will facilitate the separation although it may somewhat reduce the yield. Pure white aluminum *t*-butoxide may also be obtained by allowing it to crystallize from a benzene solution even though the latter is colored.

Summary

A method has been described whereby the rate of approach to, and the concentrations at, equilibrium may be determined in reactions of the type $R_2CO + R'_2CHOH \longleftrightarrow R_2CHOH + R'_2CO$. The relative reducing power of various alcohols and the oxidizing power of the corresponding ketones have been estimated in several cases.

The usefulness and the limitations of the polarograph as an instrument in the determination of the reduction potential and of the concentrations of aldehydes and ketones has been illustrated and discussed. The reduction potentials of forty-three representative aldehydes and ketones have been determined through the use of a polarograph. Significant relations of structure and electrolyte to the reduction potential have been pointed out. In particular, the effectiveness of unsaturation in decreasing the polarographic reduction potential has been illustrated.

The preparation and uses of aluminum *t*-butoxide and the choice of a ketone to be used in a new method for the oxidation of alcohols has been considered.

MADISON, WISCONSIN RECEIVED JANUARY 22, 1938

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NOTRE DAME]

Desaturation Products from 1,3,3-Trimethoxybutane[1]

BY R. O. NORRIS, J. J. VERBANC AND G. F. HENNION

Introduction

The numerous desaturation products of 1,3,3-trimethoxybutane are of considerable interest. The latter compound is readily prepared directly from vinylacetylene by catalytic addition of methanol.[2] It has not been found possible to isolate intermediate addition products from this reaction since three molecules of methanol add exclusively. The mono- and dimethoxy compounds are obtainable only[3] by desaturation[4] of the trimethoxy compound.

The purpose of the present investigation was threefold: (1) to obtain each desaturation product in maximum yield; (2) to determine the mechanism of progressive desaturation; and (3) to study the readdition of methanol to the desaturation products.

The results of our studies are summarized in Fig. 1. Compounds IV, V, VI and VII are interconvertible in various ways as shown. Thermal desaturation of IV at 300–320° yields VI. The same result may be accomplished at 140–150° by employing a small amount of boric acid as a catalyst. Desaturation of VI with sodium acid sulfate as a catalyst yields V and VII. Compound V is probably not a primary desaturation product but originates rather by readdition of methanol to VII. The sequence of desaturation is therefore likely IV $\longrightarrow$ VI $\longrightarrow$ VII. Compounds I, II and III react catalytically with methanol to yield IV but the reactions cannot be reversed.

The unsaturated ethers V, VI and VII react vigorously with anhydrous methanol when a trace of acid is added. In fact it was found essential, in the preparation of these compounds, to collect the crude desaturation products over dilute sodium carbonate solution and to remove the methanol formed by thorough washing with water. Otherwise, upon distillation recombination took place as evidenced by the fact that the distillation temperature fluctuated considerably and the distillate was always very warm. The six unsaturated compounds listed manifest a strong orientation influence with respect to addition of methanol. Isomers of IV have not been isolated from any reaction studied. There is probably no other instance on record (except in cases of hydrogenation) where six unsaturated compounds have been saturated to yield the same addition product.

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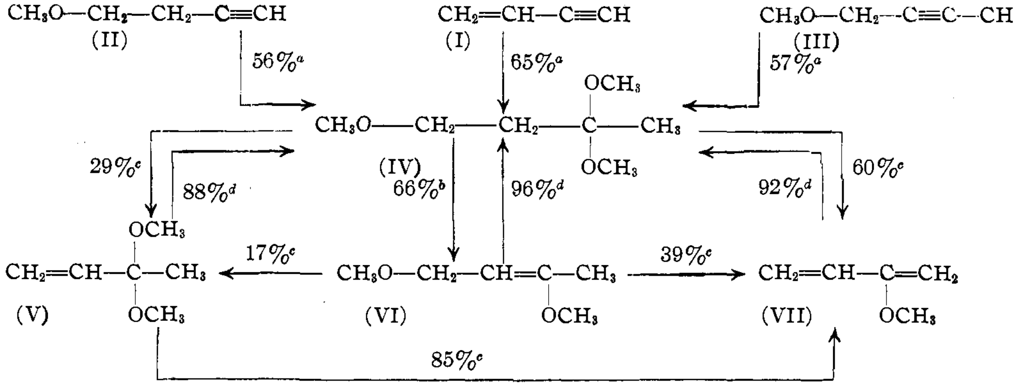
[1] Paper XXV on the chemistry of substituted acetylenes and their addition products; previous paper, THIS JOURNAL, **60**, 718 (1938).

[2] Killian, Hennion and Nieuwland, *ibid.*, **56**, 1786 (1934).

[3] A possible exception is 1-methoxy-2-butyne which may be obtained from vinylacetylene by heating with methanol and sodium methylate in a bomb tube. Jacobson, Dykstra and Carothers, *ibid.*, **56**, 1169 (1934).

