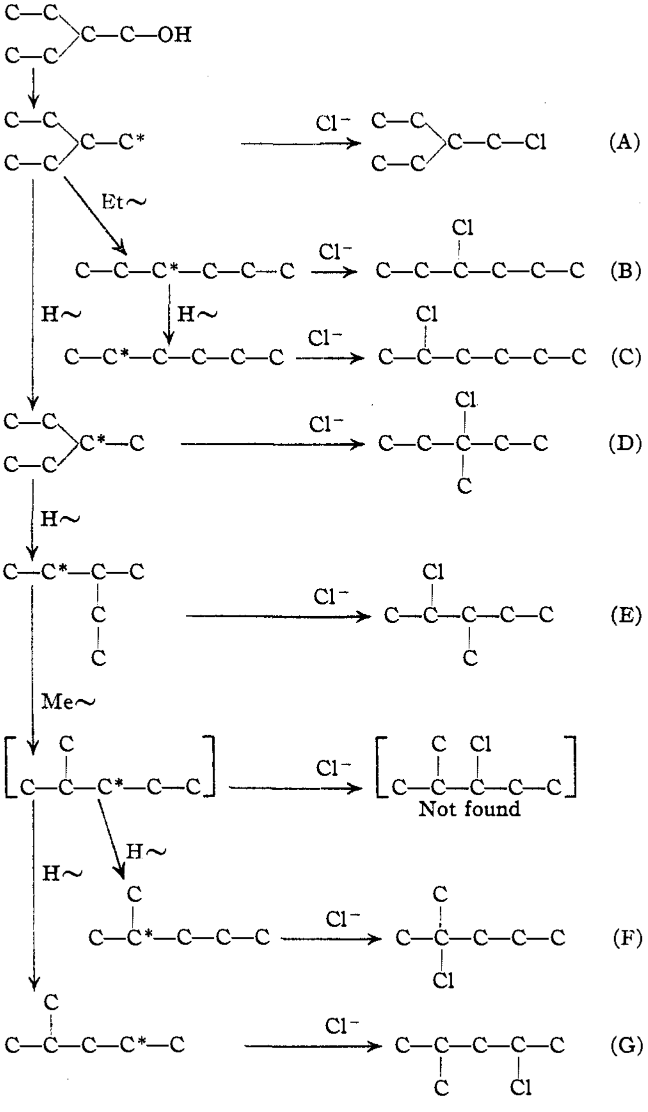
[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

Alkyl Chlorides Obtained from 2-Ethyl-1-butanol

BY FRANK C. WHITMORE AND F. A. KARNATZ

In connection with work in this Laboratory on the course of rearrangements,[1] it was decided to study the conversion of an alcohol of the type R_2CHCH_2OH to the corresponding chloride. While considerable work has been done on the rearrangement of hydrogen during the preparation of halides,[2] there are very few recorded cases of the rearrangement of the carbon skeleton during the replacement of hydroxyl by halogen.[3] Mainly rearranged halides were obtained from *t*-butyl- and *t*-butylmethyl-carbinols.[4] Wallis and Bowman[5] found no primary chloride in the product of the reaction of 2-methyl-2-phenyl-1-butanol with thionyl chloride. No instance of skeletal rearrangement during the preparation of halides from an aliphatic carbinol of the type R_2CHCH_2OH was found in the literature.

When 2-ethyl-1-butanol was treated with zinc chloride and hydrochloric acid,[6] a complex mixture of isomers was obtained in 70–80% yield. The presence of the following hexyl chlorides was established: (A) 2-ethyl-1-chlorobutane, (B) 3-chlorohexane, (C) 2-chlorohexane, (D) 3-methyl-3-chloropentane, (E) 3-methyl-2-chloropentane, (F) 2-methyl-2-chloropentane and (G) 4-methyl-2-chloropentane. The following mechanism based on the concepts current in this Laboratory[1] is given as a possible explanation of the formation of these products. The carbon with only 6 electrons is indicated as C*. The transitory existence is assumed for only one fragment for which the corresponding chloride was not found, namely, $(CH_3)_2CHC^*HCH_2CH_3$. There is strong evidence for its momentary presence in the finding of two chlorides, the structures of which can be derived from it by simple migration of hydrogen. The failure of the formation of a chloride $(CH_3)_2CHCHClCH_2CH_3$ agrees with results obtained by F. Johnston[7] of this Laboratory in which attempts to form chlorides of this type from the corresponding alcohol gave almost entirely the tertiary chloride analogous to (F).



