Reactions of Tertiary Allylamines with Dimethyl Acetylenedicarboxylate

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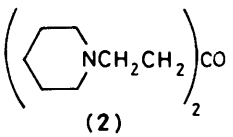
The reaction of some tertiary allylamines with dimethyl acetylenedicarboxylate in acetonitrile results in the formation of 1 : 1 adducts *via* [3,3] rearrangement of the allyl group from nitrogen to carbon.

Tertiary amines catalyse the nucleophilic addition of species HX to activated acetylenes.[1] In some other cases, adducts incorporating the amine moiety are obtained as the result of C–N bond cleavage. Winterfeldt has described a variety of such reactions involving the tertiary amino-ester (**1a**) and -ketones (**1b**) and (**2**) with methyl propiolate to give β-aminocrotonates (**3a**) and (**3b**).[1] The formation of *N*-ethylpyrrole derivatives from tertiary amines (**1b**) and (**1c**) and acetylene esters involves loss of the second *N*-ethyl group in each case. Similarly triethylamine is reported[2] to add to dimethyl acetylenedicarboxylate (DMAD) in the presence of a proton source to give compound (**4a**), for which the maleate configuration, not assigned at the time, is correct by comparison of spectral data with those of analogous compounds.[3,4] *N*-Benzylaziridine catalyses the trimerisation of DMAD in aprotic solvents, but in t-butyl alcohol a 1:1:1 adduct (**4c**) is obtained through opening of the aziridine ring.[5]

Et_2NCH_2R

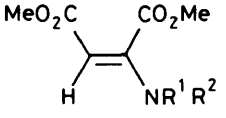
(**1**) a; R = CH_2CO_2Et
b; R = COPh
c; R = CO_2Me



(**2**)

$R^1R^2NCH{=}CHCO_2Me$

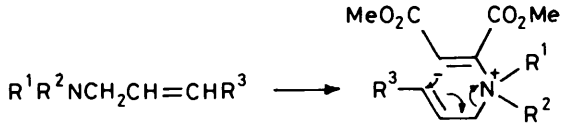
(**3**) a; $R^1 = R^2 = Et$
b; $R^1, R^2 = (CH_2)_5$



(**4**) a; $R^1 = R^2 = Et$
b; $R^1, R^2 = (CH_2)_5$
c; $R^1 = CH_2Ph$, $R^2 = CH_2CH_2OBu^t$
d; $R^1 = R^2 = Me$
e; $R^1, R^2 = (CH_2)_2$
f; $R^1, R^2 = CH_2CH{=}CHCH_2$
g; $R^1, R^2 = (CH_2)_4$

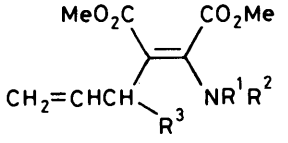
Results and Discussion

We have examined the addition of tertiary allylic amines to DMAD. Although no reaction occurs between allyldiethylamine (**5a**) and DMAD in dry ether, these compounds react readily in acetonitrile at room temperature to give the 1:1 adduct (**7a**) together with smaller amounts of the aminomaleate (**4a**). The proportion of (**4a**) increased if water was added to the system, but it still amounted to a small percentage of the main product (**7a**) even when thoroughly dry acetonitrile was used. *N*-Allylpiperidine (**5b**) reacted similarly with DMAD to give the 1:1 adduct (**7b**) and a smaller amount of (**4b**). The constitution of the adducts (**7a**) and (**7b**) was proved from their ^1H n.m.r. and mass spectra and by hydrolysis in the presence of 2,4-dinitrophenylhydrazine, when both (**7a**) and (**7b**) afforded the same derivative (**9b**). Authentic samples of the by-products (**4a**) and (**4b**) were prepared from DMAD with diethylamine and piperidine, respectively, and similarly converted into the 2,4-dinitrophenylhydrazone derivative (**9a**). Catalytic hydrogenation of the adduct (**7a**) gave the corresponding propyl compound (**8**), which was characterised both as the 2,4-dinitrophenylhydrazone (**9d**), and by degradation to 2-oxohexanoic acid (Scheme 2).



