readily crystallized. Both the barium and sodium salts were analyzed.

Anal. Calcd. for $(C_7H_{15}CHOHCH_2SO_3)_2Ba$: Ba, 23.54. Found: Ba, 23.49, 23.55. Calcd. for $C_7H_{15}CHOHCH_2SO_3Na$: Na, 9.35. Found: Na, 9.34, 9.12.

When the reaction mixture was hydrolyzed with cold sodium hydroxide, the ethylene chloride layer separated and the aqueous solution evaporated to dryness under reduced pressure in a water-bath held at 40–50° the product was the sodium sulfate–sulfonate, $C_7H_{15}CH(OSO_3Na)CH_2SO_3Na$, mixed with a few per cent. of sodium sulfate. Due to the high solubility in water of the former, purification was not possible. Hydroxysulfonates were prepared from higher olefins by the same procedure used for 1-nonene.

Sulfation and Sulfonation Reactions.—The reactions of aromatic compounds and of alcohols with the D. S. reagent require no detailed description. In the case of the anisole sulfonation the product was identified as the para compound by conversion into the sulfonamide. The other sulfation and sulfonation products are well-known compounds.

Summary

1. Dioxane reacts with either one or two molecules of sulfur trioxide to give compounds of the coördination type.

2. Either of these addition compounds serves as a reagent for sulfonation of various types of aromatic compounds. In the case of aniline, phenol and benzoic acid reaction occurs with the substituents rather than the benzene nucleus.

3. Primary alcohols are converted into alkyl hydrogen sulfates. Since the higher members of this series are valuable detergents, this reaction has practical significance.

4. Olefins are converted into compounds of the carbyl sulfate type. Hydrolysis of these yields hydroxysulfonates. Those from high molecular weight olefins have detergent properties. Further investigation of these compounds is in progress.

EVANSTON, ILLINOIS RECEIVED AUGUST 25, 1937

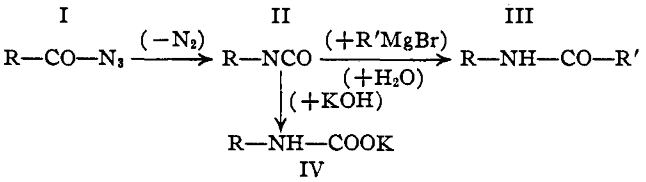
[CONTRIBUTION FROM THE CHARLES EDWARD COATES LABORATORY OF CHEMISTRY AT LOUISIANA STATE UNIVERSITY]

Preparation and Properties of Some Derivatives of 2-Aminofuran

BY H. M. SINGLETON[1] AND W. R. EDWARDS, JR.

Desiring to prepare and study derivatives of furan containing nitrogen in the α-position, and to ascertain to some extent the suitability of these products for further synthetic work, the authors applied the Curtius reaction, with variations, to furoic acid. This general means of approach has been employed by a number of investigators, but frequently the results with α-substituted furans have been discouraging. To simplify resultant observations and to make their possible application more general, the present work was confined to monosubstituted furans, though this involved waiver of the stabilizing influences sometimes exerted by additional substituent groups.

A preliminary comparison of the original method of Curtius for the preparation of 2-furoyl azide with the more recent method of Schroeter,[2] Naegeli,[3] and others, was made by reference and tested experimentally, and led to selection of the latter as more convenient, less expensive, and productive of a higher yield based on initial furoic acid. Starting with the azide, the primary reactions were



$$\begin{tikzcd}
\text{I} & \text{II} & \text{III} \\
R—CO—N_3 \arrow[r, "(-N_2)"] & R—NCO \arrow[r, "(+R'MgBr)", "(+H_2O)"'] \arrow[d, "(+KOH)"] & R—NH—CO—R' \\
 & R—NH—COOK & \\
 & \text{IV} &
\end{tikzcd}$$

In the present work, R was the α-furyl group, and R′ was either C_6H_5 or C_2H_5.

In proceeding from I to such products as III, IV and others, in the general employment of the Curtius reaction, the usual practice has been to omit isolation of II because of its objectionable nature, its instability when exposed to moist air, and the occasional difficulty of separating it from its solvent. It has been found commonly that when I has been decomposed thermally in suitable media, Grignard or other reagents can be added to the entire resultant mixtures with

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[1] This paper is an abstract of a portion of a thesis submitted by H. M. Singleton to the Graduate Faculty of Louisiana State University in partial fulfilment of the requirements for the degree of Doctor of Philosophy, in June, 1937. It was presented at the Chapel Hill meeting of the American Chemical Society, April, 1937.

