

The amount of substances used in each case was small and no attempt was made to check the method using large quantities. The method seems to be limited to the preparation of the esters of benzyl alcohol since other high-boiling alcohols were tried and gave unsatisfactory results. Two of the benzyl esters, benzyl phthalate and benzyl butyrate, required that the method be varied.

In the case of dibenzyl phthalate the condenser tube was surrounded with a jacket through which steam was passed while the pressure within the condenser tube was maintained at 200 mm. below atmospheric pressure. In the preparation of benzyl butyrate, it was necessary to apply nearly 1200 mm. pressure before the reaction took place.

Each ester was saponified and the acid and alcohol identified by the usual standard methods.

Summary

A modification of a standard method of esterification has been worked out, and applied to the preparation of esters of benzyl alcohol and acids with boiling points above the boiling point of water. The advantages of this method are three: (1) it is simple and very easily applied; (2) the product is formed in a relatively high state of purity; (3) the yield is greater in most cases than yields obtained by other methods.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF NORTHWESTERN UNIVERSITY]

THE PREPARATION OF PHENYLIMIDO-PHOSGENE, AND THE CHLORINATION OF FORMANILIDE

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Phenylimido-phosgene, because of its toxic lachrymatory properties, was used by the Germans as a war gas during the last four months of 1917. A sudden temporary revival of its use was noted again in April, 1918, which was ascribed to a clearing out of old chemical stock rather than to a change of military policy in regard to this substance. Although studied by the Allies, phenylimido-phosgene was never adopted or used by them as a weapon. The physiological symptoms are mainly those

¹ The work represented in that portion of this paper dealing with the preparation of phenylimido-phosgene, and thiocarbonyl, as well as some preliminary experiments on the chlorination of formanilide, was carried out in Organic Offense Research Unit No. 3, C. W. S., U. S. A., 1918, by G. A. Perkins, H. A. Shonle and G. A. Taylor. Chloro-phenylimido-phosgene was apparently formed but this was not definitely proved, as the emphasis in the investigation was for the moment elsewhere. The subject has been further studied by W. Lee Lewis and R. S. Bly at Northwestern University. The earlier results are included with the permission of the C. W. S., General Amos A. Fries, Director.

produced by a mild lung irritant, namely, nausea, and sometimes vomiting, soreness of throat, tightness in the chest, and pains in the stomach. A cough and bronchitis develop later, but lachrymation is not a prominent feature. The property of producing in experimental animals corneal ulcers, which do not, however, tend to permanent blindness, undoubtedly identifies this gas as the much heralded "blinding gas" of the period.

The following study was originally undertaken with a view to improving present methods or developing new methods for the preparation of phenylimido-phosgene.

This compound is ordinarily prepared by the chlorination of phenyl mustard oil as follows:² $C_6H_5NCS + 2Cl_2 \longrightarrow C_6H_5NCCl_2 + SCl_2$. Of the various methods recommended for the preparation of phenyl mustard oil from thiocarbanilide the best results were obtained by using for each part by weight of carbanilide, 3 parts by weight of diluted sulfuric acid (one volume of sulfuric acid, sp. gr. 1.84, to 2.5 volumes of water), and refluxing the mixture for several hours before distilling with steam. When the preliminary refluxing was omitted, the thiocarbanilide changed very slowly and the yields decreased. In large laboratory runs, the aniline by-product could be recovered to the extent of 83%.

The phenyl mustard oil was chlorinated to saturation in a solution with one volume of carbon tetrachloride or carbon disulfide. The solvent was removed by fractionation at 30 mm. The yields averaged 95%. The fraction boiling at 104–106° was considered pure, and identified by conversion into acetanilide melting at 113,^{2a,b} and triphenylguanidine melting at 140°.^{2b} No evidence of the chlorination in the ring, mentioned by Nef,^{2b} was noted. The procedure described by Nef of decomposing the sulfur chloride with water and drying and fractionating the resulting material, gave no better product or yield. When the reaction mixture stood with the solvent after chlorination, an amorphous solid formed. After removal of the solvent, which now contained approximately 85% of pure phenylimido-phosgene, the residue is stable on standing.

By using phenylimido-phosgene itself as a solvent for the thiocarbanilide and adding the latter in portions as the chlorination is continued, it was found that the use of carbon disulfide or tetrachloride could be dispensed with and the resulting product fractionated at once at ordinary pressure.

