[Contribution from the Department of Chemistry, University of Buffalo]

THE REACTION OF CYANOGEN WITH ORGANIC COMPOUNDS. VII. GRIGNARD REAGENTS[1]

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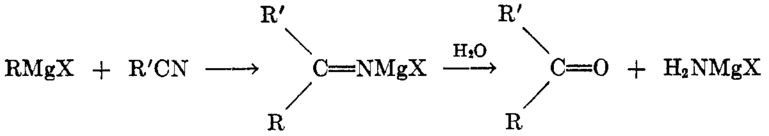
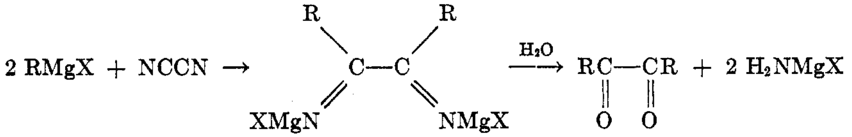
In a short paper published in 1901, which omitted many important details, Blaise (1) described the production of ketones from the reaction of nitriles and Grignard reagents.



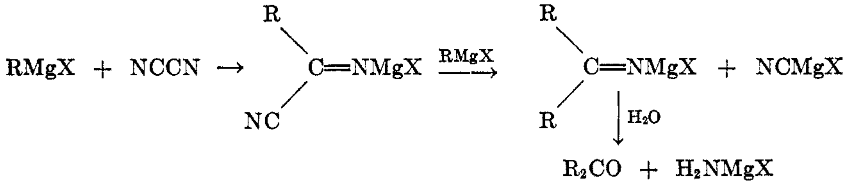
(Eq. 1)

He reasoned that substitution of cyanogen, NC—CN, for the organic nitrile RCN, should produce a diketone according to the reaction scheme:



(Eq. 2)

however, he was able to isolate only the monoketone, R_2CO. In explanation he was forced to write the equations



(Eq. 3)

In 1911, Grignard (2) reported the successful preparation of nitriles from cyanogen and Grignard reagents by a method in which the organometallic compound was added to an excess of cyanogen in ether, and in analogy to halogen reactions he wrote:

$$RMgX + NCCN \rightarrow RCN + CNMgX \qquad \text{(Eq. 4)}$$

He emphasized the point that the Grignard reagent must be added to the cyanogen and implied that ketone formation resulted from the interaction of nitriles first formed, with excess organometallic compound. Blaise did not describe his mode of addition and neither one reported the α-ketonic nitrile which could result from the hydrolysis of Blaise's first intermediate. There appeared to

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[1] From the dissertation submitted by Leo B. Lathroum in partial fulfillment of the requirements for the Ph.D. degree, February 1953.

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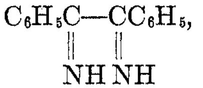
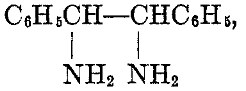
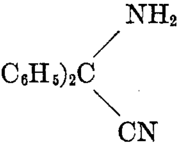
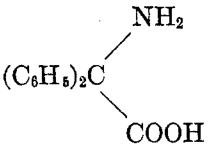
be good reason to examine more closely the reaction of cyanogen with Grignard reagents.

Because the compounds involved (benzonitrile, benzophenone, benzil, etc.) are well known, phenylmagnesium bromide was chosen as the first compound for study. Introduction of cyanogen to an excess of the Grignard reagent followed by hydrolysis with dilute mineral acid resulted primarily in benzophenone, benzoic acid, and diphenyl, however, *there was also obtained* a small amount of an unknown material melting between 97° and 100°. Because the acid hydrolysis mixture was rather difficult to handle, the hydrolyzing medium was changed to saturated ammonium chloride, whereupon the quantity of the unknown substance rose to *over 40% of the product.* This result was confirmed by several repetitions of the experiment.

Preliminary analysis of this material favored the assumption that a portion of the cyanogen had reacted according to Blaise's diketone mechanism (Eq. 2). The presence of nitrogen eliminated benzil from consideration but stilbene diimine,  $C_6H_5\underset{NH}{\underset{\|}{C}}-\underset{NH}{\underset{\|}{C}}C_6H_5$, or stilbene diamine,  $C_6H_5\underset{NH_2}{\underset{|}{CH}}-\underset{NH_2}{\underset{|}{CH}}C_6H_5$, were not unreasonable. Eventually these formulas were discarded on the basis of the following discoveries: (a) Absorption of dry hydrogen chloride was almost exactly the amount required for a *mono*hydrochloride. (b) Acetic anhydride produced a *mono*acetyl derivative. (c) Hydrolysis with concentrated hydrochloric acid produced only benzophenone.

