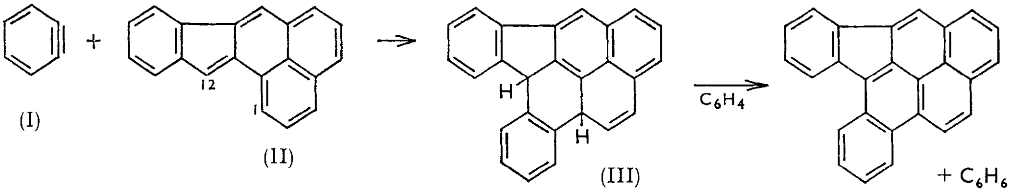
135. *Conjugated Cyclic Hydrocarbons and Their Heterocyclic Analogues. Part III.*[1] *The Addition of Benzyne and* 1-*Bromoacenaphthylene to Indeno*[2,1-a]*perinaphthene.*

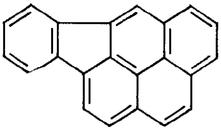
By (the late) I. M. AITKEN and D. H. REID.

Benzyne, generated *in situ* and acting as a dienophile, adds to indeno-[2,1-*a*]perinaphthene (II) but not to perylene or azulene. 1-Bromoacenaphthylene also adds to the hydrocarbon (II).

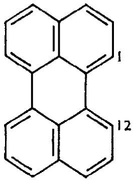
IN their studies on the function of benzyne as a dienophile in the Diels–Alder reaction Wittig and his co-workers showed that benzyne (I), generated in tetrahydrofuran by the interaction of magnesium and *o*-bromofluorobenzene [2] or of n-butyl-lithium and fluorobenzene,[3] adds to anthracene transannularly to form triptycene in 10—30% yield. This is the only reported case of benzyne adding to an aromatic hydrocarbon, although many similar reactions have been reported involving addition to incompletely conjugated hydrocarbons (cyclopentadiene [4] and 1,3-cyclohexadiene [4]) or to heterocyclic nuclei (furan,[2] 1,3-diphenylisobenzofuran,[5] 1-methylpyrrole,[4] and 2-methylisoindole [5]).



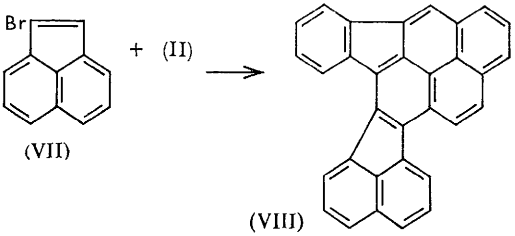
(I) (II) (III) (IV)



(V)



(VI)



(VII) (VIII)

In an earlier paper [6] it was shown that indeno[2,1-*a*]perinaphthene (II) is a highly reactive diene in the Diels–Alder reaction, addition taking place at positions 1 and 12. When maleic anhydride was the dienophile and a non-oxidising solvent (xylene) was used, the primary adduct was isolated in almost quantitative yield. In a mildly oxidising medium (nitrobenzene) aromatisation accompanied addition.

It has now been found that benzyne adds rapidly to indeno[2,1-*a*]perinaphthene (II) when the hydrocarbon and an excess of *o*-bromofluorobenzene and magnesium are boiled together briefly in tetrahydrofuran. Dehydrogenation follows addition, for the product was the fully aromatic benzo[*a*]indeno[1,2,3-*cd*]pyrene (IV). This may be the result of a purely thermal elimination of hydrogen from the nearly aromatic primary adduct (III); alternatively, two hydrogen atoms may be removed by the excess of benzyne serving as a hydrogen acceptor, and giving benzene. The latter possibility appears attractive in view of the low temperature of the reaction.

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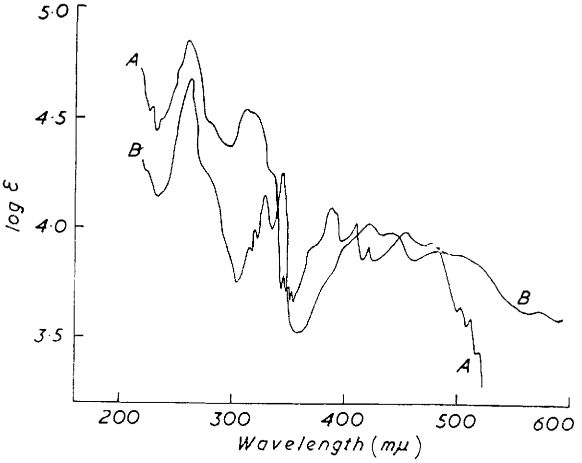
[1] Part II, Kirby and Reid, *J.*, 1960, in the press.
[2] Wittig and Ludwig, *Angew. Chem.*, 1956, **68**, 40.
[3] Wittig and Benz, *Angew. Chem.*, 1959, **71**, 166.
[4] Wittig, *Suomen Kem.*, 1956, **29**, 283.
[5] Wittig, Stilz, and Knauss, *Angew. Chem.*, 1958, **70**, 166.
[6] Aitken and Reid, *J.*, 1956, 3487.

The absorption spectrum (see Figure) of benzo[*a*]indeno[1,2,3-*cd*]pyrene resembles in its general structure that of indeno[2,1-*a*]perinaphthene (II) and indeno[1,2,3-*cd*]pyrene [6] (V). Strikingly, benzo[*a*]indeno[1,2,3-*cd*]pyrene and indeno[1,2,3-*cd*]pyrene absorb, band group for band group, at shorter wavelengths then indeno[2,1-*a*]perinaphthene although they possess, respectively, four and two more π-electrons and greater molecular areas.

