

glass wool and evaporation yielded the ether-soluble rubber. The portion insoluble in ether was similarly treated with 100 ml. of chloroform for four hours and the residue from that treatment was extracted with 100 ml. of benzene for four hours.

**Phenylsodium and Rubber.**—Phenylsodium was made from 2.5 g. (0.022 mole) of chlorobenzene and sodium sand in a total volume of 160 ml. of thiophene-free benzene in the usual way. The mixture was forced by nitrogen pressure into a solution of 1.5 g. of rubber in 100 ml. of thiophene-free benzene. The viscous mixture was allowed to stand for the period given in Table II, after which it was forced onto solid carbon dioxide. Subsequent recoveries of rubber were as described in the previous section. The operations with stirring were in general the same as when the mixture was allowed to stand. Other conditions and results are given in Table II.

**Amylsodium and Rubber.**—The quantities of amyl chloride and sodium used for preparing amylosodium were such as to give 0.044 mole in each experiment based on an 80% yield. If isopropyl alcohol was added to this mixture in order to form the isopropoxide, enough additional amylosodium was prepared to allow for this consumption. Rubber, 1.5 g., was shredded and added to the reaction mixture. For the reaction at 20° the solvent was pentane; for the higher temperatures it was cyclohexane. The products were handled as before. The results are given in Table III.

**Pentenylsodium and Rubber.**—The preparation of amylosodium was carried out in the usual manner but with 1-pentene as a solvent.<sup>4</sup> Isopropoxide was obtained when desired by addition of the requisite quantity of isopropyl alcohol to 1-pentenylsodium. Rubber was added and the products separated as described in the previous section. The results are given in Table IV. The gel, swelling volume (S. V.) and intrinsic viscosity were determined by standard methods.

**Alkali Metals and Rubber.**—Sodium (5 g.) was shaken in 100 ml. of hot sulfur-free toluene. Rubber (1.5 g.) was then added and dissolved in 60°. An atmosphere of nitrogen was maintained. After removal of as much of the toluene as possible by use of an aspirator, the remainder was removed under a molecular still. Heat and vacuum was applied as described in Table VI. Carbon dioxide was then admitted, the reaction mixture cooled, and treated with solid carbon dioxide. The rubber was washed and fractionated as described below. The results are given in Table VI.

**Reaction of Metals with Hydrocarbons.**—The hydrocarbon in the quantities specified in Tables VII and VIII was dissolved in 40 ml. of benzene or xylene. Sodium was cut into small pieces and added. Alcohol was added as specified; the mixture was refluxed under an atmosphere of dry nitrogen. After the period of time specified in the table the mixture was carbonated by forcing it onto solid carbon dioxide. Alcohol, 100 ml., was added to destroy the sodium. Water, 13 ml., was then added and the solution heated on a water-bath to evaporate the alcohol. The aqueous solution was extracted with petroleum ether and with benzene and was then acidified with hydrochloric acid. The acid solution was then extracted with three 100-ml. portions of benzene and with three 100-ml. portions of ether.

The procedure was, in general, the same when the mixtures were stirred instead of refluxed. Usually the carboxylic acid precipitated upon the addition of hydrochloric acid and a single crystallization gave fairly good material. Triphenylacetic acid, recrystallized once from benzene, melted at 256.5–258.5° (the recorded<sup>12</sup> value is 264–265° dec.), fluorene-9-carboxylic acid, recrystallized once from alcohol, melted at 216–218° (a recorded<sup>13</sup> value is 220–222°), and phenylacetic acid, as obtained by evaporation of the ether extract, melted at 70–72° (recorded<sup>14</sup> value 76.7°).

### Summary

When metalating agents act on natural or Alfin rubber, gel is formed. The amount of gel increases with the activity of the metalating agent and the severity of the conditions under which it is used.

Metallic sodium or potassium does not cause gel to form in natural rubber. Under very severe conditions these metals will metalate the highly active hydrocarbons, fluorene, triphenylmethane and diphenylmethane, in fair to poor amount, depending on the hydrocarbon, but they metalate toluene only slightly, even under highly favorable conditions.

