

gave the crude aqueous azeotrope, b.p. 88–95°, which upon analysis⁵ proved to represent a yield of 16% based on starting material or 32% on 2-methoxyethanol consumed. The ethoxyacetaldehyde azeotrope, b.p. 90–110°, was similarly made at 300–425° in yields of 8–13% based on 2-ethoxyethanol consumed, but the dehydrogenation failed for *n*-butoxyacetaldehyde. Conversion of glycerol α -monochlorohydrin to glycerol α -*n*-propyl ether, b.p. 109–114° (9 mm.) (41% yield) and oxidation with lead tetraacetate, all according to the method of Hatch and Nesbitt,⁶ gave crude *n*-propoxyacetaldehyde, b.p. 60–80° (105 mm.), in 72% yield based on the ether.

Preparation of Polyhydroxymethylated Compounds. Procedure A.—A mixture of formaldehyde (as 37% formalin), carbonyl compound, water, and calcium oxide in the molar ratio 3:1:50:0.5 was stirred and kept below 40° until the aldehyde titer⁵ was negligible; this required 7–30 hours. The mixture was neutralized with dilute sulfuric acid, treated with Super-Cel filter aid, filtered by suction, and evaporated under reduced pressure on the steam-bath to a viscous brown sirup. This sirup was dissolved in an equal volume of hot methanol, diluted with acetone until precipitation ceased, and filtered as before. Renewed vacuum evaporation, solution in a little water, extraction with ether to remove colored impurities, and vacuum distillation gave a light yellow or colorless sirup, which sometimes crystallized upon standing.

Procedure B.—The reaction mixture was like that in procedure A but additionally contained 5 ml. of 2% Aerosol OT solution per 200 ml. of water. This was caused to react at 50°, neutralized, filtered, and separated into its two layers. The organic layer was washed repeatedly with water and distilled under reduced pressure to yield a sirup which soon crystallized.

Procedure C.—A solution of formaldehyde (as 37% formalin) and the other aldehyde in ethanol was stirred and gradually treated with potassium hydroxide in 90% ethanol: the molar ratio was 3HCHO:1RCHO:1KOH:10C₂H₅OH total. Initial cooling was necessary to keep the temperature below 50°. When all the aldehyde had disappeared (20–40 hours, mostly at room temperature), the solution was neutralized with sulfuric acid, filtered, and evaporated *in vacuo* on a steam-bath. If two layers appeared, the water layer was discarded and the organic layer was washed with water before fractional vacuum distillation. This usually yielded two yellow sirup fractions, the triol and its monoethyl ether (appearing in reverse order).

The applications of these syntheses and physical properties of products are shown in Table I, and analytical data in Table II.

1,3-Dichloro-2-chloromethyl-2-methoxypropane.—This was prepared³ from 2-hydroxymethyl-2-methoxy-1,3-propanediol, pyridine and thionyl chloride in the molar ratio 1:3:3. Besides a relatively large amount of high-boiling chlorine-containing liquid, presumably a mixture of the mono- and dichlorinated compounds, the desired trichloro compound was obtained as a white solid melting at 59.0–59.2° (cor.) after recrystallization from ethanol.

Anal. Calcd. for C₅H₉OCl₃: Cl, 55.6. Found: Cl, 56.1.

Attempted preparation of the corresponding ethoxy and *n*-propoxy compounds by the same method gave only unpurifiable oils.

(5) L. H. Donnelly, *Ind. Eng. Chem., Anal. Ed.*, **5**, 91 (1933).

(6) L. F. Hatch and S. S. Nesbitt, *This Journal*, **67**, 39 (1945).

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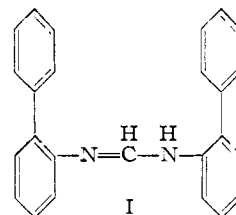
Improved Phenanthridine Syntheses with Polyphosphoric Acid

By E. C. TAYLOR, JR., AND NORMAN W. KALENDA

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The cyclization of 2-formamidobiphenyl to phenanthridine represents the simplest and most straightforward route to this compound, but the methods which have been described for effecting

this cyclization are somewhat unsatisfactory. The use of zinc chloride gives only a 42% yield of phenanthridine,¹ while an improved cyclization procedure, although raising the yield of 90%, employs a mixture of phosphorus oxychloride, nitrobenzene and anhydrous stannic chloride.² In view of the versatility of polyphosphoric acid in effecting numerous cyclization reactions,³ we have investigated its application in the present case. Phenanthridine is formed in yields consistently over 90% by heating a stirred mixture of 2-formamidobiphenyl and polyphosphoric acid for one hour at 140–160° and then pouring the reaction mixture into water. Constant stirring during the heating period is essential; without stirring, the only product isolated was a compound C₂₅H₂₀N₂, which is probably *N,N'*-bis-(*o*-biphenyl)-formamidine (I).



