Table I. Bond Lengths in Angstroms[a]

a	1.38	i	1.81	Ru(1)–C(1)	2.16
b	1.46	j	1.81	Ru(1)–C(2)	2.18
c	1.42	h	1.19	Ru(1)–C(8)	2.16
d	1.44	l	1.19	Ru(1)–C(3)	2.36
e	1.38			Ru(1)–C(7)	2.58
f	1.47	m	2.947	Ru(2)–C(5)	2.21
g	1.46	m′	2.928	Ru(2)–C(4)	2.30
h	1.42	n	2.782	Ru(2)–C(6)	2.17
				Ru(2)–C(3)	2.92
				Ru(2)–C(7)	2.42

[a] Standard deviations are 0.002 A for Ru–Ru, 0.02 A for Ru–C, and 0.03 A for C–C and C–O bonds.

2.89 A, is significantly larger and the difference between the mean Ru(1)–Ru(2) distance, 2.94 A, and the Ru(2)–Ru(2)′ distance, 2.78 A, is notable. Both these differences may be attributed to an inferior ability of cyclooctatetraene in comparison to CO to remove π antibonding electrons from the metal atom cluster.

The mode of attachment of the rings is essentially the same as that in $(C_8H_8)Fe_2(CO)_5$[5] and (1,3,5,7-tetramethylcyclooctatetraene)$Fe_2(CO)_5$,[6] except for some distortions due to intramolecular repulsions. Thus, of the twelve short Ru–C distances, corresponding to π-allyl to metal bonding, all but the two of the Ru(2)–C(4) type are in the range 2.16–2.21 A, while Ru(2)–C(4) is 2.30 A. Again, of the eight long Ru–C distances, corresponding to the multicenter fractional bonding (to C(3) and C(7)), six are in the range 2.34–2.60 A, while the two of type Ru(2)–C(3) are 2.90 and 2.94 A. Both of these distortions arise from repulsion between the CO group on one Ru(2) atom and the C(3) and C(4) atoms of the ring on the other.

Since $C_8H_8Fe_2(CO)_5$ and its 1,3,5,7-tetramethyl analog are both fluxional molecules,[7,8] it is not surprising that in $(C_8H_8)_2Ru_3(CO)_4$, where there is similar metal–ring bonding, fluxional behavior is observed. It is interesting that this unanticipated type of bonding between two metal atoms and a C_8H_8 ring has now been found in three molecules. It may be noted that there are two other molecules, $C_8H_8Ru_3(CO)_8$ and $(C_8H_8)_3Ru_3$, which might exist in view of the stability of $(C_8H_8)_2Ru_3(CO)_4$; these molecules are being sought by us.

This molecule appears to be the first fluxional molecule in which there are two "independent" rings capable of movement. It raises the question of whether the two rings can move entirely independently or whether the two movements must be correlated.

Finally, the reported structure accounts for the characteristic infrared spectrum in the CO stretching region. In C_2 symmetry four infrared-active normal modes are to be expected, with the one consisting mainly of in-phase stretching of the two CO groups approximately perpendicular to the Ru_3 plane being very weak.[9]

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(5) E. B. Fleischer, A. L. Stone R. B. K. Dewar, J. D. Wright, C. E. Keller, and R. Pettit, *J. Am. Chem. Soc.*, 88, 3158 (1966).

(6) F. A. Cotton and M. D. LaPrade, *ibid.*, in press.

(7) C. E. Keller, G. F. Emerson, and R. Pettit, *ibid.*, 87, 1388 (1965).

(8) F. A. Cotton and A. Musco, *ibid.*, in press.

(9) This work was supported by the National Science Foundation under Grant No. GP 7034X and by the Petroleum Research Fund administered by the American Chemical Society.

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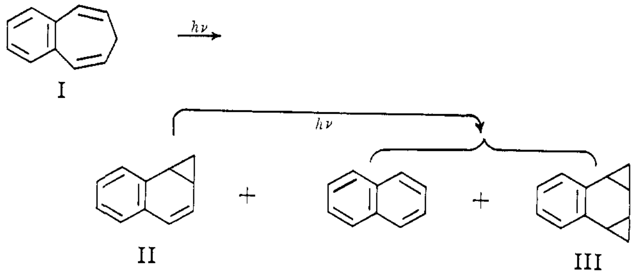
The Photochemical Reorganization of 3,4-Benzotropilidene[1]

Sir:

