fashion with those of natural eseroline, thus demonstrating the identity of the ring structure found in physostigmine with that of the synthetic products described in this and an earlier communication.

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[Contribution from the Chemical Laboratories of the University of Notre Dame]

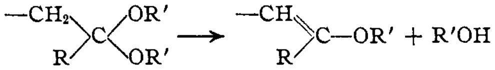
The Preparation of Some α-Unsaturated Ethers from 2,2-Dimethoxyalkanes[1]

By D. B. Killian, G. F. Hennion and J. A. Nieuwland

Introduction

In the condensation of alcohols with various acetylenes, catalyzed by a mercury salt and a suitable acid, to form acetals or ketals, it has been quite generally believed that vinyl ethers are intermediates in the reaction.[2,3,4] Such vinyl ethers, however, have never been isolated from these reactions, although they have been synthesized by other methods. It is known that such ethers are extremely reactive to alcohols in the presence of traces of acid, being converted to acetals.[5]

Faworski[6] prepared isopropenyl ethyl ether from methylacetylene and alcoholic potash at 170–180°. Alkylacetylenes other than methylacetylene rearrange to disubstituted acetylenes.[6,7,8] Phenylacetylene similarly adds one molecule of alcohol, but the addition is reversed and compounds of the type $C_6H_5CH{=}CH(OR)$ are formed.[8] Moureu[9] prepared 2-methoxy-, ethoxy- and propoxyheptene-1 by heating the alkoxyamylacrylic acid at 150–175°. Claisen[10] succeeded in splitting diethyl acetal to ethyl vinyl ether by heating with phosphorus pentoxide and quinoline. Ethyl isopropenyl ether was obtained similarly from 2,2-diethoxypropane. The thermal decomposition of acetals and ketals to α-unsaturated ethers was studied by Sigmund and Uchann.[11] Johannissian and Akunian[12] split cyclohexanone diethyl acetal to 1-ethoxycyclohexene by heating with traces of *p*-toluenesulfonic acid. These reactions may be expressed by the equation



$$\begin{matrix}-CH_2\\R\end{matrix}\!\!>\!C\!<\!\!\begin{matrix}OR'\\OR'\end{matrix} \longrightarrow \begin{matrix}-CH\\R\end{matrix}\!\!\geqslant\! C{-}OR' + R'OH$$

These interesting desaturation reactions have not been studied extensively nor has their generality been established.

Hill and Pidgeon[2] prepared the monovinyl ethers of glycol and trimethylene glycol and showed that ring closure to the ethylidene compound proceeded with explosive violence when a trace of acid was added. We have observed that ketals of the type $R(CH_3)C(OCH_3)_2$ are readily split, by merely heating with a small amount of *p*-toluenesulfonic acid, to yield substituted vinyl ethers of the type $RC(OCH_3){=}CH_2$. Readdition of methyl alcohol to the double bond is quantitative when the ether and alcohol are mixed and a trace of acid added. The ketal may be isolated readily if the acid is neutralized prior to distillation. Addition of a foreign alcohol is likewise quantitative but in this case a mixture of three ketals is obtained, *viz.*, the dimethyl ketal, the ketal of the foreign alcohol and a mixed ketal. However, by using an excess of the foreign alcohol the methyl ether or the 2,2-dimethoxyalkane may be directly converted to the ether of the foreign alcohol by distilling the mixture from a trace of acid through a suitable fractionating column so as to remove all methyl alcohol and excess foreign

Table I

α-Unsaturated Ethers, $R{-}C(OR'){=}CH_2$

(Asterisk denotes new compound)

No.	R	R′	Compound
1	C_4H_9-	CH_3-	*2-Methoxyhexene-1
2	C_4H_9-	C_2H_5-	*2-Ethoxyhexene-1
3	C_4H_9-	n-C_3H_7-	*2-Propoxyhexene-1
4	C_4H_9-	n-C_4H_9-	*2-*n*-Butoxyhexene-1
5	C_4H_9-	iso-C_4H_9-	*2-Isobutoxyhexene-1
6	$C_5H_{11}-$	CH_3-	2-Methoxyheptene-1
7	$C_5H_{11}-$	n-C_3H_7-	2-Propoxyheptene-1
8	C_6H_5-	CH_3-	α-Methoxystyrene

(1) Fifth paper on the chemistry of alkylacetylenes and their addition compounds; previous paper, This Journal, **56**, 1802 (1934).

(2) Hill and Pidgeon, *ibid.*, **50**, 2718 (1928).

(3) Nieuwland, Vogt and Foohey, *ibid.*, **52**, 1018 (1930).

(4) Hennion, Killian, *et al.*, *ibid.*, **56**, 1130 (1934).

(5) Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934, p. 679.

(6) Faworski, *J. prakt. Chem.*, [2] **37**, 531 (1888).

(7) Faworski, *ibid.*, [2] **44**, 208 (1891).

(8) Moureu, *Compt. rend.*, **138**, 288 (1904).

(9) Moureu, *Bull. soc. chim.*, [3] **31**, 522 (1904).

(10) Claisen, *Ber.*, **31**, 1021 (1898).