The only formula which both agreed with the analytical data and accounted for the results above was that of diphenylglycinonitrile,  $(C_6H_5)_2C\begin{array}{l}\diagup NH_2\\ \diagdown CN\end{array}$, a hitherto unknown compound. To prove its identity a method of hydrolysis which would not destroy the carbon skeleton was needed. It was found in the use of 70% sulfuric acid. The product, recovered in 45% yield, agreed in melting point (3) and analysis with diphenylglycine,  $(C_6H_5)_2C\begin{array}{l}\diagup NH_2\\ \diagdown COOH\end{array}$, and its structure was further proved by conversion to benzilic acid using the method of Hauser, Flur, and Kantor (4).

A number of additional Grignard reagents was examined as to their reaction with cyanogen, hydrolysis in each case being accomplished by a saturated ammonium chloride solution. Di-substituted glycinonitriles were isolated in yields from 6–34% from *m*-tolyl-, cyclohexyl-, *n*-butyl-, and *tert*-butyl-magnesium bromides. *o*-Tolylmagnesium bromide produced only 2,2′-dimethylbenzophenone and from *p*-tolylmagnesium bromide there was recovered only di-*p*-tolyl.

TABLE I

GLYCINONITRILES AND RELATED COMPOUNDS

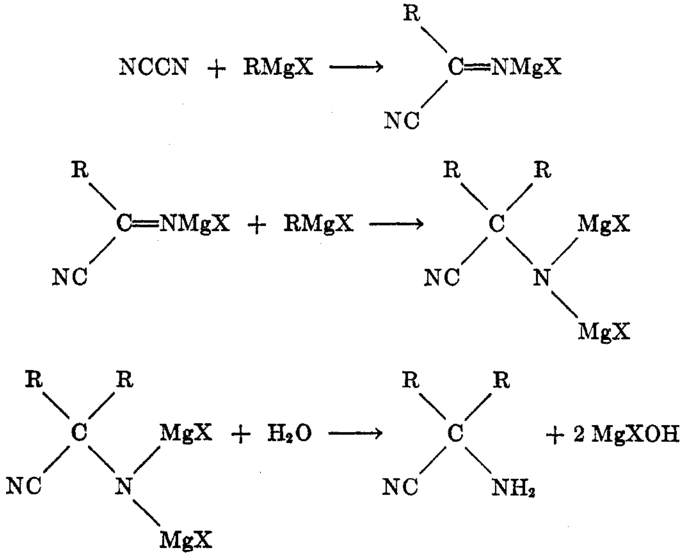
R	YIELD, %	M.P., °C.	$R_2C(NH_2)CN$ DERIVATIVES; M.P., °C.			$R_2C(NH_2)CONH_2$ M.P., °C.	$R_2C(NH_2)CO_2H$ M.P., °C.	$R_2C(OH)CO_2H$ M.P., °C.
			HCl	Acetyl	Benzoyl			
Phenyl	33	98–99	280	271			240	149
m-Tolyl	34	95–96	215	213			255	131
Cyclohexyl	6	83–84	209			143		
n-Butyl	12*				113		143	
tert-Butyl	15	43–44	298			127		

* Benzoyl derivative.

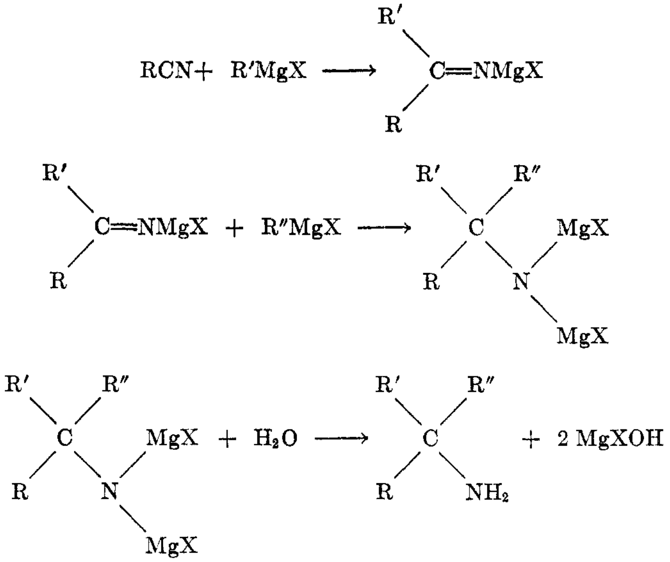
The glycinonitriles, all hitherto unreported compounds, were converted into derivatives, hydrolyzed, and where possible were converted into substituted benzilic acids. Analytical data in every case confirmed the proposed structures of the compounds.

