

Summary

1. The reactivity of the chlorine atom in *o*-, *m*- and *p*-chlorophenyl methyl sulfones toward sodium ethoxide has been determined and compared with the reactivity of the chlorine atom

in *o*-, *m*- and *p*-nitrochlorobenzenes.

2. It was found that the activation of the halogen by the sulfone group was very much less than that produced by the nitro group.

URBANA, ILLINOIS

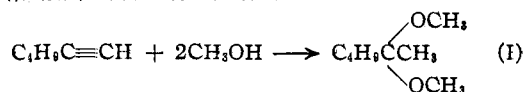
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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NOTRE DAME]

The Preparation of Some Ketals of Alkylacetylenes with Methanol

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

The authors have recently shown¹ that *n*-butylacetylene reacts with methanol to form 2,2-dimethoxyhexane (I) in the presence of mercuric oxide and boron trifluoride.



This condensation is similar to the formation of acetals from acetylenes.²

This reaction has been studied in greater detail, and ketals have been prepared from methylacetylene, ethylacetylene, *n*-propylacetylene, *n*-butylacetylene and *n*-amylacetylene in high yield. All of the ketals are colorless liquids having highly characteristic odors. Both 2,2-dimethoxypropane and 2,2-dimethoxybutane possess odors similar to that of menthol.

The 2,2-dimethoxyalkanes are extremely unstable in the presence of acid and upon hydrolysis form methanol and the corresponding ketone RCOCH_3 , where R represents the alkyl group attached to the ethynyl group in the acetylene. Since the catalyst is acidic, attempted neutralization of the reaction product with aqueous carbonate resulted in high yields of ketone. When anhydrous potassium carbonate was added to the reaction mixture before distillation, the ketal could be isolated without difficulty.¹

Addition of monohydric alcohols other than methanol to alkylacetylenes in the presence of boron fluoride and mercuric oxide occurred rapidly, but the products were to a large extent polymeric. No ketals have thus far been isolated from such reactions. Ethyl alcohol, for example, reacted vigorously with amylacetylene, producing polymeric liquids of wide boiling range in addition to non-distillable resins.

With the exception of the first two, all of the compounds in Table I are new. For the sake of the completeness of the homologous series, dimethyl acetal² has been included in this table. Using acetone, methanol and formimido ether, Claisen³ has previously prepared 2,2-dimethoxypropane.

TABLE I
PROPERTIES OF 2,2-DIMETHOXYALKANES,
 $\text{R}(\text{CH}_2)\text{C}(\text{OCH}_3)_2$

R	B. p., °C.	Mm.	Density	n_D	MR	
					Calcd.	Found
H-	84-85		0.8494 ²⁵	1.3762 ²⁵	23.96	24.20
CH ₃ -	78-80	747	.8448 ²⁰	1.3746 ²⁰	28.58	28.18
C ₂ H ₅ -	48-50	100	.8535 ²⁹	1.3899 ²⁸	33.20	32.70
<i>n</i> -C ₃ H ₇ -	30-31	15	.8494 ²⁸	1.3986 ²⁸	37.81	37.71
<i>n</i> -C ₄ H ₉ -	58-60	30	.8536 ²⁸	1.4053 ²⁸	42.44	41.96
<i>n</i> -C ₅ H ₁₁ -	74-75	27	.8543 ²²	1.4122 ²²	47.05	46.67

TABLE II
ANALYSIS OF 2,2-DIMETHOXYALKANES

R	Empirical formula	Calcd., %		Found, %	
		C	H	C	H
C ₂ H ₅ -	C ₆ H ₁₄ O ₂	60.96	11.95	60.75	11.68
<i>n</i> -C ₃ H ₇ -	C ₇ H ₁₆ O ₂	63.57	12.21	63.21	12.14
<i>n</i> -C ₄ H ₉ -	C ₈ H ₁₈ O ₂	65.69	12.41	65.56	12.18
<i>n</i> -C ₅ H ₁₁ -	C ₉ H ₂₀ O ₂	67.40	12.87	67.94	12.47

The procedure for preparing the 2,2-dimethoxyalkanes is nearly uniform except that the temperature at which the reaction was carried out varied slightly according to the acetylene used. Two typical procedures are described.

Experimental Part

Reagents.—The preparation of the boron fluoride catalyst (in the form of $(\text{C}_2\text{H}_5)_2\text{O}\cdot\text{BF}_3$), alkylacetylenes, and the purification of the methanol, etc., have been described.^{1,4} Methylacetylene and ethylacetylene were prepared by the action of the appropriate dialkyl sulfates on sodium acetylide in liquid ammonia and were purified by passing through water, dilute sulfuric acid, a calcium chloride tower and finally through soda lime. They

(3) Claisen, *Ber.*, **31**, 1012 (1898).

