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A NOVEL PRODUCT FROM THE REACTION OF BENZYNE WITH ACRIDINE

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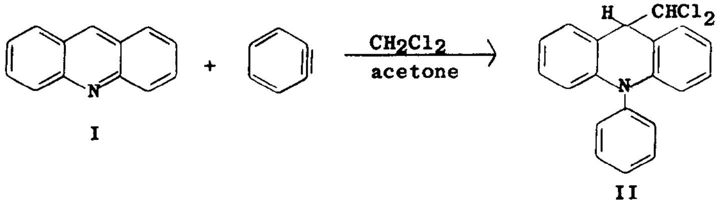
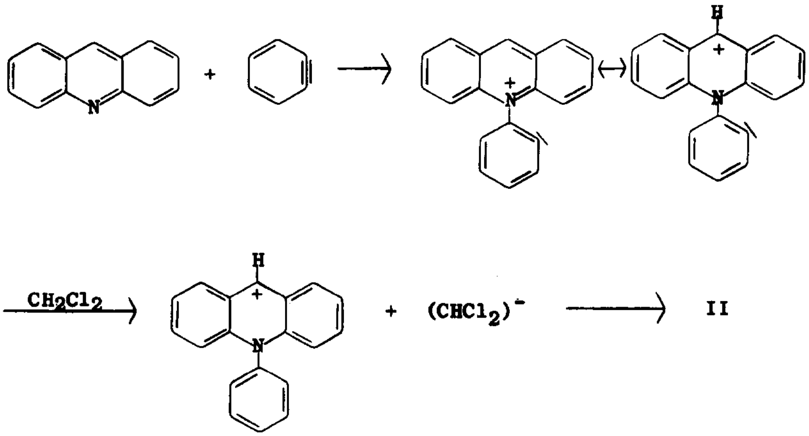
We wish to report that the reaction of acridine (I) with benzyne, generated from anthranilic acid diazotized with isopentyl nitrite in methylene chloride-acetone solution (1) leads to a novel product, 9-dichloromethyl-10-phenylacridan (II). The formation of II is significant because the aprotic solvent, methylene chloride, has entered into the reaction.



Previously, the reaction of I with benzyne, formed from o-bromofluorobenzene and magnesium in tetrahydrofuran, has been reported to yield 4-phenylacridine (2%), 9,10,9',10'-tetrahydro-9,9'-biacridyl (27%), and 10,10'-diphenyl-9,10,9',10'-tetrahydro-9,9'-biacridyl (10%), in addition to very small amounts of other products and recovered I (2).

Compound II was isolated from the neutral fraction of the reaction of acridine (25.5 g. in 1.5 ℓ. of refluxing methylene chloride) and benzyne, generated from anthranilic acid (20.5 g. in 125 ml. of acetone) and isopentyl nitrite (21.5 ml.). The dilute hydrochloric acid extract yielded predominantly I, as was shown by vapor phase chromatography. The neutral fraction was purified by column chromatography (neutralized alumina packed in petroleum ether and eluted with mixtures of petroleum ether and methylene chloride) Recrystallizations from benzene-petroleum ether and ethanol afforded 1.0 g. of II, m.p. 107-109°. In addition to elemental analyses, the composition was confirmed by the mass spectrum which showed significant peaks at m/e 339 (M^+ calcd for $C_{20}H_{15}Cl_2N$: 339), 304 (M-Cl), 269 (M-2Cl), and 256 (M-$CHCl_2$). Isotope peaks with the proper ratios were observed for 2 Cl's at m/e 341 and 343 and for 1 Cl at m/e 306. The ultraviolet spectrum (cyclohexane) exhibited a λ_{max} 285 mμ (log ϵ 4) which was consistent with the proposed structure. Conclusive evidence for the structure was provided by the n.m.r. spectrum (deuteriochloroform) which showed absorption at τ 2.3-3.1 (multiplet), 3.5-3.7 (multiplet), 4.19 (doublet), and 5.29 (doublet) with relative areas of 11, 2, 1, and 1, respectively. The doublets had identical splitting constants at 4 c.p.s. and were of proper field positions for the $C\underline{H}Cl_2$ and 9-H, respectively. 10-Phenylacridan showed a peak at τ 5.81 for the 9-H's and aromatic absorption at τ 2.4-3.3 and 3.7-3.9. The multiplets at τ 3.5-3.7 and 3.7-3.9, respectively, in the two spectra had identical fine structure and showed the ring current effect of the 10-phenyl group on the 4-H and 5-H. Therefore, II is the only structure consistent with these data.

The mode of formation of II most likely does not involve 9-azatriptycene because it would be stable under the reaction conditions employed (3). A possible pathway may be as follows:



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