75. *Interaction of Arylated Unsaturated Substances with Diazonium Salts.*

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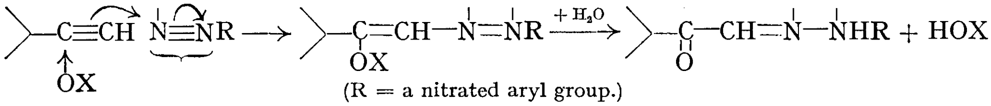
SCHARVIN and PLACHUTA (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 253) found that cuprous acetylide and benzenediazonium sulphate reacted with formation of diphenyl, tetraphenylethane, and other products. Henrich and Thomas (*Ber.*, 1907, **40**, 4924) obtained formazylacrylic acid from glutaconic acid and benzenediazonium chloride, and ethyl glutaconate gave a bisbenzeneazo-derivative, one of the azo-groups passing into the hydrazone tautomeric form. Meyer (*Ber.*, 1919, **52**, 1468) obtained nitro- and dinitro-benzeneazo-derivatives of the simpler, conjugated, doubly unsaturated hydrocarbons. Quilico and Freri (*Gazzetta*, 1928, **58**, 380) showed that anethole, *iso*safrole, and *iso*apiole are converted by nitro- or dinitro-benzenediazonium salts into the substituted phenylhydrazones of anisaldehyde, piperonal, and apiolealdehyde respectively (cf. Quilico and Fleischner, *ibid.*, 1929, **59**, 39; Quilico and Freri, *ibid.*, p. 600; *idem*, *ibid.*, 1930, **60**, 606). Another type of reaction, namely, displacement of the unsaturated side chain, was noted in the case of *p*-dimethylamino*iso*propenylbenzene, which, with *p*-nitrobenzenediazonium sulphate, was converted into *p*-nitrobenzeneazodimethylaniline (Quilico and Freri, *ibid.*, 1932, **62**, 253); the normal formation of dimethylaminobenzaldehyde-*p*-nitrophenylhydrazone had been previously observed under other conditions.

We have found that *p*-methoxystyrene undergoes Quilico's reaction with 2 : 4-dinitrobenzenediazonium sulphate in alcoholic solution and is converted into anisaldehyde-2 : 4-dinitrophenylhydrazone. This was to be anticipated in view of the close analogy with anethole; styrene, however, did not behave in a similar fashion and gave a very small yield of an unidentified substance.

p-Methoxyphenylacetylene was changed by *p*-nitrobenzenediazonium sulphate into a substance, $C_{15}H_{13}O_4N_3$, which is the *p-nitrophenylhydrazone* of *p-methoxyphenylglyoxal*, $MeO{\cdot}C_6H_4{\cdot}CO{\cdot}CH{:}N{\cdot}NH{\cdot}C_6H_4{\cdot}NO_2$. A similar substance was obtained when 2 : 4-dinitrobenzenediazonium sulphate was employed. Phenylacetylene gave *phenylglyoxal*-p-*nitrophenylhydrazone* in a like manner, but with 2 : 4-dinitrobenzenediazonium sulphate the product was of uncertain composition.

The mechanism of the process can be simply represented as follows :



(R = a nitrated aryl group.)

EXPERIMENTAL.

Anisaldehyde-2 : 4-*dinitrophenylhydrazone*.—A mixture of 2 : 4-dinitroaniline (3 g.), acetic acid (20 c.c.), and concentrated sulphuric acid (2 c.c.) was cooled in ice, and *iso*amyl nitrite (3 c.c.) introduced. The diazo-sulphate was precipitated by the addition of ether, collected, dissolved in alcohol (20 c.c.), and mixed with *p*-methoxystyrene (2·5 c.c.). A vigorous evolution of nitrogen occurred and after the solution had been kept for 24 hours at 0°, water was added and the precipitated oil was collected, washed, and dissolved in a little alcohol. The brick-red residual solid (1 g.) separated from acetic acid in bronze-red plates of anisaldehyde-2 : 4-dinitrophenylhydrazone, m. p. 249—250° (Found : C, 52·8; H, 3·8; N, 17·5. Calc. for $C_{14}H_{12}O_5N_4$: C, 53·1; H, 3·8; N, 17·7%), not depressed by an authentic specimen, m. p. 250—251°. No definite compound could be isolated from the mother-liquors.

