viscous oil gradually separated out. After two hours separation ceased and this was taken as the end of the reaction. The resulting product was an amber-yellow viscous oil which adhered to the walls of the flask. The alcoholic solution was poured off, the oil washed repeatedly with alcohol and then dissolved with warming in carbon disulfide. After cooling and distilling off part of the solvent, the substance separated in crystalline form. In order to obtain a more complete separation an equal volume of benzene may be added to the solution; yield 20 g. or 51% of the theoretical. After recrystallization from benzene and drying in a vacuum desiccator, the melting point was 114°.

Anal. Calcd. for C_2H_2ClSAs: As, 44.49; Cl, 21.05; S, 19.03. Found: As, 44.55; Cl, 21.06; S, 19.27.

β-Chlorovinylarsine sulfide crystallizes in cubes, possesses a pale yellow color and a weak, not unpleasant, odor; is easily soluble in carbon disulfide, less so in benzene and ether and insoluble in water. Under the influence of sunlight the substance acquires an orange color.

MOSCOW, U. S. S. R. S. L. WARSCHAWSKI

RECEIVED JULY 17, 1935

THE ISOLATION OF CROTYL AND METHYLVINYLCARBINYL BROMIDES

Sir:

The composition of bromide mixtures arising from the action of hydrogen bromide and phosphorus tribromide on crotyl alcohol or methylvinylcarbinol has been the subject of much discussion. Some claim that pure products [Charon, *Ann. chim. phys.*, [7] **17,** 216 (1899); Prévost, *Ann. chim.*, **10,** 113 (1928); Claisen and Tietze, *Ber.*, **59B,** 2344 (1926); Juvala, *Ber.*, **63B,** 1989 (1930)] are obtained from alcohols of this type while others report the formation of mixtures of bromides but have not separated them [Baudrenghien, *Bull soc. chim. Belg.*, **31,** 160 (1922); Meisenheimer and Link, *Ann.*, **479,** 211 (1930); Young and Prater, This Journal, **54,** 404 (1932); Gredy and Piaux, *Bull. soc. chim.*, [5] **1,** 1481 (1934)]. The bromides obtained in this Laboratory have always been mixtures. We have recently separated these mixtures into the primary (crotyl bromide) and secondary (methylvinylcarbinyl bromide) isomers by fractional distillation at 0°. The properties are $n^{23}\text{D}$ 1.4805 and 1.4612; d^{25}_4 1.3335 and 1.2998; b. p. 49° and 31.0° at 93 mm., >107° and 86.5° at 760 mm., and +2.0° at 5 mm. and −2.0° at 14 mm. for the primary and secondary isomers, respectively. Mixtures of these bromides may be analyzed from density or refractive index measurements since these properties are linear functions of the composition.

Both of the pure bromides rearranged to an equilibrium mixture of 14% secondary and 86% primary in a few days at room temperature, in less than one hour at 75° and in less than five minutes at 100°. If a mixture of the bromides is subjected to slow distillation at atmospheric pressure through a 100-cm. packed column, almost pure secondary bromide is obtained as a distillate. Equilibrium is so rapidly established in the boiler that the secondary bromide is replaced as fast as it is removed from the top of the column.

It is now evident that the bromides reported by Juvala, Baudrenghien and Gredy and Piaux having $n^{23}\text{D}$ 1.4750 to 1.4759 contained from 24–29% of secondary bromide. Their compositions were dependent on the method of distillation and had nothing to do with the method of preparation. The bromides used by Gredy and Piaux must have gone to equilibrium after the refractive index was taken and before the Raman spectra were measured, since their analysis of 90% primary and 10% secondary is qualitatively in agreement with the equilibrium composition and not with the composition calculated from the refractive index.

In the light of these developments, crotyl alcohol and methylvinylcarbinol are being converted into bromide mixtures by various reagents under conditions designed to avoid rearrangement of the product. The composition of these mixtures will be reported in the near future.

DEPARTMENT OF CHEMISTRY WILLIAM G. YOUNG
UNIVERSITY OF CALIFORNIA AT LOS ANGELES
LOS ANGELES, CALIFORNIA SAUL WINSTEIN

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