47. *The Preparation of the Mononitrobenzaldehydes.*

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o- and *p*-Nitrobenzaldehydes have been prepared by the oxidation of the corresponding nitrocinnamic acids. Nitration of benzylidene diacetate in acetic acid or anhydride solution with copper nitrate yields *p*-nitrobenzylidene diacetate, whilst nitration of the diacetate in acetic anhydride solution with nitric acid gives *o*-nitrobenzylidene diacetate. Nitration of acetophenone in acetic acid solution with copper nitrate yields *p*-nitrobenzylidene diacetate, and the mechanism of this reaction has been elucidated. Other metal nitrates are less effective than copper nitrate as nitrating agents for benzylidene diacetate. Hydrolysis of nitrobenzylidene diacetates is satisfactorily achieved by the use of suspensions of magnesium hydroxide.

Mononitrobenzaldehydes were required for the preparation of substituted benzaldehydes and of substituted chalcones; *m*-nitrobenzaldehyde is readily prepared by the direct nitration of benzaldehyde but the preparation of the *o*- and *p*-isomers presents some difficulties. Although some *o*-nitrobenzaldehyde is produced in the direct nitration of benzaldehyde (Friedländer, *Ber.*, 1881, **14**, 2803) it cannot easily be isolated from the reaction product. The preparation of *o*- and *p*-nitrobenzaldehydes has been investigated by three methods : (*a*) oxidation of the nitrotoluenes by the chromic acid–acetic acid–anhydride method, (*b*) oxidation of the nitrocinnamic acids, and (*c*) nitration of benzaldehyde and of its diacetate.

Oxidation of nitrotoluenes by the methods of *Org. Synth.*, Coll. Vol. II, p. 441, and Vol. **24**,

p. 75, gave the required products, but from *o*-nitrotoluene large amounts of tar were always obtained and the yield of aldehyde was low. In view of this and of the considerable risk of explosion attendant on the use of chromic acid in acetic anhydride (Tuey, *Chem. and Ind.*, **1948**, 766), alternative methods of preparation were investigated.

Acetyl or benzoyl nitrate has been used for selective *ortho*-nitration of organic compounds but their use is limited by the risk of explosion (Pictet and Khotinsky, *Ber.*, 1907, **40**, 1163). Menke (*Rec. Trav. chim.*, 1925, **44**, 141, 269) has shown that acetic anhydride and copper, nickel, iron, or cobalt nitrate effect *ortho*-nitration in the same way as acetyl nitrate, but without the danger of explosion. Bacharach (*J. Amer. Chem. Soc.*, 1927, **49**, 1522) has confirmed this and shown that lithium nitrate yields mainly *p*-nitro-compounds. Nitration of cinnamic acid in acetic anhydride solution by means of hydrated copper nitrate failed to give *o*- and *p*-nitrocinnamic acids, which were therefore prepared by nitration of cinnamic acid or of its ethyl ester in nitric acid alone, or preferably in sulphuric acid, the acids being separated by utilising the low solubility of ethyl *p*-nitrocinnamate in ethanol (Drewson, *Annalen*, 1882, **212**, 150). Nitration of benzylidene diacetate, prepared from benzaldehyde by the method of Wegschneider and Späth (*Monatsh.*, 1909, **30**, 840), in acetic anhydride solution by means of hydrated copper nitrate yielded *p*-nitrobenzylidene diacetate in 52% yield, but the reaction was difficult to control an dnitration was therefore effected (in 79% yield), using acetic acid as solvent. Careful purification of benzaldehyde was essential for maximum yields, even redistilled samples of the aldehyde reacted violently with acetic anhydride with excessive evolution of heat. Attempts to moderate the reaction between impure benzaldehyde and acetic anhydride by the addition of acetic acid were not successful and led to incomplete formation of diacetate. Nitration of benzylidene diacetate, formed *in situ*, from pure benzaldehyde has also been achieved by this method. Commercial samples of benzaldehyde have been nitrated in acetic acid solution with copper nitrate to give *p*-nitrobenzylidene diacetate in 12% yield, although it has not proved possible to prepare benzylidene diacetate from benzaldehyde and acetic acid by a method analogous to that using acetic anhydride (cf. Wegschneider and Späth, *loc. cit.*). Other metal nitrates were found to be less useful than copper nitrate in these reactions, lead nitrate failing to react and sodium nitrate causing deflagration.