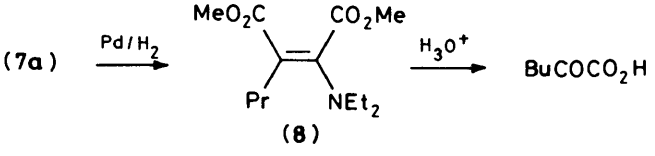
(**5**) a; $R^1 = R^2 = Et$, $R^3 = H$
b; $R^1, R^2 = (CH_2)_5$, $R^3 = H$
c; $R^1 = R^2 = Et$, $R^3 = Me$

(**6**)



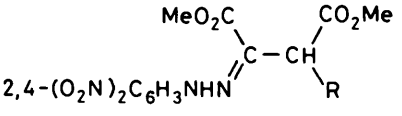
(**7**) a; $R^1 = R^2 = Et$, $R^3 = H$
b; $R^1, R^2 = (CH_2)_5$, $R^3 = H$
c; $R^1 = R^2 = Et$, $R^3 = Me$

Scheme 1.

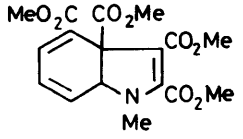


(**8**)

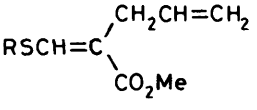
Scheme 2.



(**9**) a; R = H
b; R = $CH_2{=}CHCH_2$
c; R = $CH_2{=}CHCHMe$
d; R = Pr



(**10**)



(**11**)

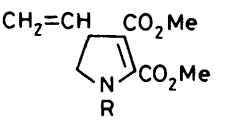
The addition of tertiary allylic amines to DMAD is assumed to proceed as depicted in Scheme 1. This pattern of addition was suggested by consideration of the mechanism proposed to account for the formation of the rearranged 1:2 adduct (**10**) from *N*-methylpyrrole and DMAD[6] and of the nature of the reaction of thebaine with methyl and ethyl propiolate in polar solvents.[7,8] Allylic sulphides react in the same manner with *acetylene esters*, but only in the presence of aluminium trichloride.[9] Formation of the intermediate zwitterion (**6**) requires a polar solvent. Inversion of the allyl group, as required by this mechanism, was confirmed using but-2-enyldiethylamine (**5c**) with DMAD, which afforded the 1:1 adduct (**7c**). The ^{1}H n.m.r. spectrum of (**7c**) included signals for three vinyl hydrogens and a doublet signal for one *C*-methyl group; there was no evidence for the formation of the isomeric adduct in which the but-2-enyl group had migrated without rearrangement. The adduct (**7c**) was also characterised by conversion into the 2,4-dinitrophenylhydrazone derivative (**9c**).

As the tertiary amines (**5a**—**c**) were demonstrably free of contamination by secondary amines, the formation of the by-products (**4a**) and (**4b**) is attributable to protonation of the carbanion centre in the intermediate (**6**), *e.g.* by water; this prevents the rearrangement leading to (**7**), but is followed by loss of the allyl group, *e.g.* by an S_N2' reaction also possibly involving water.

The second step in Scheme 1 may be compared to the [3,3] sigmatropic rearrangement of *N*-allylenammonium ions,[10] which is greatly facilitated by the positive charge. The corresponding process in *N*-allylenamines occurs only above 200 °C.[11] [2,3] And other rearrangements of allylic ammonium ylides have also been described.[12]

