and about twice this amount of unchanged *p*-iodoaniline were obtained from approximately 400 g. of crude material.

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## The Reaction of Ethylene Oxide with Acetylenic Grignard Reagents

BY JAMES P. DANEHY, RICHARD R. VOGT AND J. A. NIEUWLAND

Recently the preparation of certain acetylenic alcohols by the action of ethylene oxide on acetylenic Grignard reagents has been reported.[1,2] We can now report in a quantitative manner the products obtained from this reaction.

Two moles (192 g.) of heptyne-1 was transformed into the Grignard reagent, treated with a slight excess of ethylene oxide (90 g.) and subsequently hydrolyzed; on fractional distillation under diminished pressure 65 g. of heptyne-1, 95 g. of ethylene bromohydrin and 60 g. of 3-nonyn-1-ol were obtained. The Grignard reagents of hexyne-1 and phenylacetylene when treated with ethylene oxide give analogous products in substantially the same percentage yields.

[1] Faucounau, *Compt. rend.*, **199**, 605 (1934).

[2] Danehy, Vogt and Nieuwland, THIS JOURNAL, **56**, 2790 (1934).

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## The Fries–Rosenmund Rearrangement of N-Acetylcarbazole[1]

BY ERICH MEITZNER

3-Acetylcarbazole, in yields not stated, has been prepared by Plant and Williams[2] by heating N-acetylcarbazole with aluminum chloride. Since their method proved to be unsatisfactory, the rearrangement was carried out with nitrobenzene as solvent. With this modification in the conditions, 3-acetylcarbazole may be obtained in yields of 50 to 60%, together with tarry products, carbazole, and the hitherto unknown 1-acetylcarbazole.[3] The complexity of the process is a serious drawback to its use for large scale preparations of 3-acetylcarbazole.

The structure of 1-acetylcarbazole was demonstrated by converting the compound by potassium hydroxide fusion into the known carbazole-1-carboxylic acid.[4] The detection of 1-acetylcarbazole among the reaction products completes the parallelism of this rearrangement to that of acyl phenols to *p*- and *o*-hydroxy ketones.

### Experimental

**Rearrangement of N-Acetylcarbazole.**—Twenty-one grams of N-acetylcarbazole was dissolved in 125 cc. of nitrobenzene, 15 g. of aluminum chloride added (water cooling) and the mixture was allowed to stand for fifteen to twenty hours The observance of this delay is important, because immediate heating results in increased formation of tar. The mere standing at room temperature does not effect the conversion, however, as was shown by the quantitative recovery of carbazole when the mixture was worked up according to the process described below. The mixture was then heated in an oil-bath to 110–125° for thirty minutes, decomposed with ice, and the nitrobenzene distilled off with steam. The solidified residue was filtered, dried and dissolved in boiling ethyl alcohol. After filtration from an insoluble residue, the solution was evaporated to small bulk. About 12–13 g. of crude 3-acetylcarbazole (m. p. 155–160°) separated at this point. This product was purified by recrystallization from toluene, or sublimation at 170–180° and $10^{-2}$ mm. It forms snow white prisms, m. p. 167–168°. (3-N-Diacetylcarbazole melts at 156°; Plant and Williams, 153°.) The mother liquors were evaporated and the residue, after removal of some nitrobenzene, distilled at 170° and $10^{-2}$ mm. The distillate consisted of 3- and 1-acetylcarbazoles, carbazole and a yellow compound which proved to be *m*-dinitrobenzene, undoubtedly present as an impurity in the nitrobenzene used. This mixture was distilled at 130° and $10^{-2}$ mm.

The residue consisted chiefly of 3-acetylcarbazole, while the distillate was largely a mixture of 1-acetylcarbazole and carbazole, with a small amount of dinitrobenzene deposited farthest from the source of heat. The mixture of 1-acetylcarbazole and carbazole was sublimed at 110°, $10^{-2}$ mm., and the fine white sublimate of carbazole separated mechanically from the yellowish prisms of 1-acetylcarbazole. The sublimation and separation was repeated and the products recrystallized from ethyl alcohol.

1-Acetylcarbazole crystallizes in fine white needles of m. p. 136°.

*Anal.* Calcd. for $C_{14}H_{11}ON$: C, 80.35; H, 5.30. Found: C, 80.52; H, 5.41.

1-Acetylcarbazole oxime, white silky needles, m. p. 179–180°.

*Anal.* Calcd. for $C_{14}H_{12}ON_2$: C, 74.96; H, 5.40. Found: C, 74.59; H, 5.33.

The action of equivalent amounts of acetyl chloride and carbazole under the above conditions yields the same

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[1] The work reported in this paper is part of a unification of effort by a number of agencies having responsibility for the solution of the problem of drug addiction. The organizations taking part are: The Rockefeller Foundation, the National Research Council, the U. S. Public Health Service, the U. S. Bureau of Narcotics, the University of Virginia and the University of Michigan.