Baker and Ingold (*J.*, 1930, 431) showed that the nitration of benzaldehyde with acetic anhydride and nitric acid gave 62·6% of *o*–*p*- and 37·4% of *m*-nitration, the reaction proceeding *via* the diacetate (*p*-nitrobenzylidene diacetate was isolated from the reaction mixture). The change in position of nitration with different experimental conditions has been summarised by Baker and Moffitt (*J.*, 1931, 316). Nitration of benzylidene diacetate, formed *in situ*, in acetic anhydride solution with nitric acid was vigorous and led to *o*-nitrobenzylidene diacetate (43%) and *p*-nitrobenzoic acid (26%), whilst nitration at low temperatures gave *o*-nitrobenzaldehyde in 41% yield. A mixture of nitric and sulphuric acids, at low temperatures, gave *o*- and *m*-nitrobenzaldehyde in 33% and 43% yield, respectively. Excess of sulphuric acid led to the hydrolysis of the diacetate and formation of *m*-nitrobenzaldehyde as the main product. This *ortho*-nitrating effect of nitric acid–acetic anhydride has previously been reported by Witt and Uterman (*Ber.*, 1906, **39**, 3903) and the preparation of *o*-nitrocinnamic aldehyde in 36% yield by Mills and Evans (*J.*, 1920, 1037) is a further example for *o*-nitro-aldehydes. Nitric acid, in contrast to copper nitrate, fails to nitrate benzylidene diacetate in acetic acid solution.

Ketones do not form diacetates, but acetophenone undergoes oxidation and nitration to *p*-nitrobenzylidene diacetate in 40% yield when treated with acetic acid and copper nitrate. The mechanism of this reaction has been found to involve oxidation of the acetophenone to benzoylformic acid, loss of carbon dioxide to give benzaldehyde, formation of benzylidene diacetate, and nitration. Benzoylformic acid yields benzylidene diacetate on heating with acetic anhydride, and *p*-nitrobenzylidene diacetate on nitration with acetic anhydride or acetic acid and copper nitrate.

The results of these nitrations are summarised in the table.

Some difficulty was encountered in the hydrolysis of *p*-nitrobenzylidene diacetate by the method of *Org. Synth.*, Coll. Vol. II, p. 441. It has been found possible to hydrolyse nitrobenzylidene diacetates in high yields by means of magnesium hydroxide suspensions. Alkaline hydrolysis of aldehyde diacetates is not normally feasible as the high concentration of alkali which must be present initially to ensure complete hydrolysis leads to condensation of the aldehyde formed in the early stages of the hydrolysis. It has been found that if the hydrolysis of nitrobenzylidene diacetates is carried out at 100° with increasing concentrations of sodium hydroxide, the Cannizzaro reaction becomes appreciable when the alkali concentration reaches about 0·01N. (pH about 12 at 24°). Condensation could be avoided by adding the alkali at such a rate that the critical pH is never reached and this can be conveniently achieved by hydrolysing these diacetates with magnesium hydroxide suspensions, since the pH of its pure aqueous suspension is about 10·4 (at 24°).

Nitration of cinnamic acid, ethyl cinnamate, benzylidene diacetate and acetophenone.

Reactants.		Conditions.	Products.
1. Cinnamic acid :	HNO_3	3 hrs., <10°	49% *o*- + 39% *p*-nitrocinnamic acid
2. ,,	HNO_3–H_2SO_4	4 hrs., <20°	50% *o*- + 39% *p*-nitrocinnamic acid
3. ,,	HNO_3–AcOH	4 hrs., <20°	Unchanged
4. Ethyl cinnamate :	HNO_3	4 hrs., <20°	56% *o*- + 27% *p*-nitrocinnamic acid
5. ,,	HNO_3–H_2SO_4	4 hrs., <20°	43% *o*- + 42% *p*-nitrocinnamic acid
6. Cinnamic acid :	Ac_2O–$Cu(NO_3)_2$	Uncontrolled	68% *o*- + 15% *p*-nitrobenzoic acid
7. Benzylidene diacetate :	Ac_2O–$Cu(NO_3)_2$	,,	52% *p*-nitrobenzylidene diacetate
8. ,, ,,	AcOH–$Cu(NO_3)_2$	5 hrs., reflux	79% ,, ,,
9. Benzaldehyde :	AcOH–$Cu(NO_3)_2$	,,	79% ,, ,,
10. Benzylidene diacetate :	Ac_2O–HNO_3	118°	43% *o*-nitrobenzaldehyde + 26% *p*-nitrobenzoic acid
11. ,, ,,	,,	4 hrs., <20°	41% *o*-nitrobenzaldehyde
12. ,, ,,	AcOH–HNO_3	Uncontrolled	96% benzoic acid
13. ,, ,,	HNO_3–H_2SO_4	3 hrs., <15°	33% *o*- + 43% *m*-nitrobenzaldehyde
14. Benzaldehyde :	HNO_3–H_2SO_4	4 hrs., <15°	80% *m*- + little *o*-nitrobenzaldehyde
15. Acetophenone :	AcOH–$Cu(NO_3)_2$	5 hrs., reflux	42% *p*-nitrobenzylidene diacetate

