# CCCCX.—*The Reduction of Nitro-compounds by Aromatic Ketols. Part II. Some* o-, m-, *and* p-*Azoxy-compounds.*

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In extending the work already done (Part I, J., 1927, 2081), it has been proved that benzoin and its homologues in hot alcoholic solution under the influence of a trace of sodium ethoxide reduce nitro-groups to azoxy-groups no matter what position these occupy in the benzene ring. Whilst the reaction, as a method of preparing azoxy-compounds, still continues to be particularly successful in the case of para-compounds and more particularly in the case of para-compounds containing a carbon-to-carbon or a carbon-to-nitrogen double bond, yields of the order 50—87% being obtained, it is not so successful in the case of *o*- and *m*-compounds, the yields dropping to the order of 6—50%.

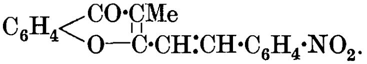
The isolation of the azoxy-compound from the accompanying diketone is the main difficulty, for only methods of fractional crystallisation can be resorted to because azoxy-compounds readily decompose when distilled, even in a vacuum, especially when in admixture with other compounds. *p*-Azoxy-compounds are usually much less soluble in common solvents than benzil and can, in general, be easily separated even in alcoholic solution. *o*- and *m*-Azoxy-compounds, however, are as soluble as or more soluble than the diketone, which is often the first product of the reaction, whilst the azoxy-compound must be isolated from the mother-liquors. In many cases it has been found impossible to isolate the azoxy-compound; but in every case examined it has been possible to separate the diketone and thus prove that the nitro-group has oxidised the ketol and has at the same time suffered reduction. This reaction is utilised in a new preparation of anisil and furil by oxidation of the corresponding ketol with nitrobenzene.

*o*-, *m*-, and *p*-Azoxy-compounds have been prepared from *o*-, *m*-, and *p*-nitrobenzylideneacetophenone, 2-*o*-, 2-*m*-, and 2-*p*-nitrostyryl-3-methylchromone, and *o*-, *m*-, and *p*-nitrobenzylidene-*p*-bromoaniline. *p*-Azoxybenzylidene-*p*-toluidine has already been described (J., 1927, 2084); the m-*azoxy*-compound has now been prepared, but the *o*-azoxy-compound could not be isolated. Ethyl *p*-nitrobenzoate is reduced to ethyl *p*-azoxybenzoate, but the isolation of the esters of *m*-and *o*-azoxybenzoic acids could not be accomplished. The preparation of *o*- and *m*-azoxybenzonitrile, of azoxybenzene, and of α-azoxynaphthalene (compare Cumming and Steele, J., 1923, **123**, 2466) failed. In each case, however, benzil was separated.

## EXPERIMENTAL.

*Preparation of 2-Nitrostyryl-3-methylchromones.*—2 : 3-Dimethylchromone was condensed with the corresponding nitrobenzaldehyde by Heilbron, Barnes, and Morton's method (J., 1923, **123**, 2565).

2-o-*Nitrostyryl*-3-*methylchromone*,



$$C_6H_4<\begin{matrix}CO\cdot \overset{}{C}Me\\ \|\\ O—C\cdot CH{:}CH\cdot C_6H_4\cdot NO_2\end{matrix}.$$

2 : 3-Dimethylchromone (2·8 g.) and *o*-nitrobenzaldehyde (2·2 g.) gave 1·6 g. of a solid which recrystallised from glacial acetic acid in yellow needles, m. p. 161° (Found : N, 4·5. $C_{18}H_{13}O_4N$ requires N, 4·55%).

2-m-*Nitrostyryl*-3-*methylchromone.* The chromone (3·4 g.) and *m*-nitrobenzaldehyde (3 g.) gave a solid which recrystallised from acetone in greenish-yellow needles (3 g.), m. p. 212° (Found : N, 4·55%).

2-p-*Nitrostyryl*-3-*methylchromone*, similarly prepared from *p*-nitrobenzaldehyde (3 g.), crystallised from glacial acetic acid in orange-yellow needles (2·8 g.), m. p. 238° (Found : N, 4·5%).

*Preparation of Azoxy-compounds. General Method and Remarks.*—The general method described in Part I (*loc. cit.*) was again employed. In those cases in which the azoxy-compound did not separate immediately or on standing for some time, some of the alcohol was distilled off and the reaction mixture was again kept until needles of benzil crystallised. These were filtered off and the mother-liquor was poured into water. The solid which separated (a mixture of benzil and azoxy-compound) was then dried and dissolved in the minimum quantity of benzene or xylene, and the azoxy-compound precipitated by addition of light petroleum.

A modification of the process, with benzene as a solvent and piperidine as an activator, was used in the preparation of 2-nitro-4-azoxytoluene.

p-*Azoxybenzylideneacetophenone*, $(C_6H_5\cdot CO\cdot CH{:}CH\cdot C_6H_4)_2N_2O$. *p*-Nitrobenzylideneacetophenone (4·2 g.) and benzoin (5·4 g.) gave 3·5 g. (87% of the theoretical yield) of the *p*-azoxy-compound, which recrystallised from xylene in yellow flakes, m. p. 211—213° (compare Vorländer, *Ber.*, 1906, **39**, 810) (Found : N, 5·8. Calc. : N, 6·1%).

m-*Azoxybenzylideneacetophenone.* *m*-Nitrobenzylideneacetophenone (4·8 g.) and benzoin (6·5 g.) gave an oily solid which crystallised after some time. Recrystallised from dilute acetone and finally purified by dissolution in hot xylene and precipitation with light petroleum, it gave a brown, microcrystalline solid, m. p. 156—157°. Yield, 0·75 g. (6%) (Found : N, 6·1. $C_{30}H_{22}O_3N_2$ requires N, 6·1%).

o - *Azoxybenzylideneacetophenone.* *o* - Nitrobenzylideneacetophenone (4·6 g.) and benzoin (6·36 g.) gave benzil (4·5 g.) as a first product, and the mother-liquor, poured into water, gave a brown solid which crystallised from benzene and light petroleum in brown flakes, m. p. 141—142° after softening at 135°. Yield, 1·2 g. (11%) (Found : N, 6·2%).

