

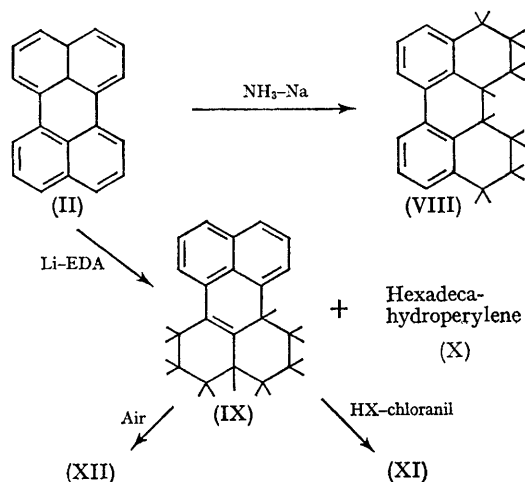
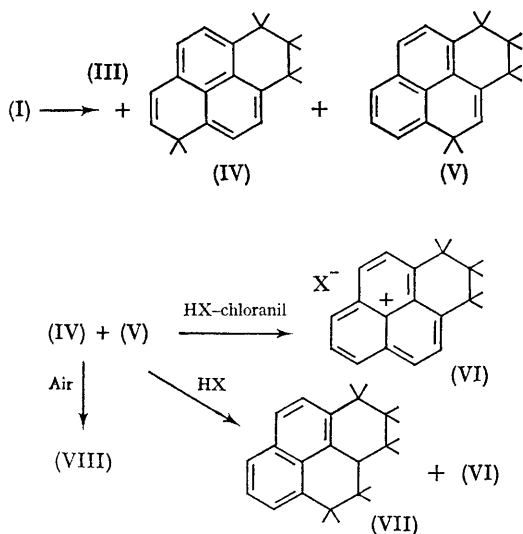
Formation of Substituted Phenalenes from the Reduction of Pyrene and Perylene

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IN an attempt to repeat the work of Neunhoeffer¹ and Brooks² on the Birch reduction of pyrene (I) and of perylene (II) we have found different products from those reported. Reduction of pyrene using 4 equiv. sodium and liquid ammonia¹ gave a mixture of three compounds.* Chromatographic separation on alumina gave two fractions.

fraction was shown by vapour-phase chromatography and n.m.r. to be a mixture (m.p. 55—50°) of two isomeric tetrahydropyrenes (89%), 1,2,3,6-tetrahydropyrene (IV), and 1,2,3,5-tetrahydropyrene (V) in approximately a 2:1 ratio [we were not able to separate (IV) and (V)]. Reduction of pyrene employing the procedure of Brooks using 8 equiv. lithium and ethylenediamine (EDA) gave only hydrocarbons (IV) and (V) in a 95% yield (2:1 ratio). Further proof for the structure of (IV) and (V) came from the ability of these compounds to form phenalenium salts (VI) in the presence of



The first fraction was identified as 1,2,3,3a,4,5,5a,6,7,8-decahydropyrene (III)³ (8.1%). The second

* All reported compounds have satisfactory analysis as well as spectral data (i.r., u.v., n.m.r., and mass spectrum) consistent with the proposed structures.

strong acids and a hydride acceptor.⁴ These salts could also be formed in the presence of strong acids by intermolecular hydride transfer with the concomitant formation of 1,2,3,3a,4,5-hexahydroperylene (VII).⁵ Exposure of (IV) and (V) to air gave the stable 6,7,8-trihydroperenyl radical (VIII).⁶

Reduction of perylene using 8 equiv. sodium and liquid ammonia gave a 90% yield 1,2,3,10,11,12,12a,12b-octahydroperylene (VIII).⁷

When perylene was reduced using 16 equiv.

lithium and ethylenediamine, a mixture of 1,2,3,3a,4,5,6,6a-octahydroperylene (IX), m.p. 141—143° (85%) and a hexadeca-hydroperylene (X) (10%) were isolated. The structure of (X) is not known with certainty at the present time.

Hydrocarbon (IX) formed phenalenium salts (XI) in the presence of a strong acid and a hydride acceptor and also formed a stable phenalenyl radical⁸ (XII) when exposed to air.

(Received, November 14th, 1966; Com. 881.)

¹ O. Neunhoffer, H. Woggon and S. Dähne, *Annalen*, 1958, **612**, 98.

² J. D. Brooks, R. A. Durie, and H. Silberman, *Austral. J. Chem.*, 1964, **17**, 55.

³ J. V. Braun and E. Rath, *Ber.*, 1928, **61B**, 956.

⁴ D. H. Reid and R. G. Sutherland, *J. Chem. Soc.*, 1963, 3295.

⁵ J. W. Cook and C. L. Hewett, *J. Chem. Soc.*, 1933, 401.

⁶ F. Gerson, E. Heilbronner, A. H. Reddoch, D. H. Paskovich and N. C. Das, to be published.

⁷ A. Zinke and O. Benndorf, *Monatsh*, 1934, **64**, 87.

⁸ A. H. Reddoch and D. H. Paskovich, to be published.