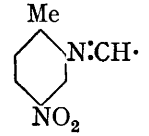
# 380. *Orientation Problems. Part I. The Effect of Nitro-groups in Schiff's Bases.*

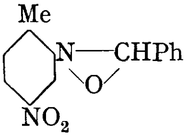
By A. McGookin.

In attempting to study the orienting effects of various amino-substituents in the nitroamines a number of Schiff's bases were prepared in good yield. These highly crystalline compounds, unlike the simple anils, were exceedingly stable towards acids. Hydrolysis could only be effected by heating them under pressure to a high temperature with ammonia.

On nitration a second nitro-group was introduced into *benzylidene*-4-*nitro*-o-*toluidine*, and the product proved to be even more stable than the original anil. Hydrolysis yielded 4-nitro-*o*-toluidine, hence nitration must have occurred in the benzylidene nucleus and not, as was hoped, in the substituted nucleus. By condensing the isomeric nitrobenzaldehydes with 4-nitro-*o*-toluidine the nitration product was identified as m-*nitrobenzylidene*-4-*nitro*-o-*toluidine*, so that the group (I) has *m*-directing influence in this case.

(I.)





(II.)

An increase in the number of nitro-groups, as well as their positions in the molecule, appears to determine the stability of the anils to ammonia, since benzylidene-4-nitro-*o*-toluidine and benzylidene-2-nitro-*p*-toluidine are hydrolysed at 100°, *m*-nitrobenzylidene-4-nitro-*o*-toluidine at 150°, whilst benzylidene- and furfurylidene-2 : 5-dinitro-*p*-toluidine are stable at 150°.

The positions of the nitro-groups with respect to the amino-group affect the capacity of the dinitrotoluidines to form Schiff's bases, for, whilst 2 : 5-dinitro-*p*-toluidine readily condenses, 3 : 5- and 4 : 5-dinitrotoluidines will not react with benzaldehyde.

In order to study the orienting effect of ·N:CHR it is obviously necessary for R to be non-nitratable; consequently a number of suitable aldehydes were used to form anils. Owing to the remarkable stability of the products, and to the unsatisfactory yields obtained during pressure hydrolysis, the study of these compounds was abandoned for some years. Interest in it revived recently when an unusual method of hydrolysis was accidentally discovered. Since Schiff's bases do not appear to have been subjected to oxidation, an attempt was made to oxidise benzylidene-4-nitro-*o*-toluidine with neutral aqueous permanganate. Oxidation seemed to be indicated by an immediate odour of benzaldehyde, but the other product of the reaction proved to be 4-nitro-*o*-toluidine.

The oxidising agent must play a preliminary part in hydrolysis, probably forming an unstable intermediate compound (II), which breaks down in the presence of water into the free base, benzaldehyde, and hydrogen peroxide, since free oxygen is not evolved during the reaction.

This view is partially confirmed by repeating the oxidation in dry acetone. A colourless solid is obtained which rapidly turns yellow on treatment with water, the smell of benzaldehyde being only then apparent. An investigation of the exact nature of this reaction and of its possible applications is being conducted.

## EXPERIMENTAL.

*Benzylidene*-4-*nitro*-o-*toluidine*.—4-Nitro-*o*-toluidine (10 g.) and benzaldehyde (7 g.) were warmed in an evaporating dish on a water-bath with rapid stirring. The mixture quickly became solid. Crystallisation from alcohol–acetone yielded faintly yellow hairs (15·5 g.), m. p. 116° (Found : N, 11·4. $C_{14}H_{12}O_2N_2$ requires N, 11·7%). Heating with ammonia (*d* 0·880) in an autoclave to 100° gave 4-nitro-*o*-toluidine, m. p. 107°. Yield, 80%.

*Attempted Oxidation of Benzylidene*-4-*nitro*-o-*toluidine*.—(a) The anil (1 g.) was shaken with an aqueous solution of potassium permanganate and kept for 2 days. Benzaldehyde was immediately evolved and 4-nitro-*o*-toluidine (0·4 g.) was isolated from the reaction mixture by ether extraction. A small amount of unchanged anil was also present.

