NOTES

A Water-Soluble Mannan from the Seeds of Daubentonia Drummondii[1]

BY A. L. CURL[2] AND E. K. NELSON[3]

In an investigation of the seeds of *Daubentonia drummondii*, a shrub of the pea family which grows in the coastal plain from Florida to Texas, a water-soluble fraction was obtained in 16% yield which consisted chiefly of a polysaccharide from which 43% of mannose (as the phenylhydrazone) was obtained on hydrolysis. The seeds also contained 4.4% of a semi-drying oil and an unidentified glycoside. It is believed that these seeds might be an important domestic source of mannose.

Experimental

The seeds used in this investigation were provided by S. B. Detwiler of the Soil Conservation Service, U. S. Department of Agriculture and were collected at Yellow Pine, La.

The ground seeds contained 6.5% moisture (dried six hours at 100°) and 2.8% ash. A test for cyanogenetic glycosides[4] was negative.

Eighty-five grams of the ground seeds was extracted in a Soxhlet extractor overnight successively with petroleum ether, ether, chloroform, and alcohol.

The petroleum ether extract on evaporation yielded 3.7 g. (4.4%) of a yellow oil which had an iodine no. (Wijs) of 122.6.[5]

The ether and chloroform extracts yielded, respectively, 1.0 g. (1.2%) and 1.6 g. (1.9%) of viscous green material which was not further investigated.

The alcohol extract yielded 6.5 g. (7.7%) of a light brown powder (I). A solution of (I) in water gave a green color with ferric chloride, but did not have an astringent taste and did not precipitate gelatin from aqueous solution; so apparently it contained little tannin, if any. A solution of (I) in water reduced Fehling solution slowly on boiling. To another portion of (I) in water, sulfuric acid was added and the mixture was warmed (a precipitate formed), neutralized, and boiled with Fehling solution, giving a strong test. The precipitate was a resinous material, soluble in ether and in petroleum ether; it was not identified. The alcohol extract evidently contained a glycoside.

The residue from the extractions in the Soxhlet apparatus was allowed to stand overnight with 300 ml. of water, filtered, and washed with 100 ml. of water. The filtrate and washings were evaporated to 100 ml., cooled and diluted to 1 liter with absolute alcohol. The resulting white precipitate (II) after filtering and drying weighed 13.4 g. (15.8%). Ten grams of (II) on neutralization required 17 ml. of 0.5 N sodium hydroxide, equivalent to 0.5 g. as citric acid. Lead acetate gave a small amount of precipitate with the neutralized solution; this was filtered off, and the filtrate was de-leaded with hydrogen sulfide, concentrated and reprecipitated with alcohol. The result-

(1) Agricultural Chemical Research Division Contribution No. 138. Not copyrighted.

(2) Present Address: U. S. Citrus Products Station, Winter Haven, Fla.

(3) Died November 9, 1940.

(4) "Official and Tentative Methods of Analysis," Association of Official Agricultural Chemists, Washington, D. C., fourth ed., 1935, p. 348, par. 46.

(5) Analysis by C. E. Swift, Fellow, National Cottonseed Products Assn.

ing product (III) contained 0.23% nitrogen[6] and 0.8% ash; it had an optical rotation $[\alpha]^{20}D$ of $+50.6°$ in water and turned brown without melting on heating to 260°. A solution of (III) in water formed a bulky light-colored precipitate with Fehling solution and no reduction occurred on heating to boiling; a similar precipitate was formed with copper sulfate and sodium hydroxide, but none formed with copper sulfate and ammonium hydroxide nor with sodium hydroxide alone. Negative tests on (III) for proteins were given by the xanthoproteic and biuret reactions. The Schotten–Baumann test yielded a white precipitate. A solution of (III) after boiling with hydrochloric acid and neutralizing reduced Fehling solution on boiling.

One gram of (III) was heated to 130° in an autoclave with 50 ml. of 0.5% hydrochloric acid for two hours; the mixture was cooled, and sodium acetate and 1.5 ml. of phenylhydrazine added. The crystalline precipitate which formed in the cold, after filtering, washing with water and alcohol, and drying, weighed 0.65 g., equivalent to a 43% yield as mannose. The filtrate, after the addition of acetic acid, was warmed for two hours on a steam-bath but only a small amount of osazone was formed. A portion of the hydrazone, after being recrystallized from pyridine and butanol, and then from phenol and butanol, had a m. p. of 193–194° (cor.) and its mixture with mannose phenylhydrazone had a m. p. of 195° (cor.).

(6) Analysis by B. Axelrod, Enzyme and Photochemistry Research Division.

