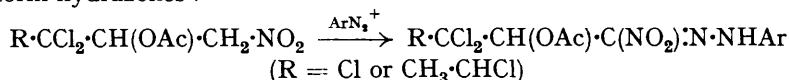


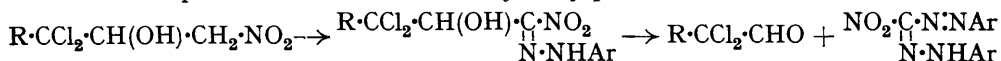
376. The Action of Diazonium Salts on the Trichloro- α -nitro- β -acetoxy-paraffins.

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LIKE many other compounds containing an activated methylene group, the trichloro- α -nitro- β -acetoxy-paraffins couple readily, under slightly acid conditions, with diazonium salts and form hydrazones:



These hydrazones are strongly coloured, stable compounds which frequently crystallise in two polymorphic forms.* They do not react further with diazonium salts, differing markedly in this respect from the hydrazones yielded as first products in the action of diazonium salts upon the trichloro- α -nitro- β -hydroxy-paraffins:



The stabilising effect of the acyl group is interesting, as the intermediate hydrazones formed from the corresponding β -hydroxy-paraffins (cf. Jones and Kenner, J., 1930, 919) can only with great difficulty be obtained unmixed with a large excess of the nitroformazyl.

The action of amines upon the hydrazone acetic esters takes the same abnormal course as that followed in the case of the trichloro- α -nitro- β -acetoxy-paraffins themselves, an amine being produced.

EXPERIMENTAL.

$\gamma\gamma\gamma$ -Trichloro- α -nitro- β -acetoxypropanalphenylhydrazone, $\text{CCl}_3\cdot\text{CH}(\text{OAc})\cdot\text{C}(\text{NO}_2)\cdot\text{N}\cdot\text{NHPh}$.—5 G. (1.5 mols.) of aniline in 25 c.c. of alcohol were mixed with 20 c.c. of concentrated hydrochloric acid (excess) and diazotised with 4 g. of sodium nitrite in 10 c.c. of water. To this cooled stirred solution was added a solution of 9 g. (1 mol.) of $\gamma\gamma\gamma$ -trichloro- α -nitro- β -acetoxypropane in 40 c.c. of alcohol, followed by a large excess (40 g.) of finely powdered, fused sodium acetate. After 15 minutes' stirring, an equal volume of water was added and the above *hydrazone*, which had separated as a bright yellow solid, was filtered off and washed with hot water and alcohol; it crystallised from boiling acetic acid or alcohol, in which it was moderately easily soluble, in compact orange prisms with a slight blue reflex, m. p. 137° (Found: C, 37.4; H, 2.9; N, 12.0; Cl, 30.1. $\text{C}_{11}\text{H}_{10}\text{O}_4\text{N}_3\text{Cl}_3$ requires C, 37.2; H, 2.8; N, 11.85; Cl, 30.0%).

In a similar manner to the above the following compounds were prepared. $\gamma\gamma\gamma$ -Trichloro- α -nitro- β -acetoxypropanal-*p*-tolylhydrazone crystallises from alcohol first as a labile form in a felted mass of pale yellow, feathery needles, which, if left in the solution, slowly redissolve whilst a stable compact form appears and grows at the expense of the labile form until the latter has completely disappeared. The whole change is complete within a few hours. The stable form separates in deep scarlet, short, compact, rhombic prisms with domed ends and possessing a slight blue reflex, m. p. 152°. The labile form also melts at this temperature (Found: Cl, 28.85. $\text{C}_{12}\text{H}_{12}\text{O}_4\text{N}_3\text{Cl}_3$ requires Cl, 28.9%).