2-p-*Azoxystyryl*-3- *methylchromone.* 2 - *p* - Nitrostyryl - 3 - methylchromone (1·5 g.) and benzoin (1·1 g.) gave 0·6 g. (43%) of the p-*azoxy*-compound, which recrystallised from xylene in orange-yellow flakes, m. p. 289° (Found : N, 5·0. $C_{36}H_{26}O_5N_2$ requires N, 4·9%).

2-m-*Azoxystyryl*-3-*methylchromone* (0·75 g. ; 62%), prepared from 2-*m*-nitrostyryl-3-methylchromone (1·3 g.) and benzoin (1·2 g.), separated from xylene as a yellowish-white, microcrystalline solid, m. p. 275·5° (Found : N, 5·0%).

2-o-*Azoxystyryl*-3-*methylchromone* (0·2 g.; 15%), obtained from 2-*o*-nitrostyryl-3-methylchromone (1·5 g.) and benzoin (1·3 g.), formed greenish-yellow needles, m. p. 202° (Found : N, 4·8%).

p-*Azoxybenzylidene*-p-*bromoaniline*, $(C_6H_4Br{\cdot}N{:}CH{\cdot}C_6H_4)_2N_2O$, (1 g. ; 55%), prepared from *p*-nitrobenzylidene-*p*-bromoaniline (2 g.) and benzoin (2 g.), recrystallised from glacial acetic acid in yellowish-red plates, m. p. 218° (Found : N, 10·15. $C_{26}H_{18}ON_4Br_2$ requires N, 10·0%).

m-*Azoxybenzylidene*-p-*bromoaniline.* m-*Nitrobenzylidene*-p-*bromoaniline* was prepared by heating *m*-nitrobenzaldehyde and *p*-bromoaniline together until no more water was given off. It crystallised from alcohol in long, yellow needles, m. p. 84° (Found : N, 9·4. $C_{13}H_9O_2N_2Br$ requires N, 9·2%).

*m*-Nitrobenzylidene-*p*-bromoaniline (4 g.) and benzoin (4 g.) gave on standing for some time 0·7 g. (19%) of the m-*azoxy*-compound, which separated from benzene and light petroleum as a yellow, microcrystalline solid, m. p. 120° (Found : N, 10·15. $C_{26}H_{18}ON_4Br_2$ requires N, 10·0%).

o-*Azoxybenzylidene*-p-*bromoaniline* (0·5 g.; 27%), obtained from *o*-nitrobenzylidene-*p*-bromoaniline (2 g.) and benzoin (2 g.) after standing for 2 days, crystallised from xylene and light petroleum in yellow needles, m. p. 299° (Found : N, 10·3%).

m-*Azoxybenzylidene*-p-*toluidine* (2 g.; 46%), obtained from *m*-nitrobenzylidene-*p*-toluidine (4·8 g.) and benzoin (5 g.) after standing for some time, was recrystallised, first from glacial acetic acid and then from benzene and light petroleum; it formed pale yellow needles, m. p. 150° after softening at 135° (Found : N, 13·0. $C_{28}H_{24}ON_4$ requires N, 13·0%).

Ethyl *p*-azoxybenzoate (2·75 g.; 78%), prepared from ethyl *p*-nitrobenzoate (4 g.) and benzoin (6·5 g.), crystallised from glacial acetic acid in salmon-pink needles, m. p. 117° (compare Meyer and Dahlem, *Annalen*, 1903, **326**, 334) (Found : N, 8·3. Calc. : N, 8·2%).

2-*Nitro*-3-*azoxytoluene*. A solution of 2 : 4-dinitrotoluene (5 g.) and benzoin (10 g.) in 15 c.c. of benzene containing 2 c.c. of piperidine was boiled under reflux for 6 hours. The solvent was then allowed to evaporate almost to dryness. The solid which separated, after being washed with a little cold benzene and recrystallised from glacial acetic acid and from benzene–light petroleum, formed yellowish-white needles, m. p. 164° (compare Brand and Zöller, *Ber.*, 1907, **40**, 3329). Yield, 1 g. (23%) (Found : N, 17·6. Calc. : N, 17·7%).

*Preparation of Anisil and Furil.*—Although azoxybenzene could not be isolated in the reduction of nitrobenzene by means of benzoin, anisoin, or furoin, by using excess of the oxidising agent it was found possible to utilise the reaction as a method of preparing anisil and furil in 80% and 90% yields, respectively. Benzil is obtained by the same reaction in yields of 30—40%.

A solution of the ketol (5 g.) and nitrobenzene (4 g.) in 50 c.c. of alcohol containing 2 c.c. of 6% alcoholic sodium ethoxide was boiled under reflux for 2—3 minutes and then allowed to cool. The diketone which separated, recrystallised from alcohol, gave 4 g. of anisil, m. p. 133°, in the case of anisoin, and 4·7 g. of furil, m. p. 162°, in the case of furoin.

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