CHEMISTRY OF ACETALS.

COMMUNICATION 19. STRUCTURE OF ACETALS AND THEIR REACTIVITY IN REACTION WITH ETHYL VINYL ETHER

(UDC 542.951.2)

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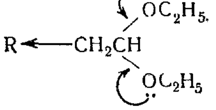
Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 9,
pp. 1638-1644, September, 1965
Original article submitted June 28, 1963

We have pointed out previously [1, 2] that the following acetals do not react with ethyl vinyl ether under the usual conditions: ethoxyacetaldehyde, bromoacetaldehyde, ethyl malonaldehydate, acetoacetaldehyde, and propiolaldehyde diethyl acetals and glyoxal and 2-butynedial bis [diethyl acetals]. The same has been observed by other authors for the diethyl acetals of ethoxy- and bromo-acetaldehydes [3], 5-alkoxy- and 5-(ethylthio)-4-penten-2-ynals [4], and ethyl malonaldehydate [5].

In the case of 5-alkoxy- and 5-(ethylthio)-4-penten-2-ynal acetals it was shown that under severe conditions in a sealed tube reaction with ethyl vinyl ether goes with formation of a mixture of telomers with a low content of the primary growth product [4].

We were interested in the cause of such behavior in these acetals, and we decided to make a more detailed study of the relation between the structure of the acetals and their reactivity in reaction with ethyl vinyl ether. For this purpose we carefully analyzed the whole of the experience accumulated in the course of our investigations and all data in the literature [1], and we also repeated a number of reactions between acetals of various structures and ethyl vinyl ether under comparable conditions and carried out some reactions for the first time.

From an examination of the results according to the types of acetals the following main characteristic features emerge. In the case of saturated monoacetals, no acetal with an electron-accepting substituent in the α-position relative to the acetal grouping (acetals No. 4, 6, 7, 10, 12) reacts with ethyl vinyl ether. Acetals with an electron-accepting substituent in the β-position relative to the acetal grouping (acetals No. 5, 8, 9) react with ethyl vinyl ether with low yields of primary growth products. The presence of an electron-accepting substituent in a more remote position relative to the acetal grouping (acetal No. 11) has scarcely any effect on the reactivity of the acetal in reaction with ethyl vinyl ether. The nature of the alkyl substituent has no appreciable effect on the reaction with ethyl vinyl ether (acetals No. 1-3; also data in the review [1]). We may conclude, therefore, that electron-accepting substitutents lower the reactivity of saturated monoacetals in reaction with ethyl vinyl ether as a result of the -I effect:

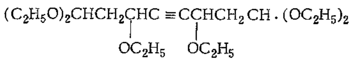
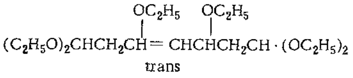
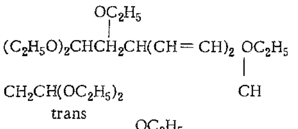
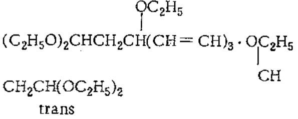


$$R \longleftarrow CH_2CH\begin{matrix}\ddot{O}C_2H_5\\ \ddot{O}C_2H_5\end{matrix}$$

This fact places a considerable limitation on the field of application of the chain growth of acetals with the aid of ethyl vinyl ether, making it impossible to use this reaction for the synthesis of ω-substituted acetals and aldehydes of the types $RCH_2CH(OC_2H_5)CH_2CH(OC_2H_5)_2$ and $RCH_2CH{=}CHCHO$, in which R is an electron-accepting substituent such as Hal, OR, COOR, and CN.

