

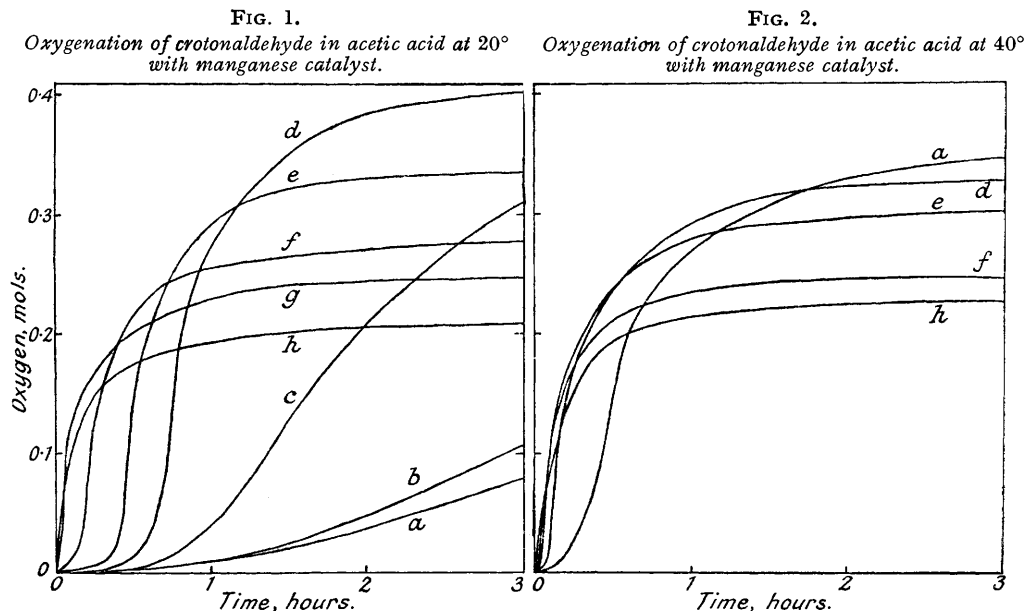
### 125. *The Oxygenation of Crotonaldehyde.*

By L. N. OWEN.

A quantitative study has been made of the absorption of oxygen by crotonaldehyde in the presence of various catalysts. In acetic acid solution, there is an optimum concentration of cobalt or manganese at which oxygenation is most efficient, but copper is ineffective at any concentration. In the absence of a solvent, cobalt and manganese are detrimental, whereas copper again has little effect. Increased temperature is also to be avoided. Crotonic acid is obtained in highest yield by the use of pure crotonaldehyde in the absence of any catalyst, precautions being taken against undue rise in temperature. Side reactions, involving attack at the double bond, lead to the formation of *dl-erythro- $\alpha$* -dihydroxybutyric acid, which has been isolated as one

of the by-products. The synthesis of *crotyl crotonate*, and the formation of a calcium chloride compound of crotonaldehyde,  $\text{CaCl}_2 \cdot 2\text{C}_4\text{H}_6\text{O}$ , are described.

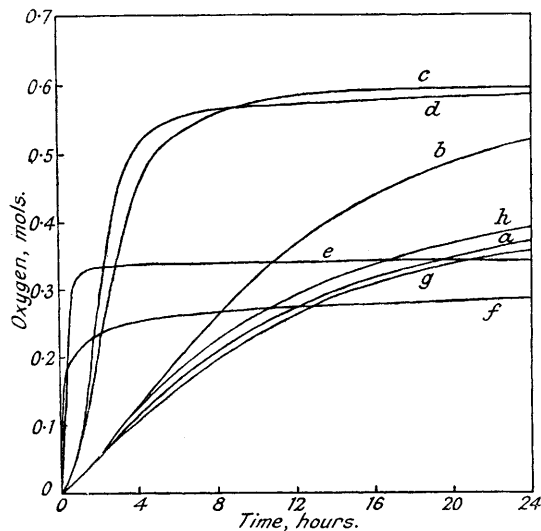
THE difficulty of obtaining a high yield of crotonic acid by treatment of crotonaldehyde with air or oxygen is well known (Duchesne and Delépine, *Bull. Soc. chim.*, 1924, 35, 1311; Rupe and Schaerer, *Helv. Chim. Acta*,