[2] Schroeter, *Ber.*, **42**, 3356 (1909).

[3] Naegeli and Stefanovitsch, *Helv. Chim. Acta*, **11**, 609 (1928); Naegeli, Grüntuch and Lendorff, *ibid.*, **12**, 227 (1929).

satisfactory results. In some of our initial preparations the same procedure was followed[4]; but for the greater part of the work, the isocyanate was isolated by distillation.[5] This was made possible by decomposing the azide in a high-boiling solvent, and by protecting the isocyanate from the atmosphere, from the time of its formation until its ultimate utilization. Under these conditions it proved sufficiently stable. While it undoubtedly has been obtained previously in solution, its isolation has not been described.[6]

In the preparation of 2-benzoylaminofuran such isolation of the isocyanate was found to be essential for the successful synthesis of a pure product. More generally, it was worth while because the isocyanate proved to be an efficient reagent for a variety of subsequent preparations. In addition to its previously indicated use for the synthesis of 2-benzoylaminofuran, 2-propionylaminofuran and potassium 2-furylcarbamate it reacted with water to form *sym*-di-2-furylurea and with methanol to form methyl-2-furylcarbamate. These reactions were all rapid, the yields were good, and side reactions were of comparatively small proportions. Treatment of the isocyanate with barium hydroxide produced barium 2-furylcarbamate, but with less success as regards yield, purity and stability of product than in the preparation of the potassium compound.

2-Benzoylaminofuran and its propionyl analog were subjected to hydrolysis under a wide variety of conditions. No 2-aminofuran was obtained. In each case the products included: benzoic (or propionic) acid or its salt, almost quantitatively; ammonia, in quantity corresponding to practically all the nitrogen present; and tarry solids, apparently representing decomposition and subsequent polymerization products of the furan nucleus.

When the undistilled mixture resulting from thermal decomposition of furoyl azide was added to phenylmagnesium bromide,[4] an interesting result was observed. The product, first supposed to be wholly 2-benzoylaminofuran, possessed the correct composition and molecular weight for that compound; but its melting point was unexpectedly low and lacking in sharpness. The cause of this appeared when it was hydrolyzed. In addition to the products mentioned above (benzoic acid, ammonia and a tarry solid) there were obtained small but definite quantities of aniline and furoic acid. Evidently the product was 2-benzoylaminofuran accompanied by its isomer, 2-furanilide. The two compounds apparently formed isomorphous crystals; repeated recrystallizations failed to separate them. When, on the other hand, the isocyanate was distilled before its addition to phenylmagnesium bromide,[5] no trace of the isomer or of the latter's hydrolysis products could be detected, and the melting point of the resultant benzoylaminofuran was higher and sharper.

The circumstance of the formation of the isomer under one set of conditions, and its non-appearance under other conditions, indicates that its source is either undecomposed 2-furoyl azide or some by-product of the decomposition of that material. Further work is being done to investigate this side reaction. Whatever its nature may be, the appearance of the isomer suggests the following points.

(1) In the production of compounds of the type R–NH–CO–R′ with the aid of the Curtius reaction, it may be necessary, in order to avoid simultaneous production of an isomer difficult to separate, either to isolate and purify the isocyanate, or, possibly, to devise measures which will give increased assurance of complete decomposition of the acid azide before addition to the Grignard reagent.

(2) If, without such precautions, the reaction is extended through the hydrolysis of the compound of R–NH–CO–R′ type, a subsequent qualitative test for an amine does not demonstrate the presence of either particular one of the two amines which might be formed from the mixture of isomers. Where such a mixture exists, either $R\text{–}NH_2$ or $R'\text{–}NH_2$ or both might be produced.

Experimental Part

2-Furoyl Azide.—The method employed was adapted from the preparation of chaulmoogryl azide by Naegeli and Stefanovitsch.[3] A solution of 26 g. of 2-furoyl chloride in 75 cc. of ether was cooled to 0°. To this was added, dropwise and with stirring, a solution of 13 g. of sodium azide dissolved in 50 cc. of water. Stirring was continued at this temperature for fifteen minutes; then the mixture was allowed to come to room temperature, and stirring continued for another hour. The ether was

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[4] Experimental Part: "2-Benzoylaminofuran (Method I)."

