constant was determined graphically by plotting $x/a(a - x)$ against t from the kinetic equation $k = 1/t \cdot x/a(a - x)$. The results are summarized in Table I. It can be seen that the *o*-methyl esters have a reaction rate approximately twice that of the isomeric ortho-isopropyl esters.

TABLE I

SAPONIFICATION RATE CONSTANTS

Isopropylbenzoates	B. p. at 5 mm. °C.	n^{20}_{D}	Yield, %	Rate of reaction in moles/liter/sec. × 10^4		
				k_{25}	k_{35}	k_{50}
Ethyl 2-methyl-5-	117.9	1.5020	50	0.505	1.32	5.53
Ethyl 3-methyl-6-	116.1	1.5001	50	.218	0.646	2.45
Methyl 2-methyl-5-	107.2	1.5101	63	.575	1.47	7.10
Methyl 3-methyl-6-	107.5	1.5071	60	.235	0.659	3.73

Summary

1. An improved method of synthesis for 2-methyl-5-iso-propylbenzoic acid is reported.

2. The rates of the saponification at three temperatures of the methyl and ethyl esters of 2-methyl-5-isopropylbenzoic acid have been found to be about twice those of the corresponding esters of 3-methyl-6-isopropylbenzoic acid.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF GALAT CHEMICAL DEVELOPMENT, INC.]

A Synthesis of α,β-Unsaturated Esters

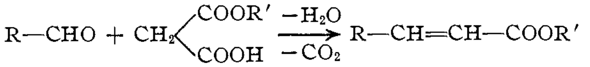
BY ALEXANDER GALAT

A general procedure for converting aldehydes directly into α,β-unsaturated esters is not available at present. The preparative value of such a method is evident, since α,β-unsaturated esters are often desired as intermediates in the syntheses of alcohols, acids, amides and in the formation of addition and substitution products. Moreover, such esters, particularly those of the aromatic series, are employed as preservatives, antioxidants, antiseptics and perfumes.

The Claisen and the Reformatsky methods which involve the interaction of an aldehyde with an acetic ester in the presence of sodium or with a haloacetic ester and zinc, are not general methods. In particular, they are not suitable for the preparation of cinnamic esters containing halogen, nitro or phenolic groups in the ring.[1]

Since a number of cinnamic esters, particularly those containing phenolic groups, was desired by this Laboratory, a new method, of wider application than the Claisen and Reformatsky, was sought.

The ease with which malonic acid and its di-esters condense with aldehydes is well known and the classical Doebner and Knoevenagel procedures have served in the past to prepare a great variety of acrylic acid derivatives. This suggested that half-esters of malonic acid would condense with similar ease to form half-esters of alkylidene- or arylidene-malonic acids. These, without isolation, would lose carbon dioxide and yield acrylic esters



$$\text{R—CHO} + \text{CH}_2\begin{cases}\text{COOR}' \\ \text{COOH}\end{cases} \xrightarrow[-\text{CO}_2]{-\text{H}_2\text{O}} \text{R—CH=CH—COOR}'$$

This method was tried with excellent results and, indeed, proved to be of a more general nature for the direct synthesis of α,β-unsaturated esters than those described in the literature. It was shown to be applicable in cases where the Claisen and the Reformatsky reactions are known to be unsuitable.[1]

The monoesters of malonic acid can be prepared from the corresponding di-esters by the action of the calculated amount of alkali, followed by acidification and extraction with a solvent,[2] or by the direct esterification of malonic acid with the corresponding alcohol.[3]

Because of the ready availability of di-ethyl malonate and also because the ethyl esters were the ones desired, most of the unsaturated esters prepared in the present investigation were ethyl esters. Several methyl esters were also prepared after it was observed that mono-methyl malonate could be easily obtained by treating di-ethyl malonate with one mole of potassium hydroxide in the presence of an excess of methanol. Apparently a quantitative interchange takes place, since by the subsequent reaction with aldehydes unsaturated methyl esters were obtained in pure state.

The following aldehydes were studied and gave the corresponding unsaturated esters in yields of 75% or higher: benzaldehyde, *p*-tolualdehyde, *p*-chlorobenzaldehyde, *m*-nitrobenzaldehyde, *p*-hydroxybenzaldehyde, protocatechuic aldehyde, anisaldehyde, 1-naphthaldehyde and furfural. The conditions, except for minor variations in the isolation of the ester, were essentially the same as those of the Doebner method for the preparation of unsaturated acids.[1]

Experimental

Methyl *m*-Nitrocinnamate.—Three and two-tenths grams (0.02 mole) of *m*-nitrobenzaldehyde, 4.8 cc. (*ca.* 0.04 mole) of monomethyl malonate, 0.25 cc. of piperidine

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[1] "Organic Reactions," Vol. 1, John Wiley & Sons, New York, 1942, Chapters I and VIII.

[2] Breslow, Baumgarten and Hauser, THIS JOURNAL, **66**, 1287 (1944).

[3] Contzen-Crowet, *Bull. soc. chim. belg.*, **35**, 183 (1926).

and 10 cc. of dry pyridine were mixed together and heated under reflux on a steam-bath for six hours. The ester crystallized out on cooling and the process was completed by keeping overnight in the refrigerator. The crystals were filtered, washed with acetone and dried in vacuum. The filtrate and the acetone washings were combined, evaporated to a small volume and, on the addition of iso-propanol, a second crop of crystals was obtained. The total yield was 3.58 g. (86.5%), m. p. 122–124°.

