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# ARYNE CHEMISTRY PART IV[1]

## TETRACHLOROBENZYNE

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Tetrafluorobenzyne shows high reactivity in the formation of Diels-Alder adducts in good yields with a variety of aromatic substrates.[1,2] It is of interest, therefore, to compare the reactivity of tetrachlorobenzyne with that of tetrafluorobenzyne. The recent suggestions that products obtained from the diazotisation of tetrachloroanthranilic acid[3] and that octachlorobiphenylene, obtained by pyrolysis of tetrachlorophthalic anhydride[4,5], involve tetrachlorobenzyne, prompts this report of some of our work in this area.

Pentachlorophenylmagnesium chloride has been prepared from hexachlorobenzene by entrainment with 1,2-dibromoethane in ether:benzene solution.[6] We have shown that this Grignard reagent is considerably more stable than pentafluorophenyl-magnesium chloride since removal of the ether followed by prolonged refluxing in benzene solution (12 hr.) gave, after hydrolysis, pentachlorobenzene. We find, however, that pentachlorophenylmagnesium chloride does lose magnesium chloride at the temperature of refluxing mesitylene to give a 50% yield of the expected tetrachlorobenzyne:mesitylene adduct, 3,4,5,6-tetrachloro-1,9,12-trimethyltricyclo[6,2,2,$0^{2,7}$]-dodeca-2(7),3,5,9,11-pentaene(I), b.p. 120-122° at $10^{-3}$ m.m., m.p. 109-110°.

The formation of pentachlorophenyl lithium in good yield from pentachlorobenzene by metallation with n-butyl lithium in tetrahydrofuran at -60° has been reported recently.[7] We have independently confirmed this result both by carboxylation and by reaction with bromine, which affords bromopentachlorobenzene in 80% yield. However, because of the rapid cleavage of tetrahydrofuran by organolithium reagents at higher temperatures[8] this solvent was considered to be unsatisfactory for aryne reactions. While the above metallation reaction does not give a good yield of pentachlorophenyl lithium in ether, the halogen-metal interconversion reaction with bromopentachlorobenzene and n-butyl lithium is successful. Pentachlorophenyl lithium prepared in ether:benzene by this method does give tetrachlorobenzyne at ambient temperature and this reacts with benzene to give a 37% yield of 3,4,5,6-tetrachlorotricyclo$[6,2,2,0^{2,7}]$-dodeca-2(7),3,5,9,11-pentaene[*] (II), b.p.97-100° at $10^{-4}$ m.m., m.p.74-75°. The yield of this compound is increased to 62.5% by removing the ether by distillation and briefly refluxing the reaction mixture in benzene.

The structures of the adducts were assigned on the basis of elemental analyses, ultra violet, infra red, proton magnetic resonance and mass spectra; and by reduction to the corresponding tetrahydro compounds.

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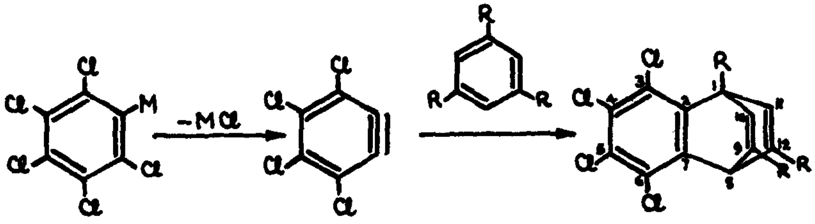
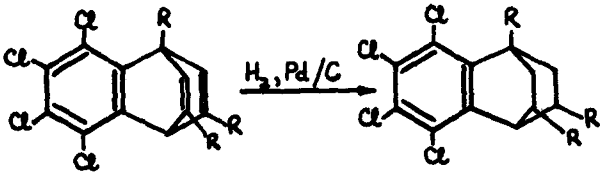
[*] J.Meinwold and J.K.Crandall in an appendix to a recent paper (J.Amer.Chem.Soc., 88, 1292 (1966) point out that serious confusion can arise due to incorrect nomenclature being used. Clearly, although the names given above do not give any impression of the chemistry involved, they should be used in preference to an attempt to fuse the Benzo-and von Baeyer systems.



a) M = MgCl
b) M = Li

I R = Me
II R = H



Further work on the reactions of tetrachlorobenzyne generated by these and other routes is at present in progress.

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