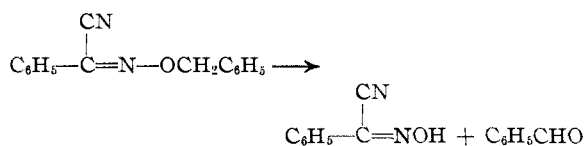


esters, compounds possessing structures related to III, are unstable substances which decompose to give oximes. This behavior is illustrated by the following example.



Furthermore, *aci*-diphenylnitromethane, which along with benzophenone oxime is a probable cleavage product of III, is also unstable, producing benzophenone and benzophenone oxime.⁶ The formation of benzophenone, benzophenone oxime and a small amount of the compound, $(\text{C}_6\text{H}_5)_2\text{C}=\text{N}-\text{O}-\text{N}=\text{C}(\text{C}_6\text{H}_5)_2$, upon treatment of the colorless oxidation product with hot solvents, therefore, becomes intelligible on the basis of this structure. A corresponding lack of stability has been observed⁷ in the case of the so-called benzaldoxime peroxide and phenylnitromethane was reported⁸ as one of the decomposition products.

In the presence of acids, the colorless oxidation product (III) is readily transformed to benzophenone, benzophenone oxime, and nitrogen, and under certain conditions a small amount of benzanilide is also obtained. A semi-quantitative study using glacial acetic acid showed that approximately equimolar amounts of benzophenone and benzophenone oxime were produced and that one-half of the nitrogen present was converted to gaseous nitrogen.

Phenylmagnesium bromide, dissolved in *n*-butyl ether, reacted at 100° with III to yield triphenylcarbinol, benzophenone oxime, phenol, $(\text{C}_6\text{H}_5)_2\text{C}=\text{N}-\text{O}-\text{N}=\text{C}(\text{C}_6\text{H}_5)_2$, and nitrogen after acidification of the Grignard reaction mixture. This behavior is manifestly complicated, but perhaps comparable to that shown⁹ by triphenyl isoxazoline oxide. Even though these products can be accounted for on the basis of the structure assigned to the colorless oxidation product, it should be noted that since benzophenone is a product of the thermal decomposition of III, the production of triphenylcarbinol may not be significant. The temperature at which the Grignard reagent was added was much lower than that at which extensive pyrolysis takes place, however.

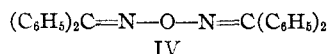
(6) Konowalow, *Ber.*, **29**, 2196 (1896).

(7) E. g., Beckmann, *ibid.*, **22**, 1588 (1889); Robin, *Ann. chim.*, **16**, 77 (1921).

(8) Clusa and Parisi, *Gazz. chim. ital.*, **55**, 416 (1925).

(9) Kohler and Richtmyer, *THIS JOURNAL*, **52**, 2038 (1930).

The compound, $\text{C}_{26}\text{H}_{20}\text{ON}_2$, obtained from III in small amount almost quantitatively yields benzophenone oxime upon treatment with acetic acid (which contains a small quantity of acetic anhydride) and subsequent hydrolysis. Therefore, it is assigned the structure



The production of the oxidation products can be accounted for on the assumption that the first step in the oxidation of benzophenone oxime involves the abstraction of a hydrogen atom to produce a radical with an odd electron. The blue color of the oil which is produced by low temperature oxidation may be attributed to a structure of this kind. It is well known that *N,N'*-diphenylhydroxylamine on oxidation gives red diphenylnitrogen oxide.¹⁰ The combination of two radicals, $(\text{C}_6\text{H}_5)_2\text{CNO}$, might account for the formation of III; the combination of two radicals, one of which has lost an oxygen would produce I, and the decomposition of one radical might conceivably yield benzophenone and nitrogen. Angeli¹¹ who reported on the decomposition of the silver salts of ketoximes, obtained metallic silver together with the ketone and nitrogen. Large amounts of benzophenone and nitrogen are always produced when benzophenone oxime is oxidized.