The adducts (**7a**—**c**) are expected to have the *E*-configuration, both on account of their formation supposedly *via* a cyclic transition state (Scheme 1) and because the maleate (*E*-) configuration of the related enamine esters (**4**) has been shown to be thermodynamically preferred.[3,13] Indeed, the *Z*-stereoisomeric adduct of a secondary amine and DMAD has been obtained pure and well characterised in only one case.[4,14] However, the experimental evidence for the stereochemistry of (**7a**—**c**) is not altogether clear. The *N*,*N*-diethylamino compound (**7a**) shows two i.r. absorption bands in the carbonyl region (1 731 and 1 691 cm^{-1} in CH_2Cl_2) comparable to those of the aminomaleates (**4b**) and (**4d**).[3,15] The single u.v. absorption band of (**7a**) in dioxane ($\lambda_{max.}$ 298 nm, ε 710 m^2 mol^{-1}) is at longer wavelength than reported for the aminomaleates (**4a**, **b**, **d**) (277—282 nm),[3,4,15] and closer to that for the *Z*-steroisomer of (**4e**) (292 nm).[4] Both (**7b**) and (**7c**) show more complicated, less well resolved i.r. absorption in the carbonyl region and two u.v. absorption maxima, one either side of that of (**7a**). Moreover, g.l.c. analysis of the piperidino compound (**7b**) revealed a subsidiary peak, enhanced in relative intensity after distillation of the sample, just preceding and overlapping the main peak for the 1:1 adduct; selective ion monitoring of the mass spectra recorded through this double peak failed to show any difference in composition. There were also additional lines of low intensity in the ^{13}C n.m.r. spectra of both compounds (**7b**) and (**7c**). All of this evidence is compatible with compound (**7a**) being a single stereoisomer, probably the maleate, but the distilled samples of compound (**7b**) and (**7c**) being mixtures of maleate and fumarate stereoisomers. Similarly, the adducts (**11**) obtained from allylic sulphides and methyl propiolate were shown to be mixtures containing 70—90% of the *E* stereoisomers.[9]

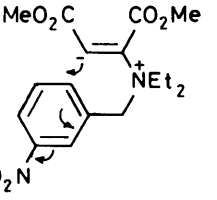
It was of interest to examine the addition of *N*-substituted derivatives of 2,5-dihydropyrrole to DMAD, which by the same mechanism should afford adducts of structure (**12**). A *ca.* 3:1 mixture of 2,5-dihydropyrrole and pyrrolidine available commercially was converted into a mixture of the *N*-benzyl derivatives (**13a**) and (**13b**), which on reaction with DMAD in aceto-



(**12**)

$XC_6H_4CH_2NR^1R^2$

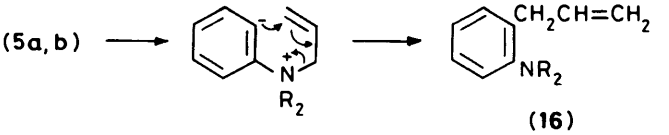
(**13**) a; X = H, R^1, R^2 = $CH_2CH{=}CHCH_2$
b; X = H, R^1, R^2 = $(CH_2)_4$
c; X = H, R^1 = R^2 = Me
d; X = 3-NO_2, R^1 = R^2 = Et



(**14**)

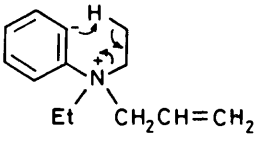
$PhNR^1R^2$

(**15**) a; R^1 = R^2 = Et
b; R^1 = Et, R^2 = $CH_2CH{=}CHCH_2$
c; R^1, R^2 = $(CH_2)_5$
d; R^1 = Me, R^2 = PhCHMe
e; R^1 = Et, R^2 = $CH_2{=}CHCHEt$

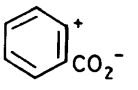


(**16**)

Scheme 3.



(**17**)



(**18**)

nitrile afforded the amino esters (**4f**) and (**4g**) as the only identifiable products. The major component (**4f**) was separated from the mixture chromatographically, and (**4g**) was identified *in situ* by comparison of its chromatographic behaviour with that of an authentic sample prepared from pyrrolidine and DMAD.[16] The readiness with which the benzyl groups of (**13a**) and (**13b**) are lost in the reaction with DMAD was also observed in the case of benzyldimethylamine (**13c**), which afforded only the *N*,*N*-dimethylaminomaleate (**4d**). The same amine (**13c**) also reacts with benzyne to give *N*,*N*-dimethylaniline as the major product, together with the 1-phenylethylamine (**15d**) resulting from a Stevens rearrangement.[17]

In the case of *N*,*N*-diethyl-3-nitrobenzylamine (**13d**) we hoped that the nitro group might facilitate rearrangement of an intermediate zwitterion, as shown in (**14**), whereby the benzyl group might be less readily lost. However, we failed to induce any reaction between the amine (**13d**) and DMAD.

