STUDIES OF DERIVATIVES OF DIACETYLENE

REPORT No.8. THE REACTIONS OF ETHYNYLVINYL AND THIOETHYNYLVINYL ETHERS WITH CARBONYL COMPOUNDS *

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Among the reactions of ethynylvinyl ethers and thioethynyl ethers that do not affect the triple bond may be included their reaction with carbonyl compounds [1]. Although the reactions of ethynylvinyl ethers with carbonyl compounds have only been described in the literature in the single case of ethylvinylmethyl ether, no description of analogous reactions with thioethynylvinyl ethers has yet appeared.

Weygand and Leube [2] studied the reaction of ethynylvinylmethyl ether with formaldehyde at various temperatures, and used the 1-methoxypentene-1-yne-3-ol-5 (equation 1) for the synthesis of 2-desoxy-d, 1-ribose and 2desoxy-d, 1-xylose.

$$CH \equiv C - CH = CH - OCH_3 + HCHO \rightarrow CH_2(OH) - C \equiv C - CH = CH - OCH_3$$
(1)

However, reactions of ethynylvinyl ethers with carbonyl compounds proceed most readily by means of the organomagnesium complex. Thus, from ethynylvinylmethyl ether and the ethyl ester of orthoformic acid, Dornow [3] obtained the diethylacetal of 1-methoxypentene-1-yne-3-al-5, which was the first etheracetal containing a pentene-1-yne-3 chain of carbon atoms that had been described in the literature. The author hydrated the etheracetal in a methyl alcohol solution, which lead to the formation of bisacetal containing a keto group; the latter cyclized to pyrone-4. In a similar manner the author [4] synthesized the ester of methoxybutenylcarboxylic acid.

The simultaneous combination of formaldehyde and secondary amines with ethynylvinylmethyl ether was used for the preparation of ethynylvinyl aminoethers or Mannich bases [5, 6]. Thus the reaction of ethynylvinyl ethers with carbonyl compounds is of considerable interest, since it makes it possible to build up the chain of carbon atoms and increase the number of reaction centers in the molecule of the original ethers, thus increasing the synthetic possibilities of diacetylene derivatives.

In the present paper, along with a description of new examples of the reaction of ethynylvinyl ethers with the ethyl ester of orthoformic acid by means of the organo-magnesium complex (equation 2)

 $CH \equiv C-CH = CH - OR \xrightarrow{C_{2}H_{6}MgBr} BrMgC \equiv C-CH = CH - OR \xrightarrow{CH(OC_{2}H_{6})_{3}}$ (I) (I) $(C_{2}H_{5}O)_{2}CH - C \equiv C-CH = CH - OR$ (I) $R = C_{4}H_{9} (Ia); C_{6}H_{5}C_{2}H_{4} (Ib),$

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and also with formaldehyde and diethylamine (equation 3)

$$CH \equiv C-CH = CH - OR + HCHO + NH (C_{2}H_{5})_{2} \longrightarrow H_{2}O +$$

$$+ (C_{2}H_{5})_{2}N - CH_{2} - C \equiv C - CH = CH - OR \xrightarrow{CH_{3} \mathbf{I}} \longrightarrow$$
(II)
$$(II)$$

$$- - \rightarrow (C_{2}H_{5})_{2}N - CH_{2} - C \equiv C - CH = CH - OR$$

$$CH_{3} = \mathbf{I}$$
(III)
(III)
(III)
(III)
(III)

a description of the reaction of thioethynylvinyl ethers with the ethyl ester of orthoformic acid is also given. This reaction leads to the formation of a series of thioether acetals containing a pentene-1-yne-3 chain of carbon atoms (equation 4)

$$CH \equiv C - CH = CH - SR \xrightarrow{C_{4}H_{5}MgBr} BrMgC \equiv C - CH = CH - SR \xrightarrow{CH(OC_{2}H_{5})_{3}}$$