It was necessary to determine whether these rearrangements took place chiefly during, rather than after, the replacement of hydroxyl by chlorine. This was accomplished by putting a

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(1) *Cf.* THIS JOURNAL, **54**, 3274 (1932).

(2) Brunel, *Ber.*, **44**, 1003 (1911); Michael and Zeidler, *Ann.*, **385**, 227 (1911); *ibid.*, **393**, 110 (1912); Shoesmith and Mackie, *J. Chem. Soc.*, 2336 (1928); Noller, THIS JOURNAL, **53**, 639 (1931).

(3) Demjanov, *J. Chem. Soc.*, **98**, 838 (1910); Kizhner, *J. Russ. Phys.-Chem. Soc.*, **40**, 994–1015; *ibid.*, **43**, 1157–1163; Favorskii, *ibid.*, **50**, 43–80 (1918).

(4) Whitmore and Rothrock, THIS JOURNAL, **54**, 3431 (1932); *ibid.*, **55**, 1106 (1933).

(5) Wallis and Bowman, *J. Org. Chem.*, **1**, 383 (1936).

(6) Compare Norris and Taylor, THIS JOURNAL, **46**, 753 (1924).

(7) Whitmore and Johnston, *ibid.*, **60**, 2265 (1938).

sample of pure 2-ethyl-1-chlorobutane through exactly the same treatment that gave the above mixture from the alcohol. While there was some isomerization of the chloride, over 70% of it was recovered unchanged.

No rearranged halides were obtained by treatment of 2-ethyl-1-butanol with thionyl chloride, 2-ethyl-1-chlorobutane of high purity being isolated in over 80% yield. This result is of interest in contrast to the work of Wallis and Bowman[5] and also to the behavior of neopentyl alcohol, which gives only a 4% yield of unrearranged chloride when treated with thionyl chloride and pyridine.[8]

Experimental

Purification of 2-Ethyl-1-butanol.—The 2-ethyl-1-butanol used in this research was kindly furnished by the Carbide and Carbon Chemicals Corporation. It was purified by two fractionations through an efficient column of the total condensation type,[9] 107 × 2.1 cm., packed with glass helices. A total of 4605 g. of pure carbinol, b. p. 145° (727 mm.) −146° (732 mm.), $n^{20}\text{D}$ 1.4220-1, d^{20}_4 0.8326, was obtained from 12,270 g. of the commercial material; yield 37.5%. This gave an α-naphthylurethan, m. p. 63.5–64.5°, which melted at 63–64.5° when mixed with the α-naphthylurethan, m. p. 63–64°, made from a known sample of 2-ethyl-1-butanol obtained by the hydrogenation of ethyl diethylacetate.[10]

Anal. Calcd. for $C_{17}H_{21}NO_2$: N, 5.17. Found: N, 5.22.

Treatment of 2-Ethyl-1-butanol with Thionyl Chloride.—The method of Darzens[11] was used. Addition of 167 g. (1.4 moles) of thionyl chloride to a solution of 102 g. (1 mole) of 2-ethyl-1-butanol in 79 g. (1 mole) of dry pyridine required two hours. The mixture was heated for three and one-half hours at 60–90°; sulfur dioxide was evolved. The crude product was washed with dilute hydrochloric acid, dried with anhydrous potassium carbonate and fractionated to give 99 g. of pure 2-ethyl-1-chlorobutane (82% yield), b. p. 88° (225 mm.), $n^{20}\text{D}$ 1.4230, d^{20}_4 0.8914. Conversion to the Grignard compound and treatment with oxygen gave 2-ethyl-1-butanol; α-naphthylurethan, m. p. and mixed m. p., 63–64°.

The only constants found[12] for 2-ethyl-1-chlorobutane are: b. p. 125–127°, $d^{23.5}_{23.5}$ 0.881. The compound was obtained in only 11% yield by the action of 45% hydrochloric acid in a sealed tube at 100°. Rothstein[13] treated 2-ethyl-1-butanol with thionyl chloride and pyridine but gave no data for the product.

