

25–45°C (in the case of *a*-chlorocyclohexyl acetate at 33–73°C) at diminished pressure and redistilled in an efficient distillation assembly. The resulting esters were colourless liquids which decomposed during a few hours or days to the acid chloride and ketone and turned yellow (it was found by a kinetic method that, *e.g.*, *ca.* 20% of a sample of *a*-chloro-*sec.*-propyl acetate decomposed in 6 h at room temperature and *ca.* 70% in 48 h at 0°C). It was not possible to distil all of them in a Todd distillation assembly and usually even the purest samples contained acid chloride and ketones as impurities. These impurities, however, did not interfere in the kinetic experiments (to be published later) for which the esters were prepared. The esters were in general more stable the larger the alkyl component and the smaller the acyl component.

For analysis, the esters were hydrolysed in water and the total amount of liberated acids was determined by titration with sodium hydroxide and the amount of the chloride ion by potentiometric titration with silver nitrate. The amounts are given as percentages of the theoretical amount. The yields of the esters varied from 5 (*a*-chloro-*sec.*-propyl esters) to 17% (*a*-chlorocyclohexyl acetate). The following esters were prepared:

a-Chloro-*sec.*-propyl acetate. From acetone (E. Merck AG., *pro analysi*) and acetyl chloride (BDH, Laboratory Reagent). B.p. 29–30°C/12 torr, n_D^{20} 1.4152, d_4^{20} 1.0662, $[R]_D$ 32.09 (calc. 4 31.59), acid 98%, chloride 94%.

a-Chloro-*sec.*-propyl propionate. From acetone and propionyl chloride (BDH, Laboratory Reagent). B.p. 28–30°C/6 torr, n_D^{20} 1.4205, d_4^{20} 1.0326, $[R]_D$ 36.95 (calc. 36.24), acid 94% chloride 97%.

a-Chloro-*sec.*-butyl acetate. From methyl ethyl ketone (Fluka AG., *puriss.*) and acetyl chloride. B.p. 31–34°C/6 torr, n_D^{20} 1.4247, d_4^{20} 1.0375, $[R]_D$ 37.09 (calc. 36.24), acid 90%, chloride 89%.

1-Chloro-1-ethylpropyl acetate. From diethyl ketone (BDH, Laboratory Reagent) and acetyl chloride. B.p. 50–52°C/7 torr, n_D^{20} 1.4293, d_4^{20} 1.0452, $[R]_D$ 40.63 (calc. 40.89), acid 98.1%, chloride 97.8%.

1-Chloro-1-methylbutyl acetate. From methyl propyl ketone (BDH, Laboratory Reagent) and acetyl chloride. B.p. 33–34°C/2 torr, n_D^{20} 1.4271, d_4^{20} 1.0261, $[R]_D$ 41.20 (calc. 40.91), acid 97.7%, chloride 98.7%.

1-Chloro-1,2-dimethylpropyl acetate. From methyl isopropyl ketone (BDH, Laboratory Reagent) and acetyl chloride. B.p. 38–

39°C/4.5 torr, n_D^{20} 1.4309, d_4^{20} 1.0309, $[R]_D$ 41.33 (calc. 40.92), acid 93.7%, chloride 93.6%.

a-Chlorocyclohexyl acetate. From cyclohexanone (BDH, technical) and acetyl chloride. B.p. 62–63°C/3 torr, n_D^{20} 1.4635, d_4^{20} 1.1208, $[R]_D$ 43.45 (calc. 43.37), acid 98.1%, chloride 98.2%.

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Favorsky Rearrangements

I. A New Synthesis of Isocrotonic Acid

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The preparation of isocrotonic acid has hitherto been a rather troublesome synthesis. The best method described was stereospecific *cis*-hydrogenation of tetrolic acid using a palladium catalyst¹ but, as many other acetylenic compounds, tetrolic acid is not simply prepared.^{2,3}

de Simó and McAllister⁴ reported in a patent that when 1,3-dichlorobutanone-2 was treated with a boiling saturated solution of sodium carbonate a mixture of crotonic and isocrotonic acids could be isolated in 46.6% yield. This is an example of the Favorsky rearrangement of a dihalogeno ketone. The authors did not separate the isomers.

Other examples of the above rearrangement were reported by Wagner and Moore who, in addition to other bromo ketones, treated 1,3-dibromo-3-methylpentanone-2

under Favorsky conditions.⁵ These authors reported that they obtained both geometric isomers of 3-methyl-2-pentenoic acid. The presently accepted theory of the Favorsky rearrangement of an α,α' -dihalogeno ketone predicts that both geometric isomers of the α,β -unsaturated acid are formed in about equal amounts.⁶

However, the first example of a Favorsky rearrangement, reported as early as 1880 by Demarcay, seems to have been neglected. He obtained only one of the possible geometric isomers, mesaconic acid, from the reaction of potassium hydroxide and 4,4-dibromo-2-methylacetoacetic ester.^{7,8} Another stereospecific Favorsky rearrangement was recently described by Kennedy, McCorkindale and Raphael.⁹ They obtained pure *cis*- α,β -unsaturated esters from the rearrangement of 1,1-dibromo methyl ketones.

