

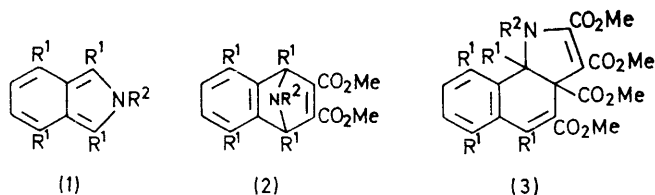
Reactions involving Deamination of Isoindole Adducts with Acetylenic Dienophiles

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Summary The formation of deaminated products is described from anomalous reactions of some isoindoles and 1,4-dihydro-1,4-iminonaphthalene derivatives with benzyne and with dimethyl acetylenedicarboxylate.

THE recent report¹ of the stepwise addition of dimethyl acetylene dicarboxylate (DMAC) to 1,3,4,7-tetramethylisoindole (**1a**) giving 1:1 and 2:1 adducts, (**2a**) and (**3a**), excited our interest in view of its relation to our work on isoindoles and to earlier studies of the 2:1 adduct from the acetylenic ester and *N*-methylpyrrole.² We have independently prepared and characterised† analogous 1:1 adducts (**2b—d**) and 2:1 adducts (**3e** and **3f**) from DMAC and the corresponding isoindoles (**1b—f**), although we were unable to isolate the intermediates (**2e** and **2f**). We report a different type of reaction of the 1:1 adducts in which the group NR² is lost from the molecule.

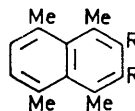


a; R¹ = Me, R² = H
b; R¹ = R² = Me
c; R¹ = Me, R² = PhCH₂

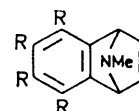
d; R¹ = Me, R² = Ph
e; R¹ = H, R² = Et
f; R¹ = H, R² = Buⁿ

Compound (**2b**) with the acetylenic ester at 110—120° failed to give the expected product (**3b**), but instead the

naphthalenedicarboxylic ester (**4a**) (33%), the structure of which was confirmed by degradation to 1,4,5,8-tetramethylnaphthalene (**4b**). This unexpected deamination is induced by DMAC, as the adduct (**2b**) is unchanged when heated alone at 110° or even briefly at 300°. The adducts (**2c** and **d**) were recovered in high yield after treatment with DMAC in similar conditions, and formation of the adducts (**3c** and **3d**) and the naphthalene derivative (**4a**) could not be detected. However, the tetrachlorobenzyne-*N*-methylpyrrole adduct (**5a**)³ with DMAC in refluxing chloroform afforded analogously 1,2,3,4-tetrachloronaphthalene (27%).



(4) a; R = CO₂Me
b; R = H



(5) a; R = Cl
b; R = H

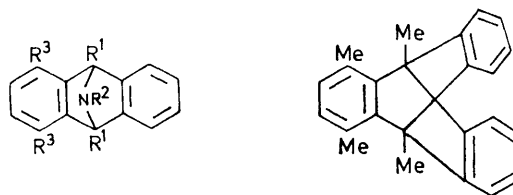
Several other 1,4-dihydro-1,4-iminonaphthalenes (**2**; H instead of CO₂Me) are aromatised spontaneously to α - or β -naphthylamine derivatives during their formation from benzyne and pyrroles,⁴ but it is unlikely that (**4a**) arises from (**2b**) via a naphthylamine intermediate. A closer analogy is the unexplained formation of a small amount of naphthalene together with 1:1 and 2:1 adducts from benzyne and *N*-methylpyrrole,⁵ where deamination of the 1:1 adduct (**5b**) is possibly brought about by further attack of benzyne. We therefore investigated reactions of some related adducts with benzyne.

† Structures are assigned to all new compounds in accord with analytical and appropriate spectroscopic evidence.

Benzyne adducts (**6a—c**) have been obtained from a number of isoindoles,^{8,7} but with *o*-bromofluorobenzene and magnesium in refluxing THF the isoindole (**1c**) gave none of the analogous adduct (**6e**). Instead a hydrocarbon product, C₂₄H₂₂, identified as the tetramethyltriptycene (**7**) was obtained. *N*-Benzylcarbazole was found among other products of the reaction, and some unchanged isoindole (**1c**) was autoxidised during work-up forming *N*-benzyl-3,6-dimethylphthalimide,⁸ the structure of which was confirmed by independent synthesis. *N*-Methylcarbazole was similarly produced in the reaction of benzyne with compound (**5a**).

Compound (**7**) presumably arises by addition of benzyne to 1,4,9,10-tetramethylantracene, formed by deamination of an intermediate adduct (**6e**). Analogously, Wittig *et al.*⁸ isolated anthracene in small yield from the reaction of *N*-phenylisoindole or the *N*-methylisoindole adduct (**6a**) with benzyne. Also the formation of 9,10-diphenylanthracene from adduct (**6d**) at 215° has been reported,⁷ but in none of these cases has the fate of the extruded fragment NR² been established. The formation of carbazole derivatives in our reactions of (**1c**) and (**5a**) with benzyne

suggests a mechanism in which the attack of benzyne accomplishes the deamination of the imino-bridged systems (**5**) and (**6**).



- (6) a; R¹ = R³ = H, R² = Me
 b; R¹ = R³ = H, R² = Ph
 c; R¹ = Ph, R² = R³ = H
 d; R¹ = Ph, R² = CO₂Et, R³ = H
 e; R¹ = R³ = Me, R² = PhCH₂

(7)

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