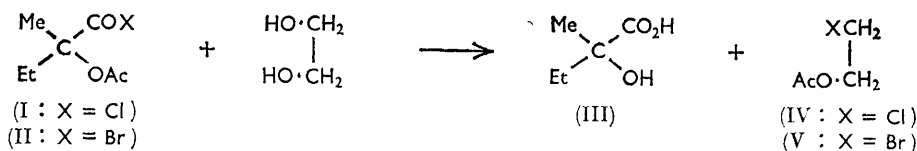


**932. Novel Reactions of Some  $\alpha$ -Acyloxy-acid Halides.**  
**Part II.<sup>1</sup> Some Further Examples.**

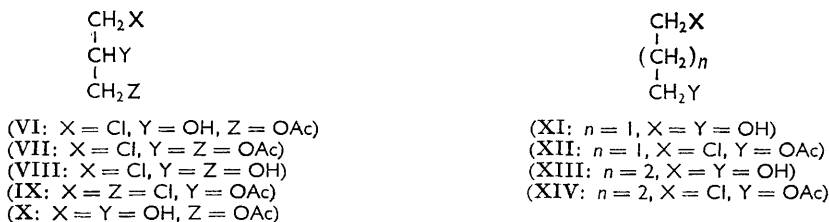
By A. R. MATTOCKS.

The scope of the "abnormal" reaction of  $\alpha$ -acetoxy- $\alpha$ -methylbutyryl chloride (I) with some diols to give chloroalkyl acetates<sup>1</sup> has been examined by using a range of diols. The reaction has been extended to other  $\alpha$ -acyloxy-acid halides, including the bromide (II).

It has been shown<sup>1</sup> that  $\alpha$ -acetoxy- $\alpha$ -methylbutyryl chloride (I) reacts with ethylene glycol "abnormally," to give  $\alpha$ -hydroxy- $\alpha$ -methylbutyric acid (III) and 2-chloroethyl acetate (IV). Some related reactions are now reported.



The reaction of the acid chloride (I) with glycerol was similar to that with ethylene glycol. No hydrogen chloride was evolved, and the main products were  $\alpha$ -hydroxy- $\alpha$ -methylbutyric acid (III) (98% yield), and 1-acetoxy-3-chloropropan-2-ol (VI). The latter was identified by acetylating it to 1,2-diacetoxy-3-chloropropane (VII), and by its boiling point.<sup>2</sup> That



glycerol here reacts as a 1,3- rather than a 1,2-diol, is attributed to the greater reactivity of the primary hydroxyl groups [glycerol, with hydrochloric acid, gives the 1-chlorohydrin (VIII)].<sup>3</sup> The acid chloride (I) can react as readily with a 1,3- as with a 1,2-diol, as demonstrated (below) with propane-1,3-diol.

The primary position was chlorinated when the acid chloride (I) reacted with two related diols. 3-Chloropropane-1,2-diol (VIII) gave 2-acetoxy-1,3-dichloropropane (IX) (82%), and 3-acetoxyp propane-1,2-diol (X) gave 1,2-diacetoxy-3-chloropropane (VII) (81%). In both cases, the hydroxy-acid (III) crystallised from the reaction mixture (93 and 68%, respectively).

Propane-1,3-diol (XI) also reacted "abnormally" with the acid chloride (I), giving 3-chloropropyl acetate (XII) (88%) and the hydroxy-acid (III) (97.5%). However, butane-1,4-diol (XIII) gave only partly the "abnormal" reaction. Some hydroxy-acid (III) was obtained, and the neutral product was a mixture of esters containing some chlorinated material. Among these, 4-chlorobutyl acetate (XIV) was identified by gas chromatography. These results are consistent with a reaction which depends for success on the proper alignment of two pairs of adjacent groups. (The proportion of molecules of a 1,4-diol, that at any time have their hydroxyl groups close enough together for the "abnormal" reaction to occur, must be much smaller than with a 1,3-diol.)