Table I summarizes by melting points the compounds isolated in this study.

The production of glycinonitriles obviously cannot arise by the mechanism for the cyanogen-Grignard reaction proposed by Blaise (Eq. 3) but must involve instead the addition of two MgX fragments to the nitrogen first attacked:



This mechanism finds support not only in the products isolated but also in Henze's study of the conversion of nitriles to amines (5) whereby the stepwise addition of two equivalents of Grignard reagent allows the introduction of three different alkyl groups into the amine. The analogy between the equations above and those given by Henze is apparent.



The changes in appearance of the reaction mixtures in these experiments parallel closely those described by Henze, the diaddition product separating out as a thick taffy-like substance in both cases. An increased rate of reflux is noted in the second stage of each reaction.

If this in reality is the mechanism of the reaction of cyanogen with Grignard reagents, why did not Blaise discover glycinonitriles among his products? Probably the answer is to be found in his mode of hydrolyzing the Grignard complex. Experimentally we have observed that contact between diphenylglycinonitrile and 10% aqueous hydrochloric acid at room temperature results in a positive test for ketone within four hours, and that hydrolysis of the Grignard mixture with water or dilute acids sharply decreases the amount of glycinonitrile that can be recovered. Had Blaise not been so intent on producing ketones but more concerned with the nature of the reaction it is probable that glycinonitriles would have been reported fifty years ago.

An attempt to replace the amino group in diphenylglycinonitrile by hydroxyl, using the nitrous acid reaction failed. Success in this experiment would have produced the cyanohydrin of benzophenone which has never been reported.

Also attempted without success was a reaction between the CN group of diphenylglycinonitrile and additional Grignard reagent.

Grignard's preparation of benzonitrile from excess cyanogen and RMgX was repeated but his order of addition was reversed, *i.e.*, the cyanogen solution was dropped into the Grignard reagent. A 50% yield of benzonitrile was recovered.

EXPERIMENTAL DETAILS

REAGENTS

Cyanogen was prepared by the reaction of aqueous sodium cyanide with a boiling solution of cupric sulfate and was purified as previously described (6). When used in solution it was dissolved in dry ether at −5°.

Grignard reagents were prepared in half-molar quantities in the usual manner, using diethyl ether as the solvent.

Sulfuric acid (70%) was prepared by carefully pouring 70 g. of concentrated sulfuric acid into 30 g. of cold distilled water. The true percentage strength of this solution is about 68.5. It is referred to as 70% as a matter of convenience.

REACTIONS OF CYANOGEN WITH GRIGNARD REAGENTS

Phenylmagnesium bromide. (a). Molar ratio Grignard reagent to cyanogen 2:1. Three methods of combining the reagents were investigated.

(A). Purified cyanogen gas (0.5 mole) was passed over the surface of the vigorously stirred solution of phenylmagnesium bromide (1.0 mole) contained in a one liter three-necked flask equipped with a stirrer, condenser, and gas inlet tube. The reaction mixture remained thin and fluid but began to assume a silvery luster when approximately one-half the quantity of cyanogen gas had been added. Eventually this changed to a golden-brown color due to the formation of a solid which, at times, caused the reaction mixture to become so viscous as to stop the stirrer.

(B). The gas inlet tube in the apparatus described above was replaced by a dropping funnel and an ice-cold ether solution of cyanogen (0.5 mole) was placed in the flask. Using mechanical stirring, but no external cooling, the phenylmagnesium bromide solution (1.0 mole) was added from the dropping-funnel at a rate which caused the ether to reflux. The first change noted was the formation of a white solid which adhered to the side of the flask. This slowly assumed the golden-brown color noted above as more of the Grignard reagent was added.