EXPERIMENTAL.

(All m p s are uncorrected.)

1. *Nitration of Cinnamic Acid with Nitric Acid Alone.*—Finely powdered cinnamic acid (30 g.) was added during 1 hour to vigorously stirred nitric acid (150 ml.; *d* 1·52) and the mixture stirred for a further 2 hours, the temperature being maintained below 10° by external cooling. The resulting paste was stirred into water (2·5 l.) and filtered, and the product washed free from mineral acid with cold water.

The air-dried product (38 g.) was suspended in ethanol (400 ml.), sulphuric acid (15 ml.; *d* 1·84) added, and the whole refluxed until dissolution was complete. The resulting solution was cooled to 0° and kept overnight in the refrigerator. The ethyl *p*-nitrocinnamate which had separated was filtered off and washed with cold ethanol (50 ml.), the filtrate and washings being combined. The ester, after recrystallisation from ethanol, was boiled with ethanol (200 ml.) and sulphuric acid [50 ml. (*d* 1·84) +350 ml. of water] for 8 hours. After addition of water (500 ml.) the precipitated acid was filtered off, and purified by dissolution in sodium carbonate solution, filtration, and reprecipitation by hydrochloric acid. Recrystallisation of the product from ethanol gave *p*-nitrocinnamic acid (15·2 g., 39%), m. p. 286° (Müller, *Annalen*, 1882, **212**, 126, gives m. p. 286°).

Hydrolysis of the filtrate was achieved by the addition of water (500 ml.) and refluxing for 12 hours. The *o*-nitrocinnamic acid was precipitated by pouring the mixture into water and purified as in the case of the *p*-nitro-acid, to give an acid (19·2 g., 49%), m. p. 240° (Müller, *loc. cit.*, gives m. p. 240°).

2. *Nitration of Cinnamic Acid with Nitric and Sulphuric Acids.*—Cinnamic acid (30 g.), dissolved in sulphuric acid (250 ml.; *d* 1·84) was nitrated by the addition of nitric acid (11 ml.; *d* 1·52) during an hour, and stirring for a further 3 hours, the temperature being kept below 20°. Isolation of the mixed acids by precipitation with water, filtration, and washing gave a product which was separated as before to give *p*- (15·5 g., 39%; m. p. 286°) and *o*-nitrocinnamic acid (19·5 g., 50%; m. p. 240°).

3. *Nitration of Cinnamic Acid with Acetic and Nitric Acids.*—Addition of nitric acid [11 ml. (*d* 1·52) or 50 ml. (*d* 1·52)] to cinnamic acid (30 g.) in glacial acetic acid (250 ml.) afforded only unchanged cinnamic acid.

4. *Nitration of Ethyl Cinnamate with Nitric Acid Alone.*—Ethyl cinnamate (50 g.) was nitrated by adding it slowly to cooled nitric acid (250 ml.; *d* 1·52) and stirring for a further 3 hours, at <20°. The mixed nitro-esters were isolated by pouring the mixture into water (2·5 l.), filtration, and washing. Separation was achieved by dissolving the mixture in ethanol (500 ml.), cooling to 0°, and allowing the *p*-ester to separate overnight in the refrigerator. Hydrolysis by the methods already described and purification of the acids gave *p*- (15 g., 27%; m. p. 286°) and *o*-nitrocinnamic acid (31 g., 56%; m. p. 240°).