It was thought that formanilide in either of its tautomeric forms, $C_6H_5.NH.CHO$ or $C_6H_5.N:CHOH$, might be chlorinated to give phenylimido-phosgene. It was found that sulfur dichloride as a possible chlorinating agent formed an apparent addition product with formanilide, but as chlorination was continued, 2,4-dichloro-formanilide only resulted. Chlorination in the presence of phosphorus trichloride and oxychloride

² (a) Sell and Zierold, *Ber.*, **7**, 1228 (1874); **26**, 2870 (1893). (b) Nef, *Ann.*, **270**, 282 (1892).

led to mixtures which could be separated with difficulty, in which no phenylimido-phosgene was found.

With thionyl chloride, the course of the reaction was profoundly affected by the character of the thionyl chloride used, particularly by the presence of traces of phosphorus oxychloride which lessened the amount of chlorine taken up. Ultimately the following products of this chlorination were isolated and identified: 2,4-dichloro-formanilide, phenylimido-phosgene, 4-chloro-phenylimido-phosgene and 2,4-dichloro-phenylimido-phosgene.

The formanilide used was prepared from formic acid and aniline by the method of Tobias³ the yields being approximately 90% of the calculated amount. The thionyl chloride obtained from the University of Illinois, was redistilled through a 38cm. column and collected between 74° and 76.5°. The formanilide was dissolved in 6 parts of an equal mixture of chloroform and thionyl chloride, and chlorinated with rapid stirring to saturation, below 10°. This required on an average 3 hours, using 100 g. of formanilide, about 100 g. of chlorine being absorbed in each case. During chlorination a white solid separated in the chlorine delivery tube, which was identified as 2,4-dichloro-formanilide by its melting point, 152° (uncorr.),⁴ and its conversion by means of boiling 5% sodium hydroxide solution into 2,4-dichloro-aniline melting at 62.5° (uncorr.).⁵ The reaction mixture was distilled up to 80° at ordinary pressure for removal of higher chlorides of sulfur and chloroform. During this process chlorine, sulfur dioxide and hydrogen chloride were freely evolved. The remainder of the reaction mixture was then repeatedly fractionated through a column at 30mm. pressure. Three main fractions were thus obtained, boiling respectively at 107–109°, 135–137° and 150–153°. All these products are colorless oils resembling phenylimido-phosgene in physical appearance and possessing similar physiologically irritating properties. The specific gravities increase with chlorine content while the lachrymatory effects decrease.

The first was identified as phenylimido-phosgene by its analysis, and boiling point of 209–212° (corr.)^{2a} at ordinary pressure. With aniline it gave triphenylguanidine hydrochloride melting at 239–242° (uncorr.) and from this was obtained the base melting at 140–141° (uncorr.).^{2b}

When heated with glacial acetic acid, it formed acetanilide^{2b} melting at 112.2°⁶ and when mixed with an equal amount of absolute alcohol, phenyl urethane⁷ melting at 50–51°⁸ was formed.

The intermediate fraction which was not found in every run and which

³ Tobias, *Ber.*, **15**, 2443 (1882).

⁴ Chattaway, Orton and Hortley, *ibid.*, **32**, 3636 (1903).

⁵ Beilstein and Kurbatow, *Ann.*, **182**, 96 (1876).

⁶ Gerhardt, *ibid.*, **87**, 164 (1853).

⁷ *Ref.* 2b, p. 280.

⁸ Wilm and Wischin, *ibid.*, **147**, 157 (1868).

boiled at 135–137° proved to be 4-chloro-phenylimido-phosgene, by analysis for chlorine and nitrogen and by molecular-weight determinations. With glacial acetic acid it gave 4-chloro-acetanilide melting at 173–174° (uncorr.).⁹ On boiling this product with 10% sodium hydroxide solution, needles of *p*-chloro-aniline formed, melting at 69–70° (uncorr.).¹⁰ With aniline a compound resulted melting at 252–255°, and yielding with ammonium hydroxide a base melting sharply at 137–138° and analyzing for monochloro-triphenyl-guanidine.

