

A similar yield of I is obtainable with a catalyst mixture of 75 cc. of concd. hydrochloric acid and 37 cc. of water, and a reaction temperature of 90–95°. With 85% phosphoric acid at 90–95° the yield is smaller and the product darker.

The amorphous product forms crystalline solvates with aromatic hydrocarbons. From benzene it crystallizes in flat, white needles, m.p. 120–122°; from toluene in stout needles, m.p. 108–109°; from *m*-xylene in flat needles, m.p. 96–98°. Removal of the solvent of crystallization *in vacuo* at 90° leaves the glass, m.p. ca. 90°. Crystallization of the benzene solvate from *m*-xylene yielded the *m*-xylene solvate.

*Anal.*² Benzene solvate: Calcd. for $C_{17}H_{18}O_4 \cdot \frac{1}{2}C_6H_6$: C, 73.82; H, 6.51. Found: C, 73.48; H, 6.62. Toluene solvate: Calcd. for $C_{17}H_{18}O_4 \cdot \frac{1}{2}C_7H_8$: C, 74.07; H, 6.67. Found: C, 74.44; H, 7.02.

After many unsuccessful attempts to obtain I crystalline and solvent-free, a large batch crystallized solvent-free from a mixture of toluene and acetone, m.p. 168–170°. It formed hard, white rosettes from water containing a trace of acetic acid, m.p. 171–172°, and could also be crystallized well from mixtures of heptane and ethyl acetate, or benzene and acetone. Hot solutions of the amorphous modification in aromatic hydrocarbons when seeded with solvent-free crystals, yielded the crystals, m.p. 171–172°, on cooling.

Anal. Calcd. for $C_{17}H_{18}O_4$: C, 71.31; H, 6.34. Found: C, 70.99, 70.94; H, 6.62, 6.46.

$\lambda_{\text{EtOH}-0.1\% \text{HOAc}}$, $\mu\mu$ 225.0 (log *E* 4.20); 227.5 (infl., log *E* 4.18)
279.0 (log *E* 3.57); 282.5 (infl., log *E* 3.53)
 λ_{min} 250.0 (log *E* 2.71)

The ultraviolet spectra of the solvates are very similar. The infrared spectrum of I in a nujol mull shows a strong band at 12.0 μ (indicative of *para* substitution), and no band at 13.2–13.4 μ .

Solvent-free, crystalline I forms a methyl ester which crystallizes from aqueous methanol with water of crystallization and melts at 87–89°.

Anal. Calcd. for $C_{18}H_{20}O_4 \cdot 3H_2O$: C, 61.00; H, 7.40. Found: C, 61.43; H, 7.60.

(2) Analyses by the Micro-Tech Laboratories, Skokie, Ill.

THE RESEARCH LABORATORIES
THE PAINT DIVISION
THE PITTSBURGH PLATE GLASS COMPANY
MILWAUKEE, WISCONSIN

3-Substituted Thiophenes. VIII.¹ 3-Thienylalkylamines²

BY E. CAMPAIGNE AND WALTER C. MCCARTHY³

RECEIVED MAY 3, 1954

β -2-Thienylethylamine was shown to have vasopressor action by Tainter.⁴ More recently, N-methyl- β -2-thienylethylamine and β -2-thienylisopropylamine and its N-methyl derivative were reported by Blicke and Burckhalter⁵ to be semi-quantitatively similar to their phenyl analogs. Related compounds were the subject of a patent by Van Zoeren,⁶ and pharmacological data have been reported by Warren, *et al.*,⁷ and Alles and Feigen.⁸

(1) Contribution No. 632. For a previous paper in this series see E. Campaigne and P. A. Monroe, *THIS JOURNAL*, **76**, 2447 (1954).

(2) Taken from part of the thesis submitted by W.C.M. in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Indiana University, August, 1949.

(3) Sterling-Winthrop Fellow in Chemistry, 1948–1949.

(4) M. L. Tainter, *Quart. J. Pharm. Pharmacol.*, **3**, 584 (1930).

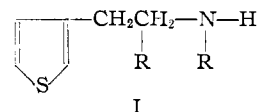
(5) F. F. Blicke and J. H. Burckhalter, *THIS JOURNAL*, **64**, 477 (1942).

(6) G. J. Van Zoeren, U. S. Patent 2,367,702; *C. A.*, **39**, 4195 (1945).

