# Reduction of Nitroarenes to Anilines in Basic Alcoholic Media

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Substituted nitrobenzenes are reduced by alkoxide ions in alcohols to the corresponding azoxy and aniline derivatives. The reaction leading to anilines has been investigated in detail. Two different processes have been identified, both initiated by the condensation between the nitrosoarene intermediate (the first product of the reduction reaction) and the product of oxidation of the solvent. The imino derivative thus formed (ArN=CH–COR) may either undergo hydrolysis (to aniline) or form, through a series of redox processes, compounds containing the ArNH–CO moiety. These are also hydrolysed to anilines in a slower reaction.

The reduction of nitroaromatic compounds to the corresponding anilines in acid media is a well established synthetic procedure[1] fundamental to the development of the organic chemical industry.[2] It is therefore not surprising that a wealth of information is available on the reaction mechanism and on several useful improvements in the experimental conditions.[3]

Reduction under basic conditions has received far less attention,[4] probably because of the formation, along with the main products of reaction (azoxy and azo derivatives[5,6]), of a relatively large number of by-products.[7] The mechanism of reduction in basic solution is, indeed, much less well defined than that in acid solution.[4]

It is known, however, that nitroarenes are converted into their radical anions when treated with alkoxides in dipolar aprotic solvents,[8] and that these radical anions are intermediates in the reduction of nitrobenzenes to azoxybenzenes by sodium methoxide in methanol[9] as well as in reactions leading to the production and oxidation of carbanions.[10]

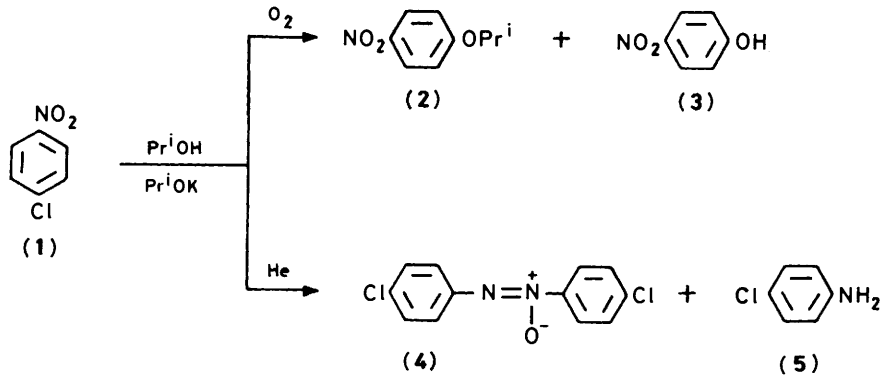
We have been able to use this information to control the reaction between potassium isopropoxide in propan-2-ol and 1-chloro-4-nitrobenzene. Indeed we do not obtain from this reaction the expected nucleophilic aromatic substitution product (4-nitrophenyl isopropyl ether[11]); a complex mixture is formed containing products both of substitution of the chlorine and of reduction of the nitro group.[12] The chloronitrobenzene radical anion, which is the intermediate leading to the reduction, may be trapped by running the reaction under oxygen. This causes the radical anion to revert to the starting material,[13] completely suppressing the reduction reaction (see Scheme 1).

Surprisingly, the reduction process, which is the only one observed under a deoxygenated atmosphere, yields only two products: 4,4′-dichloroazoxybenzene (**4**) and 4-chloroaniline (**5**). The formation of anilines in the reduction of nitroarenes in basic solutions has been previously reported,[7] without comment on the reaction mechanism. We present in this paper results which allow us to describe in detail the route leading to anilines in basic alcoholic solution.

## Results and Discussion

The reaction of substituted nitrobenzenes with $Pr^iOK$ in $Pr^iOH$ at 75 °C and in an inert atmosphere leads to the azoxy and aniline derivatives in 60—70% and 10—20% yields, respectively. Interestingly, the amount of aniline produced does not remain constant after complete disappearance of the starting material, but slowly increases to a plateau. The data reported in Table 1 indicate that anilines are produced in two processes, a fast process accounting for the largest fraction of the overall amount formed, and a slower process corresponding to reaction of some intermediate(s) unstable under the reaction conditions.