Experimental

Oxidation with Potassium Ferricyanide in Alkaline Solution

(a) **At 35°.**—A solution of 20 g. of benzophenone oxime in 100 ml. of ethyl alcohol to which 100 ml. of a 5% solution of potassium hydroxide had been added was diluted to 300 ml. and added slowly with vigorous stirring to 2200 ml. of a solution containing 50 g. of potassium ferricyanide and 100 g. of potassium hydroxide, both solutions being initially at 35°. Stirring was continued for four hours thereafter. The next morning the immediate yellow precipitate was filtered off (the filtrate evolved nitrous fumes on acidification) and boiled with alcohol, an insoluble colorless residue (1.0 g., m. p. 193° dec.) remaining. The alcohol extract was evaporated under reduced pressure and the residue was boiled with petroleum ether. After cooling to 0° and filtering, the yellow solid was crystallized from alcohol; yield 6.5 g.; m. p. 156–159°. The petroleum ether extract yielded more of this yellow solid after concentration. The filtrate therefrom, seeded with benzophenone, gave an immediate crop (7.0 g.) of benzophenone crystals.

(b) **At -3 to -8°.**—The above procedure was followed at lower temperatures. Upon mixing, a white precipitate of the oxime separated out, which soon became yellow, and finally a deep blue oil floated on the surface of the reaction mixture. After standing overnight, the blue

(10) Wieland and Offenbacher, *Ber.*, **47**, 2111 (1914).

(11) Angeli, *Atti. Accad. Lincei*, [5] **221**, 735 (1913).

semi-solid had become brownish-yellow. This brownish-yellow mass was boiled with at least 500 ml. of ethanol and the colorless residue (3 to 4 g., m. p. 193° dec.) was separated. The alcohol filtrate was concentrated and the resulting oil was extracted with petroleum ether. Benzophenone was isolated from the petroleum ether extract.

The colorless solid (m. p. ca. 193°) was identical with that obtained by oxidation at 35°, but none of the yellow compound (m. p. 156–157°) was isolated from the low-temperature oxidations.

Diphenylketazine Oxide.—This yellow oxidation product (m. p. 156–157°) was subjected to the following treatments.

(a) **Pyrolysis.**—A 2-g. sample was heated in an apparatus connected to a supply of air-free carbon dioxide. Evolution of nitrogen began at 160° and the temperature was slowly increased to 180°. The evolved gas (39.2 cc. at 27° and 737 mm.) was collected over concentrated aqueous potassium hydroxide. An alcohol solution of the residue in the reaction tube yielded diphenylketazine (0.53 g., m. p. 160–161°). After removal of the alcohol, the resulting oil was treated with petroleum ether and a small amount of diphenylketazine was obtained. Benzophenone (0.96 g.) crystallized from the petroleum ether solution after "seeding." A brown solid, which refused to crystallize, remained.

(b) **Acid Treatment.**—A sample (0.5 g.) was treated with hot concentrated hydrochloric acid. Benzophenone (0.41 g.) resulted.

(c) **Catalytic Reduction.**—An alcoholic solution (200 ml.) containing diphenylketazine oxide (1.0 g.) was reduced with hydrogen in the presence of a platinum oxide catalyst. Diphenylketazine was obtained in practically quantitative yield. The product was crystallized from alcohol and then from benzene. After warming to remove the benzene, the diphenylketazine melted at 161.5–162°.

$$\begin{array}{c} \text{O} \\ \uparrow \\ (\text{C}_6\text{H}_5)_2\text{C}=\text{N}-\text{O}-\text{N}=\text{C}(\text{C}_6\text{H}_5)_2 \end{array}$$

A sample (0.7619 g.) of the colorless oxidation product, dissolved in 32.76 g. of benzene, showed a freezing point depression of 0.295°. *Mol. wt.* Calcd. for $\text{C}_{26}\text{H}_{20}\text{O}_2\text{N}_2$: 392. Found: 406.

(a) This compound is somewhat unstable. A sample (1.0 g.) was boiled with chloroform. After removal of the chloroform, alcohol was added. The alcohol solution deposited crystals of $\text{C}_{26}\text{H}_{20}\text{ON}_2$ (0.06 g., m. p. 167°). After the separation of this substance, the alcohol was removed by evaporation and the residue was extracted with petroleum ether. The petroleum ether extract yielded benzophenone (0.68 g.). The petroleum ether insoluble portion was treated with alcohol containing a small amount of aqueous sodium hydroxide. The soluble portion was diluted with water containing sodium bicarbonate. Benzophenone oxime (0.15 g.) separated.

