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THE REACTION OF BENZYNE WITH STYRENE

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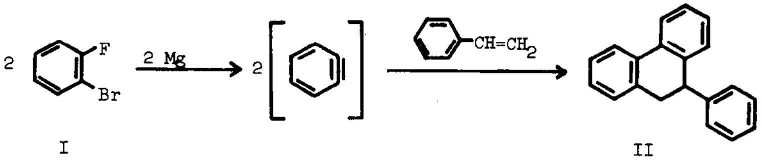
A number of cycloaddition, Diels-Alder and other types of addition reactions of benzyne with unsaturated molecules have been reported (1). We would like to report a novel addition reaction between benzyne and the olefin styrene (2). In principle several different types of addition could be visualized for this reaction. For example cycloaddition to give a cyclobutane derivative or a Diels-Alder type addition are possibilities.

o-Bromofluorobenzene (I) was added to a mixture of magnesium turnings (1d) and a five molar excess of styrene in tetrahydrofuran at 60°. Hydrolysis with water and removal of excess styrene followed by chromatography on alumina with hexane and benzene gave a hydrocarbon $C_{20}H_{16}$ (87%), m.p. 79-80° after recrystallization from hexane. This product was established to be 9-phenyl-9,10-dihydrophenanthrene (II) by elemental analysis (Calcd. for $C_{20}H_{16}$: C, 93.71; H, 6.29. Found: C, 93.71; H, 6.46) and spectral data (3). The mass spectrum showed a parent

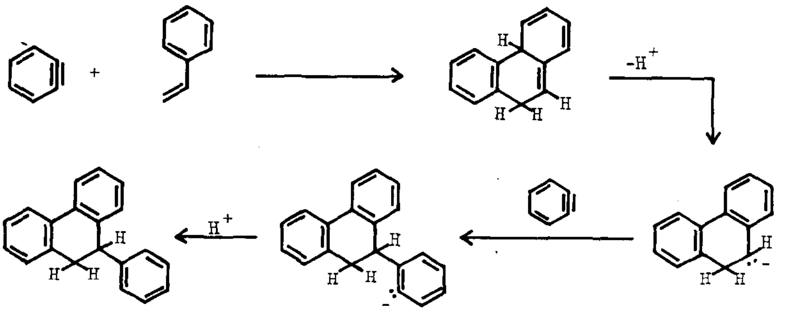


I

II

peak (m/e 256) and an intense ion at m/e 178 which was probably due to fragmentation to phenanthrene by the loss of the elements of benzene. The nuclear magnetic resonance spectrum (CCl_4) of (II) showed a multiplet centered at -7.70 (7) (2.04)(8) for the aromatic protons at positions 4 and 5, a multiplet at -7.12 (11.00) for the remaining aromatic protons, a triplet (J = 7.7 c.p.s.) at -4.09 (1.09) for the tertiary proton, and a doublet at -3.09 (1.95) for the secondary protons (9). Apparently the chemical shifts of the two structurally non-equivalent secondary protons are nearly the same. The ultraviolet spectrum of (II) $\left[\lambda_{max.}^{CH_3OH}\ (\epsilon),\ 267\ m\mu\ (16{,}300),\ 300\ m\mu\ (3{,}810);\ \lambda_{min.}^{CH_3OH}\ (\epsilon),\ 241\ m\mu\ (4{,}180),\ 296\ m\mu\ (3{,}670)\right]$ was very similar to that of 9,10-dihydrophenanthrene $\left[\lambda_{max.}^{C_2H_5OH}\ (\epsilon),\ 264\ m\mu\ (17{,}000),\ 299.5\ m\mu\ (4{,}450);\ \lambda_{min.}^{C_2H_5OH}\ (\epsilon),\ 237\ (2{,}650)\right]$ (10). One would not expect the unconjugated phenyl group to affect markedly the spectrum of the remainder of the molecule. The infrared spectrum (CCl_4) was also consistent with (II) showing major absorption maxima at 3.24, 3.46, 6.73, 6.89, and 14.23μ.

The mechanism of this reaction has not been determined, but a logical path to the product (II) would appear to be an initial Diels-Alder reaction followed by a proton loss and nucleophilic addition to another benzyne molecule (11).



II

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3. The melting point of (II) has been reported as 84° (4), 86° (5), and 121.5° (6).

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7. δ in p.p.m. from tetramethylsilane used as an internal standard.

8. Relative integrated area.

9. For comparison the proton resonances (CCl_4) of 9,10-dihydrophenanthrene showed the aromatic protons at positions 4 and 5 at -7.63, the remaining aromatic protons at -7.14, and the benzylic protons at -2.76.

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11. For related reactions see references 2f-k.