hydrous ether, and refluxed for four hours. The product was decomposed with ice and dilute sulfuric acid and the ethereal solution washed with sodium bicarbonate solution and water, dried and concentrated. The solid residue was recrystallized from benzene and melted at 125°; yield 85%.

Anal. Calcd. for $C_{16}H_{18}O_2$: C, 79.3; H, 7.4. Found: C, 79.5; H, 7.5.

2,2′-Bis-(bromomethyl)-6,6′-dimethylbiphenyl (II).—To a suspension of 9 g. of the dialcohol in 300 cc. of anhydrous benzene, which contained a few drops of pyridine, there was added at room temperature 28 g. of phosphorus tribromide (2 mole per mole of the dialcohol). During the reaction, the dialcohol dissolves. The reaction was completed by heating at 60° for two hours; the solution was washed with water, and sodium bicarbonate solution and evaporated. Trituration with cold alcohol caused the oily residue to crystallize in analytically pure form, m.p. 69.5–70°; yield 90%.

Anal. Calcd. for $C_{16}H_{16}Br_2$: Br, 43.5. Found: Br, 43.3.

4,5-Dimethyl-9,10-dihydrophenanthrene (III).—From 0.3 g. of lithium metal and 3.7 g. of bromobenzene in 35 cc. of ether, a solution of lithium phenyl was prepared (nitrogen atmosphere) and added slowly to the solution of 5.5 g. of the dibromide II in 130 cc. of ether with vigorous agitation. After one hour at room temperature and a further hour of refluxing, ice and dilute sulfuric acid was added and the ethereal layer washed with bicarbonate solution and water, dried and evaporated. The residual oil (3 g., 98%) was fractionated in a vacuum of 0.2 mm.; b.p. 115–117°, yield 2.4 g. (80%).

Anal. Calcd. for $C_{16}H_{16}$: C, 92.3; H, 7.7. Found: C, 92.4; H, 7.7.

4,5-Dimethylphenanthrene (IV).—The mixture of 0.5 g. of the dihydro compound III, and 0.5 g. of 10% palladium–charcoal was heated for 4 hours at 300° in a current of nitrogen. In order to prevent losses of the hydrocarbon, the reaction vessel was mounted with a water-cooler of finger type.[16] The reaction product was isolated by extraction with ether and purified by slow distillation under 0.1 mm. pressure at 100°. The oil which was thus obtained (0.45 g., 95%), crystallized upon trituration with alcohol; from alcohol, m.p. 76.3–76.7° (literature[4] 76.3–76.9°); mixed m.p. with an authentic specimen no depression.

The 2,4,7-trinitrofluorenone complex was prepared in alcoholic solution and recrystallized from the same solvent. It formed glistening, red needles, m.p. 122° (literature[4] 120.7–121.3°).

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[16] L. F. Fieser, "Experiments in Organic Chemistry," 2nd Edition, D. C. Heath and Co., Boston, Mass., pp. 461–462.

TEL-AVIV, ISRAEL

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF WASHINGTON]

The Thermal Rearrangement of Methyl Benzoate

BY KENNETH B. WIBERG

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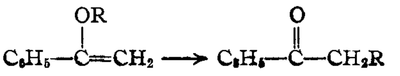
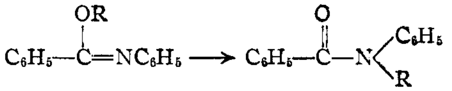
The possibility of observing a thermal rearrangement of methyl benzoate in which the methyl migrates from one oxygen to the other has been investigated using O^{18} as a tracer. No rearrangement was observed under 250°, but at 400° the reaction proceeds at a reasonable rate. A convenient preparation of O^{18}, labeled methanol is also given.

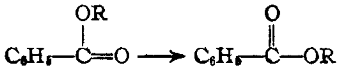
Current studies of the thermal rearrangement of vinyl ethers (A),[1] and of benzimido ethers (B),[2] have led to an investigation of the possibility of observing the corresponding rearrangement of an ester (C). Such a rearrangement, if facile, might effect partial racemization of esters of some optically active alcohols on distillation, and might have other similar consequences.



$$C_6H_5-\overset{OR}{\overset{|}{C}}=CH_2 \longrightarrow C_6H_5-\overset{O}{\overset{\|}{C}}-CH_2R \qquad (A)$$



$$C_6H_5-\overset{OR}{\overset{|}{C}}=NC_6H_5 \longrightarrow C_6H_5-\overset{O}{\overset{\|}{C}}-N\begin{matrix}C_6H_5\\R\end{matrix} \qquad (B)$$



$$C_6H_5-\overset{OR}{\overset{|}{C}}=O \longrightarrow C_6H_5-\overset{O}{\overset{\|}{C}}-OR \qquad (C)$$

