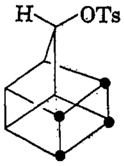
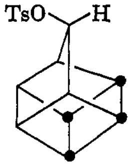
In order to follow the extent of possible rearrangement of the homocubyl ion accompanying solvolysis, the tetradeuterio derivative of homocubanol was prepared in an analogous manner starting with perdeuteriocyclobutadieneiron tricarbonyl.[8] Path a afforded an equal mixture of the two tosylates V and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

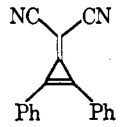
[12] Greater than five shifts are indicated.

[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

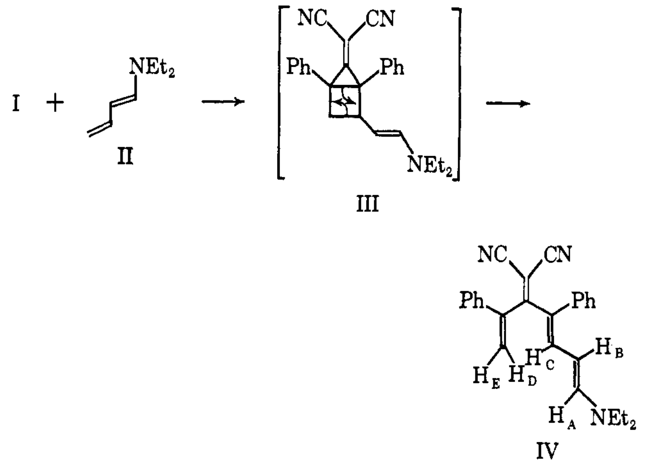
Sir:

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).

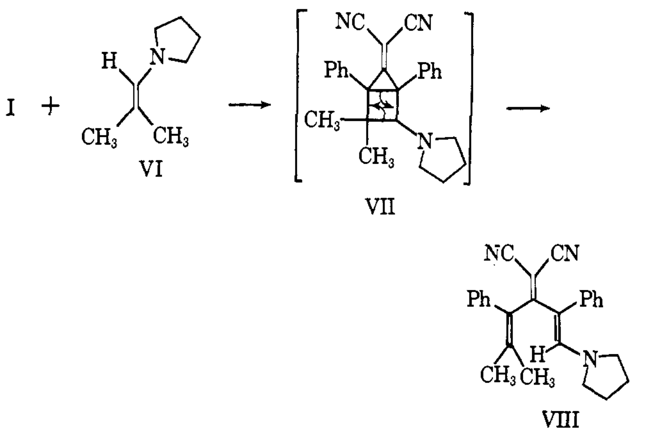
[3] S. Hünig and H. Kahanek, *Chem. Ber.*, **90**, 238 (1957).

[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).

cps), 3.11 (4 H, quartet, J = 7 cps), 4.97 (H_B, triplet, $J_{AB} = J_{BC}$ = 12 cps), 5.43 (H_D or H_E, singlet, J_{DE} = 0), 6.00 (H_E or H_D, singlet, J_{ED} = 0), 6.76 (H_C, doublet, J_{CB} = 12 cps), 7.13–7.60 (11 H, complex multiplet, aromatics and H_A).[5] *Anal.* Calcd for $C_{26}H_{25}N_3$: C, 82.29; H, 6.64; N, 11.07; mol wt, 379. Found: C, 82.41; H, 6.87; N, 11.04; (mass spectrum) *m/e* 379.

Tetraene IV[6] must arise from an initial 1,2 cycloaddition of the 3,4-double bond of II[7] to the endocyclic double bond of I[8] and subsequent ring opening of the bicyclic intermediate III.[9]

Reaction of 0.723 mmole of 1-(N-pyrrolidino)-2-methylpropene (VI) with 0.618 mmole of I in benzene under similar conditions produced triene VIII as yellow plates in 92% yield after similar work-up and recrystallization from benzene–hexane: mp 188–189°; $\nu_{max}^{CHCl_3}$ (cm^{-1}) 2210 (s), 1585 (s), 1455 (s), 1390 (s), 1310 (s); $\lambda_{max}^{C_2H_5OH}$ (mμ) 403 (ϵ 43,300), 236 (15,200), 290 (sh) (3600); nmr (CDCl$_3$) (ppm from TMS) 1.5–1.8 (4 H, –CH$_2$CH$_2$–, multiplet), 1.88 (3 H, CH$_3$–, singlet), 1.98 (3 H, CH$_3$–, singlet), 2.7–3.3 (4 H, –CH$_2$NCH$_2$–, broad singlet), 7.05–7.40 (10 H, multiplet, aromatics), 7.56 (vinyl H, singlet). *Anal.* Calcd for $C_{26}H_{25}N_3$: C, 82.29; H, 6.64; N, 11.07; mol wt, 379. Found: C, 82.29; H, 6.86; N, 11.09; (mass spectrum) *m/e* 379.



