

Aromatic hydrocarbons were present only in insignificant amount in the ebonite fractions boiling from 156–165°, since less than 1 g. of hydrocarbon (b. p. 160–163°,  $n_D^{30}$  1.472) was recovered from the sulfuric acid washing of the steam distillates.

TABLE III

AMOUNTS OF PRODUCTS RECOVERED BY PYROLYSIS OF 36,000 G. OF EBONITE			
Compound	Recovered, g.	Compound	Recovered, g.
Benzene	<0.5	2,4-Dimethylthiophene	10
2-Methylthiophene	10	<i>m</i> -Xylene	50
Toluene	1	Aromatic hydrocarbon, b. p.	
2,3-Dimethylthiophene	50	<i>ca.</i> 160°	< 1
		2-Methyl-5-ethylthiophene	240

### Summary

The following compounds have been identified in the products obtained from ebonite by destructive distillation: 2-methylthiophene, 2,3-dimethylthiophene, 2,4-dimethylthiophene, 2,5-methylethylthiophene and *m*-xylene. These results will be used to derive the structural formula of ebonite.

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## THE PREPARATION OF BENZOYLACETIC ESTER AND SOME OF ITS HOMOLOGS

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Although benzoylactic ester was first prepared by Baeyer<sup>1</sup> by the hydration of phenylpropionic ester, this method has certain disadvantages that reduce its preparative value.<sup>2</sup> The most satisfactory methods that may be found in the literature are two developed by Claisen. One of these involves the direct condensation of ethyl benzoate with ethyl acetate in the presence of sodium ethoxide,<sup>3</sup> and although a 33% yield of product is claimed, the actual weight of benzoylactic ester reported as having been obtained shows the yield to be only 26% of the theoretical. In the other method benzoylactic ester is obtained by the partial hydrolysis of benzoyl-acetoacetic ester.<sup>4</sup> Recently, failures to duplicate the yield claimed in Claisen's first method and modifications of the second method have been reported by Shriner and Schmidt.<sup>5</sup>

A number of the homologs of benzoylactic ester have been prepared

<sup>1</sup> Baeyer, *Ber.*, 15, 2705 (1882).

<sup>2</sup> Hope and Perkin, *J. Chem. Soc.*, 95, 2047 (1909).

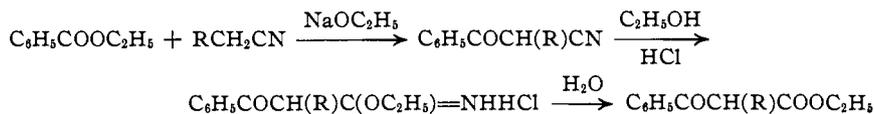
<sup>3</sup> Claisen and Lowman, *Ber.*, 20, 653 (1887).

<sup>4</sup> Claisen, *Ann.*, 291, 67 (1896).

<sup>5</sup> Shriner and Schmidt, *THIS JOURNAL*, 51, 3636 (1929).

by Perkin and co-workers<sup>6</sup> by the alkylation of this ester with an alkyl iodide in alcoholic solution in presence of sodium ethoxide. Although no yields are reported the idea is conveyed that the procedure is quite satisfactory. Experiences with the alkylation of benzoylacetic ester in this Laboratory by Perkin's method as well as with one using metallic sodium in the absence of alcohol<sup>7</sup> have been far from gratifying. Besides being obtained in quite low yields, the product was a mixture of the alkylated and unalkylated benzoylacetic esters.

This paper reports the results of a study of the preparation of benzoylacetic ester and its homologs, ethyl  $\alpha$ -benzoylpropionate, ethyl  $\alpha$ -benzoylbutyrate and ethyl  $\alpha$ -benzoylvalerate. These esters were prepared by the hydrolysis of the imino ether hydrochlorides derived from the corresponding  $\alpha$ -benzoyl alkyl cyanides. These latter compounds were obtained by the condensation of ethyl benzoate with the alkyl cyanide by means of sodium ethoxide. The steps in the preparation may be illustrated thus



The yields of the benzoyl alkyl cyanides varied from 53–60%, while the yields of the esters from the cyanides were 64–74%. The over-all yields of each of the keto esters from ethyl benzoate was 35–44% of the theoretical.