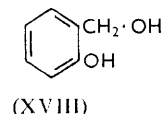
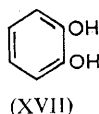
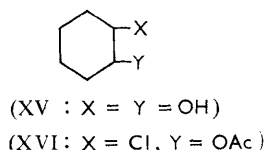
To test the reaction of the acid chloride (I) with a solid diol, cyclohexane-1,2-diol (XV)

<sup>1</sup> Mattocks, J., 1964, 1918 (to be considered as Part I).

<sup>2</sup> Bigot, *Ann. Chim. Phys.*, 1891, [6], 22, 491.

<sup>3</sup> Conant and Quayle, *Org. Synth.*, Coll. Vol. I, 2nd edn., p. 294.

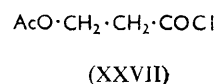
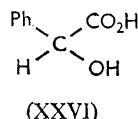
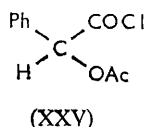
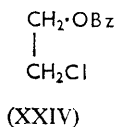
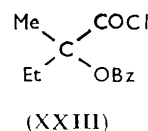
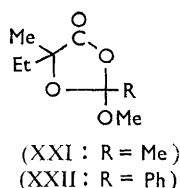
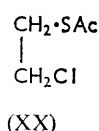
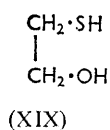
(*trans*, with a little *cis*) was used. The extent of "abnormal" reaction was indicated by the yield (55%) of hydroxy-acid (III). The neutral product, a mixture of esters containing chlorinated material, was not completely resolved by distillation, but a gas chromatogram showed four peaks, two of which corresponded with 2-chlorocyclohexyl acetate (XVI)



[mainly *cis*, with a little *trans*; reversal of configuration at one of the two reacting sites (chlorination) is consistent with both the mechanisms already proposed<sup>1</sup> for the "abnormal" reaction].

The "abnormal" reaction failed completely when phenolic compounds were used in place of glycol. Both catechol (XVII) and saligenin (XVIII) reacted vigorously with the acid chloride (I). Hydrogen chloride was produced copiously, and in neither case was there isolated any of the hydroxy-acid (III).

The "abnormal" reaction occurred when one hydroxyl group in glycol was replaced by a thiol group; esterification occurred mainly at the latter. Equimolecular amounts of the acid chloride (I), and 2-mercaptoethanol (XIX), gave the hydroxy-acid (III; 90%) and a mixture of esters [ $\nu$  1695 (thioester) and 1740  $\text{cm}^{-1}$  (weaker; ester)]. From this, 2-chloroethyl thiolacetate (XX) was isolated by chromatography on alumina; a small amount of 2-chloroethyl acetate (IV) was detected by gas chromatography.



Some further acid halides have been shown to undergo "abnormal" reactions. With ethylene glycol,  $\alpha$ -acetoxy- $\alpha$ -methylbutyryl bromide (II) gave 2-bromoethyl acetate (V) (66%), and the hydroxy-acid (III) (93%); and with methanol and triethylamine, the main product was 2,5-dimethyl-2-methoxy-5-ethyl-1,3-dioxolan-4-one (XXI).<sup>1</sup>

In the aromatic series,  $\alpha$ -benzoyloxy- $\alpha$ -methylbutyryl chloride (XXIII) with glycol gave 2-chloroethyl benzoate (XXIV; almost quantitative) and the hydroxy acid (III). With methanol and triethylamine, the chloride (XXIII) gave the new dioxolanone (XXII) and not methyl  $\alpha$ -benzoyloxy- $\alpha$ -methylbutyrate.

Acetylmandelyl chloride (XXV) also reacted "abnormally" with glycol, giving 2-chloroethyl acetate (IV) (at least 50% yield), and mandelic acid (XXVI) (72%). However, with methanol and triethylamine the only product was methyl acetylmandelate; no dioxolanone was formed. This agrees with previous work,<sup>1</sup> in which dioxolanones were only formed when the  $\alpha$ -carbon atom of the acid chloride carried *two* alkyl substituents.