Lastly, we also investigated the reaction of the tertiary allylic amines (**5a**) and (**5b**) with benzyne, where the corresponding rearrangement of an intermediate zwitterion would give rise to 2-allylanilines (**16**) (Scheme 3). The related possibility of *o*-alkylation but without allylic rearrangement is to be found in previous work by Hellmann *et al.*[17] However, we found no evidence for the formation of the expected product (**16**); instead,

formation of the tertiary amines (**15a**—**c**) accounted for 21% of the benzyne used in each reaction. *N*-Allyl-*N*-ethylaniline (**15b**), a minor product from allyldiethylamine (**5a**), is probably formed *via* an intramolecular Hofmann elimination in an intermediate zwitterion (**17**).[18] The products reported elsewhere from compound (**5a**) and benzyne under somewhat different conditions were *N*-ethylaniline and the rearranged tertiary amine (**15c**),[17] neither of which was apparent in our reaction mixture. Allyl benzoate, identified as a by-product from both (**5a**) and (**5b**), is probably formed by transfer of an allyl group to benzenediazonium-2-carboxylate or to (**18**), the intermediate in the stepwise decomposition of benzenediazonium-2-carboxylate to benzyne.

Experimental

^{1}H N.m.r. spectra were recorded at 60 MHz on a Perkin-Elmer EM-360 or at 90 MHz on a JEOL JNM-FX-90Q spectrometer, and ^{13}C n.m.r. spectra at 22.6 MHz on the latter instrument, for solutions in deuteriochloroform with tetramethylsilane as internal standard; multiplicities of ^{13}C signals in proton-coupled off-resonance spectra are given in parenthesis. Mass spectra were recorded at 70 eV on a Kratos MS30 instrument; only those fragment ions with relative intensity $\geqslant 20\%$ are recorded. G.c. analyses of the tertiary amines (**5a**—**c**) and (**13a**—**d**) were performed on a column containing Carbowax 20M (20%) and potassium hydroxide (5%), g.c. analyses of the enamine esters (**4a**, **b**, **f**, **g**), (**7a**—**c**), and (**8**) on an Apiezon column, and g.c. analyses of the benzyne reaction products on di- or poly-ethyleneglycol adipate. T.l.c. was performed on silica-coated plates developed with diethyl ether–light petroleum (1:1 v/v), and preparative t.l.c. was carried out on 1 mm coated circular plates using a Chromatotron®. Light petroleum refers to the fraction b.p. 60—80 °C. Ether refers to diethyl ether.

The tertiary amines (**5a**—**c**),[19–21] (**13d**),[22] and (**15c**)[23] were prepared according to literature methods and their purity checked by g.c. before use. 2,5-Dihydropyrrole containing 25% pyrrolidine (Aldrich) was treated with benzoyl chloride in the presence of 10% aqueous sodium hydroxide; the mixture of *N*-benzoyl derivatives was dissolved in ether and reduced with aluminium lithium hydride to give a 3:1 mixture of the *N*-benzyl derivatives (**13a**) and (**13b**) as an oil, which was distilled at 105—125 °C (bath)/15—20 mmHg. The components (**13a**) and (**13b**) were inseparable by g.c. The ^{1}H n.m.r. spectrum was characteristic for (**13a**): δ 3.46 (4 H, s, ring CH_2), 3.75 (2 H, s, CH_2Ph), 5.73 (2 H, s, =CH), and 7.79 (5 H, s, ArH), with additional peaks due to (**13b**).

The aminomaleates (**4a**, **b**, **d**, **g**) were prepared from diethylamine, piperidine, dimethylamine, and pyrrolidine, respectively, with DMAD in dry ether; the m.p.s of (**4b**, **d**, **g**) were in agreement with literature values.[3,4,16]

