Thermal Rearrangements of Benzonorcaradiene, Benzonorbornadiene, and 1,2-Benzotropilidene

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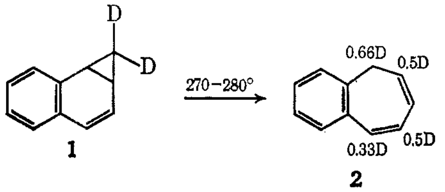
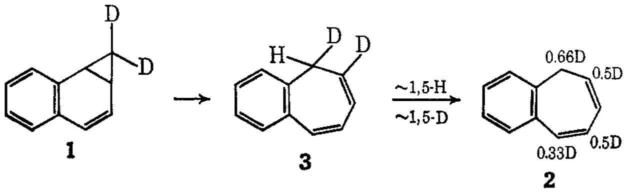
The thermal rearrangement reactions of 7,7-dideuteriobenzonorcaradiene (**1**), 5,6-dideuterio-2,3-benzonorbornadiene (**7**), and 3,5,7,7-tetradeuterio-1,2-benzotropilidene (**11**) have been studied. Pyrolysis of **1** produced 1,2-benzotropilidene with 0.33, 0.5, 0.5, and 0.66 deuteron in positions 3, 4, 6, and 7, respectively, presumably *via* either a 1,2- or a 1,5-hydrogen shift mechanism. Pyrolysis of **7** gave 1,2-benzotropilidene with, initially, 0.5, 1, and 0.5 deuteron in positions 4, 5, and 6, respectively, ruling out 6,7-benzobicyclo[3.2.0]hept-2,6-diene as a possible intermediate. Further thermal rearrangement of **7** or **11** showed that positions 3, 4, 6, and 7 completely equilibrated their hydrogens. Three mechanisms are postulated for this rearrangement; 1,2- and/or 1,5-hydrogen shift or methylene group rearrangement. In all of these thermal reorganizations 1,5-hydrogen shift, between positions 3 and 7, occurs very rapidly, even below 250°.

During the course of our study of the photochemical rearrangements of 1,2-benzotropilidene and 3,4-benzotropilidene,[1] we required a specifically deuterated 1,2-benzotropilidene to rule out a possible mechanistic pathway. We therefore looked at the known thermal rearrangements of benzonorcaradiene[2] and benzonorbornadiene[3] to 1,2-benzotropilidene.

7,7-Dideuteriobenzonorcaradiene (**1**)[4] was prepared by Doering's method of the photolysis of dideuteriodiazomethane[5] in the presence of naphthalene.[6] Upon heating **1** at 270–280° (gas phase) for 1 hr, 1,2-benzotropilidene was formed with deuterium labeling as shown in structure **2**. In addition, partial rearrangement at 260° gave **2** with the same deuterium labeling, while recovered **1** showed no scrambling. Therefore **2** is the first observable product. The location of deuterium in the product (**2**) was accomplished by nmr spectroscopy after assigning the various absorptions in 1,2-benzotropilidene. The doublet (J = 6 Hz) at τ 7.05 ppm was assigned to the methylene hydrogens, at the 7 position. Spin decoupling of the methylene hydrogens indicated that the hydrogen at the 6 position (to which the methylene hydrogens were coupled) was at τ 4.3 ppm. The aromatic hydrogens appeared at τ 2.9 ppm and partially obscured the peaks at τ 3.05 ppm. This latter absorption was shown, by spin decoupling, to be coupled only to the hydrogen at τ 3.55 ppm. Therefore, the peak at τ 3.05 ppm must be due to the hydrogen at position 3 and the one at τ 3.55 ppm is due to the hydrogen at position 4. The additional hydrogen, at the 5 position, appears at τ 3.9 ppm. This result is completely consistent with the nmr spectrum of what was proven previously to be 3,5,7,7-tetradeuterio-1,2-benzotropilidene.[1]