It was desired to attempt this reaction using methyl benzoate (I) labeled with O^{18} on the ether oxygen,[3] since it was believed that an especially convenient method of following the reaction could be found, and since the ester is known to be quite stable toward thermal decomposition[4] thus eliminating undesirable side reactions. The most convenient method for the preparation of this ester would be the reaction of benzoyl chloride with O^{18}-enriched methanol. Methanol-O^{18} has been obtained by the fractional distillation of ordinary methanol,[5] and by the hydrolysis of methyl phosphate[6] in acid solution containing H_2O^{18}. The first of these methods is inconvenient and leads to only a small degree of enrichment under practical conditions, whereas in the latter method considerable dimethyl ether forms during the reaction and a product having considerably less O^{18} than the water used is obtained. Furthermore, the conversion of water to methanol is not too favorable unless the water is repeatedly recycled.

In order to find a more convenient method for the preparation of methanol-O^{18}, the reaction between methylmagnesium bromide with O_2^{18} was investigated. This reaction is known to be satisfactory for the preparation of aliphatic alcohols when an excess of oxygen is used.[7] The labeled oxygen was obtained by the electrolysis of H_2O^{18}-enriched water[8] with sulfuric acid. Under conditions employed, 50–70% of the theoretical amount of methanol was obtained, based on the water used. The methanol had only a slightly smaller O^{18}-content than the water, the loss of O^{18} probably being due to exchange with the sulfuric acid[9] during electrolysis. The composition of the methanol was determined from the cracking pattern obtained using a mass spectrometer.

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[1] L. Claisen, *Ber.*, **29**, 2931 (1896).

[2] A. W. Chapman, *J. Chem. Soc.*, 1743 (1927).

[3] As opposed to carbonyl labeled.

[4] E. M. Bilger and H. Hibbert, THIS JOURNAL, **58**, 823 (1936).

[5] I. Roberts and H. C. Urey, *ibid.*, **60**, 2391 (1938).

[6] E. Blumenthal and J. B. M. Herbert, *Trans. Faraday Soc.*, **41**, 611 (1945).

[7] F. Runge, "Organometallverbindungen," Wissenschaftliche Verlagsgesellschaft M. B. H., Stuttgart, 1944, p. 299.

[8] Obtained from the Stuart Oxygen Co. on allocation from the Atomic Energy Commission.

[9] J. Halperin and H. Taube, THIS JOURNAL, **74**, 375 (1952).

The rearrangement of ether labeled methyl benzoate (I) was first attempted at 250° with no rearrangement being observed using the analytical method described below. The use of 360° for three hours gave approximately 5% rearrangement, whereas 400–405° for three hours gave about 66% rearrangement. The reaction thus appears to have a high activation energy. It is interesting to note that the analogous rearrangement of α-methoxystyrene to propiophenone proceeds readily at 230° (the b.p. at 2 atm. pressure),[1] thus showing a remarkable difference in the ease of the two rearrangements.

The choice of analytical method was predicated on the belief that one of the primary fragmentation reactions of I in a mass spectrometer would be that leading to the acylonium ion $(C_6H_5C{=}O)^+$ since this should have a considerable degree of resonance stabilization. If this were the case, one could analyze for excess O^{18} over normal abundance in the carbonyl oxygen by using the 107/105 ratio, corrected for the ratio found in ordinary I.[10] The total excess O^{18}-content could then be estimated by using the 138/136 ratio similarly corrected. An examination of the mass spectrum of I (Table I) shows the above expectations to be realized. The 105 peak (acylonium ion) is the strongest in the spectrum, and the 107 peak in the carbonyl labeled I[11] is more intense than that of ordinary I or ether labeled I by the expected amount based on the O^{18}-content of the water used in its preparation. The fact that the 107 peak in the ether labeled I is slightly higher than that of ordinary I may be due to a small amount of exchange during its formation. The above results illustrate a convenient use for a mass spectrometer, *the degradation of a molecule and the simultaneous analysis of the fragments obtained for their isotopic content*, when a suitably designed system is employed.