(12) Schmidlin, *Ber.*, **39**, 636 (1906).

(13) Friedländer, *ibid.*, **10**, 536 (1877).

(14) Huntress and Mulliken, "Identification of Pure Organic Compounds Order I," John Wiley and Sons, New York, N. Y., 1941.

CAMBRIDGE, MASS.

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## NOTES

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### The Preparation of Methyl Esters

BY R. O. CLINTON AND S. C. LASKOWSKI

There appears to be no description in the literature of an easily applicable general method for the preparation of the methyl esters of aliphatic and aromatic acids, especially for large-scale preparations. A large number of individual preparations have been described, involving in most cases the use of methanol-sulfuric acid or the Fischer methanol-hydrogen chloride method. In certain cases either of these methods gives excellent results; usually, however, the yields are of the order of 60–80%. The Fischer method gener-

ally gives the better yield, but is not easily adaptable to large-scale preparations. Other methods involving fractional distillation, such as the method of Weissberger and Kibler<sup>1</sup> require elaborate equipment and considerable manipulation. Baker<sup>2</sup> has described a procedure of apparently wide adaptability for small scale preparations, in which a mixture of the acid, methanol, chloroform (or benzene) and sulfuric acid is refluxed under a Soxhlet apparatus containing anhydrous magnesium sulfate. Baker<sup>2b</sup> states that continuous

(1) Weissberger and Kibler, "Organic Syntheses," **24**, 72 (1944).

(2) (a) Baker, *THIS JOURNAL*, **65**, 1577 (1943); (b) Baker, Query, *Safir and Bernstein, J. Org. Chem.*, **12**, 144 (1947).

drying of this type is essential for high yields. The limiting factors in this method are the large amounts of anhydrous magnesium sulfate required, the necessity for inclusion of a Soxhlet-type apparatus in the condensate path, and in some cases the time required for complete distillation of the water formed in the reaction, due to low concentration in the vapor phase.

A method in use in these Laboratories for some years appears to be of general applicability, and in ease of manipulation offers very evident advantages. We have found that the use of either methylene dichloride or ethylene dichloride as solvent removes the necessity for continuous drying and gives very high yields of methyl esters. The choice of solvent depends to some extent upon the boiling point of the required methyl ester; in general ethylene dichloride is the preferred solvent. A generalized procedure is as follows:

For each mole of aliphatic carboxyl group there are used 96 g. (3 moles) of commercial methanol, 300 ml. of ethylene dichloride, and 3 ml. of concentrated sulfuric acid. If the acid is aromatic, the amount of sulfuric acid is increased to 15 ml. per mole of carboxyl group.

The mixture is refluxed for from six to fifteen hours.<sup>3</sup> Progress of esterification is usually, but not invariably, indicated by the development of

cloudiness and the separation of an upper layer containing water, methanol and sulfuric acid. The cooled reaction mixture is washed successively with water, sodium bicarbonate solution<sup>4</sup> and again with water. The ethylene dichloride layer is then distilled at atmospheric pressure or *in vacuo*, and the residual methyl ester processed by distillation or crystallization.

The procedure is not limited to insensitive acids; substitution of a milder catalyst such as ethanesulfonic acid (0.5 to 1.0 ml. per mole of carboxyl group) for the sulfuric acid allows the preparation of, *e. g.*, methyl pyruvate with no difficulty.

Table I includes a few examples to indicate the versatility of the method.

(4) In large-scale preparations it is more convenient to dilute with water, siphon the upper layer, and stir the lower layer with excess solid sodium bicarbonate.

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### Condensation of Thiophene and Certain Derivatives with Chloral<sup>1</sup>

BY JAMES F. FREEMAN,<sup>2</sup> JOHN R. DOVE AND E. D. AMSTUTZ

The recent appearance of several papers<sup>3,4</sup> on the condensation of thiophene and several of its derivatives with chloral prompts us to report work which has been carried out along the same lines in this Laboratory.