Addition of DMAD to Allyldiethylamine (**5a**).—DMAD (1.42 g, 10 mmol) was added dropwise to a solution of allyldiethylamine (**5a**) (1.13 g, 10 mmol) in acetonitrile (30 ml). The mixture was left overnight; acetonitrile was then evaporated under reduced pressure, and the residual oil redissolved in ether and filtered from a small quantity of tarry solid. Analysis by g.c.—m.s. showed the presence of (**4a**) and the 1:1 adduct (**7a**) (peak area ratio 1:10); compound (**4a**) was identical with an authentic sample in respect of g.c. retention time and mass spectrum; compound (**7a**) was identified from its mass spectrum; *m/z* 255 (M^+, 31%), 214 (84), 196 (M − CO_2Me, 100), 168 (21), 166 (30), 136 (40), 108 (38), 80 (33), and 59 (63) (Found: M^+, 255.1462. $C_{13}H_{21}NO_4$ requires M^+, 255.1470). Distillation at 100—125 °C (bath)/1 mmHg gave a pale yellow oil but did not separate the two components. N.m.r. spectra were recorded for a distilled sample and (**7a**) was characterised as follows: δ_H 1.15 (6 H, t, CMe), 3.10 (4 H, q, NCH_2 overlapping 2 H, s, CCH_2), 3.68 and 3.81 (each 3 H, s, OMe), and 4.8—6.2 (3 H, m, $CH{=}CH_2$); δ_C 13.6 (q, CMe), 32.1 (t, $=CCH_2$), 45.7 (t, NCH_2), 50.9 and 51.6 (q, OMe), 108.0 (s, =C), 114.3 (t, $=CH_2$), 135.6 (d, =CH), and 166.8 and 168.5 (s, CO).

The adduct (**7a**) (0.15 g) and 2,4-dinitrophenylhydrazine (0.15 g) in methanol (7 ml) containing 2 drops concentrated hydrochloric acid were heated under reflux for 2 h, and then chilled. The yellow crystals (0.20 g) were collected and recrystallised to give the 2,4-*dinitrophenylhydrazone* (**9b**), m.p. 98—99 °C (from methanol) (Found: C, 47.3; H, 4.2; N, 15.0. $C_{15}H_{16}N_4O_8$ requires C, 47.3; H, 4.2; N, 14.7%); *m/z* 380 (M^+). T.l.c. examination of the mother liquor showed, as well as compound (**9b**), the presence of a second, slower moving component, the behaviour of which was matched by that of dimethyl oxaloacetate 2,4-DNP (**9a**), m.p. 160—161 °C (lit.,[6] m.p. 161 °C), obtained in the same way from the enamine ester (**4a**) and 2,4-dinitrophenylhydrazine.

Addition of DMAD to N-*Allylpiperidine* (**5b**).—This reaction was carried out in the same way as described above. The crude product after evaporation of ether was a reddish brown oil (2.3 g, 86%), consisting of (**4b**) and (**7b**) (g.c. peak area ratio 1:11), identified by g.c.—m.s. and, in the case of (**4b**), by comparison with an authentic sample. Distillation at 130—150 °C (bath)/1 mmHg gave a pale yellow oil, in which the adduct (**7b**) was characterised by the following spectroscopic evidence: δ_H 1.60 (6 H, br, ring CH_2), 2.43 (2 H, br, allyl CH_2), 3.07 (4 H, br, NCH_2), 3.67 and 3.81 (each 3 H, s, OMe), and 4.8—7.5 (3 H, m, $CH{=}CH_2$); δ_C 23.9 (t, CH_2), 26.2 (t, 2 × CH_2), 32.7 (t, allyl CH_2), 51.5 (q, OMe), 51.6 (t, NCH_2), 52.2 (q, OMe), 107.3 (s, =C), 115.0 (t, $=CH_2$), 136.4 (d, =CH), 153.2 (s, =C), and 167.2 and 169.0 (s, C=O); *m/z* 267 (28%), 226 (M − C_3H_5, 61), 208 (M − CO_2Me, 100), 166 (40), and 148 (50) (Found: M^+, 267.1471. $C_{14}H_{21}NO_4$ requires M^+, 267.1470).

The reaction between DMAD and the amine (**5b**) was repeated in rigorously anhydrous acetonitrile, when the same products (**4b**) and (**7b**) were formed in 1:36 ratio (g.c. peak areas). The proportion of (**4b**) increased with addition of increasing amounts of water, and in aqueous acetonitrile (1:1 v/v) the same products were formed in 1:1.3 ratio.

A distilled sample of the adduct (**7b**) was hydrolysed in the presence of 2,4-dinitrophenylhydrazine, as described for (**7a**), and afforded the same 2,4-DNP derivative (**9b**), m.p. and mixed m.p. 98—99 °C. As before, the mother liquor from recrystallisation of compound (**9b**) also contained compound (**9a**), formed from (**4b**), and identified by matching its t.l.c. behaviour with that of an authentic sample.

