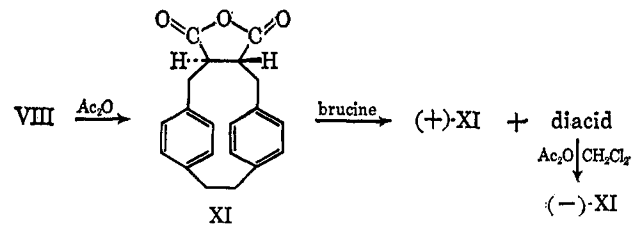
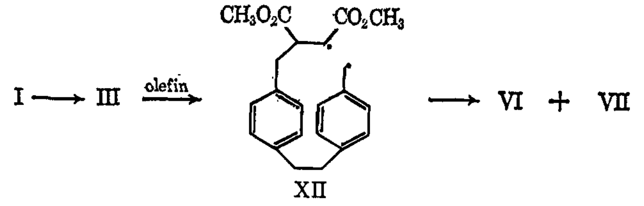


The olefin insertion reaction undoubtedly involves production of the diradical III, one benzyl carbon atom of which adds to olefin to produce a second diradical, XII, which in turn ring closes to give VI and VII. Intermediate XII must have a sufficient lifetime to destroy the stereochemical memory of the adding olefin before ring closure. The lack of stereospecificity[14] of the insertion reaction precludes any concerted addition to the diradical III or to [2.2]paracyclophane itself.



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[14] Appropriate control experiments demonstrated that dimethyl maleate, dimethyl fumarate, and VII are essentially configurationally stable under the reaction conditions.

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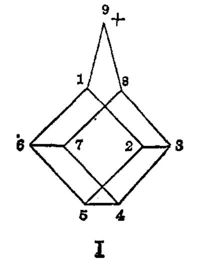
Stereospecific Rearrangements in the Homocubyl Cation

Sir:

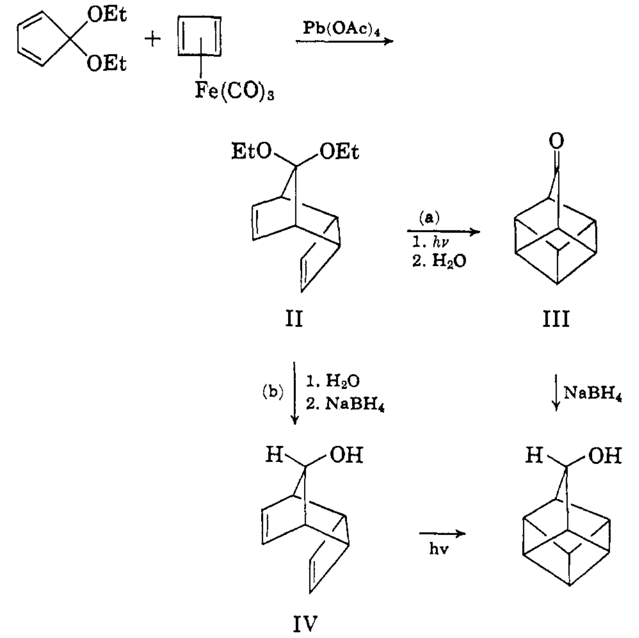
Of the fluctional molecules now known, bullvalene remains the most remarkable in that *via* a series of Cope rearrangements the system can undergo degenerate valence tautomerism which ultimately leads to complete scrambling of the carbon atoms in the framework.[1] Among other systems which can, in principle, behave similarly is the 9-homocubyl cation I; in this case, a succession of Wagner-Meerwein rearrangements continually regenerates the 9-homocubyl cation and results in scrambling of the nine methine units.



I

In a recent communication, Schleyer and co-workers[2] have reported preliminary studies dealing with the synthesis and rearrangement of the homocubyl cation. We have independently been investigating this same problem and wish to report our initial results at this time. These results, based upon both a different synthesis and method of rearrangement detection, are in agreement with those of Schleyer, *et al.*,[2] in showing that the homocubyl cation when generated in acetic acid does undergo several degenerate rearrangements before forming the acetate. In addition, evidence indicates the reaction to be stereospecific and that much of the scrambling proceeds *via* internal return of the tosylate employed.

