atomic number rule. In C_{3v} symmetry, the six filled π orbitals of the acetylene groups rearrange themselves into six filled molecular orbitals of ($A_1 + A_2 + 2$ E) symmetry. As aptly pointed out by Tate and coworkers and by King, the A_2 molecular orbital cannot overlap with the tungsten atom for the simple reason that none of the tungsten atomic orbitals has A_2 symmetry. This leaves only 10 of the 12 acetylene π electrons available for bonding to the tungsten atom, which is then forced to acquire two more electrons, in this case from a carbonyl group, to satisfy its electronic requirement.

Acknowledgment. We thank the Petroleum Research Fund (Grant No. 2059-G3), the National Institutes of Health (Biomedical Sciences Support Grant RR-07012-04), and the Research Corporation for supporting this research. The help of the University of Southern California Computer Center, in making available its IBM 360/65 computer, is also gratefully acknowledged.

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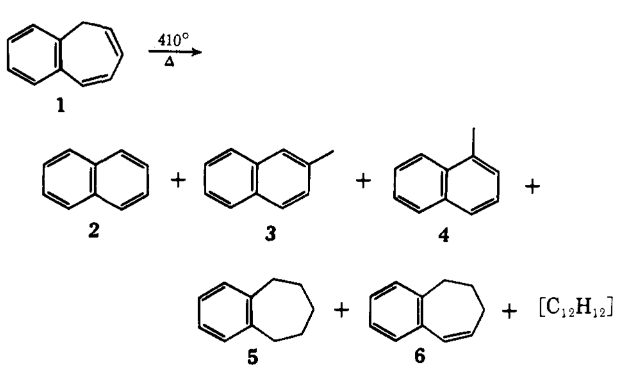
Received December 17, 1971

The Mechanism of the Pyrolytic Loss of CH_2 from 1,2-Benzotropilidene

Sir:

In view of the current interest in thermal reactions involving the extrusion of carbene fragments[1] we wish to report on our observations concerning the pyrolytic formation of naphthalene (**2**) from 1,2-benzotropilidene (**1**). Formally this can be viewed as a one- or two-step elimination of methylene, a somewhat attractive possibility since reactions of this type are allowed by orbital symmetry considerations.[2] The alternative possibility would involve free-radical transfer of a methylene fragment without the intermediacy of methylene itself. We have performed several experiments to determine which of these pathways is operative in the conversion of **1** to **2** and have demonstrated that the latter is the preferred mechanism.

We have observed that heating **1** at 410° in an evacuated Pyrex ampoule (gas phase) results[3] in the formation of naphthalene (**2**, 14% relative, 12% absolute), 2-methylnaphthalene (**3**, 18% relative), 1-methylnaphthalene (**4**, 50% relative), benzocycloheptene (**5**, *ca.* 1% relative), and 1,2-benzocyclohepta-1,3-diene[4] (**6**, 17% relative). In addition, when the low voltage mass spectrum of the pyrolysis mixture was examined there was a peak at *m/e* 156 corresponding to $C_{12}H_{12}$.



Identification of naphthalene, the methylnaphthalenes, and benzocycloheptene[5] was by preparative glpc and nmr spectral comparison with authentic samples. The structural assignment of **6**[6] rests upon spectroscopic analysis. The low-voltage mass spectrum showed a parent at *m/e* 144, and the nmr spectrum (τ 8.11 (m, 2, CH_2), 7.75 (m, 2, CH_2), 7.24 (m, 2, CH_2), 4.16 (d of t, 1, J = 12.5 and 4 Hz, vinyl H β to Ph), 3.50 (d of t, 1, J = 12.5 and 2 Hz, vinyl H α to Ph), and 2.82 (m, 4, aromatic)), was also consistent with the structure. In addition, when benzotropylium fluoroborate was reduced with lithium aluminum hydride, **6** was isolated as one of the products.

In a control experiment it was demonstrated that neither 1- nor 2-methylnaphthalene produces naphthalene under the reaction conditions.