Treatment of 2-Ethyl-1-butanol with Hydrochloric Acid and Zinc Chloride.—Many runs were made in order to obtain sufficient product for fractionation; a typical run by our technique is described. One mole, 102 g., of 2-ethyl-1-butanol was added to a solution of 1.25 moles, 171 g., of fused zinc chloride in 2 moles, 202 g., of concentrated hydrochloric acid in a 3-necked flask fitted with a reflux condenser, mercury-seal stirrer, and gas inlet tube leading to the bottom of the flask. The flask was heated in a bath to 80–85° for six and one-half hours. A slow stream of hydrogen chloride was passed into the mixture for the last four hours.

The dark halide layer was separated and washed with 15 cc. of water and 10 cc. of 10% sodium carbonate solution; the color faded markedly on washing. The product was dried with anhydrous sodium sulfate and anhydrous potassium carbonate, and was fractionated from fresh carbonate at 160 mm. pressure to give several fractions.

Fraction	Wt., g.	B. p. (160 mm.), °C.	$n^{20}\text{D}$
1	9.0	56–67.7	1.4155
2	16.3	67.7–68.5	1.4180
3	16.6	68.5–69.5	1.4190
4	10.0	69.5–69.6	1.4196
5	14.9	69.6–70.5	1.4198
6	7.4	70.5–71.6	1.4198
7	5.9	71.6–72.7	1.4198
8	7.0	72.7–74.0	1.4195
9	6.5	74.0–75.0	1.4195
10	6.2	75.0–76.5	1.4192
11	3.0	?	1.4198
12	3.0	Residue	
	105.8		

The yield of mixed hexyl chlorides, b. p. 67.7–76.5° (160 mm.), was 90.8 g., or 75%.

The fractions from five such runs were refractionated by parts three times at 160 mm. pressure. In the final distillation, referred to as Distillation B, 297 g. of chlorides was separated into 44 fractions.

Identification of 2-Methyl-2-chloropentane (F).—Fraction 2 from Distillation B, 5.3 g., b. p. 63.5–64.0° (160 mm.), $n^{20}\text{D}$ 1.4138, was converted to the Grignard reagent and this was treated with phenyl isocyanate in ether solution. The dimethyl-*n*-propylacetanilide was identified by m. p. and mixed m. p. 70.5–74°.

Anal. Calcd. for $C_{13}H_{19}NO$: N, 6.84. Found: N, 6.89.

The known sample was prepared in the same way from known 2-methyl-2-chloropentane, b. p. 64.5–64.7° (160 mm.), $n^{20}\text{D}$ 1.4126, obtained by the action of hydrochloric acid on the corresponding carbinol.

Similarly, fraction 4 from Distillation B, 4.8 g., b. p. 64.7–65.5° (160 mm.), $n^{20}\text{D}$ 1.4140, was converted to the Grignard reagent and this was treated with α-naphthyl isocyanate. The α-naphthalide of dimethyl-*n*-propylacetic acid was identified by m. p. and mixed m. p. 116–118°.

Anal. Calcd. for $C_{17}H_{21}NO$: N, 5.49. Found: N, 5.35.

Identification of 4-Methyl-2-chloropentane (G).—Fractions 9–14 from Distillation B, 35.9 g., b. p. 65.5–67.5° (160 mm.), $n^{20}\text{D}$ 1.4150–74, were converted to the Grignard reagent and this was treated with oxygen. The crude product remaining after distillation of the ether was heated with a few crystals of iodine[14] to dehydrate any tertiary

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(8) Whitmore and Karnatz, unpublished work.

(9) Whitmore and Lux, THIS JOURNAL, **54**, 3451 (1932); Wilson, Parker and Laughlin, *ibid.*, **55**, 2795 (1933).

(10) Kindly done by Prof. Homer Adkins of the University of Wisconsin.

(11) Darzens, *Compt. rend.*, **152**, 1314 (1911).

(12) Fourneau and Matti, *J. pharm. chim.*, [8] **14**, 513 (1931).

(13) Rothstein, *Bull. soc. chim.*, [5] **2**, 83 (1935).

(14) Hibbert, THIS JOURNAL, **37**, 1748 (1915).

carbinols. The residue was dried and was distilled from an 8-cc. distilling flask to obtain a fraction, weight 1.4 g., b. p. 115–128° (734 mm.), n^{20}D 1.4140. The α-naphthylurethan prepared from this material was found to melt at 94–95° after 2 crystallizations from ligroin and one from dilute alcohol. A mixture with the known α-naphthylurethan of 4-methyl-2-pentanol[15] of m. p. 93.5–94.5°[16] melted at 93.5–95°.