$$(C_{2}H_{5}O)_{2}CH - C \equiv C - CH = CH - SR$$

$$(IV)$$

$$R = C_{2}H_{5} (IVa); C_{4}H_{9}(IVb)$$

$$(IV)$$

$$(IV)$$

The formation of pentene-1-yne-3 etheracetals and thioetheracetals in good yield, which are stable on storage but undergo some conversion of the ethynylvinyl and thioethynylvinyl ethers, gives evidence that they still contain ethynylvinyl groups. Thus, 1, 1-diethoxy-5-phenylethoxypentene-4-yne-2, like ethylvinyl ether [7], partially and completely hydrogenates to the corresponding trialkoxypentadiene and trialkoxypentane derivatives (equation 5)

$$(C_{2}H_{\delta}O)_{2}CH-C \equiv C-CH = CH-OR \xrightarrow{H_{2}}$$

$$\longrightarrow (C_{2}H_{5}O)_{2}CH-CH = CH-CH = CH-OR \xrightarrow{H_{2}}$$

$$(V)$$

$$\longrightarrow (C_{2}H_{5}O)_{2}-CH-CH_{2}-CH_{2}-CH_{2}-OR$$

$$(VI)$$

$$R = C_{6}H_{5}C_{2}H_{4} (Va) \qquad R = C_{6}H_{5}C_{2}H_{4} (VIa)$$

$$(VIa)$$

1, 1-Diethoxy-5-thioethylpentene-4-yne-2 reacts with an alcohol solution (equation 6) similarly to ethynylvinyl thioethers [8].

$$(C_{2}H_{5}O)_{2}-CH-C\equiv C-CH=CH-SC_{2}H_{5}+HgCl_{2}+C_{2}H_{5}OH \longrightarrow$$

$$\longrightarrow HgClSC_{2}H_{5} \downarrow +HCl+[(C_{2}H_{5}O)_{2}-CH-C\equiv C-CH=CH-OC_{2}H_{5}].$$
(6)

EXPERIMENTAL

Preparation of ethynylvinylphenylethyl ether. 17 g (47% of theoretical) of ethynylvinylphenylethyl ether with b.p. 114 - 114.5° (4 mm); n_D^{20} 1.5522; d_4^{20} 1.0058; MR 54.73 were obtained from 10.7 g (0.21 M) of diacetylene, 52.2 g (0.42 M) of phenylethyl alcohol and 1.0 g of KOH at a bath temperature of 115 - 117° according to the method described previously [7]. The calculated value for $C_{12}H_{12}O$ is $4\downarrow_{L}$, MR 53.13. Analysis showed: C 83.47, 83.79; H 7.20, 7.22%. $C_{12}H_{12}O$, calculated: C 83.69; H 7.02%.

The reaction of ethynylvinyl ethers and thioethers with the ethyl ester of orthoformic acid. Into a three-necked flask, equipped with a stirrer, thermometer and dropping funnel, and containing an organo-magnesium compound obtained from 2.5 g Mg and 10.8 g C_2H_5Br in absolute ether, cooled to $-8 \div -10^\circ$, 6.2 g (0.04 M) of ethynylvinylbutyl ether was added drop by drop. After attaining room temperature, 14.0 g (0.09 M) of the ethyl ester of orthoformic acid were added to the mixture at such a rate that the temperature did not rise above 23 - 25°. Then the mix-

