[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

THE CATALYTIC REDUCTION OF NITRO COMPOUNDS. I. α,β-UNSATURATED NITRO COMPOUNDS

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The immediate occasion of the following investigation was our desire to prepare primary nitro compounds containing large alkyl groups. Since unsaturated nitro compounds like nitrostyrene (I) and its substitution products (II)

$$\underset{\text{I}}{C_6H_5CH:CHNO_2} \qquad \underset{\text{II}}{XC_6H_4CH:CHNO_2}$$

contain conjugated systems of double linkages it seemed not unlikely that it might be possible to convert them into saturated nitro compounds by carefully regulated catalytic reduction. We undertook, therefore, the reduction of nitrostyrene in the presence of various catalysts.

At the time this work was begun we could find no mention of any attempt to reduce an unsaturated nitro compound catalytically. Shortly afterwards, however, we received an excellent paper, published by Sonn and Schellenberg[1] during the war, describing the reduction of nitrostyrene and piperonal-nitromethane with hydrogen and platinum. They obtained a small quantity of oils from which they isolated aldoximes; but the principal product in each case was a sparingly soluble solid which, as they proved, is a dimolecular reduction product.

We reduced nitrostyrene in various solvents and in the presence of palladium black, platinum black of different degrees of activity, colloidal platinum, and the nickel catalyst devised by Kelber.[2] With all of these we obtained, in fairly constant amounts, the products described by Sonn and Schellenberg.

These results confirmed our opinion that α,β-unsaturated nitro compounds would behave towards reducing agents exactly like α,β-unsaturated aldehydes and ketones; but the formation of the dimolecular reduction product was a surprise. Such dimolecular reduction products are generally obtained when α,β-unsaturated ketones are reduced with metals and either acids or bases, and they usually constitute most of the product when the reduction is carried out with aluminum amalgam; but they are very seldom formed in catalytic reductions—so seldom that, although nearly every known unsaturated ketone has been reduced catalytically, only two such cases of dimolecular reduction have been reported.[3] It was of great interest, therefore, to determine how commonly α,β-unsaturated nitro compounds undergo this mode of reduction.

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[1] Sonn and Schellenberg, *Ber.*, **50**, 1513 (1917).

[2] Kelber, *ibid.*, **50**, 305 (1917).

[3] All cases of this kind will be discussed in a later paper.

With this end in view we have studied the reduction of a series of nitro compounds closely related to nitrostyrene (I): nitrostilbene (II), β,β-diphenyl-nitro-ethylene (III), and β,β-diphenyl-dinitro-ethylene (IV). In addition, Wieland,[4] meanwhile has reduced dinitro-stilbene in the same way. We have now, consequently, available for comparison the results obtained by reducing the following series of closely related compounds.

$C_6H_5CH:CHNO_2$, I $C_6H\ CH:C(C_6H_5)NO_2$, II $(C_6H_5)_2C:CHNO_2$ III

$C_6H_5C(NO_2):C(NO_2)C_6H_5$, IV $(C_6H_5)_2C:CH(NO_2)_2$ V

These substances give very different types of compounds when reduced catalytically. The first is reduced with great rapidity and gives principally the dimolecular product for which Sonn and Schellenberg established Formula VI. It also gives some phenyl-acetaldoxime (VII) and small quantities of indeterminate oils.

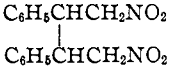
The second is reduced with equal ease but does not give a trace of any dimolecular product: it goes almost quantitatively into the oxime of desoxybenzoin (VIII).

β,β-Diphenyl-ethylene (III), likewise, goes rapidly and quantitatively into a monomolecular product: diphenyl-acetaldimine (IX)—the first representative of this type of imine.

Wieland found that the fourth gives tetraphenyl-piperazine (X), ammonia and a little desoxybenzoin oxime (VIII).

The last (V) poisoned the catalyst so seriously that it was never possible to complete a reduction. The products isolated in partial reductions were tetraphenyl-succinonitrile (XI) and a small quantity of diphenyl-acetonitrile (XII).

The formulas of these products are as follows.



