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

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[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
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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

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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).

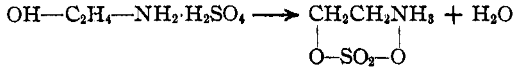
products, with a somewhat higher formation of tarry products.

UNIVERSITY, VIRGINIA RECEIVED AUGUST 9, 1935

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).

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.

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.

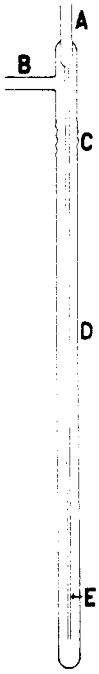

Fig. 1.

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).

Bodenstein,[2] Ramsperger,[3] and Sutton and Mayer.[4] For many purposes the valve described here is more desirable than any of these because it combines ease of construction with ease of operation.

[2] Bodenstein, *Z. physik. Chem.*, **B7**, 387 (1930).

[3] Ramsperger, *Rev. Sci. Inst.*, **2**, 738 (1931).

[4] Sutton and Mayer, *J. Chem. Phys.*, **3**, 20 (1935).

CONTRIBUTION FROM THE
LABORATORY OF PHYSICAL CHEMISTRY
UNIVERSITY OF WISCONSIN
MADISON, WISCONSIN
RECEIVED AUGUST 22, 1935

Periodic Classification of the Rare Earths

BY HERMAN YAGODA

Brauner's[1] distribution of the rare earths in the periodic system, Fig. 1, has the disadvantage of placing several of the members into groups where the other elements are chiefly of an amphoteric or acidic nature. Pearce[2] has criticized the classification on the ground that the periodicities observed by Brauner are not connected with the rest of the system. The tendency of these elements to form stable trivalent compounds seems to mask the underlying fact that the properties, of their other valence states, are a periodic function of the atomic number.

Groups	I	II	III	IV	V	VI	VII
8th series	Cs 55	Ba 56	La 57	Ce 58	Pr 59	Nd 60	Il 61
9th series	Sm 62	Eu 63	Gd 64	Tb 65	Dy 66	Ho 67	Er 68
10th series	Tm 69	Yb 70	Lu 71	Hf 72	Ta 73	W 74	Re 75

Fig. 1.

Thus, cerium and terbium are located in the fourth group in agreement with the tetravalence exhibited in their higher oxides CeO_2 and Tb_4O_7. Praseodymium forms two higher oxides, Pr_6O_{11} and PrO_2 in which, according to Prandtl,[3] the metal has a valence of five, in harmony with the position of the element in the fifth group. Again, of all the rare earths only europium[4] and ytterbium[5] form difficultly soluble bivalent sulfates and both elements are allocated to the second group along with the alkaline earths. Evidence for the division of the metals into three series is seen in the variation of the molecular volume of the oxides, Fig. 2, the curve[5a] showing distinct maxima at both samarium and thulium, the initial members of the ninth and tenth series.

If the classification has real significance it should be possible to predict the properties of the rare earth ions in those valency states corresponding with their position in the groups. Thus, Sm$^+$ and Tm$^+$ should form difficultly soluble chloroplatinates; Ce^{++++} and Tb^{++++} phosphates, that are insoluble in mineral acids,[5b] in the same way that Eu^{++} and Yb^{++} are now known to form insoluble sulfates.

Molecular volume of the rare earth oxides (R_2O_3).

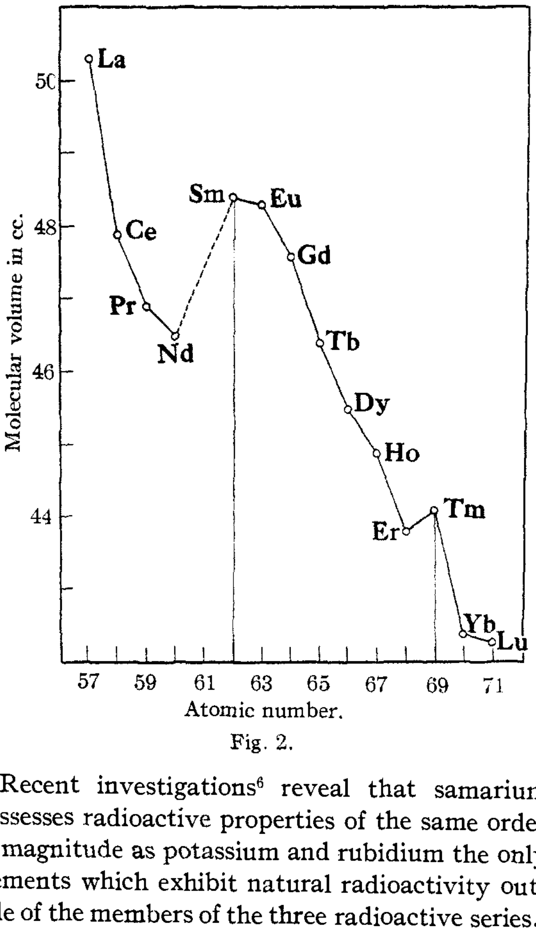

Fig. 2.