(7) M. R. Warren, D. G. Marsh, C. R. Thompson, R. S. Shelton and T. J. Becker, *J. Pharm. Exptl. Therap.*, **79**, 187 (1943).

(8) G. A. Alles and G. A. Feigen, *ibid.*, **72**, 265 (1941).

We have prepared four β -3-thienylethylamines, I, in order to compare the physiological activity of these with the corresponding 2-thienyl and phenyl analogs. β -3-Thienylethylamine (Ia) was prepared in three different ways: Curtius degradation



I
a, R = R' = H; b, R = H, R' = CH₃; c, R = Cl, R' = H; d, R = R' = CH₃

of β -3-thienylpropionic acid, reduction of ω -nitro-3-vinylthiophene with lithium aluminum hydride,⁹ and reduction of 3-thienylacetonitrile with lithium aluminum hydride.¹⁰ The second method proved best, affording a 74% yield of amine, in contrast to 53 and 50% yields by the other methods, respectively. N-Methyl- β -3-thienylethylamine (Ib) was obtained by lithium aluminum hydride reduction of N-methyl-3-thienylacetamide. The attempted methylation of N-benzal- β -3-thienylethylamine, according to the method of Decker and Becker,¹¹ gave only a trace of this secondary amine. Since reductive amination of 3-thienylacetone by the Leuckart reaction gave only an 11% yield of 1-(3-thienyl)-2-aminopropane (Ic), a second method, reduction of 1-(3-thienyl)-2-nitropropene with lithium aluminum hydride, was tried and an 85% yield of amine was obtained. The Leuckart reaction proved adequate for the preparation of 1-(3-thienyl)-2-methylaminopropane (Id).

In preliminary experiments by Dr. A. M. Lands, of the Sterling-Winthrop Research Institute, Ia was shown to have about 1/3 the pressor potency of its phenyl analog by direct comparison, and an average potency of 1/132 the assay dose of epinephrine. From this, it appears that the 3-thiophene isomer is about 3 to 4 times as active as the 2-isomer, which Tainter⁴ reported to be about 1/531 as active as epinephrine.

Experimental¹²

Diethyl 3-Thienylmalonate.—A procedure was used similar to that reported by Marvel¹³ for the benzyl analog. From 1 l. of absolute ethanol, 47.5 g. (2.07 gram atoms) of sodium, 340 g. (2.12 moles) of diethyl malonate and 354 g. (2.0 moles) of 3-thienyl bromide,¹⁴ a yield of 251 g. (48%) of a product boiling from 135° to 164° (4 mm.) was obtained. For analysis a sample was redistilled through a column. The major fraction distilled at 146° (3 mm.), n_D^{20} 1.4960, d_4^{20} 1.142.

Anal. Calcd. for $C_{12}H_{16}O_4S$: S, 12.51. Found: S, 12.51.

3-Thienylmalonic Acid.—Diethyl 3-thienylmalonate (48.7 g., 0.19 mole) was saponified by refluxing with a 20% aqueous solution of sodium hydroxide for six hours, and the reaction mixture was then acidified and extracted with ether. After evaporation of the ether and recrystallization of the crude product from benzene there were obtained 22.4 g. (59%) of white crystals, which melted at 138–139°. A second recrystallization from benzene raised the m.p. to 139–140° dec.

Anal. Calcd. for $C_8H_8O_4S$: S, 16.01. Found: S, 16.02.

β -3-Thienylpropionic Acid.—3-Thienylmalonic acid (22.4 g., 0.112 mole) was heated at 130 to 141° for one hour, until

(9) Cf. R. T. Gilsdorf and F. F. Nord, *J. Org. Chem.*, **15**, 807 (1950).

(10) This reduction was reported recently by W. Herz, *THIS JOURNAL*, **73**, 351 (1951), in low yield.

(11) H. Decker and P. Becker, *Ann.*, **395**, 362 (1913).

(12) All melting points are uncorrected.

(13) C. S. Marvel, *Org. Syntheses*, **21**, 99 (1941).

(14) E. Campaigne and B. F. Tullar, *ibid.*, **33**, 96 (1953).

evolution of carbon dioxide had practically ceased; then heated quickly to 170° and cooled. After recrystallization from water, 13.4 g. (77%) of white needles, m.p. 61–62°, was obtained.

Anal. Calcd. for $C_7H_5O_2S$: C, 53.80; H, 5.16; S, 20.53. Found: C, 53.79; H, 5.06; S, 20.62.