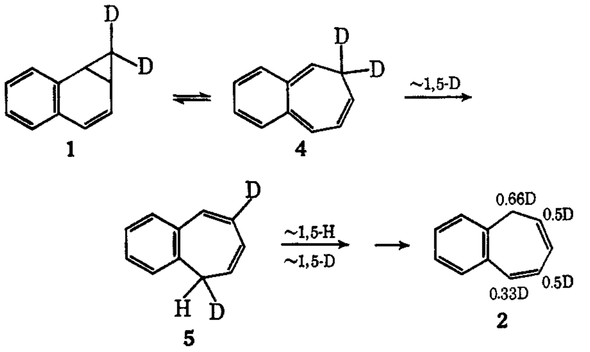


Two possible mechanisms can be formulated to account for the observed labeling pattern. First is a cyclopropane to propylene, 1,2-hydrogen migration to produce **3** (eq 1) followed by a series of rapid 1,5-hydrogen shifts (between positions 3 and 7). Such 1,5-hydrogen shifts are known to be quite rapid at these temperatures. With tropilidene itself the activation energy for this shift is 31 kcal/mol and with 7-phenyltropilidene it is 27 kcal/mol; the reaction therefore occurs very fast at temperatures below 150°.[7]



(1)

The alternative mechanism is valence tautomerization of **1** to produce **4**, followed by 1,5-hydrogen shift to give **5**. This in turn would undergo the rapid 1,5-hydrogen shifts already discussed with the production of the observed product, **2** (eq 2).



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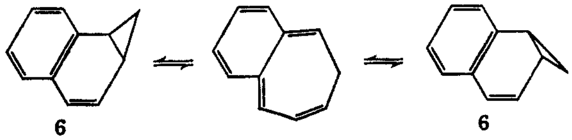
The intermediate **4** (without the deuterium atoms) has been previously implicated in the "ring-flipping" of benzonorcaradiene (eq 3) by Vogel. This reaction



(3)

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[1] M. Pomerantz and G. W. Gruber, *J. Amer. Chem. Soc.*, **89**, 6798, 6799 1967).

[2] E. Müller, H. Fricke, and H. Kessler, *Tetrahedron Lett.*, 1525 (1964).

[3] R. K. Hill and R. M. Carlson, *J. Org. Chem.*, **30**, 2414 (1965); S. J. Cristol and R. Caple, *ibid.*, **31**, 585 (1966).

[4] The deuterons here shown to be in the 7 position by nmr spectroscopy.

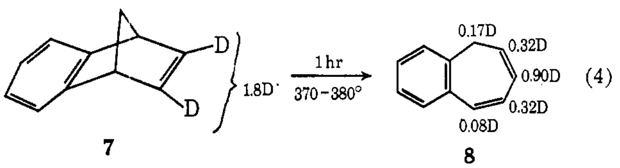
[5] W. von E. Doering and P. P. Gaspar, *J. Amer. Chem. Soc.*, **85**, 3043 (1963).

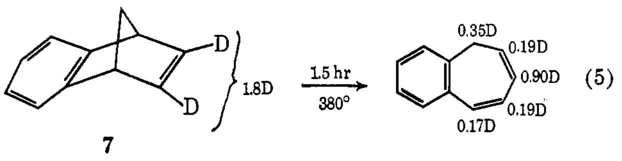
[6] W. von E. Doering and M. J. Goldstein, *Tetrahedron*, **5**, 53 (1959).

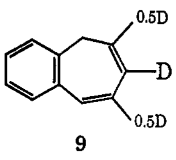
[7] A. P. ter Borg, H. Kloosterziel, and N. Van Meurs, *Proc. Chem. Soc.*, 359 (1962).

occurs quite readily at low temperatures with an activation energy of 19.4 kcal/mol.[8] It should also be pointed out that phenylcyclopropane, a compound analogous to benzonorcaradiene, undergoes thermal ring opening very much more slowly than **6** and apparently not by a cyclopropane to propylene rearrangement. The major products here were shown to be *n*-propylbenzene and 2-phenyl-1-propene and were postulated to arise by a free-radical pathway.[9] It is therefore tempting to speculate that the second mechanism (eq 2) is more reasonable, but a clear-cut choice cannot at present be made.

