Preparation of Aromatic Aldehydes and Ketones from Diazonium Salts.

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A new method for preparing aromatic aldehydes and alkyl aryl ketones is described. Diazonium salts react with formaldoxime, acetaldoxime, propionaldoxime, and acetaldehyde semicarbazone severally, under carefully controlled conditions, to give arylated derivatives which can be hydrolysed to aromatic aldehydes or ketones.

o-Nitrobenzaldehyde can be conveniently prepared in this way from *o*-nitroaniline in 33% yield.

The reaction between diazonium salts and hydroxyiminoacetone according to the equation :

$$\mathrm{Ar{\cdot}N_2Cl + CH_3{\cdot}CO{\cdot}CH{:}N{\cdot}OH \xrightarrow{\text{Aq. NaOH}} CH_3{\cdot}CO{\cdot}CAr{:}N{\cdot}OH + N_2 + HCl}$$

discovered by Borsche (*Ber.*, 1907, **40**, 737) suggested that oximes of simpler constitution might behave similarly and so provide a new and convenient method for preparing aromatic aldehydes and ketones from amines :

$$\mathrm{Ar{\cdot}NH_2 \longrightarrow Ar{\cdot}N_2Cl \longrightarrow ArRC{:}N{\cdot}OH \longrightarrow Ar{\cdot}COR}$$

Apart from a brief reference to the reaction between diazonium salts and formaldoxime in I.G. Farbenindustrie research reports (FD. 2729/46, B.I.O.S./DOCS/1156/1121), no mention is made in the literature of the use of simple oximes such as formaldoxime, acetaldoxime, and the like in this type of reaction. On investigation, however, many diazonium salts were found to react readily with formaldoxime, acetaldoxime, and propionaldoxime in this sense. It was also shown that acetaldehyde semicarbazone is arylated by certain diazonium salts similarly.

The yields of arylated oximes, and hence of aldehydes and ketones, obtained by this method vary considerably according to the conditions. More favourable results were obtained with slightly acid (pH 5·5—6·0) than with the alkaline media employed by Borsche (*loc. cit.*). In acid conditions, however, a catalyst was generally essential, a cupric sulphate–sodium sulphite mixture (cf. Philipp, *Annalen*, 1936, **523**, 285) being satisfactory. The function of the sulphite in conjunction with cupric sulphate is not clear, but in some condensations it appears to accelerate the reaction more than does cupric sulphate alone, and to lead to rather higher yields. If too high a concentration of sulphite is used, however, the yield falls; 0·032 mol. of sulphite per mol. of diazonium salt was about the optimum.

The effect of varying the molecular ratio of cupric sulphate to diazonium salt was investigated for condensations of *p*-chloro- and *o*-nitro-benzenediazonium chlorides with formaldoxime. Other factors being equal, the yield of aldehyde obtained on subsequent hydrolysis was a maximum when 0·1—0·2 mol. of cupric sulphate per mol. of diazonium salt was present. Some typical results are given in Table 1. In some cases, similar yields were obtained with cuprous chloride, but use of nickel sulphate reduced them by about one-half. As diazonium chlorides frequently yield chlorohydrocarbons in the presence of copper salts, experiments were made in which chloride ions were completely excluded. Condensation of *p*-chlorobenzenediazonium sulphate with formaldoxime, however, gave only 43% of aldehyde, *o*-nitrobenzenediazonium sulphate only 21%.

TABLE 1. *Effect of varying the ratio, cupric sulphate : diazo-compound, on the yield of aldehyde obtained* (0·032 *mol. of sodium sulphite*).

R in $R{\cdot}C_6H_4{\cdot}N_2Cl$:	*p*-Cl				*o*-NO_2		
Proportion of cupric sulphate (mol.) ...	0·02	0·1	0·2	0·5	0·1	0·2	0·3
Yield of aldehyde (%)	48	60	57	35	20	33	25

The optimum pH range (5·5—6·0) for the reaction between diazonium salts and formaldoxime was conveniently obtained by working in aqueous media strongly buffered with sodium acetate. Lower yields resulted when sodium carbonate (pH 9·5—10·0), sodium hydrogen carbonate (pH 8·0—8·5) or calcium carbonate (pH 6·5—6·8) was used to regulate the pH.

