CHEMISTRY

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1960

SovietRxiv

Abstract

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SYNTHESIS OF UNSATURATED ETHER ACETALS, THIOETHER ACETALS, AND MERCAPTALS

The synthesis of various unsaturated ether acetals, thioether acetals, and dimercaptals is of interest for synthetic chemistry, since it can serve as one of the principal stages in the process of extending a chain of carbon atoms in molecules containing alkoxy and alkylthio groups. One method for the synthesis of the named compounds may be the interaction of ethynylvinyl ethers and thioethers, obtained from diacetylene [1,2], with carbonyl compounds. Study of the reaction of ethyl orthoformate with certain simple [3] and substituted simple vinyl ethers led to the development of a general method for the synthesis of tetraethyl acetals of various β-dicarbonyl compounds [4].

For ethynylvinyl thioethers, the reaction under study has not been described in the literature. Among ethynylvinyl ethers, only ethynylvinyl methyl ether has been examined in this reaction; ethyl orthoformate was added to it through a magnesium-organic complex [5]. In the present work, we report the synthesis of alkoxyacetals and alkylthioacetals containing a pentenynic chain of carbon atoms with a conjugated system of multiple bonds, as well as an interesting reaction involving the replacement of alkoxyl groups by mercaptoalkyl radicals in these compounds. The synthesis of unsaturated ether acetals and thioether acetals was carried out according to the following scheme:

$$\mathrm{CH\equiv C{-}CH{=}CH{-}XR} \xrightarrow{\mathrm{RMgBr}} \mathrm{BrMgC\equiv C{-}CH{=}CH{-}XR} \xrightarrow{\mathrm{CH(OC_2H_5)_3}}$$

$$\rightarrow \mathrm{(C_2H_5O)_2CH{-}C\equiv C{-}CH{=}CH{-}XR}$$

RX = C_4H_9O (Ia); $C_6H_5CH_2O$ (Ib); $C_6H_5CH_2CH_2O$ (Ic); RX = C_2H_5S (IIa);

C_4H_9S (IIb)

and was completed with a good yield of final products containing alkyl and aralkyl radicals. In view of the fact that the sulfur-containing ether acetals obtained had not been studied, it was advisable to investigate their properties and, in particular, the addition of mercaptans to them, which should have led to mixed mercaptoacetals. However, in the interaction of thioether acetals with ethyl mercaptan, the main product proved to be bis-(diethylmercaptal)-pentyne-3-dial-1,5 (III), the formation of which occurs as a result of exchange of alkoxyl groups for mercaptoalkyl groups, and addition of a mercaptan molecule to the double bond of the initial thioether acetal, followed by disproportionation:

$$\left.\begin{array}{l} R'S{-}CH{=}CH{-}C\equiv C{-}CH(OC_2H_5)_2 \\ R''O{-}CH{=}CH{-}C\equiv C{-}CH(OC_2H_5)_2 \end{array}\right\} \xrightarrow{4RSH} RS\backslash CH{-}CH_2{-}C\equiv C{-}CH\backslash SR + 4R''OH$$

$$\begin{array}{c} RS/ \qquad\qquad\qquad\qquad /SR \\ \text{(III)} \end{array}$$

$$R' = R = C_2H_5 \text{ (IIIa)}; \quad R'' = C_4H_9; \quad R = C_2H_5 \text{ (IIIb)}$$

It is known ([6–9]) that alkoxy groups in acetals are mobile; however, there are no indications in the literature that they are capable of being exchanged for mercaptoalkyl radicals upon interaction with mercaptans. It was therefore of interest to determine whether this reaction is characteristic of the given acetals or is of a general nature. For this purpose we studied the reaction of various acetals of acetaldehyde, 3-butoxybutanal, and tetrolic aldehyde with ethyl mercaptan.

In all cases this reaction was accompanied by exchange of the alkoxy and aralkoxy groups of the acetal for the mercaptoalkyl radical of the mercaptan taken, as a result of which the corresponding mercaptals were obtained:

$$CH_3 - CH(OR)_2 + 2C_2H_5SH \rightarrow CH_3 - CH(SC_2H_5)_2, \text{ (IV)}$$

$$R = C_2H_5 \text{ (IVa)}; \quad C_4H_9 \text{ (IVb)};$$

$$CH_3 - CH(OC_4H_9) - CH_2 - CH(OC_4H_9)_2 + 2C_2H_5SH \rightarrow$$

$$\rightarrow CH_3 - CH(OC_4H_9) - CH_2 - CH(SC_2H_5)_2, \text{ (V)}$$

$$CH_3 - C{\equiv}C - CH(OCH_2C_6H_5)_2 + 2C_2H_5SH \rightarrow CH_3 - C{\equiv}C - CH(SC_2H_5)_2; \text{ (VI)}$$

which indicates that the reaction described is of a general nature.

