wave for tripositive antimony reveals a somewhat more complicated situation than with arsenic. The slope of the E vs. log $i/(i_d - i)$ plot gives a straight line in all cases with a slope which varies from 0.047 to 0.037 as the hydroxide ion concentration increases from 1.0 to 10.0 moles/l. These slopes are high compared to 0.030 characteristic of a reversible 2 electron change. Raising the temperature to 40° failed to alter the slope beyond the limits of experimental error, indicating the spread wave does not result from a high activation energy for the reaction. The half-wave potential varies with the molal activity of potassium hydroxide in manner characteristic of a reversible 2 electron change involving two hydroxide ions as shown in Fig. 5. Also shown in Fig. 5 is the effect of a 10° rise in temperature on the half-wave potentials in 1 M and 10 M KOH. At 30°

$$E_{1/2} = -0.453 - 0.060 \log a_{\mathrm{OH}^-} \text{ vs. S.C.E.}$$

The small negative shift with increasing temperature is characteristic of a reversible process. Whitney and Davidson[8] have shown that the complexes $SbCl_4^-$ and $SbCl_6^-$ interact to give a colored complex in strong hydrochloric acid. It would seem possible then that the corresponding hydroxy complexes, if formed, would interact. Such interaction would serve to decrease the concentrations of $Sb(OH)_4^-$ and $Sb(OH)_6^-$ at the surface of the mercury drop in such a way as to spread the wave out, increasing the slope of the E vs. log $i/(i_d - i)$ plot as observed. Solutions of high ionic strength might be expected to cut down interaction and the plot should show a trend toward a reversible slope with increasing ion strength as it does. The reaction $2OH^- + Sb(OH)_4^- \rightarrow Sb(OH)_6^- + 2e$ satisfies the dependence of $E_{1/2}$ on hydroxide ion activity. Since pentavalent antimony is not reduced under these conditions it would seem likely that the form produced by the oxidation would be an unusual form not normally encountered in solution. Pauling[9] and Beintema[10] have shown the existence of salts of $Sb(OH)_6^-$ but the species has not heretofore been identified in solution where it may polymerize to an irreducible form. Many other equations involving two hydroxide ions and two electrons are of course possible, but the correlation of the reaction given with other known phenomena of antimony complexes seems to favor it in the author's opinion. This proposed mechanism is very tentative and confirmation or rejection must wait on data from other types of experiments if such are possible.

Figure 3 shows that the 2nd antimony wave which is cathodic is 3/2 the height of the first as found by Kolthoff and Probst. The plot of E vs. $i/(i_d - i)$ for this wave gives a straight line with a slope of 0.076—nearly four times the value for a reversible 3 electron change. The small wave following may be partial reduction to stibine.

Summary.—This paper describes the nature of the chloroantimonous complex and the participation of hydroxide in the polarographic oxidation of arsenite and antimonite solutions. In addition it introduces a new technique of plotting $E_{1/2}$ vs. molal activities of ions involved in the reaction as a means for studying complexes in solutions of strong acids and bases at concentrations above 1 molal.

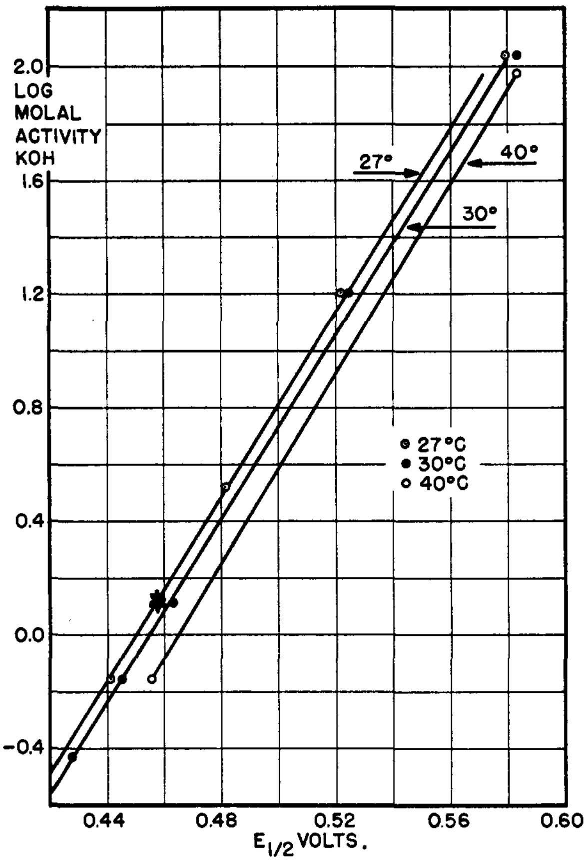

Fig. 5.—Oxidation of stibnite in KOH: *, in NaOH at 27°.