When **1** was heated at 400° in the presence of a five molar excess of benzene, in addition to compounds **2**–**6**, a small amount (*ca.* 0.2% total, 1.5% of the naphthalene) of toluene was also formed.[7] The extent of naphthalene formation was shown to be independent of the amount of initial benzene.

In an effort to increase the toluene yield a high-pressure gas-phase pyrolysis was carried out. Heating of **1** at 360° for 24 hr was in an evacuated heavy-walled Pyrex ampoule in the presence of a five molar excess of benzene, where the initial liquid volume was one-third the total available volume of the ampoule. The distribution of the major products was: **2**, 17%; **3**, 16%; **4**, 17%; and **5**, 51%. In addition, the amount of toluene formed was increased to 0.6% total and 4% of the naphthalene produced. When the pyrolysis was carried out in the presence of free-radical inhibitors such as diphenylamine and 2,6-di-*tert*-butyl-5-hydroxymethylphenol there was no change in the amounts of naphthalene or toluene formed.

These data are completely consistent with a mechanism involving thermally induced methylene extrusion and trapping with benzene. They do not, however, rule out the free-radical pathway since the ability of compounds such as diphenylamine and 2,6-di-*tert*-butyl-5-hydroxymethylphenol to inhibit radical formation at elevated temperatures is questionable.

If the conversion of **1** to **2** involves the thermal extrusion of methylene, nonaromatic compounds should be viable trapping agents. However, when **1** was heated at 400° in the presence of excess cyclohexane,

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(1) (a) R. W. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **10**, 529 (1971), and references therein; see also (b) W. H. Atwell, D. R. Weyenberg, and J. G. Uhlmann, *J. Amer. Chem. Soc.*, **91**, 2025 (1969); (c) V. Franzen and H. I. Joschek, *Justus Liebigs Ann. Chem.*, **633**, 7 (1960).

(2) (a) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie, Weinheim/Bergstr., 1970; (b) J. P. Snyder, R. Boyd, and M. A. Whitehead, presented at the 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 1971, Abstract No. ORGN 73.

(3) These results are for a typical run. Relative naphthalene yields varied from 10 to 25% and absolute yields from 5 to 15%. The yields of other products showed similar distribution.

(4) In one run a compound tentatively identified as 1,2-benzocyclohepta-1,4-diene was isolated.

(5) We wish to thank Professor Lester Friedman and Mr. James C. Day for a sample of benzocycloheptene.

(6) This compound has been previously reported: R. Huisgen and G. Seidl, *Chem. Ber.*, **96**, 2730 (1963).

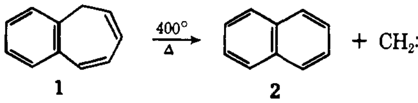
(7) Any tropilidene formed would rapidly form toluene.[8]

(8) W. G. Woods, *J. Org. Chem.*, **23**, 110 (1958).

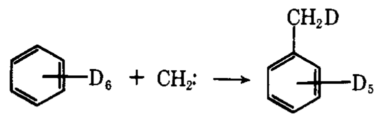
no methylcyclohexane was observed (*i.e.*, less than 0.005% under conditions where the toluene yield was 0.2%).

When the gas-phase pyrolysis of **1** was carried out with increasing pressures, it was observed that the amount of hydrogenated benzotropilidenes (*i.e.*, **5** and **6**) increased, while the methylnaphthalene (**3** and **4**) formation decreased accordingly. Hydrogenated products are well known in static pyrolyses.[9] The hydrogen is often derived from oxidative dimerization,[9] a reaction associated with free-radical polymerization. The formation of naphthalene closely parallels that of the hydrogenated benzotropilidenes, making its formation suspect of radical intermediates.