In order to investigate the scope of the reaction, a number of aromatic aldehydes were prepared from amines, the diazonium salts being condensed with formaldoxime under the conditions described. The resulting arylaldoximes were converted into the corresponding aldehydes by acid hydrolysis or by treatment with boiling aqueous ferric ammonium sulphate (cf. Gabriel and Meyer, *Ber.*, 1881, **14**, 2336). The overall yields (amine to aldehyde) obtained are given in Table 2. The yields of arylated oximes were commonly higher than those yields of aldehydes, dehydration of some aldoximes to nitriles occurring as a side-reaction during hydrolysis with boiling dilute mineral acids (cf. Hantzsch and Lucas, *Ber.*, 1895, **28**, 746). Control experiments established that the yield of *p*-chlorobenzaldoxime from *p*-chlorobenzenediazonium chloride and formaldoxime under optimum conditions was *ca.* 75%, the yield of *p*-chlorobenzaldehyde being some 15% lower.

TABLE 2. *Yields of aldehydes obtained from amines.*

Aldehyde	Yield (%)	Aldehyde	Yield (%)
Benzaldehyde	40	*o*-Methoxybenzaldehyde	34
o-Tolualdehyde	46	*p*-Anisaldehyde	42
m-Tolualdehyde	41	2-Naphthaldehyde	25
p-Tolualdehyde	46	*p*-Ethoxycarbonylbenzaldehyde	20
o-Chlorobenzaldehyde	52	Pyridine-3-aldehyde	14
m-Chlorobenzaldehyde	50	Diphenyl-2-aldehyde	Very poor
p-Chlorobenzaldehyde	60	Diphenyl-4 : 4′-dialdehyde	
o-Nitrobenzaldehyde	33	Di-*p*-formylphenyl ether	
Salicylaldehyde	9		

The diazo–formaldoxime reaction failed to give the expected aldehyde when certain *o*-substituted diazonium chlorides were used. Thus, although satisfactory results were obtained with *o*-methyl-, *o*-halogeno-, and *o*-nitro-benzenediazonium salts, none of the required aldehyde was isolated when *o*-cyano- or *o*-ethoxycarbonyl groups were present.

The use of formaldoxime with an unsubstituted hydroxyl group appears to be essential to the reaction, for *O*-substituted derivatives, *e.g.*, *O*-methylformaldoxime, failed to give any simple product on treatment with *p*-chlorobenzenediazonium chloride.

Condensation of diazonium salts with acetaldoxime, acetaldehyde semicarbazone, or propionaldoxime and subsequent hydrolysis gave alkyl aryl ketones in somewhat lower yields. The diazo–acetaldoxime reaction is especially useful for the synthesis of certain substituted acetophenones which are otherwise difficult of access, such as 4-acetylphthalic acid which was conveniently prepared by use of methyl 4-aminophthalate.

In order to test the scope of the reaction, the ketones shown in Table 3 were prepared.

TABLE 3.

Ketone	Yield (%)	Ketone	Yield (%)
o-Chloroacetophenone	43	*p*-Diacetylbenzene	33
p-Chloroacetophenone	35—45	1 : 3-Diacetyl-4-chlorobenzene	15
p-Chloropropiophenone	30	4-Acetylphthalic acid	27
m-Diacetylbenzene	27		

Synthesis of arylated oximes by the diazo-reaction was often accompanied by formation of by-products arising by replacement of the diazo-group by hydrogen. This was very noticeable when preparing 1 : 3-diacetyl-4-chlorobenzene and pyridine-3-aldehyde.

No *p*-chlorobenzophenone oxime was isolated from *p*-chlorobenzendiazonium chloride and benzaldoxime, indicating that further reaction of diazo-compound with the aromatic aldoxime cannot be responsible for limitation of yield in the reaction with formaldoxime.

The method for preparing aldehydes and ketones described above succeeds only to a limited extent with difunctional compounds. Condensation of tetrazotised *p*-phenylenediamine with acetaldoxime and subsequent hydrolysis gave less than 10% of *p*-diacetylbenzene, while attempts to prepare aromatic diketones from diazonium salts and dialdoximes such as glyoxime and succindialdoxime were unsuccessful.

