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

The Addition of Methyl Alcohol to Monovinylacetylene

BY D. B. KILLIAN, G. F. HENNION AND J. A. NIEUWLAND

Introduction

The authors have recently shown[1,2] that organic oxy compounds add to monoalkyl acetylenes in the presence of small amounts of mercuric oxide and boron fluoride to form compounds of the type $R–C(OR')_2CH_3$— where R represents the alkyl group attached to the ethynyl group of the acetylene and R′ may be an appropriate alkyl group derived from the adding molecule. Methyl alcohol in particular adds very readily under these conditions.

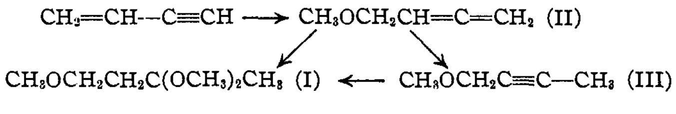
The use of monovinylacetylene in such addition reactions was thought to be of particular interest because of the conjugate unsaturated structure of this acetylene. Recently Jacobson, Dykstra and Carothers[3] reported that vinylacetylene adds *one* molecule of methyl alcohol in the presence of sodium methylate at 100° to form methoxy-4-butyne-1. The reaction was shown to involve 1,4 addition followed by rearrangement. We have succeeded in effecting addition of methyl alcohol to vinylacetylene in the presence of mercuric oxide and boron fluoride and have observed that, in this way, vinylacetylene readily adds *three* molecules of methyl alcohol, in effect, two to the triple bond and one to the double.

The addition takes place with best results if a small amount of trichloroacetic acid is used in conjunction with the boron fluoride and mercuric oxide commonly employed in our acetylene addition reactions. The over-all reaction may be formulated as follows

$$CH_2{=}CH{—}C{\equiv}CH + 3CH_3OH \longrightarrow CH_3O{—}CH_2{—}CH_2{—}C(OCH_3)_2CH_3 \quad (I)$$

On the basis of analyses and reactions there can be little doubt that the product has the structure indicated by (I).

It is possible to formulate two distinct reaction mechanisms for the addition. (*a*) Direct addition to the triple and double bonds. Such a mechanism would necessitate the assumption of a highly activated double bond in monovinyl acetylene. (*b*) 1,4 Addition followed by rearrangement, and further addition of two molecules of methyl alcohol.



The addition of the last two molecules of methyl alcohol may occur at either the allene stage (II) or at the methoxybutyne stage (III). Work on the reaction mechanism is now in progress.

The trimethoxybutane (I) hydrolyzed in good yield to a new methoxy ketone (IV).

$$CH_3OCH_2CH_2C(OCH_3)_2CH_3\ (I) + H_2O \longrightarrow CH_3OCH_2CH_2COCH_3\ (IV) + 2CH_3OH$$

Experimental Part

Reagents.—The preparation of the boron fluoride catalyst (in the form of $(C_2H_5)_2O{\cdot}BF_3$) and the purification of the methyl alcohol have been previously described.[1,2,4] Trichloroacetic acid was C. P. grade. Monovinylacetylene was passed directly into the reaction mixture in the gaseous form without further purification.

Action of Methyl Alcohol upon Monovinylacetylene.—The catalyst was prepared by warming together 15 g. of red mercuric oxide, 4.5 ml. of $(C_2H_5)_2O{\cdot}BF_3$, 2 g. of trichloroacetic acid and 10 ml. of methyl alcohol. To this was added 15 moles (480 g.) of methyl alcohol. This mixture was placed in a 3-liter 3-necked flask equipped with an inlet tube for monovinylacetylene, a mercury sealed motor-driven stirrer and a liquid ammonia reflux condenser.[5] Monovinylacetylene was passed directly into the reaction flask. The flask was cooled in a water-bath into which cold water was constantly run. Six moles (312 g.) of monovinylacetylene was passed into the reaction mixture, with constant stirring, over a period of three hours. During this time the catalyst blackened and settled as a sludge. The temperature of the bath was raised to 50° and stirring was continued for another hour. At the end of this time 10 g. of anhydrous potassium carbonate was added to the reaction product and stirring continued for another fifteen minutes. The sludge was allowed to settle and the pale yellow supernatant liquid decanted and fractionated *in vacuo* through a 125-cm. Vigreux style column of the partial condensation total take-off type. The yield of product boiling at 63–65° at 25 mm. was 487 g. (65% of the theoretical on the basis of methyl alcohol taken). The compound, 2,2,4-trimethoxybutane, had the following characteristics: b. p. 63–65° at 25 mm.; n^{26}_D 1.4082, n^{12}_D 1.4145; d_{26} 0.9332; MR'_D calcd., 39.46, MR'_D found, 39.15.

Anal. Calcd. for $C_7H_{16}O_3$: methoxy, 62.8; mol. wt., 148.13. Found: methoxy, 60; mol. wt., cryoscopic in benzene, 142, 146, 149, av. 146.

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[1] Hennion, Killian, *et. al.*, THIS JOURNAL, **56**, 1130 (1934).

[2] Killian, Hennion and Nieuwland, *ibid.*, **56**, 1384 (1934).