In order to investigate the mechanisms of production of anilines in these systems we initially studied the behaviour of conceivable precursors. The reduction of nitrobenzene to aniline in acidic solution is considered to occur through nitroso and the hydroxylamino derivatives.[14] We therefore subjected, separately, 1-chloro-4-nitrosobenzene and 4-chlorophenylhydroxylamine to our usual reaction conditions. As expected,[15] both compounds give 4,4′-chloroazoxybenzene in virtually quantitative yield. 4,4′-Dichloroazoxybenzene, in turn, undergoes very slow reduction ($t_{\frac{1}{2}}$ 40 h) to 4,4′-dichloroazobenzene, which is stable under the reaction conditions.




Scheme 1.

**Table 1.** Reduction of substituted nitrobenzenes ($XC_6H_4NO_2$; 0.03M) with potassium isopropoxide (0.23M) in propan-2-ol[a]

| X | Azoxy compd. (%) | Aniline[b] (%) | $t_{\frac{1}{2}}$[c]/min |
|---|---|---|---|
| *p*-Cl | 58.1 | 21.3 (26.0) | 17 |
| *m*-Cl | 58.9 | 14.4 (24.0) | 7 |
| H | 60.1 | 16.3 (20.9) | 58 |
| *m*-$OCH_3$ | 69.0 | 11.6 (15.3) | 36 |
| *p*-$OCH_3$[d] | 50.8 | 14.9 | 250 |
| *m*-$N(CH_3)_2$ | 60.8 | 17.1 (19.7) | 105 |

[a] Under argon at 75 °C. [b] % Yield of aniline at infinite time (*ca.* 20 h) in parentheses. [c] Half-life for the disappearance of the starting material. [d] 1-Isopropoxy-4-nitrobenzene (8%) also formed.

**Table 2.** Effect of the addition of water and ketones on the reduction of 1-chloro-4-nitrobenzene (0.03M) with potassium isopropoxide (0.25M) in propan-2-ol[a]

| Ketone[b] | $[H_2O]$/M | Reaction time[c] (min) | 4,4′-Dichloroazoxybenzene (%) | 4-Chloroaniline (%) |
|---|---|---|---|---|
| | | 90 | 56.9 | 14.2 |
| | 0.333 | 90 | 54.7 | 23.8 |
| $CH_3COCH_3$ (0.09) | 0.365 | 180 | 19.7 | 61.1 |
| $CH_3COPh$ (0.028) | 0.365 | 180 | 14.1 | 82.5 |
| PhCOPh (0.027) | 0.347 | 150 | 51.3 | 26.9 |

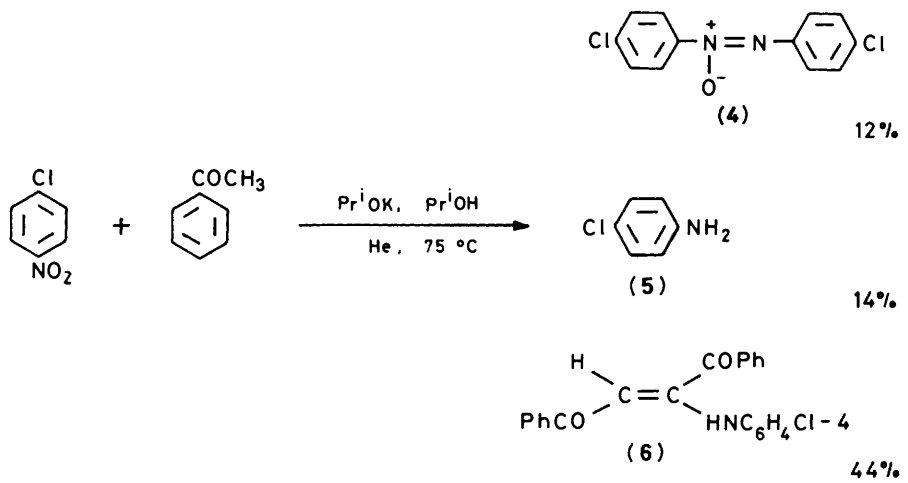
[a] At 75 °C, under helium. [b] Molarity in parentheses. [c] Time needed for the disappearance of 1-chloro-4-nitrobenzene.

accompanied by the oxidation of propan-2-ol to acetone, and formation of water. Indeed acetone can be isolated (as the 2,4-dinitrophenylhydrazone) by bubbling nitrogen first through the reaction solution and then into an alcoholic solution of 2,4-dinitrophenylhydrazine.