In the present investigation 1,3-dibromobutanone-2 was treated with various bases under different conditions. Alkoxides, the most commonly used bases in Favorsky rearrangements, were found to react with the bromo ketone. The reaction could be followed by titration, but no detectable amounts of crotonic or isocrotonic esters could be isolated when the syntheses were worked up in the usual way.¹⁰

It was also found that weaker bases, *e.g.* alkali hydroxides, carbonates and even bicarbonates reacted with 1,3-dibromobutanone-2. The reaction was performed with excess base in aqueous medium at room temperature and was followed by titration. The reaction was in general complete after one to two hours, when about two equivalents of base had been consumed. The crude product, obtained by extracting the acidified solution with ether and evaporation of the ether, was analyzed by NMR before further purification. The spectrum showed that the product consisted solely of isocrotonic acid and no crotonic acid could be detected in contradiction to the accepted theory.⁶ In an authentic mixture of isocrotonic acid (95 %) and crotonic acid (5 %) two distinct CH_3 -doublets ($\delta = 1.70$, $\delta = 1.45$) could be found.

The yields of the crude product were found to vary with the base and the results are given in Table 1 together with the reaction time needed in each case. It is noteworthy that the yield seems to be dependent on both the cation and anion used. Regarding the anion, the yield seems to vary with the strength of the base.

Table 1.

Base	Reaction time (h)	Yield % ^a
NaOH	1/2	23
KOH	1/2	21
Na_2CO_3	1 1/2	64
K_2CO_3	1	57
Li_2CO_3	1 1/4	32
NaHCO_3	2 1/2	73
KHCO_3	2 1/2	77

^a Mean values of two determinations.

Carbonates gave about 40 % better yield than hydroxides and bicarbonates about 15 % better yields than carbonates. In general sodium salts gave higher yields than the corresponding potassium salts, but as seen in the table, the best yields were obtained when sodium or potassium bicarbonates were used. Lithium carbonate gave the lowest yield of the carbonates. As could be expected the reaction times needed also varied with the strength of the base, the stronger base, the shorter time. Carbonates are in general known to give high yields of hydroxyketones,¹¹ only in a few cases are carbonates or bicarbonates reported to give high yields of rearranged products.¹²⁻¹⁵

These variations of the Favorsky rearrangement of dibromoketones have not been previously recorded. In the rearrangement of 3-bromo-heptanone-2 Venus-Daniilowa has compared the effect of potassium, barium, and calcium carbonates.¹⁵ Although the yields of rearranged product were low (3–10 %) it could be seen that potassium carbonate gave the best yield in this case. Aston and Greenberg have studied the effect of different sodium alkoxides on the rearrangement of 3-bromo-3-methylbutanone-2.¹⁶

It is known from the literature that the purification of isocrotonic acid cannot be performed by distillation owing to isomerization to crotonic acid.¹⁷ However, when used immediately or stored at -15°C , the crude isocrotonic acid could be used for further synthetic work without any purification. At room temperature the isomerization soon started and after 1–2 days the large amounts of crotonic acid caused the product to crystallize. It was also found that in small portions (5–10 g) the crude acid could be distilled at 1 mm pressure without isomerization (b.p. 36°C).

The facile isomerization seems to explain why Simo and McAllister obtained both isomers in their synthesis.⁴

The best way of purifying isocrotonic acid was found to be recrystallization. When recrystallized as described in the experimental part, a sample could be held at 30°C in the dark for 3 weeks without any detectable isomerization. A NMR-spectrum of this recrystallized product is shown in Fig. 1.

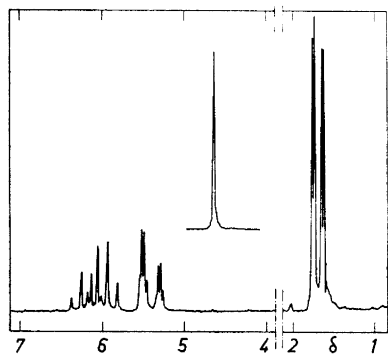


Fig. 1. NMR-spectrum of isocrotonic acid.

Preliminary results indicate that this method can be used as a standard procedure of synthesizing alifatic *cis*- α , β -unsaturated acids. Table 2 summarizes the acids prepared

Table 2.