9-Homocubyl tosylate was prepared by two related pathways. Oxidative decomposition of cyclobutadieneiron tricarbonyl with lead tetraacetate in pyridine in the presence of cyclopentadienone diethyl ketal[3] afforded the adduct II.[4] In path a irradiation of II in acetone gave 9,9-diethoxyhomocubane which upon hydrolysis yielded homocubanone III. Reduction of III with sodium borohydride produced 9-homocubanol which was converted to the tosylate in the usual manner. The tosylate (mp 73–73.5°) displayed absorptions in the nmr at τ 2.42 (area 4), 5.12 (1), 6.33–7.00 (8), and 7.56 (3).[6] In path b, hydrolysis of the ketal II followed by reduction with $NaBH_4$ afforded predominantly the alcohol IV in which the stereochemistry of the hydroxyl group is as indicated.[7] Irradiation of IV gave homocubanol.



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[1] W. von E. Doering and W. Roth, *Tetrahedron*, **19**, 715 (1963); G. Schröder, J. F. M. Oth, and R. Merenyi. *Angew. Chem. Intern. Ed. Engl.*, **4**, 752 (1965).

[2] P. von R. Schleyer, J. J. Harper, G. L. Dunn, V. J. Di Pasquo, and J. R. E. Hoover, *J. Am. Chem. Soc.*, **89**, 698 (1967).

[3] P. E. Eaton and R. A. Hudson, *ibid.*, **87**, 2769 (1965).

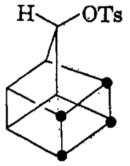
[4] Decomposition with ceric ion[5] was unsatisfactory in that the ketal was rapidly hydrolyzed and dimerized to dicyclopentadienone.

[5] J. C. Barborak, L. Watts, and R. Pettit, *J. Am. Chem. Soc.*, **88**, 1328 (1966).

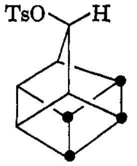
[6] The physical properties of 9-homocubanol and its acetate and tosylate were identical with those reported by Schleyer and co-workers.[2]

[7] This isomer is formed in better than 90% yield. The stereochemistry is indicated by the nmr pattern of the 7,8-olefinic protons (triplet) characteristic of 7-antisubstituted norbornenes [see E. I. Snyder and B. Franzus, *J. Am. Chem. Soc.*, **86**, 1166 (1964)]. In addition, in the mixture of tetradeuterated 9-homocubyl tosylates made *via* pathway a (see text) there exists two distinct regions of absorptions for the ring protons other than C_9; these occur in the regions τ 6.4–6.6 and 6.6–7.0 of areas 1:3, respectively. The lower field set (τ 6.4–6.6) must therefore be associated with those protons situated beneath the tosylate group rather than those β to the tosylate group. In the d_4 tosylate made *via* path b there is no absorption in the region τ 6.4–6.6 but all four protons appear at τ 6.65–6.9; therefore, the tosylate must be *syn* to two deuterium atoms, which requires the stereochemistry shown in IV.

In order to follow the extent of possible rearrangement of the homocubyl ion accompanying solvolysis, the tetradeuterio derivative of homocubanol was prepared in an analogous manner starting with perdeuteriocyclobutadieneiron tricarbonyl.[8] Path a afforded an equal mixture of the two tosylates V and VI, while path b afforded the single isomer V.



V



VI

A sample of V and another consisting of an equal mixture of V + VI was solvolyzed in acetic acid at 120° for 30 hr, and the acetates and unreacted tosylates were recovered.[10] The unique chemical shift of the C_9 proton in both the acetate and the tosylate allows a direct measure of the extent of rearrangement; however, the amount of deuterium appearing at C_9 will also depend on the stereospecificity of the process. In a stereospecific process involving repeated migration of the carbon atom *trans* to the leaving group, the sample of V should show twice as much deuterium at C_9 as that of the mixture V + VI since VI in such a process cannot generate deuterium at C_9. However, in a nonstereospecific process, the two samples should produce the same amount of deuterium at C_9.

The acetate produced from V showed 26.1 ± 3% deuterium at C_9, while that from V + VI showed 12.3 ± 3%. The scrambling process under these conditions is clearly stereoselective if not entirely stereospecific. The relationship between the number of rearrangements which occur and the amount of deuterium they generate at C_9 for the stereospecific process is shown in Table I.[11]

Table I. Percentage of D at C_9 Accompanying 1,2 Shifts of V

No. of 1,2 shifts	0	1	2	3	4	5	6	∞
% D at C_9	0	0	12.5	21.9	28.1	32.2	35.0	40.0

On the average close to four Wagner–Meerwein shifts had therefore occurred in the over-all solvolysis. The recovered tosylates also contained deuterium at C_9 and to a larger degree than that observed for the acetates;[12] again approximately twice as much deuterium appeared at C_9 in the reaction of V as with the mixture V + VI. This indicated stereospecific rearrangement *via* internal return of the tosylate ion pair.[13] The results of Schleyer and co-workers, however, clearly indicate that in formolysis, at least, stereochemical leakage can occur.[2]

Acknowledgment. We thank the National Science Foundation and the Robert A. Welch Foundation for financial support. We also thank Badische Anilin und Soda Fabrik and General Aniline and Film Corporation for generous gifts of cyclooctatetraene and iron carbonyl, respectively.