To probe the origin of the methyl substituent on the toluene formed during the pyrolysis of **1** in the presence of benzene, a labeling study was undertaken. A high-pressure pyrolysis of **1** was performed in the presence of a five molar excess of benzene-d_6. A mechanism involving methylene extrusion would be expected to result in toluene-d_6 (**7**). Collection by



1 **2**



7

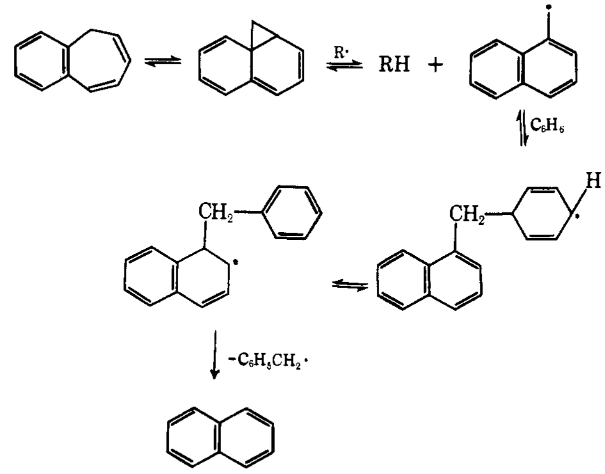
preparative glpc and low-voltage mass spectral analysis showed the major toluene component to be toluene-d_5, thus ruling out transfer of free methylene.

To substantiate the intermediacy of free radicals in the formation of **2**, a pyrolysis of **1** was carried out in the presence of di-*tert*-butyl nitroxide,[10] presumably a radical source at elevated temperatures.[11] It was observed that the amount of naphthalene formed was substantially increased. Furthermore, one of the most significant results was obtained when the pyrolysis was carried out in excess benzene at 300° where the amount of toluene formed was 0.67% of starting material (6% of naphthalene) compared to no toluene formation (*i.e.*, less than 0.005%) under the same conditions without added nitroxide.

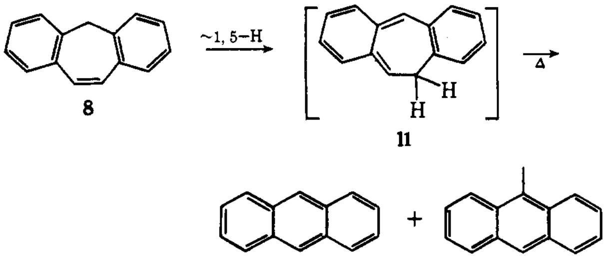
These data, therefore, are consistent with a mechanism involving free-radical transfer of the methylene fragment rather than the thermal extrusion of methylene itself. One such possibility is shown in Scheme I. Other equally reasonable possibilities can also be written.

To probe the generality of this reaction we examined the products from the pyrolysis of tropilidene at 405°. In addition to the expected toluene[8,12] (89%), we also observed benzene (3%), along with 8% of recovered starting material. It was easily shown, in a control experiment, that the source of benzene was not toluene. This is essentially the same result as was obtained by Woods[8] who postulated a dimerization–fragmentation sequence to explain the benzene.[13] When we heated cycloheptatriene with excess naphthalene, 1-methylnaphthalene was among the products. These results taken with our previous results support Woods' original dimerization–fragmentation hypothesis.

Scheme I



When 1,2,5,6-dibenzotropilidene (**8**)[14] was heated at 430° in an evacuated Pyrex ampoule (gas phase) for 2 hr, anthracene (**9**, 75%) was formed along with 9-methylanthracene (**10**, 6%) and a third product (18%) not as yet identified. When **8** was pyrolyzed in the presence of naphthalene, 1- and 2-methylnaphthalene and 1,2-benzotropilidene were observed in about a 40–60% yield based upon the amount of anthracene produced. The formation of 1,2-benzotropilidene in this reaction argues against a sequence involving direct transfer of a methyl group. These results, once again, are consistent with a radical transfer of methylene from species **11** produced by 1,5 sigmatropic migration of hydrogen,



8 **11** **9** **10**

a common reaction of benzotropilidenes.[15]

On the basis of our results one can now reasonably assume that Renfroe's report that the metacyclophane **12** gives the pyrene **13** at 250°[16] involves a free-radical transfer of the methylene fragment.

In conclusion, it should be pointed out that the thermal elimination of a CH_2 fragment from a seven-membered ring appears to have a different mechanism (free radical) than the elimination of other CR_2 groups (carbene). This occurs, in spite of the overall similarity of the two reactions.

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(9) S. W. Benson and A. Shaw, *J. Amer. Chem. Soc.*, **89**, 5351 (1967).

