91. *The Nitration of Chalkone.*

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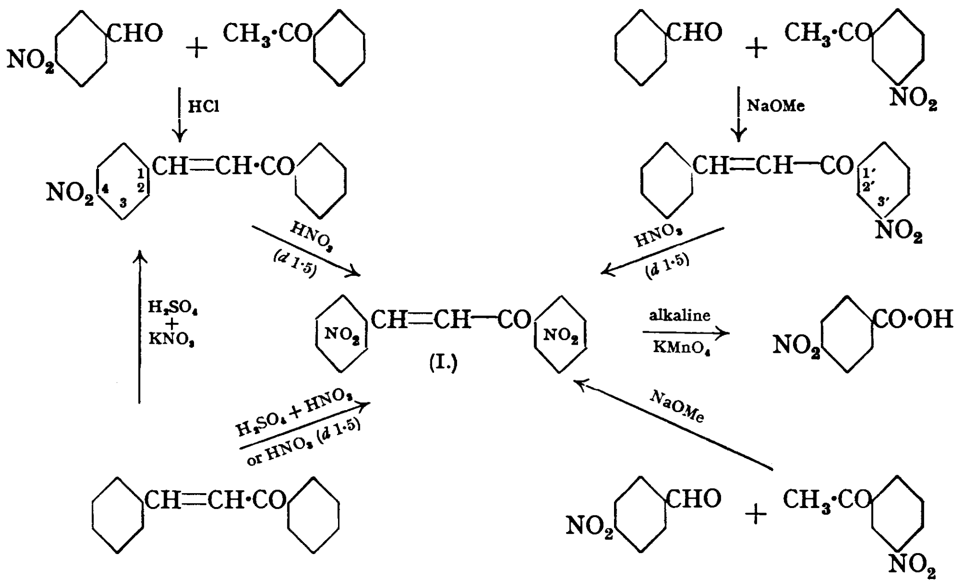
Goldschmidt (*Ber.*, 1895, **28**, 986), without giving experimental details or analyses, claimed to have isolated, by the interaction of mixed acids and chalkone, *o*-nitrobenzylideneacetophenone as a yellow oil and another nitro-compound, m. p. 159°. Since in our experience the *o*-nitro-compound has always appeared as a crystalline solid, m. p. 124°, and the *p*-nitrochalkone as a solid, m. p. 164°, Goldschmidt's experiments were repeated.

Essentially similar preparations were obtained when either mixed acids (as specified by Goldschmidt), potassium nitrate and excess of sulphuric acid, or fuming nitric acid alone was used. Goldschmidt's yellow oil was seen to be a mixture of nitration and oxidation products : it gave a very small yield of 2-phenylquinoline dichromate on reduction and therefore contained only a trace of the *o*-nitro-compound. The nitration of chalkone by fuming nitric acid at a low temperature produced the nitro-derivative (I) in almost quantitative yield, scarcely any yellow oil being formed.

The (total) solid nitrochalkone obtained by Goldschmidt's procedure usually melted well above 159° ; after purification it had m. p. 204—205°. It was a dinitrochalkone, gave *p*-nitrobenzoic acid on oxidation with alkaline potassium permanganate, and was also obtained by the nitration of either 3′- or 4-nitrochalkone.



The compound (I) is therefore 3′ : 4-dinitrochalkone : we have also obtained it by the condensation of *p*-nitrobenzaldehyde and *m*-nitroacetophenone (Dilthey, Neuhaus, Reis, and Schommer, *J. pr. Chem.*, 1930, **124**, 81, record m. p. about 225°).

We have roughly observed that, as the temperature of nitration of chalkone is reduced, the yield of 3′ : 4-dinitrochalkone increases, reaching *ca.* 100% at − 15°. Acetophenone similarly gives the highest yield of its *m*-nitro-derivative at a low temperature (cf. also propiophenone; Commanducci and Pescitelli, *Gazzetta*, 1906, **36**, ii, 789).

Mono-*p*-nitration of benzylideneacetone alone occurs even when a considerable molecular excess of nitric acid is employed (cf. Baeyer and Drewson, *Ber.*, 1882, **15**, 2859).

EXPERIMENTAL.

