CCLXXV.—*The Reduction of Nitro-compounds by Aromatic Ketols. Part I. Some* p-*Azoxy-compounds.*

By Hugh Bryan Nisbet.

That benzoin and its analogues may reduce Fehling's solution has been known for a long time, but the possibility of reducing nitro-groups by means of these agents has not hitherto been investigated. It has now been found that benzoin, anisoin, and furoin, in hot alcoholic solution in the presence of a trace of sodium methoxide or ethoxide, may be successfully used for the reduction of nitro-groups to azoxy-groups :

$$2R{\cdot}NO_2+3R{\cdot}CH(OH){\cdot}COR = R_2N_2O + 3R{\cdot}CO{\cdot}COR + 3H_2O.$$

The reduction is particularly successful in the case of *p*-nitro-compounds such as the *p*-nitrobenzylideneanilines, *p*-nitrobenzonitrile, the *p*-nitrocinnamic esters, and the *p*-nitrostilbenes, since the azoxy-compounds formed are, in general, sparingly soluble substances and may be readily separated from the 1 : 2-diketone to which the ketol is oxidised in the course of the reaction. The reduction proceeds very quickly, in some cases with ebullition of the solvent, and in a very short time the *p*-azoxy-compounds separate from solution. The 1 : 2-diketone may be recovered in each case from the mother-liquor.

With benzoin as reducing agent, 60—70% yields of *p*-azoxybenzylideneanilines can be obtained from the corresponding *p*-nitrobenzylideneanilines. *p*-Azoxybenzylideneaniline so obtained is identical with that obtained by reducing *p*-nitrobenzylideneaniline with alkali sulphides (*Chem. Zentr.*, 1900, ii, 612) or with alcoholic potash (Alway, *Ber.*, 1902, **35**, 2436), by treating *p*-nitrobenzyl chloride with caustic potash (Alway, *loc. cit.*), or by condensing *p*-azoxybenzaldehyde with aniline (Alway, *Amer. Chem. J.*, 1902, **28**, 43). *p*-Azoxybenzylidene-*p*-toluidine prepared by this method is identical with the compound prepared by reducing *p*-nitrobenzylidene-*p*-toluidine with alkali sulphides (*Chem. Zentr.*, 1900, ii, 612) or by the condensation of *p*-azoxybenzaldehyde with *p*-toluidine (Alway, *Ber.*, 1902, **35**, 2437). *p*-Nitrobenzylidene-*p*-aminoacetophenone is reduced by benzoin to *p*-azoxybenzylidene-*p*-aminoacetophenone.

Japp and Miller (J., 1893, **63**, 474) showed that benzoin and benzonitrile in the presence of concentrated sulphuric acid condense to form triphenyloxazole ; but *p*-nitrobenzonitrile is reduced by benzoin to *p*-azoxybenzonitrile.

By this method of reduction the esters of *p*-azoxycinnamic acid can be prepared directly from the esters of *p*-nitrocinnamic acid, and the azoxy-acid can be obtained by hydrolysis. The yields of the reduction products are good, usually 70%, and the reaction proceeds very quickly, whereas the reduction of the nitro-acid electrolytically (Marie, *Comp. rend.*, 1905, **140**, 1248) or by sodium arsenite (Vorländer, *Ber.*, 1906, **39**, 806) and the formation of the esters of the azoxy-acid through the silver salt (Vorländer, *loc. cit.*) are all tedious methods.

p-Nitrostilbenes also are easily reduced by this method to *p*-azoxystilbenes, which may be obtained in excellent yield. The table gives the *p*-azoxystilbenes prepared by this method, the approximate yield, usually the average of two experiments, and the molecular weights of those compounds which are sufficiently soluble in 2 : 4-dinitrotoluene to allow of the determination by the cryoscopic method in that solvent (Auwers, *Z. physikal. Chem.*, 1899, **30**, 310).

Azoxy-compounds.	Yield.	*M*, found.	*M*, calc.
p-Azoxystilbene	70%	396	402
p-Azoxy-2-nitrostilbene	70%	487	492
p-Azoxy-2 : 3′-dinitrostilbene	45%	—	—
p-Azoxy-2 : 6-dinitrostilbene	Small	—	—
p-Azoxy-2-nitro-4′-methoxystilbene	70%	512	552
p-Azoxy-2-nitro-3′ : 4′-methylenedioxystilbene	65%	586	580
p-Azoxy-2 : 6-dinitro-4′-methoxystilbene	45%	—	—
p-Azoxy-2-nitro-4′-dimethylaminostilbene	42%	—	—

Anisoin and furoin were substituted for benzoin in the reduction of 2 : 4-dinitrostilbene and gave approximately the same yield of the same azoxy-compound. The mother-liquors yielded anisil and furil, respectively. In all the reductions in which benzoin was used, benzil was recovered from the mother-liquors.