(C). In this procedure the ether solution of cyanogen was added dropwise to the well-stirred solution of phenylmagnesium bromide.

When the combining of cyanogen and Grignard reagent was complete the flask was warmed gently on a water-bath for 30 minutes and then allowed to stand overnight. Hydrolysis was effected in the original reaction flask by the addition of a saturated ammonium chloride solution through the dropping-funnel.

After hydrolysis, the reaction mixture was again warmed for 30 minutes, then cooled and the ethereal layer was decanted through a dry filter. To the filtrate was added 5–10 ml. of ethyl alcohol and the solution was set aside to permit the ether to evaporate spontaneously. After 24 hours, at room temperature, the first crop of crystals was collected and washed first with cold ethyl alcohol and then with petroleum ether. The washings were combined with the mother liquor and allowed to stand another 24 hours. A second crop of crystals was obtained. The average yield from the three experiments, of white crystalline material later identified as *diphenylglycinonitrile,* was 33% based upon the halide used. The melting point was 98–99°.

Anal. Calc'd for: $(C_6H_5)_2C(NH_2)CN$: C, 80.8; H, 5.8; N, 13.5.
Found: C, 80.6; H, 5.8; N, 13.7.

The *hydrochloride* of *diphenylglycinonitrile* was prepared by passing dry hydrogen chloride into a solution of the nitrile in dry benzene. In two separate experiments 3-g. samples gave 3.42 g. and 3.50 g. of product, almost exactly the weights expected from a compound containing but *one* amino group. The material was a white powder melting at 280–283°.

Anal. Calc'd for $C_{14}H_{13}ClN_2$: C, 68.8; H, 5.3.
Found: C, 69.1; H, 5.3.

The *picrate* was produced by mixing a solution of 0.5 g. of diphenylglycinonitrile in 10 ml. of ethanol with an equal volume of saturated alcoholic picric acid, and heating until the volume was reduced to one-half, whereupon there precipitated a reddish-brown crystalline material melting with decomposition at 270–271°.

Acetyldiphenylglycinonitrile. When 1 g. of diphenylglycinonitrile was warmed with 10 ml. of acetic anhydride, a solution resulted. On cooling, a white solid precipitated. Recrystallized from ethyl alcohol this material melted at 270–272° with effervescence. Yield 85%.

Anal. Calc'd for $C_{16}H_{14}N_2O$: C, 76.8; H, 5.6; N, 11.2.
Found: C, 76.4; H, 5.8; N, 11.3.

Hydrolysis of diphenylglycinonitrile was brought about in two ways: (a) *With concentrated hydrochloric acid,* warming at 80° for 30 minutes produced a clear solution. This on cooling precipitated *benzophenone* (2,4-dinitrophenylhydrazone, m.p. 239°) in 80% yield. By neutralization of the mother liquor with solid sodium carbonate, unchanged diphenylglycinonitrile was recovered.

(b) *With 70% sulfuric acid.* One gram of diphenylglycinonitrile was placed in a 200-ml. round-bottom flask equipped with a stirrer, and 60 ml. of 70% sulfuric acid was added. After stirring the mixture vigorously for 30 minutes a water-bath was placed beneath the flask and the temperature raised to 80°. At first the reaction mixture was a pale yellow color but this darkened after heat had been applied. After heating for six hours, the water-bath was removed and the reaction mixture was allowed to cool. It was then diluted with an equal volume of water and extracted with ether.

The cool aqueous residue was neutralized with solid sodium carbonate to *p*H 2 (pHydrion paper) while being stirred vigorously. At this *p*H a white solid began to separate. This solid was removed and the mother liquor was raised to *p*H 6 whereupon more solid was removed. The precipitates were combined and washed with warm water until free from sulfate and then were dried. Recrystallization from wet butyl alcohol raised the melting point to 240–241°. Setlur, Kothare, and Nadkarny (3) reported the melting point of *diphenylglycine* as 245°. Yield 44%.

Anal. Calc'd for $(C_6H_5)_2C(NH_2)COOH$: C, 74.0; H, 5.7; N, 6.2.
Found: C, 73.9; H, 6.1; N, 6.1.