The influence of additions of methyl ketones and water on the yields of the reduction products was studied in a series of experiments which are summarized in Table 2. The amount of aniline formed greatly increases when either acetone or acetophenone and water are added to the reaction mixture, whereas additions of benzophenone have essentially no effect. These results suggest that the reaction of nitroarenes in the presence of methyl ketones in basic solutions might represent an interesting method for the reduction of nitroaromatic compounds to amino derivatives. Addition of methyl ketones also modifies the product composition in the reduction of 1-chloro-4-nitrosobenzene in the same system, decreasing the yield of 4,4′-dichloroazoxybenzene with concurrent formation of 4-chloroaniline.[16]

Since the addition of water alone seems to affect the yield of aniline, we thought that the latter might be derived from the hydrolysis of an intermediate. In order to check this point, and in an attempt to isolate any intermediate, the reduction of nitrobenzene was carried out in the presence of acetophenone, without addition of water. The choice of acetophenone rather than acetone is dictated by the higher yield of aniline obtained with the former ketone, and by the much easier synthesis and characterization of the intermediates formed (see later).

The reaction gives the results reported in Scheme 2. The structure and some reactions of compound (**6**) and substituted




**Scheme 2.**

We conclude, therefore, that none of the foregoing four conceivable aniline precursors is directly responsible for the aniline produced in the reduction of nitroarenes promoted by $Pr^iOK$ in $Pr^iOH$.

The search for potential sources for the production of aniline was aided by close inspection of the stoicheiometry of the overall reduction processes. The stoicheiometry of the reactions leading to nitroso and azoxy compounds [equations (1) and (2)] tells us that the reduction of the aromatic substrates is

$$ArNO_2 + Pr^iOH \xrightarrow{Pr^iOK} ArNO + Me_2CO + H_2O \quad (1)$$

$$2ArNO + Pr^iOH \xrightarrow{Pr^iOK} Ar\text{–}\overset{+}{N}(O^-)\text{=}\overset{+}{N}\text{–}Ar + Me_2CO + H_2O \quad (2)$$

analogues have been described in a recent paper.[16] The possibility that compound (**6**) is the intermediate leading to 4-chloroaniline is ruled out by a basic hydrolysis experiment. Compound (**6**) is indeed hydrolysed to 4-chloroaniline, but at a much lower rate[16] than needed to account for the aniline formed in the reduction of nitro derivatives ($t_{\frac{1}{2}}$ 8 h, $[Pr^iOK]$ 0.23M, $[H_2O]$ 5.5M, reflux).

As we have shown elsewhere,[16] compound (**6**) is formed by addition of the acetophenone enolate ion to the nitrone (**7**), followed by elimination of water and tautomerization. The nitrone, in turn, can arise, as suggested in the literature,[17] through oxidation of the hydroxylamine anion (**8**) (Scheme 3).

Another reaction pathway open to compound (**8**) is elimination of water to form the imino derivative ArN=CH–COR (**9**). Compound (**9**; R = Ph, Ar = 4-$ClC_6H_4$), synthesized independently by reaction of 4-chloroaniline with phenylglyoxal

$$ArNO_2 \longrightarrow ArNO$$

$$RCOCH_3 + Pr^iO^- \longrightarrow RCOCH_2^- + Pr^iOH$$

$$ArNO + RCOCH_2^- \longrightarrow Ar\text{-}N(O^-)\text{-}CH_2\text{-}COR \quad (8)$$

$$Ar\text{-}N(O^-)\text{-}CH_2\text{-}COR \xrightarrow[(ArNO \text{ or } ArNO_2)]{\text{oxidn.}} Ar\text{-}\overset{+}{N}(O^-)\text{=}CH\text{-}COR \quad (7)$$

**Scheme 3.**

in alcoholic media,[18] readily and reversibly adds alcohols to the C=N double bond according to equilibrium (3).[18] For all

