Reaction of Diazomethane with Arylideneanilines.

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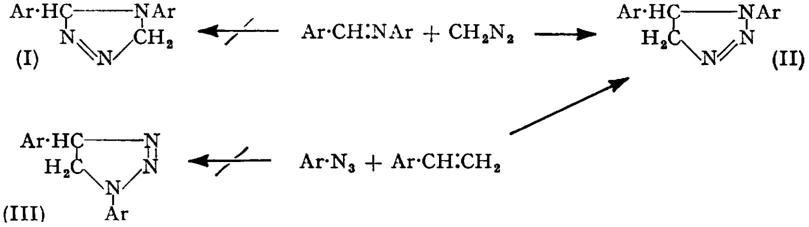
The compound obtained by the action of diazomethane on *p*-nitro-*N*-*p*′-nitrobenzylideneaniline is identical with the product of the reaction of *p*-nitrophenyl azide with *p*-nitrostyrene, and is therefore a 1 : 5-diaryl-1 : 2 : 3-triazoline.

Benzylideneaniline and *p*-chlorobenzylideneaniline with ethereal diazomethane in presence of methanol give 1 : 2 : 3-triazolines in 10—15% yield but do not react in absence of methanol.

Mustafa (*J.*, 1949, 234) has shown that certain nitro-derivatives of benzylideneaniline react with diazomethane to form heterocyclic compounds, to which he ascribes a 4 : 5-diaryl-1 : 2 : 4-triazoline structure (I) on very inadequate grounds. If Mustafa is correct the methylene group of the diazomethane has become attached to the nitrogen atom of the arylideneaniline, but this is unlikely because diazomethane normally reacts in the form $\overset{-}{C}H_2-\overset{+}{N}\equiv N$ (cf. addition to carbonyl compounds), and in nucleophilic additions to the $C{=}N$ bond the anion invariably becomes attached to the carbon atom (cf. addition of sodium cyanide, nitromethane, sodium hydrogen sulphite, etc.). It therefore seems probable that in the addition of diazomethane to arylideneanilines the methylene group will become attached to carbon rather than nitrogen, and the product will be a 1 : 5-diaryl-1 : 2 : 3-triazoline (II).



The structure of the product from diazomethane and *p*-nitro-*N*-*p*′-nitrobenzylideneaniline has been investigated. This compound must be either 4 : 5-di-*p*-nitrophenyl-1 : 2 : 4-triazoline (as I) or 1 : 5-di-*p*-nitrophenyl-1 : 2 : 3-triazoline (as II). 1 : 5-Diphenyl-1 : 2 : 3-triazoline (II; Ar = Ph) is formed by the action of phenyl azide on styrene (Wolff, *Annalen*, 1912, **394**, 68). *p*-Nitrophenyl azide was therefore treated with *p*-nitrostyrene in an attempt to synthesise (II; Ar = *p*-$NO_2{\cdot}C_6H_4$). An addition product of empirical formula $C_{14}H_{11}O_4N_5$, which must be either (II or less probably III; Ar = *p*-$NO_2{\cdot}C_6H_4$), was isolated. It was identical in melting point and infra-red spectrum with the compound obtained from diazomethane and the anil and must therefore be (II; Ar = *p*-$NO_2{\cdot}C_6H_4$).

Formula (II) was rejected by Mustafa chiefly because he found that the compound dissociated to diazomethane and the anil at 270° and he considered it unlikely that the C–C bond in the 1 : 2 : 3-triazoline ring could be disrupted so easily. This is not, however, a valid objection since it has been shown that an analogous dissociation of the 1 : 2 : 3-oxadiazolines to diazomethane and a carbonyl compound may occur at 250° (Bridson-Jones, Buckley, Cross, and Driver, *J.*, 1951, 2999).