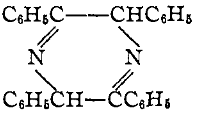
$$\begin{array}{l} C_6H_5CHCH_2NO_2 \\ \quad | \\ C_6H_5CHCH_2NO_2 \end{array}$$

VI

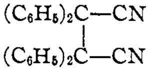
$C_6H_5CH_2CH:NOH$ VII

$C_6H_5CH_2C(C_6H_5):NOH$ VIII

$(C_6H_5)_2CHCH:NH$ IX



X



$$\begin{array}{l} (C_6H_5)_2C{-}CN \\ \qquad | \\ (C_6H_5)_2C{-}CN \end{array}$$

XI

$(C_6H_5)_2CHCN$ XII

From these results we conclude that the behavior of α,β-unsaturated nitro compounds towards reducing agents is exactly like that of α,β-unsaturated ketones. The primary reduction product is always a saturated nitro compound; in exceptional cases this is a dimolecular reduction product but as a rule it is the monomolecular reduction product formed by adding 2 atoms of hydrogen either to the ethylene linkage or, as seems much more probable, to the conjugated system. The nitro group is,

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[4] Wieland, *Ann.*, **424**, 77 (1922).

however, reduced much more easily than the carbonyl group; hence primary products can be caught much more seldom in the reduction of unsaturated nitro compounds than in that of unsaturated ketones.

The nitro group, moreover, is reducible in steps and the products intermediate between the nitro compounds and the amines vary as much in stability and solubility as in relative ease of reduction. The final result, therefore, depends in part on the structure of the nitro compound, which determines the stability and mode of rearrangement of the intermediate products, and in part on external factors—solubility, the nature of the solvent, and the activity of the catalyst—which affect the extent of the reduction.

In the reduction of nitrostyrene, for example, the complex nitro compound (VI) is so sparingly soluble and crystallizes so readily that it separates from the solution almost as rapidly as it is formed, and hence largely escapes further reduction. The monomolecular reduction product, phenyl-nitro-ethane (XIII), is doubtless, like phenyl-nitromethane, readily soluble, and consequently undergoes further reduction.

The result of reducing phenyl-nitro-ethane can be predicted from the behavior of aromatic nitro compounds. These were reduced catalytically by Cusmano[5] who showed that the successive stages are $R{-}NO_2 \longrightarrow R{-}NO \longrightarrow R{-}NHOH \longrightarrow RNH_2$. The reduction of aliphatic nitro compounds, doubtless, starts in the same way, but the later stages are quite different because, as is well known, only tertiary nitroso compounds are stable; all others undergo rearrangement to the corresponding oximes. Oximes are not as reactive as nitro compounds, but under proper conditions they can be reduced to imino compounds,[6] and these in turn to amines. The successive stages in the reduction of a primary aliphatic nitro compound, like phenyl-nitro-ethane, are, therefore,

$$\underset{\text{XIII}}{C_6H_5CH_2CH_2NO_2} \longrightarrow \underset{\text{XIV}}{C_6H_5CH_2CH_2NO} \longrightarrow C_6H_5CH_2CH{:}NOH \longrightarrow$$
$$C_6H_5CH_2CH{:}NH \longrightarrow C_6H_5CH_2CH_2NH_2$$

In accordance with this we found that when nitrostyrene is reduced in the presence of a small quantity of platinum the principal monomolecular reduction product is phenyl-acetaldoxime. When larger amounts of platinum were used, the reduction went further; but the separation of the oily products did not prove feasible.

The reduction of nitrostilbene differs from that of nitrostyrene only in that no dimolecular products are formed. With diphenyl-dinitro-ethylene, however, it was not difficult to carry the reduction a step further, and as the product is a solid we succeeded in isolating the exceedingly sensitive aldimine. $(C_6H_5)_2C{:}\ CHNO_2 \longrightarrow (C_6H_5)_2CHCH_2NO_2 \longrightarrow (C_6H_5)_2CHCH{:}\ NOH \longrightarrow (C_6H_5)_2CHCH{:}\ NH$.

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[5] Cusmano, *Atti accad. Lincei,* [5] **26,** II, 87 (1917).

[6] Mignonac, *Compt. rend.,* **170,** 936 (1920).

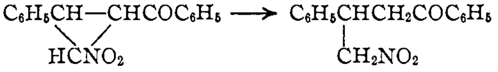
The mechanism by which tetraphenyl-piperazine is formed from dinitrostilbene is not clear; but as Wieland found that this is also the principal product obtained by reducing diphenyl-dinitro-ethane, it seems safe to assume that the first step consists in the reduction of the unsaturated to the saturated nitro compound. In the reduction of β,β-diphenyl-dinitro-ethylene all catalysts were poisoned so rapidly that the volume of the hydrogen absorbed had no significance. Nothing could be done, therefore, towards clearing up the mechanism of the reaction, but it seems impossible to account for the formation of tetraphenyl-succinonitrile without assuming that a dimolecular reduction product is formed in the first step.