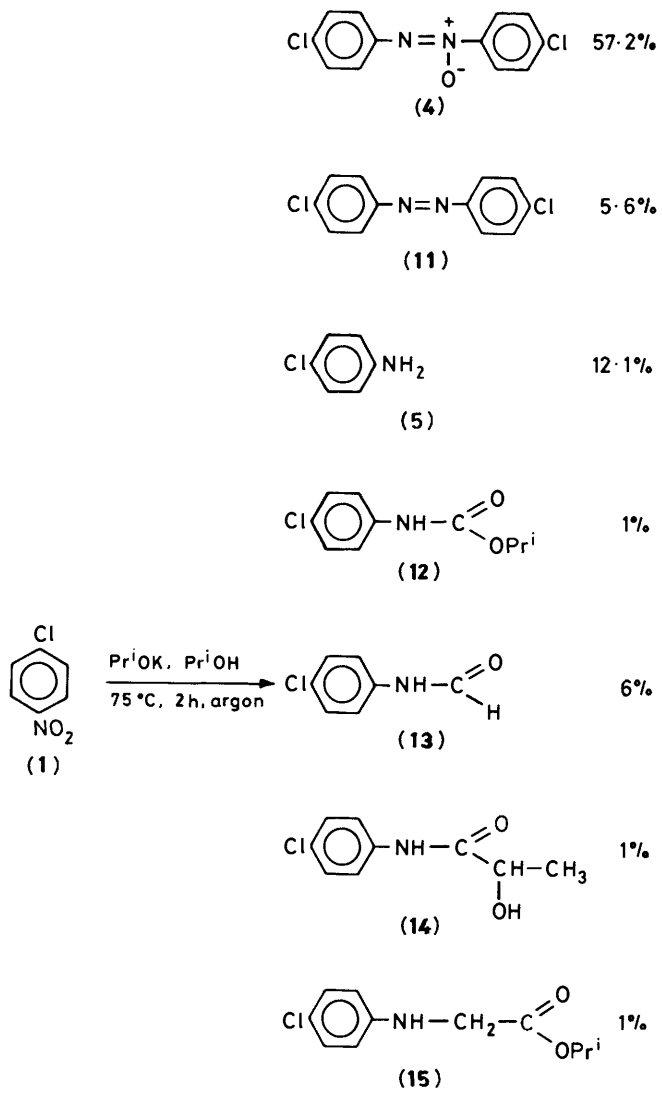
$$ArN{=}CH\text{-}COR\ (\mathbf{9}) + R'OH \rightleftharpoons Ar\text{-}N(H)\text{-}CH(OR')\text{-}COR\ (\mathbf{10}) \quad (3)$$

synthetic purposes, the imino compound, or its adducts with alcohols, or a mixture of these can be used.[18] The anil (**9**; Ar = 4-$ClC_6H_4$, R = Ph) or its methanol or ethanol adduct (**10**), affords quantitatively 4-chloroaniline when treated with basic propan-2-ol in the presence of water ([$Pr^iOK$] 0.23M, [$H_2O$] 2.23M, 75 °C) with $t_{\frac{1}{2}}$ 0.5 min. This experiment provides strong evidence for the anil (**9**) being the precursor of the aniline formed during the reduction of nitrobenzenes in basic solution.

Two questions still remain unanswered: (i) what is the source of the aniline formed in the slower process after complete disappearance of the nitroarene; and (ii) why is it that under some conditions the nitrone (**7**) is formed, leading to the diketone (**6**), whereas under others the anil (**9**) is formed, leading to an aniline?

To answer these questions, a reaction was run with 1-chloro-4-nitrobenzene on a preparative scale under our usual conditions and quenched just after the complete disappearance of (**1**). Careful work-up afforded the compounds reported in Scheme 4, in the yields indicated. Together with the expected azoxy compound (**4**) and the aniline (**5**), some 4,4′-dichloroazobenzene (**11**) was found, derived from further reduction of (**4**). More interestingly, we also isolated and identified compounds (**12**)—(**14**) all of which produce 4-chloroaniline under basic conditions in a relatively slow hydrolysis reaction. The detailed mechanism of formation of compounds (**12**)—(**15**) is still unknown. However, we know that reaction of anils in $Pr^iOK$–$Pr^iOH$ may lead, through several redox processes, to compounds such as lactanilide (**14**) or formanilide (**13**). Indeed we have reported[18] that the reaction of the phenylglyoxal anil (PhCOCH=N-$C_6H_4$Cl-4) in $Pr^iOK$–$Pr^iOH$ yields *ca.* 11% of (**13**) and 3% of mandelamide [PhCH(OH)–CONH-$C_6H_4$Cl-4). A rationalization for this reaction has been presented elsewhere.[18] We may conclude from this experiment that the aniline formed after all the nitro derivative has disappeared arises from the slow hydrolysis of compounds having the ArNHCO moiety, in turn derived from a common precursor, the anil ArN=CH–COR.

