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

The Preparation of Some Ketals of Alkylacetylenes with the Higher Alcohols[1]

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

In a recent publication,[2] the authors have described a number of ketals prepared from various alkylacetylenes with methanol using mercuric oxide and boron fluoride as a catalyst. When monohydric alcohols other than methanol were treated with monoalkylacetylenes in the presence of this catalyst, the products were found to be polymeric. No ketals have been isolated from such reactions. Ethyl alcohol, for example, reacted with amylacetylene to produce polymeric liquids of wide boiling range in addition to non-distillable resins. Temperature control or the use of solvents had no noticeable effect on the nature of this reaction, but when a small amount of trichloroacetic acid (from 0.2 to 1 g. per mole of acetylene used) was added to the catalyst mixture, reaction occurred smoothly with the formation of 2,2-dialkoxyalkanes in high yield. The ketals of *n*-butylacetylene and *n*-amylacetylene have been prepared in this way with ethanol, *n*-propanol, *n*-butanol, *n*-pentanol and *n*-hexanol.

While straight-chained monohydric alcohols react readily with monoalkylacetylenes to produce ketals when trichloroacetic acid is used, the branch-chained or isoalcohols either react not at all or only with great difficulty. Thus with isopropanol, tertiary butanol and tertiary amyl alcohol, no evidence of reaction has been observed with an alkylacetylene. With several other commonly available primary alcohols, in which the side-chain is one or two carbon atoms removed from the carbinol group, and with secondary alcohols, little if any reaction has been obtained with the possible exception of isobutanol. These rather anomalous results cannot be explained at the present time. The conditions necessary to effect addition of such alcohols to monoalkylacetylenes are being studied in this Laboratory.

Claisen[3] has reported 2,2-diethoxypropane and 2,2-dipropoxypropane prepared from acetone, formimido ethyl ester hydrochloride and ethyl alcohol and with corresponding derivatives for the propoxy compound. Using the same method and various ketones Reitter and Hess[4] have synthesized various 2,2-diethoxyalkanes. Evlampiev[5] has further extended the series using ethyl orthoformate and the appropriate ketone in the presence of a small amount of sulfuric acid. With the exception of 2,2-diethoxyhexane, previously prepared by Evlampiev,[5] all of the compounds reported in Table I are new.

TABLE I

2,2-DIALKOXYALKANES, $R-C(OR')_2-CH_3$

No.	R	R′	Compound
1	n-C_4H_9-	C_2H_5-	2,2-Diethoxyhexane
2	n-C_4H_9-	n-C_3H_7-	2,2-Dipropoxyhexane
3	n-C_4H_9-	n-C_4H_9-	2,2-Dibutoxyhexane
4	n-C_4H_9-	n-C_5H_{11}-	2,2-Dipentoxyhexane
5	n-C_4H_9-	n-C_6H_{13}-	2,2-Dihexoxyhexane
6	n-C_5H_{11}-	C_2H_5-	2,2-Diethoxyheptane
7	n-C_5H_{11}-	n-C_3H_7-	2,2-Dipropoxyheptane
8	n-C_5H_{11}-	n-C_4H_9-	2,2-Dibutoxyheptane
9	n-C_5H_{11}-	n-C_5H_{11}-	2,2-Dipentoxyheptane

The physical properties and analyses of the 2,2-dialkoxyalkanes are reported in Table II and Table III, respectively.

TABLE II

PROPERTIES OF 2,2-DIALKOXYALKANES

No.	B. p., °C.	Mm.	Density^{25}	n^{25}_D	MR′D Calcd.	MR′D Found
1	68– 69	18	0.835	1.4087	51.67	51.59
2	95– 97	18	.836	1.4160	60.91	60.71
3	115–117	18	.837	1.4240	70.15	70.16
4	141–143	18	.839	1.4285	79.39	79.30
5	143–144	8	.839	1.4322	88.63	88.45
6	81– 83	18	.834	1.4132	56.29	56.28
7	107–109	18	.836	1.4191	65.53	65.34
8	134–136	18	.837	1.4252	74.77	74.65
9	148–150	17	.839	1.4310	84.01	84.02

TABLE III

ANALYSES OF 2,2-DIALKOXYALKANES

No.	Empirical formula	Calcd., % C	Calcd., % H	Found, % C	Found, % H
1	$C_{10}H_{22}O_2$	68.89	12.73	68.59	12.88
2	$C_{12}H_{26}O_2$	71.22	12.96	71.14	13.09
3	$C_{14}H_{30}O_2$	72.97	13.13	73.03	13.06
4	$C_{16}H_{34}O_2$	74.33	13.23	74.11	13.56
5	$C_{18}H_{38}O_2$	75.12	13.41	75.29	13.39
6	$C_{11}H_{24}O_2$	70.14	12.85	69.50	12.71
7	$C_{13}H_{28}O_2$	72.10	13.05	71.99	13.25
8	$C_{15}H_{32}O_2$	73.69	13.24	73.65	13.46
9	$C_{17}H_{36}O_2$	74.92	13.32	74.93	13.31

Since the procedure for preparing the 2,2-dialkoxyalkanes is uniform, only one typical procedure is described.

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(1) Seventh paper on the chemistry of alkylacetylenes and their addition compounds; previous paper, THIS JOURNAL, **57**, 2006 (1935).

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

(3) Claisen, *Ber.*, **31**, 1012 (1898); *ibid.*, **40**, 3908, 3913 (1907).