EXPERIMENTAL.

Preparation of Nitrostilbenes.—A modification of Bishop and Brady's method (J., 1922, **121**, 2367) was used. A solution of the polynitrotoluene and the aromatic aldehyde in molecular proportion and 1 c.c. of piperidine in a small quantity of benzene is boiled under reflux until the reaction is complete, the time varying from 1 to 6 hours. The benzene is then allowed to evaporate and the crystalline mass is washed with benzene–light petroleum and recrystallised from glacial acetic acid. 2 : 4-Dinitro-4′-methoxystilbene, 75% yield, m. p. 163° (compare Pfeiffer, *Annalen*, 1916, **411**, 91). 2 : 4 : 3′-Trinitrostilbene, 50% yield, m. p. 182—183° (compare Pfeiffer, *loc. cit.*). 2 : 4 : 4′-*Trinitrostilbene*, from 2 : 4-dinitrotoluene (9 g.) and *p*-nitrobenzaldehyde (7·5 g.). Yield, 12 g. Dark orange needles, m. p. 234—235° (Found : C, 53·9; H, 3·0. $C_{14}H_9O_6N_3$ requires C, 53·3; H, 2·9%). 2 : 4-*Dinitro*-3′ : 4′-*methylenedioxystilbene* from 2 : 4-dinitrotoluene (9 g.) and piperonal

(7·5 g.). Yield, 12 g. Orange-red, squat crystals, m. p. 178—180° (Found: C, 56·9; H, 3·3. $C_{15}H_{10}O_6N_2$ requires C, 57·3; H, 3·2%). 2 : 4 : 6-*Trinitro-4'-methoxystilbene*, from 2 : 4 : 6-trinitrotoluene (11 g.) and anisaldehyde (7 g.). Yield, 9·3 g. Brown needles, m. p. 167—168° (Found: C, 51·8; H, 3·3. $C_{15}H_{11}O_7N_3$ requires C, 52·2; H, 3·2%). 2 : 4-*Dinitro-4'-dimethylaminostilbene*, from 2 : 4-dinitrotoluene (9 g.) and *p*-dimethylaminobenzaldehyde (7 g.). Yield, 11 g. Small, black, lustrous plates, m. p. 181° (Found: N, 12·8. $C_{16}H_{15}O_4N_3$ requires N, 12·8%). The base forms a *chloroplatinate*, yellowish-brown needles, m. p. 211° [Found: Pt, 18·8. $(C_{16}H_{15}O_4N_3)_2,H_2PtCl_6$ requires Pt, 18·9%].

Preparation of Azoxy-compounds. General Method and Remarks.—The nitro-compound is dissolved in the smallest possible quantity of boiling alcohol, sufficient ketol for the reduction of somewhat less than the whole of the nitro-compound is added, and then a few drops of 6% alcoholic sodium methoxide or ethoxide. The solution goes dark, but soon begins to clear and a yellow or an orange precipitate settles out. After cooling a little, this is collected, dried, and recrystallised from xylene. The azoxy-compounds so obtained are, in general, yellow or bronze-yellow, and are very slightly soluble in the common solvents, slightly soluble in boiling xylene, and more soluble in boiling pyridine. If too much reducing agent be added, the reduction products are sometimes red, probably due to the formation of traces of azo-compounds.

The constitutions of the *p*-azoxystilbenes follow from the analytical figures and the molecular-weight determinations, and from their analogy to the other compounds described in this paper. That it is the *p*-nitro-group which is reduced in stilbenes containing more than one nitro-group may be safely assumed, since it has been proved already that other alkaline reducing agents, *e.g.*, ammonium sulphide, attack the *p*-nitro-group first (Thiele and Escales, *Ber.*, 1901, **34**, 2846). The insolubility of the *p*-azoxystilbenes which have been prepared so far by this method has rendered the examination of further reduction products impossible.

p-*Azoxybenzylideneaniline*, $(C_6H_5\cdot N{:}CH\cdot C_6H_4)_2N_2O$. *p*-Nitrobenzylideneaniline (8 g.) and benzoin (8 g.) gave an almost immediate separation of yellow flakes which, recrystallised from xylene, sintered at 185° and melted and decomposed at 226°. Yield, 5 g. (Found: C, 77·2; H, 5·2; N, 13·8. Calc.: C, 77·2; H, 4·95; N, 13·8%). The compound was completely identified by treating it with 27% nitric acid; *p*-azoxybenzaldehyde, m. p. 190°, and aniline were obtained (compare Alway, *Amer. Chem. J.*, 1902, **28**, 43). The *p*-azoxybenzaldehyde recondensed with aniline to give *p*-azoxybenzylideneaniline which, when mixed with the product obtained by using benzoin as reducing agent, did not alter its melting point.