EXPERIMENTAL

Preparation of Aliphatic Aldoximes.—Formaldoxime. As this substance polymerises very readily (Scholl, *Ber.*, 1891, **24**, 573; Dunstan and Bossi, *J.*, 1898, **73**, 353), it was prepared and used as required in dilute aqueous solution without isolation. A 10% solution for use in conjunction with 0·25 mole of diazonium salt was made by heating paraformaldehyde (11·5 g.) with hydroxylamine hydrochloride (26·3 g.) in water (170 c.c.) until a clear solution was obtained, adding hydrated sodium acetate (51 g.), and boiling gently under reflux for 15 min. In cases where the diazonium sulphate was used in the subsequent condensation, hydroxylamine hydrochloride was replaced by an equivalent amount of the sulphate.

Acetaldoxime was prepared by Wieland's method (*Ber.*, 1907, **40**, 1677).

Propionaldoxime. Hydroxylamine hydrochloride (87·5 g.) in water (85 c.c.) was treated with sodium carbonate (69 g.) in water (250 c.c.), and the solution was kept at 5—10° while propaldehyde (72·5 g.) was added gradually. After 2 hr., the oxime was extracted with ether (400 c.c.) and dried ($MgSO_4$). Fractional distillation through a 4" gauze-packed column yielded propionaldoxime (70 g., 77%), b. p. 130—132°.

General Procedure for Preparing Aldehydes from Amines.—(i) p-*Chlorobenzaldehyde from* p-*chloroaniline.* A solution of *p*-chlorobenzenediazonium chloride, prepared from *p*-chloroaniline (32 g.), hydrochloric acid (57 c.c.; *d* 1·18), water (50 c.c.), and ice (100 g.) by treatment with sodium nitrite (17·5 g.) in water (25 c.c.) at 0—5°, was made neutral towards Congo-red by addition of hydrated sodium acetate (22 g.) in water (35 c.c.). The neutral diazonium solution was introduced below the surface of 10% aqueous formaldoxime, to which had been added copper sulphate (6·25 g.), sodium sulphite (1·0 g.; anhyd.), and further sodium acetate (165 g.) in water (180 c.c.), at 10—15° with stirring. Stirring was then continued for 1 hr. The mixture (*ca.* 1000 c.c.) was rendered acid to Congo-red with hydrochloric acid and, after addition of a further quantity (230 c.c.; *d* 1·18) of this acid, was boiled under reflux for 2 hr. After distillation of the *p*-chlorobenzaldehyde in steam, the distillate (1000—1500 c.c.) was neutralised with sodium hydrogen carbonate, and the aldehyde was extracted with ether (750 c.c.). The crude product obtained by distilling off the ether was shaken with aqueous sodium hydrogen sulphite (90 c.c.; 40%) at 60°, water (275 c.c.) was added, and non-aldehydic material was removed by extraction with ether (90 c.c.). After regeneration from the aqueous layer by boiling sulphuric acid (45 c.c.; *d* 1·84) and water (45 c.c.) for 0·5 hr., the aldehyde was removed in ether (300 c.c.).

The ethereal solution was dried ($MgSO_4$) and evaporated, and the residue was distilled, giving *p*-chlorobenzaldehyde (21 g., 60%), m. p. 48°, b. p. 98°/14 mm. The semicarbazone had m. p. 233° (Found : N, 21·75; Cl, 18·0. Calc. for $C_8H_8ON_3Cl$: N, 21·25; Cl, 17·95%). To estimate the losses occurring during purification, *p*-chlorobenzaldoxime (19·45 g.) was boiled under reflux for 2 hr. with 2N-hydrochloric acid. The product of hydrolysis was distilled in steam and further purified as previously, giving *p*-chlorobenzaldehyde (13·75 g., 78%).