Another sample of crude carbinol, weight 1.68 g., b. p. 100–130° (735 mm.), was obtained in the same way from a similar cut of mixed chlorides, weight 65.0 g., b. p. 65.5–68.0° (160 mm.), n^{20}D 1.4158–80, from another distillation. This carbinol was oxidized to 4-methyl-2-pentanone with sulfuric acid and dichromate; semicarbazone, m. p. and mixed m. p. 127–131°. The known derivative was obtained from the ketone, b. p. 111–113° (738 mm.), n^{20}D 1.3967, prepared by the oxidation of synthetic 4-methyl-2-pentanol, b. p. 131° (738 mm.), n^{20}D 1.4111.

Identification of 3-Methyl-3-chloropentane (D).—A sample of chlorides from the fractionation before Distillation B, b. p. 69.5° (160 mm.), n^{20}D 1.4202, was converted to the Grignard reagent and this was treated with phenyl isocyanate. Purification gave crystals melting at 86.5–88.5°. A mixture with methyldiethylacetanilide of m. p. 87.5–89° similarly prepared from known 3-methyl-3-chloropentane[17] melted at 86.5–88.5°.

Anal. Calcd. for $C_{13}H_{19}NO$: N, 6.84. Found: N, 7.01.

Identification of 3-Methyl-2-chloropentane (E).—Fractions 29, 31 and 32 of mixed chlorides from Distillation B, wt. 22.9 g., b. p. 71.1–73.3° (160 mm.), n^{20}D 1.4198–201, were converted to the Grignard reagent and this was treated with oxygen. The crude carbinols were heated with a crystal of iodine[14] for two and one-half hours. The residue was dried and fractionated: (Distillation C).

Fraction	Wt., g.	B. p., °C.	Press., mm.	n^{20}D
1	0.9	51–110	735	1.3900
2	1.2	128–132	735	1.4166
3	2.8	132–133	735	1.4188
4	1.4	?	Reduced	1.4190
5	1.3	Residue		

Yield of secondary hexanols was 5.4 g., or 28% of the theoretical. The α-naphthylurethan prepared from fraction 3 was found to melt at 72–72.5° after four crystallizations from ligroin and one from dilute alcohol. A mixture with a known sample of the α-naphthylurethan of 3-methyl-2-pentanol of m. p. 74.5–75.5°[18] melted at 72–75°. The known specimen was obtained from synthetic 3-methyl-2-pentanol, b. p. 132–132.5° (726 mm.), n^{20}D 1.4206.

A 1-cc. sample of fraction 3 of the above hexanols was oxidized to the ketones, which were fractionated and converted to 2,4-dinitrophenylhydrazones. A series of crystallizations of these from dilute alcohol gave first the impure derivative for hexanone-3 and then, from the mother liquor, the 2,4-dinitrophenylhydrazone of 3-methyl-2-pentanone, m. p. 67–71°. A mixture with a known sample, m. p. 70.5–72.5°,[19] prepared from a sample of ketone made by oxidation of the synthetic carbinol, melted at 69–72°.

By the same methods, fractions 33–36 of mixed chlorides from Distillation B, 23.9 g., b. p. 69.5–74.5° (160 mm.), n^{20}D 1.4188–94, were converted to the ketones. These were shaken with 15 cc. of a saturated solution of sodium bisulfite (to remove 2-hexanone, see below), and the addition compound was separated from uncombined ketones by dissolving it in water and extracting this solution with ether. The ether solution yielded a *m*-nitrobenzoylhydrazone melting at 143.5–144.5°. A mixture with a sample of m. p. 145–146° obtained from the known 3-methyl-2-pentanone melted at 144–145°.

Anal. Calcd. for $C_{13}H_{17}N_3O_3$: N, 15.99. Found: N, 15.97.

Identification of 3-Chlorohexane (B).—Fractions 37, 39, 41 and 42 of mixed chlorides from Distillation B, 24.8 g., b. p. 73.5–76.5° (160 mm.), n^{20}D 1.4187, were converted to the carbinols through the Grignard reagent. Fractionation gave (Distillation D): 1–2, 2.2 g., 34–123° (732 mm.), n^{20}D 1.370; 3–4, 3.5 g., 124–133.5°, 1.4144–1.4178; 5–6, 5.8 g., 133.5–141°, 1.4186; residue, 1.8 g.