Perylene (VI), although known [7] to react at positions 1 and 12 with maleic anhydride in boiling nitrobenzene, failed to react with benzyne under the conditions described above. Attempts under the same conditions to add benzyne to azulene at positions 1 and 8 (the positions of greatest π-electron excess and deficiency, respectively [8]), were also unsuccessful: the disparity between the 1,2-bond length of benzyne and the distance between positions 1 and 8 of azulene may be at least partly responsible for this.

Absorption spectra of (A) *benzo*[a]*indeno*[1,2,3-cd]*pyrene* (IV) *and* (B) *indeno*[2,1-a]*perinaphthene* (II) *in cyclohexane.*



(IV) $\lambda_{max.}$	229	259	310	346	350	353	387	409	420	453	476	503	511	520
log ε	4·55	4·85	4·54	3·78	3·73	3·71	4·09	4·02	3·91	3·98	3·94	3·64	3·59	3·44
(II) $\lambda_{max.}$................	262	315	320	329	344	420	442	484	570					
log ε	4·69	3·92	3·99	4·16	4·26	4·03	3·99	3·90	3·64					

Acenaphthylene has been used successfully, under somewhat forcing conditions, as a dienophile in the synthesis of tetrahydrofluoranthenes.[9] It is now found that 1-bromoacenaphthylene (VII) adds rapidly to indeno[2,1-*a*]perinaphthene (II) in boiling nitrobenzene: aromatisation of the primary adduct occurred and the hydrocarbon (VIII) was formed directly. The crude product contained 3% of bromine, which was eliminated by Raney nickel alloy and potassium hydroxide in boiling aqueous pyridine. Two possible explanations are suggested to account for this: migration of bromine into an aromatic ring takes place in the dissociable primary adduct; [10] alternatively, bromine atoms formed by the thermal or oxidising action of the solvent on hydrogen bromide eliminated from the primary adduct may attack the fully aromatic product.

EXPERIMENTAL

M. p.s were determined on a Kofler-type heating-stage. Absorption spectra were measured with a Unicam S.P. 500 instrument. Chromatographic purifications were effected on activated alumina.

Tetrahydrofuran was purified by boiling over sodium wire until it no longer imparted a

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[7] Clar, *Ber.*, 1932, **65**, 846.
[8] Brown, *Trans. Faraday Soc.*, 1948, **44**, 984.
[9] Bergmann, *Nature*, 1948, **161**, 889; Kloetzel and Mertel, *J. Amer. Chem. Soc.*, 1950, **72**, 4786.
[10] Clar and Zander, *J.*, 1957, 4615.

colour to the fresh metal surface, and then distilled. It was redistilled over lithium aluminium hydride (1 g./l.) immediately before use.

Light petroleum was of boiling range 40—60°.

Addition of Benzyne to Indeno[2,1-*a*]*perinaphthene.*—Indeno[2,1-*a*]perinaphthene [6] (126 mg.), *o*-bromofluorobenzene [11] (2 ml.; b. p. 158°), and magnesium (230 mg.) in tetrahydrofuran (10 ml.) were boiled under dry nitrogen for 15 min., then poured into an excess of dilute sulphuric acid, and extracted with ether (2 × 250 ml.). The extracts were washed free from acid before drying (K_2CO_3) and evaporation, finally at reduced pressure. The residual oil was eluted with benzene after adsorption from benzene (10 ml.) on an alumina column (16 × 3·2 cm.). The eluates, on concentration, deposited *benzo*[a]*indeno*[1,2,3-cd]*pyrene* (IV) which crystallised from xylene as orange-red needles (24 mg., 15%), m. p. 262—264° [Found: C, 95·7; H, 4·4%; *M* (Rast), 355. $C_{26}H_{14}$ requires C, 95·7; H, 4·3%; *M*, 326], giving a violet colour with concentrated sulphuric acid.

Addition of 1-*Bromoacenaphthylene to Indeno*[2,1-a]*perinaphthene.*—Indeno[2,1-*a*]perinaphthene (126 mg.), 1-bromoacenaphthylene [12] (260 mg.; b. p. 120—122°/0·4 mm.), and nitrobenzene (10 ml.) were boiled for 5 min. On cooling, the solution deposited the adduct (90 mg.) as golden-yellow needles. The product, recrystallised from nitrobenzene and then from nitrobenzene–xylene (1 : 1), contained 2·1% of bromine which was reduced to 1·8% by fractional sublimation at 0·1 mm. but could not thus be completely eliminated. Raney nickel alloy (4 g.) was added portionwise in 40 min. to the impure hydrocarbon (40 mg.) and potassium hydroxide (4 g.) in boiling water (10 ml.) and pyridine (100 ml.). The still boiling solution was filtered from metallic residues which were washed with boiling pyridine (2 × 10 ml.); the filtrates were concentrated to 30 ml. before dilution in water (60 ml.). The precipitated yellow solid was filtered off, washed with water and methanol, and dried at 100°. From nitrobenzene (5 ml.) it gave *acenaphthyleno*[1,2-a]*indeno*[1,2,3-cd]*pyrene* (VIII) (22 mg.), orange needles, m. p. >350° (Found: C, 96·2; H, 3·9. $C_{32}H_{16}$ requires C, 96·0; H, 4·0%).

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[11] Bergmann, Engel, and Sandor, *Z. phys. Chem.*, 1930, **10**, 120.
[12] Blumenthal, *Ber.*, 1874, **7**, 1094.