Carbon and hydrogen determinations:
(1) 0.1524 g. substance gave 0.3194 g. CO_2 and 0.1118 g. H_2O.
(2) 0.1544 g. substance gave 0.3214 g. CO_2 and 0.1122 g. H_2O.
(3) 0.1027 g. substance gave 0.2123 g. CO_2 and 0.0742 g. H_2O.
Nitrogen determinations (Dumas):
(1) 0.1330 g. substance gave 26.4 cc. N at 760 mm. and 25°.
(2) 0.998 g. substance gave 19.6 cc. N at 763 mm. and 22°.

Calc. for $C_6H_{10}ON_2$:	C, 57.0;	H, 8.0;	N, 22.2
Found:	C, 56.78;	H, 8.1;	N, 21.96
	C, 56.77;	H, 8.1;	N, 22.3
	C, 56.39;	H, 8.0	

The Formation of the Glyoxalone (XII) by Hydrolysis of the Methoxypyrimidine (IX) with Hydrobromic Acid.—Four grams of the methoxypyrimidine were heated with 20 cc. of hydrobromic acid at 150° until the evolution of carbon dioxide ceased. After the end of this operation the heating was then continued for about 6 hours and the solution finally evaporated to dryness to remove the excess of hydrobromic acid. The same procedure was then applied at this stage as we have already discussed in the previous experiments involving hydrolysis of the ethoxypyrimidine. The glyoxalone separated in a crystalline condition after trituration with dilute sodium hydroxide solution and was purified by recrystallization from boiling 95% alcohol. It was identical with the product obtained by hydrolysis of the ethoxypyrimidine (X) and melted at 270° with decomposition. The yield of the glyoxalone was 1 g.

NEW HAVEN, CONN.

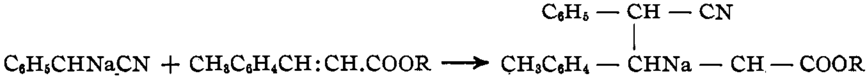
[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF NEBRASKA.]

ACTION OF SODIUM BENZYL CYANIDE WITH *p*-TOLYLCINNAMIC ESTER.[1]

BY MILO REASON DAUGHTERS.

Received June 22, 1917.

The results obtained by Auwers and Köbner,[2] Perkins,[3] and Avery,[4] in analogous reactions in the preparation of alkyl glutaric acids, did not correspond with the result obtained in this reaction. According to Michael's reaction,[5] the following result should have been obtained:



$$C_6H_5CHNaCN + CH_3C_6H_4CH{:}CH.COOR \longrightarrow CH_3C_6H_4 - \overset{C_6H_5 - CH - CN}{\overset{|}{CHNa}} - CH - COOR$$

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[1] From the thesis prepared as a part of the work required for the degree of Master of Arts.

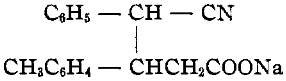
[2] *Ber.*, **24**, 1936 (1891).

[3] *J. Chem. Soc.*, **69**, 1472 (1896).

[4] *Am. Chem. J.*, **20**, 509 (1898); **28**, 48 (1902).

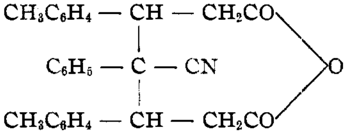
[5] *J. prakt. Chem.*, [2] **35**, 352 (1887).

When sodium benzyl cyanide reacts with *p*-tolylcinnamic ester, saponification results with the formation of two products—an observation in harmony with the results obtained by Avery and McDole[1] in the action of cinnamic ester with sodium benzyl cyanide. One of the products obtained was



$$\begin{array}{l} C_6H_5 - CH - CN \\ \qquad\quad\; | \\ CH_3C_6H_4 - CHCH_2COONa \end{array}$$

which was produced in large quantities and the other, the exact structure of which is still unknown but which by analogy from the compound obtained by Avery and McDole, would have the following formula:



Experimental.

The acetic ether used in this work was prepared by the method given in Gatterman's Organic Chemistry.

Preparation of *p*-Tolylcinnamic Ester.[2]—600 g. (an excess) of acetic ether, alcohol and water-free, were placed in a liter Erlenmeyer flask and immersed in ice. When cold, 21.81 g. of metallic sodium, cut in small thin pieces, were added a little at a time until all disappeared. The contents of the flask were shaken constantly. To this were added 60 g. of *p*-tolylaldehyde (one mol to one atom of sodium). After standing overnight it was acidified with glacial acetic acid. Water was next added, whereupon a reddish oil separated out. This mixture was neutralized with sodium carbonate, separated with a separatory funnel, washed twice with tap water, to remove the sodium carbonate, and then dehydrated by heating on a water bath for three hours with calcium chloride. After standing overnight the *p*-tolylcinnamic ester was poured from the solidified calcium chloride into a distilling flask which was connected to a brass-jacketed condenser. That portion which passed over at 260–280° was collected. It appeared as a heavy oil, light yellow in color. Yield, 50 g.

$$\text{Reaction: } 2CH_3C_6H_4CHO + 2CH_3COOC_2H_5 + 2Na \longrightarrow 2CH_3C_6H_4CH = CHCO_2C_2H_5 + 2NaOH + H_2.$$

β-*p*-Tolyl-γ-phenyl-γ-cyanbutyric Acid.—Method of Preparation and Purification. Three grams of metallic sodium in the form of dry sodium methylate were added to a warmed mixture of 17 g. of *p*-tolylcinnamic ester and 10.4 g. of benzyl cyanide in a beaker. During the reaction, which took place very rapidly, considerable heat was given off. There

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[1] THIS JOURNAL, 30, 1423 (1908).