Treatment of the oxidation product III for two weeks with boiling benzene produced benzophenone, benzophenone oxime and $\text{C}_{26}\text{H}_{20}\text{ON}_2$ (IV) in small amounts. Three-fourths of the starting material was recovered unchanged. Dioxane dissolved about 1% by weight of III and upon the addition of alcohol, III again separated. This proved to be an effective method of purification. Samples so purified showed some decomposition after standing for several months.

(b) **Action of Glacial Acetic Acid.**—A sample (0.33 g.) of the oxidation product (III) was placed in an apparatus connected on one side to a source of carbon dioxide and on the other side, through a solution of potassium iodide in dilute acetic acid, to a gas buret. Gas evolution began shortly after the addition of the acid, but no iodine was liberated from the potassium iodide. The gas (13.0 cc. at 30° and 736 mm.), collected over aqueous potassium hydroxide, would not support combustion. (The gas volume was decreased to 12.56 cc. on washing with alkaline pyrogallol. If the volume of air equivalent to the amount of oxygen found is deducted, the volume of gas produced becomes 10.9 cc.)

The acetic acid solution in the reaction vessel, after dilution with water and extraction with petroleum ether yielded benzophenone (0.16 g.). The petroleum ether insoluble portion was treated with alcohol containing a small amount of aqueous sodium hydroxide. The addition of sodium bicarbonate to this solution precipitated benzophenone oxime (0.15 g.).

The action of hydrochloric acid and of acetic anhydride likewise produced in each case benzophenone oxime, benzophenone and a small amount of benzanilide.

(c) **Pyrolysis.**—The white oxidation product III (1.0 g.) placed in a tube which was connected to a source of carbon dioxide and to a gas buret was heated gradually. At 194° gas (40.7 cc. at 22° and 746 mm.) was evolved. The gas showed no volume change after treatment with alkaline pyrogallol nor did it support combustion. Explosion studies after the addition of oxygen and hydrogen failed to reveal any oxidizing substance other than the added oxygen. The gas was nitrogen and the amount collected over potassium hydroxide corresponded to 64.7% of that present in the original sample.

The pyrolysis mixture was treated with hot alcohol. Diphenylketazine (m. p. and mixed m. p. 160–161°; 0.1 g.) separated out of the alcohol solution. The filtrate after concentration yielded $\text{C}_{26}\text{H}_{20}\text{ON}_2$, IV (m. p. 166.5–167°) and finally after "seeding" benzophenone (0.61 g.).

(d) **Grignard Studies.**—Phenylmagnesium bromide in *n*-butyl ether was added to a sample (1.0 g.) of III. The reaction mixture was heated to 100° and 68% (43.3 cc. at 31.8° and 742 mm.) of the total amount of nitrogen present in the sample was evolved. The reaction mixture was acidified with cold, dilute sulfuric acid and extracted with ether. After removal of the solvent, the residue was extracted with alcohol containing aqueous sodium hydroxide and the soluble portion was treated with sodium bicarbonate. Benzophenone oxime (0.03 g.) was obtained. After the removal of the oxime, the filtrate contained a small amount of phenol which was identified as tribromophenol.

The portion of the residue which was insoluble in the mixture of alcohol and aqueous alkali was next treated with hot alcohol. The alcohol extract yielded the compound $\text{C}_{26}\text{H}_{20}\text{ON}_2$ (0.058 g.); on cooling and after dilution with water, triphenylcarbinol (0.115 g., m. p. and mixed m. p. 158–159°) was obtained.

Methylmagnesium iodide yielded diphenylmethylcarbinol (m. p. 80–81°).

(e) **Miscellaneous Studies.**—A sample of III, dissolved in dioxane, was treated with sodium methoxide. After refluxing for several hours, the unchanged starting material

was isolated. Similar results were obtained with sodium ethoxide.

Three grams of the colorless oxidation product, dissolved in benzene (50 ml.) and then chilled in an ice-bath, showed no change when treated with sodium amalgam and ethanol. Upon addition of acetic acid slightly more than two grams of starting material was recovered.

$(C_6H_5)_2C=N-O-N=C(C_6H_5)_2$, IV.—*Anal.* Calcd. for $C_{26}H_{20}ON_2$: C, 82.98; H, 5.32. Found: C, 83.05; H, 5.36.