In the group of α,β-unsaturated acetals we must refer in the first place to the inability of propiolaldehyde acetal (No. 13) to react with ethyl vinyl ether under the usual conditions. This is probably a general property of

TABLE

No.	Acetal $RCH_2CH(OC_2H_5)_2$	Chain-growth product $R-CH_2CH(OC_2H_5)CH_2CH(OC_2H_5)_2$	Yield, % on $CH_2=CHOC_2H_5$
Saturated Monoacetals			
Reaction conditions: catalyst $BF_3(C_2H_5)_2O$, 35-40°, molar ratio acetal: $CH_2=CHOC_2H_5 = 2:1$			
1	H	H	65-70
2	C_2H_5	C_2H_5	65-70
3	$i\text{-}C_3H_7CH(OC_2H_5)_2$	$i\text{-}C_3H_7CH(OC_2H_5)CH_2CH(OC_2H_5)_2$	60-65
4	Cl	Cl	Scarcely any formed*
5	$ClCH_2$	$ClCH_2$	8-10
6	Br	Br	Scarcely any formed
7	C_2H_5O	C_2H_5O	"
8	$C_2H_5OCH_2$	$C_2H_5OCH_2$	10-12*
9	$CH_3CH(OC_2H_5)$	$CH_3CH(OC_2H_5)$	30-35
10	C_2H_5OOC	C_2H_5OOC	Scarcely any formed
11	$C_2H_5OOC(CH_2)_3$	$C_2H_5OOC(CH_2)_3$	70†
12	CH_3CO	CH_3CO	Scarcely any formed
Unsaturated Monoacetals			
Reaction conditions: catalyst $BF_3(C_2H_5)_2O$, 35-40°, molar ratio acetal: $CH_2=CHOC_2H_5 = 1:1$			
13	$HC\equiv CCH(OC_2H_5)_2$	$HC\equiv CCH(OC_2H_5)CH_2CH(OC_2H_5)_2$	Scarcely any formed
14	$CH_3CH=CHCH(OC_2H_5)_2$	$CH_3CH=CHCH(OC_2H_5)CH_2CH(OC_2H_5)_2$	65-70
15	$(CH_3)_2C=CHCH(OC_2H_5)_2$	$(CH_3)_2C=CHCH(OC_2H_5)CH_2CH(OC_2H_5)_2$	62-68‡
16	$C_2H_5OOCCH=CHCH(OC_2H_5)_2$	$C_2H_5OOCCH=CHCH(OC_2H_5)CH_2CH\cdot(OC_2H_5)_2$	35-40*
17	$C_2H_5OOC(CH=CH)_2CH(OC_2H_5)_2$	$C_2H_5COC(CH=CH)_3CH(OC_2H_5)CH_2CH\cdot(OC_2H_5)_2$	65-70
18	$C_2H_5OOC(CH=CH)_3CH(OC_2H_5)_2$	$C_2H_5COC(CH=CH)_3CH(OC_2H_5)CH_2CH\cdot(OC_2H_5)_2$	70-75
Reaction conditions: catalyst $BF_3(C_2H_5)_2O$, 35-40°, molar ratio acetal: $CH_2=CHOC_2H_5 = 2:1$			
19	$CH_2=CH$	$CH_2=CH$	20-25
20	$CH_3CH=CHCH(OC_2H_5)$	$CH_3CH=CHCH(OC_2H_5)$	20-25
21	$C_2H_5OOCCH=CH$	$C_2H_5OOCCH=CH$	Scarcely any formed*
No.	**Diacetal $(C_2H_5O)_2CHRCH(OC_2H_5)_2$**	**Chain-growth product $(C_2H_5O)_2CHRCH(OC_2H_5)-CH_2CH(OC_2H_5)_2$**	**Yield,% on $CH_2=CHOC_2H_5$**
Saturated Diacetals			
Reaction conditions: catalyst $BF_3(C_2H_5)_2O$, 35-40°, molar ratio acetal: $CH_2=CHOC_2H_5 = 1:1$			
22	–	–	Scarcely any formed
23	$-CH_2-$	$-CH_2-$	40-45
24	$-CH(CH_3)-$	$-CH(CH_3)-$	55-58
25	$-CHBr-$	$-CHBr-$	Scarcely any formed*
Unsaturated Diacetals**			
Reaction conditons: catalyst $BF_3(C_2H_5)_2O$, 35-40°, molar ratio acetal: $CH_2=CHOC_2H_5 = 1:2$			
26	$(C_2H_5O)_2CHC\equiv CCH(OC_2H_5)_2$	 $(C_2H_5O)_2CHCH_2\underset{OC_2H_5}{CH}C\equiv C\underset{OC_2H_5}{CH}CH_2CH\cdot(OC_2H_5)_2$	Scarcely any formed
27	$(C_2H_5O)_2CHCH=CHCH(OC_2H_5)_2$ cis	 $(C_2H_5O)_2CHCH_2\overset{OC_2H_5}{CH}=CH\overset{OC_2H_5}{CH}CH_2CH\cdot(OC_2H_5)_2$ trans	65-70
28	$(C_2H_5O)_2CHCH=CHCH(OC_2H_5)_2$ trans	"	65-70
29	$(C_2H_5O)_2CH(CH=CH)_2CH(OC_2H_5)_7$ trans	 $(C_2H_5O)_2CHCH_2\overset{OC_2H_5}{CH}(CH=CH)_2\,\underset{CH}{OC_2H_5}$ $CH_2CH(OC_2H_5)_2$ trans	50-55
30	$(C_2H_5O)_2CH(CH=CH)_3CH(OC_2H_5)_2$ trans	 $(C_2H_5O)_2CHCH_2\overset{OC_2H_5}{CH}(CH=CH)_3\cdot\underset{CH}{OC_2H_5}$ $CH_2CH(OC_2H_5)_2$ trans	50-55