The Absorption Spectra of Pyrrole Blue A and B

BY F. FROMM[1]

Liebermann and Häse[2] have shown that the interaction of pyrrole and isatin in presence of sulfuric acid yields a mixture of two dyestuffs, pyrrole blue A and B, while only pyrrole blue B is obtained if pyrrole and isatin react in glacial acetic acid. Pratesi[3] determined the constitution of the B compound as β-(5-pyrrolenyl)-isatin and investigated the absorption spectra of the homologous 2,3-dimethylpyrrole blue, cryptopyrrole blue and opsopyrrole blue in pyridine solution. All the three absorption curves are close together; the logarithm of their molecular extinction log ϵ rises from about 3.6 at 450 mμ to about 4.4 at 700 mμ. The logarithm of specific extinction,[4] log k for 2,3-dimethylpyrrole blue [β-(2,3-dimethyl-5-pyrrolenyl)-isatin] has been computed from Pratesi's data and has been entered as curve C in Fig. 1. Grassmann and v. Arnim[5] published a spectrum of a pyrrole blue dyestuff

(1) Present Address: Colegio del Sagrado Corazón, Santurce, Puerto Rico.

(2) Liebermann and Häse, *Ber.*, **38**, 2851 (1905).

(3) Pratesi, *Ann.*, **504**, 263 (1933).

(4) *I. e.*, the extinction for unit concentration (g./l.) and unit thickness (cm.).

(5) Grassmann and v. Arnim, *Ann.*, **519**, 197 (1935).

which is entirely different from Pratesi's diagram; it shows log k about 0.2 at 625 mμ and falls off to log k about -0.5 at 470 mμ and log k about -0.25 at 800 mμ without reaching a minimum. The solvent used is not indicated.
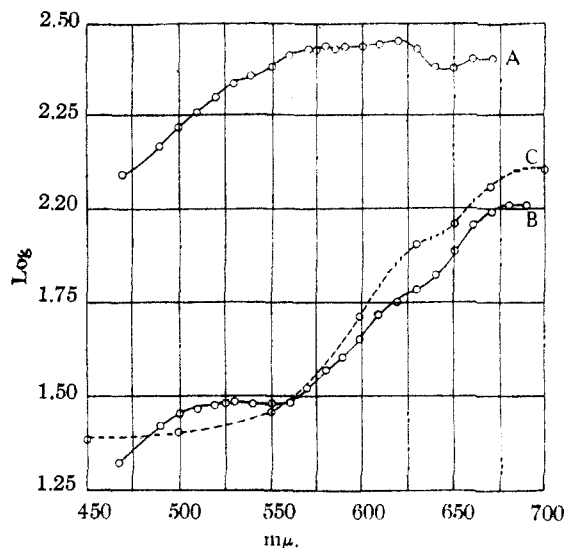

Fig. 1.—A, Pyrrole blue A, 50.94 mg. per liter of glacial acid; B, pyrrole blue B, 15.5 mg. per liter of glacial acetic acid; C, 2,3-dimethyl pyrrole blue in pyridine calculated from Pratesi's data.

The absorption curves of pyrrole blue A and B are not known since Pratesi measured only homologous substances of these dyestuffs and Grassmann and v. Arnim's curve differs so much from Pratesi's that it is improbable that it belongs to the B compound. A determination of the spectra of pyrrole blue A and B seemed therefore indicated.

Pyrrole blue B was prepared according to Liebermann and Häse[2] and dissolved in glacial acetic acid. The extinction was measured in a Hilger–Nutting spectrophotometer[6] with glacial acetic acid as a compensating liquid. The results are given in Fig. 1 curve B. Measurements in alcoholic hydrochloric acid gave a very similar picture. The curve resembles Pratesi's diagram for the homologous pyrrole blues (see curve C).

Both the acetic acid and the alcoholic solution are very unstable. They begin to change their spectrum after a few hours; the change continues through several days. The maximum at 520 mμ increases to log k about 1.9 while the maximum at 680 mμ disappears completely; no minimum could be observed in the visible range. The material represented in spectrum B seems therefore to contain some of the decomposition product.

Pyrrole blue A was prepared according to

(6) The author is greatly indebted to the Chemistry Department of the University of Michigan for the permission of using this instrument and to Dr. F. F. Blicke for the supply of pyrrole.

Pratesi and Zanetta[7]; these authors have pointed out that pyrrole· blue A is not an oxidation product or derivative of pyrrole blue B but the result of a completely different reaction between pyrrole and isatin. Its absorption spectrum measured in glacial acetic acid in the Hilger–Nutting spectrophotometer is given in curve A Fig. 1. It confirms the assumption that the structure of pyrrole blue A is different from that of the B compound. Also the solutions of dyestuffs A are extremely unstable.

