acid represented 83% of the theoretical amount. It is slightly soluble in cold water, very soluble in hot water and insoluble in organic solvents. It melts with decomposition between 190 and 194°. The molecular weight was found by titration to be 111, in good agreement with the theoretical value of 114.

The aminomethylenesulfonic acid thus obtained was converted to the sodium salt by adding 33.25 g. of the acid to a solution containing 10 g. of sodium hydroxide. The resulting solution was placed in a three-necked, round-bottom flask fitted with a mercury-seal stirrer, a reflux condenser and two dropping funnels. The reaction mixture was heated to water-bath temperature and one-third of an aqueous solution of 50.5 g. of sodium cyanide, was added. Of the total required amount of formaldehyde (43 g. of 37% solution), one-third was added, dropwise, over a period of 45 minutes. The second and third portions of these reagents were added in a similar manner and the reaction was allowed to proceed for 24 hours at the same temperature. The course of the reaction was followed by trapping the ammonia given off and titrating it with standard sulfuric acid. Approximately 97% of the theoretical amount of ammonia was evolved from the reaction mixture.

The product was isolated as a semi-solid material by evaporation of the solution under reduced pressure. It was obtained in a dry form by repeated vacuum distillation of alcoholic solutions. The crude material finally was recrystallized from a water-alcohol solution and dried in a vacuum desiccator. The final product is a colorless, crystalline very hygroscopic material.

Anal. Calcd. for $C_5H_6O_7NS_2Na_3$: N, 4.77; S, 10.9. Found: N, 4.57; S, 11.45.

Trisodium 2-Aminobenzoate-N,N-dimethylenesulfonate.—A solution consisting of 55 g. of sodium bisulfite, 73 ml. of water and 41 g. of a 37% formaldehyde solution was heated to 65° for 30 minutes. Next, a solution of 34.25 g. of anthranilic acid and 10 g. of sodium hydroxide in 200 ml. of water and 150 ml. of alcohol was added, and the reaction mixture was heated to 75° for 4 hours. The reaction solution was allowed to cool to room temperature and then was treated with ethanol, whereupon the product precipitated from the alcoholic solution.

Proper conditions for recrystallization were not found. The compound would not crystallize from water or water-alcohol solutions. The uncrystallized product is a colorless solid which is soluble in water, insoluble in organic solvents.

Anal. Calcd. for $C_9H_8O_8NS_2Na_3 \cdot H_2O$: N, 3.14; S, 14.4. Found: N, 3.0; S, 14.3.

Trisodium Nitrilotrimethylenesulfonate—An aqueous solution containing 55.2 g. of sodium hydroxide, 51 g. of aminomethylenesulfonic acid and 75.4 g. of a 37% solution of formaldehyde was prepared. The resulting mixture then was cooled down to room temperature and 58.8 g. of gaseous sulfur dioxide was added over a period of 8 hours. The reaction solution then was heated to 70° for 3 hours. After the reaction mixture had been cooled to room temperature, the product was precipitated out by the addition of a little methanol. After recrystallization from a water-alcohol solution the nitrilotrimethylenesulfonate salt was obtained as a colorless, crystalline trihydrate.

Anal. Calcd. for $C_3H_6O_9NS_3Na_3 \cdot H_2O$: N, 3.4; S, 23.07; Na, 16.5. Found: N, 3.8; S, 22.7; Na, 16.2.

Determination of Neutral Equivalent.—A weighed sample of amino acid (20 to 40 mg.) was dissolved in 250 ml. of distilled water and standard sodium hydroxide was added in small quantities to the stirred solution. After each addition of base, the *p*H was measured with a glass electrode and a saturated calomel reference electrode used in conjunction with a Beckman *p*H meter. After the *p*H reached a value of about 10, a standard solution of hydrochloric acid was added in order to bring the *p*H back to its original value. Then the sample was titrated with standard hydrochloric acid in a similar manner. After each addition the *p*H of the solution was recorded. Observation of inflections in the titration curve thus obtained made it possible to calculate a neutral equivalent in certain cases where inflections were found at positions other than that corresponding to the starting material. In such cases the neutral equivalent could be interpreted in terms of molecular weight in view of the nature of the known functional groups in the substance being studied.