[Mn]: (a), 0; (b),  $2 \times 10^{-7}$ ; (c),  $6 \times 10^{-7}$ ; (d),  $2 \times 10^{-6}$ ; (e),  $4 \times 10^{-6}$ ; (f),  $2 \times 10^{-5}$ ; (g),  $2 \times 10^{-4}$ ; (h),  $4 \times 10^{-3}$ .

1925, 8, 853; Kaufler and Halbig, *Monatsh.*, 1929, 53—54, 119). According to B.P. 165,728, oxygenation of crotonaldehyde in acetic acid containing 0.1—0.2% of manganese (as manganic acetate) leads to formation of crotonic acid in 98—99% yield; this is presumably calculated on a "weight for weight" basis, and corresponds to a yield of 80% of the theoretical. Duchesne and Delépine (*loc. cit.*) could not confirm this claim, and the present work has demonstrated that a catalyst concentration of 0.1% is not the most effective.

FIG. 3.  
Oxygenation of crotonaldehyde in acetic acid at 20°  
with cobalt or copper catalyst.



[Co]: (a), 0; (b),  $10^{-5}$ ; (c),  $10^{-4}$ ; (d),  $2 \times 10^{-4}$ ; (e),  $10^{-3}$ ; (f),  $10^{-2}$ . [Cu]: (g),  $10^{-5}$ ; (h),  $10^{-2}$ .

curves tend to approach that obtained with the highest catalyst concentration, a curve which itself is almost independent of temperature [compare Fig. 1(h) and Fig. 2(h)]. Indeed, at 60° the catalyst concentration had little effect on either the rate or the extent of the reaction, all the curves obtained being practically identical with (h), Fig. 2.

