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

CALIFORNIA RESEARCH CORPORATION
RICHMOND, CALIFORNIA

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

BY SIMON W. KANTOR AND CHARLES R. HAUSER

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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%), $[\alpha]^{29}_{D}$ −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%, $[\alpha]^{30}_{D}$ −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, $[\alpha]^{27}_{D}$ +13.28° (reported d^{30}_{4} 0.7990, n^{23}_{D} 1.3955).[5] Since the highest value reported for *d*(+)-2-butanol is $[\alpha]^{27}_{D}$ +13.52°,[5] our *d*-2-butanol was at least 98.2% optically pure.

[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).

DEPARTMENT OF CHEMISTRY
DUKE UNIVERSITY
DURHAM, N. C.

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

BY DONALD G. KUNDIGER AND KENNETH H. FROMAN[1]

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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.

[1] Work toward the M.S. degree by K. H. Froman.

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

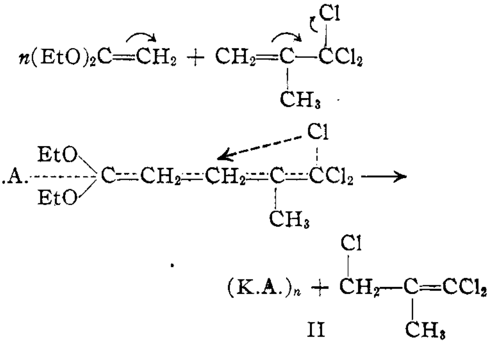
[3] S. M. McElvain, "The Characterization of Organic Compounds," The Macmillan Co., New York, N. Y., 1947, p. 90.

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

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

It seems that the most significant finding here is the facile conversion of TMP *via* an allylic rearrangement over to the allyl TMP by means of a strong electron donor agent such as ketene acetal. Previously, conversion of TMP to this allylic isomer was brought about by heating 10 g. of TMP with 0.1 g. of hydrogen chloride at 200° overnight.[6]

The mechanism for ketene acetal causing facile conversion of TMP to the allylic isomer appears interesting. The following seems reasonable, and is postulated (K. A. stands for ketene acetal).



Experimental

Starting Materials.—1,1,1-Trichloro-2-methylpropene-2 (TMP) was prepared along the lines of the method of McElvain and Stevens[6] except that a longer reaction period of 20–30 hr. was used. TMP having b.p. 132–135° was used. *Ketene acetal* was prepared by the method of McElvain and Kundiger.[7] *Ethyl orthoacetate* was prepared for a control experiment by treating 5.8 g. (0.05 mole) of ketene acetal with 100% absolute alcohol (2.8 g., slightly more than 0.05 mole). These materials were heated under anhydrous conditions at 95–100° for 15 minutes; then distillation gave 6.5 g. of ethyl orthoacetate, observed b.p. 146–150°.

Reaction of 1,1,1-Trichloro-2-methylpropene-2 (TMP) with Ketene Diethylacetal. Formation of 1,1,3-Trichloro-2-methylpropene-1 (allyl TMP).—To a 100-ml. round-bottom flask fitted with a reflux condenser connected to a Dry Ice cooled trap, a mercury sealed mechanical stirrer and a dropping funnel, there was added TMP (35.5 g., 0.221 mole). Ketene acetal (25.8 g. (0.221 mole)) was added dropwise to the TMP (constant stirring), beginning at room temperature. There was spontaneous rise of temperature in the reaction mixture to only 40°. Then, the reaction mixture was stirred and held at 100° by a bath for 48 hours. Indication of deep red dealcoholated polymers of ketene acetal was obtained because the mixture became a clear deep red solution. Ethyl chloride, b.p. 12° (3.5 g.) collected in the Dry Ice trap. Distillation of the reaction mixture through a column fractionating setup gave the following significant fractions: (a) 3.1 g., b.p. 47–49° at a pressure of 145 mm. (This material redistilled at 71–78°, had a strong odor of ethyl acetate and contained admixed ethanol since it gave the proper ceric nitrate test and also gave the 3,5-dinitrobenzoate derivative of ethanol, m.p. 95–96°, no depression of m.p. on admixture with an authentic sample); (b) 3.2 g., b.p. 100–102° (145 mm.); (c) 26.8 g., b.p. 96–100° (125 mm.); (d) 5.6 g., b.p. 50–53° (2 mm.); (e) 3.5 g., b.p. 70–129° (2 mm.) and (f) 7.5 g., b.p. rising constantly above 129° (2 mm.).