Conversion of diphenylglycine to *benzilic acid* was accomplished as follows: diphenylglycine (1 g.) was dissolved in a mixture of 3 ml. of distilled water and 3 ml. of concentrated hydrochloric acid and the solution was filtered. The filtrate was cooled to 0°, ice was added, and the stirrer was introduced. A cold solution of 5 g. of sodium nitrite dissolved in 50 ml. of water was added beneath the surface of the liquid until an excess of nitrous acid was present as indicated by starch-iodide test paper. This required about 1 ml. of sodium nitrite solution.

The solution was allowed to warm up spontaneously and white crystals soon appeared. When the temperature of the solution had reached room temperature, it was heated on a water bath for 30 minutes. On cooling, crystals of benzilic acid, m.p. 149°, were deposited in 60% yield.

Anal. Calc'd for $C_{14}H_{12}O_3$: C, 73.7; H, 5.3.
Found: C, 73.9; H, 5.4.

(*b*). *Molar ratio of Grignard reagent to cyanogen, 1:2.* One mole of cyanogen dissolved in ether was added slowly with mechanical stirring to a half-molar solution of phenylmagnesium bromide contained in the previously described apparatus. The flask was warmed for 30 minutes after the addition of the cyanogen was completed. After standing for two hours the reaction mixture was hydrolyzed with a saturated solution of ammonium chloride and the ethereal solution was decanted through a dry filter. The filtrate was placed in a current of air to evaporate and the residue was then distilled at atmospheric pressure. *Benzonitrile*, b.p. 188–190°, was obtained in 50% yielded, based upon the halide.

(*c*). *Attempted reaction of diphenylglycinonitrile with additional Grignard reagent.* Diphenylglycinonitrile (0.02 mole) was dissolved in 50 ml. of anhydrous ether contained in a three-necked flask equipped with condenser, stirrer, and dropping-funnel. Phenylmagnesium bromide (0.04 mole) was added dropwise to the vigorously stirred solution. A white to gray solid was deposited on the side of the flask just above the liquid level. After all of the Grignard reagent had been added, the flask was warmed over a water-bath for five hours. The solid attached to the side of the flask became black during the heating. Hydrolysis of the reaction mixture using a saturated solution of ammonium chloride yielded only the original diphenylglycinonitrile and some diphenyl.

m-Tolylmagnesium bromide. This Grignard reagent was cyanogenated by the method described in (A) above and was hydrolyzed with a saturated ammonium chloride solution. Evaporation of the ether layer to which had been added 10 ml. of ethanol produced *di-m-tolylglycinonitrile* in yields of 33–35% based on the halide used. The product melted at 95.2–96.4° after recrystallization from ethanol.

Anal. Calc'd for $(CH_3C_6H_4)_2C(NH_2)CN$: C, 81.3; H, 6.9; N, 11.9.
Found: C, 81.7; H, 7.1; N, 11.8.

Acetyl-di-m-tolylglycinonitrile was prepared by warming together 1 g. of di-*m*-tolylglycinonitrile and 5 ml. of acetic anhydride. The resulting solution when cooled in an ice-bath gave an 85% yield of product melting at 213–214°.

Anal. Calc'd for $C_{18}H_{18}N_2O$: C, 77.7; H, 6.5; N, 10.1.
Found: C, 77.2; H, 6.8; N, 9.9.

Hydrolysis with hot concentrated HCl produced 3,3′-dimethylbenzophenone, m.p. 45°, identified as the 2,4-dinitrophenylhydrazone, m.p. 221–223°.

Di-m-tolylglycine was obtained by hydrolysis with 70% sulfuric acid. The nitrile (1 g.) was stirred vigorously with 50 ml. of 70% sulfuric acid and was heated at 80–90° for 24 hours. A clear solution resulted. When this solution was diluted with an equal volume of water a cloudiness appeared which disappeared upon further heating and stirring. The diluted solution was cooled and extracted with ether. The ethereal extract yielded about 5% of 3,3′-dimethylbenzophenone. The solution was neutralized with solid sodium carbonate and at approximately *p*H 4 a white solid appeared in about 25% yield. This was washed with warm water until free from sulfate. The substance melted at 255°.

Anal. Calc'd for $[(CH_3)C_6H_4]_2C(NH_2)COOH$: C, 75.5; H, 6.7; N, 5.5.
Found: C, 75.5; H, 7.0; N, 5.3.