The high-boiling fraction, 150–153°, was identified as 2,4-dichloro-phenylimido-phosgene as follows. It gave the correct analysis for nitrogen and chlorine and reacted vigorously with aniline to form colorless crystals melting at 207.5–209.5° (corr.) which proved to be 2,4-dichloro-triphenyl-guanidine hydrochloride. Boiled with dil. ammonium hydroxide, this product gave the corresponding base, analyzing correctly for chlorine and nitrogen and melting at 129.5–130.5° (corr.). With acetic acid, 2,4-dichloro-acetanilide resulted, melting at 142–143° (uncorr.).¹¹ This product with 10% sodium hydroxide solution gave 2,4-dichloro-aniline, melting at 61–62° (uncorr.).¹²

The specific action of thionyl chloride in the formation of the foregoing products is noteworthy, the products being entirely different in the presence of the other chlorinating agents used. The following equation expresses the main course of the reaction, omitting the ring chlorination which occurs, in the usual manner: $C_6H_5 \cdot NH \cdot CH : O + SOCl_2 + Cl_2 \longrightarrow C_6H_5 \cdot N : C Cl_2 + SO_2 + 2HCl$.

It is also possible that phenylisocyanide, formed by dehydration of an enolic form of formanilide, adds chlorine to give the observed products.¹³

Experimental

Preparation of Phenyl Mustard Oil.—Fifteen moles of dil. sulfuric acid, 3689 g., was mixed with 5 moles, 1140 g., of thiocarbanilide and the mixture refluxed for 6 hours. The dilute acid was prepared by adding 5 parts of water by volume to 2 parts of 1.84 sulfuric acid; the temperature of refluxing ranged from 140–160°. The refluxed mixture was distilled with steam, and the mustard oil separated, dried with calcium chloride, distilled at ordinary pressure, and collected at 215–221°. The yields averaged 70%, based upon the equation, $C_6H_5NHCSNHC_6H_5 \longrightarrow C_6H_5NCS + C_6H_5NH_2$. In one run, steam and hydrogen sulfide were passed through the residue from the first steam distillation for an hour, with a view to breaking up the triphenyl-guanidine by-product into aniline and phenyl mustard oil, but no product was formed. After neutralizing the residue, 83% of the aniline was recovered in the usual manner.

Chlorination of Mustard Oil.—In a typical run 328 g. of the mustard oil was dis-

⁹ Ref. 5, p. 98.

¹⁰ Mills, *Ann.*, **176**, 355 (1875).

¹¹ Lehmann, *Jahresber.*, **1882**, 369.

¹² Ref. 5, p. 95.

¹³ Ref. 2b, p. 270.

solved in an equal volume of carbon tetrachloride and dry chlorine passed in to saturation. The reaction mixture was distilled at 80° to remove sulfur chlorides and solvent, and the resulting crude phenylimido-phosgene fractionated at 30 mm. pressure. The fraction boiling at 104–106° was taken as pure product. The yield varied from 90 to 97%. In view of the fact that 90% of the crude phenylimido-phosgene distilled above 104° at 30 mm., it is evident that the sulfur dichloride underwent little decomposition during the distillation. The procedure followed when carbon disulfide was used as a solvent was identical in all respects save that the distillation for removal of solvent in this case was carried to 60°.

With a view to determining the value of phenylimido-phosgene itself as a solvent in the chlorination of phenyl mustard oil, 59 g. of mustard oil was added to 89 g. of phenylimido-phosgene. Further additions of 16 g., 25 g., and 22 g. were made after 1, 2 and 3 hours, respectively, chlorination being continuous. Thus a total of 122 g. of mustard oil was added to 89 g. of phenylimido-phosgene during a period of 4 hours' chlorination. The reaction mixture was fractionated once at atmospheric pressure, and 148 g. of fraction obtained boiling at 207–210°. The yield was 60%. The products obtained above were tested for purity and possible ring chlorination as follows. Portions were converted into triphenyl-guanidine melting at 140° (corr.) by Nef's method,^{2b} and triphenyl-guanidine hydrochloride melting at 252° (corr.).¹⁴ By boiling with 5 parts of acetic acid for 5 hours, acetanilide was obtained, melting at 115° (corr.).^{2a}

Preparation of Formanilide.—The method of Tobias³ was followed; 745 g. (8 moles) of aniline and 410 g. (8 moles) of 90% formic acid were refluxed for 3 hours. The product was distilled under reduced pressure and the fraction boiling at 159–162° at 13 mm. collected. The product came over as a yellow oil, and solidified to a white crystalline mass, melting¹⁵ at 45–47°. The yield was 856 g. or 88%.

