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THERMAL REORGANIZATIONS OF 3,4-BENZOTROPILIDENE (1)

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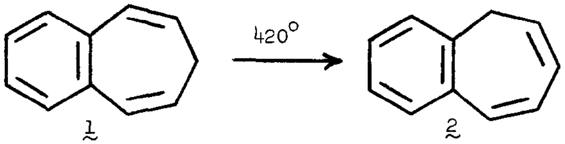
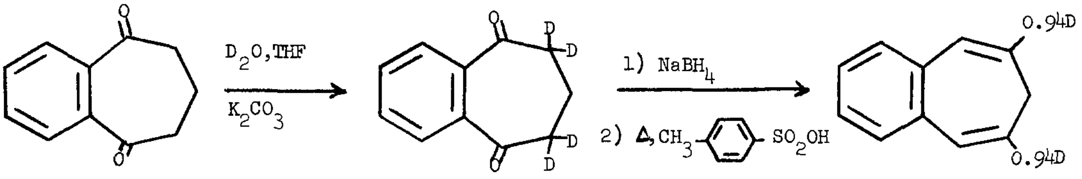
Our interest in the thermal reorganization of $C_{11}H_{10}$ hydrocarbons containing a fused benzo-ring (4,5) prompted a study of 3,4-benzotropilidene (1). When 1 was heated at 420° for 40 minutes (50 ml. Pyrex ampoule; gas phase) the major product was 1,2-benzotropilidene (2) along with lesser amounts of the pyrolysis products of 2 (6).



1 2

The mechanism of this rearrangement was probed by preparing the deuterated molecule, 3, by the sequence of reactions shown in Scheme I, starting from the diketone 4 (8). Analysis of 3 was by nmr and mass spectroscopy and showed 94% of two deuterons in the non-benzylic vinyl positions (9).

Scheme I



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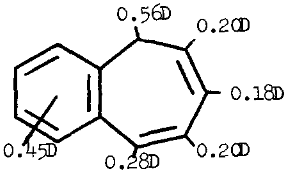
When 3 was pyrolized at 413° for 30 min. the 1,2-benzotropilidene formed (5) had the indicated deuterium labeling pattern as determined by nmr spectroscopy.



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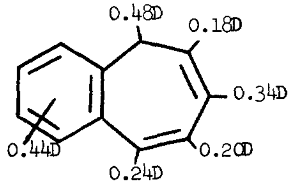

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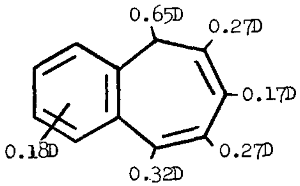

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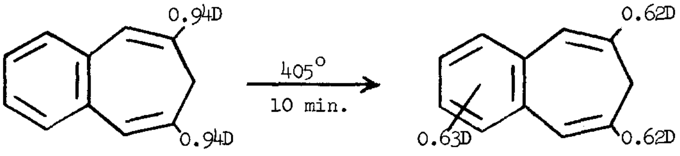
Two additional runs, one at 408° for 15 min. and the other at 659° for _ca._ 2 sec. (flow system, nitrogen carrier gas), gave the deuterated benzotropilidenes 6 and 7 respectively.

Before rationalizing the observed labeling patterns it was necessary to run the rearrangement to partial completion and determine whether the starting material had scrambled the label. When 3 was heated at 405° for 10 minutes (36% conversion) and reisolated the labeling was as indicated in 8. Deuterium had "migrated" from the original vinyl positions to the aromatic ring. A reasonable explanation would involve a 1,5-hydrogen shift (4) and a tropilidene-norcaradiene equilibration as indicated in Scheme II. Intermediates 9 and 10 might also be precursors for 1,2-benzotropilidene and can account for the appearance of deuterium in the 3,4,6,7 and aromatic positions (Scheme III; 4).



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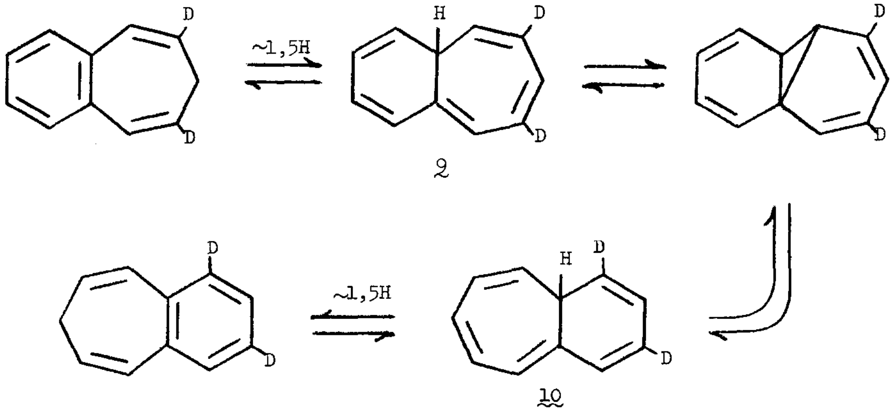
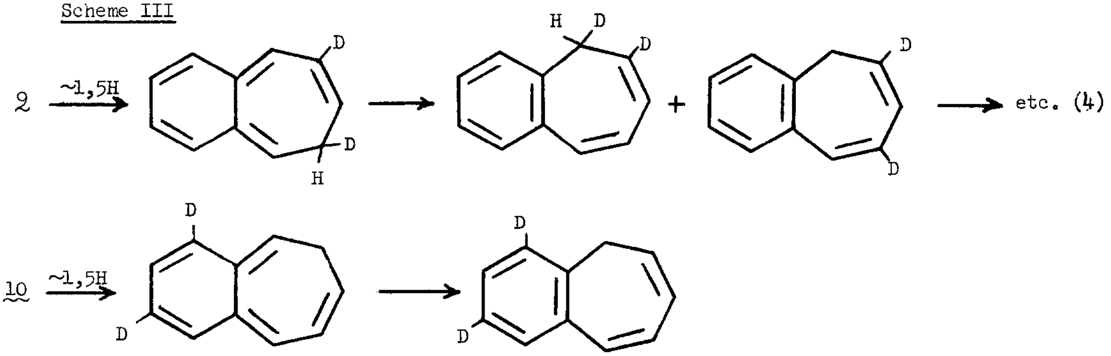
Scheme II