β -3-Thienylpropionyl Chloride.— β -3-Thienylpropionic acid (13.6 g., 0.087 mole) and 20.8 g. (0.172 mole) of purified thionyl chloride¹⁵ were refluxed for ten minutes. After removal of the excess thionyl chloride at reduced pressure, 12.3 g. of the product (81%) was collected from 90–100° at 3 mm.

ω -Nitro-3-vinylthiophene.—The procedure of Worrall¹⁶ for the benzene analog was used. Nitromethane (50.8 g., 0.833 mole) and 93.4 g. (0.833 mole) of 3-thenaldehyde¹⁷ in 167 ml. of methanol were condensed by adding 85 ml. of an aqueous solution containing 35.0 g. (0.875 mole) of sodium hydroxide. After recrystallization from ethanol, 78.2 g. of crystals melting between 86–91° was obtained. Two further recrystallizations from ethanol and one from acetic acid gave 39.3 g. (25%) of pure product, m.p. 96–97°.

Anal. Calcd. for $C_6H_5NO_2S$: S, 20.66. Found: S, 20.61.

3-Thienylacetonitrile.¹⁸—From the reaction of 280 g. (1.58 moles) of 3-thenyl bromide with 98 g. (2 moles) of sodium cyanide in aqueous alcohol, there was obtained 124.4 g. (64%) of the nitrile boiling at 77–100° (5 mm.). A sample was redistilled for analysis; b.p. 124–125° (16 mm.), n_D^{25} 1.5422, d_4^{25} 1.080.

Anal. Calcd. for C_6H_5NS : N, 11.37. Found: N, 11.05.

β -3-Thienylethylamine, Ia. A. Curtius Degradation.—A vigorous reaction occurred as 5.0 g. (0.077 mole) of sodium azide was added cautiously in portions to a solution of 12.4 g. (0.071 mole) of β -3-thienylpropionyl chloride in 100 ml. of benzene. After all the azide was added, the mixture was refluxed for 22 hours, filtered, and the residue washed with benzene. The benzene filtrates were then combined, 45 ml. of concentrated hydrochloric acid added, and the mixture refluxed for four hours longer. The water layer was separated, and the benzene layer washed with water. The two water layers were combined and made alkaline with sodium hydroxide. The oil was extracted with benzene and vacuum distilled, and the fraction boiling from 90–100° (12 mm.) which separated was collected and weighed 4.8 g. (53%). A sample was redistilled; b.p. 65–68° (3 mm.), n_D^{20} 1.5537, d_4^{20} 1.086. The benzamide derivative, recrystallized from ethyl alcohol, melted at 108–108.5°.¹⁹

B. Reduction of ω -Nitro-3-vinylthiophene.—An ether solution of 27.6 g. (0.178 mole) of ω -nitro-3-vinylthiophene was reduced with 17.8 g. (0.466 mole) of lithium aluminum hydride.²⁰ After isolation of the amine, it was vacuum distilled, b.p. 82–91° (7 mm.), and a 74% yield (16.7 g.) was obtained.

C. Reduction of 3-Thienylacetonitrile.¹⁰—An ether solution of 24.6 g. (0.20 mole) of 3-thienylacetonitrile was reduced with 7.6 g. (0.20 mole) of lithium aluminum hydride and 12.8 g. (50%) of the amine was isolated.

The hydrochloride was obtained from a solution of the amine in absolute ethanol by saturation with dry hydrogen chloride and addition of an equal volume of ether to complete the precipitation. After recrystallizing from absolute ethanol, the product melted at 214.5–216°.

Anal. Calcd. for $C_6H_{10}ClNS$: N, 8.56; S, 19.59. Found: N, 8.67; S, 20.26.

The phenylthiourea derivative was recrystallized from ethyl alcohol, m.p. 86–86.5°.

Anal. Calcd. for $C_{13}H_{14}N_2S_2$: N, 10.68; S, 24.44. Found: N, 10.85; S, 23.78.

N-Benzal- β -3-thienylethylamine.—A solution of 16.7 g. (0.131 mole) of Ia and 14.0 g. (0.132 mole) of benzaldehyde

in 50 ml. of ethanol was refluxed for 30 minutes. The alcohol was removed under reduced pressure, and the oil was vacuum distilled, to give 27.1 g. (96%) of product boiling from 170–192° (7 mm.). Subsequently, the material crystallized, melting at 33–35°.