As is known ([10]), the synthesis of acetaldehyde mercaptal from vinylethyl sulfide and ethyl mercaptan is complicated by the competing addition of the mercaptan contrary to Markovnikov' s rule, as a result of which the yield of mercaptal is very low. The side reaction is not completely suppressed even in the presence of SO_2 and with the greatest possible removal of atmospheric oxygen. The synthesis of mercaptals from acetylene and mercaptans in the presence of CuCl ([11]) also does not make it possible to obtain mercaptals in yields greater than 50%.

The structures of the isolated mercaptals were proved by reaction with an alcoholic solution of mercuric chloride ([2,10]).

1. Synthesis of ether acetals and thioether acetals. Diethyl acetal of 5-benzyloxypent-4-yn-2-al (Ib) was obtained (in a flask with a stirrer and thermometer) from the Mg-organic complex (1.0 Mg and 4.7 g of C_2H_5Br) in ether and 4.5 g (0.02 mole) of ethynylvinyl benzyl ether, added at $-10°$, followed by the addition of 6.1 g of the ethyl ester of orthoformic acid at a temperature not above 25°. After treatment of the mixture with an aqueous ammonium chloride solution, the ether layer was dried with sodium sulfate and distilled in vacuo. A 5.6 g fraction, b.p. $108 - 110°$ (0.007 mm), was isolated; after redistillation it had the constants of the diethyl acetal of benzyloxypentynal, given in Table 1.

In the same way, the diethyl acetals of 5-butoxy- and 5-phenylethoxypentynals (Ia and Ic) were synthesized; their constants and yields are presented in Table 1.

The diethyl acetals of 5-ethylmercapto- and 5-butylmercapto-pentynals (IIa and IIb) were synthesized from ethynylvinyl thioethyl and ethynylvinyl thiobutyl ethers under conditions analogous to those described. For the constants see Table 1.

2. Synthesis of bis-(diethylmercaptal) of pentyn-3-dial-1,5 (III). A sealed ampoule containing 8.3 g (0.04 mole) of diethyl acetal of 5-ethylmercaptopentynal (IIa) and 14.9 g (0.24 mole) of ethyl mercaptan was heated on an oil bath at $115 - 120°$ for 16 h. By distillation, 4.6 g of a fraction, b.p. $130 - 2°$ (0.01 mm), was isolated; on redistillation it had the constants of bis-(diethylmercaptal)-pentyn-3-dial-1,5 (IIIa), given in Table 1. The results of titration with mercuric chloride of the fraction $120 - 2°$ (0.008 mm) (IIIa) are also given there. Similarly, from the diethyl acetal of 5-butoxypentynal (IIIb), bis-(diethylmercaptal) pentyn-3-dial-1,5 (IIIa) was obtained in 50.0% of theory. B.p. $123 - 5°$ (0.01 mm); n_D^{20} 1.6030.

3. Synthesis of diethylmercaptal from acetals of acetaldehyde (IV). 1) 8 g (0.045 mole) of dibutyl acetal of acetaldehyde and 12.4 g (0.18 mole) of ethyl mercaptan were heated in an ampoule for

16 h on a boiling water bath. Distillation in vacuum gave 5.8 g (84.2%) of acetaldehyde diethyl mercaptal, which after redistillation (5.1 g) had the constants

listed in Table 1.

2) In a similar manner, from 5.9 g of acetaldehyde diethyl acetal and 12.4 g of ethyl mercaptan, on heating for 6 h, 5.7 g (76.5%) of a fraction of acetaldehyde diethyl mercaptal was obtained, b.p. 80–82° (21 mm); n_D^{20} 1.5010. Titration with sublimate of the fraction 80–82° (21 mm) showed a 94.63% content of diethyl mercaptal.

4. Synthesis of 3-butoxybutanal diethyl mercaptal (V). From 5.5 g (0.02 mole) of dibutyl acetal of 3-butoxybutanal ([6]) and 5 g (0.08 mole) of ethyl mercaptan, on heating for 16 h, 4.5 g (90% of theory) of a fraction 123–7° (5 mm) was obtained, which proved to be 3-butoxybutanal diethyl mercaptal; after redistillation it had the constants listed in Table 1.

5. Synthesis of tetrolic aldehyde diethyl mercaptal (VI). From 2.6 g (0.012 mole) of dibenzyl acetal of tetrolic aldehyde (I) and 3 g (0.05 mole) of ethyl mercaptan, after heating at 110–120° for 24 h, 1 g of a fraction 130–135° (4 mm) of tetrolic aldehyde diethyl mercaptal was isolated; after redistillation it had the constants listed in Table 1.

The reaction of the isolated mercaptals with an alcoholic solution of sublimate, followed by titration with HCl, was carried out according to the procedure described earlier ([2],[10]). The titration results are presented in Table 1.