The production of compounds IV and VIII necessitates the intermediacy of the substituted 5-methylenebicyclo[2.1.0]pentane derivatives III and VII,[10] respectively. Whether the formation as well as the ring opening of intermediates III and VII proceeds by a concerted or stepwise process is questionable.

Further investigations of these reactions employing other enamines as well as triafulvenes are in progress.

Acknowledgment. We thank the National Institutes of Health (Grant No. GM 14579-01) for generous support of this work.

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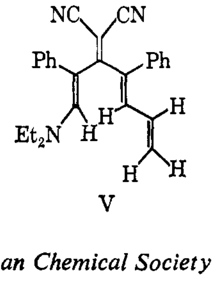
(5) The nmr spectra were recorded with a Varian A-60-A spectrometer. Mass spectral data were recorded on a Hitachi RMU-6D spectrometer. The infrared and ultraviolet data were taken on a Perkin-Elmer Model 337 grating spectrophotometer and a Cary Model 14 spectrophotometer, respectively. The A-60-A and RMU-6D spectrometers were purchased through a National Science Foundation major equipment grant to Brown University.

(6) Examination of Dreiding models reveals that the tetraene probably possesses the more favorable *trans,trans* geometry.

(7) The cycloaddition of sulfene ($CH_2{=}SO_2$) proceeds by initial attack at the 3,4-double bond of 1-dialkylamino-1,3-butadienes [G. Opitz and F. Schweinsberg, *Angew. Chem.*, **77**, 811 (1965); Leo A. Paquette, private communication]. Ketene, on the other hand, undergoes cycloaddition to the 1,2-double bond of 1-(2-ethyl-4-methyl-1,3-pentadien-1-yl)piperidine [R. H. Hasek, P. G. Gott, and J. C. Martin, *J. Org. Chem.*, **31**, 1931 (1966)].

(8) The addition of 1-diethylamino-1,3-butadiene to a dibenzocalicene derivative proceeds in 1,4 manner [H. Prinzbach, U. Fischer, and R. Cruse, *Angew. Chem.*, **78**, 268 (1966)].

(9) The simplicity of the nmr spectrum precludes the alternative possibility of an initial cycloaddition of I to the 1,2-double bond of II to give ultimately, after ring opening, tetraene V.



V

(10) The reaction of 1,2-diphenyl-3-carbethoxymethylenecyclopropene with tetracyanoethylene reportedly proceeds across the exocyclic double bond of the triafulvene to give a spirohexene derivative [M. A. Battiste, *J. Am. Chem. Soc.*, **86**, 942 (1964)]. On the other hand, 1,2-di-*n*-propyl-3-dicyanomethylenecyclopropene fails to react with tetracyanoethylene under similar conditions [A. S. Kende and P. T. Izzo, *ibid.*, **86**, 3587 (1964)].

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Catalysis of Hydrogen Exchange in *m*-Dinitrobenzene[1]

Sir:

In the interaction of aromatic nitro compounds with bases, nuclear hydrogen abstraction is the least well characterized process; the formation of charge-transfer complexes,[2a] of radical anions,[2b] and latterly of Meisenheimer adducts[3] is well substantiated. Due to the contradictory reports[4–10] as to the feasibility and significance of such proton abstraction we have undertaken a systematic study of the process. Further, it was hoped that these studies would also provide information on the nature of the catalysis of aromatic hydrogen abstraction. Whereas general-base catalysis of proton abstraction from aliphatic carbon (eq 1) is well documented,[11a] corresponding evidence for

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(10) Part III of series: E. Buncel and E. A. Symons, *Can. J. Chem.*, **44**, 771 (1966).

(11) R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1959: (a) Chapters 9 and 10; (b) Chapter 4.