(4) Hennion, Hinton and Nieuwland, *This Journal*, **55**, 2858 (1933).

(1) Hennion, Killian, *et al.*, *This Journal*, **56**, 1130 (1934).

(2) Hinton and Nieuwland, *ibid.*, **52**, 2892 (1930).

were used in the gaseous state by passing them directly into the alcohol-catalyst mixture. The other acetylenes were used in the liquid state.

Action of Methanol on Ethylacetylene.—The catalyst was prepared by heating together 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 two moles (64 g.) of methanol. The mixture was placed in a 2-liter 3-necked flask equipped with an inlet tube for ethylacetylene, a mercury sealed motor driven stirrer, and a liquid ammonia reflux condenser.⁵ Ethylacetylene was passed directly into the reaction mixture maintained at 40°; after stirring for two hours the contents of the flask was mixed with 5 g. of anhydrous potassium carbonate and fractionated at 100 mm. Forty grams of 2,2-dimethoxybutane was obtained.

Action of Methanol on Propylacetylene.—One-half mole (34 g.) of propylacetylene was added slowly with constant stirring to one and one-quarter moles of methanol (40 g.) containing the usual catalyst. The temperature of the reaction mixture was not allowed to rise above 35°. The procedures for the preparation and purification of 2,2-

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

dimethoxypentane and heptane are analogous to that already described¹ by the authors for 2,2-dimethoxyhexane.

Proof of the Structure of 2,2-Dimethoxyheptane.—Hydrolysis of 2,2-dimethoxyheptane with dilute mineral acid yielded methyl alcohol and methyl *n*-amyl ketone, b. p. 149–150°. The latter was identified by its semicarbazone, m. p. 120–121°.

Summary

1. A series of 2,2-dimethoxyalkanes has been prepared from various alkylacetylenes with methanol in the presence of mercuric oxide and boron fluoride.

2. The ketals obtained from methyl, ethyl, *n*-propyl, *n*-butyl and *n*-amyl acetylenes are described.

3. With monohydric alcohols other than methanol, no ketals have been isolated by this method.

NOTRE DAME, INDIANA

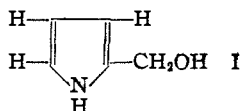
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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE RICE INSTITUTE]

Synthesis of Pyrrole Alcohols and their Derivatives

BY MILLARD S. TAGGART AND G. HOLMES RICHTER

Although the higher complex pyrrole alcohols are known in great variety, the first member of the series has not been prepared. Mingoa¹ attempted to prepare 2-pyrrolocarbinol by the action of formaldehyde on pyrromagnesium bromide and obtained a substance which seemed to be the diether of the 2,3 or 2,5 glycol. Tschelinzeff and Maxorow,² and many others, condensed formaldehyde with pyrrole and obtained several products which were considered as derivatives of the unknown 2-pyrrolocarbinol (I)



We have carefully repeated these experiments and have been able to isolate the previously unknown alcohol; however, the structure of the alcohol obtained in both cases was not the 2 isomer as expected, but the 1 isomer. This was demonstrated by preparing the unknown 2-pyrrolocarbinol by reduction of 2-pyrrolylaldehyde. This alcohol had entirely different physical prop-

erties. Additional proof of structure was afforded by preparing the 1-carbinol by the reaction of chloromethyl acetate with potassium pyrrolate and subsequent hydrolysis of the ester to the alcohol; this alcohol and its derivatives correspond in all respects to the alcohol obtained by condensing formaldehyde with either pyrrole or pyrromagnesium bromide. The determination of the number of active hydrogens by the method of Tschugaeff and Zerewitinoff also indicated that the latter was the 1 isomer as only one active hydrogen was found, whereas, if the 2 isomer were produced, two active hydrogens would be present. Several derivatives and homologs of these alcohols were prepared and are described in the experimental part.

Experimental

1. **Reaction of Pyrromagnesium Bromide with Formaldehyde.**—The Grignard solution was prepared from 9 g. of magnesium, 40.7 g. of ethyl bromide and 200 cc. of dry ether; 25 g. of pyrrole was then added to form the Grignard reagent of pyrrole. Formaldehyde, by heating 16 g. of paraformaldehyde, was passed into the solution until the contents became quite dark. The product was treated with ammonium chloride, the aqueous layer saturated with potassium carbonate and extracted with

(1) Mingoa, *Gazz. chim. Ital.*, **62**, 844 (1932).

(2) Tschelinzeff and Maxorow, *J. Russ. Phys.-Chem. Soc.*, **48**, 748 (1916).