Our interest in the photochemical behavior of *o*-divinylbenzene[2] led us to examine the photochemistry of 3,4-benzotropilidene (I).[3] Irradiation (100-w G.E. mercury lamp, H100-A4/T; Pyrex filter) of 0.02–0.2% solutions of I in ether led, in rather good yield (70–80%), to benzonorcaradiene (II). Prolonged irradiation produced naphthalene and bismethanonaphthalene (III). The benzonorcaradiene (II) was identified by spectral comparison with authentic material synthesized by the method of Doering,[5] and the naphthalene by comparison of its spectra to those of authentic material. The bismethanonaphthalene (III) was shown to be present by comparing its retention time on three gas chromatography columns with the retention time of authentic material[6] prepared by the reaction of II with methylene iodide and zinc–copper couple.

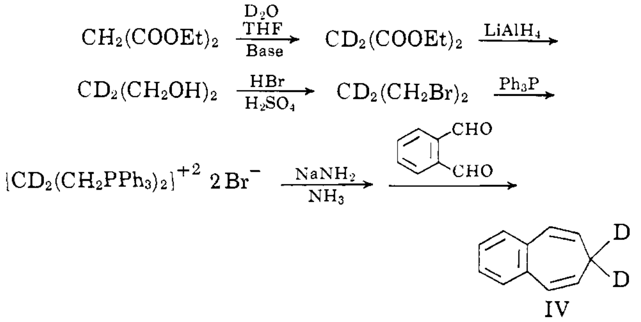


The mechanism for the conversion of II to naphthalene and III is best rationalized by assuming a photolytic cleavage of II into naphthalene and methylene, for which there is much analogy.[7] This hypothesis was borne out by a trapping experiment in which photolysis of II in cyclohexene gave norcarane and naphthalene.

The mechanism of the photoreorganization was studied by first synthesizing 7,7-dideuterio-3,4-benzotropilidene (IV) by the route shown in Scheme I. Product IV was shown by nmr analysis to contain about 80–83% of two deuterons in the 7 position. It also showed an AB pattern (J = 10 Hz) for the vinyl protons at τ 3.5 and 4.4 ppm.

In order to locate the deuterons in photoproduct II

Scheme I



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(1) Presented in part at the 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967, Abstract S25.

(2) M. Pomerantz, *J. Am. Chem. Soc.*, **89**, 694 (1967).

(3) 3,4-Benzotropilidene was prepared by the method of Wittig.[4]

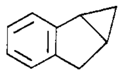
(4) G. Wittig, H. Eggers, and P. Duffner, *Ann.*, **619**, 10 (1958).

(5) W. von E. Doering and M. J. Goldstein, *Tetrahedron*, **5**, 53 (1959).

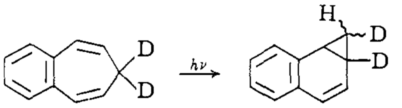
(6) E. Müller, H. Fricke, and H. Kessler, *Tetrahedron Letters*, 1525 (1964).

(7) See, *e.g.*, D. B. Richardson, L. R. Darrett, J. M. Martin, Jr., W. E. Putnam, S. C. Slaymaker, and I. Dvoretsky, *J. Am. Chem. Soc.*, **87**, 2763 (1965).

it was necessary to know the nmr chemical shifts of the aliphatic (and vinyl) protons of II. The assignments have been made previously[8] and we have confirmed this by spin decoupling along with the observation that one of the cyclopropyl CH_2 protons shows a coupling constant of $\sim$8 Hz with the vicinal protons (the other coupling constants being 3–4 Hz), which means it must be *cis* to these hydrogens,[9] and therefore *exo*. In addition the nmr spectrum of the CH_2 group is very similar to that of V.[2] The *endo*-cyclopropyl CH_2 hydrogen appears at τ 10.4 ppm, the *exo*-cyclopropyl CH_2 hydrogen at 8.6 ppm, the benzylic cyclopropyl hydrogen at 7.7 ppm, the remaining, allylic, cyclopropyl hydrogen at 8.2 ppm, the vinyl hydrogens at 3.8 ppm, and the aromatic hydrogens at 2.9 ppm.

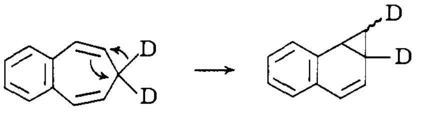

V

With these assignments the product of the photolysis of IV was shown to be VI, with 50% of the deuterium *endo* and 50% *exo* on the methylene group of the three-membered ring. Vogel[8] has demonstrated that flipping of the three-membered ring occurs with an activation energy of 19.4 kcal/mole, which means that at 0 to $-5°$ the half-life of this reaction might be long enough to observe differences in the deuterium *exo*:*endo* ratio if a stereospecific hydrogen shift mechanism obtains. The photolysis at this temperature (including work-up) gave the same 50:50 mixture of *exo*- and *endo*-deuterium and thus the reaction is either nonspecific or the ring is still flipping too fast at this temperature.