Products corresponding to those we have described have also been obtained in nearly all cases in which unsaturated nitro compounds have been reduced with metals and acids. The one exception that we have found, is the substance which Bouveault and Wahl[7] obtained when they reduced α-nitro-β-methyl-crotonic ester (XV) with zinc and acetic acid.

$$\underset{\text{XV}}{(CH_3)_2C{:}C(CO_2C_2H_5)NO_2}, \quad \underset{\text{XVI}}{(CH_3)_2C{:}C(CO_2C_2H_5)NH_2}, \quad \underset{\text{XVII}}{(CH_3)_2CHC(CO_2C_2H_5){:}NH}$$

They regarded this as the corresponding unsaturated amino ester (XVI) but the ease with which it is hydrolyzed to a glyoxylic ester indicates that it is an imino compound and it is now known that the other reactions used to establish the structure fail to distinguish between an amino and an imino compound. In our opinion, therefore, this substance is the saturated imino ester (XVII), which is formed from the nitro ester in the same way that diphenyl-aldimine is formed from diphenyl-nitro-ethylene.

In view of the close resemblance between many derivatives of ethylene and cyclopropane it was of interest to subject a nitro-cyclopropane to catalytic reduction. We found that the simplest known nitro-cyclopropane derivative (XVIII), when reduced with hydrogen in the presence of platinum black, gave as one of the products the corresponding open-chained, saturated nitro compound, (XIX).



XVIII XIX

The behavior of the cyclopropane derivative is, therefore, exactly like that of the ethylenic compounds and, because the solubility relations are favorable, the primary reduction product can be isolated.

Experimental Part

General Procedure

The procedure used in the following experiments was that which is now commonly employed in catalytic reductions that are carried out at the ordinary temperature. All reductions were made under a pressure

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[7] Bouveault and Wahl, *Bull. soc. chim.*, [3] **25,** 914 (1901).

of approximately 1 atmosphere with commercial electrolytic hydrogen which was used without purification. The volume of hydrogen absorbed was measured; this measurement was useful only for determining when absorption had ceased, because the cyclopropane derivative was the only case in which it was possible to isolate intermediate reduction products by stopping the process when definite volumes of hydrogen had been absorbed. The catalyst most frequently employed was platinum black, generally in form prepared according to Loew.[8] When this did not serve, we used the more active form prepared in accordance with the directions of Willstätter.[9]

Some of the nitro compounds, even when prepared with the greatest care, contained a small amount of some material which rapidly poisoned the small quantity of catalyst we used and stopped the process after a few hundred cc. of hydrogen had been absorbed. Attempts to revive the catalyst by the method proposed by Willstätter generally failed, but addition of another small quantity of catalyst usually started a brisk absorption which continued until reduction was complete.

Nitrostyrene

Our experiments with nitrostyrene do not add very much to the results already published by Sonn and Schellenberg. Reduction in pure alcohol or ether in the presence of Loew's platinum black gave mainly the mixture of dimolecular products they have described. We found, however, that the formation of these complex products can be prevented by reducing in the presence of mineral acid.

Thus, in one exepriment a mixture composed of 20 g. of nitrostyrene, 0.75 g. of platinum black, and 200 cc. of dry methyl alcohol into which some dry hydrogen chloride had been passed, was shaken with hydrogen in the usual way. The reduction proceeded normally; but even though the acidity had completely disappeared when the absorption of hydrogen stopped, the mixture gave only 0.8 g. of dimolecular reduction product.

The filtrate from the dimolecular reduction product yielded 2 isomeric phenylacetaldoximes. One of these crystallized in stout needles and melted at 97°. This is the *syn* oxime which was first prepared from phenyl-acetaldehyde by Dollfus.[10] The other crystallized in large plates and melted at 100°. This is the substance first obtained by Bouveault and Wahl[11] by reducing nitrostyrene with zinc and acetic acid, and then also made directly from phenyl-acetaldehyde. The two are not identical, for while their melting points lie very close together the melting point of the mixture is much lower.

The oil, left after removing the oximes, gave the nitrolic acid test for primary nitro compounds, but all attempts to isolate phenyl-nitro-ethane by distillation under very low pressures or to prove its presence by forming a solid addition product with benzalacetophenone[12] were unsuccessful.