TABLE I

Mass no.	Ordinary I	Carbonyl labeled I	Ether labeled I	Rearranged[a] ether l. I
104	0.57[b]	0.57	0.55	0.56
105	100.0	100.0	100.0	100.0
106	26.7	25.9	26.7	26.1
107	0.48	1.81	0.53	0.92
135	1.28	1.26	1.29	1.26
136	34.3	33.3	33.4	33.1
137	2.86	2.74	2.70	2.79
138	0.22	0.68	0.59	0.60
Mole %[c] excess O^{18}	0.00	1.33[d]	1.13[e]	1.17[e]

[a] Rearranged for 3 hr. at 400–405°. [b] Values given are relative intensity. [c] Excess over normal abundance (0.20%). [d] This value was calculated using the 107/105 ratio. The use of the 138/136 ratio leads to a value of 1.4% excess O^{18}. It was believed that these values would be little affected by the isotope effect since even with deuterium compounds the effect is not overly large. [e] Calculated using the 138/136 ratio.

Experimental

Methanol-O^{18}.—Oxygen enriched with O^{18} was obtained by the electrolysis of 20% sulfuric acid prepared from ordinary sulfuric acid and water containing 1.5% H_2O^{18}. The electrolysis cell was a U-tube constructed from a 33 cm. piece of 14-mm. tubing. The platinum electrodes were sealed in. Two bulbs of 30-ml. capacity were attached to the hydrogen side in such a way that the electrolyte would flow into the first bulb when the flow of oxygen became restricted during the reaction, thus stopping the electrolysis. The second bulb prevented water, which was used as a controllable head, from entering the electrolysis cell. A tube leading to the bottom of the cell made it possible to occasionally bubble nitrogen through the electrolyte, thus mixing the concentrated sulfuric acid which accumulated during the electrolysis with the body of the electrolyte. The cell was immersed in cold water during the electrolysis, and the apparatus was swept out with nitrogen before each run. The oxygen formed was passed through a Dry Ice–acetone cooled trap in order to remove water vapor.

The oxygen thus generated was introduced into 0.55 mole of methylmagnesium bromide in 500 ml. of ether (prepared under nitrogen), contained in a 1-l. three-necked flask having a stirrer and a reflux condenser. The delivery tube was of large diameter to minimize clogging by the precipitated salt. After a current of 4 amp. had been passed through the cell for seven hours (corresponding to *ca.* 0.5 atom of oxygen), the excess ether was decanted from the precipitate, and ice, followed by 25% sulfuric acid was added with external cooling. The solution thus obtained was distilled through a 18-cm. "Helipak" packed column, two fractions being collected, b.p. 60–70° and b.p. 70–99°.

The higher boiling fractions from several runs were combined and redistilled collecting material b.p. 60–70°. The lower boiling fractions were then combined and carefully redistilled, giving 50–70% of methanol, b.p. 65°. A somewhat larger amount of material having a wider boiling range could be obtained. Using water containing 1.5% O^{18}, there was obtained methanol containing 1.2% excess O^{18} (1.4% total) as determined from the mass spectrum.

Ether Labeled Methyl Benzoate.—To 8 g. (0.1 mole) of pyridine was added 3.2 g. (0.1 mole) of methanol-O^{18} followed by 14 g. (0.1 mole) of benzoyl chloride with ice-bath cooling. Water was added and the oily layer which separated was washed with water and distilled giving 10 g. (77%) of methyl benzoate b.p. 80° at 15 mm., having 1.2% excess O^{18} with essentially none in the carbonyl position, as determined from the mass spectrum.

Carbonyl Labeled Methyl Benzoate.—This was prepared from methyl benzimido ether hydrochloride and water containing 1.5% O^{18}, using the procedure previously described for the preparation of carbonyl labeled ethyl benzoate.[11]

Thermal Rearrangement of Ether Labeled Methyl Benzoate.—The reactions were carried out by sealing a small sample of the ester in a tube under nitrogen. The material was introduced into an aluminum mortar and heated to the desired temperature for three hours. After cooling, the tube was opened, and the sample analyzed with a mass spectrometer. Apparently, no significant amount of decomposition occurred at the temperatures employed.

SEATTLE, WASHINGTON

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[10] The Consolidated Engineering Corp. Model 21-103 mass spectrometer is uniquely suitable for this determination since it has four galvanometers operating simultaneously, giving sensitivities of 1, 3, 10 and 30. In obtaining the mass spectra, the pressure of the sample was adjusted so that the more intense peak could be read on the least sensitive galvanometer, and the less intense peak was read using the most sensitive galvanometer.

[11] Prepared by the reaction of methyl benzimido ether hydrochloride with water having an O^{18}-content of 1.5%. *Cf.* M. L. Bender, THIS JOURNAL, **73**, 1626 (1951).