The glycine was converted into *3,3′-dimethylbenzilic acid* as follows: Ice was added to a cooled solution of 1 g. of di-*m*-tolylglycine in 50 ml. of 10% sulfuric acid followed by a cold solution of sodium nitrite (1 g. in 25 ml. of water) slowly added beneath the surface of the well-stirred solution. A white substance began to separate soon after the addition was begun. When all of the sodium nitrite solution had been added, the mixture was allowed to warm up to room temperature and then was heated for two hours on a water-bath. Cooling caused the deposition of a white solid. The material, recrystallized from water, melted at 131–132°. It was obtained in a 60% yield.

Anal. Calc'd for $C_{16}H_{16}O_3$: C, 75.0; H, 6.3.
Found: C, 74.7; H, 6.5.

Cyclohexylmagnesium bromide. Dicyclohexylglycinonitrile was obtained from the cyanogenation of cyclohexylmagnesium bromide by the method described above. Hydrolysis with ammonium chloride solution was complicated by the formation at the beginning of a sticky, taffy-like mass which stopped the stirrer. Hand-stirring, while more ammonium chloride was added, eventually dispersed the mass and after 30–40 minutes the hydrolysis was completed without difficulty. The yield of white, solid product melting at 83–84° was only 6%.

Anal. Calc'd for: $(C_6H_{11})_2C(NH_2)CN$: C, 76.4; H, 10.9; N, 12.7.
Found: C, 76.6; H, 11.2; N, 12.8.

The *hydrochloride* was prepared by passing dry HCl into 20 ml. of dry ether containing 1 g. of dicyclohexylglycinonitrile. A cloudiness first appeared and after 30 minutes in an ice-bath an 85% yield of product was obtained. It melted at 209°.

Anal. Calc'd for $C_{14}H_{25}ClN_2$: C, 65.5; H, 9.8; N, 10.9.
Found: C, 65.6; H, 10.2; N, 10.9.

Hydrolysis of dicyclohexylglycinonitrile with 70% H_2SO_4 produced an excellent yield of *dicyclohexylglycinamide* rather than the acid expected. To 20 ml. of 70% sulfuric acid cooled in a ten-inch test tube was added 1 g. of dicyclohexylglycinonitrile. A stirrer was introduced and the tube was surrounded by a water-bath. The dicyclohexylglycinonitrile dissolved. The temperature was maintained at 95° for five hours whereupon the reaction mixture was diluted with an equal volume of water and heating and stirring were continued for another five hours.

After cooling the reaction mixture it was extracted with ether, from which nothing was obtained, and neutralized with solid sodium carbonate. As the solution approached *p*H 2 a cloudiness appeared and the reaction mixture was allowed to stand overnight. Ten hours later a white crystalline material was found floating on top of the liquid. Analysis indicated that a 50% yield of dicyclohexylglycinamide, m.p. 143°, had been obtained. Neutralizing the mother liquor to *p*H 6 precipitated more amide. The total yield of amide was 65%.

Anal. Calc'd for $(C_6H_{11})_2C(NH_2)CONH_2$: C, 70.5; H, 11.0; N, 11.8.
Found: C, 70.3; H, 11.4; N, 12.1.

Attempts to bring about a reaction between the glycinamide and nitrous acid failed to produce enough material to identify.

n-Butylmagnesium bromide. This Grignard reagent was cyanogenated and hydrolyzed without difficulty as described above. Evaporation of the ether layer left an oily residue which could not be induced to crystallize and which decomposed on distillation even at 2 mm. pressure. It was, therefore, decided to attempt the preparation of a benzoyl derivative.

The oily residue was measured and placed in a 250-ml. Erlenmeyer flask cooled in an ice-bath. An equal volume of benzoyl chloride and twice the volume of a 10% solution of sodium hydroxide were added, then the flask was stoppered and shaken vigorously for 15 minutes with short periods of cooling in the ice-bath when necessary.

Almost immediately the contents of the flask became viscous and yellow, separating into an aqueous layer and an organic layer. The aqueous layer was decanted and the residual organic layer was washed twice with 50-ml. of distilled water. The viscous organic material was recrystallized from ethyl alcohol and yielded a shiny white crystalline material which melted at 113–114°. A mixture melting point with benzoic acid caused a depression of 15° showing that the material was not benzoic acid. Analysis indicated that it was the *benzoyl derivative* of *di-n-butylglycinonitrile.* A 12% over-all yield was obtained.