The ethyl ester was similarly prepared with a yield of 85–90%, by using an equivalent quantity of monoethyl malonate in the place of the methyl ester.

Methyl *p*-Dimethylaminocinnamate.—Three grams (0.02 mole) of *p*-dimethylaminobenzaldehyde, 4.8 cc. (*ca.* 0.04 mole) of monomethyl malonate, 0.25 cc. of piperidine and 10 cc. of dry pyridine were heated under reflux on the steam-bath for four hours. The pyridine was then distilled off *in vacuo* and the crystalline residue was taken up in 10–15 cc. of boiling acetone. To this solution, water was added slowly with stirring until the precipitation of the ester was complete. The crystals were filtered off, washed with acetone and dried at 90–100°; yield 3.9 g. (95%); m. p. 130–132°. One recrystallization from hot acetone gave a pure material melting at 134–136°. The same yield of the ethyl ester was obtained by using monoethyl malonate.

Ethyl Caffeate.—Two and eight-tenths grams (0.02 mole) of protocatechuic aldehyde, 4.5 cc. (*ca.* 0.04 mole) of monoethyl malonate, 0.25 cc. of piperidine and 10 cc. of dry pyridine were mixed together and allowed to stand overnight in a stoppered flask. The mixture was then heated under reflux for two hours on a steam-bath, the pyridine distilled off *in vacuo* and the mixture diluted with 2 cc. of alcohol. Five cc. of water was then added slowly with stirring and the mixture was made acid to congo red with hydrochloric acid. The ester separated as a granular crystalline mass which was filtered, washed with dilute alcohol and dried at 60–70°. The yield of the crude ethyl caffeate was 3.82 g. (92%), m. p. 140–142°. One recrystallization from dilute alcohol brought the melting point to 149–150°. By re-using the mother liquors in the subsequent runs to secure the maximum yield, an over-all yield of 90–91% of the pure ester was obtained.

Summary

A one-step method for converting aldehydes into the α,β-unsaturated esters is described. It consists of condensing an aldehyde with a half-ester of malonic acid under the conditions of the Doebner reaction. The new synthesis gives good yields and has a wider range of applicability than the Claisen or the Reformatsky reactions.

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The Anomalous Reaction between Ammonia and 9-Chlorofluorene. Substitution of the Labile Hydrogen in Fluorene Derivatives

BY LOUIS A. PINCK AND GUIDO E. HILBERT[1]

Courtot and Petitcolas[2] in a note on the synthesis of 9-substituted aminofluorenes reported that the action of anhydrous ammonia on 9-chlorofluorene yields dibiphenylene-ethylene, 9,9′-difluorylamine and a trace of 9-aminofluorene. This reaction has now been reinvestigated, and the results obtained do not agree with those of the French workers.

9-Chlorofluorene[3] and liquid ammonia interact at room temperature to form dibiphenylene-ethylene in a yield approximately 45% of the theoretical. The nitrogenous products of the reaction are fluorylidene-imine, in fair yield, and traces of 9-aminofluorene. Any possibility of confusing 9,9′-difluorylamine with fluorylidene-imine is readily excluded by the wide difference in their melting points.[4] The formation of an unsaturated compound, such as the imine, obviously requires the simultaneous production of a fluorene derivative saturated presumably at the 9 position. This compound was isolated and found to be fluorene, the yield of which was comparable with that of the imine.

In the presence of a solvent, such as toluene, an additional nitrogenous compound, 1-aminodibiphenylene-ethane, is formed by the reactants. The structure of this compound was determined by the following reactions: (a) methylation with methyl iodide, yielding 1-methylaminodibiphenylene-ethane, and (b) treatment with nitrous acid, giving 1-hydroxydibiphenylene-ethane. These derivatives were found to be identical with specimens prepared by other procedures.[5,6]

The formation of the various compounds from the reactions of 9-chlorofluorene in ammonia may be expressed by the equations given on the next page. This theory of reaction mechanisms is advanced on the basis of experimental data reported in this paper and also on analogous reactions referred to in previous work. Reactions I and IV are analogous inasmuch as the lability of the hydrogen atom in the 9 position plays an important role in both cases. That 1-chlorodibiphenylene-ethane, the primary product of reaction I, was not found is not surprising since this compound is rapidly converted to dibiphenylene-ethylene in an alkaline

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(1) Present address: Bureau of Agricultural and Industrial Chemistry, U. S. Department of Agriculture, Peoria, Illinois. Article not copyrighted.

(2) Courtot and Petitcolas, *Compt. rend.*, **180**, 297 (1925).

(3) Thiele and Wanscheidt, *Ann.* **376**, 269 (1910); Bergmann and Hervey, *Ber.*, **62**, 893 (1929).

(4) The imine melts at 124°, whereas the melting point of difluorylamine according to Goldschmidt and Reichel [*Ann.*, **456**, 163 (1927)] is 198°.

(5) Pinck and Hilbert, THIS JOURNAL, **57**, 2398 (1935).

(6) Courtot, *Ann. chim.*, [9] **4**, 164 (1915).