(4) Reitter and Hess, *ibid.*, **40**, 3020 (1907).

(5) Evlampiev, *J. Russ. Phys.-Chem. Soc.*, **54**, 462 (1922/23).

Experimental

Reagents.—The preparations of the boron trifluoride catalyst and monoalkylacetylenes have been previously described.[6,7] The alcohols used were C. P. grade, carefully fractionated before use.

Action of *n*-Hexanol on *n*-Butylacetylene.—The catalyst was prepared by heating momentarily 5 g. of red mercuric oxide, 2 ml. of $(C_2H_5)_2O{\cdot}BF_3$ and 2 ml. of methanol. To this was added 120 g. (1.25 moles) of *n*-hexanol and 1 g. of trichloroacetic acid. The mixture was placed in a 1-liter 3-necked flask equipped with a mercury-sealed motor-driven stirrer, a reflux condenser and a dropping funnel. After heating the contents of the flask to 50–60° on a water-bath, 41 g. (0.5 mole) of *n*-butylacetylene was added dropwise at such a rate that the temperature of the reaction mixture did not exceed 70°. After addition of the acetylene, the source of heat (water-bath) was removed and the mixture stirred until it reached room temperature. Then 1 g. of sodium dissolved in a little methyl alcohol was added to neutralize acidity. Fractionation yielded 92 g. (62%) of 2,2-dihexoxyhexane.

Proof of the Structure of 2,2-Dialkoxyalkanes.—Hydrolysis of the 2,2-dialkoxyalkanes with dilute sulfuric acid yielded the corresponding alcohol and methyl *n*-butyl or methyl *n*-amyl ketone. The latter were identified by the melting points of their semicarbazones.

Summary

1. A series of 2,2-dialkoxyalkanes has been prepared from monoalkylacetylenes with the normal monohydric alcohols other than methanol in the presence of mercuric oxide, boron trifluoride and trichloroacetic acid.
2. The ketals obtained from ethanol, *n*-propanol, *n*-butanol, *n*-pentanol and *n*-hexanol with *n*-butyl and *n*-amyl acetylene are described.
3. With branch-chained monohydric alcohols, ketals have not been isolated by this method.

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[6] Hennion, Hinton and Nieuwland, THIS JOURNAL, **55**, 2858 (1933).

[7] Hennion, Killian, *et al.*, *ibid.*, **56**, 1130 (1934).

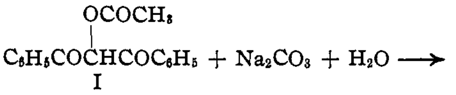
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, HOWARD UNIVERSITY]

Hydroxy Polyketones. II. Dibenzoylcarbinol

BY A. H. BLATT AND W. LINCOLN HAWKINS

As part of a study of hydroxy polyketones[1] we have prepared and examined the chemical behavior of dibenzoylcarbinol, one of the simplest of this group of compounds which might reasonably be expected to exist as an ene-diol. While our work was in progress Bigelow, Rule and Black[2] reported the preparation of this carbinol by the catalytic hydrogenation of diphenyl triketone but, evidently having a different interest in the material than we had, these authors did not attempt the reactions reported here.

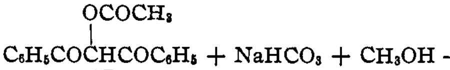
The starting material for our work was dibenzoylcarbinol acetate (I). Neufville and Pechmann,[3] who first prepared this substance, observed that its alcoholic solution gave a characteristic enol coloration with ferric chloride. We find that this alcoholic solution shows by Kurt Meyer titrations constant, though small, amounts of enol (5%). This enolic form, however, does not react with typical hydroxyl reagents. Our principal interest in the acetate was as a source of dibenzoylcarbinol and we have, therefore, examined its hydrolysis under a variety of conditions. In alkaline solution the acetate undergoes both hydrolysis and cleavage; the products obtained depend upon the solvent employed and upon the hydroxyl-ion concentration. In aqueous sodium carbonate the acetate furnishes benzoic and acetic acids and benzoylcarbinol.



$$\underset{\text{I}}{C_6H_5CO\overset{OCOCH_3}{\overset{|}{C}}HCOC_6H_5} + Na_2CO_3 + H_2O \longrightarrow$$

$$C_6H_5COCH_2OH + C_6H_5COONa + CH_3COONa + CO_2 \quad (1)$$

When the acetate is treated with aqueous sodium hydroxide, it dissolves and can be recovered if the solution is quickly acidified. After standing, however, the solution furnishes benzoic and acetic acids but no benzoylcarbinol. The absence of the carbinol is to be expected for it is destroyed by alkali hydroxides.[4] In aqueous alcoholic solution the cleavage is more interesting. Using sodium bicarbonate in methyl alcohol, benzoylcarbinol and acetic acid are formed as in aqueous solution but the third product is methyl benzoate.



$$C_6H_5CO\overset{OCOCH_3}{\overset{|}{C}}HCOC_6H_5 + NaHCO_3 + CH_3OH \longrightarrow$$

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[1] For the first paper on this subject see THIS JOURNAL, **57**, 1103 (1935).

[2] Bigelow, Rule and Black, *J. Chem. Soc.*, 83 (1935).

[3] Neufville and Pechmann, *Ber.*, **23**, 3377 (1890).

[4] (a) Hunnius, *ibid.*, **10**, 2010 (1877); (b) Zincke, *Ann.*, **216** 310 (1883).