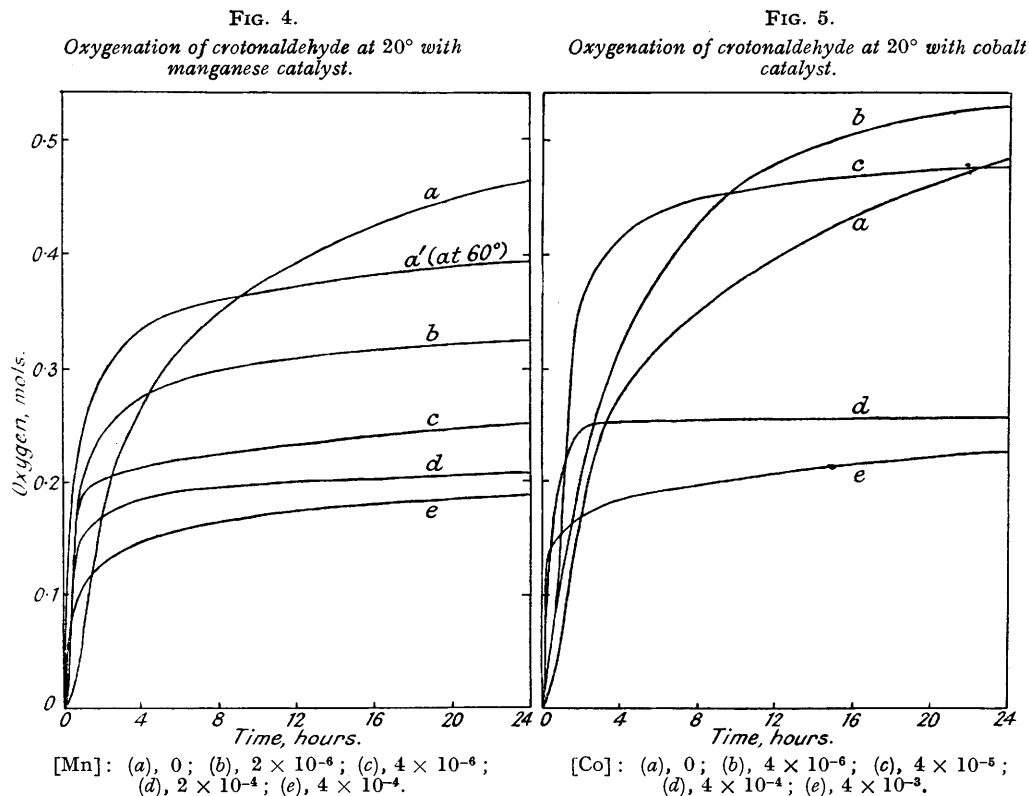
Dry crotonaldehyde, dissolved in an equal volume of acetic acid containing known amounts of manganic acetate, was shaken in oxygen at room temperature, the absorption of gas being measured. With a catalyst concentration of  $4 \times 10^{-3}$  mol./l. (*i.e.*, ca. 0.1%), absorption was rapid at first but ceased when about half the theoretical amount of oxygen had been acquired. On progressive reduction of the catalyst concentration to  $2 \times 10^{-6}$  mol./l., there was a remarkable increase in the oxygen absorption, but further reduction in concentration resulted in a diminution in the rate of reaction. The optimum value of about  $2 \times 10^{-6}$  mol./l. thus brought about the maximum absorption of oxygen in a reasonable time (about 3 hours). The curves (Fig. 1) show, as would be expected, that the induction period increases as the catalyst concentration is diminished, but it is not clear why the higher concentrations eventually inhibit the oxidation. A high rate of destruction of per-acid by the catalyst would probably bring about such a result, but the reaction products, except those from the use of the highest catalyst concentration, always showed the presence of peroxide or per-acid.

At 40°, the deleterious effect of manganese was still noticeable (Fig. 2), but with rise in temperature the curves tend to approach that obtained with the highest catalyst concentration, a curve which itself is almost independent of temperature [compare Fig. 1(h) and Fig. 2(h)].

Further experiments, carried out at room temperature only, indicated that there was a similar sensitivity to catalyst concentration when cobalt acetate was used. Copper acetate, on the other hand, was without appreciable effect at any concentration (Fig. 3).

In the absence of solvent, the presence of manganese was detrimental at all concentrations, oxidation being most efficient when no catalyst was used (Fig. 4), crotonic acid then crystallising out during the course of the oxidation. With cobalt, higher concentrations behaved in a similar manner; lower concentrations, although accelerating the initial absorption of oxygen, did not result in a yield of crotonic acid better than that obtained without a catalyst (Fig. 5). The presence of copper in various amounts did not greatly affect the course of the oxidation or the yield of acid.

Treatment of pure crotonaldehyde with oxygen under a pressure of 5 atm. resulted in an earlier separation of solid crotonic acid, and by fractional distillation of the products it was obtained in 70% yield. When the experiment was repeated on a larger scale, the heat of reaction caused a considerable rise in temperature, the product remained liquid, and the yield of crotonic acid was only 27%. The importance of temperature control was also shown by an experiment at ordinary pressure at 60°, in which the oxygen absorption was rapid at

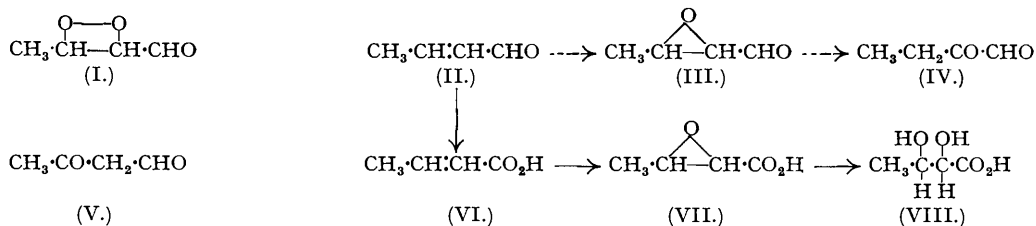


first, but was finally less than that attained in the cold [Fig. 4(a')]; furthermore, no solid separated, and a smaller amount of acid was isolated on distillation.