[2] Plant and Williams, *J. Chem. Soc.*, 1142 (1934).

[3] In a communication [*ibid.*, 743 (1935)] appearing after the completion of this work, Plant, Rogers and Williams describe the use of nitrobenzene for the rearrangement, but do not mention the formation of 1-acetylcarbazole.

[4] Ciamician and Silber, *Gazz. chim. ital.*, **12**, 272 (1882).

products, with a somewhat higher formation of tarry products.

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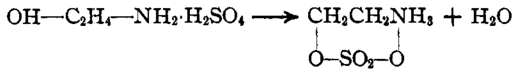
## The Preparation of Ethylene Imine from Monoethanolamine

By Henry Wenker

In view of the readiness with which compounds containing a β-aminoethyl group can be obtained from ethylene imine, a method may be of interest by which 80 g. of this base can be prepared conveniently in the laboratory in one day from inexpensive commercial material. The process consists, firstly, in preparing β-aminoethyl sulfuric acid[1,2] by thermic dehydration of monoethanolamine acid sulfate according to the equation



$$\mathrm{OH{-}C_2H_4{-}NH_2\cdot H_2SO_4} \longrightarrow \underset{\mathrm{O{-}SO_2{-}O}}{\mathrm{CH_2CH_2NH_3}} + \mathrm{H_2O}$$

secondly, in distilling this compound with alkali.

An equimolar mixture of monoethanolamine and sulfuric acid is heated rapidly over a free flame until, at a temperature of about 250°, charring begins, necessitating the end of the operation. Only 75% of the mole of water indicated by the formula can be expelled since, irrespective of the rate of heating, the product begins to turn brown rapidly when this degree of dehydration has been reached. As much as 10 moles—610 g., of monoethanolamine and 1020 g. of 96% sulfuric acid—may be used for one operation. On cooling, the thin, clear brown liquid solidifies to a hard, white crystalline cake. It is ground in a mortar with one-half its weight of 60% ethanol, filtered by suction and washed with ethanol; yield, 100 g. per mole of starting material or 71%. It is convenient to dilute both components with their own weight of water previous to mixing, and then to boil off the excess of water.

282 grams of β-aminoethyl sulfuric acid is distilled with 880 g. of 40% caustic soda solution from a 3000-cc. flask. Shortly before the boiling point is reached, a reaction occurs which keeps the mixture boiling for several minutes; during this time, heating must be discontinued. When the reaction ceases, heating is resumed and a total of 240 cc. is distilled over. One distillation requires about forty-five minutes. On addition of potassium hydroxide to the distillate, 65 cc. of base separates; this is dried repeatedly with potassium hydroxide, then with sodium, and finally fractionated. The use of an efficient distilling column is recommended since the crude base contains higher boiling by-products; yield, 23 g. of ethylene imine boiling at 55–56.5° or 26.5%.

ELIZABETH, N. J. RECEIVED JULY 29, 1935

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[1] Gabriel, *Ber.*, **21**, 1056, 2667 (1888).

[2] Fraenkel and Cornelius, *ibid.*, **51**, 1660 (1918).

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## An All-Glass Valve

By John Willard

An all-glass valve for use in systems where stopcocks are objectionable is illustrated in Fig. 1. It is easily constructed and may be opened and closed by merely heating a quartz tube which surrounds a fine Pyrex capillary. It is particularly useful for admitting a corrosive but thermally stable gas from a reservoir to a reaction.

The tube D is of quartz, about 6 mm. in diameter. Part C is a quartz-to-Pyrex graded seal and the portion of the device above C is of Pyrex. E is a fine Pyrex capillary. The outlet A is connected to a gas reservoir and the outlet B to an evacuated system to be filled from the reservoir.

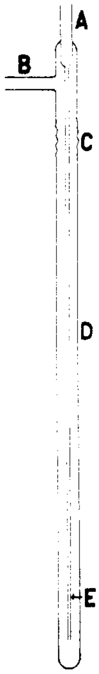

Fig. 1.

A small flame from a hand torch applied to the quartz near the tip of the capillary, when there is only a few mm. greater pressure on the A side than on the B side, will cause the capillary to blow out without affecting the quartz. When pressure has been equalized the capillary may be sealed again by similar application of heat. Repeated openings and closings of the valve may be carried out without difficulty if the capillary is long and fairly small even though it may stick to the side of the quartz tube. During an investigation in this Laboratory this device has been in constant use for several months. As many as twenty fillings have been made with it before it was necessary to seal in a new Pyrex capillary.

Alyea[1] has developed a valve which is similar in purpose to the one here described but which is made completely of Pyrex glass. It is opened by the use of a magnetic pellet and closed by sealing off the outer tube and the capillary together. Other types of greaseless valves are described by

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[1] Alyea, This Journal, **52**, 1937 (1930).