[4] Dykstra, *ibid.*, **57**, 2255 (1935).



[a] Methanol addition accomplished with small amounts of HgO and BF_3 as catalysts. [b] Heated to 140–150° with small amount of H_3BO_3. [c] Heated to about 150° with trace of $NaHSO_4$. [d] Addition of methanol occurred rapidly at room temperature, catalyzed by trace of p-CH_3—C_6H_4—SO_3H.

Fig. 1.—Desaturation products from 1,3,3-trimethoxybutane.

The formation of IV from II has not been reported previously. The preparation of IV from III was carried out in this Laboratory some time ago.[5]

The structure of VI has not been established definitely. In agreement with the conclusions of Dykstra,[4] who studied the corresponding diethoxy compound, we believe that the double bond is in the 2-position, as shown, rather than in the 1-position. Oxidation of VI with aqueous permanganate was inconclusive. Small amounts of 1-methoxy-3-butanone along with methyl vinyl ketone and acetic acid were detected.

It should be mentioned also that we occasionally obtained small amounts of a desaturation product from IV not shown in Fig. 1. Its physical characteristics were: b. p. 56° at 745 mm.; $n^{25}D$ 1.4011; d^{25} 0.8120; parachor 226.7 (obsd.). The compound added methanol readily and reverted to IV. From these data the material appears to be 3-methoxy-1,2-butadiene, isomeric with VII. Considerable time was spent in attempts to prepare this compound in quantity, but without success, nor could conditions favorable to its formation be determined.

Experimental

Reagents.—1,3,3-Trimethoxybutane[2] and 1-methoxy-3-butyne[6] were prepared by the methods previously described. All other materials were C. P. grades.

Addition of Methanol to 1-Methoxy-3-butyne.—The catalyst was prepared by heating together momentarily 5 g. of red mercuric oxide, 2 ml. of boron fluoride etherate, 1 g. of trichloroacetic acid and 10 ml. of anhydrous methanol. Methanol (90 ml.) was added to the catalyst followed by 1-methoxy-3-butyne as previously described.[2] From 42 g. of 1-methoxy-3-butyne there was obtained 41.5 g. of 1,3,3-trimethoxybutane: b. p. 63–65° at 25 mm.; $n^{26}D$ 1.4080; d^{26} 0.9337; yield 56%.

1,3-Dimethoxy-2-butene (VI).—A 250-ml. three-necked flask was equipped with a thermometer, Vigreux column with condenser and a small dropping funnel. Twenty grams of 1,3,3-trimethoxybutane was placed in the flask together with about 0.4 g. of finely powdered boric acid. The mixture was heated to boiling over an oil-bath (140–145°). As the reaction proceeded the remaining trimethoxy compound (128 g.) was added at such a rate as to keep about 20 ml. of liquid in the flask at all times. The decomposition products were collected over 5% sodium carbonate solution. At the completion of the reaction the organic material was removed from the carbonate solution, washed with water, and dried over calcium chloride. Distillation through an efficient column yielded 77 g. (66% yield) of 1,3-dimethoxy-2-butene, b. p. 130° at 748 mm.; $n^{25}D$ 1.4145; $n^{15}D$ 1.4200; d^{25} 0.8974; *MR* calcd., 32.74, *MR* found, 32.65.

Anal. Calcd. for $C_6H_{12}O_2$: methoxy, 53.5; mol. wt., 116.13. Found: methoxy, 52.6; mol. wt., cryoscopic in benzene, 113.5.

The experiment was repeated in the following manner. A 50-ml. distilling flask was provided with a condenser for distillation, dropping funnel and a heating bath of Wood's metal. The dry flask was heated to 300–320° and 148 g. of 1,3,3-trimethoxybutane added dropwise. The decomposition products were collected and purified as described above. The yield of 1,3-dimethoxy-2-butene was 80 g. (69%).

2-Methoxy-1,3-butadiene (VII) and 3,3-Dimethoxy-1-butene (V).—One mole (148 g.) of 1,3,3-trimethoxybutane was decomposed at 140–150° using 0.1–0.5 g. of powdered sodium acid sulfate as the catalyst. The procedure was identical with that described above. Distillation of the washed products yielded 50.5 g. of 2-methoxy-1,3-butadiene (60% yield) and 33.5 g. of 3,3-dimethoxy-1-butene (29% yield).

The physical properties of these products were in excellent agreement with those reported by Dykstra.[4] 2-

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[5] Hennion and Nieuwland, This Journal, **57**, 2006 (1935).

[6] McCusker and Kroeger, *ibid.*, **59**, 213 (1937).

Methoxy-1,3-butadiene: b. p. 75° at 745 mm.; $n^{20}D$ 1.4442; d^{20} 0.8281. 3,3-Dimethoxy-1-butene: b. p. 98–100° at 745 mm.; $n^{20}D$ 1.4038; d^{20} 0.8756.