The above fractions (b), (c) and (d) were found to be a mixture of allyl-TMP, b.p. 154° (Cl content 66.4%) and ethyl orthoacetate, b.p. 146°. These combined fractions (b), (c) and (d)—termed "product A"—redistilled at atmospheric pressure at b.p. 142–154° and 88% of it at b.p. 149–154°. Carius analyses of "product A" gave total Cl content: 52.5, 52.2, 52.7%. Based on these Carius analyses and the wt. of "product A" (35.4 g.), this mixture was 86.8% allyl TMP and 13.2% ethyl orthoacetate. Standard Zeisel semi-micro ethoxyl determinations were also carried out on "product A." Various samples of this product had 12.2 to 13.5% ethoxyl, also indicating the ethyl orthoacetate content.

Acid hydrolysis of "product A" to remove the ethyl orthoacetate and prove its presence was carried out thus: To a 100-ml. round-bottom 3-necked flask fitted with a reflux condenser, a mercury sealed stirrer, and a dropping funnel, there were added 20.5 g. of "product A"; and then with very rapid stirring throughout, 60 ml. of 5% hydrochloric acid was added from the dropping funnel, and the resulting mixture boiled vigorously for ten minutes. The mixture was cooled to 25°, the water-insoluble layer separated and, on distilling it, the lower fractions had no definite b.p. but had a strong odor of ethyl acetate; the major fraction came over at b.p. 153–155°, corresponding with the b.p. of the allyl TMP, *i.e.*, II. Carius analyses on this fraction gave 65.8% Cl as compared to 66.1% Cl obtained on known allyl TMP (calcd. Cl, 66.4).

Heating of 50 g. of TMP at 100° for 48 hr. resulted in practically no rearrangement to allyl TMP. The original TMP was recovered practically quantitatively.

Two other runs of TMP mixed with ketene acetal were made for 72 hr. and the methods and results checked those described above.

Acknowledgment.—We wish to thank Mr. H. Pledger, Jr., who aided materially in developing successful syntheses of TMP.

DEPARTMENT OF CHEMISTRY
KANSAS STATE COLLEGE
MANHATTAN, KANSAS

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[6] S. M. McElvain and C. L. Stevens, THIS JOURNAL, **69**, 2669 (1947).

[7] S. M. McElvain and D. G. Kundiger, *Org. Syn.*, **23**, 45 (1943).

The Dehydration of a Steroidal Δ^8-11α-Hydroxy-7-ketone

BY A. J. LEMIN,[1] G. ROSENKRANZ[2] AND CARL DJERASSI

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In a recent synthesis of cortisone,[3] there was investigated the isomerization of the unsaturated ketol I to the corresponding saturated 7,11-dione and it was found that this could be accomplished in nearly quantitative yield by treatment with a strong base such as potassium *t*-butoxide. However, all attempts to employ acidic reagents resulted in dehydration to a dienone with ultraviolet absorption maxima at 226 and 298 mμ to which was assigned the structure of a $\Delta^{8,11}$-dien-7-one II. Since this dehydration product proved to be useless as far as the synthesis of 11-keto steroids was concerned, no further work was done with this substance.

Recently, Halsall, Jones and Lemin[4] in their degradation of the triterpene polyporenic acid A were able to demonstrate that the vinylogous β-acetoxy ketone V smoothly underwent deacetoxylation on boiling with acetic acid to afford a dienone VI with an ultraviolet absorption maximum at 318 mμ (log ϵ 3.88) in excellent agreement with the maximum (314 mμ, log ϵ 3.88) found for $\Delta^{2,4}$-cholestadien-6-one.[5] Since the chromophore in the last two mentioned substances is identical with that present in the proposed[3] structure of the dehydration product II, which, however, exhibited a maximum at 298 mμ, it was considered worthwhile to reinvestigate the structure of that substance.

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[1] Syntex Postdoctorate Fellow at Wayne University, 1952–1953.

[2] Syntex, S.A., Laguna Mayran 413, Mexico City, D. F.

[3] J. Romo, G. Stork, G. Rosenkranz and C. Djerassi, THIS JOURNAL, **74**, 2918 (1952).

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