decreased, the amount of material boiling much higher than the ether is increased.

2,3-Dihydroxypropyl *n*-Dodecyl Ether.—A mixture of 3.6 g. (0.015 mole) of the 2,3-epoxypropyl *n*-dodecyl ether and 5.4 g. (0.3 mole of water) of 5% sulfuric acid was heated in the sealed tube at 160° for eight hours. The crude product was rinsed from the tube with 20–30 cc. of ether, neutralized with solid potassium carbonate and the ether layer separated. The aqueous layer was extracted with two 10-cc. portions of ether and the combined ether solutions were distilled on the steam-bath and finally under 15 mm. pressure to remove the last traces of ether and water. The residue weighed 3.0 g., 78% of the theoretical yield; n^{20}_{D} 1.4534. This compound is a wax-like solid melting about 20°, insoluble in water, soluble in methanol, ethanol, ether, acetone, carbon tetrachloride and benzene.

Preliminary hydrolysis experiments with excess water at 100° for twelve hours, 1% hydrochloric acid at 100° for eight hours, and 1% hydrochloric acid at 130° for eight hours all gave incomplete hydrolysis. The change in refractive index in going from the glycidol ether to the glycerol ether, 1.4434 to 1.4534 at 20°, was used to follow the course of the hydrolysis.

Anal. Calcd. for $C_{15}H_{32}O_3$: C, 69.12; H, 12.38. Found: C, 69.46; H, 12.39.

Samples of the ether were quantitatively oxidized at 50° with lead tetraacetate in glacial acetic acid solution according to the procedure of Criegee.[4] The following results are expressed as percentage of ether in the sample: six hours reaction time, 38.7%; twelve hours, 70.2%; twenty-one hours, 91.2%. By extrapolation of these data it appears that twenty-eight to thirty hours would be required for complete oxidation.

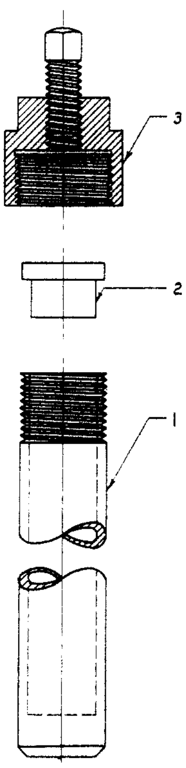

Fig. 1.—Metal bomb tube.

Reaction Tube.—Figure 1 shows a simple, convenient pressure tube made from steel tubing $1^{3}/_{16}''$ o. d., $^{15}/_{16}''$ i. d., and 15″ in length, closed at one end by a welded steel disk. The open end is machined flat so that a copper–asbestos gasket held in place by a metal plug (2) and threaded cap (3) will make a gas-tight seal.[7] A 22 mm. o. d. glass tube closed at one end is used as a glass liner.

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(7) More complete descriptions of this type of closure are given in "A High Pressure Gas-Compression System," Dilley and Edwards, Circular 61, U. S. Dept. of Agriculture, Jan., 1929; and in J. H. Perry, "Chemical Engineers' Handbook," 2nd ed., McGraw-Hill Book Co., New York, 1941, p. 2181.

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Furfuryl Furoate by Condensation from Furfural

BY ERIK R. NIELSEN

Furfuryl furoate has been prepared by the condensation of furfural in the presence of sodium furfurylate. Previous attempts to carry out this condensation have been unsuccessful and have been cited to show a breakdown in the analogy between benzaldehyde and furfural.[1] The author has modified the method described for benzyl benzoate by Kamm and Kamm[2] to the extent that the condensing agent is prepared and the reaction carried out in the presence of refluxing benzene, whereby the danger of forming the ether rather than the ester is eliminated.

Experimental.—Eighteen grams of metallic sodium was added portionwise to a mixture of 250 g. of distilled furfuryl alcohol and 750 cc. of benzene, contained in a 3-liter flask (reflux condenser). After the condensing agent had been prepared, 1350 g. of distilled furfural was added through the reflux condenser at a rate so as to maintain refluxing by the heat developed by the reaction. The reaction mixture was washed with salt brine and distilled. The ester was recovered as a fraction boiling 121° (1.5 mm.) (77.8%). The solidified ester melted at 18.5° (uncor.) and did not convert to the allotropic form melting at 27.5° which has been reported to be the stable form by Zanetti.[1] The liquid ester showed a specific gravity d^{25}_{25} of 1.2384 and a refractive index n^{20}_{D} of 1.5280. An analyses of the ester showed

	Acidity as furoic acid, %	Saponification equivalent	Carbon,[3] %	Hydrogen,[3] %
Calcd.		192	62.48	4.19
Found	0.23	195	62.25	4.32

The ester was characterized further by saponification to yield furfuryl alcohol and furoic acid.