5. *Nitration of Ethyl Cinnamate with Sulphuric and Nitric Acids.*—Nitration of ethyl cinnamate (50 g.) dissolved in sulphuric acid (150 ml.; *d* 1·84) as in (2) above, using nitric acid (20 ml.; *d* 1·52), gave *p*- (23 g., 42%; m. p. 286°) and *o*-nitrocinnamic acid (24 g., 43%; m. p. 240°).

6. *Nitration of Cinnamic Acid with Acetic Anhydride and Copper Nitrate.*—Nitration in acetic anhydride with hydrated copper nitrate, warming to 65—70°, and allowing the reaction to proceed spontaneously afforded only *o*- and *p*-nitrobenzoic acids. Under these experimental conditions *o*- and *p*-nitrocinnamic acids are oxidised to the corresponding nitrobenzoic acids. At 20° unchanged cinnamic acid and only 10% of *o*- and *p*-nitrocinnamic acid were obtained.

Oxidation of nitrocinnamic acids to nitrobenzaldehydes. *o*-Nitrocinnamic acid (10 g.) was dissolved in a solution of sodium carbonate (6 g.) in water (750 ml.), benzene (200 ml.) added, and the mixture cooled to 10° by addition of ice and external cooling. Oxidation was achieved by the addition of potassium permanganate sôlution (250 ml.; 6%) with vigorous stirring to ensure thorough mixing, the temperature being kept below 10° by the addition of ice. Stirring was continued for a further hour, the product filtered, and the manganese dioxide washed with benzene (50 ml.). The benzene layer was separated and the aqueous layer extracted with benzene (2 × 50 ml.) which was added to the main extract. After being washed with water, the benzene extract was dried, and the benzene distilled off. The residue was dissolved in toluene (10 ml.), light petroleum (70 ml.; b. p. 40—60°) added, and the solution cooled to 0°, to give *o*-nitrobenzaldehyde (5 g., 64%), m. p. and mixed m. p. 43° (oxime, m. p. 103°; acetone condensed with it in presence of sodium hydroxide to give indigo, soluble in chloroform). Extraction of the acidified aqueous layer with ether and removal of the ether gave *o*-nitrobenzoic acid, (1·7 g., 20%), m. p. and mixed m. p. 146°.

Oxidation of *p*-nitrocinnamic acid under identical conditions gave *p*-nitrobenzaldehyde (5·8 g., 74%), m. p. and mixed m. p. 106° (oxime, m. p. 132°), and *p*-nitrobenzoic acid (1·3 g., 15%), m. p. and mixed m. p. 237°.

7. *Nitration of Benzylidene Diacetate with Acetic Anhydride and Copper Nitrate.*—Benzaldehyde (12 g.) and acetic anhydride (60 g.) were stirred together, and 5 drops of sulphuric acid (*d* 1·84) added to catalyse the formation of the diacetate. After a further 15 minutes' stirring to complete the reaction, hydrated copper nitrate (30 g.) was added, the mixture warmed to 65°, and the vigorous reaction allowed to proceed spontaneously (see note below). When the temperature had fallen to 80°, water (500 ml.) and sulphuric acid [25 ml. (*d* 1·84) + 4 parts water] were added and the mixture set aside overnight. The precipitated *p*-nitrobenzylidene diacetate was filtered off, washed free from acid with water, and recrystallised from aqueous ethanol to give *p*-nitrobenzylidene diacetate (15 g., 52%), m. p. and mixed m. p. 122°. Hydrolysis of the diacetate is described later. Note: addition of copper nitrate to acetic anhydride may lead to an exothermic reaction.

Attempts to nitrate benzylidene diacetate in acetic anhydride solution with hydrated copper nitrate at <20° during 7 hours yielded only unchanged diacetate. Benzaldehyde is not nitrated by copper nitrate in acetic acid at <20°.

8. *Nitration of Benzylidene Diacetate with Acetic Acid and Copper Nitrate.*—Benzaldehyde (106 g.) was converted by acetic anhydride (250 ml.) and sulphuric acid (5 ml.; *d* 1·84) into the diacetate, which was isolated by precipitation with water. The separated diacetate was drained at the pump, dissolved in acetic acid (1 l.), and nitrated by refluxing it for 5 hours with hydrated copper nitrate (300 g.). The product was isolated as before, and the *p*-nitrobenzylidene diacetate (200 g., 79%) was hydrolysed by the method of *Org. Synth.*, Coll. Vol. II, p. 441, to give *p*-nitrobenzaldehyde (110 g., 73% based on the benzaldehyde taken), m. p. and mixed m. p. 106° (phenylhydrazone m. p. 156°; oxidation with alkaline permanganate gave *p*-nitrobenzoic acid, m. p. and mixed m. p. 237°).