*Reduction of Nitrobenzene in the Presence of Acetophenone and a Substituted Anil.*—Reduction of nitrobenzenes in the presence of acetophenone affords, under our conditions, 1,4-dioxobutenes of general structure (**6**), *via* enolate ion addition across the nitrone CH=N bond.[16] The nitrone can arise, as suggested in the literature, from the oxidation of the hydroxylamine anion (**8**) (see Scheme 4). However, another possibility is that of direct oxidation of the anil. To check this point we carried out the crossover experiment described in Scheme 5: the

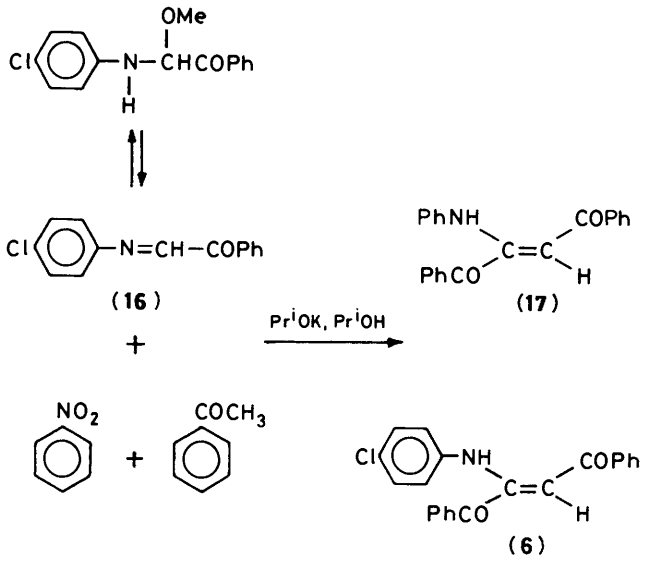



**Scheme 4.**

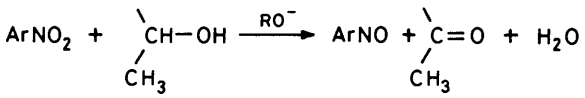
reduction of nitrobenzene was run in the presence both of acetophenone and of the imino derivative (**9**) bearing a Cl substituent, *i.e.* (**16**). Both compound (**17**), the expected 1,4-dioxobutene derived from the reduction of nitrobenzene, and compound (**6**) are formed in this reaction, thus indicating that anils can indeed be oxidized to nitrones, under our reaction conditions. Nitrones, in fact, are the intermediates needed to form the substituted 1,4-dioxobutenes. An alternative pathway can be envisaged to explain the production of (**6**), *viz.* hydrolysis of (**16**) to 4-chloroaniline and exchange of the aniline moiety in the dioxobutene. This possibility, however, has been ruled out since no exchange occurs between (**17**) and 4-chloroaniline during the time required for the reduction of nitrobenzene in the reaction of Scheme 5.

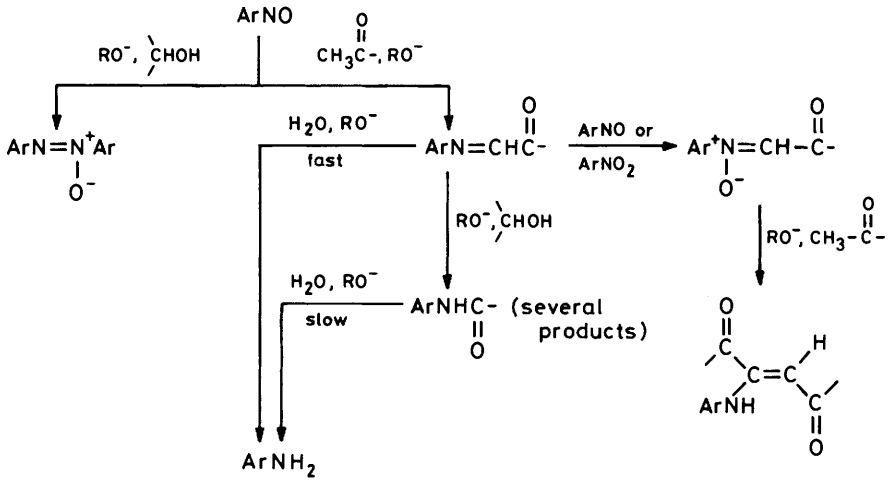
## Conclusions

The experiments described in this paper allow us to present a clear and detailed picture of what happens when nitroaromatic derivatives are reduced in basic alcoholic solution (Scheme 6). The nitro compound is reduced to its nitroso derivative at the expense of the alcohol, which is oxidized to a carbonyl compound. The nitroso compound may either reductively dimerize to the corresponding azoxy derivative or form the oxo-anil, *via* reaction with the enolate ion. The oxo-anil intermediate, in




Scheme 5.