To confirm that the "abnormal" reactions are limited to  $\alpha$ -acyloxy-acyl halides,  $\beta$ -acetoxypropionyl chloride (XXVII) was tested. With ethylene glycol, this gave no trace of 2-chloroethyl acetate (IV), as shown by gas chromatography. With methanol and triethylamine, it gave only the expected methyl  $\beta$ -acetoxypropionate.

The "abnormal" reaction, between ethylene glycol and the acid chloride (I), also occurred in a dioxan solution, though the yield was lower (about 60% of 2-chloroethyl acetate). As well as the hydroxy-acid (III), some  $\alpha$ -acetoxy- $\alpha$ -methylbutyric acid was obtained, presumably by hydrolysis of unreacted acid chloride during working up.

### EXPERIMENTAL

Paper chromatography of acids (as ethylamine salts), and infrared spectroscopy (of chloroform solutions) were as previously described.<sup>1</sup> Gas chromatograms were obtained with a Perkin-Elmer model 800 instrument. Relative retention times are given for a column containing 1.5% silicone oil (SE-30) as liquid phase. Where temperature programming was used, the starting temperature and rate of increase are given.

*Reaction of  $\alpha$ -Acetoxy- $\alpha$ -methylbutyryl Chloride.*—(a) *With glycerol.* The acid chloride<sup>1</sup> (1.78 g., 10 mmoles) and glycerol (0.92 g., 10 mmoles) were shaken together at 0–10° and the emulsion was allowed to warm slowly to room temperature, with shaking. An exothermic reaction occurred within a few minutes, giving a homogeneous syrup; no hydrogen chloride was evolved. After 30 min. at room temperature, the mixture was shaken with excess of sodium bicarbonate solution, and extracted five times with ether. When the aqueous liquor was acidified (HCl) there was extracted (5 lots of ether)  $\alpha$ -hydroxy- $\alpha$ -methylbutyric acid (1.16 g., 9.8 mmoles), forming needles (from ether–light petroleum), m. p. 71°, not depressed by an authentic sample. The combined ether extracts were dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated, giving a hygroscopic, neutral oil (1.3 g.). This nearly all distilled at 235–240° to give 1-acetoxy-3-chloropropan-2-ol,  $n_D^{20}$  1.4550 (dropping on exposure to atmospheric moisture) (Found: C, 38.8; H, 6.0; Cl, 22.7. Calc. for C<sub>5</sub>H<sub>9</sub>ClO<sub>3</sub>: C, 39.4; H, 5.9; Cl, 23.25%). Bigot<sup>2</sup> gives b. p. 240° for 1-acetoxy-3-chloropropan-2-ol; 218° for 2-acetoxy-3-chloropropan-1-ol.

The oil, on alkaline hydrolysis, gave acetic acid ( $R_F$  0.16 only). Acetylation (excess refluxing acetyl chloride) gave 1,2-diacetoxy-3-chloropropane, b. p. 228°,  $n_D^{20}$  1.4400, identical with a specimen prepared by acetylating 3-chloropropane-1,2-diol.

(b) *With 3-chloropropane-1,2-diol.* The acid chloride (10 mmoles) and the diol (1.1 g., 10 mmoles; redistilled,  $n_D^{20}$  1.4806), were allowed to react together as described in (a).  $\alpha$ -Hydroxy- $\alpha$ -methylbutyric acid crystallised from the reaction mixture and was collected, after the addition of light petroleum (b. p. 30–40°), as needles (1.1 g., 9.3 mmoles), m. p. and mixed m. p. 72°. The filtrate, worked-up as in (a), yielded 2-acetoxy-1,3-dichloropropane (1.4 g., 8.2 mmoles), b. p. 194–195°,  $n_D^{20}$  1.4540, identical with an authentic sample (lit.,<sup>4</sup> b. p. 193–195°;  $n_D^{20}$  1.4542).