[5] Experimental Part: "2-Benzoylaminofuran (Method II)," and subsequently-described preparations.

[6] In an article which has appeared since the submission of our paper, Johnson and Stevenson, THIS JOURNAL, 59, 2525 (1937), have described the isolation of this compound by decomposing 2-furoyl azide in successive small amounts, in the absence of any solvent.

evaporated by a current of air, after which the crystalline mass of 2-furoyl azide was separated by suction filtration. After washing with cold water and drying in a desiccator over phosphorus pentoxide, it was sufficiently pure for further use; yield 91.6%.

2-Furyl Isocyanate.—A 125-cc. Claisen flask was arranged in series with a short condenser, a Y-tube, and a 30-cc. dropping funnel. The open end of the Y-tube, inclined upward, was connected to a scrubber filled with benzene, and thence to the atmosphere. Air was displaced from the system by a stream of inactive gas (dry carbon dioxide or nitrogen) entering the Claisen flask and escaping through the scrubber. Ice water was circulated through the condenser jacket.

Thirteen and seven-tenths grams (0.1 mole) of 2-furoyl azide was placed in the Claisen flask, and 25 cc. of diphenyl ether (selected for its low vapor pressure at the boiling point of the isocyanate) was added. After allowing time for displacement of air, the flask was warmed cautiously on a water-bath until bubbles of nitrogen became abundant. To avoid explosion, the temperature was not allowed to exceed 75–80° at first; as the reaction progressed, this was increased gradually to 90°, the rate of increase being governed by the rate of nitrogen evolution. In the course of about two hours, the evolution of gas ceased. The 2-furyl isocyanate was distilled slowly into the dropping funnel, at atmospheric pressure, and retained there with air excluded until its further use. The yield was 8 g. (73.4%).

2-Furyl isocyanate is a colorless liquid with a very repulsive odor and a powerful lachrymatory effect. Inhalation of a very small amount of its vapor caused a lasting headache. It boiled at 111–112° at atmospheric pressure or 54° at 40 mm.

Anal. Calcd. for $C_5H_3O_2N$: C, 55.03; H, 2.77; N, 12.84. Found: C, 54.27; H, 2.85; N, 12.99.

2-Benzoylaminofuran (Method I).—A method similar to that of Burtner[7] for 3-benzoylaminofuran was employed. A solution of 27.4 g. (0.2 mole) of 2-furoyl azide, in a mixture of 200 cc. of benzene and 100 cc. of toluene, was dried over calcium chloride. After removal of the latter, the solution was refluxed cautiously until visible evolution of nitrogen ceased, and for a short additional period, meanwhile protecting it from atmospheric moisture with a calcium chloride tube. At this point, the solution was dark red and contained many suspended black particles.[8] No attempt was made to separate the isocyanate from the other constituents of the mixture.

The mixture of solvents was so composed as to provide a refluxing temperature suitable for decomposition of the azide. Blomquist and Stevenson[9] have shown the futility of attempting to separate the isocyanate by distillation when employing such solvents, with boiling points in the approximate neighborhood of that of 2-furyl isocyanate.

The entire solution was cooled to 0° and added, dropwise and with stirring, to an ether suspension of 0.2 mole of phenylmagnesium bromide, also at 0°. The resultant product was hydrolyzed with an excess of 15% ammonium chloride solution, and then extracted with ether. The combined ethereal extracts were dried over calcium sulfate and their volume reduced to 50 cc. by distillation. Pale yellow crystals of 2-benzoylaminofuran separated and were collected by suction filtration. After repeated recrystallizations from benzene, these became almost colorless, and their melting point became constant at 89–92°; yields averaged about 50%.

Anal. Calcd. for $C_{11}H_9O_2N$: C, 70.56; H, 4.85; N, 7.48; mol. wt., 187.1. Found: C, 70.26; H, 4.90; N, 7.29; mol. wt. (Rast), 190.4.

2-Benzoylaminofuran (Method II).—To a solution of 0.1 mole of phenylmagnesium bromide in 75 cc. of ether, cooled to 0°, 8.9 g. (0.082 mole) of 2-furyl isocyanate was added dropwise and with stirring. Hydrolysis, extraction, drying and crystallization proceeded as in Method I. A single recrystallization from benzene gave an almost colorless product melting sharply at 124.5°; further recrystallization did not alter melting point or appearance. Yields averaged 80%.

