[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

A NEW METHOD OF PREPARING ACETALS. II. ACETALS OF MONOHYDRIC ALCOHOLS

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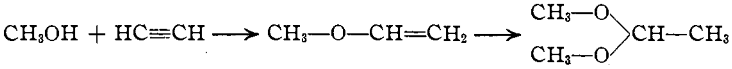
RECEIVED FEBRUARY 27, 1930 PUBLISHED JULY 3, 1930

Monohydric acetals, in limited number, have been prepared by several methods, such as the method of Reichert, Bailey and Nieuwland,[1] and the standard method described by Adkins and Nissen.[2]

The process described in this paper consists in the condensation of acetylene with the monohydric alcohols into the corresponding acetals, in the presence of a new catalyst, boron fluoride in methyl alcohol with mercuric oxide, discovered by Nieuwland and Vogt[3] and recently discussed in THIS JOURNAL.

The reaction is presumed to take place in two steps:[4] (1) the formation of a vinyl ether; (2) immediate change of the vinyl ether to the acetal, in acid solution by the addition of a second molecule of alcohol, thus



$$CH_3OH + HC{\equiv}CH \longrightarrow CH_3{-}O{-}CH{=}CH_2 \longrightarrow \begin{matrix} CH_3{-}O \\ CH_3{-}O \end{matrix}\!\!>\!CH{-}CH_3$$

By this method all of the acetals of the monohydric alcohols, from methanol through the amyl alcohols, tertiary alcohols up to nonyl alcohol and quite a number of the phenyl alcohol acetals were made. The procedure is nearly uniform for all alcohols treated and may be illustrated by the case of iso-amyl alcohol.

Experimental

Dry acetylene gas was passed into a mixture of 200 g. of iso-amyl alcohol and 10 g. of a 63% solution of the catalyst, boron fluoride in methyl alcohol with 1 g. of mercuric oxide added. After the theoretical amount of acetylene (29.5 g.) had been absorbed, the contents of the flask was treated with a small amount of water, the acid neutralized with potassium carbonate, the acetal extracted with ether and dried over potassium carbonate. The ether was distilled off, and the solution fractionated, the products obtained being unconverted alcohol and acetal. In all cases the acetal was treated with metallic sodium to prove its freedom from hydroxylic impurities.

Fractionation was the method used to recover the acetal, and this method proved satisfactory since a number of the acetals reported in the literature were successfully prepared. Methyl alcohol acetal, isopropyl alcohol acetal, methyl propyl carbinol acetal and diethyl carbinol acetal required special methods of procedure for their recovery.

According to a process by Nieuwland (unpublished) a high-boiling aromatic fraction, xylene, was used as a solvent in the case of methyl alcohol acetal. The procedure

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[1] Reichert, Bailey and Nieuwland, THIS JOURNAL, **45**, 1552 (1923).

[2] *Cf.* "Organic Syntheses," John Wiley and Sons, Inc., New York, **1923**, Vol. III, p. 1.

[3] Nieuwland, Vogt and Foohey, THIS JOURNAL, **52**, 1018 (1930).

[4] *Cf.* Hill and Pidgeon, *ibid.*, **50**, 2718 (1928).

was as follows. After the required amount of acetylene had been absorbed, the acid in the flask was neutralized with potassium carbonate. The mixture was then distilled and to the distillate was added about one-third its volume of water, with vigorous shaking. The methyl alcohol and any aldehyde present were found in the lower layer; xylene or the higher fraction of solvent naphtha was then added and after vigorous shaking the lower water layer was separated. The upper solvent layer, containing nearly all of the acetal, was treated in a flask with 50–75 g. of potassium carbonate and 20–25 g. of anhydrous barium oxide and refluxed for ten minutes on a water-bath. It was then distilled from the xylene.

In the cases of the acetals of isopropyl alcohol, methyl propyl carbinol and di-ethyl carbinol, the ether was distilled off and the solution fractionated. The distillate containing acetal and any alcohol was treated with calcium chloride and water to remove the alcohol. After separating the two layers, the acetal was dried over potassium carbonate, tested with metallic sodium and redistilled.

