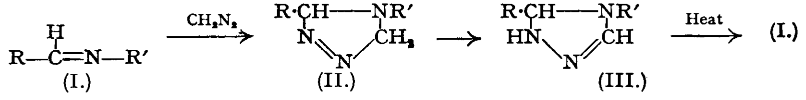
56. *Action of Diazomethane and of Diphenyldiazomethane on Nitro-anils.*

By Ahmed Mustafa.

Certain anils (Table I) are stable or very resistant towards ethereal diazomethane solution, whereas others (Table II) react readily with it, yielding 4 : 5-diaryl-4 : 5-dihydro-1 : 2 : 4-triazoles.

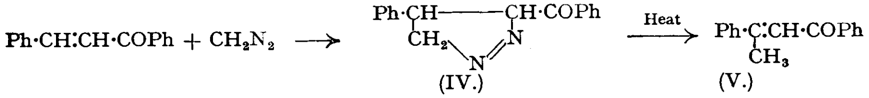
p-Nitrobenzylidene-*p*-nitroaniline (I*a*) reacts with diphenyldiazomethane to give the *triazoline* (VI).

In continuation of investigations on the action of diazomethane on aromatic compounds (Schönberg and Mustafa, *J.*, 1946, 746; 1947, 1045; 1948, 605), the anils of aromatic aldehydes and ketones listed in Table I were treated with ethereal diazomethane solution, but they failed to react. On the other hand, the anils listed in Table II reacted in molecular proportion. The products obtained by the action of diazomethane on the anils (I) could be represented by either (II) or (III), but the latter is preferred, and the former is regarded as an intermediate product :



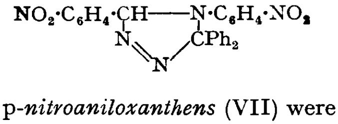
[I*a* and III*a*, R = R′ = *p*-C_6H_4·NO_2; I*b* and III*b*, R = *p*-C_6H_4·NO_2, R′ = *m*-C_6H_4·NO_2; I*c* and III*c*, R = *m*-C_6H_4·NO_2, R′ = *p*-C_6H_4·NO_2; I*d* and III*d*, R = 2 : 4-$C_6H_3(OMe)_2$, R′ = *p*-C_6H_4·NO_2; I*e* and III*e*, R = *p*-C_6H_4·NO_2, R′ = *p*-C_6H_4Br.]

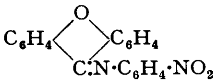
The proof of the constitution of these products may be illustrated by consideration of 4 : 5-di-(*p*-nitrophenyl)-4 : 5-dihydro-1 : 2 : 4-triazole. The structure (III*a*) accords with the fact that the substance contains active hydrogen and with its yellow colour; (II*a*), being a cyclic azo-compound, would be expected to have a more intense colour (see below). When heated, (III*a*) decomposes with evolution of gas and regeneration of (I*a*), and the latter result is produced by hydrolysis. On the basis of (III*a*), the pyrolysis can be interpreted without rupture of a C–C linkage. On the other hand, no structure involving direct attachment of the carbon atom of diazomethane to the median carbon atom of the anil would satisfy these conditions. This seems to be in favour of (III*a*) because under the experimental conditions used, *viz.*, heating at 270°, it does not seem very probable that such a C–C linkage would be ruptured [compare the thermal decomposition of 3-benzoyl-4-phenyl-Δ^1-pyrazoline (IV) (obtained by the action of ethereal diazomethane on benzylideneacetophenone), which yields the dypnone (V) (Smith and Pings, *J. Org. Chem.*, 1937, **2**, 23)].



When, instead of diazomethane, diphenyldiazomethane is used, an isomeric shift (II ⟶ III) is impossible; the deep reddish-orange *triazoline* (VI) is obtained, which when heated or hydrolysed regenerates (I*a*). Moreover, (VI) contains no active hydrogen.

(VI.)





(VII.)

The m- and p-*nitroaniloxanthens* (VII) were prepared by reaction between the corresponding nitroanilines and 5 : 5-dichloroxanthen (xanthone ketodichloride).

Table I.—*Substances stable towards ethereal diazomethane.* Benzylideneaniline, benzylidene-*p*-bromoaniline, *p*-nitrobenzylidene-β-naphthylamine, *m*-nitrobenzylidene-β-naphthylamine, *m*- and *p*-nitroaniloxanthen.

Table II.—*Substances which react with ethereal diazomethane.* *p*-Nitrobenzylidene-*p*- and -*m*-nitroaniline, *m*-nitrobenzylidene-*p*-nitroaniline, 2 : 4-dimethoxybenzylidene-*p*-nitroaniline, *p*-nitrobenzylidene-*p*-bromoaniline.