(10) R. Briere and A. Rassat, *Bull. Soc. Chim. Fr.*, 378 (1965).

(11) Di-*tert*-butyl nitroxide disproportionates above 125°: A. K. Hoffmann, A. Feldman, E. Gelblum, and W. Hodgson, *J. Amer. Chem. Soc.*, **86**, 639, 646 (1964).

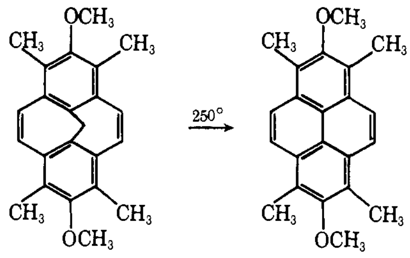
(12) W. C. Herndon and L. L. Lowry, *ibid.*, **80**, 1922 (1964), and references cited therein.

(13) Other reports of benzene or derivatives produced in small amounts from tropilidene pyrolyses are: K. W. Egger, *ibid.*, **90**, 6 (1968); O. Nefedow, N. Nowizkaja, and A. I. Waschenko, *Justus Liebigs Ann. Chem.* 707, 217 (1967); A. P. TerBorg, E. Razenberg, and K. Kloosterziel, *Recl. Trav. Chim. Pays-Bas*, **85**, 774 (1966).

(14) N. L. Wendler, D. Taub and R. D. Hoffsommer, Jr., U. S. Patent, 2,247,272 (1966); *Chem. Abstr.*, **65**, 5428c (1966).

(15) M. Pomerantz and G. W. Gruber, *J. Org. Chem.*, **33**, 4501 (1968).

(16) H. B. Renfroe, *J. Amer. Chem. Soc.*, 90, 2194 (1968).



12 **13**

Acknowledgment. We wish to thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work.

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(18) NSF Trainee 1969–1970; NDEA Graduate Fellow, 1971–1972.

(19) (a) Texaco Corporation Fellow, 1968–1969; (b) a portion of this work was taken from the Ph.D. Thesis of Gerald W. Gruber, Case Western Reserve University, Cleveland, Ohio, 1970.

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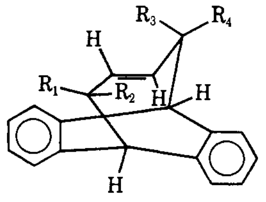
Received October 23, 1971

Photochemical Additions of Conjugated Dienes to Anthracene

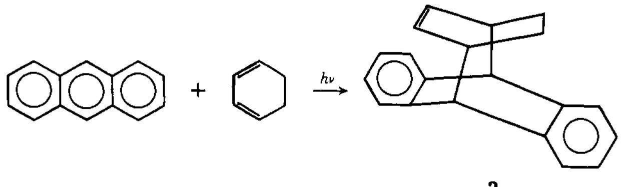
Sir:

Electronically excited molecules are susceptible to molecular complex formation, and such complexes are commonly known as excimers and exciplexes.[1] Electron transfer may occur following the complex formation which will lead to a number of interesting physical phenomena and chemical reactions. Contributions by Hammond and his coworkers showed that conjugated dienes quenched the fluorescence of naphthalene and other aromatic hydrocarbons and suggested that exciplexes were the intermediates in the quenching processes.[2,3] Although the possibility of chemical product formation had been mentioned,[2] no chemical products were characterized in these processes. Kraft and Koltzenburg reported that the photochemical reactions of benzene, alkylated benzenes and naphthalene with 1,3-butadiene or isoprene gave a complex mixture of products.[4] Anthracene has a higher electron affinity than naphthalene and benzenes[5] and may be more reactive than the simpler analogs in its excited state. The current communication deals with the photochemical 1,4 cycloaddition of conjugated dienes to anthracene and the formation of the novel 7,8,9,10-dibenzobicyclo[4.2.2]-7,9-*trans*-3-decatrienes (**1**) from acyclic 1,3-dienes and anthracene.



