unexpected, since it is only the latter which forms an insoluble ammonium salt. It is probable that the amount of the penta acid recovered represents only a small fraction of that present.

Decarboxylation.—One hundred grams of the dried acids, 200 g. of sodium hydroxide, and 100 cc. of water were placed in a 1-liter American Instrument Company bomb furnished with a nickel liner. The temperature was raised to 450° in about four hours, maximum pressure 3800 lb. After cooling, and withdrawal of a gas sample, the pressure head of the bomb was replaced by a head carrying a delivery tube for attachment to a water condenser and an inlet for steam. The steam-volatile hydrocarbons, after passage through the water condenser, were collected over a strong calcium chloride solution acidified with hydrochloric acid, and measured in a small buret calibrated to 0.05 cc. After further drying over anhydrous calcium chloride the hydrocarbons were fractionated through a 51-cm. vacuum jacketed column.

The volume of gaseous products formed in the decarboxylation was calculated from the pressure and volume of the system and their composition determined in an Orsat apparatus by standard methods.

Acknowledgment.—The authors are indebted to F. C. Silbert and T. B. Smith for determinations of ultimate composition, and to J. M. Scott for gas analyses.

Summary

The action of dilute (1 *N*) nitric acid in converting bituminous coal into soluble products has been shown to be chiefly an oxidation. The yield of humic acids reaches a maximum in a few days, while that of the soluble acids increases slowly with time. If the reaction is carried out in the presence of air, only about one-fourth as much nitric acid is consumed as in its absence.

The residue from the benzene pressure extraction of this coal oxidizes more rapidly than the original coal. Oxidation of the cokes obtained by thermal decomposition of the coal in vacuum shows no difference from the original coal with cokes up to about 440°. Cokes prepared above this temperature show markedly greater resistance to oxidation. It has been pointed out that this temperature coincides with that at which gas evolution becomes rapid.

Determinations of ultimate composition and functional groups on both types of acids formed in this oxidation show the regenerated humic acids to contain markedly less hydroxyl than is reported for other humic acids, while the soluble acids contain negligible amounts. In the humic acids only approximately half the oxygen determined by ultimate analysis can be accounted for in functional groups, while in the soluble acids only small amounts of oxygen are thus unaccounted for. The presence, in the soluble acids, of benzenepentacarboxylic and mellitic acids was shown by isolation of their esters. Of the carbon of the coal which was oxidized to soluble acids, approximately one-tenth was recovered as steam-volatile, aromatic hydrocarbons, by decarboxylation. The presence of acids more complex than the benzene carboxylics is indicated.

PITTSBURGH, PENNA. RECEIVED SEPTEMBER 9, 1935

NOTES

Decomposition of *p*-Iodoaniline

BY F. B. DAINS, R. Q. BREWSTER AND JOHN A. DAVIS

A sample of *p*-iodoaniline was prepared and carefully purified by one of us.[1]

The product stood for three years in a glass-stoppered bottle (hence a limited supply of air) in semi-diffused light, at room temperature; it had then changed to a black liquid, which was found to contain a trace of free iodine and a small amount of aniline. Further examination showed the presence of 2,4-diiodoaniline and unchanged *p*-iodoaniline. The *p*-iodoaniline was removed as its hydrochloric acid salt by extraction of the liquid with hot, dilute acid. The salt crystallized from the solution as it cooled and the free base was liberated with alkali and recrystallized from ligroin, b. p. 90–100° (m. p. 62°). The 2,4-diiodoaniline was extracted from the acid insoluble residue with hot alcohol leaving a black insoluble mass, some 80 g., which was not identified. Dark needles of the 2,4-diiodoaniline crystallized from the alcohol as it cooled. These, when recrystallized from ligroin, gave a light tan colored product (m. p. 95°). In all, 95 g. of 2,4-diiodoaniline

---

[1] R. Q. Brewster, "Organic Syntheses," John Wiley and Sons, Inc., New York City, 1931, Vol. 11, p. 62.

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

UNIVERSITY OF KANSAS
LAWRENCE, KANSAS
RECEIVED JULY 1, 1935

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).

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF NOTRE DAME
NOTRE DAME, INDIANA
RECEIVED JULY 1, 1935

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

---

(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).