the high dipole moment of iodine monochloride and the resonance between the benzene rings of the biphenyls.

It would appear in each case that iodination with iodine and nitric acid in a carbon tetrachloride solution is the best procedure for iodination of the esters studied.

AUSTIN, TEXAS RECEIVED NOVEMBER 26, 1943

[CONTRIBUTION FROM THE EASTERN REGIONAL RESEARCH LABORATORY, BUREAU OF AGRICULTURAL AND INDUSTRIAL CHEMISTRY, AGRICULTURAL RESEARCH ADMINISTRATION, UNITED STATES DEPARTMENT OF AGRICULTURE]

Pyrolysis of Lactic Acid Derivatives. Production of Phenyl and *o*-Tolyl Acrylate*

BY E. M. FILACHIONE, J. H. LENGEL AND C. H. FISHER

In recent years considerable interest has been shown in the production of acrylic esters by the pyrolysis of esters of acetoxypropionic acid. These esters can be made from lactic acid by the reactions

$$CH_3CHOHCOOH + ROH \longrightarrow CH_3CHOHCOOR + H_2O$$

$$CH_3CHOHCOOR + (CH_3CO)_2O \longrightarrow CH_3CH(OCOCH_3)COOR$$

Methyl acetoxypropionate[1,2] has been pyrolyzed to give high yields of methyl acrylate. Satisfactory yields of acrylic esters have been obtained also by pyrolysis of the benzyl[1] and tetrahydrofurfuryl[3] esters of acetoxypropionic acid. Other esters of acetoxypropionic acid, including the ethyl,[1] butyl,[1] allyl,[4] and methallyl[4] esters, have been pyrolyzed, but the yields of the corresponding acrylic esters are low, since a predominant side reaction takes place, *i. e.*, the aliphatic alcohol radical is decomposed into the corresponding olefin. For example, ethylene, carbon monoxide, acetaldehyde and acetic acid are formed when ethyl acetoxypropionate is pyrolyzed. Because of this or other side reactions, the satisfactory preparation of acrylic esters by the pyrolytic method appears limited to acetoxypropionic esters that have relatively stable alkyl groups.

Recent work[5] has shown that α-acetoxyisobutyric esters can be converted by pyrolysis into methacrylic esters more readily than α-acetoxypropionic esters can be transformed into acrylic esters.

Phenol is thermally stable, and because of their structure phenyl and substituted phenyl esters of acetoxypropionic acid would be expected to be incapable of the side reaction that occurs with ethyl acetoxypropionate and related esters. Results given in the present paper demonstrate that this expectation was reasonable.

Phenyl and *o*-tolyl acetoxypropionates were prepared by the following series of reactions and also by the methods described in the experimental section: (1) Aqueous 80% lactic acid was acetylated with acetic acid, benzene being used as an entraining agent to remove the water of esterification continuously.[6] The yields of acetoxypropionic acid were as high as 77%. (2) Acetoxypropionic acid was converted by means of thionyl chloride into acetoxypropionyl chloride in 80 to 82% yields. (3) Acetoxypropionyl chloride was converted by treatment with phenol (or *o*-cresol) into phenyl (or *o*-tolyl) acetoxypropionate in yields of almost 90%. (4) Pyrolysis of phenyl acetoxypropionate (or the corresponding *o*-tolyl ester) produced the aryl acrylate (75 to 80% yields).

Phenyl α-acetoxypropionate was pyrolyzed at temperatures and contact times that ranged from 440 to 600° and from 0.77 to 20 seconds. A pressure of 18 to 19 mm. was used in one experiment, atmospheric pressure for the others (Table I). The yield of acetic acid was always higher than the yield of phenyl acrylate. Carbon monoxide and carbon dioxide were formed in some experiments in considerable amounts. Styrene, obtained in yields as high as 20%, presumably was formed prior to decomposition of phenyl acetoxypropionate into phenyl acrylate since it has been reported by Skraup and Nietzen[7] that phenyl acrylate yields phenol, acetylene, and carbon monoxide on pyrolysis.

o-Tolyl acetoxypropionate was pyrolyzed at temperatures ranging from 500 to 591° (Table II). *o*-Tolyl acrylate was obtained in yields as high as 75%; the yields of acetic acid were even higher. No real attempt was made to detect *o*-methylstyrene in the reaction products.

