

hours. The temperature of the oil-bath was then raised to 90° and the reaction mixture held at this temperature with continuous stirring for another two hours.⁹

The reaction mixture was then cooled and treated with a cold solution of 150 cc. of glacial acetic acid in 300 cc. of water and the ester layer taken up in ether. The ether extract was washed free of acid with sodium bicarbonate and, after removal of the ether, fractionated under diminished pressure. The yield of ester boiling over a 5° range amounted to 144 g. (37% of calcd.).

When the above procedure was followed using equivalent quantities of ethyl propionate and ethyl butyrate instead of ethyl acetate the yields of the corresponding ketesters dropped to about 19 and 4% of the theoretical, respectively.

Summary

A method of preparation of a number of α -benzoyl alkyl cyanides and their conversion into the corresponding α -benzoyl substituted esters are described. The properties of the amides corresponding to certain of these esters are recorded.

A satisfactory method for the preparation of benzoylacetate ester by the direct condensation of ethyl benzoate with ethyl acetate is given.

⁹ Claisen and Lowman³ recommend mixing the reactants and heating for fifteen hours. It was found in the present work that this longer period of heating was not only unnecessary but somewhat disadvantageous since invariably 5–10% lower yields were obtained when this procedure was employed.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY, NATIONAL TSINGHUA UNIVERSITY]

ESTERS OF ORTHOFORMIC ACID

BY PETER P. T. SAH AND TSU SHENG MA

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The discovery of the first orthoformic ester was connected with the famous Williamson synthesis.¹ The product from sodium ethoxide and chloroform was really an ether with three ethoxy groups attached to the same carbon atom. The reaction was further studied by a number of investigators,² notably Deutsch,³ who synthesized five members of the homologous series (methyl, ethyl, *n*-propyl, *i*-butyl and *i*-amyl) and determined roughly their boiling points and densities. Pinner,⁴ allowing various alcohols to react on form-imino-ether-hydrochlorides, succeeded not only in confirming Deutsch's work but also isolating a number of mixed ortho-

¹ Williamson and Kay, *Ann.*, **92**, 346 (1854).

² (a) Sawitsch, "Jahresbericht über die Fortschritte der Chemie," 391 (1860); (b) Bassett, *Ann.*, **132**, 54 (1864); (c) Ladenburg and Wichelhaus, *ibid.*, **152**, 164 (1869); (d) Stapff, *Z. Chem.*, 186 (1871); (e) Arnold, *Ann.*, **240**, 193 (1887); (f) Kaufmann and Dreger, "Organic Syntheses," John Wiley and Sons, Inc., New York, 1925, Vol. V, p. 55.

³ Deutsch, *Ber.*, **12**, 115–119 (1879).

⁴ Pinner, *ibid.*, **16**, 1643–1647 (1883).

formates. Of these, little was known regarding their physical properties except their boiling points.

By allowing metallic sodium to react with a mixture of chloroform and various alcohols, we have prepared seven tri-alkyl orthoformates in a very pure condition and determined carefully their simple physical constants.

Experimental

Preparation of Tri-alkyl Orthoformates.—Into a one-liter round-bottomed flask, with a reflux condenser, containing 150 g. of dry chloroform and 500 cc. of absolute alcohol (methyl, ethyl, *n*-propyl, *i*-propyl, *n*-butyl, *i*-butyl and *i*-amyl), 69 g. of metallic sodium cut into sticks was introduced gradually in the course of two hours. For methyl and ethyl derivatives, the reactants were well cooled in ice water. The higher homologs showed retardation of reaction and initial heating was necessary. When the reaction was over, the flask was allowed to cool at room temperature for four hours. The

TABLE I
SIMPLE PHYSICAL CONSTANTS OF TRI-ALKYL ORTHOFORMATES

| Tri-alkyl | Formula | B. p., °C. | d_4^{20} | d_4^{25} | n_D^{20} | n_D^{25} | From literature ⁸ | |
|------------------|--|------------|------------|------------|------------|------------|------------------------------|--|
| | | | | | | | B. p., °C. | d_4^{25} |
| Methyl | C ₄ H ₁₀ O ₃ | 103–105 | 0.9676 | 0.9623 | 1.3793 | 1.3773 | 101–102 | 0.974 |
| Ethyl | C ₇ H ₁₆ O ₃ | 145–147 | .8909 | .8858 | 1.3922 | 1.3900 | 145–147 | .897 ₄ ¹⁸ . ⁸ |
| <i>i</i> -Propyl | C ₁₀ H ₂₂ O ₃ | 166–168 | .8621 | .8600 | 1.4000 | 1.3980 | New compound | |
| <i>n</i> -Propyl | C ₁₀ H ₂₂ O ₃ | 196–198 | .8805 | .8783 | 1.4072 | 1.4052 | 196–198 | .879 |
| <i>i</i> -Butyl | C ₁₃ H ₂₈ O ₃ | 224–226 | .8582 | .8550 | 1.4120 | 1.4100 | 220–222 | .861 |
| <i>n</i> -Butyl | C ₁₃ H ₂₈ O ₃ | 245–247 | .8693 | .8687 | 1.4180 | 1.4160 | New compound | |
| <i>i</i> -Amyl | C ₁₆ H ₃₄ O ₃ | 267–269 | .8628 | .8578 | 1.4233 | 1.4217 | 265–267 | .864 |