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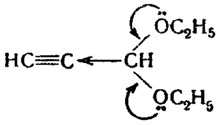
*The reaction was carried out for the first time in this work.

†Data from literature [6]; the reaction was conducted at 50°.

‡Data in literature; see the review [1].

**For unsaturated diacetals even with a large excess of the diacetal the product of growth at only one of the acetal groupings was scarcely formed at all; the yields evaluated here, therefore, refer to products of growth at both ends of the diacetal.

α,β -acetylenic acetals, for not a single case of the growth of acetylenic acetals under the usual conditions has been described in the literature; as stated above [4], under severe conditions the yield of primary growth product is small. The low reactivity of propiolaldehyde acetal in reaction with ethyl vinyl ether must probably be attributed to the electron acceptor nature of the ethynyl group:

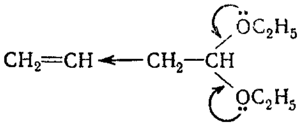


$$HC\equiv C\leftarrow CH(OC_2H_5)_2$$

From our own data and numerous data in the literature [1] it follows that all α,β -olefinic acetals react with ethyl vinyl ether. Even when electron-accepting substituents are present in the acetal molecule (see, e.g., acetal No. 16), the reaction goes, though in this case the yield is somewhat lower than in the case of acetals containing a more remote ethoxycarbonyl group. The high reactivity of α,β -olefinic acetals in reaction with ethyl vinyl ether is explained by the favorable influence of the + M effect arising in the molecules of these acetals:

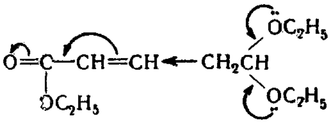
$$R-CH{=}CH-CH(OC_2H_5)_2$$

In fact, the displacement of the double bond from the α,β - to the β,γ -position relative to the acetal grouping with consequent removal of the + M effect immediately results in a fall in the reactivity of the acetals in reaction with ethyl vinyl ether (acetal No. 19), all the more in that a vinyl group in the β,γ -position may have a weak -I effect:



$$CH_2{=}CH\leftarrow CH_2-CH(OC_2H_5)_2$$

When a suitable substituent is present a strong -M effect may arise, e.g. (acetal No. 21),



$$O{=}C(OC_2H_5)-CH{=}CH\leftarrow CH_2CH(OC_2H_5)_2$$

and the acetal loses its ability to react with ethyl vinyl ether under the usual conditions, as occurs in saturated acetals substituted in the α-position by powerful electron-accepting substituents.

If we compare the data on the growth of saturated and unsaturated diacetals (see table), it is obvious in the first place the whereas saturated diacetals can be caused to grow preferentailly at one of the acetal groupings (acetals No. 23, 24), this type of growth does not occur for unsaturated diacetals. All our attempts to produce unsymmetrical growth of the diacetals of malealdehyde and fumaraldehyde on one end only by the use of one mole of ethyl vinyl ether per mole of the diacetal were unsuccessful. Irrespective of the conditions growth occurs at both ends, and as a result 1,1,3,6,8,8-hexaethoxy-4-octene is formed in 50% yield, based on the vinyl ether. This peculiarity in the behavior of diacetals can be explained if we examine the reaction scheme for the growth of unsaturated and saturated acetals: (see structure on top of the following page).