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(1) H. Gilman and Clarence C. Vernon, THIS JOURNAL, **46**, 2578 (1924); J. E. Zanetti, *ibid.*, **47**, 1452–1453 (1925).

(2) O. Kamm and W. F. Kamm, "Organic Syntheses," Coll. Vol. I, pp. 99–101.

(3) These analyses are by Dr. T. S. Ma, University of Chicago.

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The Preparation of Potassium Triphenylmethide and its Use in Certain Condensations[1]

BY ROBERT LEVINE, ERWIN BAUMGARTEN AND CHARLES R. HAUSER

Sodium triphenylmethide is a useful reagent for the acylation[2] and alkylation[3] of esters and for the carbonation and carbethoxylation of esters[4] and ketones.[5] The sodium triphenylmethide has been prepared from triphenylchloromethane and sodium amalgam. While this method is quite satisfactory, there would be an advantage in preparing sodium triphenylmethide from triphenylmethane which would be regenerated when the reagent is used to effect condensations.

Sodium triphenylmethide is readily prepared from triphenylmethane and sodium amide in liquid ammonia[6] but the reagent is destroyed[7]

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(1) Paper XXVII on "Condensations"; paper XXVI, THIS JOURNAL, **66**, 1220 (1944).

(2) See especially Hauser and Hudson, "Organic Reactions," Roger Adams, Editor-in-Chief, John Wiley and Sons, Inc., New York, N. Y., 1942, Chapter IX.

(3) Hudson and Hauser, (a) THIS JOURNAL, **62**, 2457 (1940); (b) **63**, 3156 (1941).

(4) Baumgarten and Hauser, *ibid.*, **66**, 1037 (1944).

(5) Baumgarten, Levine and Hauser, *ibid.*, **66**, 862 (1944).

(6) Kraus and Kahler, *ibid.*, **55**, 3538 (1933).

(7) Kraus and Rosen, *ibid.*, **47**, 2739 (1925).

when the ammonia is replaced by ether in order to obtain a medium suitable for acylations with acid chlorides and for alkylations or carbonations.

Potassium triphenylmethide, which is readily prepared from triphenylmethane and potassium amide in liquid ammonia, is not destroyed when the ammonia is replaced by ether and the mixture refluxed. By means of this reagent four typical condensations for which the triphenylmethide reagent is particularly useful have been effected. Ethyl isovalerate has been self-condensed to form ethyl isovalerylisovalerate in 64% yield, ethyl isobutyrate has been benzoylated with benzoyl chloride to form ethyl benzoyldimethylacetate in 55% yield, and ethyl isobutyrate has been ethylated with ethyl iodide to give ethyl α,α-dimethylbutyrate in 53% yield. Also, methyl ethyl ketone has been carbonated, followed by esterifications with diazomethane, to form methyl propionylacetate in 39% yield. In addition to the condensation products, approximately 90% of the triphenylmethane used in the preparation of the potassium triphenylmethide has been recovered. Essentially these yields of condensation products have previously been obtained using sodium triphenylmethide.[2,3,5]

The triphenylmethide reagent can be prepared in considerably less time from triphenylmethane than from triphenylchloromethane. Moreover, the triphenylmethane which is recovered in condensations may be used repeatedly for the preparation of potassium triphenylmethide, whereas new triphenylchloromethane is required for each preparation of sodium triphenylmethide. However, only the sodium triphenylmethide, which is obtained in ether solution, is suitable when a standardized solution of the triphenylmethide ion is required. The potassium triphenylmethide reagent, which is obtained as a precipitate, is not readily dissolved in ether.[8] When a series of small scale (0.1–0.2 mole) syntheses is contemplated, it may be more advantageous to use aliquots from a standardized large scale preparation of the sodium triphenylmethide reagent than to prepare the potassium triphenylmethide reagent several times.

Experimental

Preparation of Potassium Triphenylmethide.—A 500-cc. three-necked round-bottomed reaction flask having ground-glass joints was equipped with a mercury-sealed stirrer, a Dry-Ice condenser (having a soda-lime tube), and an inlet tube of wide diameter (12 mm.) leading from a second 500-cc. round-bottomed flask containing about 300 cc. of commercial anhydrous ammonia. The ammonia (150 cc.) was distilled from sodium into the reaction flask and the inlet tube replaced by a ground glass stopper. To the stirred ammonia was added in small pieces 7.8 g. (0.2 gram-atom) of clean potassium which was converted to potassium amide by means of a piece of rusty iron gauze.