The highest yield of crotonic acid is therefore produced by the simple procedure of oxygenating pure crotonaldehyde, with precautions against undue rise in temperature. Even so, however, the yield is less than that calculated from the volume of oxygen absorbed, an observation which applies indeed to all the experiments, including those in acetic acid, and suggests that some side reaction occurs, probably involving the ethylenic linkage. Duchesne and Delépine (*loc. cit.*) postulated the formation of the peroxide (I), followed by breakdown to acetic acid, which they identified as one of the products, and a fragment "CH·CHO" which would presumably appear as glyoxal or one of its oxidation products; Young (*J. Amer. Chem. Soc.*, 1932, 54, 2498) also claimed to have isolated acetic acid, but the yield and mode of identification were not recorded. It has now been shown that during the oxidation there is a diminution in unsaturation value, thus confirming that the double bond is attacked, and efforts have been made to identify the reaction products.

Distillation in steam removed crotonic acid and unchanged crotonaldehyde, and from later portions of the distillate there was obtained a *bis*-2 : 4-dinitrophenylhydrazone,  $C_{16}H_{14}O_8N_8$ , m. p. 298°. With warm aqueous or cold alcoholic alkali it gave the intense violet colour typical of a dinitrophenylosazone, which suggested that it was the derivative of ethylglyoxal (IV), possibly formed from crotonaldehyde (II) *via* the glycidic aldehyde (III). Ethylglyoxal-2 : 4-dinitrophenylosazone was prepared; it had m. p. 247°, as stated by Ingold, Pritchard, and Smith (*J.*, 1934, 79), and behaved similarly. The isomeric derivative from diacetyl had m. p. 335° (Mat-

thiessen and Hagedorn, *Mikrochem.*, 1941, **29**, 55) and gave the colour only with alcoholic alkali. An alternative, though highly improbable, isomerisation of (III) would yield acetoacetaldehyde (V), which in the acid medium



would be rapidly converted into 1 : 3 : 5-triacetylbenzene (Claisen and Stylos, *Ber.*, 1888, **21**, 1144). The substance of m. p. 298° cannot therefore be derived from (V), and it is suggested that it may be a stereoisomer of the ethylglyoxal osazone.

The portion non-volatile in steam yielded crystalline *dl*-erythro- $\alpha\beta$ -dihydroxybutyric acid (VIII), from which the *p*-phenylphenacyl ester was prepared. This acid is obtained by the action of water on  $\beta$ -methylglycidic acid (VII), which is readily formed from crotonic acid (VI) in the presence of per-acids (Braun, *J. Amer. Chem. Soc.*, 1929, **51**, 228; 1930, **52**, 3185). Such oxidising agents are usually produced during the autoxidation of aldehydes, and this mechanism is supported by the fact that the reaction products liberated iodine from an acidified solution of potassium iodide.

Analysis of a reaction mixture gave an appreciable ester value, but in view of the presence of unchanged crotonaldehyde, which is easily resinified by treatment with hot alkali, it is doubtful whether this observation is of much value. A distinct ester-like odour was noticeable with some fractions, but the cause of this could not be ascertained. The absence of any appreciable quantity of *crotyl crotonate* was established by synthesis of this ester from *crotyl bromide* and silver crotonate: its properties were entirely different from those of any fraction.

Crotonaldehyde was found to form with calcium chloride a *compound*,  $\text{CaCl}_2 \cdot 2\text{C}_4\text{H}_6\text{O}$ .