The two-end growth reactions of the symmetrical diacetals (I) and (IV) are undoubtedly stagewise reactions. In the case of the acetal (I), in the first stage the saturated diacetal (II) containing an electron-accepting substituent in the β -position relative to both acetal groupings is formed; and the further growth of the diacetal (II) leads to the diacetal (III) in which there are two electron-donating substituents, each in the β -position relative to an acetal grouping. As already stated above, the presence of an electron-accepting group in the β -position relative to the acetal grouping lowers the reactivity of the latter somewhat toward ethyl vinyl ether, and it may be expected that in the stagewise reaction (1) k_1 will be greater than k_2, so that when excess of the acetal (I) is used it can be expected that the acetal (II) will accumulate in the mixture, which is what is actually observed.

$$1)\ (C_2H_5O)_2CHCH_2CH(OC_2H_5)_2 \xrightarrow[k_1]{CH_2=CHOC_2H_5}$$

(I)

$$(C_2H_5O)_2CHCH_2CH(OC_2H_5)CH_2CH(OC_2H_5)_2 \xrightarrow[k_2]{CH_2=CHOC_2H_5}$$

(II)

$$(C_2H_5O)_2CHCH_2CH(OC_2H_5)CH_2CH(OC_2H_5)CH_2CH(OC_2H_5)_2$$

(III)

$$2)\ (C_2H_5O)_2CHCH=CHCH(OC_2H_5)_2 \xrightarrow[k_3]{CH_2=CH(OC_2H_5)_2}$$

(IV)

$$(C_2H_5O)_2CHCH=CHCH(OC_2H_5)CH_2CH(OC_2H_5)_2 \xrightarrow[k_4]{CH_2=CHOC_2H_5}$$

(V)

$$(C_2H_5O)_2CHCH_2CH(OC_2H_5)CH=CHCH(OC_2H_5)CH_2CH(OC_2H_5)_2$$

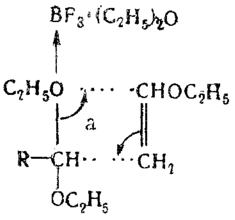
(VI)

We find a quite different situation when we examine the stagewise growth reaction of the unsaturated diacetal (IV). In this case at the first stage the unsymmetrical diacetal (V) is formed, and this contains an α,β-unsaturated acetal grouping and a saturated acetal grouping in the β-position relative to which there is an electron-accepting substituent. It has been stated above that no substituents (apart from those able to show a mesomeric effect, such as the ethoxycarbonyl group) have any effect on the reactivity of α,β-unsaturated acetals, so that it would not be expected that k_3 would differ greatly from k_4 for reaction at the unsaturated acetal grouping; but if $k_3 \approx k_4$, then it will be practically impossible to arrest the growth reaction at the first stage, and this is actually found.

The difference in behavior between saturated and unsaturated monoacetals may be explained analogously. It is known [1] that to attain maximum yields of primary products in the case of saturated monoacetals it is necessary to use two-and three-fold excesses of the acetal, for otherwise a mixture of telomers of various compositions is formed. On the other hand, unsaturated acetals give primary growth products in high yield when equimolecular proportions of acetal and ethyl vinyl ether are used.

A certain difference between saturated mono- and di-acetals must also be mentioned. In the case of saturated monoacetals, by increase in the acetal: vinyl ether ratio the formation of higher telomers can be suppressed almost completely [7], whereas for diacetals of the malonaldehyde diacetal type the formation of products of further growth cannot be suppressed even by the use of a fivefold excess of the diacetal.