Bromo ketone Acid

$\text{CH}_3\text{CHBrCOCH}_2\text{Br}$	$\begin{array}{c} \text{CH}_3 \\ \\ \text{C}=\text{C} \\ \quad \\ \text{H} \quad \text{COOH} \end{array}$
$\text{CH}_3\text{CH}_2\text{CHBrCOCH}_2\text{Br}$	$\begin{array}{c} \text{CH}_3\text{CH}_2 \\ \\ \text{C}=\text{C} \\ \quad \\ \text{H} \quad \text{COOH} \end{array}$
$\text{CH}_3(\text{CH}_2)_2\text{CHBrCOCH}_2\text{Br}$	$\begin{array}{c} \text{CH}_3\text{CH}_2\text{CH}_2 \\ \\ \text{C}=\text{C} \\ \quad \\ \text{H} \quad \text{COOH} \end{array}$
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH} \\ \\ \text{CH}_3 \end{array} \text{CHBrCOCH}_2\text{Br}$	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH} \\ \\ \text{CH}_3 \end{array} \begin{array}{c} \text{C}=\text{C} \\ \quad \\ \text{H} \quad \text{COOH} \end{array}$
$\text{CH}_3(\text{CH}_2)_3\text{CHBrCOCH}_2\text{Br}$	$\begin{array}{c} \text{CH}_3(\text{CH}_2)_3 \\ \\ \text{C}=\text{C} \\ \quad \\ \text{H} \quad \text{COOH} \end{array}$
$\text{CH}_3\text{CHBrCOCHBrCH}_3$	$\begin{array}{c} \text{CH}_3 \\ \\ \text{C}=\text{C} \\ \quad \\ \text{H} \quad \text{CH}_3 \end{array} \begin{array}{c} \text{COOH} \\ \\ \text{C} \\ \\ \text{H} \end{array}$

and the bromo ketones used. α,α' -Dibromo ketones can be prepared in good yields from the acid catalyzed bromination of the corresponding ketone.¹⁸

Experimental. 46.0 g of 1,3-dibromobutane-2¹⁸ were added to a solution of 0.3 mole of the required carbonate or 0.6 mole of the hydroxide in 450 ml of water, or 1.0 mole of the bicarbonate in 1 l of water, during 5 min. In the case of lithium carbonate a suspension of 0.5 mole (37 g) in 2 l of water was used. The mixture was thoroughly stirred and after about 1–2 h (see Table 1), when constant titration-values against methylorange were obtained, the solution was extracted with ether (2 \times 100 ml), acidified with dilute hydrochloric acid and again extracted with ether (6 \times 100 ml). After drying, the ether phase was evaporated *in vacuo* (water pump) to prevent superheating and isomerization. When the pressure had fallen to 10 mm, the last traces of ether were removed with an oil pump (0.4 mm) during 30 min. The yields of the crude products are given in Table 1.

13.0 g of the crude product were dissolved in 25 ml of petroleum ether at 5°C. When left at –15°C for some days, crystals separated which were filtered off at +5°C. 9.3 g of m.p. 12.5–14°C were obtained, $n_D^{25} = 1.4453$. Bourguel¹ gave m.p. 14°C and $n_D^{15} = 1.446$. The NMR-spectrum is given in Fig. 1. (Found: C 55.44; H 6.93. Calc. for $\text{C}_4\text{H}_6\text{O}_2$ (86.1): C 55.81; H 7.02.)

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Crystallographic Data on N,N,N',N'-Tetrakis(2-aminoethyl) ethylenediamine Pentahydrochloride = [Penten,5HCl], Hydroxy-Penten-Cobalt(III) Iodide and Hydroxy-Penten-Cobalt(III) Perchlorate

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Gauss, Moser and Schwarzenbach¹ prepared "penten", 5HCl in connection with investigations of metal complexes with polyamines. Crystallographic data on this compound (1) and on the cobalt(III) complexes [Co(OH)penten]I₂ (2) and [Co(OH)penten](ClO₄)₂ (3) were obtained from rotation and Weissenberg photographs recorded with CuK α radiation and from precession photographs recorded with

CuK α and MoK α radiation. The densities of the crystals were measured by the flotation method.

The crystals of all three compounds are monoclinic; from systematic absences (1) and (2) must have the space group $P2_1/c$ (No. 14, C_{2h}^5), although (3) has space group $P2$ (No. 3, C_2^1) or Pm (No. 6, C_s^1) the reflections $h0l$ with $l = 2n + 1$ and $0k0$ with $k = 2n + 1$ are very weak and so (2) and (3) are nearly isomorphous.

Detailed studies of these three compounds are in progress.

The crystals were kindly supplied by professor G. Schwarzenbach, Zürich.

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A Conversion of D-Glucose to D-Mannose under Acidic Conditions

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In an attempt to prepare D-mannofuranose pentaacetate, 2,3:5,6-di-O-isopropylidene-D-mannose was treated with a mixture of acetic acid, acetic anhydride and sulphuric acid at room temperature. When the deacetylated product was investigated by paper chromatography, however, it gave two spots, which corresponded to D-glucose and D-mannose. By fractionation of the mixture these two sugars were

Table 1.

	(1)	(2)	(3)
Formula	C ₁₀ H ₃₃ N ₆ Cl ₅	CoC ₁₀ H ₂₉ N ₆ OI ₂	CoC ₁₀ H ₂₉ N ₆ O ₉ Cl ₂
Formula wt.	414.7	562.2	507.2
D_m (g·ml ⁻¹)	1.34	2.07	1.71
D_x (g·ml ⁻¹)	1.35	2.07	1.71
Space group	$P2_1/c$	$P2_1/c$	
Z (calc.)	4	4	4
a (Å)	10.19	10.52	10.57
b (Å)	23.18	15.31	15.99
c (Å)	9.96	11.31	11.76
β (°)	120.0	98.4	98.4
V (Å ³)	2037	1802	1966