Anal. Calcd. for $C_{13}H_{13}NS$: S, 14.89. Found: S, 14.97.

N-Methyl-3-thienylacetamide.—3-Thienylacetyl chloride was prepared in 87% yield by the action of purified thionyl chloride on 3-thienylacetic acid,¹⁸ and distilled between 71–76° (4 mm.). This oil (35.2 g., 0.22 mole) was dropped cautiously into 80 ml. of liquid methylamine which was kept cold in a Dry Ice-acetone-bath. After the reaction was completed, the mixture was allowed slowly to warm up to room temperature, then heated on a water-bath to remove excess methylamine. Water was added to dissolve the methylamine hydrochloride, and ether to dissolve the N-methyl-3-thienylacetamide. The ether layer was washed with dilute alkali, and after the solvent was evaporated, there was obtained 20.3 g. (60%) of a solid, m.p. 72–74°. Recrystallization from benzene raised the m.p. to 75–75.5°.

Anal. Calcd. for C_7H_9NOS : N, 9.02. Found: N, 8.70.

N-Methyl- β -3-thienylethylamine (Ib).—An ether solution of 15.7 g. (0.1 mole) of N-methyl-3-thienylacetamide was reduced with 5.8 g. (0.152 mole) of lithium aluminum hydride. The isolated amine was vacuum distilled, b.p. 87–91° (7 mm.), and yielded 7.7 g. (54%) of an oil, n_D^{20} 1.5310, d_4^{20} 1.036.

Anal. Calcd. for $C_7H_{11}NS$: N, 9.92; S, 22.70. Found: 9.77; S, 21.93.

The hydrochloride crystallized from absolute alcohol and melted at 148–149°.

Anal. Calcd. for $C_7H_{12}ClNS$: N, 7.88. Found: N, 8.13.

The phenylthiourea derivative was recrystallized from ethyl alcohol, m.p. 105–105.5°.

Anal. Calcd. for $C_{14}N_2S_2$: C, 60.84; H, 5.84. Found: C, 61.00; H, 6.17.

1-(3-Thienyl)-2-nitropropene.—A mixture of 83.5 g. (0.745 mole) of 3-thenaldehyde, 56.7 g. (0.756 mole) of nitroethane, 134 ml. of absolute ethanol and 15 ml. of *n*-butylamine was allowed to stand for three days in the dark at room temperature. The mixture was then cooled in a refrigerator, filtered by suction and the crystalline product washed with cold ethanol, yielding 91 g. (72%) of canary-yellow needles, which melted at 72.5–73.5°. Recrystallization from ethanol did not raise the melting point.

Anal. Calcd. for $C_7H_7NO_2S$: S, 18.95. Found: S, 18.68.

3-Thienylacetone.—A procedure was employed similar to that used by Hoover and Hass²¹ for the preparation of the *p*-methoxyphenyl analog. A mixture of 81.1 g. (0.48 mole) of 1-(3-thienyl)-2-nitropropene, 200 g. of iron filings (60 mesh), 1 g. of ferric chloride and 500 ml. of water was refluxed, with continuous vigorous stirring, for seven hours; 90 ml. of concd. hydrochloric acid was added in five portions during the first six hours. The mixture was steam distilled until 3 l. of distillate were collected. The distillate was extracted with ether and the ether extract was dried over anhydrous calcium sulfate. The ether was evaporated and the product vacuum distilled; the fraction boiling from 93° (8 mm.) to 101° (6 mm.) weighed 48.9 g. (73%). Redistillation through a column gave 46.4 g. of a chartreuse-colored distillate boiling at 83° (5 mm.), n_D^{20} 1.5335, d_4^{20} 1.116.

Anal. Calcd. for C_7H_8OS : S, 22.91. Found: S, 22.87.

The 2,4-dinitrophenylhydrazone was recrystallized from ethyl alcohol and from nitromethane, and melted at 111.5–112°.

Anal. Calcd. for $C_{13}H_{12}N_4O_4S$: N, 17.49. Found: N, 17.33.

The oxime melted at 73–73.5° after being recrystallized from dilute ethanol and from benzene.

Anal. Calcd. for C_7H_9NOS : N, 9.02. Found: N, 9.01.

1-(3-Thienyl)-2-propylamine, Ic. A. Leuckart Reaction.—Water was distilled out of a mixture of 25.5 g. (0.5 mole) of 90% formic acid and 30.6 g. (0.5 mole) of 28% aqueous ammonia heated in a 3-neck flask equipped with dropping funnel, thermometer and condenser set for distillation.