The thionyl chloride, obtained from the University of Illinois, was redistilled through a 38cm. glass column, and the fraction used which came over at 74–76.5°.

It was noted that the presence of even traces of phosphorus oxychloride in the thionyl chloride affected markedly the course of the action, 1 to 2% of this impurity reducing the chlorine absorption approximately 50%.

Chlorination of Formanilide.—Formanilide was chlorinated with sulfur dichloride and chlorine in the cold, with and without solvents. In all cases the final product was 2,4-dichloro-formanilide,¹⁶ melting at 158–159°. This was confirmed by conversion into dichloro-aniline⁵ which melted correctly at 63°. On first adding sulfur dichloride to a carbon tetrachloride solution of formanilide there is formed a hygroscopic solid, probably an addition product, accompanied by little heat formation or gas evolution. This product reacts with water, going into solution on warming, with deposition of sulfur, this and the aqueous solution gives chloride and sulfide tests. Chlorination of a carbon tetrachloride suspension of this product gave 2,4-dichloro-formanilide, melting⁷ at 151°. Addition of sulfur dichloride to solid formanilide gave the same solid noted above in the carbon tetrachloride solution. However, after chlorination, during which heat was liberated and gas was evolved and a solution formed, the product did not precipitate on addition of carbon tetrachloride. Further chlorination gave 2,4-dichloro-formanilide melting at 151°. Some uncompleted attempts to chlorinate formanilide in the presence of phosphorus trichloride and oxychloride led to the following preliminary observations. Phosphorus trichloride reacts vigorously with formanilide, producing a gummy mass even in the presence of a diluent and with cooling. A crystalline compound, recrystallizable with difficulty from dil. alcohol, forms on refluxing. A crystalline product resulted when

¹⁴ Merz and Weith, *Chem. Zentr.*, **1863**, 513, 602.

¹⁵ Ref. 3, p. 2444.

¹⁶ Wheeler and Boltwood, *Am. Chem. J.*, **18**, 385 (1896).

chlorination was attempted in a carbon tetrachloride solution in the presence of phosphorus oxychloride.

Formanilide was chlorinated in the presence of thionyl chloride with and without chloroform as a diluent.

One hundred g. of formanilide was dissolved in 300 g. of chloroform and cooled to about 5°; 300 g. of thionyl chloride was added, and the mixture chlorinated to saturation below 10°, with vigorous stirring.

The average length of time for saturation of 6 runs with this apparatus was 8 hours, the gain in weight varying from 87 g. to 113 g. and averaging approximately 100 g. The chlorine affluent tube, finally made wide to obviate the difficulty, at first became clogged with white, needle-like crystals. When purified, this substance melted at 152° (uncorr.), and with 5% sodium hydroxide solution gave an oil which solidified on cooling. Recrystallized from 50% alcohol, the crystals melted at 62.5°, thus identifying the original compound as 2,4-dichloro-formanilide.⁴

Fractionation of the Reaction Mixture.—The chlorinated reaction mixtures were distilled at ordinary pressure and 80°, the distillate averaging 442 g. and varying from 406 g. to 485 g. The residual material from this first fractionation averaged 156 g. This was completely distilled at 30 mm., leaving an average tarry residue of 44 g. and an average distillate at 155° of 113 g.

The first distillate was now subjected to repeated fractionation at a constant pressure of 30 mm. in a small flask equipped with a 30cm. column and a side-neck dropping funnel, to enable addition of fractions without breaking the vacuum. The pressure was kept constant by a wash bottle half filled with mercury and tilted at will to correct the pressure. After some 6 fractionations in this apparatus, the combined material was resolved into 3 portions boiling, respectively, at 107–109°, 135–137°, and 150–153°.