EXPERIMENTAL.

p-*Nitroaniloxanthen.*—Xanthone (2 g.) was refluxed with thionyl chloride (30 c.c.) for 12 hours; the excess of thionyl chloride was distilled off by means of the pump, and the residual oil dissolved in dry benzene (30 c.c.) and refluxed with *p*-nitroaniline (1 g.) for 3 hours (cf. Schönberg and Asker, *J.*, 1942, 725). The solid which separated was filtered off, washed with water and dilute hydrochloric acid, and crystallised from benzene–light petroleum (b. p. 30—50°), forming yellow crystals, m. p. 182° (Found : C, 72·1; H, 3·6; N, 8·5. $C_{19}H_{12}O_3N_2$ requires C, 72·2; H, 3·8; N, 8·8%). The p-*nitroaniloxanthone* was easily soluble in benzene or hot ethyl alcohol, and difficultly soluble in light petroleum (b. p. 70—80°), and gave an orange-red colour with sulphuric acid.

m-*Nitroaniloxanthen.*—Similarly, this *compound* was obtained by use of *m*-nitroaniline; it formed pale yellow crystals from benzene–light petroleum (b. p. 30—50°), m. p. 178° (Found : C, 72·0; H, 3·7; N, 8·6%), was difficultly soluble in light petroleum (b. p. 70—80°), and gave an orange-red colour with sulphuric acid.

Treatment of Anils (*Table* I) *with Ethereal Diazomethane.*—Ethereal solutions of 1 g. of each of benzylideneaniline, benzylidene-*p*-bromoaniline (Hantzsch and Schwab, *Ber.*, 1901, **34**, 831), *p*-nitrobenzylidene-β-naphthylamine (Zenoni, *Gazzetta*, 1893, **23**, ii, 519), *m*-nitrobenzylidene-β-naphthylamine (*idem, ibid.*), and the two nitroaniloxanthens were treated with excess of cold ethereal diazomethane solution (prepared from nitrosomethylurea, 8 g., followed by distillation), and the mixture left for 48 hours at 0°, during which fresh amounts of ethereal diazomethane solution were added. The ether was then evaporated, and in every case the crude products showed the properties of the starting materials and after recrystallisation showed the same m. p. and mixed m. p.

2 : 4-*Dimethoxybenzylidene*-p-*nitroaniline.*—This *anil* was prepared by heating 2 : 4-dimethoxybenzaldehyde and *p*-nitroaniline together without a solvent (bath temp. 150°) until water ceased to be evolved (about 30 minutes). The solid product obtained on cooling was washed with hot ethyl alcohol and crystallised from benzene–light petroleum (b. p. 30—50°) in pale yellow crystals, m. p. 148° (Found : C, 62·6; H, 4·8; N, 9·6. $C_{15}H_{14}O_4N_2$ requires C, 62·9; H, 4·9; N, 9·8%). It is soluble in hot benzene and difficultly soluble in ethyl alcohol.

Action of Ethereal Diazomethane on Anils listed in Table II.—(*a*) *p*-Nitrobenzylidene-*p*-nitroaniline (1 g.) (Ingold and Piggott, *J.*, 1922, **121**, 2793) was treated with excess of cold ethereal diazomethane exactly as for the anils of Table I. The resulting yellow crystals were filtered off, washed with light petroleum (b. p. 30—50°), and crystallised from benzene, forming yellow crystals, m. p. 180—181° (decomp.; red melt) (Found : C, 53·7; H, 3·5; N, 22·0; active hydrogen, 0·31. $C_{14}H_{11}O_4N_5$ requires C, 53·7; H, 3·5; N, 22·4; active hydrogen, 0·32%). 4 : 5-*Di*-(p-*nitrophenyl*)-4 : 5-*dihydro*-1 : 2 : 4-*triazole* is soluble in hot benzene, difficultly soluble in hot methyl alcohol, and gives no colour with sulphuric acid. On hydrolysis (see below) or on heating at 270° (bath temp.), it affords the original anil. In the thermal decomposition, 1 g. was heated in a stream of dry carbon dioxide for ½ hour; the yellow sublimate which formed on the walls of the reaction tube was extracted with hot benzene and on concentration of the benzene extract, yellow crystals of the anil were obtained (m. p. 199° and mixed m. p.).

