

proportionation caused the phosphorus analysis to be 0.5–0.6% too low.

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The Behavior of Diphenylmagnesium Bromide with Benzoquinone

BY DAVID E. WORRALL AND SUMNER COHEN

Bamberger and Blangey¹ got tars only by the action of methylmagnesium iodide on benzoquinone, although small amounts of several crystalline products were obtained from xyloquinone. Using duroquinone, Smith and Crawford² found that a non-tractable oil was the principal product with phenylmagnesium bromide. It occurred to us that the substitution of a heavier radical (diphenyl) not only would raise the melting point but might act as a brake on the reactivity, thereby facilitating the isolation of the primary addition product or products. Actually it increased the Wurtz-like effect inherent in the Grignard reagent and the principal products, aside from unchanged reactants, are diphenyl and hydroquinone.

Experimental

The reagent was prepared from 0.1 g. mole of *p*-bromo-

(1) Bamberger and Blangey, *Ann.*, **384**, 272 (1911).

(2) Smith and Crawford, *This Journal*, **50**, 869 (1928).

diphenyl, using activated magnesium with a small volume of ether. An average of about 2 g. of diphenyl separated out, an amount that varied somewhat in different preparations. Benzoquinone (0.4 m. equiv.) dissolved in ether was added to the mixture. A dark blue precipitate formed, doubtless a molecular compound, that reacted with excess of reagent on shaking, losing its color and depositing a yellow oil that partially solidified. A permanent blue color was reached before all of the material was introduced. After decomposition with dilute acid the portion insoluble in ether and in water yielded 6.8 g. or 44% of crude diphenyl, which was recrystallized from nitrobenzene and identified by analysis. Hydroquinone was identified in the aqueous portion although most of the original quinone turned up as a tar after steam distillation of the ether layer. A mixture of 6–7 g. of diphenyl with bromodiphenyl was recovered by steam distillation. Slightly more than a gram of non-volatile material soluble in hot water and in alkali was isolated and identified as *p*-hydroxydiphenyl. About the same amount of hydrocarbon was obtained by treating the Grignard reagent with azobenzene. If the reactants in the original experiment were mixed rapidly or in the reverse order, little decolorization of the blue precipitate was observed and even after standing overnight no increase was noted in the quantity of hydrocarbon normally present in the reagent. No attempt was made to isolate addition products from the oil. Similar experiments with phenyl and *n*-butylmagnesium bromides failed to reveal any hydrocarbon formation from the action of benzoquinone. Small amounts of phenol and butyl alcohol from the action of atmospheric oxygen were formed.

PEARSON MEMORIAL LABORATORY

TUFTS COLLEGE

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MEDFORD, MASSACHUSETTS

COMMUNICATIONS TO THE EDITOR

l-EPHEDRINE, A DEGRADATION PRODUCT OF ALKALOIDS IN *ACONITUM NAPELLUS*

Sir:

We have been engaged in a study of degradation reactions of aconitine and its accompanying alkaloids in *aconitum napellus*. The latter, according to H. Schulze and G. Berger [*Arch. d. Pharm.*, **262**, 553 (1924)], is a mixture of the following bases: aconitine, benzoyleaconine, homoisacotinine, aconine and neopollin. This material was available in the form of aconitin hydrochloricum, amorph. (Merck).

The destructive distillation of aconitine hydrochloride, amorph., over four to five its amount of crystalline barium hydroxide yields besides a large fraction of hydrocarbons and methylamine, a

strongly basic oil which ultimately can be separated by steam distillation.

For purification it is distilled in a vacuum of 0.5 mm. and the fraction obtained at the bath temperature of 50–70° is collected. The analysis showed the presence of one methylimide group, no methoxy, a content of carbon, hydrogen and nitrogen corresponding to the formula C₁₁H₁₇ON. The mixture boils at 260–262° (uncorr.) it is slightly levorotatory and has a refractive index of *n*²⁰ 1.528. The total yield is 2%. *Anal.* Calcd. for C₁₁H₁₇ON: C, 73.74; H, 9.50; N, 7.82; (N)-CH₃, 8.37. Found: C, 74.52; H, 8.98; N, 7.70; (N)-CH₃, 7.82.

