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).