Fractions 4 and 5 failed to give an α-naphthylurethan. The remaining portions of fractions 2, 3 and 4 from Distillation C (described under 3-methyl-2-chloropentane) and fractions 4, 5 and 6 above were combined and oxidized to the ketones. Fractionation gave at 730 mm. (Distillation E): 1, 1.2 g., 67–113°, 1.3978; 2, 1.3, 113–117°, 1.4010; 3, 1.7, 117–124°, 1.4030; 4, 1.0, 124–126°, 1.4080; residue, 1.1 g.

Fraction 2 gave the 2,4-dinitrophenylhydrazone of 3-hexanone, m. p. and mixed m. p., 146.5–148.5°.

Anal. Calcd. for $C_{12}H_{16}N_4O_4$: N, 20.00. Found: N, 19.89.

The known specimen was prepared from the ketone obtained by the oxidation of synthetic (Grignard) 3-hexanol, b. p. 133–134° at 740 mm.

All of the material of the proper boiling range obtained from Distillation B was consumed in unsuccessful attempts to isolate a second derivative for 3-chlorohexane. Hence, it was necessary to make 4 additional runs of 2-ethyl-1-butanol with hydrochloric acid and zinc chloride and to refractionate the hexyl chlorides by parts through column A. A sample of these chlorides, weight 60.1 g., b. p. 74–76° (160 mm.), n^{20}D 1.4190–97, was converted to carbinols through the Grignard reagent. These were dried and fractionated at 734 mm. pressure to give 5 fractions, 33.2 g., b. p. 131–145° (734 mm.), n^{20}D 1.4176–1.4210. The carbinols were oxidized to the ketones, washed with sodium bisulfite solution and fractionated. A fraction was obtained, 0.9 g., 110° (733 mm.), n^{20}D 1.4010, which gave the semicarbazone of 3-hexanone, m. p. and mixed m. p., 110.5–111.5°.

Identification of 2-Chlorohexane (C).—Fraction 4 of the ketones from Distillation E (described under 3-chlorohexane) gave the 2,4-dinitrophenylhydrazone of 2-hexanone, m. p. and mixed m. p., 106–107°.

The aqueous solution of the sodium bisulfite addition compound described under the identification of 3-methyl-2-

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(15) Kindly furnished by F. Johnston of this Laboratory.

(16) Levene and Walti, *J. Biol. Chem.*, **94**, 869 (1931) give m. p. 86–89°; Brooks, THIS JOURNAL, **56**, 1999 (1934), gives m. p. 87–88°.

(17) Kindly furnished by D. E. Badertscher of this Laboratory.

(18) Cottle and Powell, THIS JOURNAL, **58**, 2270 (1936), give 72°.

(19) Drake and Veitch, *ibid.*, **57**, 2624 (1935), give 71.2°.

chloropentane was made alkaline with sodium carbonate and the liberated ketone was distilled. The semicarbazone prepared from this melted at 122–123.5°. A mixture with the known semicarbazone of 2-hexanone of m. p. 124–125° melted at 122.5–124°.

Identification of 2-Ethyl-1-chlorobutane (A).—Fraction 7 of the hexanols from Distillation D (described under 3-chlorohexane) gave the α-naphthylurethan of 2-ethyl-1-butanol, m. p. and mixed m. p. 63–64°.

Fraction 43 of the mixed chlorides from Distillation B, 13.5 g., b. p. 76.5–77.5° (160 mm.), n^{20}D 1.4198, was shaken with 50 cc. of normal aqueous silver nitrate solution for three hours at room temperature to remove secondary and tertiary halides. The organic material was distilled from the mixture, separated, washed with carbonate solution, dried and fractionated. Treatment of the Grignard reagent with phenyl isocyanate gave crystals melting at 80.5–81.5°. Mixture with a known sample of β-ethylvaleranilide of m. p. 83–84° melted at 80.5–82.5°. The known specimen was prepared in the same way from a sample of 2-ethyl-1-chlorobutane made by the action of thionyl chloride on the carbinol.

Anal. Calcd. for $C_{15}H_{19}NO$: N, 6.84. Found: N, 6.93.

The other fractions were studied without obtaining any evidence for the presence of chlorides other than the seven identified.

