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THE REACTION OF BENZYNE WITH CYCLOOCTATETRAENE

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Several groups have published indirect evidence pointing to the existence of [10]annulene as a reaction intermediate in thermal (1b, d) and photochemical (1a, c) rearrangements of $C_{10}H_{10}$ hydrocarbons. Also, a stable tribenz-[10]annulene has been prepared by Sondheimer et al (1e). We now describe the reaction of benzyne with cyclooctatetraene, a reaction which appears to involve a benz[10]annulene intermediate.

RESULTS:

Benzenediazonium-2-carboxylate (2) was decomposed in a large excess of cyclooctatetraene containing 25% (by volume) acetonitrile at 40° and the products were separated by preparative layer chromatography (silica gel, hexane). Nonpolar hydrocarbons were isolated in a combined yield of 25% (based on benzenediazonium-2-carboxylate) and are listed in Table 1 in order of increasing polarity:

TABLE 1

	M.P.	UV $\lambda_{max}^{CH_3OH}$ (mμ)	Molecular Formula	Relative Yield
VII	98-99°	--	$C_{14}H_{10}$	4%
II	36-37°	279 (2300) 272 (2700) infl. 266 (2600)	$C_{14}H_{12}$ (m/e 180)	20%
VIII	117-118°	281 (2900) 270 (4200) 260 (3900)	$C_{14}H_{12}$ (m/e 180)	3%
I (most polar)	84-85°	266 (17,800) 299 (4150)	$C_{20}H_{16}$ (m/e 256)	68%
				5% unidentified

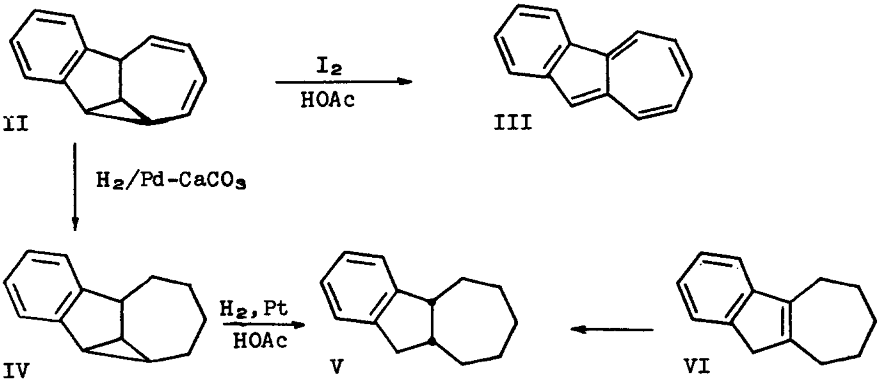
TABLE 2

A-60-A NMR Spectra (τ) in CCl_4/TMS

	Aromatic C-H	Olefinic C-H	Saturated C-H
II	2.9-3.2 (4H) multiplet	3.8 (1H) multiplet 4.1-4.7 (3H) multiplet	5.96 (1H) multiplet 7.7-7.95 (2H) multiplet 8.37 (1H) multiplet
VIII	3.01 (4H) (A_2B_2)	3.83 (2H) sextet 4.22 (2H) quartet 4.53 (2H) quartet	6.27 (2H) octet
I	2.05-2.3 (2H) multiplet 2.5-3 (11H) multiplet		5.84 (1H) triplet, J = 7.7 cps 6.87 (2H) doublet, J = 7.7 cps

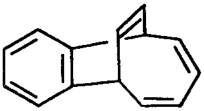
The predominant product I is an adduct of 2 moles of benzyne with 1 mole of cyclooctatetraene, and the physical and spectral properties of I are in accord with those reported for 9-phenyl-9,10-dihydrophenanthrene (3). This structure has been confirmed by direct comparison of I with known material prepared by the method of Dilling (3a).

