drolyzing directly the original reaction mixture obtained by treating 5-chlorovanillin acetate with diazomethane.

The mechanism of the formation of the chalcone as an intermediate in these reactions was proved by repeating the reactions with unchlorinated compounds to obtain previously known products.

Experimental

All melting points are uncorrected.

1-(6-Chloro-4-hydroxy-3-methoxyphenyl)-1-ethanol.—6-Chlorovanillin[4] was treated with methylmagnesium iodide essentially according to the procedure employed by Roberti, York and MacGregor for the preparation of analogous vanillin derivatives.[5] The carbinol, after crystallization from benzene–petroleum ether (b.p. 65–110°), melted at 128–128.5°.

Anal. Calcd. for $C_9H_{11}O_3Cl$: CH_3O, 15.3. Found: CH_3O, 15.4.

6-Chlorovanillin Acetate.—6-Chlorovanillin was treated with acetic anhydride essentially according to the preparation of vanillin acetate by Pisovschi.[6] The product was crystallized from absolute ethanol to give white needles melting at 97–97.5°.

Anal. Calcd. for $C_{10}H_9O_4Cl$: CH_3O, 13.6. Found: CH_3O, 13.7.

1,3-Bis-(4-acetoxy-6-chloro-3-methoxyphenyl)-3-hydroxy-1-propanone (I).—The diazomethane,[7] generated from 6.8 g. of nitrosomethylurea, was introduced beneath the surface of a solution of 8.6 g. of 6-chlorovanillin acetate in 250 ml. of ether kept at 0°. After 1.5 hours at 0° and 0.5 hour at 20°, the ether and excess diazomethane were removed by distillation leaving 9.0 g. of crude product melting at 115–145°. Repeated crystallization from ethanol raised the melting point to 157–158°.

Anal. Calcd. for $C_{21}H_{20}O_8Cl_2$: C, 53.52; H, 4.28; CH_3O, 13.2. Found: C, 53.72; H, 4.38; CH_3O, 13.2.

6,6′-Dichloro-4,4′-dihydroxy-3,3′-dimethoxychalcone (II).—I (4 g.) was warmed with 30 ml. of 5% sodium hydroxide solution. The deep orange solution was cooled, saturated with carbon dioxide and extracted with chloroform. Concentration of the chloroform extract yielded a crude product which, after several crystallizations from benzene–petroleum ether (b.p. 65–110°) and dilute ethanol, melted at 198.5–200° and weighed 150 mg.

Anal. Calcd. for $C_{17}H_{14}O_5Cl_2$: C, 55.30; H, 3.82; CH_3O, 16.8. Found: C, 55.38; H, 3.97; CH_3O, 16.5.

The residue from the chloroform-extracted solution was dissolved in 5% sodium hydroxide, acidified with sulfur dioxide and extracted with ether; the ether extract was concentrated to yield an additional 170 mg. of the 6-chlorochalcone melting at 194–195°.

The ether-extracted bisulfite solution was acidified and boiled; 0.4 g. of 6-chlorovanillin was obtained melting at 167–169°.

6-Chloroacetovanillone.—A solution of 2.1 g. of (I) in 80 ml. of 15% potassium hydroxide solution was refluxed for 20 hours. The solution was saturated with sulfur dioxide and the precipitate removed by filtration. The filtrate yielded a crop of white crystals during several hours under reduced pressure; the crystals weighed 150 mg. and melted from 100–105°. Crystallization from dilute ethanol raised the melting point to 109–110°.

Anal. Calcd. for $C_9H_9O_3Cl$: C, 53.88; H, 4.52; CH_3O, 15.5. Found: C, 53.70; H, 4.57; CH_3O, 15.8.

The 4,4′-Diacetoxy-6,6′-dichloro-3,3′-dimethoxychalcone (III).—Approximately 0.5 g. of I was dissolved in 2 ml. of hot pyridine, and 4 ml. of acetic anhydride was added. After standing for 20 hours, the mixture was poured onto ice. The oil which formed soon solidified; it melted at 129 to 133°. Several crystallizations from 95% ethanol raised the melting point to 137.5–138.5°.

Anal. Calcd. for $C_{21}H_{19}O_7Cl_2$: C, 55.64; H, 4.00; CH_3O, 13.7. Found: C, 55.61; H, 4.05; CH_3O, 13.7.