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[8] Prepared by repeated treatment of cyclobutadieneiron tricarbonyl with CF_3COOD.[9] Analysis by nmr methods indicated the starting perdeuterio complex contained at least 98% deuterium.

[9] J. D. Fitzpatrick, L. Watts, G. F. Emerson, and R. Pettit, *J. Am. Chem. Soc.*, 87, 3254 (1965).

[10] Under these conditions approximately 80% of the tosylate had reacted. The acetates were purified by repeated crystallization from pentane (mp 10–12°).

[11] This table ignores the isotope effect.

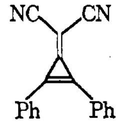
[12] Greater than five shifts are indicated.

[13] Concerning the question of possible bridged ion intermediates, it is of interest to note the stereospecificity of these rearrangements together with the enhanced rate of acetolysis found by Schleyer and coworkers.[2]

Cycloaddition Reaction of a Triafulvene with Enamines. Intermediacy of a 5-Methylenebicyclo[2.1.0]pentane

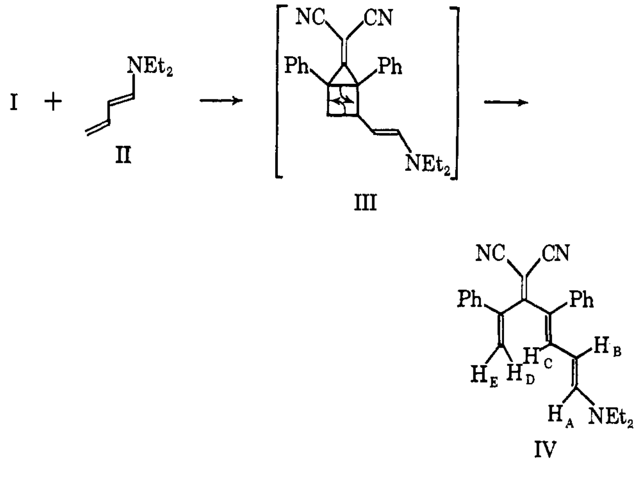
Sir:

Our recent study of the reaction of diphenylcyclopropenone with enamines[1,2] prompted our investigation of the electronically similar triafulvene I.



I

Addition of 1.03 mmoles of freshly distilled 1-diethylamino-1,3-butadiene (II)[3] in 3 ml of anhydrous benzene to 0.928 mmole of 1,2-diphenyl-3-dicyanomethylenecyclopropene (I)[4] in 7 ml of benzene under a nitrogen atmosphere followed by heating at 50–60° for 2 hr produced a deep red color. Dilution with methylene chloride, extraction with aqueous 5% hydrochloric acid and saturated sodium chloride, removal of solvent, and recrystallization from benzene–hexane afforded brilliant orange needles in 82% yield, mp 200.5–201.0°. Structure IV is assigned on the basis of the following data: $\nu_{\max}^{\mathrm{CHCl_3}}$ (cm^{-1}) 2215 (s), 1610 (s), 1555 (m), 1450 (s), 1415 (s), 1350 (m); $\lambda_{\max}^{\mathrm{C_2H_5OH}}$ (mμ) 493 (ϵ 92,500), 247 (13,100), ~290 (5520); nmr ($CDCl_3$) (ppm from TMS) 1.05 (6 H, triplet, J = 7



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[1] J. Ciabattoni and G. A. Berchtold, *J. Am. Chem. Soc.*, 87, 1404 (1965).

[2] J. Ciabattoni and G. A. Berchtold, *J. Org. Chem.*, 31, 1336 (1966).

[3] S. Hünig and H. Kahanek, *Chem. Ber.*, 90, 238 (1957).

[4] (a) S. Andreades, *J. Am. Chem. Soc.*, 87, 3941 (1965); (b) E. D. Bergmann and I. Agranat, *ibid.*, 86, 3587 (1964); (c) Y. Kitahara and M. Funamizu, *Bull. Chem. Soc. Japan*, 37, 1897 (1964).