Anal. Calcd. for $C_{11}H_9O_2N$: C, 70.56; H, 4.85; N, 7.48. Found: C, 70.30; H, 4.91; N, 7.35.

Hydrolysis of samples of 2-benzoylaminofuran, prepared by Methods I and II, respectively, showed the former to be contaminated with 2-furanilide, and the latter to be free from this substance. The hydrolyses were conducted under various conditions[10] with substantially similar results. The following is a typical example.

Hydrolysis of 2-Benzoylaminofuran from Method I.—Forty-five grams of 2-benzoylaminofuran in a one-liter round-bottomed flask was digested under reflux for fifteen minutes with 300 cc. of 5% sulfuric acid. From the cooled solution, a large quantity of benzoic acid precipitated, and was removed by filtration. The filtrate was made barely alkaline with solid sodium carbonate, and then steam distilled, the distillate being received in an excess of 6 *N* hydrochloric acid. A crystalline residue (22.9 g.) was obtained after slow evaporation of the solvent.

This residue was dissolved in liquid ammonia, and the latter allowed to evaporate. This treatment was expected to release from their hydrochlorides the greater part of any amines present less basic than ammonia.[11] It was hoped that 2-aminofuran, if present, might thus be released without decomposition. When evaporation of the ammonia was complete, the residue (chiefly ammonium chloride) was extracted with dry ether, which was then removed by cautious distillation; 0.6 g. of a liquid boiling at 178° was obtained. Treatment of this liquid

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[7] Burtner, This Journal, **56**, 666 (1934).

[8] The appearance of a dark red color accompanied by black solid particles was observed in a large proportion of the reactions described here, and in other reactions involving alpha furan derivatives. It seems to be an almost invariable result, and an indication, of at least partial nuclear decomposition. *Cf.* Freundler, *Bull. soc. chim.*, [3] **17**, 419 (1897).

[9] Blomquist and Stevenson, This Journal, **56**, 146 (1934).

[10] Including use of different acids and bases, various concentrations, times and temperatures, and various ways of separating the products. A non-apropos but interesting observation was that in one hydrolysis with 3% potassium hydroxide, there was formed in addition to the usual products a small amount of the potassium salt of an acid which, from its Duclaux constants, appeared to be formic acid.

[11] Preliminary tests of this method showed it to be effective in releasing from their salts aniline and *o*-toluidine; partially effective with the more basic benzylamine; ineffective with ethylamine, which is more basic than ammonia. Under ideal conditions, the recovery of aniline was 87% of the theoretical.

with benzoyl chloride gave a crystalline product melting at 159.5–160.5°. A mixture of these crystals with benzanilide from other sources melted within the same range. Therefore this liquid product, which appeared to be the only stable base, less basic than ammonia, formed in the initial hydrolysis, was aniline. As discussed earlier in this paper, this indicated the presence of 2-furanilide in the 2-benzoylaminofuran. The method employed lacks quantitative accuracy; but the proportion of 2-furanilide was probably about 3%.

To verify the existence of the isomer, the residue from the steam distillation was examined for furoic acid. A small amount of the latter was separated and identified in the form of the ethyl ester. The total quantity was not determined.

The complete list of hydrolysis products recognized included: ammonia, obtained as ammonium chloride in nearly quantitative amount; benzoic acid in large quantity; small quantities of aniline and furoic acid. There was also isolated a small quantity of an unidentified material, in the form of small, colorless, plate-like crystals, m. p. 68.5–69°; b. p. 115–125° at 8 mm.

Anal. C, 82.20; H, 6.42; N, 0.00.

No basic products other than ammonia and aniline could be detected. A tarry residue was conspicuous. Immediately following hydrolysis, the mixture was tested for carbonyl oxygen, and for acetylenic linkages; the results were negative.

Hydrolysis of 2-Benzoylaminofuran from Method II.—The procedure followed in the hydrolysis just described was repeated with 2-benzoylaminofuran (m. p. 124.5°) prepared from the isolated isocyanate. Neither aniline nor furoic acid could be discovered in the hydrolysis products. In every other respect, the results of hydrolysis and subsequent treatment were the same.

2-Propionylaminofuran.—This was prepared from 2-furyl isocyanate and ethylmagnesium bromide, by a procedure similar to Method II for the preparation of 2-benzoylaminofuran. When the extracting ether was removed by distillation, the residue was a liquid. This was distilled at reduced pressure; the pale yellow oil thus obtained turned to a solid mass on standing. It was recrystallized from dilute alcohol: m. p. 80.5–81.0°; b. p. 134° at 12 mm. The yield was 88.5% of the theoretical.