Phenylimido-phosgene, C₆H₅N:Cl₂.—The first fraction, which showed the physical and physiological properties of phenylimido-phosgene and gave characteristic reactions, did not, however, analyze for this substance. Analyses by Carius' method gave 2.13% and 2.14% of sulfur. Phenyl mustard oil was suspected as an impurity, particularly as when the sulfur content was corrected for its equivalent of phenyl mustard oil; the analyses then totaled 100% and were correct for phenylimido-phosgene. The low-boiling fraction was accordingly dissolved in an equal weight of chloroform and again chlorinated at room temperature in a stirring apparatus. Chlorine was absorbed, heat given off, and the color of the reaction mixture changed from yellow to the deep orange characteristic of the higher chlorides of sulfur. The chloroform and sulfur chlorides were removed by fractionation at atmospheric pressure up to 130°, and the residue once more fractionated at 30 mm. The fraction distilling at 107–109° was now free from sulfur.

Analyses. Subs., 0.1341, 0.2009: AgCl, 0.3208, 0.3293. Calc. for C₆H₅NCCl₂: Cl, 40.77. Found: 40.80, 40.55.

The presence of phenyl mustard oil finds probable explanation in the formation of phenylisocyanide by dehydration of formanilide; C₆H₅N(OH)H—H₂O → C₆H₅NC. The odor of the iso-nitrile was repeatedly noted during the preparation of formanilide. This compound could add free sulfur¹⁷ present in the thionyl chloride, thus forming the phenyl mustard oil.

The first fraction so purified was irritating and lachrymatory and boiled correctly at atmospheric pressure for phenylimido-phosgene, at 209–210° (corr.).^{2a} It was further identified as phenylimido-phosgene as follows. Three g. was mixed with an equal weight of redistilled aniline, with cooling. The resulting crystalline solid was thrice recrystallized from 60% aqueous alcohol, when it melted at 239–240° (uncorr.), the melting point of triphenyl-guanidine hydrochloride.^{2b} From this the base was prepared by

¹⁷ Weith, *Ber.*, **6**, 211 (1873).

treatment with dil. ammonium hydroxide. The needle-like crystals, purified by alcohol, melted at 142–143° (corr.), the melting point of triphenyl-guanidine.^{2b}

Three g. of the fraction was mixed with an excess of glacial acetic acid and refluxed. The reaction, accompanied by evolution of hydrogen chloride, started immediately. The solid product was recrystallized from water and melted at the melting point of acetanilide,^{2b} 112.2° (corr.). A further 3g. portion was converted into phenyl-urethane melting at 50–51° (uncorr.),^{2b} by mixing with an equal amount of absolute alcohol and, after the spontaneous reaction had subsided, purifying the solid by recrystallization from water.

p-Chloro-phenylimido-phosgene, $\text{ClC}_6\text{H}_4\text{N}:\text{C}:\text{Cl}_2$.—The intermediate fraction boiling at 135–137° at 30 mm. pressure was identified as chloro-phenylimido-phosgene by the following series of reactions. *p*-Chloro-acetanilide melting at 173–174° (uncorr.)¹⁸ was prepared by refluxing 3 g. of the fraction with 12 g. of glacial acetic acid, for 4½ hours. The solid obtained by pouring the mixture into water was recrystallized from 6 *N* acetic acid. A portion of the *p*-chloro-acetanilide was heated with 10% sodium hydroxide solution for 2 hours. The product recrystallized from alcohol gave needle-like crystals of *p*-chloro-aniline, melting at 69–70° (uncorr.).¹⁰

A third portion of the intermediate fraction was converted into a chloro-triphenyl-guanidine hydrochloride, which melted at 247–250°. Three g. was mixed with 2.8 g. of redistilled aniline and the resulting vigorous reaction controlled by cooling. The gummy mass was washed with benzene and recrystallized from dil. alcohol. The hydrochloride on treatment with dil. ammonium hydroxide gave *p*-chloro-triphenyl-guanidine base, melting at 135–136°. As these compounds are not described in the literature the base was analyzed for chlorine.

Analyses. Subs., 0.2111, 0.2303: AgCl, 0.0935, 0.1030. Calc. for $\text{C}_{19}\text{H}_{15}\text{N}_3\text{Cl}$: Cl, 11.02. Found: 10.95, 11.06.

2,4-Dichloro-phenylimido-phosgene, $\text{Cl}_2:\text{C}_6\text{H}_3\text{N}:\text{C}:\text{Cl}_2$.—This fraction, boiling at 150–153° at 30 mm., was free from sulfur.

Analyses. Subs., 0.2055, 0.1925: AgCl, 0.4809, 0.4522. Calc. for $\text{C}_7\text{H}_3\text{NCl}_3$: Cl, 58.30. Found: 57.89, 58.11.