The powerful influence of electronic factors on the reactivity of acetals in reaction with vinyl ethers is undoubtedly related to the mechanism of this reaction. We consider it logical to regard the mechanism of the addition of acetals to vinyl ethers as a cyclic electron transfer process with four centers:



This scheme shows the effect of the group R on the case of reaction with ethyl vinyl ether in a particularly clear and graphic manner. In fact, since the second reaction component (ethyl vinyl ether) does not change and constant reaction conditions are used (in particular, boron trifluoride etherate is used as catalyst), the reactivities of the acetals will differ only in virtue of their dependence on the nature of the group R. If this group R promotes withdrawal of electrons from the acetal grouping, then it is quite obvious that electron transfer in the direction "a" will be hindered right up to the point at which such a transfer is quite impossible, and the reactivity of the acetal in reaction with ethyl vinyl ether will fall correspondingly. On the other hand, if the group R donates electrons, electron transfer in the direction "a" will be facilitated.

EXPERIMENTAL

The same type of procedure was used in all the experiments on the chain growth of acetals. In the case of saturated monoacetals: to 0.05 mole of the acetal (the diethyl acetal of acetaldehyde, butyraldehyde, isobutyraldehyde, chloroacetaldehyde, 3-chloropropionaldehyde, bromoacetaldehyde, ethoxyacetaldehyde, 3-ethoxypropionaldehyde, ethyl malonaldehydate, acetoacetaldehyde, or 3-ethoxybutyraldehyde) we added five drops of boron trifluoride etherate and then a solution of 0.05 mole of ethyl vinyl ether in 0.05 mole of the acetal dropwise at such a rate that the temperature did not exceed 35-40° (cooling was applied when necessary). The mixture was heated for one hour at 45-50°, cooled, and treated with shaking with a 10-15% solution of sodium hydroxide. The organic layer was separated, and the aqueous layer was extracted 2-3 times with ether; the combined organic layer was dried with magnesium sulfate and then fractionated. The purities of the chain-growth production obtained were checked by the formation of one spot in thin-layer chromatography on unbound alumina in various solvent systems (mixtures of diethyl ether with benzene or petroleum ether) and the formation of one peak on the gas-liquid chromatogram (2-m column containing 1% of silicone elastomer on NaCl at 70-85°). We obtained: 1,1,3-triethoxybutane. b.p., 72-75° (15 mm), n_D^{20} 1.4080 [8]; 1,1,3-triethoxyhexane, b.p. 95-100° (10 mm); n_D^{20}1.4140 [8]; 1,1, 3-triethoxy-4-methylpentane, b.p. 93-97° (12 mm), n_D^{20} 1.4142 [8]; 1,1,3-triethoxy-5-chloropentane, b.p. 76-79° (0.42 mm), n_D^{20} 1.4420 (found: C 55.70; 55.53; H 9.81; 9.77%. $C_{11}H_{23}O_3Cl$. Calculated: C 55.31; H 9.66%); 1,1,3,5-tetraethoxypentane, b.p. 75-79° (0.42 mm), n_D^{17} 1.4225 (found: C 62.87; 62.91; H 11.25; 11.31%. $C_{13}H_{28}O_4$. Calculated: C 63.02; H 11.36%); 1,1,3,5-tetraethoxyhexane, b.p. 69-71° (1 mm), n_D^{20} 1.4182 [7].