TABLE II
MOLECULAR REFRACTIONS OF TRI-ALKYL ORTHOFORMATES

| Structures | Mol. wt. | Molecular refractions | | | | | |
|--|----------|-----------------------|--------|--------|----------------|--------|-------|
| | | Gladstone–Dale | | | Lorenz–Lorentz | | |
| | | Calcd. | Found | Calcd. | Found | Calcd. | Found |
| HC(OCH ₃) ₃ | 106.078 | 41.49 | 41.56 | 41.56 | 25.60 | 25.34 | 25.35 |
| HC(OC ₂ H ₅) ₃ | 148.125 | 64.44 | 65.21 | 65.21 | 39.45 | 39.64 | 39.61 |
| HC(OCH(CH ₃) ₂) ₃ | 190.172 | 87.39 | 88.24 | 88.01 | 53.31 | 53.47 | 53.37 |
| HC(OCH ₂ CH ₂ CH ₃) ₃ | 190.172 | 87.39 | 87.95 | 87.74 | 53.31 | 53.19 | 53.10 |
| HC(OCH ₂ CH(CH ₃) ₂) ₃ | 232.218 | 110.34 | 111.64 | 111.36 | 67.16 | 67.33 | 67.29 |
| HC(O(CH ₂) ₃ CH ₃) ₃ | 232.218 | 110.34 | 111.66 | 111.20 | 67.16 | 67.32 | 67.08 |
| HC(OC ₅ H ₁₁ - <i>i</i>) ₃ | 274.265 | 133.29 | 134.62 | 134.82 | 81.02 | 81.09 | 81.19 |

TABLE III
ANALYSES OF TRI-ALKYL ORTHOFORMATES

| Tri-alkyl | Formula | Subs., g. | H ₂ O, g. | CO ₂ , g. | H, % | | C, % | |
|------------------|--|-----------|----------------------|----------------------|--------|-------|--------|-------|
| | | | | | Calcd. | Found | Calcd. | Found |
| Methyl | C ₄ H ₁₀ O ₃ | 0.1489 | 0.1286 | 0.2474 | 9.50 | 9.66 | 45.24 | 45.30 |
| Ethyl | C ₇ H ₁₆ O ₃ | .1185 | .1179 | .2446 | 10.89 | 11.13 | 56.71 | 56.28 |
| <i>i</i> -Propyl | C ₁₀ H ₂₂ O ₃ | .1481 | .1525 | .3411 | 11.66 | 11.52 | 63.10 | 62.81 |
| <i>n</i> -Propyl | C ₁₀ H ₂₂ O ₃ | .0825 | .0888 | .1909 | 11.66 | 12.04 | 63.10 | 62.95 |
| <i>i</i> -Butyl | C ₁₃ H ₂₈ O ₃ | .1498 | .1658 | .3668 | 12.15 | 12.38 | 67.17 | 66.77 |
| <i>n</i> -Butyl | C ₁₃ H ₂₈ O ₃ | .1877 | .1986 | .4604 | 12.15 | 11.84 | 67.17 | 66.91 |
| <i>i</i> -Amyl | C ₁₆ H ₃₄ O ₃ | .1033 | .1189 | .2636 | 12.49 | 12.88 | 69.98 | 69.61 |

sodium chloride was filtered off. The clear filtrate was fractionated at atmospheric pressure. The lower fractions consisted of unreacted chloroform and alcohol and could be used over again. The higher constant boiling fraction was collected and redistilled three times. The product was considered to be pure; yield, 30%. The simple physical constants were then determined.

Tri-alkyl orthoformates are colorless liquids with a faint characteristic odor, insoluble in water but soluble in all organic solvents. They could be distilled at atmospheric pressure without any decomposition.

Summary

1. Seven simple tri-alkyl orthoformates have been synthesized from chloroform and sodium alkoxides. Among these, the *i*-propyl and *n*-butyl ortho-esters are new compounds. The rest have been mentioned in the literature, but their simple physical constants are for the first time accurately determined.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

STEREOCHEMISTRY OF DIPHENYL. XXIII.¹ OPTICALLY ACTIVE 2,5-DIMETHOXY-2'-NITRO-6'- CARBOXYDIPHENYL AND THE MUTAROTATION OF ITS SALTS

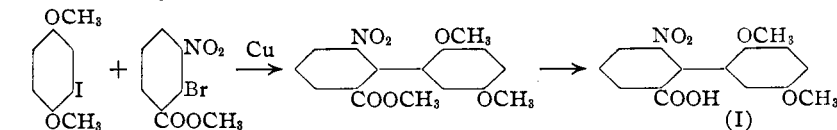
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On the assumption that the size of the 2,2',6,6' groups is the primary factor in preventing free rotation of the aryl groups in substituted diphenyls, the relative rates of racemization of various derivatives should lead to conclusions concerning the relative size of groups. Since the tetra-substituted derivatives, except in very few instances, present molecules which cannot be racemized at all or only with great difficulty, the 2,2',6-trisubstituted diphenyls offer the most promising field for this study.

In the present investigation a compound was selected containing one group, the methoxyl, which from previously published and unpublished results, was known to be small. The specific compound prepared was 2,5-dimethoxy-2'-nitro-6'-carboxydiphenyl (I).



¹ The last five papers in this series are as follows: (a) Hill and Adams, *THIS JOURNAL*, **53**, 3453 (1931); (b) Bock and Adams, *ibid.*, **53**, 3519 (1931); (c) Woodruff and Adams, *ibid.*, **54**, 1977 (1932); (d) Roll and Adams, *ibid.*, **54**, 2494 (1932); (e) White and Adams, *ibid.*, **54**, 2104 (1932).

² This communication is an abstract of a portion of a thesis submitted by H. C. Yuan in partial fulfillment of the requirements for the Degree of Doctor of Philosophy in Chemistry at the University of Illinois.