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[8] Loew, *Ber.*, **23**, 289 (1890).

[9] Willstätter, *ibid.*, **54**, 122 (1921).

[10] Dollfus, *ibid.*, **25**, 1917 (1892).

[11] Bouveault and Wahl, *Bull. soc. chim.*, [3] **29**, 519 (1903).

[12] THIS JOURNAL, **38**, 889 (1916).

Reduction in the Presence of a Nickel Catalyst.—When nitrostyrene is reduced in the presence of platinum, the rate of absorption of hydrogen is represented by a smooth curve, showing that the rate of reduction of the nitro goups cannot be very different from that of the conjugated system. We also tried the less active nickel catalyst proposed by Kelber; but the results were practically the same as those obtained with platinum.

A solution of 5 g. of nitrostyrene in 125 cc. of alcohol was poured into a suspension of 4.5 g. of the catalyst in 125 cc. of water. This mixture, when shaken with hydrogen, absorbed approximately 1 molecular equivalent in the course of 8 hours. The gray solid suspended in the liquid was then filtered off, dried and extracted with chloroform in a Soxhlet apparatus. The chloroform yielded 3.2 g. of solid composed mainly of the dimolecular reduction product that melts at 235–240°. The filtrate on slow evaporation first deposited 0.6 g. of the *syn* aldoxime of phenyl-acetaldehyde and finally a small quantity of a yellow oil that gave a feeble reaction for primary nitro compounds.

Nitrostilbene

A solution of 4.6 g. of carefully purified nitrostilbene[13] in 100 cc. of ether was shaken with hydrogen and 0.1 g. of Loew's platinum black. The hydrogen was absorbed briskly, but the rate soon fell off. Another 0.1 g. of platinum black was therefore added and the reduction continued until the solution became colorless. No dimolecular reduction product separated during the process and none was found in the clear solution left after filtering off the platinum. This solution was dried with calcium chloride, concentrated, and mixed with petroleum ether. It deposited a solid which melted at 94–96° and which was identified as the oxime of desoxybenzoin by comparison with a specimen made from the ketone. The combined filtrates, on complete evaporation, left only a trace of oil; the reduction, therefore, gave neither saturated nitro compounds nor dimolecular reduction products.

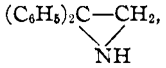
β,β-Diphenyl-nitro-ethylene

When β,β-diphenyl-nitro-ethylene was reduced in alcohol or ether in the presence of Loew's platinum black it gave an oil which contained no saturated nitro compound and evidently was not diphenyl-acetaldoxime. Assuming that the reduction in this case went beyond the oxime, we turned, therefore, to the more active platinum black of Willstätter, operated in dry ether and used dry hydrogen. Under these conditions we obtained a well-crystallized solid whose composition and molecular weight are represented by $C_{14}H_{13}N$.

Unsymmetrical diphenyl-ethylene derivatives frequently rearrange to isomeric derivatives of stilbene, but in the substance $C_{14}H_{13}N$ the phenyl groups must still be in their original position, because chromic acid oxidizes it to benzophenone. There are, therefore, only 3 possible formulas for the substance.

$(C_6H_5)_2C:CHNH_2$,

XX



$(C_6H_5)_2\underset{\diagdown\ \diagup \atop NH}{C-CH_2}$,

XXI

$(C_6H_5)_2CHCH:NH$

XXII

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[13] Knoevenagel and Walter, *Ber.*, **37**, 4508 (1904).

Only one of the types of compounds represented by these formulas is known. When Gabriel[14] first made "vinylamine" he regarded it as an unsaturated amine of Type XX, but Marckwald and Howard[15] showed later that it is a cyclic imine of Type XXI. Busch,[16] by passing hydrogen chloride into solutions of biazolone sulfim and hydrobenzamide obtained a salt which he regarded, quite correctly doubtless, as the hydrochloride of benzaldimine, $C_6H_5CH:NH$, a representative of Type XXII. All his attempts to isolate the free base were unsuccessful; but his results indicate that the properties of aldimines are quite different from those of cyclic imines. In the air benzaldimine hydrochloride soon smelled of benzaldehyde; in solution it gave the characteristic aldehyde reactions; when warmed it readily lost ammonia and passed into hydrobenzamide.