Addition of DMAD to N,N-*Diethylbut-2-enylamine* (**5c**).—This reaction was carried out using 10 mmol of each reactant, as before. The crude product after evaporation of ether was a reddish brown oil (2.2 g, 82%) consisting of (**4a**) and (**7c**) (g.c. peak area ratio 1:17), identified by g.c.—m.s. and, in the case of (**4a**), by comparison with an authentic sample. Distillation at 100—130 °C (bath)/0.6 mmHg gave a pale yellow oil, in which the adduct (**7c**) was characterised by the following spectroscopic evidence: δ_H 1.10 (6 H, t, CH_2*Me*), 1.28 (3 H, d, CH*Me*), 3.94 (4 H, q, CH_2Me), 3.68 and 3.74 (each 3 H, s, OMe), 4.8—5.2 (2 H, m, $=CH_2$), and 5.7—6.3 (1 H, m, =CH); δ_C 13.8 and 18.1 (q, *CMe*), 37.3 (d, CH), 47.3 (t, NCH_2), 50.9 and 51.3 (q, OMe), 113.5 (t, $=CH_2$), 131.2 (s), 140.3 (d, =CH), 146.1 (s), and 166.3 and 168.0 (s, C=O); *m/z* 269 (M^+, 25%), 254 (M − Me, 47), 214 (83), 210 (M − CO_2Me, 100), 180 (30), 150 (24), 94 (20), 72 (20), and 59 (62) (Found: M^+, 269.1627. $C_{14}H_{23}NO_4$ requires M^+, 269.1627).

A distilled sample of the adduct (**7c**) was hydrolysed in the

presence of 2,4-dinitrophenylhydrazine, as described for (**7a**), and afforded the corresponding 2,4-*DNP derivative* (**9c**), yellow needles, m.p. 104—106 °C (from methanol) (Found: C, 48.8; H, 4.5; N, 14.4. $C_{16}H_{18}N_4O_8$ requires C, 48.7; H, 4.6; N, 14.2); *m/z* 394 (M^+, 4%), 348 ($M - NO_2$, 65), 335 (28), 308 (28), 307 (56), and 195 (ArN_2^+, 100). As before, the mother liquor from recrystallisation of (**9c**) also contained (**9a**), formed from (**4a**), and was identified by t.l.c. comparison with an authentic sample.

Degradation of the Adduct (**7a**) *to 2-Oxohexanoic Acid.*—The adduct (**7a**) (3.7 g) in methanol (150 ml) with palladium–charcoal (5%, 0.17 g) was shaken under hydrogen at atmospheric pressure until the uptake of the calculated volume of hydrogen was complete. The solution was filtered, the methanol evaporated off under reduced pressure, and the residue distilled to afford an oil (3.2 g), b.p. 86—88 °C (bath)/0.6 mmHg, in which the dominant component (**8**) was identified by g.c.—m.s.: *m/z* 257 (M^+, 24%), 228 (M – Et, 85), 214 (24), 198 ($M - CO_2Me$, 100), 142 (22), 140 (22), 111 (28), and 59 (45). A sample of (**8**) was characterised by conversion into the 2,4-*DNP derivative* (**9d**) by the same procedure as described above for (**7a**)→(**9b**); clustered yellow rod-like crystals, m.p. 127—128 °C (from methanol) (Found: C, 47.3; H, 4.8; N, 14.6. $C_{15}H_{18}N_4O_8$ requires C, 47.1; H, 4.7; N, 14.7); *m/z* 382 (M^+).

Another sample of the dihydro derivative (**8**) (1.0 g) was heated under reflux for 20 h with dilute sulphuric acid (10 ml, 14%). The mixture was cooled and extracted with ether; the ether was washed, dried ($MgSO_4$), and evaporated under reduced pressure. The residual oil (0.37 g) was subjected to short-path distillation to give 2-oxohexanoic acid, b.p. 60—90 °C (bath)/1 mmHg, which solidified below room temperature; δ_C 13.4 (q, Me), 21.8, 24.8, and 37.7 (each t, CH_2), and 161.4 and 195.6 (each s, C=O). On treatment with hydroxylamine in aqueous ethanol it afforded the oxime derivative, m.p. 135—137 °C (from ethanol) (lit.,[24] m.p. 137 °C).