(c) *With 3-acetoxypropane-1,2-diol.* The acid chloride (10 mmoles) and the diol (1.34 g., 10 mmoles) were allowed to react as above. Working up in the usual way gave  $\alpha$ -hydroxy- $\alpha$ -methylbutyric acid (0.8 g., crystallising from the reaction mixture), and 1,2-diacetoxy-3-chloropropane (1.58 g., 8.1 mmoles), b. p. 226–228°,  $n_D^{20}$  1.4410, identical (infrared spectrum) with authentic material (see above).

(d) *With propane-1,3-diol.* The acid chloride (10 mmoles) and the diol (0.76 g., 10 mmoles) were allowed to react as described in (a).  $\alpha$ -Hydroxy- $\alpha$ -methylbutyric acid (0.85 g.) crystallised from the reaction mixture, m. p. and mixed m. p. 72°; further hydroxy-acid (0.3 g.) was recovered from the bicarbonate solution (total, 9.75 mmoles). The ether extract yielded a neutral oil (1.2 g., 8.8 mmoles), which almost all distilled at 173.5°,  $n_D^{20}$  1.4295, identical (infrared spectrum) with authentic 3-chloropropyl acetate, b. p. 173–175°,  $n_D^{20}$  1.4297 (Bogert and Slocum<sup>5</sup> give b. p. 165–166°; Conant, Kirner, and Hussey<sup>6</sup> give 168–169°).

(e) *With butane-1,4-diol.* The acid chloride (10 mmoles) and the diol (0.9 g., 10 mmoles) were allowed to react as described in (a). Some hydrogen chloride was evolved. No crystallisation occurred. From the bicarbonate solution was obtained a semi-crystalline acid (1.1 g.),  $R_F$  0.36 ( $\alpha$ -hydroxy- $\alpha$ -methylbutyric acid) and 0.52 ( $\alpha$ -acetoxy- $\alpha$ -methylbutyric acid, small spot). Recrystallisation from ether–light petroleum gave the pure hydroxy-acid, m. p. and mixed m. p. 71.5°. The ether extract yielded a neutral oil (1.1 g.),  $\nu_{\max}$ , 1725s (ester), 3450w cm.<sup>-1</sup> (OH), containing about 8% chlorine. Gas chromatography (120°; 10.4°/min.) revealed two main components, in a ratio of about 1 : 2 (retention times 0.89, 1.28 min.). The b. p. varied

<sup>4</sup> Humnicki, *Bull. Soc. chim. France*, 1929, [4], **45**, 279.

<sup>5</sup> Bogert and Slocum, *J. Amer. Chem. Soc.*, 1924, **46**, 763.

<sup>6</sup> Conant, Kirner, and Hussey, *J. Amer. Chem. Soc.*, 1925, **47**, 488.

continuously from about  $190^\circ$  to  $>212^\circ$  (distillate,  $n_D^{20}$  1.428—1.437). An authentic sample of 4-chlorobutyl acetate<sup>7</sup> had b. p.  $191^\circ/1$  atm.;  $n_D^{20}$  1.4370; retention time, 0.89 min.