As a second approach to a suitable deuterated 1,2-benzotropilidene we examined the thermal rearrangement of 5,6-dideuterio-2,3-benzonorbornadiene (**7**). The starting deuterated compound (**7**) was prepared by a series of metalations of benzonorbornadiene with *n*-butylsodium followed by quenching of the vinyl carbanion with D_2O.[10] Six such reactions gave **7** with 1.8 deuterons in the vinyl positions and 0.2 deuteron in the benzene ring. Pyrolysis of this compound at 370–380° for $\sim$1 hr resulted in 85% conversion into **8** with the labeling as indicated (eq 4). In addition, the recovered starting material (**7**) had not scrambled any deuterium. When the reaction was allowed to proceed for 1.5 hr at 380° there was essentially total scrambling among positions 3, 4, 6, and 7 as indicated (eq 5). Therefore compound **9** is the first-formed product and this subsequently goes on to scramble deuterium. While the results of these labeling experiments are not unique for one particular mechanism, they do serve to rule out 6,7-benzobicyclo[3.2.0]hepta-2,6-diene as an intermediate.[11] As shown in eq 6, the anticipated product from such a pathway would have been **10** and not **9**.







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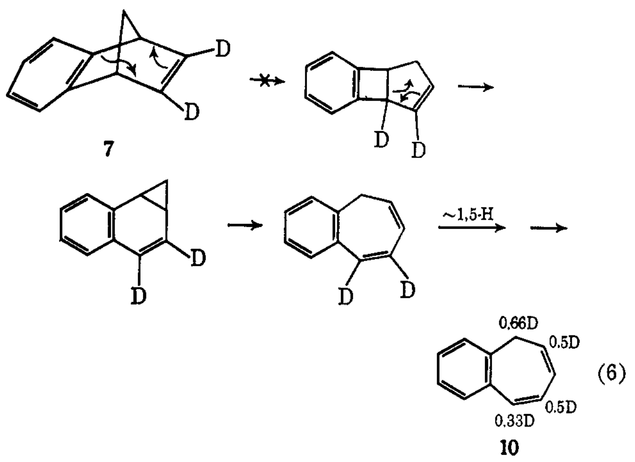
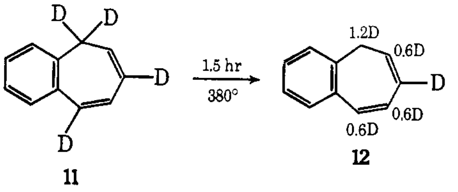


The apparent 1,2 shift of hydrogen in compound **9** (and **8**) is rather interesting. Exactly the same phenomenon was observed in the pyrolysis of 3,5,7,7-tetradeuterio-1,2-benzotropilidene (**11**).[1] Heating **11** at 380° for 1.5 hr resulted in the scrambling of deuterium among positions 3, 4, 6, and 7 to give **12**.



Three mechanisms can be postulated for these hydrogen rearrangements. First is a simple propylene to cyclopropane ring closure with 1,2-hydrogen migration followed by rapid rearrangement by the known benzonorcaradiene to 1,2-benzotropilidene reaction (*vida supra*) to give a partially scrambled 1,2-benzotropilidene (**13**). This would then undergo a series of rapid 1,5-hydrogen shifts and additional propylene to cyclopropane ring closures and reversals to give, finally, the

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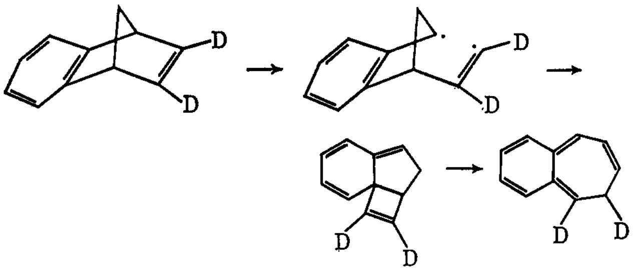
[8] E. Vogel, D. Wendisch, and W. R. Roth, *Angew. Chem. Intern. Ed. Engl.*, **3**, 442 (1964).

