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*-biphenylyl)-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

BY W. J. CROXALL AND J. O. VAN HOOK

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Liquid ammonia solutions of sodium vinylacetylide have been used for the introduction of vinylethinyl 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-vinylethinylcyclohexanol 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 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^{20}_{D} 1.4958 (lit.[6] b.p. 68–69° (10 mm.), n^{18}_{D} 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^{21}_{D} 1.4752 (lit.[2] b.p. 67° (24 mm.), n^{20}_{D} 1.4778).

1-Vinylethinylcyclohexanol.—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-vinylethinylcyclohexanol, b.p. 83–87° (3 mm.), n^{20}_{D} 1.5145 (lit.[2] b.p. 84–85° (2 mm.), n^{20}_{D} 1.5169).

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[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).

[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]

BY E. C. HORNING AND G. N. WALKER[3]

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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 mμ 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 mμ).

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[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).