#### EXPERIMENTAL.

Crotonaldehyde (A. Boake, Roberts and Co., Ltd.) was dried over calcium chloride and redistilled, the fraction of b. p. 103—105° being used. Oxygen was stored over water in a graduated cylinder, connected through a sulphuric acid drying bottle to the 10-c.c. reaction vessel, attached to a shaking machine and fitted with a small electric heater for work at higher temperatures. The heater was controlled by a variable resistance in series with an ammeter, which had been calibrated by preliminary experiments so that at a fixed rate of shaking (300 r.p.m.) the contents of the vessel could be maintained at any desired temperature. In view of the great effect produced by slight traces of catalysts, particular care was necessary to ensure that the reaction vessel and its connecting tubes were thoroughly cleaned before each experiment. After introduction of the material to be oxidised, air was replaced by oxygen, any necessary adjustments of temperature made, and the shaker set in operation at 300 r.p.m.

*Catalyst Solutions.*—A stock solution of manganese acetate was prepared by a slight modification of B.P. 165,728: To manganese acetate (1 g.), dissolved in boiling acetic acid (50 c.c.), was added a solution of potassium permanganate (0.15 g.) in hot water (5 c.c.). After cooling, the volume was made up to 500 c.c. with acetic acid, the catalyst concentration thus being 0.2%, calculated as manganese acetate, *i.e.*,  $8 \times 10^{-3}$  mol./l. Stock solutions of cobalt and copper acetates, each containing  $2 \times 10^{-2}$  mol./l., were made by dissolving the solids in acetic acid. Other concentrations were prepared by progressive dilution with acetic acid of portions of the stock solutions. The catalyst concentrations given in Figs. 1—5 refer to the net concentrations in the reaction mixtures employed.

*Oxygenations in Acetic Acid.*—(A) *With manganese catalyst* (see Figs. 1 and 2). The experiments were carried out in each instance on dry crotonaldehyde (3.5 c.c.) mixed with the catalyst solution (3.5 c.c.). With the higher concentrations there was an appreciable rise in temperature during the early stages of the reaction, but on repetition with a cooling bath surrounding the vessel there was little alteration in the ultimate absorption of oxygen, *e.g.*, 0.21 mol. after 2 hours with a catalyst concentration of  $4 \times 10^{-3}$  mol./l. [cf. curve (h), Fig. 1]. At 60°, with [Mn] ranging from 0 to  $4 \times 10^{-3}$ , all oxygenations took the same course, approximately that of curve (h), Fig. 2.

With the exception of the experiment in which the concentration was  $4 \times 10^{-3}$  mol./l., the reaction mixtures obtained by oxygenation at room temperature contained appreciable amounts of per-acid or peroxide (see above). In some instances, the total acidity of the final reaction mixture was determined by titration with standard alkali. The increased acidity was always less than that calculated on the basis of oxygen absorption, *e.g.*, the product from (h), Fig. 1 (Found: crotonic acid, 1.05 g. Calc.: 1.54 g.), and from (d), Fig. 1 (Found: 1.76 g. Calc.: 2.95 g.).

*Examination of oxidation products.* The combined products from a number of experiments at 20° were steam-distilled. Acetic acid, crotonic acid, and unchanged crotonaldehyde distilled first, and from later portions 2 : 4-dinitrophenylhydrazine sulphate afforded in small yield a *bis*-2 : 4-dinitrophenylhydrazone, forming orange-red needles, m. p. 298° (Found: C, 42.7; H, 3.1; N, 25.1.  $\text{C}_{16}\text{H}_{14}\text{O}_8\text{N}_8$  requires C, 43.0; H, 3.2; N, 25.1%), from nitrobenzene; its properties are discussed above.