(b) The anil (1 g.), dissolved in dry acetone (10 c.c.), was shaken in a closed flask with powdered potassium permanganate (10 g.). On filtration and removal of the solvent in an exsiccator a nearly colourless solid remained which had no odour of benzaldehyde. Immediately on addition of water the solution became yellow and benzaldehyde was formed. On standing, yellow crystals (0·56 g.) of 4-nitro-*o*-toluidine separated.

m-*Nitrobenzylidene*-4-*nitro*-o-*toluidine*.—Benzylidene-4-nitro-*o*-toluidine (22 g.) was dissolved in sulphuric acid (50 c.c., *d* 1·8) and nitric acid (50 c.c., *d* 1·5) was gradually dropped in with mechanical stirring at 0°. After ½ hour the solution was poured into ice-water (1 l.). The yellow solid was filtered off, washed, and crystallised from alcohol, then from benzene, forming buff plates (13 g.), m. p. 184°. Unchanged benzylidene-4-nitro-*o*-toluidine (10 g.) was recovered from the mother-liquor.

The same anil was obtained from 4-nitro-*o*-toluidine (1 g.) and *m*-nitrobenzaldehyde (1 g.) as colourless plates (1·7 g.) from acetone, m. p. 185°, mixed m. p. 184° (Found : N, 14·4.* $C_{14}H_{11}O_4N_3$ requires N, 14·7%). This compound, on heating with ammonia (*d* 0·880) in an autoclave at 150°, yielded 4-nitro-*o*-toluidine.

o-*Nitrobenzylidene*-4-*nitro*-o-*toluidine*, prepared from the aldehyde (1 g.) and the base (1 g.), crystallised from alcohol in faintly coloured flakes (1·7 g.), m. p. 155° (Found : N, 14·3. $C_{14}H_{11}O_4N_3$ requires N, 14·7%). p-*Nitrobenzylidene*-4-*nitro*-o-*toluidine* was obtained similarly in yellow crystals (1·8 g.) from acetone, m. p. 227° (Found : N, 14·45%).

*Furfurylidene*-4-*nitro*-o-*toluidine*.—Furfuraldehyde (6·4 g.) and 4-nitro-*o*-toluidine (10 g.) yield pale felted needles (14·9 g.) from alcohol–acetone, m. p. 153° (Found : N, 11·9. $C_{12}H_{10}O_3N_2$ requires N, 12·2%). This compound tends to darken when its solutions are boiled.

*Chloral*-4-*nitro*-o-*toluidine*.—Chloral hydrate (4·1 g.) and 4-nitro-*o*-toluidine (3·8 g.) formed bright yellow cubes (7 g.) from acetone, m. p. 105° (Found : N, 10·2. $C_9H_7O_2N_2Cl_3$ requires N, 9·94%).

*Benzylidene*-2-*nitro*-p-*toluidine*.—Benzaldehyde (7 g.) and 2-nitro-*p*-toluidine (10 g.) formed pearly plates (15·7 g.) from acetone, m. p. 77—78° (Found : N, 11·45. $C_{14}H_{12}O_2N_2$ requires N, 11·7%). Aqueous ammonia (*d* 0·880) at 100° in an autoclave gave 2-nitro-*p*-toluidine.

*Benzylidene*-2 : 5-*dinitro*-p-*toluidine*.—The aldehyde (2·65 g.) and 2 : 5-dinitro-*p*-toluidine (4·9 g.) gave pale yellow flakes or hairs (7 g.) from aqueous acetone, m. p. 71—72° (Found : N, 14·9. $C_{14}H_{11}O_4N_3$ requires N, 14·7%).

*Furfurylidene*-2 : 5-*dinitro*-p-*toluidine*.—The aldehyde (2·4 g.) and the base (4·9 g.) yielded yellow laminæ (6·3 g.), m. p. 208° (Found : N, 14·8. $C_{12}H_9O_5N_3$ requires N, 15·3%).

*Nitration of Chloral*-4-*nitro*-o-*toluidine*.—Powdered chloral-4-nitro-*o*-toluidine (9 g.) was slowly added to mechanically stirred nitric acid (50 c.c., *d* 1·5) at 0°. After 1 hour the solution was poured into ice-water (1 l.), and the yellow precipitate washed and fractionally crystallised from aqueous acetone; unchanged anil (3 g.) was then obtained, and buff-coloured pearly plates (5·2 g.), m. p. 170°, which have not yet been identified.

The author thanks Mr. W. Doran, M.Sc., and his assistant, Mr. Boston, for kindly undertaking the microanalysis marked with an asterisk.

THE UNIVERSITY, LIVERPOOL. [*Received, August* 8*th*, 1934.]