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[8] J. Whitney and N. Davidson, THIS JOURNAL, **71**, 3809 (1949).

[9] L. Pauling, *ibid.*, **55**, 1895 (1933).

[10] J. Beintema, *Rec. trav. chim.*, **56**, 931 (1937).

The Reaction of Methanesulfonyl Chloride with Alcohols in the Presence of Pyridine

BY C. R. NOLLER, C. A. LUCHETTI, E. M. ACTON AND R. A. BERNHARD

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The reaction of methanesulfonyl chloride with an alcohol in the presence of pyridine might be expected to yield either the alkyl methanesulfonate or the alkyl chloride. As subsequent reactions the pyridine may remove methanesulfonic acid from the ester or hydrogen chloride from the alkyl chloride to give the olefin, or may form alkylpyridinium salts.

The reaction of methanesulfonyl chloride with an alcohol in the presence of pyridine at room temperature or below is the usual method for preparing alkyl methanesulfonates.[1] 1-Hydroxy-2-octyne does not yield the ester by this procedure, but a

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[1] V. C. Sekera and C. S. Marvel, THIS JOURNAL, **55**, 345 (1933); M. Zief, H. G. Fletcher and H. R. Kirshen, *ibid.*, **68**, 2743 (1946); M. F. Clarke and L. N. Owen, *J. Chem. Soc.*, 315 (1949); 2103, 2108 (1950).

poor yield of the chloride is obtained.[2] A double bond can be introduced into triterpenes by heating methanesulfonates with pyridine.[3]

The present work was undertaken to determine whether the decomposition of alkyl methanesulfonates by heating with pyridine may be used as a general method for preparing olefins. For this purpose the ester was not isolated, but the methanesulfonyl chloride merely was added to the alcohol in the presence of an excess of pyridine, and the resulting mixture heated.

The standard procedure adopted was the addition of 0.2 mole of methanesulfonyl chloride slowly with stirring to a solution of 0.2 mole of the alcohol in 0.4 mole of dry pyridine under a reflux condenser. During the addition the heat of reaction caused the mixture to boil. After the addition the mixture was heated on the steam-bath for 30 minutes, allowed to cool, and decomposed with water. The organic layer was separated, washed with dilute hydrochloric acid and water, dried over sodium sulfate, and distilled at 15 mm. until the residue in the flask began to decompose. A cold trap was inserted between the condenser and the vacuum pump. The distillate then was fractionated at atmospheric pressure into the lower-boiling fraction of olefin and a higher-boiling fraction, which consisted of a mixture of the chloride and, depending on the difference in the boiling points, more or less unreacted alcohol. The chloride was purified by washing with cold concentrated sulfuric acid, then with water, drying, and distilling. The olefins and halides were identified by their boiling points and refractive indexes. 2-Chloroöctane was characterized further by conversion through the Grignard reagent to the anilide of 2-methyloctanoic acid. The results are summarized in Table I.

TABLE I

Alcohol used	Yield of products, % Olefin	Chloride	Alcohol used	Yield of products, % Olefin	Chloride
n-Hexyl alcohol	0	59	*n*-Butyl alcohol	..	58
2-Octanol	24	28	*s*-Butyl alcohol	..	40
2-Methyl-2-heptanol	56	0	*t*-Butyl alcohol	..	0
Cyclohexanol	29	18	*i*-Butyl alcohol	..	53

For the four higher alcohols, which were chosen for the initial work because the olefins could be isolated readily, the primary alcohol gives chiefly chloride, the secondary alcohols about equal amounts of chloride and olefin, and the tertiary alcohol chiefly olefin. The butyl alcohols behave similarly since, although no attempt was made to isolate the olefins, the yield of chloride decreases from primary, to secondary to tertiary. It is of interest to note that whereas *n*-butyl alcohol is reported[1] to give a 79% yield of ester at 0°, at temperatures in the neighborhood of 100° a 58% yield of the chloride is obtained.

Although not recorded in the table, the behavior of pinacolyl alcohol also was investigated. The yield of isolable products was very low. About 14% of olefins and 4% of chloride were obtained, the remainder being high-boiling material. The olefins boiled in the range 38–73°, and fractionation and color reactions with tetranitromethane indicated that the mixture contained *t*-butylethylene, *unsym*-methylisopropylethylene and tetramethylethylene, and hence was similar to that obtained by the acid-catalyzed dehydration of pinacolyl alcohol.[4] Thus although an excess of pyridine was present at all times, a mixture of rearranged olefins was produced.

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[2] R. A. Raphael and F. Sondheimer, *J. Chem. Soc.*, 2101 (1950).

[3] F. A. Alves, Ph.D. Thesis, Stanford University, 1950; C. R. Noller and P. J. Hearst, THIS JOURNAL, **72**, 625 (1950).