TABLE I

PREPARATIVE DATA AND PHYSICAL CONSTANTS OF COMPOUNDS (ASTERISKS DENOTE NEW COMPOUNDS)

	Taken,	Yield				
Ethylidene compound	g.	g.	%	B. p., °C.	d_4	n_D
Methyl alcohol	200	104	37	64–65	0.8494^{26}	1.3762^{26}
Ethyl alcohol	200	104	40	101–102	0.8250^{23}	1.3789^{30}
Propyl alcohol	203	90	37	146–148.5	0.8256^{26}	1.3938^{26}
Isopropyl alcohol*	200	97	40	82–84	0.7855^{25}	1.3790^{25}
Butyl alcohol	100	39.5	33.6	197–198	0.8312^{26}	1.4090^{26}
n-*Sec.*-butyl alcohol*	33	14	35	55–60 (16 mm.)	......	1.3965^{29}
Primary isobutyl alcohol	200	102	43.4	168–169	0.8123^{24}	1.4037^{24}
n-Amyl alcohol	200	117	51.5	114–116 (16 mm.)	0.8282^{26}	1.4159^{26}
Isobutyl carbinol	200	117	51.5	210–211	0.8278^{23}	1.4175^{23}
Sec.-butyl carbinol	200	100	43.6	205–206	0.8262^{25}	1.4165^{25}
Methylpropyl carbinol*	130	45	30	120–123	0.8128^{24}	1.4069^{24}
Methylisopropyl carbinol*	59	21	30	142–145	......	1.4095^{27}
Diethyl carbinol*	78	36	40	120–121	0.8120^{27}	1.4050^{27}
Dimethyl ethyl carbinol*	200	123	53.7	90–93	0.8278^{26}	1.3965^{26}
Diethyl methyl carbinol*	...	...	..	96–99	......	1.3872^{23}
Triethyl carbinol*	...	...	..	114–116	......	1.4135^{26}
Methylethyl butyl carbinol*	...	...	..	125–128	......	1.4145^{25}
Allyl alcohol	...	...	..	90–93 (16 mm.)	......	1.4351^{28}
Tetrahydrofurfuryl alcohol*	104	37	31.6	153–155 (18 mm.)	1.3700^{27}	1.4563^{26}
Cyclohexanol*	...	...	..	131–134 (16 mm.)	0.9560^{25}	1.4651^{25}
Benzyl alcohol*	200	102	45.5	187–189 (16 mm.)	1.0455^{25}	1.5397^{25}
Diphenyl carbinol*	...	...	..	201–202 (18 mm.)	......	1.5545^{25}
Phenyl ethyl alcohol*	122	68	50.4	204–205 (16 mm.)	1.0180^{26}	1.5302^{26}
Phenyl methyl carbinol*	...	...	..	164–166 (17 mm.)	......	1.5365^{25}
Phenyl ethyl carbinol*	70	31	40	185–187 (16 mm.)	......	1.5495^{25}
Phenyl methyl ethyl carbinol*	...	...	..	200 (14 mm.)	......	1.5801^{25}

Physical constants and analyses were determined as soon as possible after the acetal was recovered, since the acetals had a tendency to decompose on standing.

Table I shows the ethylidene compounds prepared by this new method, their physical constants and the yields obtained. Blank spaces in the table are the result of incomplete data since in these cases it was not possible to recover the acetal completely.

In explanation of this table, it might be said that Eastman purified chemicals were used, and those alcohols not obtained from the above source were prepared and purified in our laboratories, mostly by the Grignard method of making alcohols.

Tertiary butyl alcohol acetal was prepared from a technical grade of the alcohol. It was found to have the following physical constants: b. p. 78–81, d_4^{28} 0.8528, n_D^{28} 1.4050. However, technical tertiary butyl alcohol obtained from petroleum cracked gases contains isopropyl alcohol, which is difficult to remove, and it is conceivable that the acetal formation observed with this grade of tertiary butyl alcohol was due to the presence of this impurity. Attempts to make tertiary butyl alcohol acetal from the pure alcohol, melting at 25°, failed.

Triphenyl carbinol acetal was also prepared, using glycol acetal as a solvent. The reaction was rapid and vigorous, and a white solid, having the following physical constants, was obtained: b. p. 211° at 18 mm., m. p. 93°, yield 43%. It had a melting point in close proximity to triphenylmethane but the following evidence pointed to acetal formation. The crystalline structure of the acetal was uniform throughout, separating from ethyl alcohol in long needle crystals. Crystals were also obtained using benzene as the solvent. These crystals gave a melting point of 93–94°. Triphenylmethane forms a molecular compound with one molecule of benzene, melting at 75°. Molecular weight determinations showed the acetal to be approximately twice that of triphenylmethane. The analysis of the acetal closely checked the calculated amount of carbon and hydrogen. The acetal when first formed gave the characteristic aldehyde test when hydrolyzed with dilute hydrochloric acid.

If during the course of the reaction in the preparation of these acetals, the absorption of acetylene slowed down, mercuric oxide and catalyst were added to speed up the reaction. When the absorption was very rapid, the flask was cooled to prevent the decomposition of the acetal and the formation of tarry residues. In some cases the reaction proceeded slowly until about one-half of the theoretical amount of acetylene had been absorbed and then the absorption was quite rapid until the reaction was completed. It seemed that the acetal itself acted as a solvent, hastening the reaction.

The acetylene and alcohol were thoroughly dried before they entered the reaction; otherwise, the presence of water in the reaction caused the formation of acetaldehyde and crotonaldehyde, tars or resins were formed and the yield of acetal was lowered.