The *m*-tolylhydrazone forms clusters of small yellow needles from alcohol, m. p. 127° (Found: Cl, 28.8%). The *o*-tolylhydrazone separates first from alcohol as a labile form in slender, pale yellow prisms, m. p. 109°, and transforms on standing in the mother-liquor into the compact, deep orange-red, six-sided rhombic plates of the stable form, m. p. 115° (Found: Cl, 29.0%). The *p*-chlorophenylhydrazone forms a felted mass of pale orange needles from alcohol, m. p. 165° (Found: Cl, 36.3. $\text{C}_{11}\text{H}_9\text{O}_4\text{N}_3\text{Cl}_4$ requires Cl, 36.5%). The 2:4-dichlorophenylhydrazone crystallises from acetic acid in orange-red irregular plates, m. p. 155° (Found: Cl, 42.0. $\text{C}_{11}\text{H}_8\text{O}_4\text{N}_3\text{Cl}_5$ requires Cl, 41.9%). The *p*-nitrophenylhydrazone first separates from acetic acid as a labile form in clusters of small, slender, yellow needles, m. p. 187°, and on standing for several weeks in the mother-liquor at the ordinary temperature completely transforms into the orange, compact, short, six-sided prisms with domed ends of the stable form, m. p. 189° (Found: Cl, 26.2. $\text{C}_{11}\text{H}_8\text{O}_6\text{N}_4\text{Cl}_3$ requires Cl, 26.1%).

$\gamma\gamma\delta$ -Trichloro- α -nitro- β -acetoxy-pentanalphenylhydrazone forms pale yellow needles from

* Many of the geometric isomers among hydrazones which have been stated to exist are probably unrecognised polymorphs.

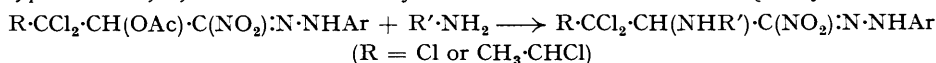
alcohol, m. p. 152° (Found: Cl, 27.7; N, 10.9. $C_{13}H_{14}O_4N_3Cl_3$ requires Cl, 27.8; N, 11.0%); the *p*-tolylhydrazone, clusters of slender, orange-red prisms from alcohol-acetic acid, m. p. 166° (Found: Cl, 26.7. $C_{14}H_{16}O_4N_3Cl_3$ requires Cl, 26.86%); and the *p*-chlorophenylhydrazone, a felted mass of golden needles from alcohol-acetic acid, m. p. 177° (Found: Cl, 34.1. $C_{13}H_{13}O_4N_3Cl_4$ requires Cl, 34.1%). The *p*-nitrophenylhydrazone crystallises from acetic acid-alcohol in a labile form in clusters of small yellow needles, which on standing in the mother-liquor for a few hours completely dissolve and transform into orange-yellow irregular plates of a stable form, m. p. 187° (Found: Cl, 25.0. $C_{13}H_{13}O_6N_4Cl_3$ requires Cl, 24.9%).

Nitroformazyl.—To a cooled stirred solution of benzenediazonium chloride, an alcoholic solution of $\gamma\gamma\gamma$ -trichloro- α -nitro- β -hydroxypropane was added under much the same conditions as those used with $\gamma\gamma\gamma$ -trichloro- α -nitro- β -acetoxypropane. The liquid became red and a viscid mass of nitroformazyl separated; after 30 minutes' stirring, this became crystalline. It formed clusters of red needles, m. p. 161°, from alcohol, identical with a specimen prepared by the action of benzenediazonium chloride on nitromethane.

pp'-Dichloronitroformazyl was prepared in a similar way to the above from *p*-chlorobenzenediazonium chloride and the nitro-alcohol. It separated from ethyl acetate in dark purple-red, slender needles, m. p. 188° (Found: Cl, 21.2. $C_{13}H_9O_2N_5Cl_2$ requires Cl, 21.0%). From this compound, which was the main product of the reaction, a very small amount of $\gamma\gamma\gamma$ -trichloro- α -nitro- β -hydroxypropanal-*p*-chlorophenylhydrazone was isolated by extracting the crude reaction product with a little alcohol, precipitating the hydrazone with water, and crystallising it from alcohol. It separated in clusters of minute orange-red needles, m. p. 160° (Found: Cl, 40.5. $C_9H_7O_3N_3Cl_4$ requires Cl, 40.9%).