[4] K. C. Laughlin, C. W. Nash and F. C. Whitmore, *ibid.*, **56**, 1395 (1934).

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Substituted Alkyltrimethylammonium Bromides

BY NORMAN RABJOHN AND P. D. STRICKLER[1]

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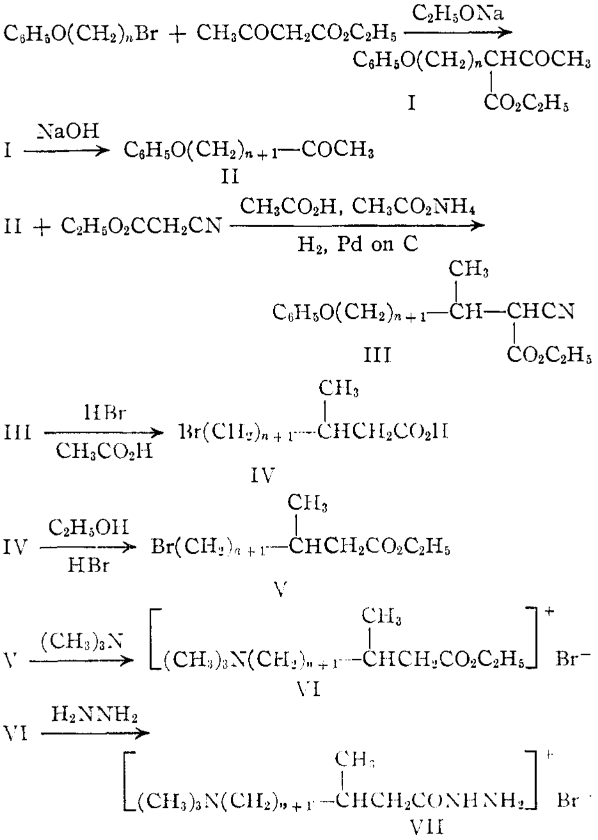
It is known that branched chain fatty acids, hydrazides and quaternary ammonium salts possess properties of physiological significance and it appeared to be of interest to combine all of these functions in a single molecule.

The present work describes the methods of preparation of two such compounds as well as some related substances. The synthetic scheme employed is summarized by the equations



$$C_6H_5O(CH_2)_nBr + CH_3COCH_2CO_2C_2H_5 \xrightarrow{C_2H_5ONa} \underset{\text{I}}{C_6H_5O(CH_2)_nCH(CO_2C_2H_5)COCH_3}$$

$$\text{I} \xrightarrow{NaOH} \underset{\text{II}}{C_6H_5O(CH_2)_{n+1}—COCH_3}$$

$$\text{II} + C_2H_5O_2CCH_2CN \xrightarrow[H_2,\ Pd\ on\ C]{CH_3CO_2H,\ CH_3CO_2NH_4} \underset{\text{III}}{C_6H_5O(CH_2)_{n+1}—\overset{CH_3}{\overset{|}{C}}H—CH(CO_2C_2H_5)CN}$$

$$\text{III} \xrightarrow[CH_3CO_2H]{HBr} \underset{\text{IV}}{Br(CH_2)_{n+1}—\overset{CH_3}{\overset{|}{C}}HCH_2CO_2H}$$

$$\text{IV} \xrightarrow[HBr]{C_2H_5OH} \underset{\text{V}}{Br(CH_2)_{n+1}—\overset{CH_3}{\overset{|}{C}}HCH_2CO_2C_2H_5}$$

$$\text{V} \xrightarrow{(CH_3)_3N} \underset{\text{VI}}{\left[(CH_3)_3N(CH_2)_{n+1}—\overset{CH_3}{\overset{|}{C}}HCH_2CO_2C_2H_5\right]^+ Br^-}$$

$$\text{VI} \xrightarrow{H_2NNH_2} \underset{\text{VII}}{\left[(CH_3)_3N(CH_2)_{n+1}—\overset{CH_3}{\overset{|}{C}}HCH_2CONHNH_2\right]^+ Br^-}$$

where n = 3 and 5.

The ω-phenoxy bromides were prepared by conventional procedures and caused to react with ethyl acetoacetate in the usual fashion. The resulting substituted acetoacetic esters underwent a facile hydrolysis to give the desired methyl ketones. The method of Cope and Alexander[2] was used to convert these to the α-cyano-β-methyl-ω-phenoxy

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[1] Abstracted in part from a thesis submitted by P. D. Strickler to the Graduate College of the University of Missouri, 1951, in partial fulfillment of the requirements for the Degree of Master of Arts.

[2] A. C. Cope and E. R. Alexander, THIS JOURNAL, **66**, 886 (1944).