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.; $n^{20}\text{D}$ 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.; $n^{20}\text{D}$ 1.5160; d^{20}_4 1.050; M_R (calcd.) 45.96; M_R (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.

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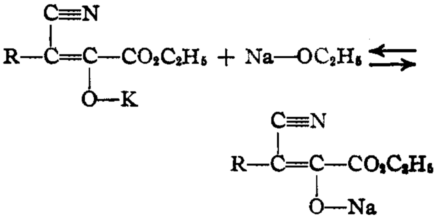
[1] Skinner, THIS JOURNAL, **59**, 322 (1937).

TABLE I

Ethyl alkylcyanopyruvate		Equivs. alkoxide	Yield, %	B. p., °C.	B. p., Mm.	Nitrogen, % Found	Nitrogen, % Calcd.
Methyl	$C_7H_9O_3N$	50% Na:50% K.	79	119–21	14		
Ethyl	$C_8H_{11}O_3N$	K	65	127–9	15	8.25	8.28
n-Propyl	$C_9H_{13}O_3N$	K	55	137–9	15	7.58	7.65
n-Propyl		90% Na:10% K.	31	135–7	15		
n-Propyl		Na	13	135–9	15		
n-Propyl		Na ribbon (ether)	15	132–5	13		
n-Butyl	$C_{10}H_{15}O_3N$	K	58	148–50	15	6.87	7.10

Melting points: methyl, 68° (Wislicenus gives 68°); ethyl, 46–48°. Densities: *n*-propyl, 1.073 (20°), 1.068 (25°); *n*-butyl, 1.050 (20°), 1.046 (25°). Refractive indices: *n*-propyl, 1.477 (20°), 1.476 (25°); *n*-butyl, 1.479 (20°), 1.478 (25°).

causing the condensation of ethyl phenylacetate with ethyl carbonate or ethyl oxalate. Accordingly mixtures of sodium and potassium ethoxides have been applied to nitriles that do not satisfactorily condense with ethyl oxalate under the influence of sodium ethoxide alone, there being the possibility that once the potassium derivative is formed it might undergo double decomposition with sodium ethoxide and thus avoid to some extent the use of potassium.



$$R-C(C\equiv N)=C(OK)-CO_2C_2H_5 + Na-OC_2H_5 \rightleftarrows R-C(C\equiv N)=C(ONa)-CO_2C_2H_5 + K-OC_2H_5$$

Fleischauer[2] was unable to isolate cyanopyruvic ester from the condensation products formed by the action of sodium ethoxide on a mixture of methyl cyanide and ethyl oxalate although he did show that a small amount had been formed. Wislicenus and Silberstein[3] using potassium ethoxide obtained an 83% yield of cyanomethylpyruvic ester from propionitrile. Later investigators[4] have used potassium ethoxide. Thus it would appear that the activation of the α-hydrogen in aliphatic nitriles by the nitrile group alone is not sufficient to permit a satisfactory reaction if sodium ethoxide is the condensing agent.

In phenylacetonitrile, which readily condenses,[5] this hydrogen is also in the reactive position with respect to the double bond in the ring. It is significant also that ethylene cyanide reacts readily with two moles of oxalic ester to give a fair yield of the diketo ester while trimethylene cyanide reacts with only one mole.[6] This difference may be understood if one considers that the hydrogen of the second methylene group in the case of ethylene cyanide is activated also by the double bond of the enolic form present as the salt. In the case of trimethylene cyanide these two influences activate different hydrogen atoms.

The results of our experiments indicate that with valeronitrile a very poor yield (13%) of cyano-*n*-propylpyruvic ester is obtained with sodium ethoxide as the sole condensing agent, that if one-tenth of the sodium ethoxide is replaced by potassium ethoxide the yield is raised to 31% and that the yield is 55% if potassium ethoxide is the sole condensing agent. On this basis the yield should be increased to approximately 17% by the substitution of the equivalent weight of potassium for 10% of the sodium, whereas the yield is actually increased to 31%. An equimolecular mixture of sodium and potassium ethoxides gave a 79% yield of cyanomethylpyruvic ester which is almost as good as that obtained by Wislicenus and Silberstein who used potassium ethoxide. According to the procedure we employed the greater solubility of the sodium enolate causes no error in isolating the product. The ethylation of cyanopropylpyruvic ester yields the ether of the enol form which confirms more recent results.[4,7]

Preparation of Alkylcyanopyruvic Esters.—In a typical experiment, 14.0 g. of sodium was caused to react with absolute alcohol (182 cc.) dissolved in 805 cc. of absolute ether. The potassium (23.8 g.) was then added to the cooled mixture. After all of the metal had reacted a solution of 67.1 g. of propionitrile in 178.1 g. of ethyl oxalate was added at once and the whole was thoroughly mixed. A deep red color developed within a half hour. The amount of precipitate appearing after standing for four days was much less than it was when the equivalent amount of potassium ethoxide was used. The reaction mixture was then quickly mixed with a freezing mixture prepared from 115 cc. of hydrochloric acid (d. 1.19) and 440 g. of finely crushed ice. The ether layer was dried over sodium sulfate and distilled, finally under diminished pressure. Upon standing several months in a closed container the esters partially decomposed to a yellow oil. Redistillation of such a sample gave oxalic ester, the alkylcyanopyruvic ester and a high boiling residue that did not contain nitrogen. The sample for the analysis of cyanoethylpyruvic ester was prepared by cooling an ether–ligroin solution in an ice–salt mixture.

Ethyl 3-Cyano-2-ethoxy-2-hexenoate.—This compound was prepared in 52% yield by alkylating cyano-*n*-propylpyruvic ester in alcohol with sodium ethoxide and ethyl sulfate. The unalkylated ester was removed by extraction with sodium carbonate solution; b. p. 137–139° (9.3 mm.); 114° (1 mm.).

Anal. Calcd. for $C_{11}H_{17}O_3N$: N, 6.63; OC_2H_5, 42.66. Found: N, 6.48; OC_2H_5, 42.76.

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[2] Fleischauer, *J. prakt. Chem.*, [2] **47**, 375 (1893).

[3] Wislicenus and Silberstein, *Ber.*, **43**, 1825 (1910).

[4] Borsche and Manteuffel, *Ann.*, **512**, 97 (1934).

[5] Erlenmeyer, Jr., *Ber.*, **22**, 1483 (1889).

[6] Michael, *Am. Chem. J.*, **30**, 156 (1903).

[7] Skinner and Green, THIS JOURNAL, **62**, 2882 (1940).