(ii) o-*Nitrobenzaldehyde from* o-*nitroaniline*. A solution of *o*-nitrobenzenediazonium chloride, prepared from *o*-nitroaniline (34·5 g.), hydrochloric acid (57 c.c.; *d* 1·18), water (50 c.c.), and ice (100 g.) by treatment with sodium nitrite (17·5 g.) in water (25 c.c.) at 0—2°, was made neutral towards Congo-red by addition of hydrated sodium acetate (22 g.) in water (35 c.c.). The neutral diazonium solution was introduced below the surface of a 10% aqueous formaldoxime solution, to which had been added copper sulphate (12·5 g.), sodium sulphite (1·0 g.; anhyd.) and further sodium acetate (165 g.) in water (180 c.c.), at 10—15° with stirring. Stirring was then continued for 1 hr. The mixture was rendered acid to Congo-red with hydrochloric acid, and the liquor was decanted from the crude, tarry oxime which was then boiled under reflux with ferric ammonium sulphate (300 g.) in water (500 c.c.) for 1 hr. The crude aldehyde (20 g.), which was isolated by steam-distillation, extraction of the distillate (*ca.* 1500 c.c.) with ether (750 c.c.), and subsequent distillation of the ether, was shaken with aqueous sodium hydrogen sulphite (50 c.c.; 40%), and water (100 c.c.) at 50° was added. After removal of non-aldehydic material by extraction of the cooled solution with ether (80 c.c.), the aldehyde was regenerated by treatment of the aqueous solution with sufficient 10N-sodium hydroxide to render it faintly alkaline to Clayton-yellow. The product was then removed in ether (300 c.c.) and dried ($MgSO_4$) and the solvent removed by distillation, finally under reduced pressure. The residue consisted of almost pure *o*-nitrobenzaldehyde (12·3 g., 33%), m. p. 43—44°, characterised by formation of indigo with warm acetone and dilute aqueous sodium hydroxide.

(iii) *Other aromatic aldehydes*. The remaining aldehydes listed in Table 2 were prepared similarly, with copper sulphate (12·5 g.) and sodium sulphite (1·0 g.; anhyd.) as catalyst for 0·25-mole preparations. The aldehydes were characterised as the derivatives shown in Table 4, identities being established either by mixed m. p., or by analysis where no authentic sample was available. *p*-Ethoxycarbonylbenzaldehyde was prepared from ethyl *p*-aminobenzoate as described for *o*-nitrobenzaldehyde. After the oxime had been boiled with aqueous ferric ammonium sulphate, however, the aldehyde was extracted with chloroform. The crude aldehyde was purified through the bisulphite compound as with *o*-nitrobenzaldehyde. Subsequent distillation under reduced pressure gave *p*-ethoxycarbonylbenzaldehyde as a liquid, b. p. 142—144°/15 mm.

TABLE 4. *Derivatives prepared for characterisation.*

Aldehyde, or R in $R\cdot C_6H_4\cdot CHO$	Derivative	M. p. of deriv.	Found (%) C	Found (%) H	Found (%) N	Required (%) C	Required (%) H	Required (%) N
H	Phenylhydrazone	158°	—	—	—	—	—	—
o-Me	Phenylhydrazone, $C_{14}H_{14}N_2$	105—106	79·5	6·9	12·9	80·0	6·65	13·3
m-Me	Semicarbazone, $C_9H_{11}ON_3$	216—217	—	—	23·75	—	—	23·7
p-Me	Phenylhydrazone, $C_{14}H_{14}N_2$	114	—	—	13·0	—	—	13·3
o-Cl	α-*Oxime* *	74	—	—	—	—	—	—
m-Cl	Phenylhydrazone, $C_{13}H_{11}N_2Cl$	134	—	—	11·9	—	—	12·15
p-MeO	Semicarbazone	210—211	—	—	—	—	—	—
p-CO_2Et	Phenylhydrazone, $C_{16}H_{16}O_2N_2$	142—143	71·95	6·0	10·6	71·65	5·95	10·45
2-Naphthaldehyde	Phenylhydrazone	206	—	—	—	—	—	—
Pyridine-3-aldehyde	Phenylhydrazone, $C_{12}H_{11}N_3$	157—158	72·7	5·65	21·65	73·1	5·6	21·3
Diphenyl-2-aldehyde	Semicarbazone, $C_{14}H_{13}ON_3$	208—209	70·2	5·2	17·9	70·3	5·45	17·55
Di-*p*-formylphenyl ether	Dianil, $C_{26}H_{20}ON_2$	155	82·85	5·45	7·4	83·0	5·3	7·45

* Found : Cl, 22·85. C_7H_6ONCl requires Cl, 22·85%.