(21) F. W. Hoover and H. B. Hass, *J. Org. Chem.*, **12**, 501 (1947).

(15) D. L. Cottle, *THIS JOURNAL*, **68**, 1380 (1946).

(16) D. E. Worrall, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 413.

(17) E. Campaigne, R. C. Bourgeois and W. C. McCarthy, *Org. Syntheses*, **33**, 93 (1953).

(18) E. Campaigne and W. M. LeSuer, *THIS JOURNAL*, **70**, 1555 (1948).

(19) Previously reported, 108.5–109°, reference 10.

(20) Cf. R. F. Nystrom and W. G. Brown, *THIS JOURNAL*, **70**, 3738 (1948).

When the temperature reached 175°, heating was stopped, and the condenser set for refluxing. A single addition of 14.0 g. (0.1 mole) of 3-thienylacetone was made and the temperature was maintained at 160–170° for seven hours. The reaction mixture was cooled, and upon adding 60 ml. of water, the formyl derivative of the amine separated as an oil. The mother liquor was extracted with benzene, the benzene evaporated, and the two portions of the formyl derivative were mixed. This formyl derivative was refluxed with 100 ml. of 3 *N* sodium hydroxide for 20 hours, and the amine extracted with benzene. The benzene solution was extracted with dilute hydrochloric acid, the acid solution was made alkaline with concd. ammonia, and the amine was again extracted with benzene. The solvent was removed under reduced pressure and the product was vacuum distilled, b.p. 64–71° (3 mm.), to yield 1.6 g. (11%).

B. Reduction of 1-(3-Thienyl)-2-nitropropene.—1-(3-Thienyl)-2-nitropropene (33.8 g., 0.2 mole) was reduced in ether solution with 22.8 g. (0.6 mole) of lithium aluminum hydride. After isolation of the amine, it was vacuum distilled, b.p. 79° (12 mm.) to 85° (5 mm.), to yield 23.9 g. (85%). Fractionation through a short column gave a product, b.p. 70–74° (7 mm.), n_D^{20} 1.5349, d_4^{20} 1.037.

Anal. Calcd. for $C_8H_{11}NS$: S, 22.70. Found: S, 23.03.

The hydrochloride was recrystallized from absolute ethanol, m.p. 135–136°.

Anal. Calcd. for $C_8H_{11}ClNS$: N, 7.88. Found: N, 7.91.

The benzamide was recrystallized from ethanol, m.p. 118–118.5°.

Anal. Calcd. for $C_{10}H_{13}NOS$: C, 68.53; H, 6.16; S, 13.07. Found: C, 68.54; H, 5.88; S, 13.07.

The phenylthiourea derivative was recrystallized from ethanol, m.p. 110.5–111°.

Anal. Calcd. for $C_{11}H_{13}N_2S_2$: N, 10.14. Found: N, 10.07.

N-Methyl-1-(3-thienyl)-2-propylamine (Id).—From 25.5 g. (0.5 mole) of 90% formic acid, 54 ml. (0.5 mole) of 9.34 *M* methylamine solution and 14.0 g. (0.1 mole) of 3-thienylacetone, 7.5 g. (48%) of an amine fraction, b.p. 89–92° (9 mm.), was obtained *via* the Leuckart procedure previously described. Redistillation gave a product, b.p. 67–69° (3 mm.), n_D^{20} 1.5233, d_4^{20} 1.009.

Anal. Calcd. for $C_8H_{13}NS$: S, 20.65. Found: S, 20.35.

The hydrochloride was recrystallized from a mixture of absolute alcohol and dry ether, m.p. 97–98°.

Anal. Calcd. for $C_8H_{14}ClNS$: C, 50.11; H, 7.36; S, 13.72. Found: C, 50.65; H, 7.55; S, 16.28.

The phenylthiourea derivative was recrystallized from ethyl alcohol, m.p. 122–122.5°.

Anal. Calcd. for $C_{15}H_{15}N_2S_2$: N, 9.65; S, 22.08. Found: N, 9.36; S, 22.39.