(*b*) Similarly, 4-(p-*nitrophenyl*)-5-(m-*nitrophenyl*)-4 : 5-*dihydro*-1 : 2 : 4-*triazole* was obtained from *p*-nitrobenzylidene-*m*-nitroaniline (Ingold and Piggott, *loc. cit.*) in yellow crystals from benzene–light petroleum (b. p. 30—50°), m. p. 128—129° (decomp.; yellow melt) (Found : C, 53·4; H, 3·3; N, 22·1%). It is soluble in hot benzene and ethyl alcohol and difficultly soluble in light petroleum (b. p. 30—50°) and gives no colour when treated with concentrated sulphuric acid. When heated at 270° (bath temp.) it yields the anil (I*b*) (m. p. and mixed m. p.).

(*c*) 4-(m-*Nitrophenyl*)-5-(p-*nitrophenyl*)-4 : 5-*dihydro*-1 : 2 : 4-*triazole*, similarly prepared, readily crystallised from benzene–light petroleum (b. p. 30—50°) in yellow crystals, m. p. 170° (decomp.; red melt) (Found : C, 53·4; H, 3·4; N, 22·2%). It is easily soluble in hot benzene and difficultly soluble in ethyl alcohol.

(*d*) Similarly, 4-(2 : 4-*dimethoxyphenyl*)-5-(p-*nitrophenyl*)-4 : 5-*dihydro*-1 : 2 : 4-*triazole* separated from ethyl alcohol in yellow crystals, m. p. 160° (decomp.) (Found : C, 58·3; H, 4·7; N, 16·8. $C_{16}H_{16}O_4N_4$ requires C, 58·5; H, 4·9; N, 17·1%), soluble in benzene and difficultly soluble in light petroleum (b. p. 30—50°), and giving a yellow-orange colour with sulphuric acid.

(*e*) In the usual manner, *p*-nitrobenzylidene-*p*-bromoaniline (Ingold and Piggott, *loc. cit.*) was converted into 5-(p-*bromophenyl*)-4-(p-*nitrophenyl*)-4 : 5-*dihydro*-1 : 2 : 4-*triazole*, which formed yellow crystals from ethyl alcohol, m. p. 161° (decomp.) (Found : C, 48·0; H, 3·2; N, 16·0; Br, 22·8. $C_{14}H_{11}O_2N_4Br$ requires C, 48·4; H, 3·2; N, 16·1; Br, 23·1%). It is readily soluble in ether and benzene and difficultly soluble in light petroleum (b. p. 50—70°).

Action of Diphenyldiazomethane on p-*Nitrobenzylidene*-p-*nitroaniline*.—The anil (1 g.), dissolved in benzene (20 c.c.), was treated with diphenyldiazomethane (Staudinger and Gaule, *Ber.*, 1916, **49**, 1897) (prepared from benzophenone hydrazone, 1·2 g., and yellow mercuric oxide, 3 g., suspended in benzene, 50 c.c.). The mixture was refluxed for 4 hours and the deep red colour faded. After 24 hours at room temperature, the benzene was evaporated off, the solid residue extracted with hot ethyl alcohol, and the extract concentrated; reddish-brown crystals separated, and when recrystallised from ethyl alcohol–benzene, these had m. p. 230° (deep red melt) (Found : C, 66·9; H, 4·0; N, 14·9. $C_{26}H_{19}O_4N_5$ requires C, 67·1; H, 4·1; N, 15·1%). 2 : 2-*Diphenyl*-1 : 5-*di*-(p-*nitrophenyl*-1 : 2-*dihydro*-1 : 3 : 4-*triazine* (VI) is soluble in hot benzene and alcohol and difficultly soluble in light petroleum (b. p. 30—50°). When heated at 270° or hydrolysed by acid (see below), it regenerated the anil (m. p. and mixed m. p.) and an amorphous product which could not be identified.

Hydrolysis of Triazoles.—(a) 0·5 G. of the triazole (III*a*) was refluxed with hydrochloric acid (*d* 1·18; 20 c.c.) for 6 hours, during which fresh amounts of the acid were added (about 40 c.c.). On cooling, the oily product separated and solidified; it was filtered off, washed with water, and extracted with ether. The ethereal extract was washed with aqueous sodium carbonate solution, dried (Na_2SO_4), and the ether evaporated off. The residue crystallised from benzene in yellow crystals of the anil (m. p. 198° and mixed m. p.) (Found : C, 57·5; H, 3·3; N, 15·3. Calc. for $C_{13}H_9O_4N_3$: C, 57·6; H, 3·3; N, 15·5%).

(b) Similarly, 0·5 g. of (VI) was treated as described in the preceding paragraph, and (I*a*) was obtained (m. p. and mixed m. p.).

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