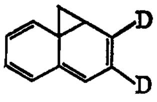
[9] P. A. Leermakers and M. E. Ross, *J. Org. Chem.*, **31**, 301 (1966).

[10] T. Goto, A. Tatematsu, Y. Hata, R. Muneyuki, H. Tanida, and K. Tori, *Tetrahedron*, **22**, 2213 (1966).

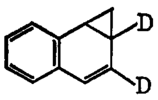
[11] A referee has pointed out that these results also rule out the following possible mechanism.



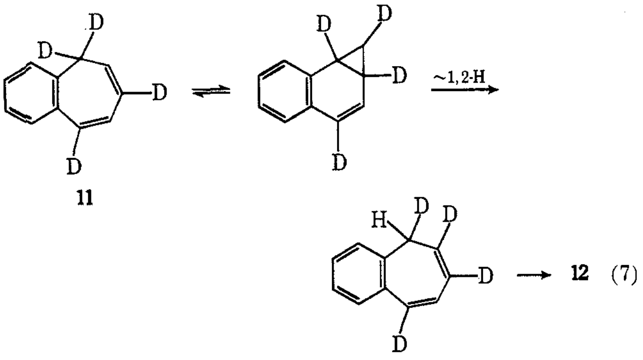
However, at least two additional mechanisms are allowed by our data: cleavage of the 1,7 bond followed by reclosure at either position 3 or position 5 to produce i or ii, respectively. These processes might be diradical or concerted, but in either case these intermediates would lead to the 1,2-benzotropilidene with the deuterium labeling that we have observed. Experiments to distinguish between these possibilities are in progress.



i



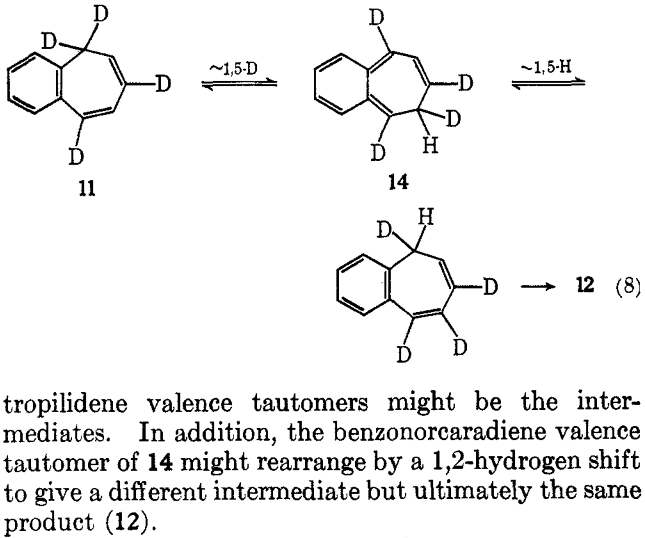
ii



11 **13**

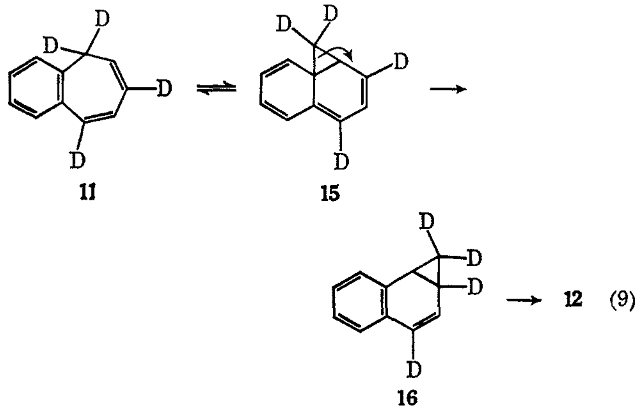
observed product (**12** in the case of **11**, eq 7). It should be pointed out that the deuterium distribution in **13** might be different depending upon the exact mechanism of the benzonorcaradiene to 1,2-benzotropilidene rearrangement; the end product, however, would still be the same (**12**). Also, rather than, or in addition to, structures such as benzonorcaradiene it is possible that their valence tautomers are the intermediates.