In the case of unsaturated acetals: to 0.05 mole of the unsaturated acetal (the diethyl acetal of propiolaldehyde, crotonaldehyde, ethyl malealdehydate, ethyl muconaldehydate, ethyl 7-formyl-2,4,6-heptatrienoate, 3-butenal, or ethyl 4-formylcrotonate) we added five drops of boron trifluoride etherate and then 0.05 mole of ethyl vinyl ether dropwise at not above 35-40°. The mixture was stirred for one hour at 45-50°, and the treatment and isolation were conducted as in the case of the saturated acetals. The products were characterized by conversion into 2,4-dinitrophenylhydrazones (the formation of the hydrazone was accompanied by the elimination of an ethoxy group) and by thin-layer chromatography on alumina (solvents–mixtures of diethyl ether with benzene or petroleum ether). We obtained: 4,4,6-Triethoxy-2-hexene, b.p. 94-98° (11 mm), n_D^{19} 1.4254 [9]. Ethyl 4-ethoxy-5-formyl-2-pentenoate diethyl acetal, b.p. 117-122° (3 mm), n_D^{17} 1.4428 (found: C 61.43; 61.47; H 9.60; 9.44%. $C_{14}H_{26}O_5$. Calculated: C 61.31; H 9.51%); 2,4-dinitrophenylhydrazone, m.p. 149-150° (from alcohol) (found: N 18.04; 18.15%. $C_{12}H_{12}N_4O_6$. Calculated: N 18.18%). Ethyl 8,10,10-triethoxy-2,4,6-decatrienoate, b.p. 122-127° (0.4 mm) n_D^{18} 1.5300 (found: C 66.09; 66.14; H 9.19; 9.27%. $C_{18}H_{30}O_5$. Calculated: C 66.27; H 9.25%). Ethyl 6,8,8-triethoxy-2,4-octadienoate, b.p. 130-135° (1.5 mm), n_D^{19} 1.4850, on hydrolysis by heating in a water bath for three hours with a mixture of acetic acid, water, and sodium acetate it was converted into ethyl 7-formyl-2,4,6-heptatrienoate, m.p. 65-67° (from hexane); 2,4-dinitrophenylhydrazone, m.p. 201-202°; preparations identical to those obtained here were prepared previously from ethyl 8-ethoxy-6,8-dimethoxy-2,4-octadienoate [10]. 4,4,6-Triethoxy-1-hexene, b.p. 50-53° (0.5 mm), n_D^{20} 1.4228 [8].

Saturated Diacetals. Reaction was conducted as described for the case of saturated monoacetals with the bis [diethyl acetals] of malonaldehyde, methylmalonaldehyde, and bromomalonaldehyde. We obtained: 1,1,3,5,5-pentaethoxypentane, b.p. 120-122° (3 mm), n_D^{20} 1.4213 [11]; 1,1,3,5,5-pentaethoxy-2-methylpentane, b.p. 124-126° (3 mm), n_D^{20} 1.4258 [11].

Unsaturated Diacetals. Five drops of boron trifluoride etherate were added to 0.05 mole of the unsaturated diacetal, the mixture was warmed to 30°, and 0.1 mole of ethyl vinyl ether was added dropwise at such a rate that the temperature did not rise above 35-40°. The mixture was heated for one hour at 40-50° and then treated in the usual way (see description above). As diacetals we used the bis[diethyl acetals] of butynedial, malealdehyde, fumaraldehyde, cis-and trans-muconaldehydes, and trans-2,4,6-octatrienedial. From the diacetals of malealdehyde and fumaraldehyde we obtained the same 1,1,3,6,8,8-hexaethoxy-4-octene (its configuration was confirmed by a study of its infrared and Raman spectra), b.p. 134-138° (0.5 mm), n_D^{20} 1.4346 [12]. Judging from the infrared spectrum, cis-muconaldehyde diacetal formed a mixture of cis- and trans-1,1,3,8,10,10-hexaethoxy-4,6-decadienes [13]; from trans-muconaldehyde diacetal we obtained fully trans 1,1,3,8,10,10-hexaethoxy-4,6-decadiene, b.p. 134-138° (0.5 mm), n_D^{18} 1.4359. Found: C 65.58; 65.44; H 10.47; 10.56%. $C_{22}H_{42}O_5$. Calculated: C 65.63; H 10.52%. From 2,4,6-octatrienedial diacetal we obtained 1,1,3,10,12,12-hexaethoxy-4,6,8-dodecatriene, b.p. 189-195° (0.06 mm), n_D^{17} 1.4852. Found: C 67.24; 67.40; H 10.33; 10.33%. $C_{24}H_{44}O_6$. Calculated: C 67.25; H 10.35%.

SUMMARY

1. From a comparison of data from our own work and from the literature on the yields of the primary products of chain-growth reactions of mono- and di- acetals of various structures it is shown that in the case of saturated acetals the cause of the different reactivities of the acetals lies mainly in the presence or absence of electron-accepting substituents in the α- or β-position relative to the acetal grouping.

2. On this basis the different behaviors of various mono- and di-acetals in the chain-growth reaction with ethyl vinyl ether are explained.

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