Pyridine-3-*aldehyde*.—A diazonium solution, prepared from 3-aminopyridine (23·5 g.), hydrochloric acid (68 c.c.; *d* 1·18), sodium nitrite (17·5 g.), and water (75 c.c.), was condensed with 10% aqueous formaldoxime in the presence of an excess of sodium acetate in the usual manner. The mixture was then made slightly acid to Congo-red with hydrochloric acid, a solution of ferric chloride (150 g.; anhyd.) in water (150 c.c.) was added and the solution was boiled under reflux for 1 hr. Sodium carbonate was then added in slight excess and the aldehyde was distilled in steam. The distillate (*ca.* 1500 c.c.) was treated with hydrochloric acid (50 c.c.; *d* 1·18), after which it was concentrated to 30 c.c. under reduced pressure. The concentrated solution was saturated with potassium carbonate, the aldehyde was extracted with chloroform (150 c.c.), and the chloroform solution dried (K_2CO_3). After distillation of the chloroform, pyridine-3-aldehyde (3·6 g., 14%) was distilled under reduced pressure, having b. p. 95—100°/16 mm. (Harries and Lenárt, *Annalen*, 1915, **410**, 115 give b. p. 95—97°/15 mm.).

*Diphenyl-2-aldehyde and Di-*p*-formylphenyl Ether.*—Prepared in the usual manner from 2-aminodiphenyl and 4 : 4′-diaminodiphenyl ether respectively, these aldehydes were obtained in poor yields in the form of derivatives. Likewise, from benzidine was obtained a very poor yield of a substance, m. p. 140°. Ullmann and Loewenthal (*Annalen*, 1904, **332**, 76) give m. p. 145° for diphenyl-4 : 4′-dialdehyde.

Preparation of Ketones from Amines.—p-*Chloroacetophenone.* (*a*) A diazonium solution, prepared from *p*-chloroaniline (32 g.) and neutralised with sodium acetate as previously described, was condensed with a solution of acetaldoxime (22·5 g.) in water (200 c.c.) containing copper sulphate (12·5 g.), sodium sulphite (1·0 g.; anhyd.), and sodium acetate (165 g.) at 10—15° as described for aldehydes. After acidification (Congo-red) with hydrochloric acid and addition of a further quantity (230 c.c.; *d* 1·18), the mixture was boiled under reflux for 3 hr. and the ketone was distilled in steam. After extraction of the neutralised distillate with ether (750 c.c.) and recovery, the ketone was purified through its derivative with Girard T reagent. Regeneration, followed by distillation under reduced pressure, gave *p*-chloroacetophenone (13·75 g., 36%), b. p. 101°/9 mm. The semicarbazone had m. p. 202—203° (Found: N, 19·8. Calc. for $C_9H_{10}ON_3Cl$: N, 19·85%).

Purification through the derivative with Girard T reagent may in other cases often be replaced with advantage by fractional distillation through a metal-packed column. In this manner, *o*-chloroacetophenone, b. p. 104—105°/15 mm., was prepared in 43% yield from *o*-chloroaniline.

(*b*) A hot solution of acetaldehyde semicarbazone (38 g.) in water (200 c.c.) was poured into a solution of sodium acetate (136 g.) in water (140 c.c.) with stirring. After addition of copper sulphate (12·5 g.) and sodium sulphite (1·0 g.; anhyd.) and cooling to 10°, a diazonium solution, prepared from *p*-chloroaniline (32 g.) and neutralised by sodium acetate (51 g.) in water (75 c.c.), was introduced below the surface at 10—20°. When the vigorous evolution of nitrogen had subsided, *p*-chloroacetophenone semicarbazone, m. p. 187—189° was isolated by filtration. After one recrystallisation from ethanol, it (20·6 g., 40%) had m. p. 196°. By hydrolysis of the crude product with boiling 2N-hydrochloric acid and purification as above, *p*-chloroacetophenone was obtained in 40—45% overall yield.

p-*Diacetylbenzene.*—(*a*) *p*-Aminoacetophenone (33·8 g.) was diazotised at 0° in sulphuric acid (17 c.c.; *d* 1·84) and water (200 c.c.) by addition of sodium nitrite (17·5 g.) in water (25 c.c.). The diazonium solution, after neutralisation with sodium acetate (22 g.) in water (35 c.c.), was condensed with acetaldoxime (22·5 g.) in water (180 c.c.) containing copper sulphate (12·5 g.), sodium sulphite (1·0 g.; anhyd.), and sodium acetate (165 g.) at 10—15°. The crude, tarry oxime was separated and boiled under reflux with 2N-sulphuric acid (500 c.c.) for 2 hr. The crude *p*-diacetylbenzene, after extraction with chloroform (600 c.c.) and recovery, was distilled in superheated (170°) steam. The product was removed from the distillate by chloroform-extraction and was, after recovery, purified by crystallisation from light petroleum (b. p. 100—120°), giving *p*-diacetylbenzene (13·5 g., 33%), m. p. 106°, raised to 113° by one further crystallisation (Ingle, *Ber.*, 1894, **27**, 2527, gives m. p. 114°).