The second mechanism involves 1,5-hydrogen shifts as indicated in eq 8. Once again, norcaradiene or tropilidene valence tautomers might be the intermediates. In addition, the benzonorcaradiene valence tautomer of **14** might rearrange by a 1,2-hydrogen shift to give a different intermediate but ultimately the same product (**12**).



11 **14**

The third alternative involves the valence tautomer of **11** (**15**) rearranging, in a reaction similar to that discovered by Berson and Willcott[12] to **16** which, by pathways previously discussed, would yield the observed product (eq 9). The reverse reaction, **16** → **11**, has already been ruled out. A similar mechanism has been proposed for the thermal rearrangement of 1,6-methano[10]annulene to 1,2-benzotropilidene.[13] A choice between these three alternatives cannot be made at present.



11 **15** **16**

It should also be pointed out that the three thermal reorganization reactions discussed were run with and without powdered Pyrex present. In all cases the extent of reaction for a particular rearrangement and for a given reaction time was the same with and without the glass. The reactions, therefore, are not surface catalyzed.

Experimental Section

7,7-Dideuteriobenzonorcaradiene (1).[5,6]—To a mixture of 95 g of naphthalene in 300 ml of benzene and 45 ml of 40% KOH solution, in an erlenmeyer flask cooled in ice, was added slowly, with magnetic stirring, 15 g of N-methyl-N-nitrosourea. The diazomethane solution was decanted onto KOH pellets and the aqueous layer extracted with an additional 50 ml of benzene. After the combined organic solution was dried over solid KOH (ice bath, 20 min), it was treated with 85 ml of 20% KOD in D_2O, while stirring (ice bath) for 7 hr. This solution was then irradiated (100-W GE Hg lamp; Pyrex filter) for 4.5 hr and filtered and the benzene distilled through a 30-cm Heli-pak column until *ca.* 150 ml remained. Crystallization afforded a solid which was filtered and washed with cold pentane. The combined mother liquor and pentane solution was distilled through a 30-cm Heli-pak column until *ca.* 40 ml remained. Crystallization afforded additional solid which was filtered and washed with cold pentane. The mother liquor and the pentane solution were combined and the concentration–crystallization procedure was repeated four additional times. At this point the mother liquor (*ca.* 2 ml) contained about 40–50% of 7,7-dideuteriobenzonorcaradiene. Further purification was by vlpc (2 m × 0.25 in., 15% triisodecyl trimellitate on 60–80 mesh Chromosorb P column). Nmr analysis indicated 82% deuteration of the cyclopropylmethylene hydrogens.

5,6-Dideuterio-2,3-benzonorbornadiene (7).[10]—In a 500-ml three-necked flask equipped with a mechanical stirrer, reflux condenser, nitrogen inlet and a dropping funnel was placed 6 g (0.26 g-atom) of dispersed sodium and 300 ml of pentane. To this was added 12 g (0.13 mol) of *n*-butyl chloride at 0° with rapid stirring, followed by 9 g (0.063 mol) of benzonorbornadiene.[14] The resulting slurry was refluxed for 8 hr, cooled, cautiously quenched with 25 ml of deuterium oxide, refluxed for 30 min, and further diluted with 100 ml of water. After separation, the aqueous layer was extracted five times with 100-ml portions of ether. The combined organic material was dried ($MgSO_4$) and concentrated to *ca.* 40 ml. This was then allowed to react, as above, with butylsodium and the procedure repeated an additional five times. The resulting solution was fractionally distilled through a 6-in. Vigreux column, pure **7** (3.5 g, 39%) being collected at 30–31° (0.2 mm). Nmr analysis indicated 90% two vinyl deuterons and 5% four aromatic deuterons.