The most convenient route to phenanthridone reported involves aluminum chloride cyclization of *o*-biphenyl isocyanate.⁴ It has now been found that this cyclization may be carried out conveniently and in improved yields (87%) by heating a stirred mixture of polyphosphoric acid and *o*-biphenyl isocyanate for two hours at 140–160° and pouring the reaction mixture into water. Some di-(*o*-biphenyl)-urea is also formed, probably as a result of hydrolysis of a small amount of unreacted *o*-biphenyl isocyanate during the isolation procedure.

Experimental⁵

Phenanthridine.—A mixture of 20 ml. of polyphosphoric acid and 2.0 g. of 2-formamidobiphenyl in a 100-ml. round-bottom flask was heated at 140–160° for one hour with constant stirring. The viscous reaction mixture was then poured into 200 ml. of cold water, the resulting milky solution adjusted to pH 10 with strong sodium hydroxide solution and allowed to stand several hours at room temperature. The light pink solid which separated was collected by filtration and washed well with water; yield 1.70 g. (93.4%), m.p. 104.5–106°. One recrystallization from ligroin using Norit gave colorless needles, m.p. 106–107°.

***N,N'*-Bis-(*o*-biphenyl)-formamidine (I).**—A mixture of 2.00 g. of 2-formamidobiphenyl and 20 ml. of polyphosphoric acid was heated at 175–180° without stirring for a period of one hour. The reaction mixture was then cooled, diluted with 200 ml. of water and the resulting solution adjusted to pH 10 with strong sodium hydroxide solution. This basic solution was extracted several times with 100-ml. portions of ether and the combined ether extracts extracted with three 80-ml. portions of 6 *N* hydrochloric acid. The combined acid extracts were adjusted to pH 10 with strong sodium hydroxide solution and allowed to stand for several

(1) G. T. Morgan and L. P. Walls, *J. Chem. Soc.*, 2225 (1932).

(2) D. W. Ockenden and K. Schofield, *ibid.*, 717 (1953).

(3) See for example: H. R. Snyder and F. X. Werber, *This Journal*, **72**, 2962, 2965 (1950); E. C. Horning, J. Koo and G. N. Walker, *ibid.*, **73**, 5826 (1951).

(4) J. M. Butler, *ibid.*, **71**, 2578 (1949).

(5) The polyphosphoric acid was generously supplied by the Victor Chemical Works, Chicago, Illinois, and the *o*-biphenyl isocyanate by Dr. J. H. Saunders, Monsanto Chemical Company, Anniston, Alabama.

hours. The pink solid which separated was recrystallized first from ligroin and then from aqueous dimethylformamide to give 0.59 g. (33.4%) of colorless crystals, m.p. 156.5–157.5°.

Anal. Calcd. for $C_{25}H_{20}N_2$: C, 86.2; H, 5.8; N, 8.0. Found: C, 85.9; H, 6.1; N, 8.2.

Phenanthridone.—A mixture of 2 ml. (2.20 g.) of *o*-biphenyl isocyanate and 4.5 ml. of polyphosphoric acid was heated for two hours with constant stirring in an oil-bath held at 140–160°. Addition of the top liquid layer to water yielded 0.02 g. of di-(*o*-biphenyl)-urea, m.p. 184–185°, while addition of the bottom liquid layer to water and recrystallization of the resulting solid from aqueous dimethylformamide gave 1.92 g. (87.3%) of colorless phenanthridone, m.p. 291–292°.

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A Preparation of Liquid Ammonia Solutions of Sodium Vinylacetylide

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Liquid ammonia solutions of sodium vinylacetylide have been used for the introduction of vinyl-ethynyl groups into molecules.^{1–3} The solutions were prepared by treating sodium or sodium amide with vinylacetylene in liquid ammonia. Vinylacetylene, however, is difficult to store and handle in the laboratory.⁴ We have found that liquid ammonia solutions of sodium vinylacetylide are conveniently prepared in the laboratory by the reaction of sodium amide in liquid ammonia with either 1,4-dichloro-2-butene or 1,2-dichloro-3-butene or a mixture of both. The existence of the sodium vinylacetylide was established by its reaction with (1) ethylene oxide to produce hex-5-en-3-yn-1-ol in 24.5% yield, (2) acetone to produce 1,1-dimethylpent-4-en-2-yn-1-ol in 56% yield and (3) cyclohexanone to produce 1-vinylethynylcyclohexanol in 52% yield.

Experimental

Dichlorobutenes.—A 60:40 mixture of 1,4-dichloro-2-butene and 1,2-dichloro-3-butene was obtained from E. I. du Pont de Nemours and Company, Inc. It was separated into 1,2-dichloro-3-butene (b.p. 47–53° (60 mm.)) and 1,4-dichloro-2-butene (b.p. 78–80° (60 mm.)) by distillation.

Sodium Amide.—This was prepared according to the method of Vaughan, Vogt and Nieuwland.⁵

Sodium Vinylacetylide.—To a stirred solution of sodium amide in 1.5 l. of liquid ammonia, prepared from 33 g. (1.5 moles) of sodium, was added 63 g. (0.5 mole) of 1,4-dichloro-2-butene or 1,2-dichloro-3-butene or a mixture of both over a period of 30 minutes at –35°. The resulting solution was stirred for 3 hours at –30 to –35° to ensure complete reaction.

