

**Methyl Ester of Indene-2-carboxylic Acid.**—Indene-2-carboxylic acid was prepared by hydrolysis of diethyl indene-2,3-dicarboxylate, obtained by treatment of diethyl benzyloxalacetate with cold sulfuric acid.<sup>16</sup> The acid (3 g.) was esterified with diazomethane in ethereal solution. The solid (2.9 g.), obtained by evaporation of the organic solvent, was purified by crystallization in petroleum ether (b.p. 60–80°) and by sublimation *in vacuo*, m.p. 82–83.5°. The product was homogeneous by gas chromatography and could be separated from methyl indene-3-carboxylate on the above mentioned column.

*Anal.* Calcd. for C<sub>11</sub>H<sub>10</sub>O<sub>2</sub>: C, 75.84; H, 5.79. Found: C, 75.73; H, 5.76.

The n.m.r. and double resonance spectra in deuteriochloroform were obtained on a Varian Associates H. R. 100 spectrometer using the method of Johnson.<sup>17</sup>

(16) J. Bougault, *Compt. rend.*, **159**, 745 (1914).

(17) L. F. Johnson, "Varian Technical Information Bulletin," Vol. III, No. 3, 5, 1962.

## A Convenient Preparation of Methanol-*d*<sup>1</sup>

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The  $\alpha$ -hydrogens of esters are conveniently exchanged with methanol-*d* (CH<sub>3</sub>OD) as the solvent, but a good preparation of this alcohol has been lacking.

Among the methods used previously are the hydrolysis of dimethyl oxalate with D<sub>2</sub>O and sodium carbonate,<sup>3</sup> the exchange of methanol with D<sub>2</sub>O,<sup>4</sup> the hydrolysis of trimethyl borate with D<sub>2</sub>O,<sup>5</sup> and the reaction of sodium methoxide or magnesium methoxide with D<sub>2</sub>O.<sup>6</sup> We have used most of these methods and have also utilized the acid-catalyzed hydrolysis of 2,2-dimethoxypropane.<sup>7</sup>

None of these methods is really satisfactory, especially for the preparation of reasonable quantities of methanol-*d* of high isotopic purity. Such objections do not apply to the preparation described below.

This method involves the hydrolysis of commercially available dimethyl carbonate. However, in one experiment a mixture of 800 g. of dimethyl carbonate, 20 g. of D<sub>2</sub>SO<sub>4</sub> and 196 g. of D<sub>2</sub>O required 3 weeks of refluxing for complete reaction. The reaction rate could undoubtedly be increased by using more acid, but a separate preparation of D<sub>2</sub>SO<sub>4</sub> is an important limitation. This inconvenience was avoided by an *in situ* preparation of the acid catalyst using dimethyl sulfate since hydrolysis of this ester is rapid. The experimental procedure below uses quantities such that reaction is complete in 3 days of refluxing. A somewhat larger ratio of dimethyl sulfate could undoubtedly be used but a too rapid hydrolysis rate should be avoided because of the evolution of CO<sub>2</sub>.

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(2) (a) National Institutes of Health Postdoctoral Fellow, 1963–1964; (b) National Science Foundation Summer Cooperative Predoctoral Fellow, 1964.

(3) H. O. House and V. Kramer, *J. Org. Chem.*, **28**, 3362 (1963).

(4) K. Wiberg, *J. Am. Chem. Soc.*, **77**, 5987 (1955).

(5) C. G. Swain and M. M. Labes, *ibid.*, **79**, 1084 (1957).

(6) C. G. Swain, J. T. McKnight, and V. P. Kreiter, *ibid.*, **79**, 1088 (1957).

(7) F. R. Jensen, unpublished results.

Since diethyl carbonate and diethyl sulfate are also available commercially, a similar preparation of ethanol-*d* should be feasible.<sup>8</sup>

## Experimental

Dimethyl carbonate (Eastman White Label), 400 g. (4.44 moles), and deuterium oxide (Bio-rad Labs., Richmond, Calif.), 100 g. (5.00 moles), were placed in a carefully dried 1-l. one-necked flask. Dimethyl sulfate (Eastman practical grade), 16 g. (0.13 mole), was added and the flask was attached to two reflux condensers arranged in series (initial rapid evolution of carbon dioxide may entrain some liquid). The flask contents were heated to reflux with provision for moisture exclusion. After 72 hr. the disappearance of the carbonyl stretching frequency of dimethyl carbonate in the infrared indicated that the reaction was complete. The methanol-*d* was distilled directly from the reaction flask through a 30-cm. Vigreux column. One further distillation from a small amount of sodium sufficed to yield 275 g. (8.34 moles, 94% yield) of gas chromatographically pure (Carbowax 20M column) methanol-*d*, b.p. 66–66.5°.

The amount of deuterium substitution was obtained conveniently from the n.m.r. spectrum<sup>9</sup> of methanol-*d*. The area under the hydroxyl peak was compared with one of the two peaks due to C<sup>13</sup> splitting. From the relative intensities, the methanol-*d* was found to contain 98.6 ± 0.4% deuterium.

(8) NOTE ADDED IN PROOF.—This preparation has now been carried out successfully. Because of a slower hydrolysis rate, double the quantity of diethyl sulfate is convenient.

(9) A Varian A-60 nuclear magnetic resonance spectrometer was used.

## Stability of the Carbon-Phosphorus Bond in Trichloromethylphosphonate Esters. Ether Formation in Reactions with Alcohols and Phenols

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Esters of phosphonic acids containing a trichloromethyl group attached to phosphorus are sensitive to alkali, liberating chloroform,<sup>1</sup> but it is now generally accepted that in the absence of alkali the C–P bond is stable. The reaction of trichloromethylphosphonate esters with primary amines was believed at first to be a case of C–P bond scission,<sup>2</sup> but later work,<sup>3</sup> which has been amply substantiated,<sup>4</sup> showed that the products were not amides but amine salts, the esters behaving in this reaction as alkylating agents. The products of the reaction of diethyl trichloromethylphosphonate with aniline, for example, were N-ethylaniline and the aniline salt of ethyl hydrogen trichloromethylphosphonate.<sup>3,4</sup>

More recently, the reaction of diethyl trichloromethylphosphonate with ethanol was examined to determine

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(4) (a) K. C. Kennard and C. S. Hamilton, *J. Am. Chem. Soc.*, **77**, 1156 (1955); (b) C. E. Griffin, *Chem. Ind. (London)*, 415 (1958); (c) Tzeng-Shou Tung and Shyh-Tsong Chern, *Hua Hsüeh Hsüeh Pao*, **24**, 30 (1958); *Chem. Abstr.*, **53**, 3113, 2114s (1959).