Nitration has also been effected to give similar yields of diacetate and aldehyde by adding the acetic acid and copper nitrate to the acetic anhydride solution of the aldehyde without isolating the diacetate, and this is the most satisfactory method.

9. *Nitration of Benzaldehyde with Acetic Acid and Copper Nitrate, without Intermediate Diacetate Formation.*—Benzaldehyde (25 g.) was refluxed with glacial acetic acid (200 ml.) and hydrated copper nitrate (60 g.) for 5 hours, and the product poured into water, made alkaline with aqueous ammonia and then just acid to litmus with dilute sulphuric acid. The precipitate, on recrystallisation from aqueous ethanol, gave *p*-nitrobenzylidene diacetate (7 g., 12%), m. p. and mixed m. p. 122°.

Reaction between Benzaldehyde and Acetic Acid.—Benzaldehyde (12 g.), glacial acetic acid (60 g.), and sulphuric acid (0·5 ml.; *d* 1·84) were stirred together for periods up to 3 hours at room temperature or up to 30 minutes at the b. p. of the mixture. In no case was benzylidene diacetate obtained on dilution with water, benzaldehyde separating in all cases; there was no evidence of appreciable reaction from time–temperature measurements, typical results being :—

	Temperature.	
Time, min.	Mixture as above.	Acetic acid replaced w./w. by acetic anhydride.
0	18°	18°
0·25	20	50
15	19·5	35

The use of mixtures of acetic acid and anhydride led in all cases to incomplete formation of benzylidene diacetate.

Use of Other Metal Nitrates.—Nitrations of benzylidene diacetate (21 g.) in acetic acid (100 ml.) using various metal nitrates under the conditions previously described were carried out with the following results:

Metal nitrate and wt. (g.) used.		Yield of *p*-nitrobenzylidene diacetate. Wt. (g.).	%.	Metal nitrate and wt. (g.) used.		Yield of *p*-nitrobenzylidene diacetate. Wt. (g.).	%.
Zinc,	30	6·0	23	Cobalt,	35	1	4
Ferric,	40	5·0	19	Calcium,	25	0	0
Bismuth,	50	5·0	19	Lead,	50	0	0
Nickel,	35	3·0	12	Sodium,	25	deflagration	
Magnesium,	30	2·0	8				

10. *Nitration of Benzylidene Diacetate with Acetic Anhydride and Nitric Acid.*—Benzaldehyde (120 g.) was added to acetic anhydride (500 ml.), and sulphuric acid (10 ml.; *d* 1·84) added slowly with vigorous stirring. The solution was stirred for a further 30 minutes and nitric acid (200 ml.; *d* 1·42) added at the rate of 25 drops per minute, the vigorous reaction maintaining the temperature at 118°. More nitric acid (50 ml.) was then added more rapidly, and the mixture then allowed to cool and poured into a large excess of water. The separated material was filtered off, washed with cold water, and refluxed with ethanol (400 ml.), water (400 ml.), and sulphuric acid (40 ml.; *d* 1·84) for 1 hour. The product was then rapidly steam-distilled to leave a residue of *p*-nitrobenzoic acid (49 g., 26%), m. p. and mixed m. p. 237° (*p*-nitrobenzyl ester m. p. 167°). Extraction of the distillate with ether and removal of the ether gave

a residue which after crystallisation from toluene and 4 volumes of light petroleum (b. p. 40—60°) gave *o*-nitrobenzaldehyde (74 g., 43%), m. p. 42—43° (oxidised by alkaline permanganate to *o*-nitrobenzoic acid, m. p. 147°; acetone condensed in presence of sodium hydroxide to give indigo, soluble in chloroform).

11. *Nitration of Benzylidene Diacetate with Acetic Anhydride and Nitric Acid at Low Temperatures.*—Benzaldehyde (12 g.), dissolved in acetic anhydride (100 ml.), was nitrated by the slow addition of nitric acid (30 ml.; *d* 1·52) with rapid stirring and external cooling, the temperature being kept at <20°. After a further 3 hours' stirring the nitration mixture was set aside at room temperature overnight. The product was poured into water (2 l.), and the separated solid filtered off, washed free from acid and crystallised from toluene–light petroleum, to give *o*-nitrobenzaldehyde (6 g., 41%), m. p. and mixed m. p. 42—43°. In this preparation hydrolysis of the diacetate occurred during isolation, and the above method represents the most convenient method of preparation of *o*-nitrobenzaldehyde by direct nitration of benzaldehyde.

