

Polymerisation of Benzene

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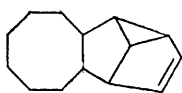
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Two recent independent reports have shown that benzene can undergo photochemical 1,3-cycloaddition of various unconjugated olefins.^{1,2} Mechanistic proposals and predictions have been made.^{2,3} Since the 1:1 adducts [*e.g.* (I) from cyclo-octene and benzene²] are themselves mono-olefins, they should in turn photo-add to benzene, as has indeed been reported.² Accordingly, olefins such as cyclo-octene should be able to initiate the photopolymerisation (strictly phototelomerisation) of benzene. This expectation has now been confirmed.

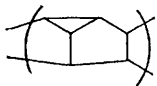
Irradiation of benzene (100 g.) with either 0.35 mol. % of cyclo-octene or 0.06 mol. % of the preformed adduct (I) (100w medium-pressure

Hanovia lamp) for 100 hr. under nitrogen gave *ca.* 1 g. of a mixture of polymers which was fractionated by treatment with hexane, acetone, benzene, and chloroform successively to give fractions H, A, B (main reaction product), and C respectively. The average molecular weights (Mechrolab Osmometer) were as follows: H, < 500; A, *ca.* 750 (8 benzene units); B, *ca.* 1500 (18 benzene units); C, *ca.* 2000 (24 benzene units). Fraction H was an oil, A, a gum, and B and C were colourless solids: fraction C was insoluble in benzene, but gave viscous solutions in chloroform. All these polymers darkened slowly when heated above 200° in air. The n.m.r. spectrum of the major fraction B in CDCl₃ showed no sign of the presence of aromatic

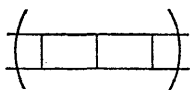
protons: ethylenic protons were just detectable at extreme sensitivity. Apart from slight $-OH$ absorption the infrared spectrum was in general that expected for saturated aliphatic hydrocarbons, and the six observable C-H stretching frequencies corresponded closely to six of the seven reported for the adduct (I).² The ultraviolet spectrum of



(I)



(II)



(III)

fraction B in ethanol or dioxan showed no peak at wavelengths longer than $210\text{ m}\mu$.

The genesis and the properties of these polymers are consistent with structures which, apart from end-groups, are ladder-like and contain the repeating C_6H_6 unit (II). In view of results given and cited in ref. 2, the presence of a minor proportion of units of type (III) is not excluded.

Even with the trace proportions of olefins used in these experiments, the normal production of fulvene from benzene was almost completely suppressed, in conformity with the previous mechanistic suggestions.^{2,3}

Polymers having different properties are formed from liquid benzene by the action of radiation of wavelength *ca.* $200\text{ m}\mu$, and from benzene vapour subjected to a microwave-generated discharge.⁴

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¹ K. E. Wilzbach and L. Kaplan, *J. Amer. Chem. Soc.*, 1966, **88**, 2066.

² D. Bryce-Smith, A. Gilbert, and B. H. Orger, *Chem. Comm.*, 1966, 512.

³ D. Bryce-Smith and H. C. Longuet-Higgins, *Chem. Comm.*, 1966, 593.

⁴ D. Bryce-Smith and A. Gilbert, unpublished work.