ture of 1.0068 centistokes. Two viscometers were used at each temperature, and the results were averaged. At 0, −40, −62° two completely independent sets of determination involving different samples, resetting the bath temperature, etc., were made. The standard deviation was less than 0.15% for all temperatures.

Results.—The results are summarized in Table I.

TABLE I

t, °C.	Viscosity, cs.	Number of detn.	Standard deviation
−17.78	0.936	14	0.00092
−28.88	1.100	6	.00074
−40.01	1.321	13	.0015
−51.09	1.637	6	.0022
−62.17	2.092	24	.0028
−73.25	2.823	5	.0033

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A Rapid Method for the Resolution of *s*-Butyl Alcohol[1]

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In connection with another study we needed large quantities of optically pure *s*-butyl alcohol. The resolution of *s*-butyl alcohol through the acid phthalate ester has previously been a rather tedious process. In the usual procedure[2] the pure acid phthalate salt is dissolved in a large volume of refluxing acetone and an equimolar amount of brucine slowly added in increments, each increment being added only after the previous one has dissolved. On cooling the resulting solution, the first crop of the brucine salt of the acid phthalate ester is obtained in only relatively low degree of resolution and six to eight recrystallizations are usually required to give the pure diastereoisomer.

We have found that when equimolar quantities of the acid phthalate ester and brucine are mixed and acetone then added to the mixed solids, followed by 24 hours of refluxing the solid obtained on filtering the hot mixture is 82% optically pure. Only two or three recrystallizations of this solid are required to give the pure isomer in yields of 19–25%. Apparently continuous recrystallization takes place during the refluxing period to leave the relatively insoluble brucine salt of the *d*-isomer. It is possible that the method may be generally applicable.

Experimental

***d*-2-Butanol.**—Redistilled Eastman Kodak Co. 2-butanol, b.p. 98–99.5°, was converted to the acid phthalate ester by the procedure of Pickard and Kenyon.[3] A mixture of 447 g. (2.01 moles) of *s*-butyl hydrogen phthalate (m.p. 58.5–59.5°) and 790 g. (2.0 moles) of brucine (m.p. 177–178°) was intimately mixed in a 6-l. erlenmeyer flask. Acetone (2 l.) was added and the mixture was refluxed for 24 hours. During this time, a definite change was observed in the physical appearance of the insoluble solid. Since the success of this procedure depends on all of the solid coming in contact with the acetone, care was taken to break up any solid cake that formed on the walls of the flask. The mixture was filtered hot to get the first crop of brucine salt. The solid weighed 306 g. (50%), $[\alpha]^{29}_{\mathrm{D}}$ −5.6° (*c* 4, ethanol); this corresponds to a salt of 82% optical purity. Two or three recrystallizations from 500 ml. of methanol gave the very pure brucine salt of the *d*-isomer in yields of 19–25%, $[\alpha]^{30}_{\mathrm{D}}$ −2.75° to −2.94° (*c* 4, ethanol). The filtrate of the first crop on cooling deposited more salt which was recrystallized in the usual manner[3] to give an additional 20–30% yield of the pure brucine salt.

The brucine salt was hydrolyzed by sodium hydroxide[4] to give the pure *d*-2-butanol, b.p. 98–99.5°, d^{30}_4 0.799, n^{23}_{D} 1.3955, $[\alpha]^{27}_{\mathrm{D}}$ +13.28° (reported d^{30}_4 0.7990, n^{23}_{D} 1.3955).[5] Since the highest value reported for *d*(+)-2-butanol is $[\alpha]^{27}_{\mathrm{D}}$ +13.52°,[5] our *d*-2-butanol was at least 98.2% optically pure.

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(1) Supported by the Office of Naval Research.

(2) A. W. Ingersoll, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, pp. 400–404.

(3) R. H. Pickard and J. Kenyon, *J. Chem. Soc.*, **99**, 45 (1911).

(4) See ref. 2, p. 402.

(5) J. Timmermans and F. Martin, *J. chim. phys.*, **25**, 431 (1928).

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Reactions of Ketene Diethylacetal with 1,1,1-Trichloro-2-methyl-2-propene

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A large number of publications[2] have dealt effectively with the chemistry of ketene diethylacetal and related ketene acetals. We have been interested particularly in the chemistry of 1,1,1-trichloro-2-methyl-2-propene (called herein TMP) because of its trichloromethyl structure coupled with its allylic placed bond, and interested in its allylic rearrangement to 1,1,3-trichloro-2-methyl-1-propene (called herein allyl TMP or II). Accordingly, it seemed of interest to investigate the reaction of TMP with ketene diethylacetal.

It was found that pure TMP did not react appreciably *as such* with ketene acetal when equimolar amounts were heated at 100° for 48 to 72 hours. This finding is in keeping with the fact that a common class in the inert halogen group consists of those halogenated aliphatic compounds with three or more halogens on the same carbon.[3] However, the TMP did undergo allylic rearrangement to the allyl TMP, and a 5.8% conversion to ethyl chloride *via* this allyl TMP was obtained.

At the same time a typical major portion of product in each of three runs was found as a co-distilling mixture of the allyl TMP *and* ethyl orthoacetate. This orthoester arose because either the allyl-TMP, the original TMP—or both—had caused the initial ketene acetal to polymerize accompanied by elimination of ethanol[4,5] from the various polymers. The ethanol then reacted at once with the ketene acetal still present as monomer to form the ethyl orthoacetate.

The co-distilling mixture of the allyl TMP and ethyl orthoacetate consisted of about 86% of the allyl TMP and (13–14%) of this orthoester. About 85% of the initial TMP was rearranged to the product, the allyl TMP. An over-all accounting of approximately 80% of the total initial chlorine was made in the form of obtained allyl TMP and of ethyl chloride.

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(1) Work toward the M.S. degree by K. H. Froman.

(2) S. M. McElvain, in *Chem. Revs.*, **45**, 453 (1949).

(3) S. M. McElvain, "The Characterization of Organic Compounds," The Macmillan Co., New York, N. Y., 1947, p. 90.

(4) S. M. McElvain and D. G. Kundiger, THIS JOURNAL, **64**, 254 (1942).

(5) P. R. Johnson, Barnes and McElvain, *ibid.*, **62**, 964 (1940).