Recent investigations[6] reveal that samarium possesses radioactive properties of the same order of magnitude as potassium and rubidium the only elements which exhibit natural radioactivity outside of the members of the three radioactive series.[7] If Brauner's classification of the rare earths is correct, the radioactivity of samarium would seem to indicate that the tendency for nuclear instability in the case of atoms of low atomic weight is centered in the first periodic group. Von Hevesy examined all the members of the rare earths with

[1] B. Brauner and E. Švagr, *Collection Czechoslov. Chem. Comm.*, **4**, 49, 244 (1932).

[2] D. W. Pearce, *Chem. Rev.*, **16**, 135 (1935).

[3] W. Prandtl and K. Huttner, *Z. anorg. Chem.*, **149**, 235 (1925).

[4] L. F. Yntema, THIS JOURNAL, **52**, 2782 (1930); P. W. Selwood, *ibid.*, **57**, 1145 (1935).

[5] R. W. Ball and L. F. Yntema, *ibid.*, **52**, 4264 (1930); J. K. Marsh, *J. Chem. Soc.*, 1972 (1934); W. Prandtl, *Z. anorg. Chem.*, **209**, 13 (1932).

[5a] The molecular volumes were derived from density measurements recorded by von Hevesy in his "Seltenen Erden von Standpunkte des Atombaues," Berlin, 1927, p. 53. The molecular weights were computed from the International Atomic Weights of 1935.

[5b] Cerium can be separated electrolytically from nitric acid solutions as ceric phosphate [J. W. Neckers, THIS JOURNAL, **50**, 955 (1928)].

[6] G. von Hevesy and M. Pahl, *Nature*, **130**, 846 (1932); M. Curie and F. Joliot, *Compt. rend.*, **198**, 360 (1934).

[7] "Radiation from Radioactive Substances," Rutherford, Chadwick and Ellis, Cambridge, 1930, p. 541.

the exception of illinium and thulium and concluded that samarium was the only one of the group whose radioactivity persisted after purification.[8] As thulium is classified in the first group, it also may possess radioactive properties of a magnitude comparable with that of samarium. Hence, a study of the radioactivity of thulium preparations is well worth investigating.

CONTRIBUTION FROM THE
DEPARTMENT OF CHEMISTRY
COLUMBIA UNIVERSITY,
NEW YORK CITY

RECEIVED JULY 16, 1935

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[8] G. von Hevesy and M. Pahl, *Nature*, **131**, 434 (1933); *ibid.*, *Z. physik. Chem.*, **A169**, 147 (1934).

COMMUNICATIONS TO THE EDITOR

ATTEMPTED PREPARATION OF VANILLOYLFORMIC ACID

Sir:

In an attempt to repeat the oxidation of apocyanin to vanilloylformic acid with nitrobenzene in alkaline solution as described by H. O. Mottern [THIS JOURNAL, **56**, 2107 (1934)] no action whatever was observable under the conditions described by the author. Nitrobenzene was recovered quantitatively from the reaction mixture and neither aniline nor azobenzene was detectable by qualitative means.

Difficulty was also experienced in repeating the author's description of the preparation of apocyanin by means of the Fries reaction. The aluminum chloride double compound with guaiacol acetate is quite solid at the temperatures described (0–5°). Before a third of the required amount of aluminum chloride has been added, the mass is so hard as to be impenetrable to a stirring rod, making it impossible to incorporate the balance. The apocyanin used was prepared by the method for low temperature Fries isomerizations described by Baltzly and Bass [*ibid.*, **55**, 4293 (1933)] which differs from the authors in the use of nitrobenzene as a solvent.

FARMINGDALE, L. I. W. E. BARCH

RECEIVED MARCH 12, 1935

NOTE BY THE EDITOR

After the receipt of this Communication a repetition of the oxidation of apocyanin to vanilloylformic acid with nitrobenzene in alkaline solution as described by H. O. Mottern was attempted by a member of the Editorial Board and independently by the Director of Research of a firm manufacturing vanillin on a large scale. Both were unsuccessful; their concordant conclusion is expressed by the latter's statement: "The synthesis of vanillin cannot be carried out following the disclosures of the paper published in THIS JOURNAL, 1934, page 2107."

OCTOBER 10, 1935 ARTHUR B. LAMB, *Editor*

THERMAL DECOMPOSITION OF $CrO_4 \cdot 3NH_3$

Sir:

Some unusual observations recently made in this Laboratory, and which we hope to study in greater detail, should prove of considerable general interest. While attempting the preparation of the tetroxide of chromium, CrO_4, by deammonating $CrO_4 \cdot 3NH_3$ (I) [made according to Riesenfeld, *Ber.*, **38**, 4070 (1905)], the following was noted. (1) Compound (I) loses practically no ammonia upon standing for four months over concentrated sulfuric acid *in vacuo* and at room temperature. (2) If the pressure in a tube containing some (I) is reduced to less than 1 mm. and the tube, still attached to the vacuum line, is immersed in a bath whose temperature may be controlled, a vigorous reaction ensues at 120 ± 10°. Particles of (I) become incandescent and dart about in spectacular fashion. The action is reminiscent of the thermal decomposition of ammonium dichromate and also of certain models that have been constructed to portray molecular motion in gases. (3) The solid residue of the above mentioned decomposition of (I) is composed of microscopic, elongated square prisms of black $CrO_3 \cdot NH_3$ (II). Analysis of (II) for ammonia was made by distilling into standard acid and for chromium by forming lead chromate. The re-