p-*Azoxybenzylidene*-p-*toluidine*, $(C_7H_7N{:}CH{\cdot}C_6H_4)_2N_2O$. *p*-Nitrobenzylidene-*p*-toluidine (2·5 g.) and benzoin (2·1 g.) gave an immediate separation of yellow flakes, which were recrystallised from boiling xylene. M.p. 217° (decomp.; sintering at 189—190°). Yield, 1·7 g. (Found: C, 77·9; H, 5·9; N, 12·5. Calc.: C, 77·7; H, 5·55; N, 12·9%).

p-*Azoxybenzylidene*-p-*aminoacetophenone*,

$$(CH_3{\cdot}CO{\cdot}C_6H_4{\cdot}N{:}CH{\cdot}C_6H_4)_2N_2O.$$

p-Nitrobenzylidene-*p*-aminoacetophenone (2·7 g.) and benzoin (2·1 g.) gave an immediate separation of yellow flakes. Recrystallised from xylene, the substance sintered at 187° and melted and decomposed at 217°. Yield, 1·8 g. (Found: C, 73·4; H, 5·15; N, 11·3; *M*, cryoscopic in 2 : 4-dinitrotoluene, 486. $C_{30}H_{24}O_3N_4$ requires C, 73·8; H, 4·9; N, 11·6%; *M*, 488).

p-*Azoxybenzonitrile*.—*p*-Nitrobenzonitrile was prepared by Sandmeyer's method (*Ber.*, 1885, **18**, 1492), but was isolated, not by sublimation, but by extracting the cuprocyanide reaction mixture several times with much boiling water; it was deposited in flakes on cooling and recrystallised from alcohol (yield, 8·2 g. from 13·8 g. of *p*-nitroaniline).

p-Nitrobenzonitrile (6 g.) and benzoin (8·5 g.) were dissolved in 100 c.c. of alcohol, and a few drops of 6% alcoholic sodium ethoxide added. p-*Azoxybenzonitrile* soon began to separate and after cooling it was collected and recrystallised from boiling toluene (yield, 5 g.); m. p. 221° (Found: C, 67·9; H, 3·5; N, 22·5; *M*, cryoscopic in 2 : 4-dinitrotoluene, 247. $C_{14}H_8ON_4$ requires C, 67·7; H, 3·2; N, 22·5%; *M*, 248).

Esters of p-*azoxycinnamic acid*. Ethyl *p*-nitrocinnamate (3 g.) and benzoin (3 g.) gave ethyl *p*-azoxycinnamate (2·1 g.), which crystallised from xylene in yellow, flocculent needles, m. p. 240°, sintering at 140° (Found: C, 67·1; H, 5·5; N, 7·1. Calc.: C, 67·1; H, 5·5; N, 7·2%).

Methyl *p*-nitrocinnamate (2 g.) and benzoin (2 g.) gave 1·4 g. of methyl *p*-azoxycinnamate, which crystallised from xylene in yellow, flocculent needles, m. p. 246°, sintering at 220° (Found: C, 65·8; H, 4·8; N, 7·35. Calc.: C, 65·6; H, 4·9; N, 7·6%).

p-Azoxycinnamic acid was obtained, by hydrolysis of either of the esters, as a yellow, amorphous solid insoluble in the common organic solvents but soluble in alkali; it decomposed at a high temperature (Found: C, 64·2; H, 4·3; N, 7·8. Calc.: C, 63·9; H, 4·1; N, 8·2%).

p-*Azoxystilbene*, $(C_6H_5{\cdot}CH{:}CH{\cdot}C_6H_4)_2N_2O$. 4-Nitrostilbene (1·7 g.)

and benzoin (1·6 g.), treated according to the general method, gave a green solution which in a short time turned yellow and deposited a yellow, flocculent precipitate. This, after recrystallisation from xylene, sintered at 259° and melted and decomposed at 271—272° (Found: C, 83·2; H, 5·6; N, 6·9; *M*, 396. $C_{28}H_{22}ON_2$ requires C, 83·5; H, 5·5; N, 6·9%; *M*, 402).