Anal. Calc'd for $C_{17}H_{24}N_2O$: C, 75.0; H, 8.9; N, 10.3.
Found: C, 75.4; H, 8.9; N, 10.7.

Hydrolysis of the compound with 70% sulfuric acid converted the CN group to COOH but did not remove the benzoyl radical. For hydrolysis 20 ml. of 70% sulfuric acid in a ten-inch test tube was cooled in an ice-bath and 1 g. of benzoyldi-*n*-butylglycinonitrile was added. When warming to room temperature and shaking did not cause the material to dissolve, the test tube was placed in a 1-l. beaker of water on a hot plate and a stirrer was introduced. The water-bath was heated to boiling and maintained at that temperature for eight hours. At this time 20 ml. of water was added to the test tube and the stirring and heating were continued for 12 hours. Addition of the water caused the contents of the tube to become cloudy but this cleared as the temperature of the tube rose again.

Upon cooling, a white crystalline material separated and was removed. Recrystallized from diluted alcohol the material melted at 143° and represented a 40% yield of *benzoyldi-n-butylglycine.*

Anal. Calc'd for $C_{17}H_{25}NO_3$: C, 70.0; H, 8.7; N, 4.8.
Found: C, 70.2; H, 8.8; N, 4.7.

tert-Butylmagnesium bromide. The Grignard reagent prepared from *tert*-butyl chloride was thicker and more viscous than the other Grignard reagents which were prepared; however, cyanogenation was carried out smoothly and the usual silvery color developed. After standing 12 hours, hydrolysis was effected with a saturated solution of ammonium chloride. Evaporation of the ethereal layer to which had been added 10 ml. of alcohol gave a 15% yield of *di-tert-butylglycinonitrile* based upon the halide used. It was recrystallized from diluted alcohol as a volatile solid melting at 43–44°. If left in an open vessel it evaporated without leaving any residue.

Anal. Calc'd for: $(C_4H_9)_2C(NH_2)CN$: C, 71.4; H, 12.0; N, 16.7.
Found: C, 71.6; H, 12.1; N, 16.4.

The *hydrochloride* was produced in 90% yield by passing dry hydrogen chloride into 20 ml. of a solution of 1 g. of the glycinonitrile in 20 ml. of ether. Recrystallized from alcoholic solution by precipitation with ether the hydrochloride melted at 298°d.

Anal. Calc'd for $C_{10}H_{21}ClN_2$: C, 58.7; H, 10.3; N, 13.7.
Found: C, 58.9; H, 10.2; N, 13.8.

Attempts to prepare the acetyl derivative with acetic anhydride, the benzoyl derivative with benzoyl chloride, and the benzenesulfonyl derivative with benzenesulfonyl chloride failed. The original material was recovered in each case.

Hydrolysis with 70% sulfuric acid produced *di-tert-butylglycinamide* instead of the free acid. Hydrolysis of 1 g. of di-*tert*-butylglycinonitrile was begun as for the *n*-butyl analog. The material dissolved slowly. The test tube with its contents was placed in a 1-l. beaker of water on a hot plate and a stirrer was introduced into the test tube. The water-bath was heated to 95–98° and maintained at this temperature for the balance of the reaction time. Stirring was continuous. After eight hours 20 ml. of water was added to the reaction mixture and heating and stirring were continued for another eight hours.

Upon cooling, the reaction mixture was extracted with ether and then neutralized with solid sodium carbonate. The white solid which appeared at *p*H 2, crystallized from 50% alcohol as shiny platelets and melted at 127°. Analysis indicated that it was di-*tert*-butylglycinamide (17% yield).

Anal. Calc'd for $C_{10}H_{22}N_2O$: C, 64.5; H, 11.8; N, 15.1.
Found: C, 64.7; H, 12.1; N, 15.1.

SUMMARY

The product of the reaction of cyanogen with two moles of Grignard reagent is a disubstituted glycinonitrile, if the hydrolyzing agent is saturated ammonium chloride solution. Hydrolysis by acids yields only the ketone. A cyanogen-Grignard reaction mechanism which explains both results is proposed.

Glycinonitriles can be converted to glycinamides or glycines with 70% sulfuric acid.

Sixteen new compounds are reported.

BUFFALO 14, NEW YORK

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