Hex-5-en-3-yn-1-ol.—Ethylene oxide (114 g., 2.6 moles) was added, over a ten-minute period, under the surface of

(1) W. H. Carothers and R. A. Jacobson, *THIS JOURNAL*, **55**, 1097 (1933).

(2) R. A. Jacobson and W. H. Carothers, *ibid.*, **55**, 1622 (1933).

(3) I. M. Heilbron, E. R. H. Jones and B. C. L. Weedon, *J. Chem. Soc.*, 140 (1944).

(4) Vinylacetylene is available from E. I. du Pont de Nemours and Company, Inc., as a 50% solution in xylene, and is shipped in cylinders of approximately one quart. The manufacturer states that the solution in unopened cylinders is relatively stable for approximately one month at ordinary room temperatures but that it is a very dangerous material to handle.

(5) T. H. Vaughan, R. R. Vogt and J. A. Nieuwland, *THIS JOURNAL*, **56**, 2120 (1934).

a stirred solution of 2 moles of sodium vinylacetylide in 3.5 l. of liquid ammonia at –35°. The mixture was stirred at –35° for seven hours and then neutralized by the cautious addition of 107 g. (2.0 moles) of ammonium chloride in small portions, after which the ammonia was allowed to evaporate. To the residue was added slowly 1 l. of water and the mixture was subjected to steam distillation. The 2 l. of distillate was saturated with potassium carbonate and the resulting oil was removed by extraction with ether. The extracts were dried over anhydrous potassium carbonate and distilled to produce 48 g. (24.5%) of hex-5-en-3-yn-1-ol which boiled at 65–70° (10 mm.) and had n_D^{20} 1.4958 (lit.⁶ b.p. 68–69° (10 mm.), n_D^{18} 1.4968).

1,1-Dimethylpent-4-en-2-yn-1-ol.—Redistilled anhydrous acetone (29 g., 0.5 mole) was added to a solution of 0.5 mole of sodium vinylacetylide in 1.5 l. of liquid ammonia over a 15-minute period at –35°. The mixture was stirred for 3 hours at –35° and then neutralized by the cautious addition of 80 g. (1.5 moles) of ammonium chloride, after which the ammonia was allowed to evaporate. To the residue there was added 1 l. of ether and then 300 cc. of water. The ether layer was separated, dried over magnesium sulfate and distilled to give 31 g. (56%) of 1,1-dimethylpent-4-en-2-yn-1-ol, b.p. 65° (24 mm.), n_D^{20} 1.4752 (lit.² b.p. 67° (24 mm.), n_D^{20} 1.4778).

1-Vinylethynylcyclohexanol.—From the reaction of 0.5 mole of sodium vinylacetylide with 0.5 mole of redistilled cyclohexanone and 1.5 l. of liquid ammonia there was obtained 12 g. of recovered cyclohexanone and 31 g. (52% yield, 40% conversion) of 1-vinylethynylcyclohexanol, b.p. 83–87° (3 mm.), n_D^{20} 1.5145 (lit.² b.p. 84–85° (2 mm.), n_D^{20} 1.5169).

(6) I. N. Nazarov and A. N. Elizarova, *Bull. acad. sci. U.R.S.S., Classe sci. chim.*, 189 (1940); *C.A.*, **36**, 742 (1942).

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Dimethoxyindanyl and -indenyl Derivatives^{1,2}

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During the course of a study of colchicine and its degradation products we became interested in reactions of methoxyindenes as a class of compounds containing a bicyclic ring system in which the A-ring contained methoxyl groups. A number of products were obtained in reactions designed to introduce various side-chains into the 6,7-dimethoxy-3-indenyl nucleus.

Condensation of ketone I with ethyl cyanoacetate gave an indanylidene cyanoacetate (II). The position of the double bond as illustrated was expected by analogy with 1-indanylidene cyanoacetate, the product of reaction of 1-indanone with ethyl cyanoacetate,⁴ and was confirmed by the ultraviolet spectrum of II. Absorption at 343 $m\mu$ was in agreement with structure II rather than that of an indenyl derivative. Compound II was methylated in the presence of sodium amide, and the product was hydrolyzed (alkali) and decarboxylated. A nitrile was obtained which had an ultraviolet spectrum consistent with an indene structure IV (maximum of principal peak, 311 $m\mu$).

(1) Supported in part by a grant-in-aid from the American Cancer Society, recommended by the Committee on Growth of the National Research Council.

(2) Taken from the Ph.D. thesis of G. N. Walker, University of Pennsylvania, 1951.

(3) American Cancer Society Predoctoral Assistant, 1949–1950; du Pont Predoctoral Fellow, 1950–1951.

(4) A. C. Cope and L. Field, *THIS JOURNAL*, **71**, 1589 (1949).