TABLE 1														
						MR			Found,	9%		Cal	culate	1, %
Formula	Yield,	(B.p. C; pressure in mm)	n_D^{20}	d_{4}^{20}	four	ld La	lcu- ted	υ	н			U	H	S
$C_4H_6O-CH=CH-C=C-CH(OC_2H_5)_2$ (1a)	70	133(3)	1,4698	0,9422	66,9	66	14,63	69,00 68,92	9,64 9,56			38,99	9,78	
$C_{4}H_{3}C_{2}H_{4}OCH = CH - C \equiv C - CH(OC_{2}H_{5})_{2}$ (1b)	45,3	112(7.10 ⁻³)	1,5223	1,0202	82,(90	9,50	74,05 74,09	8,10			74,42	8,08	ł
$C_2H_5S-CH=CH-C\equiv C-CH(OC_2H_5)_2$ (1Va)	58,8	127(4)	1,5125	0,9908	64,5	90	1,72	61,67 61,85	8,71 8,33	, 14, 14,	35.	61,64	8,46	14,96
$C_4H_9SCH=CH-C\equiv CCH(OC_2H_5)_2$ (1Vb)	80,0	147(4)	1,5045	0,9713	73,9		0,95	64,03 64,08	0,25 0,25		19	64,42	9,15	13, 23
TABLE 2														
		(IW			Foun	d, %		Ĭ	Calcul	ated, 9	
Compound	<u>d</u> i	۰۹، د: essure in m)	n_D^{20}	$d_{\frac{4}{4}}^{20}$	found	calcu- lated	U		z		0	H	z	-
$C_{10}H_{17}O-CH=CH-C\equiv C-CH_2-N(C_2H_6)_2$ (11b)	11	(4-174,5) (2,3)	1,5108	0,9657	89,72	88,59	78,41 78,57	11,01	4,90 4,77		8,84 1	0,80	4,84	1
$C_6H_6CH_2O-CH=CH=CH_2C-CH_2-N(C_2H_5)_2$	<u></u>	159(3)	1,5345	0,9786	77,36	75,54	78,76	8,88		7	8,97	8,69	5,76	١
(11c) Iodomethyl derivatives		M.P.		ļ	!	1	79,04 52,76	8,85 6,31					1	
(IIIc)		33-83, 5					52,63	6,29	<u></u>	2,80 52,99	2,99	6,27		32,93

ture was stirred for four hours and allowed to stand over night. The thick reaction mixture was treated with an aqueous solution of ammonium chloride until two layers appeared. The upper layer, after drying over sodium sulfate and removal of the solvent, was distilled in vacuo. Obtained: fraction I, b.p. $35 - 45^{\circ}$ (3 mm); 1.2 g; fraction II, b.p. $122 - 126^{\circ}$ (3 mm); 11.7 g; residue - 3.8 g.

Fraction I consisted of original unreacted materials. Fraction II consisted of 1, 1-diethylxy-5-butoxypentene-4-yne-2 (Ia) or of the diethyl acetal of butoxybutenylal, b.p. 133° (4mm); n_D^{20} 1.4698; d_4^{20} 0.9422; found MR 66.61; calculated for $C_{13}H_{22}O_{3,j=j}MR$ 63.53; yield 70.0% of theoretical. In similar fashion 1, 1-diethoxy-5-phenyl-ethoxy-pentene-4-yne-(2) (Ib), 1, 1-diethoxy-5-thioethylpentene-4-yne-2 (IVa) and 1, 1-diethoxy-5-thiobutylpentene-4-yne-2 (IVb) were prepared from ethynylvinylphenylethyl, ethynylvinylthioethyl and ethynylvinylthiobutyl ethers. The yields, constants and analytical results are shown in Table 1.

TABLE &

Y Lyn (1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 19	Fo of	un th	d, % eoret.
Original substance	thioether	acetal	ethylmer captomer curochlo ride
$C_{2}H_{5}S-CH=CH-C\equiv C-CH(OC_{2}H_{5})_{2}$ $C_{4}H_{9}S-CH=CH-C\equiv C-CH(OC_{2}H_{5})_{2}$	97, 97,	34 79 -	99,0 100,0 99,8 99,1