Mustafa (*loc. cit.*) reported that benzylideneaniline failed to react with ethereal diazomethane at 0°, and this has been confirmed. However, the addition of a little methanol to the mixture caused reaction to take place, and after ten days about 15% of the anil had been converted into 1 : 5 diphenyl-1 : 2 : 3-triazoline (II; Ar = Ph), which was identified by comparison with a specimen prepared by the action of phenyl azide on styrene. *p*-Chlorobenzylideneaniline reacted similarly with diazomethane in presence, but not in absence, of methanol to give 5-*p*-chlorophenyl-1-phenyl-1 : 2 : 3-triazoline in small yield.

EXPERIMENTAL

Microanalyses are by Dr. A. F. Colson. M. p.s are corrected.

1 : 5-*Di*-(p-*nitrophenyl*)-1 : 2 : 3-*triazoline*.—(*a*) *p*-Nitro-*p'*-nitrobenzylideneaniline (2 g.) was finely powdered and added to an ice-cold solution of diazomethane (4 g.) in ether (100 c.c.). The mixture was held at 0° for 10 days, and the crystals (2·1 g.) were collected and washed with ether. Recrystallisation from ethyl acetate gave faintly yellow needles of 1 : 5-*di*-(p-*nitrophenyl*)-1 : 2 : 3-*triazoline*, m. p. 178° (decomp.) (Found: C, 53·6; H, 3·4; N, 22·2. $C_{14}H_{11}O_4N_5$ requires C, 53·65; H, 3·5; N, 22·35%).

(*b*) A mixture of *p*-nitrophenyl azide (3 g.), *p*-nitrostyrene (3 g.), and ethyl acetate (10 c.c.) was refluxed on a steam-bath for 4 hr. After the mixture had been cooled, the crystalline product (1·1 g.) was collected and washed with ethanol. Recrystallisation from ethyl acetate gave pale yellow crystals, m. p. 177° (decomp.) (Found: C, 53·6; H, 3·4; N, 22·6. Calc. for $C_{14}H_{11}O_4N_5$: C, 53·65; H, 3·5; N, 22·35%). Its infra-red absorption spectrum was identical with that of a specimen prepared by method (*a*).

1 : 5-*Diphenyl*-1 : 2 : 3-*triazoline*.—(*a*) A solution of benzylideneaniline (2 g.) in methanol (10 c.c.) was added to an ice-cold solution of diazomethane (4 g.) in ether (100 c.c.) and held at 0° for 10 days. The solvents were then allowed to evaporate at 20°, and the residue was extracted with 50 c.c. of cold ligroin (b. p. 40—60°). The insoluble material (0·25 g.) was collected and washed with ligroin. A duplicate experiment gave 0·3 g. Crystallisation from methanol gave colourless needles of 1 : 5-diphenyl-1 : 2 : 3-triazoline, m. p. 128° (decomp.) (Found: C, 75·2; H, 5·7; N, 18·8. Calc. for $C_{14}H_{13}N_3$: C, 75·3; H, 5·85; N, 18·85%).

(*b*) A mixture of phenyl azide (10 g.), styrene (9·3 g.), and ethyl acetate (20 c.c.) was refluxed on a steam-bath for 4 hr. The ethyl acetate was removed by distillation under reduced pressure. The residue, which partly crystallised on cooling, was treated with a little methanol and the crystals (2·4 g.) were collected. Recrystallisation from methanol gave colourless needles, m. p. 128° (decomp.), undepressed on admixture with a specimen prepared by method (*a*) (Found: C, 75·05; H, 5·7; N, 18·9. Calc. for $C_{14}H_{13}N_3$: C, 75·3; H, 5·85; N, 18·85%).

5-p-*Chlorophenyl*-1-*phenyl*-1 : 2 : 3-*triazoline*.—*p*-Chlorobenzylideneaniline (2 g.) was treated with diazomethane, as described above for benzylideneaniline. After removal of the ether and extraction of the residue with cold ligroin, crude 5-p-*chlorophenyl*-1-*phenyl*-1 : 2 : 3-*triazoline* (0·2 g.) was collected. Crystallisation from methanol gave colourless crystals, m. p. 128° (decomp. *ca.* 145°) (Found: N, 16·2; Cl, 13·2. $C_{14}H_{12}N_3Cl$ requires N, 16·3; Cl, 13·4%).

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