The properties of our reduction product are likewise quite different from those of cyclic imines. They are like those of the more sensitive of the ketimines that were studied by Moureu and Mignonac.[17] When exposed to the air it soon turns into a resin. With hydroxylamine it forms the oxime and with semicarbazide the semicarbazone of diphenyl-acetaldehyde. It very readily loses ammonia and forms a product analogous to the ketisoketimines of Moureu and Mignonac. It is, therefore, diphenyl-acetaldimine (XXII). It is, doubtless both more reactive and more unstable than the simpler ketimines, but we succeeded in isolating it because it happens to be a solid.

Preparation.—The diphenyl-ethylene used in the preparation of the nitro compound was made by dehydrating diphenylmethyl carbinol. This is easily accomplished by dissolving the pure carbinol in about twice its weight of glacial acetic acid, adding 0.5 cc. of conc. sulfuric acid per 100 cc. of solvent, and then distilling in a good vacuum, first the acetic acid and finally the hydrocarbon which, under a pressure of 2–3 mm., boils at 113°.

The nitration of diphenyl-ethylene has recently been studied by Anschütz[18] and by Wieland;[19] hence it need not be discussed here. Our preliminary investigations indicated, however, that by working at a low temperature and stirring vigorously while nitric acid that has been freshly distilled from conc. sulfuric acid is added drop by drop, better yields can be obtained than by the procedure of Anschütz. In order to convert the nitro alcohol, which is obtained as a by-product of this reaction, into the unsaturated compound, it was dissolved in a small quantity of acetic anhydride containing a few drops of sulfuric acid. The solution was diluted with a large quantity of water, neutralized with sodium carbonate and extracted with ether. This, on evaporation, left almost the calculated quantity of the pure unsaturated nitro compound.

The reduction of β,β-diphenyl-nitro-ethylene was carried out in the presence of platinum black made according to Willstätter.[9] Ether dried over sodium was used as

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[14] Gabriel, *Ber.*, **21**, 1049, 2664 (1888). Gabriel and Stelzner, *ibid.*, **28**, 2929 (1895).

[15] Marckwald, *ibid.*, **33**, 764 (1900). Howard and Marckwald, *ibid.*, **32**, 2031 (1899).

[16] Busch, *ibid.*, **29**, 2143 (1896).

[17] Moureu and Mignonac, *Ann. chim.*, [9] **14**, 322 (1920).

[18] Anschütz, *Ber.*, **54**, 1855 (1921).

[19] Wieland and Rahn, *ibid.*, **54**, 1773 (1921).

solvent and the hydrogen was dried by passing it through a tower filled with sticks of potassium hydroxide. As the reduction product is unstable, the operation was conducted on a small scale —2 g. of nitro compound in 50 cc. of ether containing 0.07 g. of platinum black. Reduction proceeded rapidly and regularly, approximately 3 moles of hydrogen being absorbed in a little more than an hour.

Diphenyl-acetaldimine, $(C_6H_5)_2CHCH:NH$.—On completion of a reduction more ether was added, if necessary, to dissolve any of the product which had separated, and the solution freed from catalyst by filtration. Most of the ether was then rapidly evaporated on a steam-bath, whereupon diphenyl-acetaldimine separated in beautiful long, white needles. The yield was 1.5 g. from 2.0 g. of nitro compound.

Analyses. Calc. for $C_{14}H_{13}N$: C, 86.15; H, 6.7. Found: C, 86.1, 86.2; H, 6.9, 6.9.

Mol. wt. (benzene). Subs., 0.3644; solvent, 29.64; Δt, 0.340°. Calc. for $C_{14}H_{13}N$: mol. wt., 195. Found: 185.

Active hydrogen (Zerewitinoff's method). Subs., 0.1379; gas, 17.39 cc. 769 mm.; 23.6° A. Calc. for 1 active hydrogen: 17.01 cc. Found: 17.39 cc.

Oxidation.—A small quantity of the substance was dissolved in glacial acetic acid and oxidized with a slight excess of chromic acid. The solution was neutralized with sodium carbonate and distilled with steam. The distillate contained benzophenone, which was identified by comparing its melting point with that of a mixture made with a known sample of the ketone.

Reaction with Hydroxylamine and Semicarbazide.—A solution of the aldimine in alcohol was boiled with hydroxylamine and alkali according to the procedure used for making oximes. Ammonia was given off, and the solution after neutralization deposited a crystalline solid. By recrystallization from alcohol this was separated into 2 products, 1 of which melted at 117.5–120°, while the other, which was obtained only in a very small quantity, melted at about 85°. The composition and properties of the principal product show that it is the oxime of diphenyl acetaldehyde for which Auwers[20] gives the melting point as 120°, Klages[21] as 106°.