Possibly because of the presence of small amounts of phenol or some other inhibitor, the phenyl acrylate purified by distillation showed little tendency to polymerize. Samples of phenyl acrylate that had been washed with dilute sodium

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* Not copyrighted. This paper was presented before the Division of Industrial and Engineering Chemistry of the 106th meeting of The American Chemical Society at Pittsburgh, Pa., Sept., 1943.

(1) R. Burns, D. T. Jones and P. D. Ritchie, *J. Chem. Soc.*, 400–406, 714–717 (1935).

(2) L. T. Smith, C. H. Fisher, W. P. Ratchford and M. L. Fein, *Ind. Eng. Chem.*, **34**, 473 (1942).

(3) H. V. Claborn, U. S. Patent 2,222,363, Nov. 19, 1940; 2,229,997, Jan. 28, 1941.

(4) C. H. Fisher, C. E. Rehberg and L. T. Smith, THIS JOURNAL, **65**, 763 (1943).

(5) C. E. Rehberg, C. H. Fisher and L. T. Smith, *ibid.*, **65**, 1003 (1943).

(6) E. M. Filachione and co-workers, "Preparation of Methyl α-Acetoxypropionate from Lactic Acid, Acetic Acid and Methanol," presented at the Pittsburgh meeting of the American Chemical Society, September, 1943.

(7) S. Skraup and F. Nietzen, *Ber.*, **57**, 1294 (1924).

TABLE I

PYROLYSIS OF PHENYL α-ACETOXYPROPIONATE

Expt.	Amount pyrolyzed, g.	Temp., °C.	Contact time, sec.	Ester dec. %	Yields, moles per mole of ester decomposed				
					Acetic acid	Phenyl acrylate	Styrene	CO_2	CO
77	37	500	18	60	0.65	0.50	..	0.08	0.26
81	49	550	14	96	.81	.64	..	.12	.24
82	39	550	20	100	.88	.66	0.16	.21	.28
84	57	600	10	100	.91	.54	.07	.27	..
90	56	600	6	100	.90	.61	.12	.18	.21
102	56	583	3.7	95	.75	.64	.21	.07	.07
128	45	594	5.5	100	.86	.72	.07	.08	.08
H-170	82	522	19	65	.94	.76	.04	.07	.10
H-172	116	531	12	55	.94	.76	.03	.05	.09
H-173	123	548	15	73	.98	.76	.08	.08	.10
H-174	114	565	12	78	.97	.76	.11	.10	..
H-176	92	440	20	13	.64	.32	..	.01	.14
360[a]	78	541	0.77	34	.88	.80	..	..	..

[a] A pressure of 18 to 19 mm. was used.

TABLE II

PYROLYSIS OF *o*-TOLYL α-ACETOXYPROPIONATE

Expt.	Amount pyrolyzed, g.	Temp., °C.	Contact time, sec.	Ester dec., %	Yields, moles per mole of ester decomposed			
					Acetic acid	*o*-Tolyl acrylate	CO_2	CO
134	49	500	15	61	0.83	0.72	0.03	0.09
141	40	547	21	100	.90	.67	.04	.05
363	122	591	7	71	.64	.55	..	..
368	111	542	11	67	.97	.66	..	..
370[a]	76	549	2.3	82	.97	.75	..	..

[a] A pressure of 18 to 20 mm. was used.

hydroxide solution, however, polymerized readily (mass polymerization at 75°) in the presence of 1% benzoyl peroxide, forming a transparent product that was hard at room temperature but became soft at approximately 60°.

When a sample of *o*-tolyl acrylate isolated from the pyrolysis products by distillation was heated with approximately 1% benzoyl peroxide, a soft and viscous polymer was formed. Samples of the *o*-tolyl ester that had been washed with alkali polymerized readily (mass polymerization at 67°) when treated with 1% benzoyl peroxide. The polymer thus obtained, which was hard at room temperature, softened at approximately 60°.

The authors gratefully acknowledge the assistance of Dr. W. P. Ratchford, under whose direction the pyrolyses were carried out, and also the assistance of the other members of the Carbohydrate Division and of the Analytical and Physical Chemistry Division.

