their nitrogen determinations and stability tests; to Capt. M. L. Cushing[17] formerly of this Laboratory and initially connected with this development; and to Dr. N. Gruenhut for her able assistance.

Summary

Complete nitration of starches and modified starches by means of nitrogen pentoxide in solution in a suitable non-aqueous solvent, such as chloroform, is described, together with an effective laboratory method of producing crude nitrogen pentoxide. A simple and effective means of removal of nitric acid, the by-product of pentoxide nitrations, is accomplished by use of sodium fluoride, a hydrogen-bonded complex, $NaF\ldots HONO_2$, being probably formed, by which the efficiency of the nitration reaction is greatly increased. Trinitrates of corn starch, potato starch, thin-boiling corn starches, and corn dextrins are readily obtained and stabilization of the nitric esters is relatively simple and rapid. Owing to the completely anhydrous character of the nitration and the relatively low temperatures involved, the nitric esters produced are considered to reflect the degree of polymerization of the original materials. It is believed that nitrogen pentoxide nitration offers a new and important means of investigation of the structure of starch and modified starch, and, possibly, of other polysaccharides.

(17) Chemical Warfare Service, U. S. A.

LONG ISLAND CITY, N. Y. RECEIVED OCTOBER 9, 1945

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF EMORY UNIVERSITY]

Studies in *p*-Cymene. I. The Saponification Rate of Isomeric Benzoates Derived from *p*-Cymene[1]

BY CHARLES T. LESTER AND CARROLL F. BAILEY[2]

In connection with studies on *p*-cymene, we had prepared the two well-known isomeric acids, 2-methyl-5-isopropylbenzoic acid and 3-methyl-6-isopropylbenzoic acid.[3] It seemed to us of interest to determine what difference in the rate of saponification the esters of these two acids would show. Accordingly, we converted these into their known methyl and ethyl esters[3] and determined the rate of saponification of each of the four esters at three temperatures.

Experimental Preparations

Isomeric Acids.—2-Methyl-5-isopropylbenzoic acid was prepared by a series of steps starting with *p*-cymene, which we found more satisfactory than the procedure of Bogert and Tuttle[3] starting with crude 2-bromo-*p*-cymene, since our method avoids the tedious separation of the isomeric acids by fractional crystallization. *p*-Cymene was first converted into 2-aceto-*p*-cymene by a previously reported method[4]; then by its reaction with sodium hypochlorite, following also a previously described procedure for preparing β-naphthoic acid,[5] we obtained the desired acid in a 61% yield, b. p. 171° at 20 mm., m. p. 71°. These values checked with those reported[3] for the compound.

3-Methyl-6-isopropylbenzoic acid was prepared by a series of reactions starting with thymol. 3-Bromo-*p*-cymene, obtained in 71% yield by the reaction of thymol with phosphorus pentabromide, as described by Fileti and Crosa,[6] was treated with magnesium in dry ether to give the Grignard reagent. Dry Ice was then added to the ether solution over a period of one hour until the solution became very viscous. Additional Dry Ice was added as needed for a period of eight hours. On working up in the usual manner, 3-methyl-6-isopropylbenzoic acid, m. p. 84°, was obtained in 56% yield, based on the bromo compound. This series of reactions was almost identical with that reported by Bogert and Tuttle.[3] They reported the same melting point and a 55% yield for the acid. We found the use of Dry Ice an easier method of carbonation than the use of carbon dioxide under pressure, as reported by them.

Isomeric Esters.—The chlorides of the above acids were prepared by the procedure described by Bogert and Tuttle.[3] Our yields and boiling points agreed with their values. To a solution of 5 cc. of absolute ethanol in 50 cc. of dry pyridine was added slowly 20 g. of 2-methyl-5-isopropylbenzoyl chloride. The mixture warmed spontaneously and pyridine hydrochloride crystallized from the mixture. When all the acid chloride had been added, the solution was heated until the pyridine hydrochloride re-dissolved. It was then refluxed for ten minutes, cooled and 100 cc. of dilute hydrochloric acid added. The ester was then extracted with ether. The ether extract was washed repeatedly with dilute acid until free of pyridine, then with water, three times with 5% sodium bicarbonate solution, water again, and then dried over anhydrous sodium sulfate. The ether was removed on a water-bath, the ester fractionally distilled through a Penn State column,[7] and finally fractionally distilled through a Smith semi-micro column. The sample used was the middle cut of the final distillation. There was no range of temperature in this fraction.

The other esters were prepared and purified in the same manner. Their yields and physical properties are given in Table I. Bogert and Tuttle[3] reported the boiling points of the esters at a variety of pressures. They did not report yields or refractive indices.

Rate of Saponification

The method of Evans, Gordon and Watson was followed in detail.[8] Duplicate samples were used in each run. The duplicate values showed an average deviation of 2.6%. The reaction rate

(1) Presented before the Meeting-in-Miniature of the Georgia Section of the American Chemical Society, Atlanta, Ga., September 28, 1945.

(2) Community Trust Fellow, 1944–1945.

(3) Bogert and Tuttle, THIS JOURNAL, **38**, 1349 (1916).

(4) "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 3.

(5) Ref. 4, p. 428.

(6) Fileti and Crosa, *Gazz. chim. ital.*, **16**, 292 (1886).

(7) Whitmore and Lux, THIS JOURNAL, **54**, 3451 (1932).

(8) Evans, Gordon and Watson, *J. Chem. Soc.*, 1430 (1937).

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. $\times 10^4$ 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.

EMORY UNIVERSITY, GEORGIA

RECEIVED NOVEMBER 13, 1945

[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 diesters 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

$$R{-}CHO + CH_2\begin{cases}COOR'\\COOH\end{cases} \xrightarrow[-CO_2]{-H_2O} R{-}CH{=}CH{-}COOR'$$

This method was tried with excellent results and, indeed, proved to be of a more general nature 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

(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).