(*b*) *p*-Phenylenediamine (13·5 g.) was added gradually to a mixture of sulphuric acid (45 g., 100%), water (22 c.c.), and nitrososulphuric acid (66 g., 50% solution in sulphuric acid), the temperature being kept at 20—25°. The tetrazonium salt was precipitated when the solution was poured on ice (75 g.) and the whole cooled to −15° to −20°. After isolation by filtration, the salt was suspended in ice-water and the suspension was made neutral to Congo-red by sodium acetate, then added to a solution of acetaldoxime (22·5 g.) in water (140 c.c.) containing sodium acetate (136 g.), copper sulphate (12·5 g.), and sodium sulphite (1·0 g.; anhyd.) during 0·5 hr. at 10—15°. After hydrolysis of the crude oxime with boiling 2N-hydrochloric acid, extraction with chloroform, and recovery, the product was distilled under reduced pressure. The slightly moist crystals (2·1 g.) thus obtained had m. p. and mixed m. p. 113—114° after recrystallisation from light petroleum (b. p. 100—120°).

m-Diacetylbenzene was prepared from *m*-aminoacetophenone by the method (*a*). Its dioxime had m. p. 206° (Ruggli and Staub, *Helv. Chim. Acta*, 1936, **19**, 972, give m. p. 204°) (Found: C, 62·3; H, 5·9; N, 14·2. Calc. for $C_{10}H_{12}O_2N_2$: C, 62·5; H, 6·25; N, 14·6%).

1 : 3-*Diacetyl*-4-*chlorobenzene* was similarly obtained in rather poor yield from 3-amino-4-chloroacetophenone. Recrystallised from *cyclo*hexane, it had m. p. 54° (Found: C, 60·7; H, 4·5; Cl, 17·95. $C_{10}H_9O_2Cl$ requires C, 61·05; H, 4·6; Cl, 18·05%). A considerable amount of *p*-chloroacetophenone was obtained as by-product.

4-*Acetylphthalic Acid*.—A diazonium solution (300 c.c.) prepared from dimethyl 4-aminophthalate (52·75 g.) and neutralised by addition of sodium acetate was condensed with an aqueous solution of acetaldoxime (22·5 g.) containing copper sulphate (12·5 g.), sodium sulphite (1·0 g.; anhyd.), and excess of sodium acetate in the usual manner. The liquor was decanted from the crude oxime which was boiled under reflux for 2 hr. with ferric ammonium sulphate (300 g.) in water (500 c.c.). The crude keto-ester was extracted with chloroform (750 c.c.) and, after drying, the product was recovered and fractionally distilled; the fraction, b. p. 180—200°/15 mm., was collected. The keto-ester was hydrolysed for 4 hr. with boiling 11N-sodium hydroxide (50 c.c.), water (50 c.c.), and ethanol (50 c.c.). After removal of the ethanol and addition of water (50 c.c.), the solution was treated with hydrochloric acid (*d* 1·18) until only a faint alkalinity remained, then clarified with carbon, and further hydrochloric acid was added to give a strong acidity towards Congo-red. 4-Acetylphthalic acid (13·1 g.) separated at 0°. A further 0·9 g. of product was obtained by evaporating the filtrate to dryness and extracting the residue with boiling methanol. The crude product (14 g., 27%) had m. p. 196—200° (decomp.), raised to 210° (decomp.) by crystallisation from acetic acid (Found: C, 57·3; H, 3·95. Calc. for $C_{10}H_8O_5$: C, 57·7; H, 3·85%). [Mayer, Stark, and Schön, *Ber.*, 1932, **65**, 1336, give m. p. 210—211° (decomp.).]

p-Chloropropiophenone, prepared from *p*-chloroaniline as described for *p*-chloroacetophenone, propaldoxime being used in place of acetaldoxime, melted at 35° and formed a *semicarbazone*, m. p. 178° (Found: N, 18·85. $C_{10}H_{12}ON_3Cl$ requires N, 18·6%) (Collet, *Compt. rend.*, 1898, **126**, 1577, gives m. p. 35—36° for the ketone).

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