12. *Nitration of Benzylidene Diacetate with Acetic and Nitric Acids.*—Attempts to nitrate benzylidene diacetate in acetic acid at elevated temperatures led to the formation of benzoic acid, whilst at <20° there was no nitration during 2 days.

13. *Nitration of Benzylidene Diacetate with Sulphuric and Nitric Acids.*—Nitration of benzylidene diacetate (21 g.), dissolved in sulphuric acid (100 ml.; *d* 1·84), with nitric acid (10 ml.; *d* 1·52) at <15° led to *o*- (5 g., 33 %) m. p. 42°, and *m*-nitrobenzaldehyde (6·5 g., 43%), m. p. and mixed m. p. 58°. Increase in the proportion of sulphuric acid or the use of mixed acid for the nitration led to the formation of *m*-nitrobenzaldehyde as the main product, hydrolysis of the diacetate occurring before nitration.

14. *Preparation of* m-*Nitrobenzaldehyde.*—Nitration of redistilled benzaldehyde (106 g.), dissolved in sulphuric acid (300 ml.; *d* 1·84), with mixed acid [70 ml. of nitric (*d* 1·52) + 150 ml. of sulphuric acid (*d* 1·84)] at <15° gave *m*-nitrobenzaldehyde (121 g., 80%), m. p. and mixed m. p. 58°. Small amounts (*ca.* 5 g.) of impure *o*-nitrobenzaldehyde were isolated from the acid liquors by ether-extraction, but the product was extremely difficult to purify.

15. *Nitration of Acetophenone with Acetic Acid and Copper Nitrate.*—Acetophenone (25 g.) was refluxed for 5 hours with acetic acid (250 ml.) and hydrated copper nitrate (60 g.), and the mixture poured into a large excess of water and set aside overnight. The product was made alkaline with aqueous ammonia and then just acid with dilute sulphuric acid, and the precipitate filtered off, washed with water, and recrystallised from aqueous ethanol to give *p*-nitrobenzylidene diacetate (22 g., 42%), m. p. and mixed m. p. 122°.

Reaction Mechanism.—Benzoylformic acid (5 g.) was refluxed with acetic anhydride or acid (50 ml.) and hydrated copper nitrate (10 g.). Pouring the mixture into water gave *p*-nitrobenzylidene diacetate (3·1 g.; 2·2 g.), m. p. and mixed m. p. (after crystallisation from ethanol) 122°.

Benzoylformic acid (5 g.) was refluxed for 2 hours with acetic anhydride (50 ml.) and one drop of sulphuric acid, or glacial acetic acid (50 ml.). Benzylidene diacetate (3 g.; m. p. and mixed m. p. 46°) and benzaldehyde (2·2 g., identified as 2 : 4-dinitrophenylhydrazone) respectively were obtained on pouring the mixtures into water.

Oxidation of o- *and* p-*Nitrotoluenes.*—Oxidation of *p*-nitrotoluene by the method of *Org. Synth.*, Coll. Vol. II, p. 441, gave *p*-nitrobenzylidene diacetate in 46% yield, whilst oxidation of *o*-nitrotoluene gave 20—25% yields of the *o*-nitro-diacetate and always led to the formation of much tar.

Hydrolysis of Diacetates.—Difficulty was encountered in the acid hydrolysis of *p*-nitrobenzylidene diacetate by the method of *Org. Synth.* but rapid and complete hydrolysis of diacetates was effected as follows. The diacetate (50 g.) was refluxed with a 2·5% suspension (800 ml.) of magnesium hydroxide for 2 hours. The product was cooled, the excess of magnesium hydroxide dissolved in dilute sulphuric acid (50—60 ml.; 5N.), and the mixture chilled in ice. The aldehyde which separated was filtered off and recrystallised. Additional small amounts of aldehyde could be recovered by ether-extraction of the mother-liquors. Yields of 90—95% have been obtained.

" Milk of magnesia," diluted with 2½ parts (vol.) of water, was most suitable, as the particles are very finely dispersed but the suspension is free from any added dispersing agent.

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