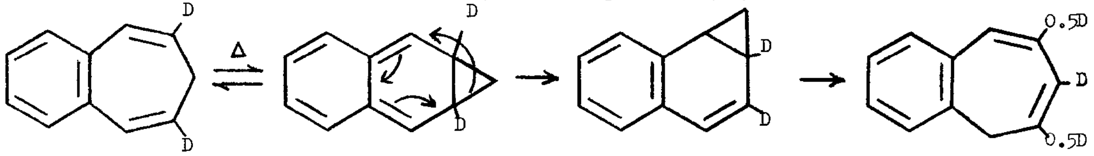


Scheme III



An alternative, less plausible, mechanism for deuterium scrambling in 3 would involve elimination-readdition of methylene. Any free methylene would be expected to add to the much more abundant and reactive C_{11} hydrocarbons than naphthalene, however no C_{12} products could be detected (10).

The mechanistic details of 1,2-benzotropilidene formation are, of course, complicated by deuterium scrambling in the starting material. Also 3 (and 1) is prone to catalyzed rearrangement as evidenced by the production of 1,2-benzotropilidene with deuterium in positions 4 and 6 on some gas chromatography columns at temperatures around 200°. In spite of these complications at least one conclusion can be reached with respect to the formation of 2 from 1 (or of 5,6, and 7 from 3). In the previously studied rearrangements of 1,2-benzotropilidene position 5 was never seen to equilibrate with any of the other hydrogens (4). (Under the reaction conditions positions 3,4,6 and 7 equilibrate; 4). We have also shown that the catalyzed rearrangement of 1 to 2 is not reversible (i.e. the rearrangemnt of 2 to 1 is not surface catalyzed; 4) and therefore is ruled out as a pathway for placing deuterium in position 5 in 5, 6 and 7. These observations (and those mentioned previously) argue for a Berson-Willcott skeletal rearrangement (12; eqn 1) for placing deuterium into the 5-position of 1,2-benzotropilidene (13).



(1)

The difference in labeling of 5,6 and 7 in the three pyrolysis runs is probably due to a combination of many factors. We will, however, not speculate at this time on these results.

REFERENCES

1. This work is taken from the Dissertation of Gerald W. Gruber submitted in partial fulfillment of the requirements for the Degree of Doctor of Philosophy to Case Western Reserve University, 1970.
2. Texaco Corporation Fellow, 1968-9.
3. Author to whom correspondence concerning this work should be sent at Yeshiva University.
4. M. Pomerantz and G.W. Gruber, *J. Org. Chem.*, **33**, 4501 (1968).
5. M. Pomerantz, G.W. Gruber and P.M. Hartman, *Trans. N.Y. Acad. Sci.*, **30**, 1052 (1968).
6. While the pyrolysis products of **2** have been reported to be α- and β-methylnaphthalene (7), the situation is considerably more complex. M. Pomerantz and G.W. Gruber, results to be published.
7. S.J. Cristol and R. Caple, *J. Org. Chem.*, **31**, 585 (1966).
8. A.M. Kahn, G.R. Proctor and L. Rees, *J. Chem. Soc.*, 990 (1966).
9. The nmr spectrum of **1** shows, in addition to four aromatic hydrogens (τ 2.88), a doublet (J=10.5Hz, τ3.5) due to the benzylic vinyl hydrogen, a doublet of triplets (J=10.5Hz and 6.5Hz) at τ4.4 due to the non-benzylic vinyl hydrogens and a triplet at τ7.55 (J=6.5Hz) for the allylic hydrogens.
10. The observation that *ca.* 33% of the label in **3** rearranges while 36% of 1,2-benzotropilidene is formed is inconsistent with methylene extrusion-readdition since it is known that the 1,2-bond in naphthalene is the most reactive toward methylene (11). This would produce mainly benzonorcaradiene which would rapidly give 1,2-benzotropilidene (4).
11. W. von E. Doering and M.J. Goldstein, *Tetrahedron*, **5**, 53 (1959); E. Müller, H. Fricke and H. Kessler, *Tetrahedron Lett.*, 1525 (1964).
12. J.A. Berson and M.R. Willcott, III, *J. Amer. Chem. Soc.*, **88**, 2494 (1966); J.A. Berson, *Accounts Chem. Res.*, **1**, 152 (1968); see also: G.W. Gruber and M. Pomerantz, *J. Amer. Chem. Soc.*, **91**, 4004 (1969).
13. Here, as in the previous case, methylene extrusion-readdition is a possibility but is made less likely by the observation that there is only a small amount of naphthalene produced [which can be accounted for by pyrolysis of **2**(6)] and no detectable C_{12} products. Since these are gas phase reactions one would not expect "cage" effects and hence there should be larger amounts of naphthalene than are actually observed.