An interesting variation in the behavior of the benzoyl alkyl cyanides was noted in their conversion into the esters. When the intermediate imino ether hydrochlorides were treated with alcohol containing the theoretical amount of water for their hydrolysis, benzoylacetic ester was obtained from benzoyl methyl cyanide with no side product, but from  $\alpha$ -benzoyl ethyl cyanide a considerable amount of benzoyl propionamide was isolated along with the keto ester. From  $\alpha$ -benzoyl propyl cyanide and  $\alpha$ -benzoyl butyl cyanide practically the entire yield in each case was the corresponding amide. This amide formation could be considerably reduced, but not completely prevented, if about three times the required amount of water, containing a small amount of hydrochloric acid, was used for the hydrolysis.

A study also was made of the direct condensation of ethyl benzoate with ethyl acetate and certain of its homologs in the presence of sodium ethoxide. Not only was it possible in the case of benzoylacetic ester to duplicate the yields reported by Claisen and Lowman,<sup>3</sup> but by certain modifications the yield was raised to 37% of theory. With such a yield the direct condensa-

<sup>6</sup> Perkin and co-workers, *J. Chem. Soc.*, **45**, 179 (1884); **49**, 160 (1886); **95**, 2047 (1909).

<sup>7</sup> Cf. Folkers and Adkins, *THIS JOURNAL*, **53**, 1416 (1931).

tion procedure is to be preferred over the method involving the intermediate benzoyl methyl cyanide. The yields of the higher homologs by direct condensation were, however, much lower, being in the cases of ethyl  $\alpha$ -benzoylpropionate and ethyl  $\alpha$ -benzoylbutyrate 19 and 4%, respectively. The procedure through the  $\alpha$ -benzoyl cyanides seems to be the most satisfactory method of preparation of these higher homologs not only because of the yield but on account of the high purity of the product which it affords due to the fact that the unalkylated and dialkylated products are necessarily absent.

### Experimental

**Materials Used.**—The esters and cyanides which were used were dried over and distilled from phosphorus pentoxide. Sodium ethoxide was prepared by two previously described procedures.<sup>8</sup>

**$\alpha$ -Benzoylalkyl Cyanides.**—In a 3-necked 1-liter flask fitted with a mercury-seal stirrer, a long-stem dropping funnel and a reflux condenser were placed 150 g. (1 mole) of ethyl benzoate and 68 g. (1 mole) of sodium ethoxide. The mixture was warmed by an oil-bath to about 80° and stirred until it became a homogeneous gelatinous mass. Then 1.25 moles of the alkyl cyanide was added slowly under the surface of this mass from the dropping funnel over a period of two hours. The temperature of the oil-bath was then raised to and maintained at 110–120°, in the case of methyl and ethyl cyanide, for ten hours with continuous stirring. When propyl and butyl cyanides were used it was found advantageous at this point to replace the reflux condenser with a short (18-cm.) Vigreux column, raise the temperature of the oil-bath to 140–160° and to allow the alcohol formed in the condensation to distil out slowly from the reaction mixture.

The reaction mixture was then cooled to about 0° in an ice-bath, treated with 400 cc. of ice water and 100 cc. of ether and shaken until the solid material had dissolved. The aqueous layer was then separated from the ether layer and acidified with dilute sulfuric acid. The precipitated benzoyl alkyl cyanide together with a small amount of benzoic acid was taken up in ether and the resulting ethereal solution washed with a saturated sodium bicarbonate solution to remove the benzoic acid. After drying over anhydrous sodium sulfate, the ether was removed by distillation. Benzoyl methyl

TABLE I  
 $\alpha$ -BENZOYLALKYL CYANIDES

Alkyl group	M. p., °C.	B. p., °C.	Yield, %	Analyses, N, %	N, % Found
Methyl <sup>a</sup>	80–81		56	..	..
Ethyl <sup>b</sup>		128–130 (3 mm.)	53	8.81	8.79
Propyl <sup>c</sup>		134–135 (3 mm.)	60	8.09	8.24
Butyl <sup>c</sup>		139–140 (3 mm.)	59	7.48	7.47

<sup>a</sup> Haller, *Compt. rend.*, **104**, 1448 (1887), reports this compound as melting at 80.5°.

<sup>b</sup> Walther and Schickler, *J. prakt. Chem.*, [2] **55**, 306 (1897), obtained by the above procedure a small amount of  $\alpha$ -benzoyl ethyl cyanide which they isolated as the phenylhydrazone, m. p. 100–104°. They could not obtain any satisfactory results with the higher cyanides. Meyer, *J. prakt. Chem.*, **147**, 190 (1889), reports this compound as a liquid but gives no physical constants. <sup>c</sup> These compounds do not appear to have been described previously in the literature.

<sup>8</sup> McElvain, *THIS JOURNAL*, **51**, 3128 (1929); Houben-Weyl, Vol. II, 1922, p. 578.

cyanide is a solid and was purified by recrystallization from naphtha (b. p. 90–125°). The higher homologs are liquids and were purified by distillation under diminished pressure.