Treatment of 2-Ethyl-1-chlorobutane with Zinc Chloride in Hydrochloric Acid.—One mole, 120.5 g., of 2-ethyl-1-chlorobutane, n^{20}D 1.4228–30, prepared by the action of thionyl chloride and pyridine on 2-ethyl-1-butanol, was stirred vigorously with a solution of 1.25 moles, 171 g., of fused zinc chloride in 2 moles, 202 g., of concentrated hydrochloric acid at 79–87° for seven hours. The halide layer was separated, washed with water and carbonate solution, dried and fractionated. The yield of chlorohexanes recovered was 108.6 g., or 90.0% of the starting material. The yield of unchanged 2-ethyl-1-chlorobutane was 86.1 g.; this is 71.4% of the starting material and 79.2% of the recovered halides. The remainder was rearranged hexyl chlorides.

Approximation of the Percentage of Individual Hexyl Chlorides Present.—Only a rough estimate, based on fractionation data, can be given. 3-Methyl-3-chloropentane (D), present in 35–40% yield, was the most abundant isomer. 2-Chlorohexane (C), 2-methyl-2-chloropentane (F) and 3-methyl-2-chloropentane (E) were present in 5–10%; the remaining isomers, 1–5% each. It is quite possible that other hexyl chlorides, present in smaller quantities, were not identified.

Summary

1. 2-Ethyl-1-chlorobutane is produced by the action of thionyl chloride and pyridine on 2-ethyl-1-butanol without any detectable rearrangement.

2. The action of zinc chloride in hydrochloric acid solution on 2-ethyl-1-butanol gives at least seven different chlorohexanes, namely, 3-methyl-3-chloropentane, 2-methyl-2-chloropentane, 3-methyl-2-chloropentane, 4-methyl-2-chloropentane, 3-chlorohexane, 2-chlorohexane, and 2-ethyl-1-chlorobutane.

3. At least the major part of the rearrangements occurred during the formation of the chlorides.

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Preparation and Properties of 2- and 3-Chloropentanes

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Much work has been done on the secondary chlorides and bromides of *n*-pentane.[1] In the present study, it was found that both 2-pentanol and 3-pentanol gave mixtures of 2- and 3-chloropentanes even with as mild treatment as the action of hydrogen chloride gas at room temperature. The amount of rearrangement was considerably less with 2-pentanol.

In order to obtain pure samples of 2- and 3-chloropentanes for the determination of physical constants, it was necessary to use thionyl chloride in the presence of pyridine.[2] There is evidence[3] that this reaction gives least rearrangement. Samples of the two chlorides were obtained, the properties of which showed a maximum difference; namely, for 2-chloropentane, n^{20}D 1.4069 and d^{20}_4 0.8695, and for 3-chloropentane, n^{20}D

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(1) Wagner and Saizew, *Ann.*, **179**, 321 (1875); Przewalski, *J. Russ. Phys.-Chem. Soc.*, **41**, 464–469 (1909); Clough and Johns, *Ind. Eng. Chem.*, **15**, 1032 (1923); Norris and Taylor, THIS JOURNAL, **46**, 753 (1924); Grignard and Ono, *Bull. soc. chim.*, [4] **39**, 1589 (1926); Norris and Reuter, THIS JOURNAL, **49**, 2630 (1927); Sherrill, Otto and Pickett, *ibid.*, **51**, 3027 (1929); Sherrill, Baldwin and Haas, *ibid.*, **51**, 3036 (1929); Ayres, *Ind. Eng. Chem.*, **21**, 899 (1929); Boord and Soday, THIS JOURNAL, **55**, 3296 (1933); Tabern and Volwiler, *ibid.*, **56**, 1139 (1934); Shonle, *ibid.*, **56**, 2490 (1934); Hass and Weber, *Ber.*, **67**, 974 (1934); Underwood and Gale, THIS JOURNAL, **56**, 2118 (1934); Lauer and Stodola, *ibid.*, **56**, 1215 (1934); Hass, McBee and Weber, *Ind. Eng. Chem.*, **27**, 1190 (1935); Hass and Weber, *Ind. Eng. Chem., Anal. Ed.*, **7**, 231 (1935).

(2) (a) Darzens, *Compt. rend.*, **152**, 1314 (1911); (b) Clark and Streight, *Trans. Roy. Soc. Can.*, **23**, 77 (1929).

(3) McKenzie and Clough, *J. Chem. Soc.*, **103**, 687 (1913); Gilman and Harris, *Rec. trav. chim.*, **50**, 1052 (1931); Kirner, THIS JOURNAL, **50**, 1958 (1928); Ref. 2a; also, unpublished work in this Laboratory.