Anal. Calcd. for $C_7H_9O_2N$: C, 60.43; H, 6.52; N, 10.07. Found: C, 59.98; H, 6.61; N, 9.93.

2-Propionylaminofuran was hydrolyzed under a variety of conditions, with results similar to those obtained from hydrolysis of the pure 2-benzoylaminofuran. Ammonia, propionic acid, and a tarry solid were produced, the two former in practically quantitative amounts. Except for ammonia, no basic hydrolysis product could be detected.

Potassium 2-Furylcarbamate.—To 75 cc. of 35% potassium hydroxide, heated to 50° and kept in an atmosphere of nitrogen, 8.7 g. of 2-furyl isocyanate was added slowly, in small drops, with vigorous stirring. After stirring for an additional fifteen minutes, the mixture was cooled in an ice-bath, and the crystalline product separated by suction filtration and washed with cold methanol. The crystals were then colorless, but turned brown after standing a few hours. The yield was 81.8% of the theoretical.

Anal. Calcd. for $C_5H_4O_3NK$: C, 36.34; H, 2.44; N, 8.48; K, 23.68. Found: C, 36.03; H, 2.90; N, 8.60; K, 23.49.

Barium 2-Furylcarbamate.—To 300 cc. of 3.5% solution of barium hydroxide cooled to 0°, 9.4 g. of 2-furyl isocyanate was added dropwise with vigorous stirring. A mass of nearly colorless rhombic plates appeared; these were separated by suction filtration, washed with cold water, and dried in a desiccator over barium oxide. Attempts to free the product completely from barium hydroxide were unsuccessful; recrystallization from warm water could not be employed, as the carbamate decomposed when this was attempted. The crystals turned brown after standing for a few hours.

Anal. Calcd. for $C_{10}H_8O_6N_2Ba$: C, 30.84; H, 2.07; N, 7.19; Ba, 35.27. Found: C, 30.10; H, 2.65; N, 6.91; Ba, 35.30.

In analyses of the two carbamates, corrections were made for the carbon remaining as carbonates of potassium and barium, respectively. A further correction was made of all values in the analysis of the barium 2-furylcarbamate, on account of the small quantity of barium hydroxide present.

Methyl-2-furylcarbamate.—To prove that the furan nucleus had remained intact during the formation of potassium 2-furylcarbamate, a portion of the latter was converted into methyl-2-furylcarbamate. Four grams of the potassium carbamate was dissolved in 100 cc. of water containing 0.5 g. of sodium hydroxide; and 3.5 g. of dimethyl sulfate was added, with stirring. The stirring was continued for thirty minutes at room temperature and then for an equal time on a steam-bath. The solution was then extracted with ether; the extract dried over solid sodium hydroxide; the ether distilled off; and the residue distilled under reduced pressure (b. p. 115–120° at 18 mm.). A 21% yield was obtained of a product identical with a sample of methyl 2-furylcarbamate separately prepared by the method of Curtius and Leimbach.[12]

Methyl 2-furylcarbamate also was prepared by the present authors by addition of 2-furyl isocyanate, in ether, to excess absolute methanol at 0°. A yield of 95.1% was obtained by this method.

Di-2-furylurea (Symmetrical).—Four and six-tenths grams of 2-furyl isocyanate was added slowly, with rapid stirring, to 50 cc. of water previously cooled to 5°. Colorless crystals (presumably 2-furylcarbamic acid) appeared quickly. These were extremely unstable, and decomposed spontaneously at room temperature with evolution of carbon dioxide and liberation of heat. The residue consisted of small, pale yellow crystals, which were separated by suction filtration and recrystallized from dilute alcohol. They melted, with decomposition, at 190°. The yield was 70% of the theoretical.

Anal. Calcd. for $C_9H_8O_3N_2$: C, 56.23; H, 4.15; N, 14.58. Found: C, 55.70; H, 3.85; N, 14.28.

This material was formed whenever the isocyanate was exposed to atmospheric moisture.

Summary

2-Furyl isocyanate, 2-benzoylaminofuran, 2-propionylaminofuran, potassium 2-furylcarba-

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[12] Curtius and Leimbach, *J. prakt. Chem.*, [2] **65**, 32 (1902).

mate and barium 2-furylcarbamate have been prepared; and certain reactions of the first four have been studied.