Reaction of DMAD with N-*Benzyl-2,5-dihydropyrrole* (**13a**).—DMAD (0.09 g) was added to the 3:1 mixture of *N*-benzyl-2,5-dihydropyrrole (**13a**) and -pyrrolidine (**13b**) (0.10 g) in dry acetonitrile (10 ml). After 2 days the solvent was evaporated under reduced pressure and the residual oil redissolved in ether. Analysis by g.c.—m.s. suggested the presence of the enamine esters (**4f**) and (**4g**), the latter identical in respect of g.c. retention time and mass spectrum with an authentic sample.[16] Preparative t.l.c. eluting with light petroleum afforded *dimethyl 2,5-dihydropyrrol-1-ylmaleate* (**4f**) (25 mg), m.p. 97—99 °C (from light petroleum) (Found: M^+, 211.0846. $C_{10}H_{13}NO_4$ requires M^+, 211.0844); $\lambda_{max.}$(EtOH) 282 nm ($\varepsilon_{max.}$ 1 550 m^2 mol^{-1}); $\nu_{max.}$(KBr) 1 740, 1 695, and 1 635 cm^{-1}; δ_H 3.65 and 3.95 (each 3 H, s, OMe), 4.08 (4 H, s, NCH_2), 4.53 (1 H, s, =CH), and 5.85 (2 H, s, ring =CH); *m/z* 211 (M^+, 59%), 180 (M – OMe, 49), 179 (M – MeOH, 100), 164 (20), 152 ($M - CO_2Me$, 38), 151 (67), 150 (27), 120 (35), 93 (42), 92 (50), 68 (35), 54 (21), 53 (27), and 39 (27).

Reaction of DMAD with Dimethylbenzylamine (**13c**).—DMAD (1.42 g, 10 mmol) was added dropwise to the amine (**13c**) (1.35 g, 10 mmol) in dry acetonitrile. After being left overnight, the acetonitrile was evaporated under reduced pressure. Preparative t.l.c. of the residual oil eluting with light petroleum afforded dimethyl dimethylaminomaleate (**4d**) (0.3 g), m.p. 79—80 °C alone or admixed with an authentic sample (lit.,[3] m.p. 83—84.5 °C), with which it was also identical in respect of t.l.c. behaviour and i.r., n.m.r., and mass spectra.

Reaction of Benzyne with N,N-*Diethylallylamine* (**5a**).— A slurry of benzenediazonium-2-carboxylate [prepared[25] from anthranilic acid (1.37 g, 10 mmol), isopentyl nitrite (2.0 g), and trichloroacetic acid (10 mg)] in dry tetrahydrofuran was added in portions over 0.5 h to the amine (1.13 g, 10 mmol) in tetrahydrofuran (50 ml). The mixture was stirred and heated under reflux during this addition and for a further 0.5 h. The solvent was removed under reduced pressure, the residue was redissolved in ether and filtered, and this filtrate analysed by g.c. and the analyses quantified using 1,2-diphenylethane as internal standard. *N,N*-Diethylaniline (**15a**) (15% based on benzyne precursor) [*m/z* 149 (M^+, 35%) and 134 (M – Me, 100)], *N*-allyl-*N*-ethylaniline (**15b**) (6%) [*m/z* 161 (M^+, 63%) and 146 (M – Me, 100)], and allyl benzoate (5%) [*m/z* 162 (M^+, 10%) and 105 ($PhCO^+$, 100)] were identified by comparison of g.c. retention times and mass spectra with those of authentic samples.

Reaction of Benzyne with N-*Allylpiperidine* (**5b**).—The above procedure was repeated using *N*-allylpiperidine (**5b**) (1.25 g, 10 mmol) in place of (**5a**). G.c. analyses of the reaction mixture on diethyleneglycol adipate were quantified using 1,2-diphenylethane as internal standard. Unchanged (**5b**) (74%) [*m/z* 125 (M^+, 34%) and 98 (100)], allyl benzoate (9%), and *N*-phenylpiperidine (**15c**) (15%) [*m/z* 161 (M^+, 73%) and 160 (100)] were identified by comparison of g.c. retention times and mass spectra with those of authentic samples.

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