Dinitration of Chalkone.—(a) *Attempted repetition of Goldschmidt's experiment.* Chalkone (5 g.) was dissolved in a mixture of HNO_3 (*d* 1·42; 30 c.c.) and H_2SO_4 (30 c.c.) at − 7°, the solution poured on ice, and after 24 hr. the solid was collected, stirred with Et_2O (200 c.c.), and recrystallised four times from AcOH, 3′ : 4-dinitrochalkone being obtained as light yellow needles, m. p. 204—205°.

Goldschmidt's yellow oil, isolated from the ethereal extract, was reduced in boiling EtOH (150 c.c.) and conc. HCl (10 c.c.) with Fe filings (8 g.), the filtered solution diluted to 300 c.c. with H_2O and made alkaline with NH_3 aq., and the pptd. solid dried, boiled with EtOH–norit for 10 min., and repptd. by excess of $K_2Cr_2O_7$ aq. as 2-phenylquinoline dichromate (0·5 g.), m. p. 135—140° (mixed with authentic material, m. p. 137—145°).

(b) *Nitration with fuming nitric acid.* Chalkone (5 g.) was dissolved in HNO_3 (*d* 1·5; 55 c.c.) at − 15° and at once poured on ice. Treatment as described under (a) produced 4·5 g., m. p. 204—205° after four crystns. (Found : N, 9·5. Calc. for $C_{15}H_{10}O_5N_2$: N, 9·4%).

(c) *Nitration in excess of sulphuric acid.* Chalkone (10 g.), dissolved in H_2SO_4 (100 c.c.), was treated below 0° with KNO_3 (10 g.) in H_2SO_4 (50 c.c.). After 3 hr., by the procedure described under (a), 10 g. of a pale yellow powder were obtained which gave 3′ : 4-dinitrochalkone on recrystn.

Mononitration of Chalkone.—(a) Chalkone in AcOH at 100° was unaffected by the calc. quantity of HNO_3 (*d* 1·5).

(b) To a solution of chalkone (5 g.) in H_2SO_4 (50 c.c.) was added KNO_3 (2·5 g.) in H_2SO_4 (5 c.c.), the temp. being kept at − 10° for 1¾ hr.; the solution was then poured on ice. The solid obtained (5·6 g.) had m. p. 136—138°, and m. p. 153—157° (raised slightly by admixture with authentic 4-nitrochalkone) after crystn. from AcOH–H_2O.

4-*Nitrochalkone.*—Into a mixture of acetophenone (1·6 g.) and *p*-nitrobenzaldehyde (2 g.), made liquid at 15° with sufficient Ac_2O, dry HCl was passed for 2·5 hr. After 24 hr., by freezing and pressing on tile, 4-nitrochalkone was obtained, m. p. 163—164° after crystn. from AcOH aq. (Sorge, *Ber.*, 1902, **35**, 1067, gives 164°). Yield, 2·9 g.

3′-*Nitrochalkone.*—To benzaldehyde (2·2 g.) and *m*-nitroacetophenone (3·4 g.), dissolved in the minimal quantity of abs. MeOH, NaOMe (from 1 g. Na and 10 c.c. MeOH) was added. After 15 min. the white ppt. was collected, washed with MeOH (yield, 1·7 g.), and crystallised from AcOH aq.; m. p. 131°.

Nitration of 4- *and* 3′-*Nitrochalkone.*—HNO_3 (*d* 1·5; 20 c.c.) at – 10° converted 4-nitrochalkone (0·5 g.) into a product, m. p. *ca.* 160°, and 203—204° after four crystns. from AcOH aq.

3′-Nitrochalkone (0·5 g.) was converted by HNO_3 (*d* 1·5; 10 c.c.) at 0° into 3′ : 4-dinitrochalkone, m. p. 203—204° (alone or mixed with authentic material) after one crystn.

3′ : 4-*Dinitrochalkone.*—*p*-Nitrobenzaldehyde (1·5 g.) and *m*-nitroacetophenone (1·6 g.), condensed in abs. MeOH by means of NaOMe (from 1 g. Na and 8 c.c. MeOH), gave a product (1·4 g.), m. p. 193—194°; this could not be raised above 203—204° by repeated crystn. from AcOH aq.

Nitration of Benzylideneacetone.—This compound (1 g.) was converted by a mixture of H_2SO_4 (20 c.c.) and HNO_3 (20 c.c.; *d* 1·5) below – 15° into *p*-nitrobenzylideneacetone, m. p. 109—110°. Oxidation of the product by alkaline $KMnO_4$ gave *p*-nitrobenzoic acid, m. p. (crude) 236—238°

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