(7) Pratesi and Zanetta, *Atti Acad. nasion. Lincei. Ren.*, [6] **22**, 159 (1935).

SAN GERMAN, PUERTO RICO   RECEIVED JANUARY 7, 1944

The Basic Nitrite of Lanthanum

By G. R. SHERWOOD

In 1914 Holden and James[1] reported that they got unusually rapid separation of yttrium from the other yttrium earths by the method of fractional precipitation with sodium nitrite. The method has been used and improved by other workers, but there seems to be no record of a quantitative study of the precipitate nor of the most favorable conditions under which it should be produced.

The lanthanum material used for these experiments showed only very faint spectral lines of praseodymium and neodymium. In addition it contained traces of cerium and manganese. It was therefore of satisfactory purity.

Some of the lanthanum solutions used were chlorides, others were nitrates. Either salt seemed to work about equally well. The lanthanum basic nitrite was prepared from these approximately 0.05 molar lanthanum solutions using the method as modified by Sherwood and Hopkins.[2]

The precipitated basic nitrite liberated iodine from hydroiodic acid, reduced acidified permanganate, and behaved in general as one would expect a nitrite to behave. All but the merest trace of sodium salts could be removed from it by simply washing it with water. The basic nitrite was surprisingly stable toward heat, at least up to approximately the boiling point of concentrated sulfuric acid.

It was found that the speed of precipitation increased with increased nitrite ion concentration, being too slow in half molar nitrite solution but satisfactory if the nitrite ion concentration was two molar.

Attempts were made to dry the first precipitates to constant weight in an oven at 110°. This was difficult to accomplish and the results did not seem significant. So subsequent precipitates were analyzed for La_2O_3 and N_2O_3 and the ratio of La_2O_3 to N_2O_3 determined for each sample.

A study was made to see whether the composi-

(1) Holden and James, THIS JOURNAL, **36**, 1418 (1914).
(2) Sherwood and Hopkins, *ibid.*, **55**, 3117 (1933).

tion of the precipitate was affected by the concentration of nitrite ion. A solution of lanthanum chloride was divided into three equal parts, one being made 0.5 molar, the second 1 molar, and the third 2 molar with sodium nitrite. There was no appreciable difference in the analyses of the precipitates produced from the three parts. Within these limits of nitrite ion concentration (0.5 molar to 2 molar) the precipitates consistently showed a molar ratio of La_2O_3 to N_2O_3 of between 1.01 and 1.02 for the purest lanthanum material. However, if the nitrite ion concentration became much less than 0.5 molar, a precipitate could be produced by boiling which contained almost no nitrite. This presumably was lanthanum hydroxide.

Methods were tried for the production of colloidal precipitates which have bothered previous workers so much. One method was the addition of a large excess of sodium chloride along with the sodium nitrite. This did not produce a colloid. However, the addition of a high concentration of sodium nitrite to a solution containing practically no free acid did produce a precipitate on boiling which was colloidal. In this case it was found that the initial pH had been allowed to become too high and that it fell as boiling started. The lanthanum solution should have a pH of approximately 5 before the sodium nitrite solution is added. Both the solutions should be at or only slightly above room temperature when they are mixed.

Using the above procedure the basic nitrite starts to precipitate from a 0.05 molar lanthanum solution at a pH of approximately 6.3 as compared to pH of approximately 8.3 required to precipitate its hydroxide.

This study indicates that a basic nitrite of lanthanum of very desirable properties can consistently be obtained by making a very faintly acidic solution of lanthanum chloride from 0.5 molar to 2 molar with sodium nitrite and subsequently boiling.

DEPARTMENT OF CHEMISTRY
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2,3-Dihydroxypropyl n-Dodecyl Ether

BY OLIVER GRUMMITT AND ROBERT F. HALL[1]

Although a number of the lower aliphatic and aromatic alpha mono-ethers of glycerol have been described,[2] the higher aliphatic derivatives are mentioned only briefly in the patent literature.[3] In order to obtain a typical member of this class of compounds the preparation of 2,3-dihydroxypropyl n-dodecyl ether (α-glycerol lauryl

(1) Present address: United Co-Operatives, Inc., Alliance, Ohio.
(2) For example, the α-ethyl ether by Nef, *Ann.*, **335**, 232 (1904), and the α-phenyl ether by Lindeman, *Ber.*, **24**, 2146 (1891).
(3) Henkel and Co., French Patent 751,923, Sept. 12, 1933; *C. A.*, **28**, 777 (1934).