Determination of Copper Complex Formation.—To the acid solution obtained in the determination of neutral equivalent was added a stoichiometric amount of copper(II) nitrate. In most cases the amount of metal added was calculated on the basis of a 1:1 molar ratio of ligand to copper salt, although in the case of ligands having a small number of functional groups, the molar equivalent of copper salt used was reduced to one-half of this value. The resulting solution was then titrated potentiometrically with small increments of standard sodium hydroxide until the *p*H reached a value above 10 or until a precipitate formed.

Acknowledgment.—The authors are indebted to F. C. Bersworth of Versenes, Inc., for financial support of this research, and for helpful suggestions and continued interest in the problem.

WORCESTER, MASSACHUSETTS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

Synthesis of Methyl-d_3 Alcohol and Methyl-d_3 Fluoride

BY WALTER F. EDGELL AND L. PARTS

RECEIVED DECEMBER 10, 1954

Tribromomethyl fluoride, carbon dioxide, phosgene and 1,2-propylene carbonate have been reduced with lithium aluminum hydride. The reduction of tribromomethyl fluoride yielded methane and methyl fluoride. From carbon dioxide and phosgene low yields of methanol, based on lithium aluminum hydride, were obtained. The reduction of 1,2-propylene carbonate gave a satisfactory yield of methanol and the method was adopted for the synthesis of methyl-d_3 alcohol, using lithium aluminum deuteride as the source of deuterium. Methyl-d_3 *p*-toluenesulfonate, prepared from methyl-d_3 alcohol led to methyl-d_3 fluoride on reaction with potassium fluoride.

Introduction

Continued progress in this Laboratory on the theoretical aspects of the rotation-vibration spectra of fluorinated hydrocarbons suggested a study of the infrared and Raman spectra of methyl-d_3 fluoride.[1] The results of microwave studies on methyl-d_3 fluoride have been reported[2] without a reference to its preparation.

In the course of the study of reactions which would lead to methyl-d_3 fluoride a new synthesis of methyl-d_3 alcohol was discovered. It was found that methyl-d_3 alcohol can be prepared in a high yield on reduction of 1,2-propylene carbonate with lithium aluminum deuteride. No special apparatus is required for this reaction.

Since methyl-d_3 alcohol is a convenient starting material for compounds containing the CD_3 group we are reporting its preparation prior to the publi-

---

[1] Walter F. Edgell and L. Parts, to be published.

[2] C. M. Johnson, R. Trambarulo and W. Gordy, *Phys. Rev.*, **84**, 1178 (1951); W. Gordy, *Ann. N. Y. Acad. Sci.*, **55**, 774 (1952).

cation of the complete results of spectroscopic studies on methyl-d_3 fluoride.

Discussion and Results

In the exploratory stages of this work we studied several lithium aluminum hydride reductions which either directly, or indirectly *via* methanol, would lead to methyl fluoride.

The reduction of tribromomethyl fluoride yielded methane, methyl fluoride and an unidentified product. From 0.203 mole of tribromomethyl fluoride with an excess of lithium aluminum hydride in dibutyl ether, 0.95 g. of product was obtained whose components were identified by means of infrared spectra. A similar experiment carried out in diethyl ether led to analogous results, except for a relatively larger amount of methyl fluoride. To our knowledge this is the first time that the cleavage of a carbon–fluorine bond has been effected with lithium aluminum hydride.[3] Due to the low yield of methyl fluoride obtained by this method it was considered as unsatisfactory for our purpose.

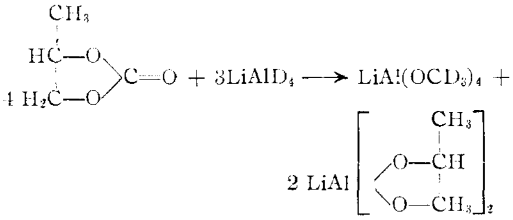
Methanol was found to be a convenient intermediate for the synthesis of methyl fluoride.[4] However the path to methyl-d_3 fluoride was complicated by the fact that no simple and economical synthesis of methyl-d_3 alcohol has been reported in the literature. The previously reported syntheses of methyl-d_3 alcohol[5–7] have been reviewed by Anderson,[8] and Nolin and Leitch.[9]