Thus, conditions have been found for the synthesis of ether acetals and thioether acetals of the pentynal series containing alkyl and aralkyl radicals. The reaction of acetals of various aldehydes with mercaptans has been studied. It has been shown that this reaction is general in character and can serve as a convenient method for the synthesis of various mercaptals and bismercaptals from the corresponding

Table 1

Compound obtained	Yield from theory, %	B.p., °C (mm)	n_D^{20}	d_4^{20}	MR_D found	MR_D calc.	Found, % C	Found, % H	Found, % S	Calculated, % C	Calculated, % H	Calculated, % S	Titration with 0.1 N $HgCl_2$, weighed, g	Titration with $HgCl_2$: NaOH, ml	Titration with $HgCl_2$: mercaptal, %
Ia. $C_4H_9OCH(R)CH=CH-C\equiv CH(OC_2H_5)_2$	70.0	133 (3)	1.4698	0.9426	86.99	84.63	69.00	9.64	—	68.99	9.78	—	—	—	—
Ib. $C_4H_9OCH(R)CH=CH-C\equiv CH(OC_2H_5)_2$	60.8	119.5 (0.01)	1.5247	1.1242	70.90	69.69	68.29	9.65	—	73.82	7.74	—	—	—	—
Ic. $C_6H_5CH_2OCH(R)CH=C\equiv C-CH(OC_2H_5)_2$	45.3	112 (0.007)	1.5228	1.0202	82.06	79.50	73.86	7.90	—	74.42	8.08	—	—	—	—

Compound obtained	Yield from the theory, %	B.p., °C (mm)	n_D^{20}	d_4^{20}	MR_D found	MR_D calc.	Found, % C	Found, % H	Found, % S	Calculated, % C	Calculated, % H	Calculated, % S	Titration with $HgCl_2$, weighed, g	Titration with 0.1 N NaOH, ml	Titration with $HgCl_2$: mercaptal, %
IIa. $C_2H_5SCH(CH=CH-C\equiv C-CH(OC_2H_5)_2$	58.8	127 (4)	1.5126	0.9908	84.96	61.72	74.64	8.72	14.85	61.64	8.46	14.96	–	–	–
IIb. $C_4H_9SCH(CH=CH-C\equiv C-CH(OC_2H_5)_2$	80.0	147 (4)	1.5046	0.9717	93.95	70.95	74.09	8.10	14.95	64.42	9.15	13.23	–	–	–
III. $(C_2H_5S)_2CH-CH_2-C\equiv CH(SC_2H_5)_2$	50–60	122 (0.08)	1.6035	1.0890	97.25	92.05	67.64	8.77	39.23	50.61	7.83	41.55	0.1491	15.77	79.73
IV. $CH_3-CH(SC_2H_5)_2$	84.2	78.5 (16)	1.5020	0.9724	46.72	45.85	64.03	9.24	31.39	47.94	9.37	42.66	0.1492	24.79	97.45
V. $CH_3-CH(SC_4H_9)-CH_2-CH(SC_2H_5)_2$	90.0	123.5–124 (4)	1.4830	0.9497	75.34	75.20	64.08	9.99	13.81	57.52	10.49	25.60	0.1912	25.14	98.82
VI. $CH_3-C\equiv C-CH(SC_2H_5)_2$	50.0	128–130 (3.5)	1.5479	1.0482	52.82	53.02	64.38	10.44	25.71	57.43	10.49	25.60	0.2113	31.76	99.04
													0.1891	19.86	99.06

···corresponding acetals, ether acetals, and thioether acetals. The addition of mercaptan to the thioalkylvinyl end of the molecule, leading to a mercaptal grouping, is evidence of the special features of the double bond, which is conjugated with the triple bond in molecules of ether- and thioether acetals.

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Received
13 VI 1960

REFERENCES

1. M. F. Shostakovskii, A. V. Bogdanova, G. I. Krasil' nikova, *Usp. khim.*, **28**, 1053 (1959); *DAN*, **114**, 1250 (1957).

2. A. V. Bogdanova, M. F. Shostakovskii, G. I. Plotnikova, *DAN*, **120**, 301 (1958); **124**, 107 (1959).

3. T. V. Protopopova, A. P. Skoldinov, *ZhOKh*, **27**, 57 (1957).

4. L. A. Yanovskaya, S. S. Yufit, V. F. Kucherov, *Izv. AN SSSR, OKhN*,

1960, No. 8.

5. A. Dornow, F. Ische, *Angew. Chem.*, **67**, 653 (1955).
6. A. E. Chichibabin, *ZhRFKhO*, **35**, 1284 (1903); **37**, 180 (1905).
7. M. F. Shostakovskii, V. A. Gladyševskaya, *Izv. AN SSSR, OKhN*, **1955**, 140, 344.
8. M. F. Shostakovskii, A. V. Bogdanova, *DAN*, **100**, No. 1, 89 (1955).
9. M. F. Shostakovskii, M. R. Kulibekov, *ZhOKh*, **28**, 578 (1958).
10. M. F. Shostakovskii, E. N. Prilezhaeva, N. I. Uvarova, *Izv. AN SSSR, OKhN*, **1954**, 517, 526.
11. W. Reppe, *Ann.*, **601**, 111 (1956).

Note: Figure translations are in progress. See original paper for figures.