Scheme 6.

turn, may undergo any of several competitive reactions: (i) hydrolysis to aniline (water is formed in the two reduction steps); (ii) an internal redox process to form products containing the ArNHCO moiety (lactanilide, formanilide, *etc.*) which are then slowly hydrolysed to aniline; (iii) oxidation to a nitrone which, in the presence of an excess of methyl ketone, reacts with the enolate anion to form the 1,4-dioxobutene derivative.

The general features of the rather complex series of reactions occurring during the reduction of nitroaromatic compounds in basic alcoholic solution are now well understood. These results open the way to further studies aimed at exploring the synthetic possibilities of these reactions (*e.g.* synthesis of anilines bearing acid-sensitive substituents) as well as at extending mechanistic investigation of the electron-transfer steps which occur during the reactions of alkoxides with nitroaromatic derivatives.[19]

## Experimental

N.m.r. spectra were recorded with a WP 200 Bruker spectrometer, with $Me_4Si$ as internal standard. Mass spectra were recorded with a V.G. MM 16 F instrument. G.l.c. analyses were performed with a Varian 3700 gas chromatograph (FID) linked to a Perkin-Elmer Sigma 10 digital integrator (2 m × 2 mm glass column filled with UCW 982 10% on Chromosorb W AW DMCS 80—100 mesh). Linear chain hydrocarbons ($C_{12}$—$C_{24}$) were used as internal standards and concentrations were determined by calibration curves.

*Materials and Solvents.*—Propan-2-ol was purified by distillation from magnesium turnings. 1-Chloro-4-nitrobenzene, 1-chloro-3-nitrobenzene, 1-methoxy-3-nitrobenzene, 1-dimethylamino-3-nitrobenzene, 1-methoxy-4-nitrobenzene, 4-chloroaniline, 4-methoxyaniline, 3-chloroaniline, aniline, nitrobenzene, 3-methoxyaniline, and 3-dimethylaminoaniline were commercial products recrystallized or distilled until pure (by g.l.c.). 4-Chlorophenyl isocyanate was used as purchased. 4,4′-Dichloroazobenzene (m.p. 186—187 °C),[20] 4,4′-dichloroazoxybenzene (m.p. 154—155 °C),[21] 4,4′-dimethoxyazoxybenzene (m.p. 117—118 °C),[21] 3,3′-bis(dimethylamino)azoxybenzene (m.p. 88—89 °C),[22] 3,3′-dichloroazoxybenzene (m.p. 97—98 °C),[20] 3,3′-dimethoxyazoxybenzene (m.p. 51—52 °C),[23] azoxybenzene (m.p. 35—36 °C),[21] 4-chlorophenylhydroxylamine (m.p. 87—88 °C),[24] 1-chloro-4-nitrosobenzene (m.p. 92—93 °C),[25] and 2-(4-chlorophenylamino)-2-methoxy-1-phenylethanone[18] were prepared and purified according to published procedures.

*Reactions of Substituted Nitrobenzenes in* Pr$^i$OH–Pr$^i$OK *under Argon.*—The reaction of 1-chloro-4-nitrobenzene is described as an example of the general procedure. A solution of 1-chloro-4-nitrobenzene (1.2 mmol) and of appropriate standards [tridecane (70 mg) and tetracosane (50 mg)] in propan-2-ol (20 ml) and a solution of potassium isopropoxide in propan-2-ol (20 ml; 0.5M) were added separately to the side arms of an inverted Y-shaped tube. The solutions were carefully and repeatedly deaerated under argon (thaw–freeze procedure) and then thermostatically maintained at 75 °C. At zero time the

solutions were mixed by inverting the Y-tube. Samples were withdrawn at appropriate time intervals, diluted with ethyl alcohol–diethyl ether, quenched with solid $CO_2$, and analysed by g.l.c.