Bis-2 : 4-dichloronitroformazyl, prepared similarly, crystallised from acetic acid in purple-red, slender, silky needles, m. p. 189° (decomp.) (Found: Cl, 34.9. $C_{15}H_7O_2N_5Cl_4$ requires Cl, 34.9%).

The Action of Amines on $\gamma\gamma\gamma$ -Trichloro- α -nitro- β -acetoxypropanal- and $\gamma\gamma\delta$ -Trichloro- α -nitro- β -acetoxypropanal-arylhydrazones.—These hydrazones react in the following way with amines:



$\gamma\gamma\gamma$ -Trichloro- α -nitro- β -*p*-toluidinopropanal-*p*-nitrophenylhydrazone.—10 G. of the *p*-nitrophenylhydrazone (1 mol.) and 6 g. of *p*-toluidine (2 mols.) were dissolved in 400 c.c. of alcohol and refluxed on a water-bath for 12 hours. A deep red solution resulted, which was evaporated to about 150 c.c. On cooling, the above compound separated as deep purple crystals; it was recrystallised from boiling acetic acid, separating as purple rhombs with a blue reflex, m. p. 189° (decomp.) (Found: C, 43.3; H, 3.3; Cl, 23.7. $C_{16}H_{14}O_4N_5Cl_3$ requires C, 43.1; H, 3.1; Cl, 23.85%).

The following compounds were prepared similarly to the above. $\gamma\gamma\gamma$ -Trichloro- α -nitro- β -*p*-toluidinopropanalphenylhydrazone formed rosettes of red needles from alcohol, m. p. 164° (decomp.) (Found: Cl, 26.6. $C_{16}H_{15}O_2N_4Cl_3$ requires Cl, 26.5%); the *o*-tolylhydrazone, slender, pale orange-yellow needles from acetic acid, m. p. 127° (Found: Cl, 25.8. $C_{17}H_{17}O_2N_4Cl_3$ requires Cl, 25.6%); and the *p*-chlorophenylhydrazone, red prisms from acetic acid, m. p. 164° (Found: Cl, 32.4. $C_{16}H_{14}O_2N_4Cl_4$ requires Cl, 32.6%). $\gamma\gamma\delta$ -Trichloro- α -nitro- β -*p*-toluidinopropanalphenylhydrazone crystallised from alcohol in pale orange needles, m. p. 178° (decomp.) (Found: Cl, 24.8. $C_{18}H_{19}O_2N_4Cl_3$ requires Cl, 24.8%).

$\gamma\gamma\gamma$ -Trichloro- α -nitro- β -methylaminopropanalphenylhydrazone hydrochloride. 3.6 G. (4 mols.) of a 33% solution of methylamine in anhydrous alcohol were added to 3.5 g. (1 mol.) of $\gamma\gamma\gamma$ -trichloro- α -nitro- β -acetoxypropanalphenylhydrazone, partly dissolved in 100 c.c. of alcohol. The solution became red and after 3 days was heated on a water-bath for 10 minutes and then poured into water. The viscid mass that separated was extracted in ether and dried (sodium sulphate), most of the ether evaporated, and excess of concentrated alcoholic hydrogen chloride added to the residue. The above hydrochloride separated; recrystallised from dilute aqueous-alcoholic hydrochloric acid, it formed slender yellow prisms, m. p. 189° (decomp.) (Found: Cl, 39.1. $C_{10}H_{11}O_2N_4Cl_3 \cdot HCl$ requires Cl, 39.2%).

The mother-liquor from the recrystallisation of the hydrochloride was made just neutral with ammonia and the $\gamma\gamma\gamma$ -trichloro- α -nitro- β -methylaminopropanalphenylhydrazone that separated was extracted in ether, dried, and recrystallised from alcohol, forming long, slender, pale orange prisms, m. p. 104° (Found: Cl, 32.6. $C_{10}H_{11}O_2N_4Cl_3$ requires Cl, 32.7%).