III (180 mg.) was warmed on the steam-bath for 10 minutes with 5 ml. of ethanol and 3 ml. of 5% sodium hydroxide and then neutralized with dilute sulfuric acid. Upon cooling, a crop of yellow needles was formed which weighed 150 mg. and melted at 202–203.5°. No depression was observed in a mixed melting point with the previously described II.

5-Chlorovanillin Acetate.—5-Chlorovanillin acetate was prepared in a manner similar to that described for the 6-chloro compound. Crystallization from petroleum ether (b.p. 30–60°) gave a product melting at 63–64°.

Anal. Calcd. for $C_{10}H_9O_4Cl$: CH_3O, 13.6. Found: CH_3O, 13.8.

5-Chloroacetovanillone.—A large excess of diazomethane prepared from 45 g. of nitrosomethylurea was added to an ether solution of 7.15 g. of 5-chlorovanillin acetate at room temperature. The reaction mixture stood for several weeks. The residue was boiled briefly with 5% sodium hydroxide causing a portion of the oil to dissolve. Saturation of the alkaline solution with sulfur dioxide and extraction with ether gave an extract which was concentrated and applied to a column of acid-washed Magnesol.[8] The chromatogram was developed with 100:1 benzene–ethanol; elution of the major zone with acetone yielded a product melting at 122–125°. Its analysis and the analogy to the vanillin–diazomethane reaction showed it to be 5-chloroacetovanillone in 23% of the theoretical yield based on 5-chlorovanillin acetate. Treatment with charcoal and crystallization from dilute ethanol raised the melting point to 124–125°.

Anal. Calcd. for $C_9H_9O_3Cl$: C, 53.88; H, 4.52; CH_3O, 15.5. Found: C, 54.01; H, 4.53; CH_3O, 15.4.

6-Chlorovanillonitrile.—6-Chlorovanillonitrile acetate, (5.0 g.) was treated with methylmagnesium iodide; decomposition of the complex yielded 3.2 g. of crude 6-chlorovanillonitrile. Treatment with charcoal and crystallization from benzene gave a product melting at 151.5–152°.

Anal. Calcd. for $C_8H_6O_2ClN$: CH_3O, 16.9. Found: CH_3O, 16.7.

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[4] L. C. Raiford and J. G. Lichty, THIS JOURNAL, **52**, 4576 (1930).

[5] P. C. Roberti, R. F. York and W. S. MacGregor, *ibid.*, **72**, 5760 (1950).

[6] I. J. Pisovschi, *Ber.*, **43**, 2139 (1910).

[7] F. Arndt, *Org. Syntheses*, **15**, 3 (1935).

[8] I. A. Pearl and E. E. Dickey, THIS JOURNAL, **73**, 863 (1951).

[9] L. C. Raiford and D. J. Potter, *ibid.*, **55**, 1682 (1933).

THE INSTITUTE OF PAPER CHEMISTRY
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Kinematic Viscosity of *n*-Heptane at Low Temperature

BY J. F. JOHNSON AND R. L. LETOURNEAU

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The kinematic viscosity of *n*-heptane has been measured at several temperatures below 0°. The results at the lower temperatures are very appreciably different from the values tabulated by the American Petroleum Institute Project 44,[1] which we understand represent a long extrapolation of the previously available data. Because there is increasing interest in low temperature viscosities, it is hoped that this note will be of interest.

Experimental

All viscosities were measured in the Zeitfuchs cross arm-type capillary viscometer.[2] Temperatures were measured by a platinum resistance thermometer and were constant to ±0.01°. Four samples of *n*-heptane were used. The purity was established as 99.8 mole % or better by cooling curves. Viscometers were calibrated using water at 20° with an assumed value for the viscosity of water at this tempera-

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[1] American Petroleum Institute Research Project 44, Selected Values of Properties of Hydrocarbons Table 20c-E (Part 2).

[2] J. F. Johnson, R. L. LeTourneau and Robert Matteson, *Anal. Chem.*, **24**, 1505 (1952).

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]

BY SIMON W. KANTOR AND CHARLES R. HAUSER

RECEIVED NOVEMBER 28, 1952

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, $n^{23}\mathrm{D}$ 1.3955, $[\alpha]^{27}\mathrm{D}$ +13.28° (reported d^{30}_4 0.7990, $n^{23}\mathrm{D}$ 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).

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

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

RECEIVED DECEMBER 4, 1952

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).