An interesting fact was noticed with respect to all tri-carbinols with which we experimented, *i. e.*, the acetals formed from tri-carbinols all gave boiling points below the boiling points of the alcohols. It is also noteworthy that although the formation of the Grignard reagent becomes increasingly difficult as the carbon content increases, due to the formation of alkenes, with acetals the reaction is just the reverse. Tertiary alcohols, in general, as the carbon content increased, formed acetals with increasing ease.

Furfuryl alcohol, which is a weak ring compound, decomposed during acetal formation. Tetrahydrofurfuryl alcohol, however, reacted quite smoothly and gave a very stable acetal. Cyclohexanol gave the acetal over a long period of time and also left a resin, soluble in ether. Oximes did not react, since the hydroxyl of an oxime evidently is different from the hydroxyl of an alcohol. Tetramethyldiaminobenzhydrol did not react, since the diamino groups attacked the catalyst in the solution. Benzhydrol, on the other hand, reacted quite rapidly and gave a high-boiling and stable acetal. Borneol and terpineol did not form acetals. Secondary octyl alcohol gave an acetal, but could not be recovered as it decomposed above 180° at 20 mm.

Although several of these acetals had been made by the sulfuric acid method, yet quite a number of acetals made by this new method probably could not have been made by the old method, since the sulfuric acid would have destroyed the alcohol before the reaction could have taken place. Benzyl alcohol acetal, for example, could not have been made by the sulfuric acid method for the above reason.

Acetals have a distinctive ethereal odor, which was noticed in almost all cases. The odors of the aliphatic alcohol acetals were similar, while the aromatic acetals varied. For instance, phenylethyl alcohol, used in perfumes, gave an acetal having an odor of horse-radish. The acetals also were found to be stable in the presence of alkalies, but hydrolyzed into acetaldehyde and the corresponding alcohol in the presence of dilute acids.

Nine representative acetals were analyzed, both molecular weight and carbon and hydrogen determinations being made. The molecular weight determinations were made by the boiling-point method, ethyl alcohol being used as a solvent. There were three possibilities as to the compound in considering molecular weight determinations; (1) the alcohol from which the acetal was made; (2) the vinyl ether (we found no evidence of vinyl ether formation); (3) the acetal. Since our molecular weight determinations showed that it could not be the alcohol or vinyl ether, we concluded that it was the acetal. The analyses of the same compounds came fairly close to the theoretical, as calculated, but since the alcohol and the acetal vary in percentage composition only by the weight of the acetylene, in most cases the difference in the per cent. of carbon and hydrogen of both the alcohol and the acetal was so small as to be within the range of experimental error for both.

Table II shows the data obtained on the molecular weights and analyses of the nine respective acetals.

TABLE II

ANALYTICAL DATA

				Analyses, %			
		Mol. wts.		Calcd.		Found	
Acetals	Formula	Calcd.	Found	C	H	C	H
Isoamyl alcohol	$C_{12}H_{26}O_2$	202.2	215.9	71.21	12.96	70.86	12.62
Sec.-butyl carbinol	$C_{12}H_{26}O_2$	202.2	209.0	71.21	12.96	70.67	12.48
n-Amyl alcohol	$C_{12}H_{26}O_2$	202.2	205.0	71.21	12.96	71.88	12.68
Tetrahydrofurfuryl alcohol	$C_{12}H_{22}O_4$	230.2	242.6	62.56	9.63	62.53	9.59
Triphenyl carbinol	$C_{40}H_{34}O_2$	546.3	527.8	87.86	6.27	87.92	6.07
Benzyl alcohol	$C_{16}H_{18}O_2$	242.1	255.5	79.29	7.49	80.18	7.07
Diphenyl carbinol	$C_{28}H_{26}O_2$	394.2	402.9	85.23	6.65	86.01	6.78
Phenylethyl alcohol	$C_{18}H_{22}O_2$	270.2	264.4	79.95	8.28	79.08	8.07
Cyclohexanol	$C_{14}H_{26}O_2$	226.2	224.0	74.27	11.58	73.75	11.24

Summary

1. Using a solution of boron fluoride in methyl alcohol with mercuric oxide as a catalyst, a series of acetals of the monohydric alcohols has been prepared.
2. A number of these compounds have been prepared for the first time, and cannot be made by any other known methods from acetylene or from acetaldehyde.
3. Furfuryl alcohol, oximes, borneol, terpineol and tetramethyldiaminobenzhydrol do not give acetals by this method.
4. Tertiary alcohols, in general, as the carbon content increases, give acetals with increasing ease of formation.
5. Attempts to make tertiary butyl alcohol acetal with the pure alcohol melting at 25° failed.
6. Acetals formed from tri-carbinols give boiling points below the boiling points of their alcohols.

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