Isolation of 2-furyl isocyanate in syntheses in which it is an intermediate compound has been shown to be advantageous in some instances.

The usefulness of the Curtius reaction for the introduction of nitrogen into the alpha position in the furan series has been demonstrated further, and some of the favoring conditions have been determined.

BATON ROUGE, LA. RECEIVED OCTOBER 18, 1937

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WASHINGTON]

Raman Spectra of Sodium Alkyl Sulfonates and Sulfinates

BY HAROLD G. HOULTON[1] AND H. V. TARTAR

Introduction

The constitution of the sulfinic acids has long been an open question. In addition, further confirmatory evidence concerning the structure of the sulfonates also should be of considerable interest. The purpose of this investigation was to establish, if possible, their type of valence bonds. The Raman effect has always been characterized by the attribution of certain wave number shifts to certain bonds in the molecule. It is possible by this means to establish the bonds existing in the sulfonic and sulfinic acid groups. In order to have the most rigorous solution to the problem, the simplest molecules containing these groups were taken for investigation, *i. e.*, the lower members of the saturated alkyl series.

Little work has been done in recent years on the lower members of the alkyl sulfonates and sulfinates. One of the first investigations on the structure of sulfinic acid was that of P. Claesson[2] in 1877, on sodium ethyl sulfinate. From that time until 1931 practically no work was done on this series of compounds. Von Braun and Weissbach[3] in 1931 prepared butyl sulfinic acid but did nothing to establish its constitution. In no case have definite directions been given for the preparation of this series of sulfinates and it is deemed advisable to include the details herein.

Some of the earliest work on alkyl sulfonic salts was carried out by Hemilian[4] who reported yields of 90%. Wagner and Reid[5] using the same method obtained only 50–60%. In this investigation we substituted sodium sulfite for the ammonium sulfite used by these workers and the yields ranged 85–90%. Consequently, the details of preparation are also included.

Experimental

Preparation of Sulfonates.—The bromides used were either supplied by the Eastman Kodak Company or were prepared by the method outlined in Gilman.[6] One mole of the bromide, 1.15 moles of sodium sulfite and 750 cc. of water were refluxed for approximately twelve hours, *i. e.*, until the bromide disappeared.

The resulting solution was evaporated to dryness on a steam-bath, dried at 110°, pulverized, and finally extracted twice with petrol ether. The excess of this solvent was removed by heating on a steam-bath. The solid thus obtained was placed in a five-liter, round-bottomed flask, two liters of alcohol (denatured, formula No. 30) added, heated to boiling, and filtered with suction to remove the excess sodium sulfite. The alcoholic solution was then cooled overnight in a refrigerator and again filtered with suction. By this procedure the yield was 75%. The remaining 25% was obtained by distilling the excess alcohol and cooling. The salt was then dried at 110° and recrystallized using one liter of alcohol per mole, 85% yields being obtained. The excess sodium sulfite sometimes approached the colloidal state and consequently all filters, with the exception of suction, clogged badly. If the salt is dried thoroughly after the addition of the petroleum ether the colloidal properties are greatly reduced. By this method, ethyl, propyl, butyl, and amyl sodium sulfonates were prepared.

Preparation of Sulfinates.—To a three-necked, three-liter flask were connected a separatory funnel, a mercury-sealed mechanical stirrer, and a reflux condenser. Three moles of magnesium turnings, previously washed with anhydrous ether, 500 cc. of anhydrous ether, 5 cc. of the bromide concerned (previously distilled from phosphorus pentoxide) and a crystal of iodine were added in the order given. The remainder of the three moles of the bromide dissolved in 500 cc. of anhydrous ether was added from the separatory funnel to the top of which was connected a calcium chloride drying tube. A similar tube was also placed in the top of the reflux condenser. The ether solution of the bromide may be added as fast as the refluxing will permit, and the addition may therefore be decidedly

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(2) Claesson, *J. prakt. Chem.*, **15**, 222 (1877).

(3) Von Braun and Weissbach, *Ber.*, **63**, 2836 (1930).

(4) Hemilian, *Ann.*, **168**, 146 (1873).

(5) Wagner and Reid, THIS JOURNAL, **53**, 3407 (1931).

(6) Gilman, "Collected Organic Syntheses," John Wiley and Sons, Inc., New York, N. Y., 1934.