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.[3] 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[4] 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.

TABLE I

METHYL ESTERS[a]

Acid	Size of experiment, moles	Yield,[b] %	Properties of methyl ester[c]
Cyclohexylacetic[d,e]	20	93	B. p. 64–65° (18 mm.), $n^{25}\text{D}$ 1.4450
Adipic[f]	14	87	B. p. 113–113.5° (13 mm.), $n^{25}\text{D}$ 1.4265
Benzoic	2	95	B. p. 80–80.5°, $n^{25}\text{D}$ 1.5155
Coumarin-3-carboxylic	2	98	M. p. 114–115°
Salicylic[g]	1	92	B. p. 104–105° (14 mm.), $n^{25}\text{D}$ 1.5360
2,4-Dinitrophenylacetic[h]	1	91	M. p. 82–83°
Pyruvic[i]	1	73	B. p. 136–140°, $n^{25}\text{D}$ 1.4046

[a] The general procedure, with ethylene dichloride as solvent, was used unless otherwise specified. [b] The yields given are for material with the properties indicated. [c] These properties agree well with those recorded in the literature for the pure compounds. [d] Preparation by Dr. E. D. Homiller. [e] Using methylene dichloride as solvent, a 95% yield of pure ester was obtained after seven hours of reflux. [f] Preparation by Dr. Bill Elpern. [g] Methylene dichloride as solvent, forty-eight hours reflux period. [h] Methylene dichloride as solvent, fifteen hours reflux period. Time for complete solution of the acid was seven hours. [i] 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.

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.

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[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.

[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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RECEIVED MARCH 16, 1948

Condensation of Thiophene and Certain Derivatives with Chloral[1]

BY JAMES F. FEEMAN,[2] JOHN R. DOVE AND E. D. AMSTUTZ

The recent appearance of several papers[3,4] 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[5] 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[3,4] 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.[3,4,5]

TABLE I

SUBSTITUTED DITHIENYL-TRICHLOROETHANES, R_2—CH—CCl_3

Compound	R =	M. p., °C.	Yield, %	Sulfur, % Calcd.	Sulfur, % Found
I	C_4H_3S—	77.5–78.0	73.2	21.54	21.63
II	5-Cl-C_4H_2S—	64–64.5	62.0	17.49	17.86
III	5-Br-C_4H_2S—	92.5–93.0	35.1	14.08	14.31
IV	2,5-di-Cl-C_4HS—	109.5–109.7	66.1	14.74	14.44
V	5-*t*-C_4H_9-C_4H_2S—	90.5–91.0	13.9	15.65	15.41

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[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).

Metcalf and Gunther[3] have shown, by oxidation of the dehydrochlorinated dithienyltrichloroethane to the corresponding 2,2′-dithienyl ketone, that condensation in this case takes place in the expected 2 position of thiophene, and have substantiated this with evidence of failure of the indophenine test on the condensation products of the 2-substituted thiophenes, while the parent compound gave a positive test.

We have obtained evidence which indicates the above conclusions are correct, *i. e.*, that the 2-substituted thiophenes condense with chloral at the reactive 5 position. It is well known that mercuration of thiophene and its derivatives takes place first at an open α-position. By mercuration of 2,2-bis-(2-thienyl)-1,1,1-trichloroethane (I) with mercuric acetate in ethanol and acetic acid, and subsequent bromination of the di-mercurated product we obtained a compound (III) which proved to be identical with the product of condensation of 2-bromothiophene and chloral.

All attempts to condense 2-*t*-octyl-thiophene, 2,5-di-*t*-butyl-thiophene, 2-benzoyl-thiophene and 2,3,5-trichloro-thiophene with chloral by this method failed.

Acknowledgments.—The authors express their thanks to the Lehigh Institute of Research for funds which permitted carrying out this investigation, to the Michigan Chemical Corp. for the sample of 2-bromothiophene used in some of the work, and to the Research and Development Department of the Socony–Vacuum Oil Co., Inc., Paulsboro, N. J., for generous samples of the remainder of the thiophene derivatives used in this study.

Experimental[6]

In general the procedure followed for the condensations involved mixing sulfuric acid of the proper concentration with the calculated quantity of chloral hydrate in a three-necked flask fitted with mechanical stirrer and dropping funnel, and cooled by means of an ice-bath. The thiophene derivative (calculated amount) was then added at once with stirring, and a second quantity of sulfuric acid dropped into the reaction mixture over a period of one hour. Stirring was then continued for five hours, when the mixture was poured into ice-water, and the crude product either filtered off or the acid solution decanted. The crude material was washed with water, 10% bicarbonate solution, and water again, and then dried over phosphorus pentoxide overnight in a vacuum desiccator. Purification was effected by several recrystallizations from ethanol, including treatment with active charcoal.

2,2-bis-(2-Thienyl)-1,1,1-trichloroethane (I).—Thiophene (16.8 g., 0.2 mole), chloral hydrate (16.6 g., 0.1 mole), 20 ml. of sulfuric acid and 20 ml. of water were allowed to react as above. Concentrated sulfuric acid (50 ml.) was dropped in during one hour.