(f) *With cyclohexane-1,2-diol*. The finely powdered diol [L. Light and Co. Ltd. (recrystallised from ethanol-ether), m. p.  $103$ — $105^\circ$ , mainly *trans* with some *cis*, 1.16 g., 10 mmoles] was added in one lot to the acid chloride (10 mmoles) below room temperature. Warming and stirring initiated a vigorous reaction; some hydrogen chloride was evolved. After 30 min., the clear liquor was dissolved in ether, shaken twice with sodium bicarbonate solution, and the ether solution dried and concentrated to give an oil (2 g.). During distillation *in vacuo* the b. p. varied continuously ( $80$ — $130^\circ$ ), the distillate having  $n_D^{20}$  1.469—1.459. The first fraction,  $n_D^{20}$  1.4682 (about 0.5 g.) had b. p.  $215^\circ/1$  atm.,  $\nu_{\max}$  1725  $\text{cm}^{-1}$  (ester) (Found: Cl, 15.4. Calc. for 2-chlorocyclohexyl acetate: Cl, 20.1%). Gas chromatography ( $120^\circ$ ;  $10.4^\circ/\text{min.}$ ) revealed four components, in a ratio of about 2 : 6 : 1 : 2 (retention times 0.85, 1.26, 1.46, and 1.81 min., respectively). A sample of 2-chlorocyclohexyl acetate, prepared by acetylating *trans*- (mainly) 2-chlorocyclohexanol, had b. p.  $216$ — $217^\circ$ ,  $n_D^{20}$  1.4690, retention times 0.85 (weak: *cis*) and 1.26 min. (*trans*) (lit.,<sup>8</sup> b. p.  $95$ — $96^\circ/11$  mm.,  $n_D^{25}$  1.4619).

From the bicarbonate washings, after acidification, was extracted  $\alpha$ -hydroxy- $\alpha$ -methylbutyric acid (0.65 g., 5.5 mmoles), m. p.  $71^\circ$ , after recrystallisation.

(g) *With saligenin*. Finely powdered saligenin (0.62 g., 5 mmoles) was added in one lot to the ice-cold acid chloride (0.9 g., 5 mmoles). A vigorous reaction set in and much hydrogen chloride was evolved. After 30 min. at room temperature, the syrup was dissolved in ether and worked up as in (f). The ether extract yielded a semi-crystalline gum (0.75 g.). The bicarbonate solution, acidified and extracted with ether, yielded only  $\alpha$ -acetoxy- $\alpha$ -methylbutyric acid (0.5 g.),  $n_D^{20}$  1.412,  $R_F$  0.51, identical with an authentic sample.<sup>1</sup>

(h) *With catechol*. Catechol (0.55 g., 5 mmoles) and the acid chloride (5 mmoles) were allowed to react as described in (g); the reaction was less vigorous than with saligenin. After 1 hr. at room temperature and then 10 min. at  $100^\circ$ , the mixture was worked up as before to give a neutral, red syrup (0.96 g.), and a liquid acid,  $n_D^{20}$  1.4340, almost entirely  $\alpha$ -acetoxy- $\alpha$ -methylbutyric acid ( $R_F$  0.51), with only a trace of the  $\alpha$ -hydroxy-acid ( $R_F$  0.36).

(j) *With 2-mercaptoethanol*. The acid chloride (10 mmoles), and 2-mercaptoethanol (L. Light and Co. Ltd., redistilled, b. p.  $157^\circ$ ,  $n_D^{20}$  1.5005), were allowed to react as described in (a). A vigorous reaction occurred; very little hydrogen chloride was evolved. After 0.5 hr. at room temperature, light petroleum (b. p.  $30$ — $40^\circ$ ) was added and  $\alpha$ -hydroxy- $\alpha$ -methylbutyric acid (1.05 g., 9 mmoles) was collected,  $R_F$  0.35, m. p. and mixed m. p.  $69$ — $70^\circ$  after one recrystallisation. From the filtrate, washed with sodium bicarbonate solution, was obtained an oil (1.25 g.),  $n_D^{20}$  1.495, b. p.  $176$ — $180^\circ$  (most),  $\nu_{\max}$  1740  $\text{cm}^{-1}$  (ester), 1695  $\text{cm}^{-1}$  (thiolester). Hydrolysis (6*N*-NaOH) of the crude oil gave acetic acid ( $R_F$  0.16 only). Gas chromatography (isothermal,  $125^\circ$ ) showed two components, with retention times 0.77 and 0.62 min. (weaker). The latter was identical with 2-chloroethyl acetate. The mixture was not separated by distillation. When chromatographed on alumina (B.D.H. chromatographic grade) an oil was eluted with light petroleum (b. p.  $30$ — $40^\circ$ ),  $n_D^{20}$  1.4978, retention time 0.77 min.,  $\nu_{\max}$  (in CO region) 1695  $\text{cm}^{-1}$  only. This was unchanged by distillation *in vacuo*, giving 2-chloroethyl thiolacetate, b. p.  $182^\circ/1$  atm. (lit.,  $54^\circ/4$  mm.;<sup>9</sup>  $76^\circ/17$  mm.<sup>10</sup>) (Found: Cl, 25.1; S, 23.5. Calc. for  $\text{C}_4\text{H}_7\text{ClOS}$ : Cl, 25.65; S, 23.15%).