[2] H. C. Parmelee, Master's Thesis, Univ. of Nebraska, 1899, p. 8.

resulted a reddish yellow, semi-liquid mass, which was allowed to stand on a water bath for one-half hour. After cooling, the resulting mass was acidified with concentrated hydrochloric acid. A yellowish mass separated. This was thoroughly washed with water to remove the excess of salt present and the excess of water was removed by decantation and by filter paper. The sticky yellow mass was dissolved in benzene and the solution heated to boiling. All went into solution readily except a small portion which would dissolve only upon prolonged boiling and in an excess of benzene. The benzene solutions were heated on a flame protector consisting of wire gauze, with fine mesh, rolled or made up in the form of a cylinder, which was set on top of the burner.

The first crystals had a melting point of 158–168°. Three recrystallizations resulted in confining the melting point to narrower limits, 166–169°. A qualitative test for nitrogen proved its presence. Titration with 0.1 *N* KOH, the silver salt, and the quantitative estimation of carbon, hydrogen and nitrogen were all below theory, which indicated the presence of an impurity or that there was a mixture of compounds.

The remainder was recrystallized from benzene in three fractions, melting at 168–180°, 162–164°, and 162°, respectively.

Fraction 2 of the above was recrystallized from benzene and fractionated in like manner into two fractions, which melted at 162–166° and 162°.

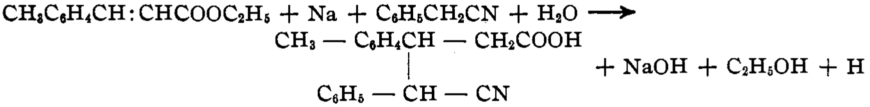
The two crops of crystals having the same melting point at 162° were placed together and thoroughly dried in a steam oven.

Analysis: C, 77.65; H, 6.032; N, 5.14. Calc. for $C_{18}H_{17}O_2N$: C, 77.41; H, 6.09; N, 5.017.

Titration: 0.0702 g. of substance required 2.51 cc. of 0.1 *N* KOH. Theory for $C_{18}H_{17}O_2N$: 2.52 cc.

Silver salt: 27.68% Ag. Theory for $C_{18}H_{16}O_2NAg$: 27.96%.

The formation of this compound is represented by the following reaction:



$$CH_3C_6H_4CH{:}CHCOOC_2H_5 + Na + C_6H_5CH_2CN + H_2O \longrightarrow \begin{array}{l} CH_3 - C_6H_4CH - CH_2COOH \\ \qquad\qquad\quad | \\ \quad C_6H_5 - CH - CN \end{array} + NaOH + C_2H_5OH + H$$

Several attempts were made to saponify the β-*p*-tolyl-γ-phenyl-γ-cyanbutyric acid. A gram was placed in a sealed tube along with 20 cc. of concentrated hydrochloric acid and heated for four hours at a temperature ranging from 120–140°. When the tube was removed from the furnace a large portion had decomposed into a brownish black mass, from which nothing of satisfactory composition could be obtained. When heated in the tube furnace at a temperature below 120° C., with concentrated hydrochloric acid for six hours, it did not produce a nitrogen-free product.

Two grams of substance were heated with concentrated KOH for four hours in a round bottom flask with a return condenser. Ammonia was given off. When cold it was acidified with concentrated hydrochloric acid, filtered, washed thoroughly with distilled water, dried in a steam oven, and then an attempt was made to recrystallize it from benzene. Only a very small portion would go into solution even in a large excess of the solvent. After drying, it was dissolved in alcohol and recrystallized twice. The product melted at 174–183° but was not nitrogen-free. A second attempt was made to saponify with KOH by prolonged treatment but the resulting compound was not free from nitrogen. All attempts to saponify the nitrile were unsuccessful.

Considerable work has been done to isolate the second product formed in the interaction of sodium benzyl cyanide with *p*-tolylcinnamic ester, but without satisfactory results. This problem will occupy our attention in the near future.

[CONTRIBUTION FROM CHEMICAL LABORATORY OF JOHNS HOPKINS UNIVERSITY.]

STUDIES IN ESTERIFICATION. IX. THE ESTERIFICATION OF ACETIC AND PROPIONIC ACIDS BY METHYL, ETHYL, PROPYL, ISOBUTYL AND ISOAMYL MERCAPTANS.

BY EDGAR M. FABER[1] AND E. EMMET REID.

Received July 2, 1917.

Historical.

Ever since Berthelot and Pean de St. Gilles[2] so carefully investigated the formation of esters, the problem of esterification, with and without a catalyst, has been one of great interest to the chemist.

This was followed by the work of Menschutkin[3] in which the question of the influence of the structure of both the acid and of the alcohol was extensively studied.

Reid[4] in a study of the mechanism of esterification found that mercaptan esterifies benzoic acid and that a well-defined limit is reached.

This work was extended by Pratt and Reid[5] who studied the esterification of benzoic acid by various mercaptans, and further by Sachs and Reid[6] and Kimball and Reid[7] who took up the question of isomerism of the acids and of the mercaptans.

All of this work on mercaptans has gone to show that mercaptans esterify acids as do alcohols and that the relations between the limits reached are

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[1] From dissertation of Edgar M. Faber.

[2] *Ann. chim. phys.*, [3] **65**, 385 (1862); **66**, 5 (1862); **68**, 225 (1863).

[3] *Ber.*, **11**, 1510 (1878); *Ann. chim. phys.*, **23**, 58 (1881).

[4] *Am. Chem. J.*, **43**, 489 (1910).

[5] THIS JOURNAL, **37**, 1934 (1915).

[6] *Ibid.*, **38**, 2746 (1916).

[7] *Ibid.*, **38**, 2757 (1916).