The reduction of carbon dioxide with lithium aluminum hydride has been studied on several occasions.[9–16] Even though the highest reported yields of methanol, as based on lithium aluminum hydride introduced as reagent, have been slightly lower than 50%,[12,14] the results of Finholt and Jacobsen[15] suggest that at higher lithium aluminum hydride concentration a higher yield of methanol could be expected. In most of the earlier work on the reduction of carbon dioxide with lithium aluminum hydride carbon-14 enriched carbon dioxide has been used. Therefore the conservation of the hydride has not been of great concern, and with sufficiently high excess of the hydride (100–600%) almost quantitative yields of methanol, as based on carbon dioxide, have been obtained. The decrease of the hydride–carbon dioxide molar ratio, and the simultaneous decrease of the hydride concentration, increases the relative amounts of the intermediate reduction products,[15] formic acid and formaldehyde. An experiment carried out here at the highest feasible lithium aluminum hydride concentration, using an excess of carbon dioxide, yielded only 36.2% methanol as based on the hydride.

Since acid chlorides are the most easily reduced derivatives of carboxylic acids,[17] phosgene was reduced with lithium aluminum hydride. However, the yield of methanol obtained from the survey reaction, carried out in diethyl Carbitol with 42% excess of lithium aluminum hydride, was only 22%. Due to inconveniences, and precautions which had to be taken, the reduction of phosgene was carried out only once.

Satisfactory results were obtained from the reduction of 1,2-propylene carbonate. A 10% excess of lithium aluminum hydride was used. Methanol was obtained in 84.8% yield based on the carbonate; the yield on the basis of lithium aluminum hydride was 77.1%. The method was adopted for the synthesis of methyl-d_3 alcohol. The corresponding yields were 89.6 and 81.5%. The synthesis is applicable on both micro and macro scales. 1,2-Propylene carbonate was used as the starting material because it was readily available at the time when the experiments were undertaken. There is no obvious reason why other organic carbonates could not be used in place of 1,2-propylene carbonate.

Methyl-d_3 alcohol was converted to methyl-d_3 *p*-toluenesulfonate, which on reaction with potassium yielded methyl-d_3 fluoride.[4] The synthesis of methyl-d_3 fluoride is represented by the following scheme of reactions.



$$4\ \text{CH}_3\text{CH(O)CH}_2\text{O}{>}\text{C=O} + 3\text{LiAlD}_4 \longrightarrow \text{LiAl(OCD}_3)_4 + 2\ \text{LiAl}[\text{OCH(CH}_3)\text{CH}_2\text{O}]_2$$

(1a)[18]

$$\text{LiAl(OCD}_3)_4 + 4\text{CH}_3(\text{CH}_2)_3\text{O(CH}_2)_2\text{O(CH}_2)_2\text{OH} \rightleftarrows 4\text{CD}_3\text{OH} + \text{LiAl}[\text{O(CH}_2)_2\text{O(CH}_2)_2\text{O(CH}_2)_3\text{CH}_3]_4 \quad (1b)$$

$$\text{CD}_3\text{OH} + p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{Cl} + \text{C}_5\text{H}_5\text{N} \longrightarrow p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{CD}_3 + \text{C}_5\text{H}_5\text{N:HCl} \quad (2)$$

$$p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{CD}_3 + \text{KF} \longrightarrow \text{CD}_3\text{F} + p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{K} \quad (3)$$

A complete trial run was carried out with methanol obtained from the reductions of 1,2-propylene carbonate prior to the synthesis of methyl-d_3 fluoride. The results are found in Table I. Similar yields were obtained when the same reactions were carried out with methyl-d_3 alcohol.

Acknowledgment.—The authors wish to thank the Atomic Energy Commission and the Purdue Research Foundation for the financial support of the above described work.

---

(3) L. M. Trevoy and W. G. Brown, THIS JOURNAL, **71**, 1675 (1949), have reported an attempted reduction of *p*-fluorotoluene with lithium aluminum hydride.

(4) Walter F. Edgell and L. Parts, Abstracts of the 125th National Meeting of the American Chemical Society, Kansas City, Mo., March-April, 1954; THIS JOURNAL, **77**, 4899 (1955).

(5) H. D. Noether, *J. Chem. Phys.*, **10**, 693 (1942).

(6) J. Beersmans and J. C. Jungers, *Bull. soc. chim. Belges*, **56**, 72 (1947).

(7) M. Corval and M. R. Viallard, *Bull. soc. chim. France*, 484 (1954).

(8) F. I. Anderson, *Proc. Conf. Applications Isotopes Sci. Research, Univ. Melbourne*, **1950**, 183 (1951).

(9) B. Nolin and L. C. Leitch, *Can. J. Chem.*, **31**, 153 (1953).