Peter<sup>5</sup> in 1884 found that thiophene reacts with chloral in acetic acid solution in the presence of sulfuric acid giving "at most a 30% yield of the desired product which melted at 76°." Recent investigators<sup>3,4</sup> have in general employed the same reaction conditions with corresponding results. In the present work we have made use of aqueous sulfuric acid of varying concentrations which, in two cases at least, appears to make possible better yields than those previously reported.

In search of new insecticidal materials, we have prepared five dithienyltrichloroethanes, listed in Table I, analogous to DDT and related compounds. Two of these are new compounds while the other three have been reported by the investigators mentioned above.<sup>3,4,5</sup>

TABLE I  
METHYL ESTERS<sup>c</sup>

Acid	Size of experiment, moles	Yield, <sup>b</sup> %	Properties of methyl ester <sup>c</sup>
Cyclohexyl-acetic <sup>d,e</sup>	20	93	B. p. 64–65° (18 mm.), <i>n</i> <sub>D</sub> <sup>20</sup> 1.4450
Adipic <sup>f</sup>	14	87	B. p. 113–113.5° (13 mm.), <i>n</i> <sub>D</sub> <sup>20</sup> 1.4265
Benzoic	2	95	B. p. 80–80.5°, <i>n</i> <sub>D</sub> <sup>20</sup> 1.5155
Coumarin-3-carboxylic	2	98	M. p. 114–115°
Salicylic <sup>g</sup>	1	92	B. p. 104–105° (14 mm.), <i>n</i> <sub>D</sub> <sup>20</sup> 1.5360
2,4-Dinitrophenylacetic <sup>h</sup>	1	91	M. p. 82–83°
Pyruvic <sup>i</sup>	1	73	B. p. 136–140°, <i>n</i> <sub>D</sub> <sup>20</sup> 1.4046

<sup>a</sup> The general procedure, with ethylene dichloride as solvent, was used unless otherwise specified. <sup>b</sup> The yields given are for material with the properties indicated. <sup>c</sup> These properties agree well with those recorded in the literature for the pure compounds. <sup>d</sup> Preparation by Dr. E. D. Homiller. <sup>e</sup> Using methylene dichloride as solvent, a 95% yield of pure ester was obtained after seven hours of reflux. <sup>f</sup> Preparation by Dr. Bill Elpern. <sup>g</sup> Methylene dichloride as solvent, forty-eight hours reflux period. <sup>h</sup> Methylene dichloride as solvent, fifteen hours reflux period. <sup>i</sup> Time for complete solution of the acid was seven hours. <sup>j</sup> Fifteen hours reflux period, substituting 0.5 ml. of ethanesulfonic acid for the sulfuric acid. No tar formation was noted. Extension of the reflux period to forty-eight hours gave the same yield.

(3) It is usually convenient to reflux overnight. The lower time limit varies for each compound, and may be as short as one-half hour. In certain cases where the initial acid is quite insoluble in the mixture the full time specified may be required.

TABLE I

Compound	R =	M. p., °C.		Yield, %		Sulfur, %	
		Calcd.	Found	Calcd.	Found	Calcd.	Found
I	C <sub>6</sub> H <sub>5</sub> S—	77.5–78.0	73.2	21.54	21.63		
II	5-Cl-C <sub>6</sub> H <sub>4</sub> S—	64–64.5	62.0	17.49	17.86		
III	5-Br-C <sub>6</sub> H <sub>4</sub> S—	92.5–93.0	35.1	14.08	14.31		
IV	2,5-di-Cl-C <sub>6</sub> H <sub>3</sub> S—	109.5–109.7	66.1	14.74	14.44		
V	5-t-C <sub>6</sub> H <sub>4</sub> -C <sub>6</sub> H <sub>4</sub> S—	90.5–91.0	13.9	15.65	15.41		

(1) Taken in part from the senior research thesis of John R. Dove, June, 1947.

(2) Lehigh Institute of Research Fellow in Organic Chemistry, 1947.

(3) Metcalf and Gunther, *THIS JOURNAL*, **69**, 2579 (1947).

(4) Truitt, Mattison and Richardson, *ibid.*, **70**, 79 (1948).

(5) Peter, *Ber.*, **17**, 1341 (1884).