Further elution of the column with diethyl ether gave a mixture of ester and thiolester.

(k) *With ethylene glycol in dioxan*. The acid chloride (10 mmoles) in dioxan (4 ml.) was mixed with glycol (0.62 g., 10 mmoles) in dioxan (4 ml.). After 30 min. at room temperature, the solvent was removed at  $50^\circ$  under slightly reduced pressure. The residue was dissolved in ether, washed with sodium bicarbonate solution, dried ( $\text{Na}_2\text{SO}_4$ ), and concentrated to give an oil (0.9 g.). On distillation the main fraction had b. p.  $145$ — $147^\circ$ ,  $n_D^{20}$  1.4230, identical (infrared spectrum) with 2-chloroethyl acetate (b. p.  $145^\circ$ ,  $n_D^{20}$  1.4240), but containing a little dioxan ( $\nu_{\max}$  1125, 893, 877  $\text{cm}^{-1}$ ). From the bicarbonate solution was extracted (after acidification) a semi-crystalline acid (1.42 g.), consisting mainly of  $\alpha$ -hydroxy- $\alpha$ -methylbutyric acid ( $R_F$  0.35), with a little of the  $\alpha$ -acetoxy-acid ( $R_F$  0.51).

$\alpha$ -Acetoxy- $\alpha$ -methylbutyryl Bromide.— $\alpha$ -Acetoxy- $\alpha$ -methylbutyric acid (8.5 g.) was heated

<sup>7</sup> Bennett and Heathcoat, *J.*, 1929, 272.

<sup>8</sup> Bedos, *Compt. rend.*, 1926, 183, 562.

<sup>9</sup> Moggridge, *J.*, 1946, 1105.

<sup>10</sup> Dawson, *J. Amer. Chem. Soc.*, 1947, 69, 1211.

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with phosphorus tribromide (30 g.) under reflux on a steam-bath for 4 hr. Excess of reagent was removed at about 50° under reduced pressure, and the residue was distilled at 50—60°/0.4—0.8 mm. (yield 5.2 g., 44%). Redistillation gave the pure *acid bromide*, b. p. 50—51°/0.45 mm.,  $n_D^{20}$  1.4610 (Found: C, 38.1; H, 5.1; Br, 35.4.  $C_7H_{11}BrO_3$  requires C, 37.7; H, 4.5; Br, 35.9%).

*Reaction of  $\alpha$ -Acetoxy- $\alpha$ -methylbutyryl Bromide.*—(a) *With ethylene glycol.* The acid bromide (2.23 g., 10 mmoles) and glycol (0.62 g., 10 mmoles) were mixed below room temperature, and allowed to warm up whilst being shaken vigorously. An exothermic reaction occurred, with evolution of a little hydrogen bromide, and crystals of  $\alpha$ -hydroxy- $\alpha$ -methylbutyric acid separated. After 15 min. at room temperature, the mixture was dissolved in ether and washed with sodium bicarbonate solution; from the washings there was obtained in the usual way the hydroxy-acid (9.3 mmoles), m. p. and mixed m. p. 72°. The neutral product was an oil (1.1 g.) which nearly all distilled at 159° to give 2-bromoethyl acetate,  $n_D^{20}$  1.4555, identical (infrared spectrum) with an authentic sample (prepared by acetylating 2-bromoethanol), b. p. 159—160°,  $n_D^{20}$  1.4560 (lit.,<sup>11</sup> b. p. 162—163°).