3,5,7,7-Tetradeuterio-1,2-benzotropilidene (11).—In a 15-ml test tube was placed 1 ml of *t*-butyl alcohol-O-*d* and enough potassium to make a saturated solution of potassium *t*-butoxide. To this was added 800 μl of DMSO-d_6 and *ca.* 250 μl of 1,2- (or 3,4-) benzotropilidene.[3,15] The resulting solution was allowed to stand at room temperature for 8 hr before being quenched with 2 ml of water and extracted three times with 3-ml portions of pentane. The combined pentane solution was dried ($MgSO_4$) and concentrated to *ca.* 500 μl under a stream of nitrogen. Pure **11** was obtained by preparative vlpc.[16]

In addition to four aromatic hydrogens (τ 2.9 ppm) the nmr spectrum showed two broad singlets (τ 3.55 ppm, 1 H, and τ 4.3 ppm, 1 H) as well as a trace (*ca.* 3% 2 H) absorption at τ

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[12] J. A. Berson and M. R. Willcott, III, *Rec. Chem. Progr.*, **27**, 139 (1966); *J. Amer. Chem. Soc.*, **88**, 2494 (1966); J. A. Berson, *Accounts Chem. Research*, **1**, 152 (1968).

[13] V. Rautenstrauch, H. J. Scholl, and E. Vogel, *Angew. Chem. Intern. Ed. Engl.*, **7**, 288 (1968).

[14] We wish to thank Professor L. Friedman and Mr. D. Smith for a generous gift of benzonorbornadiene.

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

[16] An 8 ft × 0.25 in. 20% Carbowax 20M on 45/60 mesh Chromosorb P column at 160° was employed.

7.05 ppm confirming the presence of a dideuteriomethylene moiety.

Pyrolysis of 7,7-Dideuteriobenzonorcaradiene (1).—In a partial rearrangement reaction 100 μl of 1 was sealed in an evacuated 50-ml Pyrex vessel, heated at 260–270° for 2 hr (40% rearrangement), and cooled; it was then opened. Preparative vlpc[16] afforded a pure sample of **2**. Nmr analysis provided this ratio for the hydrogens at positions 3–7, respectively: 0.73:0.59:1.0:0.59:1.46. In the same reaction, recovery of unreacted 1 allowed an nmr demonstration that no deuterium scrambling occurred in the starting material.

Pyrolysis of 5,6-Dideuterio-2,3-benzonorbornadiene (7).—In typical reactions to completion, 100–200 mg of **7** was sealed in an evacuated 50-ml glass vessel and heated at 370–390° for 50–70 min. Nmr data were in some cases obtained directly from the crude reaction mixture. Alternatively, purification was achieved by preparative vlpc.[16] In either case, nmr analysis showed that the ratio of hydrogens at positions 3–7, respectively, was 0.83:0.81:0.10:0.81:1.65.

A partial completion reaction (375°, 30 min, 70% rearrangement) showed that deuterium scrambling into positions 3 and 7 lagged considerably behind rearrangement. The ratio of hydrogens at positions 3–7, respectively, was 0.94:0.65:0.10:0.64:1.87. Starting material recovered from this reaction was shown by nmr analysis to have undergone no deuterium scrambling.

Pyrolysis of 3,5,7,7-Tetradeuterio-1,2-benzotropilidene (11).—In a typical run, 30 μl of **11** was sealed in an evacuated 50-ml glass vessel and heated at 380–400° for 80 min. The vessel was then cooled and opened. Pure 1,2-benzotropilidene-d_4 was then obtained by preparative vlpc.[16] An nmr spectrum (CCl_4 solution) afforded the following protium ratio for positions 3–7, respectively: 0.40:0.40:0.03:0.40:0.80.

Surface Catalysis Experiments.—Samples of **1**, **7**, and **11** were partially pyrolyzed in the presence of powdered glass, simultaneously with samples without added glass. Gas chromatography revealed that the ratio of reactant to product in the pyrolysis of **1** and **7** was the same with and without the powdered glass. Preparative vlpc[16] afforded pure samples in each case, which by nmr analysis were shown to have scrambled, within experimental error, the same amount of deuterium (Table I).

