Co. through the courtesy of Dr. H. E. Simmons, whose cooperation we gratefully acknowledge.

dicyanoacetylene and diethyl azodicarboxylate, we have been able to isolate only one further bisadduct. It is formed by using the potent *N*-phenyltriazolinedione (**8**) as dienophile, and its nmr spectrum again shows two sharp methyl singlets, consistent with the assignment of its structure as **7b**.

Fortunately, **8** is such a reactive dienophile that the rate of the initial Diels–Alder reaction is competitive with rate of rearrangement of **3b**. When the reaction of **2** with 1 equiv of **8** is conducted at 0° in chloroform, a monoadduct can be isolated by chromatography. Its nmr spectrum is wholly consistent with structure **6b** and excludes **4b**. In particular, the methyl group which resonates at lowest field (δ 1.51, $CDCl_3$) is coupled with $J = 2$ Hz to a proton which appears centered at δ 3.71 as half of an AB quartet. The chemical shift and allylic coupling are indicative of a methyl group on a double bond. Since in **4b** none of the methyl groups are located on double bonds, the nmr spectrum demands structure **6b**. Compound **6b** reacts with another equivalent of **8** to give **7b**.

The rapidity of the initial Diels–Alder reaction has enabled us to prepare **3b** at low temperature and measure its rate of rearrangement to **6b**. When equimolar **2** and **8** are mixed in $CDCl_3$ and allowed to warm to +10° in an nmr probe, a reaction occurs as evidenced by the disappearance of the resonances of **2** and the appearance of new singlets at δ 0.67 (6 H), 1.14 (6 H), 4.32 (4 H), 4.85 (2 H), and 5.48 (2 H). When the sample is allowed to warm to 30°, these resonances, ascribed to **3b**, diminish in intensity as those of **6b** become larger. The half-time for the rearrangement is approximately 10 min at this temperature.

In summary, we have shown that a ${}_{\sigma}2_a + {}_{\sigma}2_s$ mechanism is ruled out in the very rapid rearrangement of an ethylene-bridged cyclobutane. The demonstration of the nonintervention of a transition state of purported special stability suggests that the facility with which such molecules undergo rearrangement results from their high energy content. In addition to the large amount of strain presumably present in a cyclobutane ring 1,3 bridged by ethylene,[15] unfavorable π interaction between the orbitals of the ring and bridge also contributes to the instability of molecules containing this moiety.[17]

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[15] The unusually long carbon–carbon bonds present in tricyclo-[3.3.0.0^{2,6}]octene[16] give evidence of the highly strained nature of this molecule.

[16] D. L. Zebelman, S. H. Bauer, and J. F. Chiang, *Tetrahedron*, **28**, 2727 (1972).

[17] In cyclobutane rings 1,3 bridged by ethylene the highest occupied molecular orbitals (HOMO's) of the ring and the bridge have the same symmetry and consequently mix.[18] Interaction between such filled orbitals is shown to be destabilizing by calculations which include overlap.[8] Although stabilizing interactions between occupied and unoccupied orbitals—for instance, between the second highest filled MO of the ring and π^* of the bridge—do occur, they are cancelled by the "overlap repulsion" between the HOMO's.

In contrast, the orbital interactions in cyclobutane 1,3 bridged by butadiene result in net stabilization, because the symmetries of the HOMO and LUMO in butadiene are the reverse of those in ethylene. We attribute the reluctance of **2** and **3** to undergo Diels–Alder reactions, at least in part,[19] to the favorable orbital interactions between ring and bridge when butadiene, rather than ethylene, is the bridging group.

A fuller discussion than that possible here will be published along with the results of calculations that have been carried out in this laboratory by W. L. Jorgenson and which support these conclusions.

[18] R. Hoffmann and R. B. Davidson, *J. Amer. Chem. Soc.*, **93**, 5699 (1971). The authors have suggested that interaction between these orbitals is responsible for the unusual uv spectrum of **1**. The effect of this mixing on the total energy of the molecule is implicit in their interaction diagram.

[19] The shorter bond in an ethylene bridge (1.34 *vs.* 1.48 Å in butadiene) probably results in a more strained system; therefore, strain may also contribute to the energetic preference for butadiene as the 1,3-cyclobutane bridging group.

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The Reaction of Oxazoles with Singlet Oxygen. The Mechanism of the Rearrangement of Triamides

Sir:

Among the unusual transformations observed in the reaction of singlet oxygen with organic substrates has been the facile conversion of oxazole derivatives to triamides.[1-3] This remarkable rearrangement takes place in high yields under mild conditions when the excited oxygen is generated both by chemical[4] and photooxidative methods. We now wish to report tracer studies which clarify the mechanism of this conversion.

We had suggested earlier that the oxidative change takes place by initial formation of a transannular peroxide, followed by a Baeyer–Villiger-like rearrangement to an intermediate imino anhydride, Chart I, path a. An *O*-acyl to *N*-acyl migration would then lead to the triamide. The ease with which imino anhydrides rearrange to triamides is well known.[5]

A very reasonable alternate route to an intermediate imino anhydride (path b) would involve addition of oxygen at the 4,5 position of the oxazole followed by cleavage of the dioxetane ring. This (isomeric) imino anhydride could then rearrange, as described above, to form the triamide.

There are many precedents for both types of singlet oxygen reaction with heterocyclic systems. In the furan series, oxygen insertion products of the Baeyer–Villiger type have been commonly observed,[6-8] while with substituted imidazoles and imidazolones ring cleavage through dioxetanes appears to be the predominant reaction course.[9,10] In other highly electron-rich unsaturated systems, stable intermediate dioxetanes have been isolated.[11-13]

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[4] H. H. Wasserman, J. R. Scheffer, and J. L. Cooper, *J. Amer. Chem Soc.*, **94**, 4991 (1972).

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[10] M. L. Wolff, Ph.D. Thesis, Yale University, 1970.

[11] P. D. Bartlett and A. D. Schaap, *J. Amer. Chem. Soc.*, **92**, 3223 (1970).

[12] S. Mazur and C. S. Foote, *ibid.*, **92**, 3225 (1970).

[13] K. R. Kopecky and C. Mumford, *Can. J. Chem.*, **47**, 709 (1969).