The ground-glass stopper was replaced by a dropping funnel containing 48.8 g. (0.2 mole) of triphenylmethane (m. p. 93–94°) dissolved in 250 cc. of absolute ether. This solution was added to the stirred 0.2 mole of potassium amide as rapidly as the ammonia was efficiently condensed. The mixture acquired an orange color. After one hour, the Dry-Ice in the condenser was replaced by crushed ice. The reaction mixture was allowed to come to room temperature and finally refluxed on a steam-bath for two hours to expel the ammonia, sufficient ether being added gradually so that the volume of the mixture remained approximately 300 cc. The potassium triphenylmethide reagent was obtained as a blood-red suspension in ether.

The conversion of the potassium to potassium triphenylmethide was assumed to be quantitative, producing 0.2 mole of the reagent. Carbonation of the reagent gave a 91% yield (based on either triphenylmethane or potassium) of triphenylacetic acid, m. p. 263–265°.[9]

Condensations. General Procedure.—To the potassium triphenylmethide reagent contained in the flask in which it was prepared was added the ester or ketone dissolved in absolute ether. After a few minutes, when the red color of the reagent had faded or disappeared, the resulting mixture containing the ester anion was siphoned under nitrogen pressure into a nitrogen-filled 1-liter bottle having a ground-glass stopper and the flask rinsed with absolute ether.[10] The self-condensation of ethyl isovalerate and the benzoylation and ethylation of ethyl isobutyrate were carried out in the bottle essentially as described previously using sodium triphenylmethide.[2,3] The mixture (at −10°) containing the anion of methyl ethyl ketone was immediately siphoned onto Dry-Ice as described previously using sodium triphenylmethide.[5]

The residue remaining in the flask after distilling the condensation products consisted essentially of triphenyl methane, which after one recrystallization from 95% alcohol melted at 93–94°; recovery 90%.[11]

Ethyl Isovalerylisovalerate.—This compound (b. p. 118–119° at 15 mm.)[12] was obtained in a yield of 13.7 g. (64% based on the 0.2 mole of potassium triphenylmethide used) from 52.4 g. (0.4 mole) of ethyl isovalerate, after shaking the reaction mixture in a mechanical shaker for fifteen hours and allowing it to stand at room temperature for an additional fifty hours. Ketonic cleavage of the β-keto ester yielded di-isobutyl ketone, b. p. 164–165°; m. p. of the 2,4-dinitrophenylhydrazone, 92.0–92.5°.[13]

Ethyl Benzoyldimethylacetate.—This substance (b. p. 146–148° at 15 mm.)[14] was obtained in yield of 55% (24.2 g.) from 23.2 g. (0.2 mole) of ethyl isobutyrate and 31 g. (0.24 mole) of benzoyl chloride. A sample of the β-keto ester was converted to the isoxazolone, m. p. 69–70°.[14]

Ethyl α,α-Dimethylbutyrate.—This compound (b. p. 141–142°)[15] was obtained in a yield of 53% (15.1 g.) from 23.2 g. (0.2 mole) of ethyl isobutyrate and 46.8 g. (0.3 mole) of ethyl iodide. A sample (2 g.) of the ester was converted to α,α-dimethylbutyramide which melted at 101–102°.[16]

Methyl Propionylacetate.—This substance (b. p. 73.5–74.0° at 15 mm.)[5] was obtained in a yield of 39% (10.0 g.) from 14.4 g. (0.2 mole) of methyl ethyl ketone by carbonation followed by esterification with diazomethane.[5] A sample of the β-keto ester was converted to the copper salt, m. p. 160–160.5°.[5]

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[8] See Schlenck and Marcus, *Ber.*, **47**, 1664 (1914).

[9] Elbs and Tolle, *J. prakt. Chem.*, **32**, 624 (1885).

[10] Traces of potassium and potassium amide left on the walls of the reaction flask may be safely destroyed by the addition of Dry-Ice and absolute alcohol.

[11] The crude triphenylmethane recovered from certain other condensations (in which higher boiling condensation products were obtained) has been distilled in a Claisen–von Braun flask, the fraction boiling at 170–190° at 10 mm. being collected. The distillate consisted of a yellow liquid solidifying to a light yellow solid which, after one recrystallization from 95% alcohol and fusion *in vacuo*, melted at 93–94°.

[12] Hudson and Hauser, THIS JOURNAL, **63**, 3163 (1941).

[13] Morgan and Hardy, *Chemistry and Industry*, **52**, 518 (1933).

[14] Renfrow and Hauser, THIS JOURNAL, **60**, 463 (1938).

[15] Bouveault and Blanc, *Bull. soc. chim.*, [3] **31**, 749 (1904).

[16] Haller and Bauer, *Compt. rend.*, **148**, 129 (1909).