The aqueous residue from the steam distillation was neutralised with barium carbonate, filtered from some tarry impurities, and evaporated to small bulk. The barium salts were precipitated with alcohol, filtered off, and dried in a vacuum. The powdered product (30 g.) was added to 8% methyl-alcoholic hydrogen chloride (200 c.c.), and after a few hours the precipitated barium chloride was filtered off. The solution, which now contained about 3% of hydrogen chloride, was refluxed for 9 hours, cooled, neutralised with silver carbonate, and filtered. The esters obtained on removal of the solvent were fractionated under 15 mm. to give: (i), 0.40 g., b. p. 55—85°,  $n_D^{20}$  1.3840; (ii), 0.85 g., b. p. 85—120°,  $n_D^{20}$  1.4288; (iii), 1.45 g., b. p. 120—122°,  $n_D^{20}$  1.4492. Fraction (iii) was methyl *dl*-erythro- $\alpha\beta$ -dihydroxybutyrate (Found: OMe, 22.9; equiv., 132. Calc. for  $\text{C}_8\text{H}_{10}\text{O}_4$ : OMe, 23.2%; equiv., 134). It was heated on the water-bath for 2 hours with excess of baryta, cooled, and treated with a slight deficiency of sulphuric acid. The filtered solution was evaporated under reduced pressure, and the residue extracted with hot ethyl acetate. Removal of the solvent gave a syrup from

which crystals of *dl*-erythro- $\alpha\beta$ -dihydroxybutyric acid slowly separated. These were triturated with ether and recrystallised from ethyl acetate, forming needles, m. p. and mixed m. p.  $81^\circ$  (Found: equiv., 121. Calc.: 120). The *p*-phenylphenacyl ester crystallised from methyl alcohol in rosettes of needles, m. p.  $130^\circ$  (Found: C, 68.6; H, 6.2.  $C_{18}H_{18}O_5$  requires C, 68.8; H, 5.8%).

(B) *With cobalt and copper catalysts.* The results shown in Fig. 3 were obtained with mixtures of crotonaldehyde (3.0 c.c.) and the catalyst solution (3.0 c.c.) of appropriate concentration. A further quantity of the above osazone, m. p.  $297^\circ$  from acetic anhydride, was isolated after steam distillation of the products (Found: C, 42.5; H, 3.0%).

*Oxygenations without Solvent.*—To dry crotonaldehyde (5.0 c.c.) was added a catalyst solution (0.1 c.c.) of concentration 50 times that required for the experiment.

(A) *With manganese catalyst* [see Fig. 4, (b), (c), (d), and (e)]. All reaction mixtures remained liquid.

(B) *With cobalt catalyst* (see Fig. 5). The heat developed in the first few minutes of experiments (d) and (e) was sufficient momentarily to cause the liquid to boil; only in the other experiments did crystalline crotonic acid separate during the oxidation. Repetition of (d) and (e), with a cooling-bath surrounding the vessel, resulted in a slower rate of reaction, but the final uptake of oxygen was hardly affected, being 0.27 and 0.24 mol. respectively, proportions which are almost identical with those shown in Fig. 5.

(C) *With copper catalyst.* [Cu] was varied from 0 to  $5 \times 10^{-3}$ , but the course of the reaction was unaffected. Solid crotonic acid separated during each oxidation, and the yield obtained on distillation was approximately the same as in the absence of a catalyst (see below).

(D) *No catalyst.* Dry crotonaldehyde (5.0 c.c.) was used. Crotonic acid began to separate after about 8 hours. The curve (a) showing the course of the oxidation is included in Figs. 4 and 5. Distillation of the product at 60 mm. gave: (i), 0.8 g., b. p.  $45-110^\circ$ ; (ii), 3.1 g., b. p.  $110-112^\circ$ , crystallising as crotonic acid; (iii), 0.4 g., residue. A further quantity of crotonic acid, estimated by titration to be 0.5 g., was present in fraction (i).