(11) Sigmund and Uchann, *Monatsh.*, **51**, 234 (1929).

(12) Johannissian and Akunian, *C. A.*, **25**, 921 (1931).

alcohol. The ethylidene acetals $RCH(OR')_2$ could not be split in this way.

The α-unsaturated ethers prepared, along with their physical properties and analyses, are reported in Tables I, II and III.

TABLE II

PROPERTIES OF α-UNSATURATED ETHERS

No.	B. p. °C.	mm.	Density	n_D	MR_D Calcd.	MR_D Found
1	119-120	740	0.813^{19}	1.4179^{19}	35.71	35.38
2	132-133	745	$.797^{23}$	1.4170^{23}	40.33	40.38
3	155-156	748	$.798^{23}$	1.4215^{23}	44.94	45.21
4	177-178	745	$.802^{25}$	1.4250^{25}	49.56	49.47
5	166-168	745	$.798^{23}$	1.4228^{23}	49.56	49.78
6	142-143	745	$.806^{24}$	1.4198^{24}	40.33	40.23
7	181-183	745	$.807^{23}$	1.4260^{24}	49.56	49.55
8	191-193	745	$.994^{23}$	1.5395^{23}	41.34	41.62

TABLE III

ANALYSES OF α-UNSATURATED ETHERS

No.	Empirical formula	Calcd., % C	Calcd., % H	Found, % C	Found, % H
1	$C_7H_{14}O$	73.61	12.37	72.9	12.2
2	$C_8H_{16}O$	74.90	12.59	74.4	12.60
3	$C_9H_{18}O$	75.99	12.77	75.68	12.79
4	$C_{10}H_{20}O$	76.84	12.91	76.65	12.99
5	$C_{10}H_{20}O$	76.84	12.91	76.40	12.91

Experimental

Reagents.—The *p*-toluenesulfonic acid required as a catalyst was Eastman C. P. grade. The 2,2-dimethoxyalkanes were prepared as previously described by the authors.[13] The alcohols were purified by drying over lime and distilling before use.

Preparation of 2-Methoxyhexene-1.—To 123 g. of 2,2-dimethoxyhexane in a 250-ml. wide-mouthed flask was added approximately 0.05 g. of *p*-toluenesulfonic acid. The flask was provided with an efficient fractionating column (8 mm. i. d., 110 cm. long), packed with a single nichrome spiral and equipped with a controllable dephlegmator. The flask contents was heated to boiling and the methyl alcohol removed as formed. When nearly the theoretical quantity had been removed, the residue was distilled through a short Vigreux column; yield 95 g., boiling between 117-121°. Upon redistillation it boiled at 119-120° at 740 mm.; yield of pure product 92%.

Preparation of 2-Propoxyhexene-1.—To 73 g. (0.5 mole) of 2,2-dimethoxyhexane was added 60 g. (1 mole) of propanol and about 0.05 g. of *p*-toluenesulfonic acid. The mixture was treated as described above and the excess propyl alcohol removed after all of the methyl alcohol had distilled. The yield of pure 2-propoxyhexene-1, b. p. 155-156° at 748 mm., was 58 g. (82% of the theoretical).

Ethylidene Acetals.—Upon treating diethyl acetal or dipropyl acetal in a similar manner, most of the ethylidene acetal distilled unchanged with the exception of a small amount of polymerized residue. No α-unsaturated ethers were isolated by this method.

Summary

1. α-Unsaturated ethers may be obtained in high yield by distilling 2,2-dimethoxyalkanes with *p*-toluenesulfonic acid.

2. A method is described for the preparation of α-unsaturated ethers from a 2,2-dimethoxyalkane or a 2-methoxyalkene-1.

3. Ethylidene acetals were not able to be split in this way.

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(13) Killian, Hennion and Nieuwland, THIS JOURNAL, **56**, 1384 (1934).

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

Ethoxybenzyl Ureas

BY E. WERTHEIM

This paper reports further work on the problem of structure *vs.* taste of Dulcin (I). The previously reported preparation of *d*-ethoxybutylurea apparently shows that the aromatic character of dulcin is essentially connected with its sweet taste.[1]

This point has been tested further in the preparation of *p*-ethoxybenzylurea (II), in which the carbamido group is removed from the ring. The compound is practically tasteless in contrast with *a*-methyldulcin (III) which is sweet.[2]

In *m*-ethoxybenzylurea (IV) and *o*-ethoxymethylbenzylurea (V) (having, respectively, one and two aliphatic attachments for the taste groups) the sequence of four carbons between taste groups as found in dulcin has been retained. In addition the latter has a space orientation of these groups similar to that found in dulcin.[3] Both compounds are practically tasteless. The removal of the carbamido group from the ring destroys sweetness despite the spatial similarity of these compounds to dulcin.

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(1) Wertheim, THIS JOURNAL, **56**, 735 (1934).

(2) Lorang, *Rec. trav. chim.*, **47**, 183 (1928).

(3) *Cf.* discussion in a previous paper of this series, THIS JOURNAL, **55**, 2540 (1933).