DEPT. OF CHEMISTRY
INDIANA UNIVERSITY
BLOOMINGTON, INDIANA

Triphenylmethyl Nitrate¹

By STANLEY J. CRISTOL AND JOHN E. LEFFLER

RECEIVED MARCH 29, 1954

One of the possible modes of organic nitrate ester decomposition or reduction involves oxygen-nitrogen fission leading to the formation of alkoxy free radicals. We have been interested in the reductive denitration of nitrate esters with alkaline hydrosulfides,² and wished to conduct experiments to determine the possibility of free-radical intermediates. Although mixtures of *n*-butyl nitrate and sodium hydrosulfide with the radical detectors acrylonitrile and methyl methacrylate failed to

give any polymer, *n*-butyl nitrate appeared to inhibit the benzoyl peroxide-catalyzed polymerization of acrylonitrile. It was of interest to obtain triphenylmethyl nitrate for use in similar experiments, since the triphenylmethoxy free radical, if formed, should reveal itself by β -cleavage to benzophenone or by the Wieland rearrangement.³

Attempts to make triphenylmethyl nitrate from the chloride and silver nitrate in dimethylformamide as a solvent gave only triphenylcarbinol. A similar experiment in acetonitrile gave *N*-triphenylmethylacetamide by way of an intermediate, probably the nitrate of the imidol form of this amide. Even in benzene the reaction gave only the carbinol, by decomposition at higher temperatures or by hydrolysis on exposure of the solution to air at lower temperatures. The nitrate appeared to be inordinately sensitive to hydrolysis. When prepared in carbon tetrachloride, only the carbinol was isolated when the solvent was allowed to evaporate in air. Vacuum-line technique, using carbon tetrachloride as the solvent, gave a solid which melted with decomposition at 73° and re-solidified at a higher temperature.

Exposure of this solid to the laboratory air even for a few minutes converted it almost entirely to the carbinol. We therefore heated freshly prepared solutions of the nitrate in sealed ampoules and isolated the decomposition products without any further attempt to purify the nitrate itself. In carbon tetrachloride and in nitrobenzene the decomposition products were benzophenone, triphenylcarbinol, picric acid and oxides of nitrogen. These products are consistent with β -cleavage of some of the triphenylmethoxy radicals to phenyl radicals and benzophenone, nitration and oxidation of the cleaved phenyl radical by nitrogen dioxide and reduction of some of the triphenylmethoxy radicals by hydrogen atoms supplied in the nitration reaction. In addition some of the alcohol may have resulted from hydrolysis.

Experimental

Formation and Decomposition of Triphenylmethyl Nitrate in Carbon Tetrachloride.—To 5 g. of silver nitrate and 2.0 g. of triphenylmethyl chloride in an ampoule was added 50 ml. of carbon tetrachloride by distillation from phosphorus pentoxide. The mixture was frozen, degassed, sealed, shaken overnight, then heated to 110° for 15 minutes. The filtrate was concentrated and put onto an alumina column with ordinary chloroform. There was isolated a trace of benzophenone, 1.44 g. of triphenylcarbinol, m.p. and mixed m.p. 162–164°, and 0.4 g. of triphenylmethyl ethyl ether (evidently from alcohol in the chloroform), m.p. and mixed m.p. 83–84°, and 40 mg. of picric acid. From a second experiment in which the heating period was three hours, there was obtained 250 mg. of benzophenone, m.p. and mixed m.p. 47–49° (oxime, m.p. 141–142°), 1.38 g. of carbinol, and 140 mg. of picric acid, m.p. and mixed m.p. 119–121°. Similar results were obtained when the triphenylmethyl nitrate solution was decanted into an ampoule of calcium oxide before sealing. A mixture of carbon tetrachloride and styrene as solvent gave polymer, benzophenone, carbinol and nitrophenols.

Nitrobenzene.—A similar experiment in which the product of the reaction in nitrobenzene was decanted, sealed and decomposed at 110–125° gave oxides of nitrogen, benzophenone, carbinol and picric acid.

(3) J. E. Leffler, *Chem. Revs.*, **45**, 385 (1949); H. Wieland, *Ber.*, **44**, 2550 (1911).

(4) J. Herzig and P. Wengraf, *Monatsh.*, **22**, 601 (1901).

(1) This research was supported by a contract between the University of Colorado and the U. S. Naval Ordnance Test Station, Inyokern, U. S. Navy Bureau of Ordnance.

(2) R. T. Merrow, S. J. Cristol and R. W. Van Dolah, *This Journal*, **75**, 4259 (1953).

(5) A. Janny, *Ber.*, **15**, 2718 (1882); E. Bamberger and R. Seligmann, *ibid.*, **36**, 685 (1903).