The oxidation was repeated, and the semi-solid reaction product diluted to 100 c.c. with water. Titration with alkali indicated an acid content equivalent to 4.1 g. of crotonic acid. The apparent ester value corresponded to a further 0.4 g. of crotonic acid, and the unsaturation value to 4.5 g. of crotonic acid or 3.7 g. of crotonaldehyde. There had been, therefore, a diminution in the unsaturation value (since the amount of crotonaldehyde originally present was 4.3 g.), indicating some side reactions involving the double bond. The solution liberated iodine from acidified potassium iodide, but equivalent to a content of only 0.04 g. of percrotonic acid. The remainder of the aqueous solution was steam-distilled, and again there was isolated a bis-2:4-dinitrophenylhydrazone, m. p.  $295^\circ$  (Found: C, 42.6; H, 3.3%). The non-volatile portion contained a trace of oxalic acid, identified by formation of its calcium salt.

An oxidation at  $60^\circ$  [curve (a'), Fig. 4] gave a liquid product which on distillation at 60 mm. yielded: (i), 2.1 g., b. p.  $45-110^\circ$ ; (ii), 2.0 g., b. p.  $110-113^\circ$ , crystallising as crotonic acid; (iii), 0.7 g., residue. The total crotonic acid was estimated to be 2.7 g.

*Oxidation under pressure.* Dry crotonaldehyde (10 c.c.) was oxidised in a thick-walled glass bottle fitted to a shaking machine and connected by pressure tubing to a small reservoir containing oxygen under a pressure of about 5 atm. A pressure gauge on the reservoir gave a rough indication of the rate of absorption of oxygen, but no quantitative measurements were made. The rate was greater than at ordinary pressure, and solid crotonic acid separated after 4 hours, but the reaction was allowed to proceed for 24 hours to ensure the maximum yield. The products from 5 such experiments were combined, and solid crotonic acid (6.5 g.) filtered off (much of it had been unavoidably dissolved in transference from the reaction vessel). Fractionation under 60 mm. then gave: (i), 9.0 g., b. p.  $45-110^\circ$ ; (ii), 30.5 g., b. p.  $110-112^\circ$ , crystallising as crotonic acid; (iii), 4.0 g., residue. The yield of crotonic acid was thus 37.0 g., *i.e.*, 70% of the theoretical. It is probable that fraction (i) also contained an appreciable amount.

When the oxidation under pressure was repeated on a larger amount (50 c.c.) of crotonaldehyde, the heat of reaction caused a pronounced rise in temperature and a yellow colour developed. After 24 hours, the product, from which no solid had separated, was fractionated. The crotonic acid amounted to only 14 g., *i.e.*, 27%.

*Preparation of Crotyl Crotonate.*—Crotyl alcohol, b. p.  $119-121^\circ$ ,  $n_D^{17} 1.4290$ , was prepared by the method of Young, Hartung and Crossley (*J. Amer. Chem. Soc.*, 1936, **58**, 100). From light petroleum (b. p.  $60-80^\circ$ ), the phenylurethane crystallised in colourless needles, m. p.  $79^\circ$  (Verhulst, *Bull. Soc. chim. Belg.*, 1931, **40**, 85, gives m. p.  $80^\circ$ ; Newman and Rydon, *J.*, 1936, 261, give m. p.  $65^\circ$ ), and the  $\alpha$ -naphthylurethane in needles, m. p.  $96-97^\circ$  (Hess and Wustrow, *Annalen*, 1924, **437**, 256, give m. p.  $89^\circ$ ). The 3:5-dinitrophenylurethane, prepared by heating the alcohol (0.2 g.) with 3:5-dinitrobenzamide (0.6 g.) in toluene (3 c.c.) at  $100^\circ$  for 1 hour (see Smith and Sprung, *J. Amer. Chem. Soc.*, 1942, **64**, 433), crystallised from toluene in plates, m. p.  $106-108^\circ$  (Found: C, 47.6; H, 4.0; N, 14.5.  $C_{11}H_{11}O_6N_3$  requires C, 47.1; H, 4.0; N, 15.0%).