1

When a solution of anthracene (280 mg) and 1,3-cyclohexadiene (10 ml) in benzene (120 ml) was irradiated with a Hanovia 450-W lamp through a Pyrex filter, anthracene was rapidly consumed. The quantum yield of anthracene consumption at 313 nm was found to be 0.26. The nmr of the reaction mixture showed the presence of only one 1:1 adduct and the dimers of cyclohexadiene (170 mg). The yield of the adduct was estimated to be 96%, a pure sample of which was isolated by chromatography on alumina followed by recrystallization:[6] mp 197–200° dec (CH_2Cl_2-petroleum ether); uv max (cyclohexane) 279 (ϵ 2460), 276 (ϵ 1425), and 272 nm (ϵ 1635); ir (KBr) 718 cm^{-1}; nmr ($CDCl_3$) δ 1.42 (m, 4, CH_2), 3.08 (m, 2, $CHCH{=}CH$), 4.16 (d, 2, J = 10 Hz, ArC*H*Ar), 5.62 (sextet, 2, $CH{=}CH$), and 7.08 ppm (m, 8, Ar*H*). The olefinic protons exhibit a sextet with the two outer peaks of very low intensity and the four inner peaks of almost equal intensity which is characteristic of an A_2X_2 system similar to that in bicyclo[2.2.2]-octenes.[7] First-order analysis gives the following coupling constants: $J_{CH=CH}$ = 8.7 Hz, $J_{C=CHCH}$ = 7.0 Hz, and $J_{CH=CCH}$ = 1.4 Hz.[8] The adduct is therefore identified to be the 1,4 adduct **2** (reaction 1). The reaction was extended to 9,10-dimethylanthracene and 9-cyanoanthracene, and crystal line adducts were isolated in good yields in both cases (66 and 87%).



2 (1)

When the irradiation of anthracene was carried out with 2,5-dimethyl-2,4-hexadiene under similar conditions, an adduct was again formed in high yield. In contrast to the adduct formed from cyclohexadiene, this adduct decomposes rapidly upon chromatography or other attempted purification.[9,10] A crystalline material of about 90% purity was, however, obtained by crystallizing the crude reaction mixture from ethanol: 87–95°; uv max (cyclohexane) 275 (ϵ 909), 266 (ϵ 1020), and 258 nm (ϵ 1150); ir (CCl_4) 1005 cm^{-1};[11] nmr (CCl_4)

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(1) For reviews on excimers and exciplexes, see: (a) J. B. Birks, "Photophysics of Aromatic Molecules," Wiley, New York, N. Y., 1970; (b) A. Weller, *Pure Appl. Chem.*, **16**, 115 (1968).

(2) L. M. Stephenson and G. S. Hammond, *ibid.*, **16**, 125 (1968); *Angew. Chem., Int. Ed. Engl.*, **8**, 261 (1969); L. M. Stephenson, D. G. Whitten, G. F. Vesley, and G. S. Hammond, *J. Amer. Chem. Soc.*, **88**, 3665, 3893 (1966).

(3) T. R. Evans, *ibid.*, **93**, 2081 (1971).

(4) K. Kraft and G. Koltzenburg, *Tetrahedron Lett.*, 4357, 4723 (1967).

(5) Reference 1a, p 462.

(6) All crystalline new products in this communication gave satisfactory elemental analyses.

(7) K. Tori, Y. Takano, and K. Kitahonoki, *Chem. Ber.*, **97**, 2798 (1964).

(8) J. A. Pople, W. G. Schneider, and H. J. Bernstein, *Can. J. Chem.*, **35**, 1060 (1957).

(9) A major decomposition product appears to be the corresponding epoxide which was detected as the only contaminant in our crude product. The epoxide was characterized by its elemental analysis, molecular weight, uv, ir, and nmr spectra. The mechanism of its formation will be investigated.

(10) Neither **1a** nor **1b** showed any tendency to dimerize under our experimental conditions.

(11) The ir spectra of *trans*-cyclooctenes and *trans*-cycloheptenone exhibit a band between 9.9 and 10.1μ: A. C. Cope, R. A. Pike, and C. F. Spencer, *J. Amer. Chem. Soc.*, **75**, 3212 (1953); P. E. Eaton and K. Lin, *ibid.*, **86**, 2087 (1964); **87**, 2052 (1965).