**$\alpha$ -Benzoyl Esters and Amides.**—A solution of 50 g. of the benzoyl alkyl cyanide in 250 cc. of absolute alcohol was cooled to 0° and saturated with dry hydrogen chloride. After standing at room temperature for about twelve hours, the excess alcohol and hydrogen chloride were removed under diminished pressure. Then 100 cc. of absolute alcohol containing three times the theoretical quantity of water necessary for the hydrolysis of the imino ether hydrochloride and 3 cc. of concentrated hydrochloric acid were added to the residue and the resultant solution heated for thirty minutes on a steam-bath. The solution was then cooled and poured into 800 cc. of cold water. The ester layer which separated was taken up in ether and separated from the water layer. In certain cases a small amount of the solid amide remained insoluble in both the ether and water layers and was removed by filtration. The ether extract of the  $\alpha$ -benzoyl esters was dried over sodium sulfate and after removal of the ether the ester was distilled under diminished pressure. It is advisable to use as low pressures as possible for these distillations in order to minimize the formation of the dehydro compounds. The boiling points and yields of these esters are summarized in Table II.

If only the theoretical quantity of water were employed for the hydrolysis of the imino ether hydrochlorides instead of three times the required amount as described above, the yield of benzoyl acetic ester was unaffected but the yields of the higher homologs were considerably reduced. In each of these latter cases a sufficient amount of the corresponding amide was obtained to compensate for the reduction in the yield of the ester. These amides, which are summarized in Table II, were characterized by hydrolysis into the phenyl alkyl ketones.

TABLE II  
 $\alpha$ -BENZOYL ESTERS AND AMIDES

$C_6H_5COCH(R)COOC_2H_5$ , R is	B. p., °C.	Yield, %, from cyanide	$C_6H_5COCH(R)CONH_2$ , R is
H <sup>a</sup>	118–120 (1 mm.)	72	...
CH <sub>3</sub> <sup>b</sup>	128–130 (1 mm.)	64	CH <sub>3</sub> <sup>c</sup>
C <sub>2</sub> H <sub>5</sub> <sup>b</sup>	134–135 (3 mm.)	74	C <sub>2</sub> H <sub>5</sub> <sup>c</sup>
C <sub>3</sub> H <sub>7</sub> ( <i>n</i> ) <sup>b</sup>	138–140 (3 mm.)	64	C <sub>3</sub> H <sub>7</sub> <sup>c</sup>
M. p., °C.		Nitrogen analyses, %	
.....		Calcd.	Found
145–146		7.91	7.83
148–149		7.33	7.22
157–158		6.83	7.02

<sup>a</sup> Haller, *Bull. soc. chim.*, [2] 48, 23 (1887), reports the preparation of benzoyl acetic ester from benzoyl methyl cyanide. <sup>b</sup> Cf. Hope and Perkin, *J. Chem. Soc.*, 45, 179 (1884); 47, 241 (1885); 49, 156–160 (1886); 95, 2045 (1909). <sup>c</sup> Not previously described in the literature.

**Direct Condensation of Ethyl Benzoate with Ethyl Acetate and its Homologs.**—A mixture of 136 g. (2 moles) of sodium ethoxide and 300 g. (2 moles) of ethyl benzoate was placed in a 1-liter 3-necked flask fitted with a mercury-seal stirrer, a dropping funnel extending below the surface of the liquid, and a reflux condenser carrying a calcium chloride tube in the upper end. This mixture was stirred and heated in an oil-bath to 70–80° until the mass became a fairly homogeneous paste. Then 176 g. (2 moles) of ethyl acetate was added slowly from the dropping funnel over a period of about two

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.<sup>9</sup>

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  $\alpha$ -benzoyl alkyl cyanides and their conversion into the corresponding  $\alpha$ -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 benzoylactic ester by the direct condensation of ethyl benzoate with ethyl acetate is given.

<sup>9</sup> Claisen and Lowman<sup>3</sup> 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.

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## ESTERS OF ORTHOFORMIC ACID

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The discovery of the first orthoformic ester was connected with the famous Williamson synthesis.<sup>1</sup> 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,<sup>2</sup> notably Deutsch,<sup>3</sup> 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,<sup>4</sup> 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-

<sup>1</sup> Williamson and Kay, *Ann.*, **92**, 346 (1854).

<sup>2</sup> (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.

<sup>3</sup> Deutsch, *Ber.*, **12**, 115–119 (1879).

<sup>4</sup> Pinner, *ibid.*, **16**, 1643–1647 (1883).