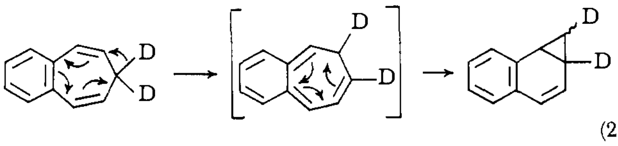


IV VI

The deuterium-labeling experiment thus conclusively proves that a hydrogen shift mechanism is operative. Two mechanisms, which are subtly different, can now be postulated. They are (1) hydrogen shift with concurrent formation of a three-membered ring or (2) hydrogen shift with formation of a product with a rearranged π system followed by rapid valence tautomerization of the first-formed tropilidene to a norcaradiene.

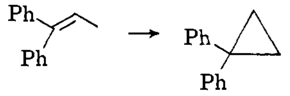


(1)

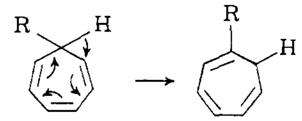


(2)

There is one authentic analogy for the first mechanism in the literature[10] and that involves the rearrangement of 1,1-diphenyl-1-propene (VII) to 1,1-diphenylcyclopropane (VIII), among other products. There are a number of analogies for the second mechanism in the 7-substituted tropilidene series.[11] Photorearrangement of many compounds of this type gives, among the products, the tropilidene having undergone a 1,2-hydrogen shift, presumably by the following mechanism.



VII VIII



One cannot, however, rule out a mechanism analogous to (1) for these rearrangements.

It should also be pointed out that the photochemistry of I differs markedly from the closely related compound *o*-divinylbenzene, which gives V upon irradiation.[2,12] The difference may be due to one or both of two factors. First, the rigidity of I precludes (except perhaps as reactive intermediates) conformations allowed for *o*-divinylbenzene; second, hydrogen shift in the latter compound is of course impossible. One therefore does not known which of these reactions would be the most favorable for a compound having no restrictions on any of these pathways.

The following communication describes the photochemical reorganization of 1,2-benzotropilidene and its relationship to the 3,4-benzotropilidene rearrangement.[13]

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[8] E. Vogel, D. Wendish, and W. R. Roth, *Angew. Chem. Intern. Ed. Engl.*, 3, 442 (1964).

[9] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Pergamon Press, New York, N. Y., 1966, p 695.

[10] G. W. Griffin, A. F. Marcantonio, H. Kristinsson, R. C. Pettersen, and C. S. Irving, *Tetrahedron Letters*, 2951 (1965).

[11] See, *e.g.*, G. J. Fonken, "Organic Photochemistry," Vol. 1, Marcel Dekker, Inc., New York, N. Y., 1967, pp 231–232; T. Mukai, H. Kubota, and T. Toda, *Tetrahedron Letters*, 3581 (1967).

[12] J. Meinwald and P. H. Mazzocchi, *J. Am. Chem. Soc.*, 89, 695 (1967).

[13] M. Pomerantz and G. W. Gruber, *ibid.*, 89, 6799 (1967).

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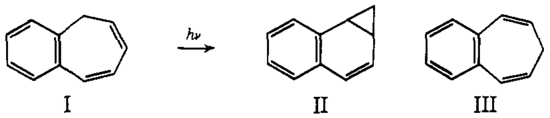
The Photochemical Reorganization of 1,2-Benzotropilidene

Sir:

1,2-Benzotropilidene (I) has been shown to rearrange photochemically (100-w G.E. mercury lamp; Pyrex filter) to benzonorcaradiene (II), the same product one obtains from the photochemical reorganization of 3,4-benzotropilidene (III).[1] In addition, one sees the results of further photorearrangement of II, as indicated in the previous paper.[1] With the knowledge that both I and III give the same product (II) on irradiation, the first questions to be answered are: is there a photoequilibrium between I and III (by, presumably, a 1,3-hydrogen shift) and is only one of these rearranging



I II III

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[1] M. Pomerantz and G. W. Gruber, *J. Am. Chem. Soc.*, 89, 6798 (1967).