Analyses. Calc. for $C_{14}H_{13}ON$: C, 79.6; H, 6.2. Found: C, 79.5; H, 6.2.

When the aldimine was treated with semicarbazide hydrochloride and potassium acetate in the usual manner it gave a semicarbazone which melted at 158–160°. The melting point of the semicarbazone of diphenyl-acetaldehyde is 160°.

Behavior on Heating.—The aldimine begins to lose ammonia rapidly at about 90°, and passes into a substance that crystallizes from methyl alcohol in beautiful, fine white needles, and melts with decomposition at about 129°. This is probably constituted like hydrobenzamide which is formed when benzaldimine hydrochloride is heated in the same way. $3(C_6H_5)_2CHCH:NH = NH_3 + [(C_6H_5)_2CHCH:N]_2CHCH(C_6H_5)_2$.

Analyses. Calc. for $C_{42}H_{36}N_2$: C, 88.8; H, 6.3. Found: C, 89.1; H, 6.3.

β,β-Diphenyl-dinitro-ethylene

When alcoholic or ethereal solutions of the dinitro compound were shaken in the presence of Loew's or Willstätter's platinum, the absorption of hydrogen started briskly but very soon came to an end. Additional catalyst started the process again, but it now stopped sooner and, after 3 or 4 additions, fresh catalyst brought no response, even though the solution still contained unchanged nitro compound. The catalyst was then removed and the clear solution allowed to evaporate. It contained, besides unchanged substance, two colorless solids that melted at 72° and 215°, and an oil that gave benzophenone when distilled with steam. The solid proved to be diphenyl-acetonitrile and

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[20] Auwers, *Ber.*, **24**, 1780 (1891).

[21] Klages and Kessler, *ibid.*, **39**, 1755 (1906).

tetraphenyl-succinonitrile. Each of these substances was identified by its melting point and the melting point of a mixture with samples of known structure.

Benzoyl-phenyl-nitrocyclopropane

Five and three-tenths g. of the cyclopropane derivative was reduced in 50 cc. of methyl alcohol in the presence of 0.25 g. of platinum black. The reduction was stopped when 740 cc. of hydrogen had been absorbed. The platinum was removed after boiling the suspension to redissolve a white solid which had separated during the reduction. On cooling the clear solution, it deposited 1.9 g. of a colorless solid which crystallized in needles and melted at 98–99°. A mixed melting point showed that this was β-phenyl-γ-nitro-butyrophenone.

Summary

1. This paper gives an account of the results obtained by reducing a series of α,β-unsaturated nitro compounds with hydrogen and platinum.

2. In a discussion of the results it is shown that the behavior of α,β-unsaturated nitro compounds on catalytic reduction is essentially the same as that of α,β-unsaturated ketones. The resulting saturated nitro compounds, however, generally undergo further reduction; the successive steps are $RCH{:}CHNO_2 \longrightarrow RCH_2CH_2NO_2 \longrightarrow [RCH_2CH_2NO] \longrightarrow RCH_2CH{:}NOH \longrightarrow RCH_2CH{:}NH \longrightarrow RCH_2CH_2NH_2$.

3. The primary reduction product of a cyclopropane derivative which has a nitro group in direct union with one of the ring carbon atoms is likewise a saturated nitro compound.

CAMBRIDGE 38, MASSACHUSETTS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

THE HIGHLY UNSATURATED FATTY ACIDS OF FISH OILS

BY J. B. BROWN[1] WITH G. D. BEAL

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Introduction

While engaged in the preparation of pure fatty acids for use in medical research during the late war under the auspices of the National Research Council, the writers had occasion to prepare pure clupanodonic acid, $C_{18}H_{28}O_2$. The information contained in the literature regarding this acid was vague, and a number of preliminary studies were made in order to divise a cheap and convenient method for its preparation. The method finally adopted was a modification of that of Riedel.[2] The methyl esters, which were prepared by debromination with zinc of the polybromides of the methyl esters of menhaden oil, had a molecular weight too high for methyl clupanodonate, and furthermore distilled over too wide a range to be a pure compound. These facts indicated that we were dealing with

[1] Abstracted from a thesis submitted by J. B. Brown in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry in the Graduate School of the University of Illinois.

[2] Riedel, Ger. pat., 266,350.