Crotyl bromide was prepared from the alcohol (4.5 g.) by addition of hydrobromic acid (15 c.c., *d* 1.7). There was an immediate separation of a dark oil, and after 4 hours at room temperature this was removed, washed with water, sodium carbonate solution, again with water, dried over calcium chloride, and distilled: (i), 1.5 g., b. p.  $100-105^\circ$ ,  $n_D^{25} 1.4745$ ; (ii), 4.8 g., b. p.  $105-110^\circ$ ,  $n_D^{25} 1.4760$ . Fraction (ii), which distilled with a constant refractive index, was used for the following esterification.

To finely powdered silver crotonate (8 g.), suspended in dry ether (40 c.c.), was added crotyl bromide (4.8 g.). Reaction was vigorous, causing the ether to boil gently, and after standing for 2 hours the silver bromide was filtered off. Removal of ether from the filtrate gave an oil which was distilled under 60 mm.: (i), 1.0 g., b. p.  $95-100^\circ$ ,  $n_D^{25} 1.4400$ ; (ii), 2.4 g., b. p.  $100-105^\circ$ ,  $n_D^{25} 1.4450$ ; (iii), 1.0 g., b. p.  $105-107^\circ$ ,  $n_D^{25} 1.4490$ . Fraction (ii), an oil with a pleasant odour, had b. p.  $ca. 175/770$  mm. (Found: C, 67.6; H, 8.5; equiv., 137;  $[\eta]_{25}^{25}$ .  $C_8H_{12}O_2$  requires C, 68.5; H, 8.6%; equiv., 140;  $[\eta]_{25}^{25}$ ). This crotyl crotonate was probably contaminated with a small proportion of methylvinylcarbinyl crotonate ( $\alpha$ -methylallyl crotonate), for Winstein and Young (*J. Amer. Chem. Soc.*, 1936, **58**, 104) have shown that crotyl bromide, as usually prepared, is in equilibrium with *ca.* 15% of methylvinylcarbinyl bromide.

*Search for Crotyl Crotonate in the Oxidation Products.*—From the b. p. of the synthetic ester it was evident that it might have been present either in admixture with the crystalline crotonic acid distillates or in the preceding fraction, usually collected at  $45-110^\circ/60$  mm. A quantity of the latter material, collected from several oxidations, was dissolved in ether and shaken with aqueous sodium carbonate to remove traces of acid. The ethereal layer was dried and evaporated to an oil (6 g.) from which, on distillation, however, crotyl crotonate could not be isolated.

The solid crotonic acid distillates often had an ester-like odour. Some of this material (48 g.) was crystallised once from water to give pure crotonic acid, m. p.  $72^\circ$ . The mother-liquors were basified with sodium carbonate solution and extracted with ether. Evaporation of the dried extract gave an oil (0.5 g.) which was distilled: (i), 0.2 g., b. p.  $120-170^\circ$ ,  $n_D^{20} 1.4325$ ; (ii), 0.2 g., b. p.  $170-180^\circ$ ,  $n_D^{20} 1.4460$ . Both fractions had negligible ester values and gave oily products with aqueous 2:4-dinitrophenylhydrazine sulphate.

*Calcium Chloride Compound of Crotonaldehyde.*—Finely powdered anhydrous calcium chloride (7 g.) was shaken in a stoppered bottle with an excess (17 g.) of dry crotonaldehyde. After standing overnight, the pasty mass was shaken with dry ether (50 c.c.), rapidly filtered off, washed with more dry ether (50 c.c.), transferred to a vacuum desiccator, and kept under reduced pressure until no further loss in weight occurred. The compound so obtained (Found: Cl, 28.6;

loss on heating, 55.1;  $\bar{1.97}$ .  $\text{CaCl}_2 \cdot 2\text{C}_4\text{H}_6\text{O}$  requires Cl, 28.3; loss, 55.8%;  $\bar{2.0}$ ) slowly decomposed in moist air with evolution of crotonaldehyde. On heating, it left a residue of calcium chloride.

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