(10) R. F. Nystrom, W. H. Yanko and W. G. Brown, THIS JOURNAL, **70**, 441 (1948).

(11) R. F. Nystrom, W. J. Shraba and R. G. Mansfield, ORNL-395, USAEC (1949); U. S. Atomic Energy Comm., *Nuclear Sci. Abstr.*, **4**, 5669 (1950).

(12) J. D. Cox, H. S. Turner and R. J. Warne, *J. Chem. Soc.*, 3167 (1950).

(13) J. D. Cox and R. J. Warne, *Nature*, **165**, 563 (1950).

(14) D. E. Pack and B. M. Tolbert, UCRL-1957, USAEC (1952).

(15) A. E. Finholt and E. C. Jacobsen, THIS JOURNAL, **74**, 3943 (1952).

(16) G. I. Feklisov, *Izvest. Akad. Nauk S.S.S.R.*, 587 (1953).

(17) U. Solms, *Chim. Switz.*, **5**, 25 (1951).

(18) The representation of complexes formed in this reaction is only symbolic and may not correspond to their actual composition.

TABLE I

SYNTHESIS OF CH_3F AND CD_3F

Step	Product, moles		Yield, %[a]	
	CH_3	CD_3	CH_3	CD_3
1a, 1b	0.424	0.448	84.8	89.6
2	.362	.369	85.4	82.4
3	.276	.297	76.2	80.5
Total	.276	.297	55.2	59.4

[a] The reported yields are based on 1,2-propylene carbonate. On the basis of lithium aluminum hydride and lithium aluminum deuteride the corresponding total yields are 50.2 and 54.0%.

Experimental

Preparation of Methyl-d_3 Alcohol.—Lithium aluminum deuteride (17.3 g., 0.412 mole) and 200 g. of diethyl Carbitol (refluxed over and distilled twice from sodium) were treated under nitrogen with 51 g. (0.500 mole) of 1,2-propylene carbonate (Jefferson Chemicals) which was added in 93 g. of diethyl Carbitol. The addition of the propylene carbonate solution was regulated to maintain a reaction temperature of 45-55°, and required four hours. With continued stirring the temperature of the reaction mixture was raised to 73° during four hours following the addition of the propylene carbonate. The mixture was then cooled to 4° and 389 g. (2.40 moles) of butyl Carbitol were added during a period of 30 minutes with cooling by an ice-bath. Some gas (HD) was evolved during the beginning of the butyl Carbitol addition, indicating the presence of unreacted lithium aluminum deuteride. The methyl-d_3 alcohol was then removed by passing a slow stream of dry nitrogen through the solution held at 90 to 110°, and condensed in two traps, one immersed in Dry Ice, the other in liquid nitrogen. The distillation was continued for two hours, then the crude distillates from both traps were combined and redistilled through an 18-plate column. A 0.4-g. forerun, containing heavy formaldehyde, was discarded. The fraction boiling between 58.0 and 64.4° was collected. The major portion of the methyl-d_3 alcohol had b.p. 64.4° (ref. 6 gives b.p. 64.6°) and $n^{20}D$ 1.3280. The yield was 15.7 g., 89.6% on the basis of 1,2-propylene carbonate or 81.5% on the basis of the lithium aluminum deuteride.

Preparation of Methyl-d_3 *p*-Toluenesulfonate.—The reaction of 15.7 g. (0.448 mole) of methyl-d_3 alcohol and 94.0 g. (0.493 mole) of tosyl chloride was carried out essentially under the conditions given by Edgell and Parts.[4] The yield of methyl-d_3 *p*-toluenesulfonate was 69.9 g. (82.4%), $n^{20}D$ 1.5179.

Preparation of Methyl-d_3 Fluoride.—All of the methyl-d_3 *p*-toluenesulfonate prepared above was treated with 64.3 g. (1.11 moles) of anhydrous KF essentially as indicated earlier[4] in the method for the absence of a solvent. The yield was 11.0 g. (80.5%). The product contained about 5% methyl-d_3 chloride, presumably due to the presence of some tosyl chloride in the methyl-d_3 tosylate. The product was purified by distillation through a Podbielniak Heli-Robot column. Assuming the boiling point of methyl fluoride as −78.414°,[19] that of methyl-d_3 fluoride was −77.9°.