The other major product II is a 1:1 adduct of benzyne and cyclooctatetraene as shown by a strong molecular ion (m/e 180) in the mass spectrum. The NMR spectrum of II (Table 2) reveals the presence of 3 cyclopropyl, 1 doubly allylic, 4 olefinic and 4 aromatic protons. Upon treatment with a mole of iodine in acetic acid, II is transformed in 40% yield to an intensely green hydrocarbon III to which we assign the structure of benz[a]azulene, based upon comparison of ultraviolet-visible spectra and thin layer chromatography behavior with an authentic sample (4). Also, catalytic hydrogenation of II over Pd/$CaCO_3$ in methanol affords a tetrahydro derivative IV (m/e 184) which is reduced further to a mixture of hexahydro derivatives by hydrogenation over platinum in acetic acid. The major reduction product V (m/e 186) can be purified by GLC (20% DC 710 silicone/chromosorb P, 175°) and all criteria (IR, NMR, GLC retention time) show that V is identical with octahydrobenz[a]azulene. For comparison, a known sample of V was prepared by hydrogenation of 5,6,7,8,9,10-hexahydrobenz[a]azulene VI (4). These chemical and spectroscopic properties are satisfied by the structure 8,9-benzotricyclo[5.3.0.0.^{2,10}]deca-3,5,8-triene for II, but not by isomers such as benzobullvalene, 3,4-benzo-, or 5,6-benzotricyclo[5.3.0.0.^{2,10}]deca-3,5,8-triene.

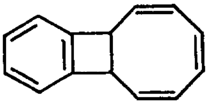


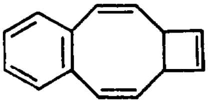
+ 2 isomers

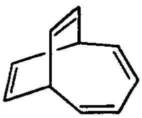
Of the minor products, VII is easily identified as phenanthrene by comparison with an authentic sample. The other minor product VIII is tentatively assigned the structure of 7,8-benzobicyclo[4.2.2.]deca-2,4,7,9-tetraene on the basis of its very characteristic spectral properties (Tables 1 and 2). Product VIII is a 1:1 adduct (m/e 180) with six olefinic hydrogens and a plane of symmetry as shown by the NMR spectrum. Since the details of the NMR and UV spectra of VIII are highly analogous to those of XI (1c, 5), but not of XII (1b) or XIII (11), the other possible symmetrical structures IX and X can be excluded. This assignment is also in accord with the relative thermal stability of VIII (unchanged after several hours at 150°). It is to be noted that VIII is the second known example of 1,4- cycloaddition to cyclooctatetraene (6).


VIII

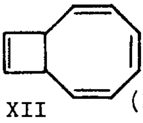
λ^{CH_3OH}
281 (2900)
270 (4200)
260 (3900)


IX

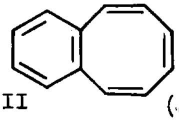

X


XI

$\lambda^{C_2H_5OH}$
280 (2900)
268 (4200)
258 (4200)
(Jones, et al)