2,2-bis-(5-Chloro-2-thienyl)-1,1,1-trichloroethane (II).—Chloral hydrate (34.0 g., 0.22 mole), and 2-chlorothiophene (50.0 g., 0.44 mole) were condensed in the presence of 50 ml. concd. sulfuric acid; yield, 50.0 g. of a colorless crystalline substance with a fruity odor.

2,2-bis-(5-Bromo-2-thienyl)-1,1,1-trichloroethane (III).—2-Bromothiophene (81.5 g., 0.5 mole) was condensed with 41.4 g. (0.25 mole) of chloral hydrate in the presence of 200 ml. of concd. sulfuric acid; yield, 40.0 g. of colorless crystals with a slight fruity odor.

2,2-bis-(2,5-Dichloro-3-thienyl)-1,1,1-trichloroethane (IV).—Chloral hydrate (41.4 g., 0.25 mole) and 78.0 g. (0.52 mole) of 2,5-dichlorothiophene were condensed in the presence of half of a solution of 100 g. of concd. sulfuric acid and 200 g. of oleum (15% sulfur trioxide). The remainder of the acid was dropped in during one hour. The crude product weighed 99 g. (90.9%) (m. p. 93–104°). Two recrystallizations from ethanol gave colorless crystals.

2,2-bis-(2,5-Dichloro-3-thienyl)-1,1-dichloroethylene.—(2,2-bis-(2,5-Dichloro-3-thienyl)-1,1,1-trichloroethane (17.4 g., 0.04 mole) was refluxed with 200 ml. of 7.5% ethanolic potassium hydroxide for one hour. The solution was poured into 500 ml. of cold water, and the oil which separated was taken up in ether, the extracts dried over calcium chloride, and the ether evaporated. The oil solidified upon standing in the cold, and two recrystallizations from methanol gave colorless prisms, 11.1 g. (69.5%), m. p. 64.5–65.5°.

Anal. Calcd. for $C_{10}H_6S_2Cl_6$: S, 16.07. Found: S, 16.06.

Attempted Oxidations.—Several attempts were made to oxidize the above ethylene derivative with chromic anhydride in glacial acetic acid to the corresponding dithienyl ketone. These gave only yellow oils which could not be crystallized. Similar oxidations of the oil formed by alkaline hydrolysis of 2,2-bis-(5-*t*-butyl-2-thienyl)-1,1,1-trichloroethane produced only yellow oils which could not be crystallized nor distilled (1 mm. pressure).

2,2-bis-(5-*t*-Butyl-2-thienyl)-1,1,1-trichloroethane (V).—2-*t*-Butylthiophene (70.0 g., 0.50 mole) and 41.4 g. (0.25 mole) of chloral hydrate were condensed in a similar manner to that for 2,5-dichlorothiophene. The product was a yellow resinous material which was triturated with cold ethanol, leaving the desired product undissolved. Three recrystallizations from ethanol gave colorless crystals.

2,2-bis-(5-Acetoxymercuri-2-thienyl)-1,1,1-trichloroethane.—To a solution of 10 g. (0.03 mole) of dithienyltrichloroethane in 100 ml. of ethanol at 70° in a 500-ml. flask fitted with a reflux condenser was added a solution of 19.2 g. (0.06 mole) of mercuric acetate in 100 ml. of ethanol and 10 ml. of acetic acid. After fifteen minutes refluxing a white precipitate began forming. At the end of an hour it was filtered off, washed twice with 25-ml. portions of ethanol, and dried at 110° in the oven, giving 23.5 g. (94.0%) of fine white powder, m. p. 192–193°, dec.

Anal. Calcd. for $C_{14}H_{11}O_4S_2Cl_3Hg_2$: Hg, 49.23. Found:[7] Hg, 48.27, 48.10.

Bromination of Dichloromercuri-Dithienyl Trichloroethane.—The diacetoxymercuri-dithienyl-trichloroethane (15.5 g., 0.019 mole) was suspended with stirring in a saturated solution of 25 g. of sodium chloride for a half-hour at 40–50°. The white product was then filtered off, washed well with water and dried in the 110° oven, giving 14.6 g. of fine white powder, m. p. 188–190° dec. A solution of 7.7 g. (0.01 mole) of 2,2-bis-(5-chloromercuri-2-thienyl)-1,1,1-trichloroethane in 150 ml. of carbon tetrachloride was placed in a 300-ml. three-necked flask, fitted

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[6] All melting points have been corrected for thermometer stem-emergence unless otherwise noted.