p-*Azoxy-2-nitrostilbene.* Reduction of 2 : 4-dinitrostilbene (Bishop and Brady, J., 1922, **121**, 2367) (2·6 g.) with benzoin (2·1 g.), anisoin (2·6 g.), or furoin (1·9 g.) gave 1·8 g., 1·75 g., or 1·8 g., respectively, of the p-*azoxy*-compound, which crystallised from xylene in orange plates, m. p. 208—210° (Found: C, 68·2; H, 4·2; N, 11·4; *M*, 487. $C_{28}H_{20}O_5N_4$ requires C, 68·3; H, 4·1; N, 11·3%; *M*, 492). Anisil, m. p. 133°, and furil, m. p. 162°, were obtained from their respective mother-liquors.

p-*Azoxy-2 : 3′-dinitrostilbene.* 2 : 4 : 3′-Trinitrostilbene (1·6 g.) and benzoin (1·1 g.) gave 0·75 g. of the reduction compound, which crystallised from xylene in yellow flakes, m. p. 212° (Found: C, 58·1; H, 3·4; N, 14·4. $C_{28}H_{18}O_9N_6$ requires C, 57·7; H, 3·1; N, 14·4%).

p-*Azoxy-2 : 4′-dinitrostilbene.* Only traces of this reduction compound could be isolated, since it was difficult to find a suitable solvent for the nitrostilbene.

p-*Azoxy-2 : 6-dinitrostilbene.* 2 : 4 : 6-Trinitrostilbene (Bishop and Brady, *loc. cit.*) (3·2 g.) and benzoin (2·1 g.) gave on standing over-night a small yield of a solid which, recrystallised from glacial acetic acid, had m. p. 270° (Found: N, 14·6. $C_{28}H_{18}O_9N_6$ requires N, 14·4%).

p-*Azoxy-2-nitro-4′-methoxystilbene.* 2 : 4-Dinitro-4′-methoxystilbene (3·1 g.) and benzoin (2·1 g.) gave 2·2 g. of the *azoxy*-compound, which is only slightly soluble in boiling xylene and is an orange-red, microcrystalline powder, m. p. 208° (Found: C, 65·8, 64·75, 64·75; H, 4·7, 4·5, 4·6; N, 10·0; *M*, 512. $C_{30}H_{24}O_7N_4$ requires C, 65·2; H, 4·3; N, 10·1%; *M*, 552).

p-*Azoxy-2-nitro-3′ : 4′-methylenedioxystilbene.* 2 : 4-Dinitro-3′ : 4′-methylenedioxystilbene (2·8 g.) and benzoin (2·1 g.) gave 1·7 g. of the p-*azoxy*-compound which, recrystallised from xylene, formed a red, microcrystalline solid, m. p. 230° (Found: C, 62·1; H, 4·0; N, 9·4; *M*, 586. $C_{30}H_{20}O_9N_4$ requires C, 62·0; H, 3·5; N, 9·6%; *M*, 580).

p-*Azoxy-2 : 6-dinitro-4′-methoxystilbene.* 2 : 4 : 6-Trinitro-4′-methoxystilbene (2·8 g.) and benzoin (2·1 g.) gave 1·25 g. of the p-*azoxy*-compound, which forms bronze plates from xylene. It changes colour at 252° and melts with decomposition at 297° (Found: C, 55·6; H, 3·6; N, 13·2. $C_{30}H_{22}O_{11}N_6$ requires C, 55·9; H, 3·4; N, 13·06%).

p-*Azoxy-2-nitro-4′-dimethylaminostilbene.* 2 : 4-Dinitro-4′-dimethylaminostilbene (1·5 g.) and benzoin (1 g.) gave black, flaky crystals of the p-*azoxy*-compound which were washed with hot alcohol. The compound is so slightly soluble in boiling xylene that it cannot be recrystallised from that solvent. The substance without further purification remained unchanged at 305° (Found : N, 14·3. $C_{32}H_{30}O_5N_6$ requires N, 14·5%). The compound is soluble in hot concentrated hydrochloric acid, but the hydrochloride is readily hydrolysed on addition of water. Two attempts to prepare a chloroplatinate failed owing to the almost colloidal nature of the hydrochloric acid solution.

The mother-liquors from each of the above reductions in which benzoin was used yielded benzil, m. p. 95°, on standing or when poured into water and the needles so obtained were recrystallised from alcohol. The compound was identified by its characteristic reaction with alcoholic potash and by its oxidation to benzoic acid, m. p. 122°, by means of alkaline permanganate.

The investigation is being continued with a view to establishing the generality of this method of reducing nitro- to azoxy-groups and determining its value as a method of preparing azoxy-compounds.

In concluding this part of the work, the author desires to thank Professor A. Archibald Boon for his kind interest and for providing the facilities which have rendered this research possible.

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