Isotopic Purity.—The isotopic purity of the methyl-d_3 fluoride was determined mass spectrometrically[20]. The following distribution of isotopic species was found: CD_3F 94.4 ± 0.5%, CD_2HF 5.2 ± 0.5%, CDH_2F 0.4 ± 0.5%, corresponding to a maximum of 2 atom per cent. light hydrogen in the sample. The percentage of CD_3F and CD_2HF was obtained from the corresponding molecule-ion peaks. The absolute amount of CDH_2F could be determined with lower accuracy due to interference by ionization fragments. The mass spectroscopic data are in agreement with an approximate isotopic analysis of methyl-d_3 alcohol by means of its infrared spectra. The results also indicate that the extent of isotopic contamination in the reactions leading from methyl-d_3 alcohol to methyl-d_3 fluoride is negligible within the limits of error of the experimental measurements.

---

[19] A. Michels and T. Wassenaar, *Physica*, **14**, 104 (1948).

[20] We are indebted to Dr. F. W. Lafferty of the Dow Chemical Company for this analysis.

LAFAYETTE, INDIANA

[CONTRIBUTION FROM THE CHEMISTRY DIVISION OF OAK RIDGE NATIONAL LABORATORY]

Molecular Rearrangements. V. The Relative Phenyl/Hydrogen Migration Abilities in the Pinacol Rearrangement of Triphenylethylene Glycol[1,2]

BY CLAIR J. COLLINS

RECEIVED MAY 2, 1955

The pinacol rearrangement of triphenylethylene glycol (I) has been investigated. The reaction was studied by comparing the fates of the chain- and ring-labels in the glycols Ia and Ic when these glycols were subjected to the influence of five different acid catalysts. It was possible to determine with high precision: (a) the yields of benzhydryl phenyl ketone (II) and triphenylacetaldehyde (III) and (b) the extent of carbon-14 migration of each label. From the foregoing data the contribution of each of four reaction paths has been calculated under each set of conditions. It is shown that the ratio of phenyl/hydrogen migration may vary by a factor of 180 (7.33 to 0.041), depending on the catalyst used for the rearrangement. These data are explainable if it is assumed that the phenyl group can migrate more readily than hydrogen in this reaction when open, or "classical" carbonium ions are the intermediates, and less readily than hydrogen when the process is concerted.

Introduction

It has been known for some time that triphenylethylene glycol (I) may be converted to phenyl benzhydryl ketone (II). Thus Gardeur,[3] Tiffeneau[4] and Lagrave[5] all reported that this transformation occurs when I is placed under the influence of various acidic catalysts. Danilov[6] reported that the glycol I, when dehydrated with 40% sulfuric acid, yields II and triphenylacetaldehyde (III) in the ratio of 4:1. Danilov reported also that III is quantitatively converted to II in the presence of concentrated sulfuric acid.

$$\underset{\mathrm{I}}{\mathrm{Ph_2COHCHOHPh}} \qquad \underset{\mathrm{II}}{\mathrm{Ph_2CHCOPh}} \qquad \underset{\mathrm{III}}{\mathrm{Ph_3CCHO}}$$

Considerable knowledge concerning the pinacol rearrangement of derivatives of triphenylethylene glycol was adduced next by McKenzie and coworkers[7,8] and by Roger and McKay.[9] These

---

[1] This paper is based upon work performed under Contract Number W-7405-eng-26 for the Atomic Energy Commission at Oak Ridge National Laboratory.

[2] Papers III and IV, C. J. Collins and W. A. Bonner, THIS JOURNAL, **77**, 92 (1955); W. A. Bonner and C. J. Collins, *ibid.*, **77**, 99 (1955).

[3] A. Gardeur, *Bull. acad. roy. Belg.*, [3] **34**, 67 (1897); *Chem. Zentr.*, **68**, II, 622 (1897).

[4] M. Tiffeneau, *Compt. rend.*, **146**, 29 (1908).

[5] R. Lagrave, *Ann. chim.*, [10] **8**, 416 (1927).

[6] (a) S. Danilov, *J. Russ. Phys. Chem. Soc.*, **49**, 282 (1917); (b) S. Danilov and E. Venus Danilova, *Ber.*, **59B**, 377 (1926).

[7] A. McKenzie, A. K. Mills and J. R. Myles, *Ber.*, **63**, 904 (1930).

[8] A. McKenzie, R. Roger and W. B. McKay, *J. Chem. Soc.*, 2597 (1932).

[9] R. Roger and W. B. McKay, *ibid.*, 332 (1933).