Reactions involving Deamination of Isoindole Adducts with Acetylenic Dienophiles

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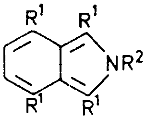
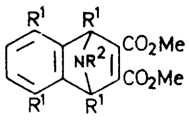
Summary The formation of deaminated products is described from anomalous reactions of some isoindoles and 1,4-dihydro-1,4-iminonaphthalene derivatives with benzyne and with dimethyl acetylenedicarboxylate.

THE recent report[1] 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 NR^2 is lost from the molecule.



(1)



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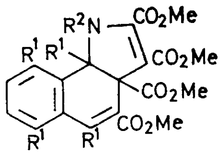
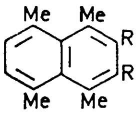


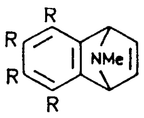
(3)

a; R^1 = Me, R^2 = H
b; R^1 = R^2 = Me
c; R^1 = Me, R^2 = PhCH$_2$
d; R^1 = Me, R^2 = Ph
e; R^1 = H, R^2 = Et
f; R^1 = H, R^2 = Bu^n

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 = CO$_2$Me
b; R = H



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

Several other 1,4-dihydro-1,4-iminonaphthalenes (**2**; H instead of CO$_2$Me) 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.

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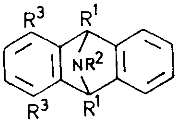
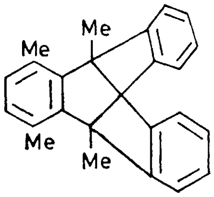
† Structures are assigned to all new compounds in accord with analytical and appropriate spectroscopic evidence.

Benzyne adducts (**6a**—**c**) have been obtained from a number of isoindoles,[6,7] but with *o*-bromofluorobenzene and magnesium in refluxing THF the isoindole (**1c**) gave none of the analogous adduct (**6e**). Instead a hydrocarbon product, $C_{24}H_{22}$, 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-tetramethylanthracene, formed by deamination of an intermediate adduct (**6e**). Analogously, Wittig *et al.*[6] 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 NR^2 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; $R^1 = R^3 = H$, $R^2 = Me$
b; $R^1 = R^3 = H$, $R^2 = Ph$
c; $R^1 = Ph$, $R^2 = R^3 = H$
d; $R^1 = Ph$, $R^2 = CO_2Et$, $R^3 = H$
e; $R^1 = R^3 = Me$, $R^2 = PhCH_2$



(**7**)

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