In another experiment 65 g. of 3,3-dimethoxy-1-butene was decomposed in a similar manner. There was obtained 40 g. of 2-methoxy-1,3-butadiene (85% yield).

Similar decomposition of 148 g. of 1,3-dimethoxy-2-butene gave 25 g. of 3,3-dimethoxy-1-butene (17% yield) and 42 g. of 2-methoxy-1,3-butadiene (39% yield).

Hydrolysis of 1,3-Dimethoxy-2-butene.—Thirty grams (0.25 mole) of 1,3-dimethoxy-2-butene was added to 20 ml. of water containing 1 drop of hydrochloric acid. After standing for fifteen minutes the product was dried over anhydrous potassium carbonate and distilled. There was obtained 17 g. (65% yield) of 1-methoxy-3-butanone, previously described:[2] b. p. 139° at 745 mm.; $n^{26}D$ 1.4019; d^{26} 0.9125.

Addition of Methanol to 1,3-Dimethoxy-2-butene.—To a mixture of 20 g. of 1,3-dimethoxy-2-butene and 10 g. of anhydrous methanol was added a few crystals of *p*-toluenesulfonic acid. The reaction was quite vigorous and it was necessary to cool in a water-bath. After the reaction was complete (few minutes) the acid was neutralized with a small amount of sodium methylate solution. Distillation gave 25 g. (96% yield) of 1,3,3-trimethoxybutane, b. p. 63–65° at 25 mm.; $n^{20}D$ 1.4110; d^{20} 0.9395.

Addition of methanol to 3,3-dimethoxy-1-butene and to 2-methoxy-1,3-butadiene was accomplished in a similar manner.

Acknowledgment.—The authors acknowledge the kind assistance of the du Pont Company for furnishing the vinylacetylene used in this work.

Summary

The thermal catalytic desaturation of 1,3,3-trimethoxybutane has been investigated and the products described. Three reversible and three non-reversible reactions leading to 1,3,3-trimethoxybutane are given.

NOTRE DAME, IND. RECEIVED MARCH 12, 1938

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE UNIVERSAL OIL PRODUCTS COMPANY]

Phosphoric Acid as Catalyst in the Ethylation of Phenol

BY V. N. IPATIEFF, HERMAN PINES AND LOUIS SCHMERLING

That sulfuric acid is a catalyst for the reaction of phenol with olefins has long been known.[1] An exhaustive study of its use in the alkylation of phenol has been made in recent years by Niederl and co-workers.[2] However, sulfuric acid does not catalyze the reaction between phenol and ethylene.

Ipatieff and Pines[3] have shown that phosphoric acid is a catalyst for the alkylation of phenol with olefins including ethylene. In the present investigation the reaction with the latter was studied in greater detail. It was found that the product consists of ethylphenols, phenetole and ethylphenetoles, and that the yield of the former may be increased at the expense of the latter by carrying out the reaction in the presence of cyclohexane as solvent.

This is somewhat analogous to Claisen's method[4] of inducing C-allylation of phenol by the reaction of sodium phenoxide with allyl bromide in the presence of a non-dissociating solvent.

In order to determine whether the nuclear alkylation had necessarily taken place by way of the intermediate formation of the ether, phenetole was alkylated with propene. The product consisted entirely of propylated phenetole. Dealkylation of this product with hydriodic acid yielded only ethyl iodide and *o*- and *p*-isopropylphenols, as well as more highly propylated phenols. This agrees with the results of Sowa, Hinton and Nieuwland,[5] who showed that propene could be condensed readily with anisole in the presence of boron fluoride, with the isolation of 2-isopropylphenyl methyl ether and higher condensation products. It may be concluded, then, that contrary to the opinion of Niederl and Natelson[2] and the more positive subsequent statement of Natelson,[6] ether formation is not *necessarily* an intermediate step in nuclear alkylation with olefins and that direct C-alkylation can occur in the presence of phosphoric acid.

It was further shown that phenetole does not rearrange under the conditions of the alkylations.

Experimental

Reaction of Ethylene with Phenol.—The alkylations were carried out in a rotating Ipatieff type autoclave of 850-cc. capacity. Phenol and phosphoric acid were weighed into a glass liner equipped with a capillary seal which was then placed in the bomb. The latter was charged with ethylene to an intial pressure of 50 atmos-

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(1) Koenigs, *et. al.*, *Ber.*, **23**, 3144 (1890); **24**, 179, 3889 (1891).

(2) Niederl and Natelson, THIS JOURNAL, **53**, 272, 1928 (1931); and subsequent papers.

(3) Ipatieff, "Catalytic Reaction at High Pressure and Temperature," The Macmillan Co., New York, N. Y., 1936, p. 668.

(4) Claisen, *Ber.*, **58**, 279 (1925); *Ann.*, **442**, 210 (1925).

(5) Sowa, Hinton and Nieuwland, THIS JOURNAL, **55**, 3402 (1933).

(6) Natelson, *ibid.*, **56**, 1583 (1934).