Subs., 0.6673, 0.4877: N, 0.03993, 0.02803. Calc. for $\text{C}_7\text{H}_3\text{NCl}_4$: N, 5.77. Found: 5.86, 5.75.

Mol. wt. Calc. for $\text{C}_7\text{H}_3\text{NCl}_4$: 242.8. Found: 242, 246.

A 3g. portion was mixed with 2.4 g. of aniline and cooled. The product, washed with benzene and recrystallized from dilute alcohol, gave small colorless crystals of 2,4-dichloro-triphenyl-guanidine hydrochloride, melting at 207–209° (corr.). From this the 2,4-dichloro-triphenyl-guanidine base was prepared by boiling it with dil. ammonium hydroxide. This base melted at 129.5–130.5° (corr.).

Analyses. Subs., 0.2002, 0.2117: AgCl, 0.1638, 0.1722. Calc. for $\text{C}_{19}\text{H}_{15}\text{N}_3\text{Cl}_2$: Cl, 19.93. Found: 20.24, 20.12.

Subs., 0.1502, 0.1975: N, 0.01763, 0.02314. Calc. for $\text{C}_{19}\text{H}_{15}\text{N}_3\text{Cl}_2$: N, 11.79. Found: 11.73, 11.72.

This proves the presence of 2 of the 4 original chlorine atoms in the phenyl radical.

A further 3g. fraction was refluxed with 12 g. of glacial acetic acid for 5 hours. The reaction mixture was poured into 200 cc. of water and recrystallized from 6 *N* acetic acid. The white, granular product melted at 142–143° (uncorr.).¹⁹

Analyses. Subs., 0.2010, 0.1536: AgCl, 0.2809, 0.2144. Calc. for $\text{C}_8\text{H}_7\text{NOCl}_2$: Cl, 34.80. Found: 34.58, 34.53.

¹⁸ Ref. 5, p. 98.

¹⁹ Ref. 11, p. 359.

The position of the nucleus chlorines was established by preparing 2,4-dichloro-aniline from the above substance. A small portion was heated for 2 hours with 10% sodium hydroxide solution, and the oil repeatedly washed with water. After solidification, it was recrystallized from 50% aqueous alcohol and gave finally long needle-like crystals of 2,4-dichloro-aniline, melting at 61-62° (uncorr.).⁵

Summary

1. A study of the preparation of phenylimido-phosgene from phenyl mustard oil and from formanilide has been made.
2. Phenyl mustard oil is best prepared from thiocarbanilide by using 3 parts by weight of dil. sulfuric acid and refluxing the mixture before distillation with steam.
3. Phenylimido-phosgene was prepared in 95% yields by chlorination of phenyl mustard oil, using carbon disulfide or carbon tetrachloride as a solvent, and omitting the addition of water as recommended by Nef.
4. Formanilide, chlorinated in the presence of sulfur chlorides, gives 2,4-chloro-formanilide.
5. Formanilide, chlorinated in the presence of thionyl chloride gives a series of products identified, respectively, as 2,4-dichloro-formanilide, phenylimido-phosgene, *p*-chloro-phenylimido-phosgene and 2,4-dichloro-phenylimido-phosgene.

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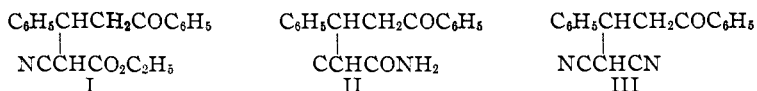
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

DELTA KETONIC NITRILES AND THEIR RELATION TO CYCLIC COMPOUNDS. II

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In continuation of the study of δ ketonic nitriles we have added cyano-acetamide and cyano-acetonitrile to benzalacetophenone, and have thus secured 2 related nitriles to compare with the methyl cyano-acetate addition product described in the earlier paper.¹



The behavior of these 3 closely related substances towards most reagents is surprisingly different: indeed, the only reaction in which all behave exactly alike is esterification. Thus while all 3 form cyclic compounds when subjected to the action of halogen acids in indifferent media, only the first forms a tetrahydropyridine (IV) derivative by molecular rearrangement. The second also forms a tetrahydropyridine derivative (V); but in accordance with the mechanism proposed in the first paper,

¹ THIS JOURNAL, 44, 2536 (1922).