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

# 1,3,3-Trialkoxybutanes[1]

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## Introduction

The 1,3,3-trialkoxybutanes have been prepared by the action of orthoformates with the 1-alkoxy 3-butanones.[2] The trimethoxy derivative also has been obtained by direct catalytic addition of methanol to vinylacetylene.[3] No homologs could be prepared by direct addition.[4] It has now been observed that if the catalyst is prepared with methanol, the higher alcohols add to vinylacetylene quite readily, at about 40°, in accordance with the equation

$$CH_2{=}CH{-}C{\equiv}CH + 3ROH \longrightarrow RO{-}CH_2{-}CH_2{-}C(OR)_2{-}CH_3$$

The required catalyst, presumably $Hg(OCH_3{\cdot}BF_3)_2$, is prepared by warming mercuric oxide with boron fluoride etherate and methanol, using a little trichloroacetic acid to increase the acidity.[3]

The trialkoxy compounds may be desaturated thermally to dialkoxybutenes and to "oxyprenes."[2,5] Ketals also undergo desaturation upon reacting with acetic anhydride.[6] This reaction has been extended to the 1,3,3-trialkoxybutanes, which were found to lose only one alcohol molecule as follows

$$RO{-}CH_2{-}CH_2{-}C(OR)_2{-}CH_3 + (CH_3CO)_2O \longrightarrow RO{-}CH_2{-}CH{=}C(OR){-}CH_3 + CH_3{-}COOR + CH_3{-}COOH$$

Data for the compounds prepared are given in Table I. The tripropoxy compound is new.

## Experimental

**1,3,3-Triethoxybutane.**—In a 500-ml. three-necked flask, equipped with a mechanical stirrer, reflux condenser and inlet tube, were placed 4 g. of red mercuric oxide, 5 ml. of boron fluoride etherate, 20 ml. of anhydrous methanol and 2 g. of trichloroacetic acid. The mixture was warmed momentarily, with stirring, to dissolve a little of the mercuric oxide. Then 265 g. of absolute aldehyde-free ethyl alcohol was added. Vinylacetylene was passed in at 40° with stirring, until 146 g. had been absorbed (excess). After cooling, 30 g. of powdered anhydrous potassium carbonate was added, the mixture stirred for one hour and allowed to stand overnight. The liquid was separated and fractionated *in vacuo*. The yield of 1,3,3-triethoxybutane, b. p. 107–111°, 54 mm., was 200 g. or 55%, based on ethyl alcohol.

Tripropoxybutane (44% yield) and the tributoxybutane (54% yield) were prepared in a similar manner.

**Reaction of Triethoxybutane with Acetic Anhydride.**—A solution of 51 g. (0.5 mole) of acetic anhydride in 95 g. (0.5 mole) of 1,3,3-triethoxybutane was refluxed gently over an oil-bath for five hours. Distillation gave 42 g. (95% yield) of ethyl acetate, b. p. 77–78°, 28 g. (93% yield) of acetic acid, b. p. 115–120°, and 40 g. (56% yield) of 1,3-diethoxy-2-butene, b. p. 70–74° at 20 mm. There was 22 g. of polymeric residue.

In a similar manner 26 g. (0.25 mole) of acetic anhydride and 69 g. (0.25 mole) of 1,3,3-tributoxybutane gave 38.2 g. of butyl acetate–acetic acid mixture, b. p. 118–127°, and 22 g. of 1,3-dibutoxy-2-butene. The ester–acid mixture was washed with water, sodium carbonate, etc., and the free butyl acetate recovered. The yield of purified butyl acetate was 26 g. (90%).

TABLE I

A. TRIALKOXYBUTANES, $RO{-}CH_2{-}CH_2{-}C(OR)_2{-}CH_3$

| R | B. p., °C. | Mm. | $d_4^{20}$ | $n^{20}D$ |
|---|---|---|---|---|
| $C_2H_5$ | 70–71 | 5 | 0.8936 | 1.4142 |
| $n$-$C_3H_7$[a] | 118–120 | 7 | .8855 | 1.4215 |
| $n$-$C_4H_9$ | 120 | 3 | .8745 | 1.4308 |

B. DIALKOXYBUTENES, $RO{-}CH_2{-}CH{=}C(OR){-}CH_3$

| | | | | |
|---|---|---|---|---|
| $C_2H_5$ | 70–74 | 20 | .8709 | 1.4242 |
| $n$-$C_4H_9$ | 96–97 | 5 | .8627 | 1.4339 |

[a] *Anal.* Calcd. for $C_{13}H_{28}O_3$: C, 67.18; H, 12.15. Found: C, 67.6; H, 11.96.

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

## Summary

1. Three 1,3,3-trialkoxybutanes have been prepared by direct addition of alcohols to vinylacetylene.

2. The trialkoxybutanes react with acetic anhydride by loss of one alcohol molecule to yield 1,3-dialkoxy-2-butenes.

NOTRE DAME, IND. RECEIVED FEBRUARY 8, 1939

(1) Paper XXXI on the Chemistry of Substituted Acetylenes; previous paper, THIS JOURNAL, **61**, 572 (1939).

(2) Dykstra, *ibid.*, **57**, 2255 (1935).

(3) Killian, Hennion and Nieuwland, *ibid.*, **56**, 1786 (1934).

(4) Ethylene glycol adds to vinylacetylene readily to give two dioxolane derivatives. Killian, Hennion and Nieuwland, *ibid.*, **58**, 1658 (1936).

(5) Norris, Verbanc and Hennion, *ibid.*, **60**, 1159 (1938).

(6) Baum and Hennion, *ibid.*, **60**, 568 (1938).