[7] Analyses for mercury were carried out gravimetrically by decomposition with fuming nitric acid in a sealed tube, and quantitative precipitation in the form of the complex $[HgI_4][Cu\ en_2]$ from the neutralized solution (ammonia) according to the method of Spacu and Suciu, *Z. anal. Chem.*, **92,** 247 (1933). Rauscher's method (Rauscher, *Ind. Eng. Chem., Anal. Ed.*, **10,** 331 (1938)) for determination of mercury was attempted but the presence of sulfur interfered with the reduction.

with a dropping funnel, stirrer and thermometer, and cooled with an ice–salt-bath. Bromine (3.2 g., 0.02 mole) was then dropped in with stirring over a period of one-half hour. The solution was filtered and the carbon tetrachloride removed under reduced pressure. There remained a dark-colored oil which solidified to a brown solid (crude yield, 4.9 g.). Several recrystallizations from ethanol with activated charcoal treatment afforded 3.7 g. of colorless crystals with a fruity odor, m. p. 92–93°. A mixed melting point with the product of condensation of chloral and 2-bromothiophene gave no depression.

Anal. Calcd. for $C_{10}H_5S_2Br_2Cl_3$: S, 14.08. Found: S, 14.15.

Attempted Condensations.—Attempts were made to condense 2-*t*-octylthiophene, 2,5-*t*-butylthiophene, 2,3,5-trichlorothiophene and 2-benzoylthiophene with chloral using conditions reported above for the successful condensations and also using acetic acid as solvent in the reaction. 2-Benzoylthiophene was unaffected by these reaction conditions, being isolated quantitatively unchanged, while the other thiophene derivatives gave dark oils which we were not able to crystallize or to distill under reduced pressure (1 mm.).

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RECEIVED MARCH 30, 1948

2-Ethylpyridine and Derivatives

BY EARL C. GREGG, JR., AND DAVID CRAIG

2-Ethylpyridine has been prepared in this Laboratory by two independent methods; the hydrogenation of 2-vinylpyridine and the reaction of methyl iodide with α-picolyl lithium. Nevertheless, derivatives (picrate[1] and mercuric chloride[2]) reported by others for 2-ethylpyridine do not agree in their properties with our derivatives.

Since our methods of preparation appear unequivocal, we believe that previously recorded preparations of this compound have been impure or unauthentic.

Experimental

2-Vinylpyridine[3] was hydrogenated at 60 lb. hydrogen pressure at room temperature over old Raney nickel. One-tenth mole of hydrogen was absorbed by one-tenth mole of 2-vinylpyridine in 35 ml. of alcohol. The hydrogenation product distilled at 70–73° at 50 mm. or 144° at atmospheric pressure, $n^{20}D$ 1.4978. The picrate melted at 108.5–110° (uncor.) when crystallized from alcohol instead of 187° (uncor.) reported by Bergstrom.[1] It was established that no other picrate forming substance was present.

Analytical

Calculated picric acid content for $C_5H_4O_7N_3 \cdot C_7H_9N$ is 68.1%. Picric acid found by polarographic analysis in 0.1 *N* hydrochloric acid solution is 68.1 ± 0.3%.

The chloroplatinic acid derivative melted at 165–166° (uncor.) as reported by Ladenburg.[2] However, the mercuric chloride derivative melted at 113–114° (uncor.) instead of 103–106° (uncor.) reported by Ladenburg.[2] α-Picolyl lithium was prepared according to Walter.[4]

Dry methyl iodide was added dropwise to the α-picolyl lithium in the reaction flask which was immersed in ice. The resulting ether mixture was extracted with water to remove lithium iodide and some of the unreacted α-picoline. The ether layer was extracted with dilute hydrochloric acid to remove the 2-ethylpyridine and remaining unreacted α-picoline. The hydrochloric acid layer was neutralized and the resulting 2-ethylpyridine was drawn off and steam distilled. The 2-ethylpyridine was dried over anhydrous sodium sulfate and fractionated to remove α-picoline at 77–79° at 80 mm. The picrate from the higher boiling (70–73° 50 mm.) fraction melted at 108.5–110° (uncor.). The mixed melting point of the picrates prepared by the two methods was 108.5–110° (uncor.).

The ultraviolet absorption spectrum of the 2-ethylpyridine prepared above was characteristic of a monoalkyl pyridine.

We wish to acknowledge the measurement and interpretation of the ultraviolet absorption spectrum of 2-ethylpyridine by Laura Schaefgen.

A CONTRIBUTION FROM THE
RESEARCH CENTER OF THE
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BRECKSVILLE, OHIO
RECEIVED APRIL 15, 1948

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Small Angle X-Ray Scattering of Various Cellulose Fibers

BY A. N. J. HEYN

The study of diffraction and scattering of X-rays at small angles by various substances has been undertaken only very recently and may be considered negligible in comparison with the studies at larger angles.

Small angles studies of fibrous material have been mainly confined to proteins[1–7] which give *discontinuous* scattering indicating the presence of a large (super-identity) period, inside the large molecules.

Only very preliminary work has been done on scattering of cellulose fibers, although it has been long known that ramie fiber gives a *continuous* small angle scattering.[2,8] Kratky and collaborators (1938–1942)[9,10] recently ventured a quantitative evaluation of the scattering in this material and related the identity period calculated to the size and distance of the cellulose micelles, which they found to be 50–60 Å. Besides ramie they also studied a special regenerated cellulose product derived from viscose. (Other authors[11–14]

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