From this, besides other salts, a hydrochloride was obtained in crystalline form which, after

two recrystallizations from absolute ethyl alcohol and alcohol-ether, melted at 220–22° (uncorr.). It had a specific rotation in alcohol of $[\alpha]_{20}^D -36.25^\circ$ ($\alpha = -0.98^\circ$, $c = 3.4$). The analysis revealed the formula $C_{10}H_{15}ON \cdot HCl$. A mixed melting point with ephedrine hydrochloride (Merck) gave no depression. *Anal.* Calcd. for $C_{10}H_{15}ON \cdot HCl$: C, 59.56; H, 7.94; N, 6.96; Cl, 17.59. Found: C, 59.81; H, 7.58; N, 7.52; Cl, 17.39.

The possibility that *l*-ephedrine as such is an alkaloid of aconitum napellus appears impossible as the free base, being water soluble, would remain in the mother liquors on precipitation of the whole alkaloids. In addition we were unable to detect ephedrine in aconitine, amorph., omitting the barium hydroxide distillation.

It appears probable that ephedra bases or indole derivatives are part of the molecular arrangement in aconite alkaloids. Each base, however, has to be degraded individually before final conclusions can be drawn.

We express our appreciation to E. Merck, Darmstadt, Germany, for a supply of the amorphous bases, to Merck and Co., Inc., Rahway, for crystalline aconitine.

DEPARTMENT OF CHEMISTRY WERNER FREUDENBERG
FORDHAM UNIVERSITY E. F. ROGERS
NEW YORK

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THE THERMAL DECOMPOSITION OF ETHYLENE OXIDE AND AN INDUCED ACETALDEHYDE DECOMPOSITION

Sir:

The thermal decomposition of ethylene oxide [Heckert and Mack, *THIS JOURNAL*, **51**, 2706 (1929)] presents certain features which hitherto have not been satisfactorily explained. It appears that the reaction from 380 to 450° proceeds in two consecutive stages with the intermediate formation of an aldehyde; but that the aldehyde decomposes at a temperature over 100° lower than that for pure aldehydes [Fletcher and Hinselwood, *Proc. Roy. Soc. (London)*, **A141**, 41 (1933); Fletcher, *ibid.*, **A146**, 357 (1934); Thomson and Frewing, *J. Chem. Soc.*, 1443 (1935)]. It was originally suggested that an isomerization of ethylene oxide to acetaldehyde occurs, and that the aldehyde undergoes a unimolecular decomposition in virtue of the energy it possesses when it is formed, *viz.*, the energy of activation (52,000

cal.) and heat of isomerization (23,300 cal.). But it has been pointed out [Kassel, "The Kinetics of Homogeneous Gas Reactions," p. 285] that this hypothesis is untenable as the aldehyde would decompose immeasurably fast, and, furthermore, similar decompositions which result in the intermediate formation of an aldehyde, *e. g.*, methyl alcohol [Fletcher, *Proc. Roy. Soc. (London)*, **A147**, 119 (1934)], do not show this behavior.

Now when ethylene oxide is passed through a hot tube it is known [F. O. Rice and K. K. Rice, "The Aliphatic Free Radicals," 1935, p. 160] that free radicals are produced in greater quantities and at temperatures considerably lower than they are from the simple aldehydes, ketones and ethers. It is suggested therefore that at 400° one or more reactions, which constitute the first and slow stage of the decomposition, take place with the production of free radicals and aldehydes; and that in the second stage such aldehydes are catalytically decomposed by the free radicals present. We have carried out tests and analyses which indicate that the aldehyde is mainly acetaldehyde, but that smaller quantities of acrolein and formaldehyde are present. The different aldehydes may be formed by alternative reactions of the ethylene oxide or by secondary processes.

As might be expected on the above hypothesis, small quantities of ethylene oxide can induce a decomposition of acetaldehyde below 500°, analogously to azomethane, which is also known to yield free radicals [Allen and Sickman, *THIS JOURNAL*, **56**, 2031 (1934)]. Thus we find that at 443° acetaldehyde at a pressure of 184 mm. is half decomposed in the presence of its isomer, ethylene oxide, at 17 mm. pressure, in three minutes; in its absence in approximately 350 minutes. This induced acetaldehyde decomposition is proportional to the square root of the ethylene oxide pressure, and to rather less than the first power of the aldehyde pressure; it is retarded by foreign inert gases, *e. g.*, helium (as is the second stage of the ethylene oxide decomposition), but the final pressure increase is not changed.

The presence of free radicals from ethylene oxide also accounts for the induced decompositions of methyl bromide, *n*-butane and isopentane found by Heckert and Mack, as, for instance, *n*-butane is known to be sensitive to methyl radicals [Frey, *Ind. Eng. Chem.*, **26**, 200 (1934)].