*Complete Product Analysis of the Reaction of* 1-*Chloro*-4-*nitrobenzene with Potassium Isopropoxide in Propan*-2-*ol*.—1-Chloro-4-nitrobenzene (2.85 g) was dissolved at room temperature in a solution of potassium isopropoxide in propan-2-ol (580 ml; 0.25M). After three thaw–freeze cycles under argon, the reaction mixture was thermostatically maintained at 75 °C for 2 h. The cold mixture was poured into water (200 ml), acidified with HCl (4M), neutralized with aqueous $NaHCO_3$, and extracted with chloroform (3 × 200 ml). The aqueous layer, acidified with conc. HCl, was extracted again with chloroform (200 ml). From this second extraction only tars (64 mg) were recovered. The organic layer obtained from the first extraction was dried ($Na_2SO_4$) and the solvent removed under reduced pressure. Chromatography of the residue on silica gel [Merck 7729; eluant light petroleum (b.p. 40—60 °C)–ethyl acetate (from 97:3 to pure ethyl acetate)] afforded in the following order: 4,4′-dichloroazobenzene (0.125 g), 4,4′-dichloroazoxybenzene (1.289 g), mixture A (0.068 g; two products), 4-chloroaniline (0.343 g), and mixture B (0.206 g; two products).

Chromatography of mixture A (silica gel; chloroform–light petroleum, 1:1) afforded isopropyl *N*-(4-chlorophenyl)carbamate (**12**) (35 mg) and isopropyl *N*-(4-chlorophenyl)glycinate (**15**) (25 mg), both identified by comparison with authentic samples.

Chromatography of mixture B (silica gel; methylene dichloride–ethyl acetate, 9:1) yielded 4-chloroformanilide (**13**) (0.170 g); δ($^1$H) ($CDCl_3$) 7.03—7.53 (arom., 4 H) and 8.35 (*J* 2 Hz) and 8.66 (*J* 11 Hz) (two d, 1 H, *cis* and *trans*); *m*/*z* 155 ($M^+$); m.p. 101—103 °C (lit.,[26] 102—103 °C), and 4-chlorolactanilide (**14**) (0.030 g); δ($^1$H) ($CDCl_3$) 1.50 (d, $CH_3$, *J* 7 Hz), 2.64 (s, OH), 4.34 (q, H, *J* 7 Hz), 7.18—7.59 (arom., 4 H), and 8.5 (s, NH); *m*/*z* 199 ($M^+$); m.p. 98—100 °C (lit.,[27] 100—101 °C).

*Isopropyl* N-(4-*Chlorophenyl*)*glycinate* (**15**).—A solution of α-chloroacetic acid (23.6 g) in anhydrous propan-2-ol (20 ml) and carbon tetrachloride (20 ml) was saturated with $BF_3$ and then refluxed for 1 h. The mixture was allowed to cool, poured into saturated aqueous $NaHCO_3$ (150 ml), and neutralized with solid $NaHCO_3$. The layers were separated and the aqueous phase was extracted with $CHCl_3$ (3 × 100 ml). Removal of the solvent at reduced pressure followed by distillation gave isopropyl α-chloroacetate (10 g), b.p. 73—74 °C at 35 mmHg. Isopropyl α-chloroacetate (3 g) and 4-chloroaniline (5.5 g) were mixed and kept at 95—100 °C for 1 h (oil-bath). After cooling, the solid formed was removed by filtration and the brown mixture was extracted with $CHCl_3$ (3 × 40 ml). After washing with 4M-HCl and then with water, the $CHCl_3$ was removed under reduced pressure to give a *solid* (1.70 g), which was recrystallized from light petroleum; m.p. 87—88 °C; δ($^1$H) ($CDCl_3$) 1.27 (d, 2 $CH_3$, *J* 6.2 Hz), 3.83 (s, $CH_2$), 5.11 (sept, CH, *J* 6.2 Hz), and 6.45—7.26 (arom., 4 H); *m*/*z* 227 ($M^+$) (Found: C, 57.9; H, 6.3; Cl, 15.6; N, 6.2. $C_{11}H_{14}ClNO_2$ requires C, 58.0; H, 6.2; Cl, 15.6; N, 6.15%).

