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MECHANISM OF THE CYCLISATION OF HALOGENATED α-PHENYL CINNAMIC ACIDS AND STILBENES WITH METAL AMIDES IN LIQUID AMMONIA

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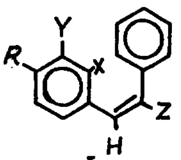
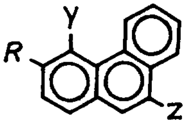
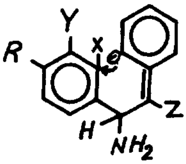
Reaction of the ortho-halogenated α-phenyl cinnamic acids (Ia; X=Cl or Br, Z=COOH, Y=R=H) and stilbenes (Ib; X=Cl, Z=C_6H_5, Y=R=H) with excess potassium amide in liquid ammonia gives the corresponding phenanthrenes (II) in good yields.[1,2]



I



II



For these cyclisations intermediacy of benzyne was assumed since the conditions used were typical for its generation. However, it was discovered later that a similar reaction with the meta-halogenated compounds Ic and Id (Y=Cl or Br, Z=COOH or C_6H_5, X=R=H) did not give phenanthrenes in detectable (t.l.c) amounts. This observation was perplexing[3] since Ic and Id can form the same benzyne as obtained from Ia and Ib. To exclude the possibility that here, due to steric or some other reasons, benzyne was being formed entirely on the wrong side, the reaction was studied with a compound in which the para position was blocked (Ie, Y=Cl, Z=COOH, X=H, R=OCH_3; $C_{16}H_{13}ClO_3$, m.p. 219-221°). Again no phenanthrene formation was observed although the halogen was lost as usual. Finally, the compound If (X=Cl, Z=COOH, Y=OCH_3, R=H) was synthesised[4] and when it was treated with KNH_2(14 mole) in liquid ammonia for 3 hrs., the corresponding phenanthrene carboxylic acid IIf (Y=OCH_3, Z=COOH, R=H; $C_{16}H_{12}O_3$, m.p. 218-9°, m/e 252 (M^+) was formed in 45 % yield. This crucial experiment clearly showed that the above cyclisations were not benzyne mediated.

A cyclisation mechanism based on addition of amide ions across the C=C bond followed by nucleophilic displacement of the halogen by the highly activated ortho carbon of the other ring (III) was then considered. However, it too could be discounted[5] in view of the failure of the fluoro compound Ig (X=F, Z=COOH, Y=R=H, Y=R=H, $C_{15}H_{11}FO_2$, m.p 183-4°) to react with KNH_2/NH_3. In this context cyclisation through a sequence involving loss of halide ion from initially formed ion-radical seems to remain the only tenable mechanism[6,7,8]. It is becoming increasingly evident that many reactions of aryl halides[9,10,11], including those of chlorides, with metal amides in liquid ammonia may not involve a benzyne intermediate.

REFERENCES AND FOOT-NOTES

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2. S.V.Kessar, M. Singh, R. Chander, D. Pal and U.K. Nadir, *Tetrahedron Letters*, 467 (1971).
3. In contrast, meta halogenated Schiff bases afford phenanthridines readily; S.V.Kessar, R. Gopal and M. Singh, *Tetrahedron*, 29, 167 (1973).
4. The α-phenylcinnamic acids were prepared by condensation of appropriate aromatic aldehydes with phenylacetic acids. The α-phenylstilbenes were synthesised through Grignard reaction of substituted benzyl chlorides with benzophenone followed by dehydration. All compounds gave satisfactory analysis.
5. Nucleophilic displacement reactions of aromatic fluorides proceed even faster than those of chlorides and bromides; J.F.Bunnett and R.E.Zahler, *Chem. Reviews*, 49, 273 (1951).
6. For a discussion of electron source in reaction of iodides under these conditions see J.K.Kim and J.F. Bunnett, *J. Amer. Chem. Soc.*, 92, 7463 (1970).
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