(b) *With methanol and triethylamine.* The acid bromide (0.9 g., 4 mmoles) was allowed to react with a mixture of methanol (1.5 ml.) and triethylamine (0.5 ml.) for 10 min., in the way previously described<sup>1</sup> for the reaction of  $\alpha$ -acetoxy- $\alpha$ -methylbutyryl chloride. An oil was obtained (0.35 g., 5 mmoles),  $n_D^{20}$  1.4220, which (from its infrared spectrum) was mainly 5-ethyl-2,5-dimethyl-2-methoxy-1,3-dioxolan-4-one<sup>1</sup> ( $\nu_{\max}$ , *inter alia*, 1802, 1037, 1056, and 911  $cm^{-1}$ ), but contained some ester (weak band at 1740  $cm^{-1}$ ).

*$\alpha$ -Benzoyloxy- $\alpha$ -methylbutyric Acid and Chloride.*— $\alpha$ -Hydroxy- $\alpha$ -methylbutyric acid<sup>12</sup> (30 g.), and benzoyl chloride (50 ml.) were heated on a steam-bath under reflux for 3 hr. After the solution was cooled and diluted with light petroleum (b. p. 40—60°), the crystals (46 g.) were collected and washed with light petroleum, being a mixture of the  $\alpha$ -benzoyloxy-acid with benzoic acid, m. p. 93—105°. This crude material (20 g.) was heated under reflux with thionyl chloride (35 ml.) for 2.5 hr. The excess of reagent was removed under reduced pressure; benzene was added, and removed under reduced pressure. The residue, distilled *in vacuo*, yielded  $\alpha$ -benzoyloxy- $\alpha$ -methylbutyryl chloride (8 g.), b. p. 112°/0.5 mm.,  $n_D^{20}$  1.5155,  $\nu_{\max}$ . 1790, 1725  $cm^{-1}$  (acid chloride, ester) (Found: C, 59.9; H, 5.4; Cl, 14.8.  $C_{12}H_{13}ClO_3$  requires C, 59.9; H, 5.4; Cl, 14.8%).

The acid chloride was rapidly hydrolysed on being shaken with water, to give  $\alpha$ -benzoyloxy- $\alpha$ -methylbutyric acid, m. p. 136—137° (from aqueous ethanol),  $\nu_{\max}$ . 1725  $cm^{-1}$  (acid, ester) (Found: C, 65.0; H, 6.4.  $C_{12}H_{14}O_4$  requires C, 64.85; H, 6.3%).

*Reaction of  $\alpha$ -Benzoyloxy- $\alpha$ -methylbutyryl Chloride.*—*With ethylene glycol.* The acid chloride (2.4 g., 10 mmoles) and glycol (0.62 g., 10 mmoles) were allowed to react in the usual way. No hydrogen chloride was evolved;  $\alpha$ -hydroxy- $\alpha$ -methylbutyric acid crystallised. After 15 min. at room temperature, there were isolated the hydroxy-acid (8.6 mmoles), m. p. and mixed m. p. 69—71°, and 2-chloroethyl benzoate (1.85 g., theor. yield), b. p. 262—263°,  $n_D^{20}$  1.5270, identical (infrared spectrum) with an authentic specimen (prepared by benzoylating 2-chloroethanol; b. p. 262—263°,  $n_D^{20}$  1.5280 lit.,<sup>13</sup> b. p. 256—257°/752 mm.).