Hydregenation of 1, 1-diethoxy-5-phenylethoxybutene- 4-yne-2. 3.2 g of the diethyl acetal of phenylethoxybutenylal were hydrogenated over platinum oxide at room temperature (according to Adams). In the course of 11 hours, 820 ml of hydrogen were consumed. 0.9 g (28.1% of theoretical) of 1, 1-diethoxy-5-phenylethoxypentadiene-2,4 (Va) were obtained by fractional distillation; b.p. 117 - 117.5° (3 mm); n_D^{20} 1.5043; d_4^{20} 1.0004; found MR 81.15; calculated for C₁₇-H₂₄O₃5 F MR 81.10. Found: C 74.01, 73.88; H 8.73, 8.68%. C₁₇H₂₄O₃. Calculated: C 73.88; H 8.75%. 0.7 g (30.4% of theoret.) of 1, 1-diethoxy-5-phenylethoxypentane (VIa), b.p. 128° (3 mm), n_D^{20} 1.4858 were also obtained. Found: C 72.57, 72.82; H 9.44, 9.62%. C₁₇H₂₈O₃. Calculated: C 72.81; H 10.00%.

Decomposition of thioetheracetals by an alcoholic solution of mercuric chloride. The decomposition was carried out by the method described in [8]. The results of the experiment are shown in Table 3.

Preparation of Mannich bases from ethynylvinyl ethers (equation 3). In a flask supplied with a stirrer, thermometer and reflux condenser, were placed 6.7 g (0.054 M) of freshly distilled ethynylvinylbutyl ether, 2.1 g (0.07 M) of paraformaldehyde, 5.4 g (0.07 M) of diethylamine and 8 ml of ethyl alcohol. The reaction mixture was stirred and heated to boiling (82°) for five hours. After cooling, the mixture was fractionally distilled and 2 g of the original ethynylvinylbutyl ether b.p. 55° (9 mm) were recovered and 5.1 g of a substance that was found to be 1-butoxy-5diethyl-aminopentene-1-yne-3 (IIa). Its yield was 64.6% of theoret.; b.p. 130 - 130.5° (8 mm); n_D^{20} 1.4782; d_4^{20} 0.8854; found MR 66.92; calculated for $C_{13}H_{23}$ ON MR 64.69. Found: C 74.58, 74.30; H 11.22, 11.17; N 7.06, 7.18%. $C_{13}H_{23}$ ON, calculated: C 74.53; H 11.16; N 6.69%.

<u>Preparation of the iodomethyl derivative of the base.</u> 0.8 g of the Mannich base were mixed with an ether solution of 0.6 g of methyl iodide while the mixture was cooled with ice water and stirred. The solution, which had become turbid, was heated to boiling for one hour. Colorless crystals of the iodomethyl derivative (IIIa) deposited from the lower oily layer on standing which, after being twice recrystallized from an ether solution of ethyl alcohol had a m.p. of 75 - 75.5°. Found: C 47.98, 47.80; H 7.20, 7.34; N 36.34, 36.21%. C₁₄H₂₆ON, calculated: C 47.78; H 7.46; N 36.12%.

In a similar manner the corresponding bases were obtained from ethynylvinyl- β -decalyl and ethynylvinylbenzyl ethers: 1- β -decaloxy-5-diethylaminopentene-1-yne-3 (IIb) with a yield of 56.6% and also their iodomethyl derivatives (IIIb) and (IIIc). Their constants and analytical data are shown in Table 2. The iodomethyl derivative of decahydroxydiethylaminopentenyne (IIIb) was separated as an uncrystallizable oil.

SUMMARY

1. The conditions for the reaction of thioethylvinyl ethers with the ethyl ester of orthoformic acid by means of the organo-magnesium complex were studied.

2. A series of new etheracetals and thioetheracetals containing a pentenyne chain of carbon atoms was synthesized. Trialkoxypentadienes-1, 3 and saturated etheracetals, not previously described, were obtained. Ethynylvinylphenylethyl ether was also synthesized. 3. New Mannich bases were synthesized by the reaction of ethynylvinyl ethers with paraformaldehyde and diethylamine, and iodomethyl derivatives of them were obtained.

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