Experimental

Preparation of Acetoxypropionyl Chloride.—A mixture of 4 moles of lactic acid (80%), 28.0 moles of glacial acetic acid, 200 ml. of benzene, and 1 ml. of concentrated sulfuric acid was refluxed, with the continuous removal of water by means of a modified Dean and Stark tube. After twenty-one hours the mixture was neutralized with 4.0 g. of sodium acetate and distilled in vacuum. A 77% yield of acetoxypropionic acid resulted. By heating the acetoxypropionic acid with thionyl chloride (1.1 mole) gradually for approximately two hours to a final temperature of 95°, followed by distilling in vacuum, an 82% yield of acetoxypropionyl chloride was isolated.

Preparation of Phenyl α-Acetoxypropionate.—Phenyl acetoxypropionate was prepared by heating equimolar quantities of phenol and acetoxypropionyl chloride on a steam-bath until evolution of hydrogen chloride ceased. The ester was then isolated in 86 to 88% yields by distillation in vacuum: b. p. 110 to 111° (2 to 3 mm.) and 143° (12 mm.); n^{20}_D 1.4860; d^{20}_4 1.134. *Anal.* Calcd. for $C_{11}H_{12}O_4$: C, 63.45; H, 5.81; M_R, 52.70. Found: C, 62.63; H, 6.05; M_R, 52.65.

Phenyl acetoxypropionate was prepared also by (a) the reaction of acetoxypropionyl chloride with aqueous sodium phenolate (65% yield); (b) the interaction of acetoxypropionyl chloride, phenol, and phosphorus oxychloride (30%); and treatment of phenyl acetate with acetoxypropionic acid in the presence of a small amount of concentrated sulfuric acid (45% yield on the basis of unrecovered acetoxypropionic acid).

Preparation of *o*-Tolyl α-Acetoxypropionate.—A mixture of 1.0 mole of *o*-cresol and 1.0 mole of α-acetoxypropionyl chloride was heated on the steam-bath until evolution of hydrogen chloride ceased. The mixture was then distilled in vacuum, a Claisen flask being used. The *o*-tolyl α-acetoxypropionate boiled at 112 to 113° below 1 mm.; n^{20}_D 1.4860; d^{20}_4 1.124. *Anal.* Calcd. for $C_{12}H_{14}O_4$: C, 64.85; H, 6.35; saponification equivalent, 111.1. Found: C, 64.01; H, 6.56; saponif. eq., 111.2.

Pyrolysis.—The pyrolysis of the acetoxypropionates was carried out by allowing the liquid to run into a Pyrex glass tube having a bore of 30 mm. and heated over a length of 13 inches. The vertical tube, packed with short lengths of Pyrex glass tubing, was heated by an electric furnace[2] controlled automatically. The apparatus[2] was swept with nitrogen before the pyrolysis started and also after all the ester had been added. A small amount of hydroquinone was added to the condensate to prevent premature polymerization.

Titration of the crude pyrolysis product showed the amount of acetic acid present. The acrylate and undecomposed acetoxypropionate were isolated by vacuum distillation of the crude pyrolysis product. Styrene was also formed in the pyrolysis of phenyl acetoxypropionate. It was collected with the acetic acid fraction in the distillation and was isolated by adding salt water to the acetic acid fraction.

Further data on the pyrolysis of phenyl and *o*-tolyl acetoxypropionate are given in Tables I and II.

Properties of Phenyl Acrylate and *o*-Tolyl Acrylate.—Phenyl acrylate[7] as obtained by the pyrolysis of phenyl α-acetoxypropionate was a virtually colorless liquid that boiled at 63 to 64° at 1- to 2-mm. pressure and 87 to 94° at approximately 12 mm.; n^{20}_{D} 1.5210; d^{20}_{4} 1.0762. *Anal.* Calcd. for $C_9H_8O_2$: C, 72.97; H, 5.44; M_R, 41.35. Found: C, 72.77; H, 5.66; M_R, 41.92. Neither the phenyl nor the *o*-tolyl acrylate polymerized readily until it had been washed with dilute alkali.