[3] Jacobson, Dykstra and Carothers, *ibid.*, **56**, 1169 (1934).

[4] Hennion, Hinton and Nieuwland, *ibid.*, **55**, 2858 (1933).

[5] Vaughn and Pozzi, *J. Chem. Ed.*, **8**, 2433 (1931).

Hydrolysis of 2,2,4-Trimethoxybutane.—One mole (148 g.) of 2,2,4-trimethoxybutane was mixed with 20 ml. of water containing 1 ml. of concentrated hydrochloric acid. Hydrolysis was apparently extremely rapid as evidenced by the fact that the temperature of the mixture dropped from 23 to −15° in a few minutes. The mixture was warmed for a few minutes under a reflux condenser, the acid neutralized with solid carbonate, and the liquid product fractionated at atmospheric pressure through a short column. The yield of 4-methoxybutanone-2 was 76 g. (75% of the theoretical). The following constants were determined for this compound: b. p. 139–140° at 745 mm.; n^{27}_{D} 1.4025, n^{12}_{D} 1.4091; d_{27} 0.9182; MR'_D, calcd. 26.95, MR'_D, found, 27.10.

Anal. Calcd. for $C_5H_{10}O_2$: methoxy, 30.4; mol. wt., 102.1. Found: methoxy, 30.4; mol. wt., cryoscopic in benzene, 101.

Proof of the Structure of 2,2,4-Trimethoxybutane.—From the evidence thus far presented the trimethoxybutane obtained from monovinylacetylene might be formulated either as 2,2,3-trimethoxybutane or 2,2,4-trimethoxybutane. Hydrolysis of the first compound would have yielded 3-methoxybutanone-2, which has been previously described by Gauthier,[6] and for which a boiling point of 113–114° at 759 mm. has been reported. The ketone prepared from our trimethoxybutane reacted with phenylhydrazine to form a phenylhydrazone. It oxidized readily with alkaline permanganate to form acetic acid in small yield as the only identified product, thus showing the presence of a CH_3—CO— group. It is evident that the methoxy group must be in the 4 position in the ketone (II) and therefore also in the trimethoxybutane (I).

Acknowledgment.—The authors gratefully acknowledge the assistance of E. I. du Pont de Nemours and Co. in supplying us with the monovinylacetylene used in this work.

Summary

1. Monovinylacetylene reacts with methyl alcohol in the presence of boron fluoride, mercuric oxide and trichloroacetic acid to yield 2,2,4-trimethoxybutane in good yield.

2. A new ketone, 4-methoxybutanone-2, prepared by the hydrolysis of 2,2,4-trimethoxybutane has been described.

3. This work is being continued with other oxy compounds.

NOTRE DAME, INDIANA RECEIVED MAY 23, 1934

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[6] Gauthier, *Ann. chim.*, [8] **16**, 322 (1909).

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

Stereochemistry of Diphenyls. XXXV.[1] The Effect of 3′ Substituents on the Rate of Racemization of 2-Nitro-6-carboxy-2′-methoxydiphenyl

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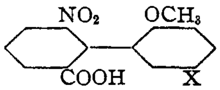
Although it is fair to assume from the experimental evidence already available that in a diphenyl molecule the effect of the 2,2′,6,6′-substituted groups is the principal factor governing the rate of racemization of the active forms, nevertheless it has been demonstrated that substituents in other positions contribute to the stability of racemization of the active diphenyls. Kuhn and Albrecht[3] found that the half-life period of active 2,4′-dinitro-6,6′-dicarboxydiphenyl was only one-third of that of the 2,4,4′-trinitro-6,6′-dicarboxydiphenyl, when observed under similar conditions.

Yuan and Adams[4] studied a series of substituted 2-nitro-6-carboxy-2′-methoxydiphenyls in which the groups methoxyl, methyl, chloro, bromo and nitro were in the 5′-position. By a comparison of the half-life periods of the active forms of these compounds with that of the unsubstituted diphenyl[5] it was demonstrated that a group in the 5′-position increased the antipodal stability of the molecule. The order of the stability to racemization is represented as follows: unsubstituted $< OCH_3 < CH_3 < Cl < Br < NO_2$. Four possible effects on the molecule due to the 5′ substituents were discussed by Yuan and Adams.

The present investigation was undertaken to produce the analogous active 3′ substituted 2-nitro-6-carboxy-2′-methoxydiphenyl (II) in order to compare the relative effects of groups in 3′ and



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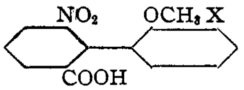

II

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[1] For the previous paper in this field see Knauf and Adams, THIS JOURNAL, **55**, 4704 (1933). See also Adams and Yuan, *Chem. Rev.*, **12**, 261 (1933).

[2] Submitted as a thesis for the Degree of Doctor of Philosophy in Chemistry at the University of Illinois. Research Fellow of the China Foundation for the Promotion of Education and Culture, 1933–34.

[3] Kuhn and Albrecht, *Ann.*, **458**, 221 (1927).

[4] Yuan and Adams, THIS JOURNAL, **54**, 2966, 4434 (1932).

[5] Stoughton and Adams, *ibid.*, **54**, 4426 (1932).