A sample (1.0 g.) was boiled for one-half hour with acetic acid containing a small amount of acetic anhydride. The solution was then made alkaline and heated for one hour.

The addition of water containing sodium bicarbonate caused the separation of benzophenone oxime (0.09 g.).

Summary

The oxidation of benzophenone oxime is described. The products of oxidation are nitrogen, benzophenone, diphenylketazine oxide and the benzophenone oxime ester of *aci*-diphenylnitromethane. The behavior of some of these oxidation products has been investigated and an attempt has been made to account for their formation.

MINNEAPOLIS, MINNESOTA

RECEIVED APRIL 6, 1942

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

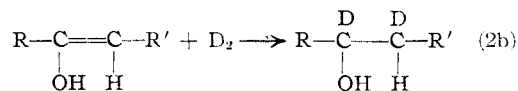
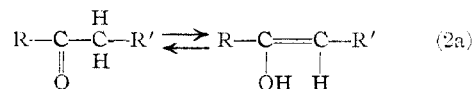
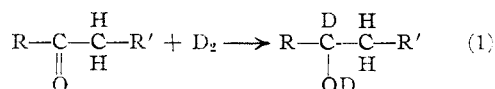
The Mechanism of the Catalytic Reduction of Some Carbonyl Compounds¹

BY LEIGH C. ANDERSON AND N. W. MACNAUGHTON

Deuterium oxide has been used by many investigators for studying reactions of hydrogen. Much of the work has dealt with inorganic compounds and in reactions where the deuterium ion was involved. Among the studies involving deuterium and organic compounds, it might be mentioned that exchange reactions between ethylene and deuterium² were found to accompany hydrogenation. It was found, also, that rapid exchange with deuterium took place with benzene in the presence of catalysts.³ Farkas and Farkas⁴ have stated that in the vapor phase both acetone and isopropyl alcohol are converted to propane with either hydrogen or deuterium over a platinum catalyst. From the relative rates of the reactions of the two organic compounds they concluded that the reduction to the hydrocarbon takes place directly from acetone rather than through the alcohol as an intermediate.

This paper presents a discussion of the mechanism of the reactions which occur when butyraldehyde, acetone, and several other aldehydes and ketones were catalytically reduced to alcohols with a mixture of hydrogen (80 parts) and deuterium (20 parts).⁵ Two mechanisms may be

postulated for the manner in which a carbonyl group is converted to an alcohol group by the use of deuterium: (1) direct addition of deuterium to the carbonyl group (Eq. 1), and (2) enolization of the carbonyl compound followed by addition of deuterium to the resulting ethylenic linkage (Eqs. 2a and 2b).



The difference in the deuterio compounds that would be formed according to these two mechanisms is readily apparent because the product from Eq. 1 contains an OD bond and a CD bond whereas that from Eq. 2b contains two CD bonds. The former compound on oxidation should yield a compound free from deuterium and the latter compound, in the absence of exchange during oxidation, should oxidize to a compound with a deuterium on the alpha carbon atom. The presence of either a CD bond or an OD bond in the compound under investigation is readily ascertained by the appearance of the characteristic bands at about $\Delta\nu$ 2150 and $\Delta\nu$ 2500 in the Raman spec-

of the Horace H. Rackham School of Graduate Studies. Preliminary experiments indicated that a mixture of deuterium and hydrogen would yield results as conclusive as pure deuterium and the mixture was used, therefore, in order to conserve the heavy isotope.

(1) The material presented in this paper constitutes a portion of a dissertation submitted by N. W. MacNaughton to the Horace H. Rackham School of Graduate Studies of the University of Michigan in partial fulfillment of the requirements of the Ph.D. degree, August, 1941.

(2) Horiuchi and Polanyi, *Nature*, **134**, 377-8 (1934); Farkas, Farkas and Rideal, *Proc. Roy. Soc. (London)*, **A146**, 630 (1934).

(3) Horiuchi, Ogden and Polanyi, *Trans. Faraday Soc.*, **30**, 663-5 (1934); Horiuchi and Polanyi, *ibid.*, **30**, 1164-72 (1934).

(4) Farkas and Farkas, *This Journal*, **61**, 1336-41 (1939).

(5) The deuterium oxide used in the preparation of deuterium for this investigation was purchased by a grant from the Research Funds