Table I

Compound	Temp, °C	Time, min	Extent of reaction, %	1,2-Benzotropilidene nmr ratios by position 3	4	5	6	7
1[a]	400	5	80	0.69	0.65	1.0	0.65	1.38
1 + powdered glass[a]	400	5	80	0.68	0.66	1.0	0.68	1.36
7	400	14	89	0.87	0.75	0.1	0.75	1.74
7 + powdered glass	400	14	87	0.87	0.75	0.1	0.75	1.74
11	380–400	20		0.10	0.85	0.0	0.85	0.20
11 + powdered glass	380–400	20		0.11	0.83	0.0	0.83	0.22

[a] Since these reactions were run at 400° partial equilibration of positions 4 and 6 with 3 and 7 occurred by the same mechanism which accounts for deuterium scrambling observed in **7** and **11**.

Registry Nos.—**1**, 17790-63-5; **7**, 17818-07-4; **11**, 17790-64-6; benzonorcaradiene, 3463-79-4; benzonorbornadiene, 4453-90-1; 1,2-benzotropilidene, 264-08-4.

Retro Diels–Alder Reactions. IV.[1]

Kinetics of the Thermal Decomposition of Bornylene and the Thermal Rearrangement of 1,5,5-Trimethylcyclopentadiene[2]

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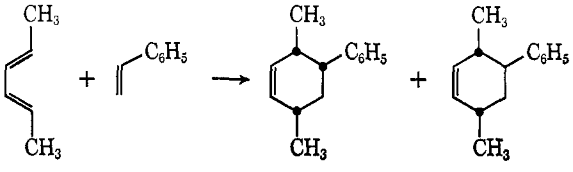
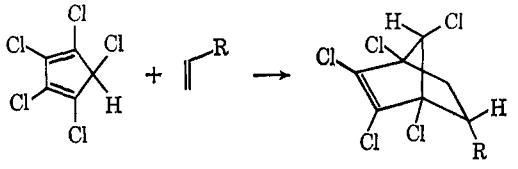
The temperature dependence of the gas phase rate of decomposition of bornylene to produce 1,5,5-trimethylcyclopentadiene and ethylene has been determined. The rate equation for this homogeneous first-order reaction is $\log k = 14.1 - (46{,}000/2.3RT)$. Comparisons are made with other retro Diels–Alder reactions, and the results are considered to support a concerted cycloaddition mechanism. The thermal rearrangement of 1,5,5-trimethylcyclopentadiene is interpreted as involving a rate-determining 1,5-sigmatropic methyl shift. This reaction is also first order and homogeneous; the rate equation is $\log k = 13.7 - (45{,}100/2.3RT)$.

Over 30 years have elapsed since the classic paper by Alder and Stein on the mechanism of the Diels–Alder reaction.[5] Hundreds of Diels–Alder reactions have been carried out in the laboratory since that time; yet the precise details of the mechanism are still obscure, and the lack of detail still continues to beguile the organic chemist.

One of the perplexing features is the effect of substituent groups on the course of the reaction. The specific problem that we refer to is evident in two recently reported investigations. Korver, *et al.*,[6] found that the reaction of styrene with *trans,trans*-2,4-hexadiene (eq 1) gave the all-*cis* adduct **1** and the *trans* adduct **2** in an 8:5 ratio, respectively, and Williamson, *et al.*,[7] reported that pentachlorocyclopentadiene undergoes reactions with various dienophiles (eq 2), in most cases



1 **2** (1)



3 (2)

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[1] Previous papers: (a) W. C. Herndon and L. L. Lowry, *J. Amer. Chem. Soc.*, **86**, 1922 (1964); (b) W. C. Herndon, W. B. Cooper, and M. J. Chambers, *J. Phys. Chem.*, **68**, 2016 (1964); (c) W. C. Herndon, C. R. Grayson, and J. M. Manion, *J. Org. Chem.*, **32**, 526 (1967).

[2] Taken in part from a dissertation by J. M. Manion submitted to the faculty of the University of Mississippi in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[3] Author to whom inquiries should be addressed at Texas Technological College.

[4] National Defense Education Act Fellow, 1962–1965.

[5] K. Alder and G. Stein, *Angew. Chem.*, **50**, 510 (1937).

[6] O. Korver, T. L. Kwa, and C. Boelhouwer, *Tetrahedron*, **24**, 1025 (1968).

[7] K. L. Williamson, Y.-F. Hsu, and R. E. Lacko, Abstracts, 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, P-45.