*Isopropyl* N-(4-*Chlorophenyl*)*carbamate* (**12**).—Anhydrous propan-2-ol (3.65 ml) was added dropwise with stirring to 4-chlorophenyl isocyanate (13.2 g) warmed to the m.p. The exothermic reaction mixture was cooled in water and the mixture was set aside for 3 h. The white precipitate was recrystallized from light petroleum (b.p. 80—100 °C) to give *isopropyl* N-(4-*chlorophenyl*)*carbamate* (8 g), m.p. 101—102 °C; δ($^1$H) ($CDCl_3$) 1.28 (d, 2 $CH_3$, *J* 6.2 Hz), 5.01 (sept, CH, *J* 6.2 Hz), 6.72 (s, NH), and 7.28 (arom., 5 H); *m*/*z* 213 ($M^+$) (Found: C, 56.3; H, 5.6; Cl, 16.65; N, 6.5. $C_{10}H_{12}ClNO_2$ requires C, 56.2; H, 5.7; Cl, 16.6; N, 6.6%).

*Alkaline Hydrolysis of* 2-(4-*Chlorophenylamino*)-2-*methoxy*-1-*phenylethanone*.—The title compound[18] (0.130 g, 0.472 mmol) was dissolved in a 10:1 propan-2-ol–water (11 ml) and thermostatically maintained at 75 °C. To the solution, Pr$^i$OK in Pr$^i$OH (0.46M; 10 ml) was added. Samples (1 ml) were withdrawn at intervals, neutralized with solid carbon dioxide, diluted with equal amounts of diethyl ether, and analysed by g.l.c. for 4-chloroaniline content (99.5% after 2 min).

*Reduction of Nitrobenzene in the Presence of Acetophenone and a Substituted Anil* (**9**).—To a refluxing solution of potassium isopropoxide (0.72M) in propan-2-ol (20 ml), a solution of nitrobenzene (0.222 g, 0.0018 mol) and 2-(4-chlorophenylamino)-2-methoxy-1-phenylethanone (0.458 g, 0.0018 mol) in Pr$^i$OH (40 ml) was added. After 80 min the reaction was quenched with solid carbon dioxide, and the resulting mixture chromatographed on silica gel (eluant light petroleum ether–diethyl ether, 7:3). The fraction containing the 1,4-dioxobutene derivatives was further analysed by h.p.l.c., to give, after repeated injections, two major products identified by comparison with authentic samples as (**6**) and (**17**). The overall yield of (**6**) + (**17**) was 34% (from the first chromatography) in 1:2 ratio (from the h.p.l.c. analysis).

*Reaction of* 1-*Chloro*-4-*nitrosobenzene with* Pr$^i$OK *in* Pr$^i$OH.—A solution of 1-chloro-4-nitrosobenzene (0.072 g, $5.1 \times 10^{-4}$ mol) in propan-2-ol (12 ml) was added to a solution of Pr$^i$OK in Pr$^i$OH (0.79M; 5 ml) at 75 °C. The solution was quenched with solid $CO_2$ after 1 min and analysed by g.l.c. (tetracosane as internal standard); the yield of 4,4′-dichloroazoxybenzene was 92%.

*Reaction of* 4-*Chlorophenylhydroxylamine with* Pr$^i$OK *in* Pr$^i$OH.—A solution of 4-chlorophenylhydroxylamine (0.097 g, $6.78 \times 10^{-4}$ mol) in propan-2-ol (10 ml) was added to a solution of Pr$^i$OK in Pr$^i$OH (0.52M; 5 ml). The solution was quenched with solid $CO_2$ after 1 min, and analysed by g.l.c. (tetracosane as internal standard); the yield of 4,4′-dichloroazoxybenzene was 98%.

*Reaction of* 4,4′-*Dichloroazoxybenzene with* Pr$^i$OK *in* Pr$^i$OH.—A solution of 4,4′-dichloroazoxybenzene (0.362 g, 0.0014 mol) in propan-2-ol (20 ml) was added to a solution of Pr$^i$OK in Pr$^i$OH (0.46M; 20 ml) at 75 °C. Samples withdrawn at various times were quenched with solid $CO_2$ and analysed by g.l.c. (tetracosane as internal standard). The following yields of 4,4′-dichloroazobenzene were determined: 138 h, 16%; 338 h, 63%; 424 h, 84%. No trace of 4-chloroaniline was found by g.l.c. even after 50 days.

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