(b) *With methanol and triethylamine.* The acid chloride (10 mmoles), methanol (6 ml.), and triethylamine (2 ml.) were allowed to react in the usual way for 15 min. at room temperature. An oil (2.3 g., 9.7 mmoles) was obtained, which was distilled *in vacuo* to give 5-ethyl-2-methoxy-5-methyl-2-phenyl-1,3-dioxolan-4-one, b. p. 110—111°/0.7 mm.,  $n_D^{20}$  1.4939 (Found: C, 66.0; H, 6.6.  $C_{18}H_{16}O_4$  requires C, 66.1; H, 6.8%). The infrared spectrum had (*inter alia*) a single carbonyl band at 1802  $cm^{-1}$ , typical of this type of dioxolanone.<sup>1</sup>

*Reaction of Acetylmandelyl Chloride.*—(a) *With ethylene glycol.* The acid chloride<sup>14</sup> (2.125 g., 10 mmoles) and glycol (0.62 g., 10 mmoles) were shaken to an emulsion, which, on gently warming, underwent a vigorous reaction; some hydrogen chloride was evolved. After 30 min. at room temperature, the liquor was seeded with mandelic acid, and, with the addition of light petroleum (b. p. 30—40°), mandelic acid (1.1 g., 7.2 mmoles) was collected, m. p. and mixed m. p. 118—120° after one recrystallisation from ether—light petroleum. The filtrate, when washed with sodium bicarbonate solution, dried, and concentrated, yielded an oil (1.05 g.).

<sup>11</sup> Henry, *Rec. Trav. chim.*, 1901, **20**, 243.

<sup>12</sup> Young, Dillon, and Lucas, *J. Amer. Chem. Soc.*, 1929, **51**, 2532.

<sup>13</sup> Jones and Major, *J. Amer. Chem. Soc.*, 1927, **49**, 1527.

<sup>14</sup> Thayer, *Org. Synth.*, Coll. Vol. I, 2nd edn., p. 12.



At least one-half of this distilled readily under reduced pressure, giving 2-chloroethyl acetate,  $n_D^{20}$  1.4243, b. p. 144°/1 atm., identical (infrared spectrum) with an authentic sample. The residue after distillation was a syrupy ester ( $\nu_{\max}$  1740  $\text{cm}^{-1}$ ), b. p. >200° (decomp.),  $n_D^{20}$  1.5030.

(b) *With methanol and triethylamine.* The acid chloride (10 mmoles) was allowed to react with methanol and triethylamine in the way described for  $\alpha$ -benzoyloxy- $\alpha$ -methylbutyryl chloride. The product was methyl acetylmandelate (1.7 g., 8.1 mmoles),  $n_D^{20}$  1.4998, identical (infrared spectrum) with the ester prepared from acetylmandelic acid and diazomethane.

*Reactions of  $\beta$ -Acetoxypropionyl Chloride.*—The acid chloride<sup>15</sup> had b. p. 57–60°/0.1 mm.,  $n_D^{20}$  1.4380 (Found: Cl, 23.3. Calc. for  $\text{C}_5\text{H}_7\text{ClO}_3$ : Cl, 22.7%). With methanol and triethylamine, it gave only methyl  $\beta$ -acetoxypropionate, b. p. 191–192°,  $n_D^{20}$  1.4172,  $\nu_{\max}$  1735  $\text{cm}^{-1}$  (ester), identical (infrared spectrum) with an authentic specimen (from  $\beta$ -acetoxypropionic acid and diazomethane). The acid chloride reacted vigorously with ethylene glycol (copious evolution of HCl), to give a mixture of esters ( $\nu_{\max}$  1735  $\text{cm}^{-1}$ ), b. p. 170–>270°/1 atm. A gas chromatogram showed that 2-chloroethyl acetate (b. p. 145°) was not present in the crude mixture.

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<sup>15</sup> Gresham, Jansen, and Shaver, *J. Amer. Chem. Soc.*, 1948, **70**, 1003.