XII

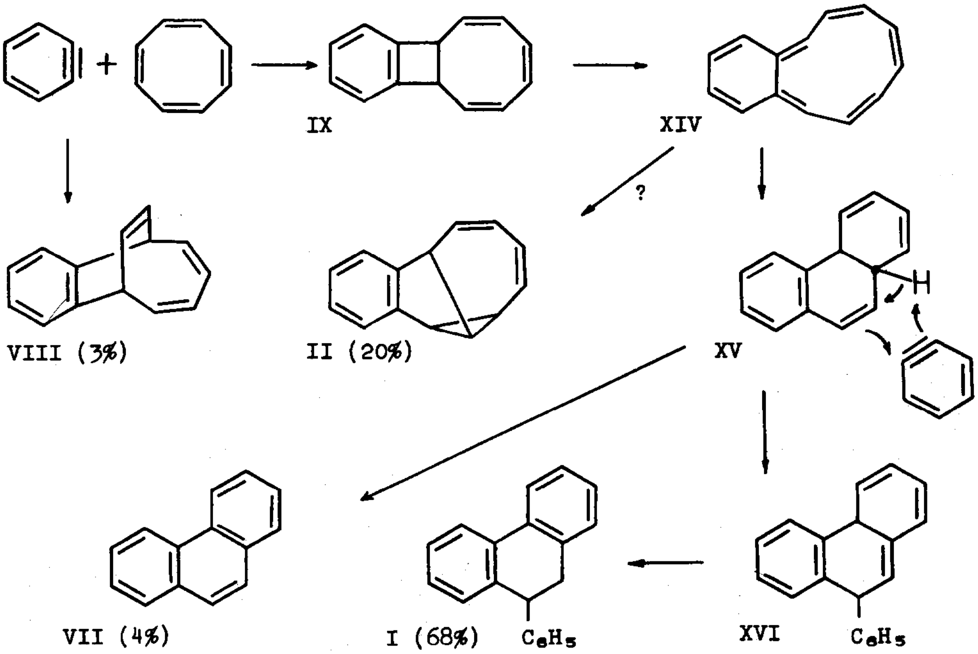
$\lambda^{C_2H_5OH}$
258 (1300)
(Masamune, et al)


XIII

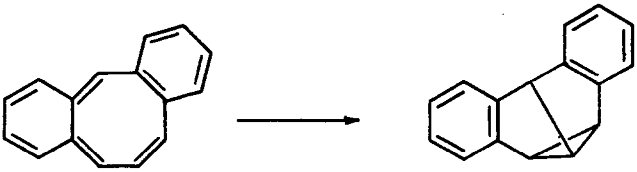
$\lambda^{C_2H_5OH}$
233
(23,300)
275
(1030)
(Stiles, et al)

DISCUSSION:

Benzyne is known to attack suitably isolated double bonds by 1,2 addition (7, 8, 11) a process which should lead to IX in the case of cyclooctatetraene. By analogy to the work of Masamune *et al* (1b), IX is expected to rearrange thermally to dihydrophenanthrene XV, presumably via the benz[10]annulene XIV. Under the reaction conditions, XV is transformed either to phenanthrene (by an unknown pathway) or to the major product 9-phenyl-9,10-dihydrophenanthrene I. The formation of I from XV is rationalized by attack of benzyne at C-9 via a cyclic transition state (8) to yield XVI which then aromatizes to I by double bond migration. Efforts to isolate intermediates IX or XV have so far been fruitless.

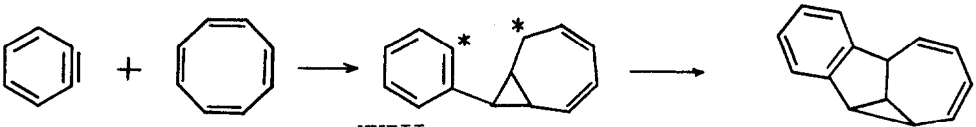


The formation of the interesting hydrocarbon II can be visualized as an intramolecular Diels-Alder reaction of the highly reactive benz[10]annulene. In fact, an analogous reaction has been proposed by Pettit and Merk to account for the formation of benzocyclobutadiene dimer XVII (9):



XVII

However, Dreiding models show that the anticipated (1b) trans double bond in XIV prevents a concerted reaction of the Diels-Alder type. An alternative mechanism is therefore preferred, namely a stepwise addition of benzyne to cyclooctatetraene to afford a homotropylium species XVIII which then closes to yield II. A similar intermediate has been proposed by Schröder (10) for the dimerization of cyclooctatetraene.



XVIII II

* indicates diradical or
charge-separated intermediate

Further studies of the chemistry of adducts II and VIII are in progress and will be described in a subsequent publication (12).

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5. We thank Professor M. Jones, Jr. for sending us NMR spectra of bicyclo-[4.2.2]-decatetraene (1c).

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12. We thank Badische Anilin und Soda Fabrik for a generous supply of cyclooctatetraene.