The *o*-tolyl acrylate was a virtually colorless liquid: b. p. 55 to 57° at 0.5 mm.; 78 to 79° at 3 mm.; n^{20}_{D} 1.5160; d^{20}_{4} 1.050; MR (calcd.) 45.96; MR (obs.) 46.59.

Summary

1. Satisfactory methods have been developed for converting lactic acid into α-acetoxypropionyl chloride, phenyl α-acetoxypropionate and *o*-tolyl α-acetoxypropionate.

2. Pyrolysis of the phenyl and *o*-tolyl esters of acetoxypropionic acid yielded phenyl and *o*-tolyl acrylate, respectively. Styrene also was formed in the pyrolysis of phenyl acetoxypropionate.

3. Relatively hard resins were obtained by polymerizing phenyl and *o*-tolyl acrylate.

PHILADELPHIA, PA. RECEIVED DECEMBER 17, 1943

NOTES

Polarographic Behavior of Aniline Oxidation Products

BY DAVID LESTER AND LEON A. GREENBERG

A recent paper by Levitan, Kolthoff, Clark and Tenenberg[1] describes the polarographic behavior of some of the oxidation products of sulfanilamide. For some time we have been interested in the possible use of the polarograph for the analysis of the intermediary products of the metabolism of aniline and therefore investigated the behavior of β-phenylhydroxylamine, *p*-aminophenol, and azoxybenzene at the dropping mercury electrode. Since we concluded at that time that this method of analysis was better replaced by specific and more sensitive colorimetric methods in the case of the first two compounds, our study was not pursued further.

Our study, however, yielded results which appear to be at variance with those published on the hydroxylamino derivative of sulfanilamide. We find that in 0.07 *M* phosphate buffer (*p*H 6.3) β-phenylhydroxylamine does not give a cathodic wave but does give an anodic oxidation wave with an $E^{1}/_{2}$ *vs.* the S. C. E. of −0.02 volt. Levitan, Kolthoff, Clark and Tenenberg do not mention an anodic wave but do find a cathodic wave in 0.1 *M* sodium hydroxide. It has been our experience with β-phenylhydroxylamine that in the presence of alkali it is converted quite completely and rapidly to the azoxybenzene derivative, which then exhibits a cathodic wave; it is therefore impossible to polarograph alkaline β-phenylhydroxylamine solutions. It would be noteworthy if hydroxylaminobenzenesulfonamide, through the presence of a sulfonamide group, would not undergo this same transformation. This point is supported by the fact that the half-wave potentials for the hydroxylamino and azoxy derivatives of sulfanilamide are practically identical. It is unfortunate that the electrode reduction of the azoxy compound had to be carried out in 50% methanol, thus making impossible comparisons of the diffusion currents.

With our apparatus (Fisher Scientific Co. Electropode) and capillary an anodic diffusion current of 5.23 μa. per 0.001 *M* solution was found for hydroquinone and *p*-aminophenol with the 0.07 *M* phosphate buffer (*p*H 6.3). Since it is known that two electrons are involved in this reaction, two electrons are probably also involved in the anodic oxidation of β-phenylhydroxylamine, which gives a diffusion current of 5.3 μa. per 0.001 *M* solution. We have found that with the same buffer, but containing 20% ethanol, the diffusion current of azoxybenzene is 7.5 μa. per 0.001 *M* solution, with an $E^{1}/_{2}$ *vs.* the S. C. E. of −0.63 volt. Since the addition of alcohol decreases the diffusion current, it is quite likely that four electrons or more may be involved in the reduction: thus $C_6H_5NONC_6H_5 \rightarrow C_6H_5NHNHC_6H_5 + H_2O$, that is, the reduction to hydrazobenzene and water.

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RECEIVED JANUARY 7, 1944

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(1) N. I. Levitan, I. M. Kolthoff, W. G. Clark and D. J. Tenenberg, THIS JOURNAL, **65**, 2265 (1943).

Alkylcyanopyruvic Esters from Aliphatic Nitriles

BY GLENN S. SKINNER, J. H. TAYLOR AND J. L. ERNST

It was reported[1] that mixtures of sodium and potassium are more effective than sodium alone in

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(1) Skinner, THIS JOURNAL, **59**, 322 (1937).