In a similar experiment with styrene there was much less evidence of immediate reaction (such as darkening, gas evolution), but after 2 days at 0° small clusters of buff crystals, m. p. 76° (decomp.), had separated. The substance decomposed in alcohol, was readily soluble in water to a yellow solution, and gave a bluish-purple azo-compound with alkaline β-naphthol.

p-*Methoxyphenylglyoxal*-p-*nitrophenylhydrazone*.—A mixture of *p*-nitroaniline (5 g.), acetic acid (30 c.c.), and concentrated hydrochloric acid (5 c.c.) was cooled to 0°, and *iso*amyl nitrite (5 c.c.) gradually added. The oil precipitated by ether was washed with more ether, then mixed with alcohol (20 c.c.) and a solution of *p*-methoxyphenylacetylene (4 g.) in alcohol (20 c.c.). Separation of a brownish-yellow solid commenced almost at once and after 24 hours (some deterioration) it was collected (2·5 g.). It was extremely sparingly soluble in alcohol, very sparingly soluble in acetic acid, and moderately readily soluble in nitrobenzene. After several crystallisations from acetic acid, the *substance* was obtained in small, golden-yellow, rectangular plates, m. p. 261° (Found : C, 60·1; H, 3·9; N, 13·8. $C_{15}H_{13}O_4N_3$ requires C, 60·2; H, 4·3; N, 14·0%). It was insoluble in aqueous sodium hydroxide, but dissolved in the presence of acetone to a deep reddish-violet solution, the colour of which faded during 2—3 minutes to pale yellow. Water added to the orange-red solution in concentrated sulphuric acid precipitated the unchanged substance.

The analogous experiment with phenylacetylene (2·5 g.) gave a pale yellow solid (0·7 g.), which crystallised from acetic acid in long, thin, brownish-yellow plates, m. p. 252° (Found : C, 61·5, 61·3; H, 3·9, 3·8; N, 14·3. $C_{14}H_{11}O_3N_3,\frac{1}{4}C_2H_4O_2$ requires C, 61·3; H, 4·2; N, 14·8%). This substance is probably *phenylglyoxal*-p-*nitrophenylhydrazone*; its solubility relations and its behaviour with acetone and aqueous alkali and with sulphuric acid (crimson coloration) resemble those of the methoxy-derivative of more precise composition.

p-*Methoxyphenylglyoxal*-2 : 4-*dinitrophenylhydrazone*.—2 : 4-Dinitrobenzenediazonium sulphate (3 g. of the base) was prepared as above and mixed with alcohol (20 c.c.) and *p*-methoxyphenylacetylene (2 g.) at 0°. The solution quickly became dark reddish-brown and crystallisation began after 15 minutes. After 24 hours at 0° the solid was collected (3·1 g.) and crystallised from acetic acid, forming canary-yellow needles, m. p. 235° (Found : C, 52·2; H, 3·4; N, 16·2. $C_{15}H_{12}O_6N_4$ requires C, 52·3; H, 3·5; N, 16·3%). The *substance* is very sparingly soluble in alcohol or cold acetic acid and moderately readily soluble in hot acetic acid or cold nitrobenzene. It is insoluble in hot aqueous sodium hydroxide, but dissolves in the presence of alcohol or acetone to a deep cherry-red solution. On oxidation with potassium permanganate it afforded anisic acid, m. p. 181—182°.

The corresponding experiment with phenylacetylene (2 g.) gave less visible sign of reaction, but after 3½ days, rosettes of dark brown-red prisms with a greenish lustre had separated (0·7 g.). This substance exploded violently at 115° and for this reason the analytical results were inconsistent (Found : C, 45·3, 44·6; H, 3·0, 3·6; N, 23·3, 23·5%). It was certainly not a simple phenylhydrazone, because it decomposed with gas-evolution and tar-formation when treated with sodium hydroxide, and in the presence of sodium acetate it coupled with β-naphthol to a red azo-compound.

p-*Methoxyphenylglyoxalbis*-2 : 4-*dinitrophenyhydrazone*.—(A) The preparation of *p*-methoxyphenylglyoxal by an adaptation of the method of Riley, Morley, and Friend (J., 1934, 1875) gave very poor results in the absence of a solvent as recommended for the oxidation of acetophenone by selenium dioxide. In the presence of alcohol a small yield was obtained, but the keto-aldehyde was not completely separated from *p*-acetylanisole. A small fraction of nearly pure material was used and, by condensation with 2 : 4-dinitrophenylhydrazine (a little less than 1 mol.) in cold acetic acid solution containing a trace of hydrogen chloride, *p*-methoxyphenylglyoxal-2 : 4-dinitrophenylhydrazone was obtained. This specimen was crystallised from acetic acid; m. p. 234° alone or mixed with that obtained as described above (Found : C, 52·2; H, 3·4; N, 16·0%).

On condensation of *p*-methoxyphenylglyoxal with an excess of 2 : 4-dinitrophenylhydrazine in boiling acetic acid solution, a deep red, crystalline solid separated. This was almost insoluble in acetic acid, but crystallised from nitrobenzene in dark crimson needles, m. p. 292° alone or mixed with the specimen obtained as described in (B).

(B) The substance (0·3 g.), m. p. 235°, derived from *p*-methoxyphenylacetylene and 2 : 4-dinitrobenzenediazonium sulphate was refluxed for 1 hour with 2 : 4-dinitrophenylhydrazine (0·2 g.), concentrated hydrochloric acid (1 c.c.), and acetic acid (24 c.c.). The separated crystals (0·3 g.) were recrystallised from nitrobenzene; m. p. 292° (Found: C, 48·2; H, 3·2; N, 20·7. $C_{21}H_{16}O_9N_8$ requires C, 48·1; H, 3·1; N, 21·3%).

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