ether) was undertaken. Epichlorohydrin and excess lauryl alcohol in the presence of anhydrous ferric chloride reacted at 160° to give a 39% yield of 3-chloro-2-hydroxypropyl n-dodecyl ether. The corresponding epoxy compound (glycidol ether) was obtained in a 74% yield by removal of the units of hydrogen chloride with sodium hydroxide in n-butyl ether as a diluent. Hydrolysis of this intermediate to the glycerol ether, 2,3-dihydroxypropyl n-dodecyl ether, was unexpectedly slow—practically no hydrolysis occurred with excess dilute hydrochloric acid after eight hours of refluxing, but at 160° in a closed tube the hydrolysis was complete in eight hours.

2,3-Dihydroxypropyl n-dodecyl ether is a wax-like solid melting at about 20°. As do other 1,2-glycols, it undergoes quantitative oxidation with lead tetraacetate.[4] The rate of oxidation, however, is low in comparison with that of a glycerol mono-ester; for example, α-monostearin is quantitatively oxidized in six hours at 50°,[5] but the ether required more than twenty-one hours at the same temperature.

Experimental

3-Chloro-2-hydroxypropyl n-Dodecyl Ether.—A mixture of 9.7 g. (0.1 mole) of Eastman Kodak Co. epichlorohydrin, 37.2 g. (0.2 mole) of lauryl alcohol (E. K., m. p. 23–24°) and 0.4 g. of anhydrous ferric chloride was heated in a sealed, glass-lined metal tube for eighteen hours in an oil-bath held at 160°. The reaction mixture was transferred to a Claisen flask with a small amount of ether for rinsing, and the ether distilled on the steam-bath. The residue was distilled at 1–2 mm. pressure to give 10.9 g. at 114–150°, consisting mostly of unreacted epichlorohydrin and lauryl alcohol, 11.4 g. of product at 150–160° (39% of the theoretical yield), and a residue of 6.2 g. Redistillation gave 157° (1 mm.) as the approximate boiling point. The ether was a water-white liquid of faint odor showing $n^{25}D$ of 1.4525.[6]

In the absence of the ferric chloride catalyst the yield was only 16%. With equimolar quantities of reactants and in the presence of 1% of catalyst the yield was 27%. A 2/1 mole ratio of epichlorohydrin to alcohol and in the presence of the catalyst raised the yield to 35%, and reversing the relative quantities taken to a mole ratio of 1/2 gave a 39% yield, as described above.

2,3-Epoxypropyl n-Dodecyl Ether.—A mixture of 12 g. (0.043 mole) of 3-chloro-2-hydroxypropyl n-dodecyl ether, 3.9 g. (0.098 mole) of pulverized sodium hydroxide, and 36 cc. of anhydrous n-butyl ether was heated under reflux with frequent shaking on the steam-bath for one hour. The pulverized sodium hydroxide was made from the pellets with a mortar and pestle and a few cc. of n-butyl ether to protect the surface against carbonate formation. The n-butyl ether was dried by distilling the technical grade to give the 138–141° fraction. After heating, the reaction solution was transferred to a Claisen flask with anhydrous ether for rinsing, and distilled: 7.7 g. at 132–135° (1–2 mm.) were collected; $n^{20}D$ 1.4434; 74% yield.

Anal. Calcd. for $C_{15}H_{30}O_2$: C, 74.25; H, 12.47. Found: C, 74.61; H, 12.06.

Experiments with no diluent gave much lower yields. Longer reaction time and/or higher temperature likewise gave lower yields (10–55%). When the yield of ether is

(4) Criegee, *Ber.*, **64**, 260 (1931).
(5) Hilditch and Rigg, *J. Chem. Soc.*, 1774 (1935).
(6) Henkel and Co., French Patent 744,749, April 26, 1933; *C. A.*, **27**, 4242 (1933).

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.

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) 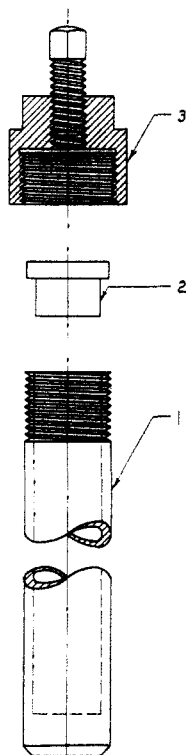and threaded cap (3) will make a gas-tight seal.[7] A 22 mm. o. d. glass tube closed at one end is used as a glass liner.

Fig. 1.—Metal bomb tube.

(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.

(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]

(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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DURHAM, NORTH CAROLINA   RECEIVED MARCH 15, 1944

(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).