Reactions of Some Benzyne Precursors and Cyclo-octyne with a Zerovalent Platinum Complex

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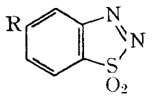
COOK and JAUHAL have reported attempts to stabilize benzyne by co-ordination to platinum.[1] In their conditions, the benzyne precursors, 1,2,3-benzothiadiazole 1,1-dioxide (Ia)[2] and benzenediazonium-2-carboxylate (IIIa),[3] were trapped by the zerovalent platinum species, bis(triphenylphosphine)(ethylene)platinum(0), before they could decompose. Our similar experiments with tetrakis(triphenylphosphine)platinum(0)[4] confirm and extend their observations and show that the reactions of benzyne, generated in the presence of the latter complex, are greatly altered.

Compound (Ia) and its 5-methyl derivative (Ib)[5] react readily with $(Ph_3P)_4Pt$ in benzene at 5° to give complexes (IIa), m.p. 177—179° (79%) and (IIb), m.p. 177—181° (71%). The spectral data for (IIa) are the same as those reported;[1] additional evidence for structure (IIb) is provided by the ^1H n.m.r. spectrum which integrated correctly and showed a singlet at τ 8·3.

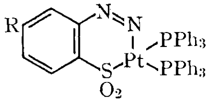
Unlike Cook and Jauhal,[1] we find that complex (IIa) does generate benzyne on photolysis. When (IIa) was irradiated (300 w sunlamp for 24 hr.) in a mixture of furan and tetrahydrofuran the benzyne adduct, 1,4-dihydronaphthalene endoxide, m.p. 53—54° (9%) and its rearrangement product, 1-naphthol (14%) were isolated. Complex (IIa) is thus a new, stable, benzyne precursor, requiring only irradiation for its decomposition. However, no adduct could be obtained by the thermolysis of (IIa) in furan.

When the reaction between complex (Ia) or (Ib) (3 mmol.) and $(Ph_3P)_4Pt$ (1 mmol.) was carried out in a mixture of ether and benzene at 35°, the reaction took a different course. Triphenylene, m.p. 192—196° [38% based on (Ia)] or 2,6,11-trimethyltriphenylene,[6] m.p. 132–133° [(35% based on (Ib)] was isolated by chromatography on alumina. Complex (Ia) usually gives small yields of biphenylene, and no triphenylene, when decomposed thermally in solution.[2]

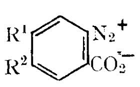
No triphenylene was formed when (Ia) was similarly decomposed in the absence of the platinum complex but in the presence of triphenylphosphine.



(I)
a; R=H
b; R=Me

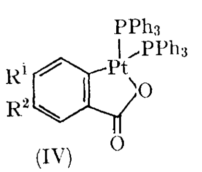


(II)
a; R=H
b; R=Me



(III)

a; $R^1 = H, R^2 = H$
b; $R^1 = H, R^2 = NO_2$
c; $R^1 = H, R^2 = Me$
d; $R^1 = H, R^2 = Cl$
e; $R^1 = Cl, R^2 = H$

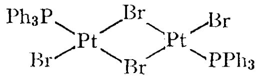


(IV)

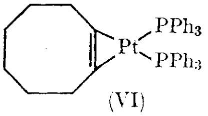
a; $R^1 = H, R^2 = H$, m.p. 260—264°
b; $R^1 = H, R^2 = NO_2$, m.p. 285—287°
c; $R^1 = H, R^2 = Me$, m.p. 261—262°
d; $R^1 = H, R^2 = Cl$, m.p. 268—270°
e; $R^1 = Cl, R^2 = H$, m.p. 270—272°

Benzenediazonium-2-carboxylate (IIIa) decomposes in 1,2-dichloroethane under reflux to give benzyne;[7] in the presence of $(Ph_3P)_4Pt$, however, complex (IVa) was obtained (80%). The structure (IVa) was assigned on the basis of the i.r. spectrum which was identical to that reported,[1] and its reaction with bromine in chloroform; with an aqueous work-up this gave *o*-bromobenzoic acid and a platinum complex, m.p. 320°, assigned structure (V). An attempt to labilize the carboxylate function in the diazonium-carboxylate by introducing suitable substituents was unsuccessful; the zwitterions (IIIb–e) gave good yields of the complexes (IVb–e) as the only products. Complex (IVa) is unchanged by irradiation or by heating at temperatures up to 200°; it is not, therefore, a benzyne precursor.

Thus all attempts to isolate a benzyne–platinum complex analogous to acetylene–platinum complexes[8] have failed at the stage of generation of benzyne. We are encouraged in this general approach, however, by the isolation in high yield (70%) of a stable cyclo-octyne–platinum complex, m.p. 180—182°, by the addition of cyclo-octyne[9] to $(Ph_3P)_4Pt$ in benzene. Structure (VI) is supported by the n.m.r. and i.r. spectra and, like all other new compounds reported, by correct analytical data.



(V)



(VI)

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