PRINS REACTIONS OF ALLYL ALCOHOL AND ALLYL ACETATE

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THE CONDENSATIONS OF ALLYL ALCOHOL AND ALLYL ACETATE WITH CH_2O WERE STUDIED. THE MAIN REACTION PRODUCTS DEPARTED FROM THE USUAL MAIN PRODUCTS OF PRINS REACTIONS.

Introduction

The condensations of allyl alcohol and allyl acetate with formaldehyde in the presence of an acid catalyst were studied. The main reaction products were found to be linear formals of allyl alcohol, *trans*–1,4–diacetoxybutene–2 from allyl acetate and, as a result of secondary reactions, 1,2,4–triacetoxy–3–acetoxymethylbutane. The addition products of formaldehyde to the double bonds of allyl alcohol were formed in negligible amounts. Attention was paid to the effects of the reaction conditions (temperature, catalyst concentration, reagent ratio, reaction time) on the yield and product distribution in the reaction of allyl acetate with CH_2O.

Experimental

GLC analysis was performed on an LHM–8MD instrument fitted with a 2m·3mm column of 5% SE–301 on Chromatone N–AW–HMDS and with a flame ionization detector. The column temperature was 373 K or was programmed in the interval

323–423 K, with helium as carrier gas (30 ml/min). ^{1}H–NMR spectra were measured in CCl_4 with a Tesla–BS–487 C spectrometer, and are reported in ppm (δ) relative to internal HMDS. IR spectra were run on a Microlab–620MH spectrometer in neat film. GC/MS spectra were recorded on a Finnigan–4021 instrument (EI 68––70 eV) with a 50 m x 0.32 mm glass capillary column coated with SE–54SIL, temperature–programmed from 50 K to 493 K with helium as carrier gas.

Reaction of allyl alcohol (I) and formalin: A mixture of 238 ml (3.4 mole) I, 290 ml (3.5 mole) 30 % formalin and 8.4 ml cc. H_2SO_4 was heated and stirred at 358–360 K for 2.5 hours. After cooling, the acid was neutralized, the unreacted formaldehyde was bound with gaseous ammonia, and the mixture was extracted with 3x100 ml ether. The organic layer was dried, the solvent was distilled off, and the residue was fractionated on a 15 cm column, to yield 35 g III and 176 g II. The formaldehyde conversion, determined by the sulphite method, was 88–89 %.

Synthesis of IV: A mixture of 46.9 g (1.56 mole) paraformaldehyde, 82 ml water, 13.9 ml cc. H_2SO_4, 144 ml (1.56 mole) butanol–1 and 88.5 g (1.3 mole) I was stirred at 353 K for 9 hours. After the standard working–up, the residue was fractionated, to yield 89 g IV and 37 g dibutylformal.

Reaction of I and formalin in the presence of HOAc: A mixture of 191 ml (1.91 mole) 30 % formalin, 65 ml (0.95 mole) I, 109 ml HOAc and 10.2 ml cc. H_2SO_4 was stirred at 348 K for 4 hours. After cooling, neutralizing and working–up the residue was distilled and separated to yield 62.5 g VIII. This compound was termally unstable above 413 K.

Reaction of I and paraformaldehyde in the presence of $AlCl_3$: To a mixture of 63 ml $CHCl_3$, 10.5 g $AlCl_3$ and 11.8 g (0.39 mole) paraformaldehyde at 273 K 27 ml (0.39 mole) I was added in small portions and the mixture was then stirred at 353 K for 3.5 hours. After the working–up and distilling–off of unreacted I, the residue was fractionated leading to separation of a fraction with b.p. 343–393 K/3,99 kPa (mainly II) and another one with b.p. 398–423 K/0,799 kPa (a mixture of compounds resulting from the addition of HCl to II).

Reaction of I and paraformaldehyde in the presence of HCl: A mixture of 53.6 g (1.79 mole) paraformaldehyde, 101 ml (1.49 mole) I, 94 ml water and 126 ml cc. HCl was stirred at 343 K for 2 hours. After the working–up and the distilling–off unreacted I (32 g), the residue was fractionated. TLC analysis (on alumina, benzene–EtOH = =10:1, R_F = 0.28) and the ^{1}H–NMR spectrum indicated, that the first fraction (8.6 g) was IX, while the second fraction (16 g, b.p. 429–473 K/1,86 kPa) was a mixture (3:1) of IX and an unknown compound (R_F = 0.63). The total yield of IX was 27 %; the conversion of I was 63 %.

Reaction of I and paraformaldehyde in HOAc: A mixture of 70 g (2.34 mole) paraformaldehyde, 159 ml (2.34 mole) I, 134 ml HOAc and 12.4 ml cc. H_2SO_4 was stirred at 353 K for 6.5 hours. After the working–up and the distilling–off the light fractions (unreacted I, formals II and VIII and allyl acetate), the residue was fractionated. The main fraction (34 g), with b.p. 371–463 K/1,73 kPa was separated by column chromatography (on silicagel, benzene–EtOH = 10:1) into two fractions. The first fraction (R_F = 0.48, n_D^{20} = 1.4516, 5.4 g) was identified as a mixture (5:1) of dioxacyclanes X and XI; the second fraction (R_F = 0.53) was XII.

Reaction of XIII and paraformaldehyde in HOAc: To a mixture of 27 g (0.9 mole) paraformaldehyde, 128 ml HOAc and 16 ml cc. H_2SO_4, 160 ml (1.5 mole) XIII was added dropwise and the mixture was then stirred at 363 K for 3.5 hours. After working–up, the residue was fractionated. In the first fraction (b.p. 346–383 K/3,99 kPa, after redistillation, XVI and 1,2–diacetoxypropane were identified. The second fraction was XVII.

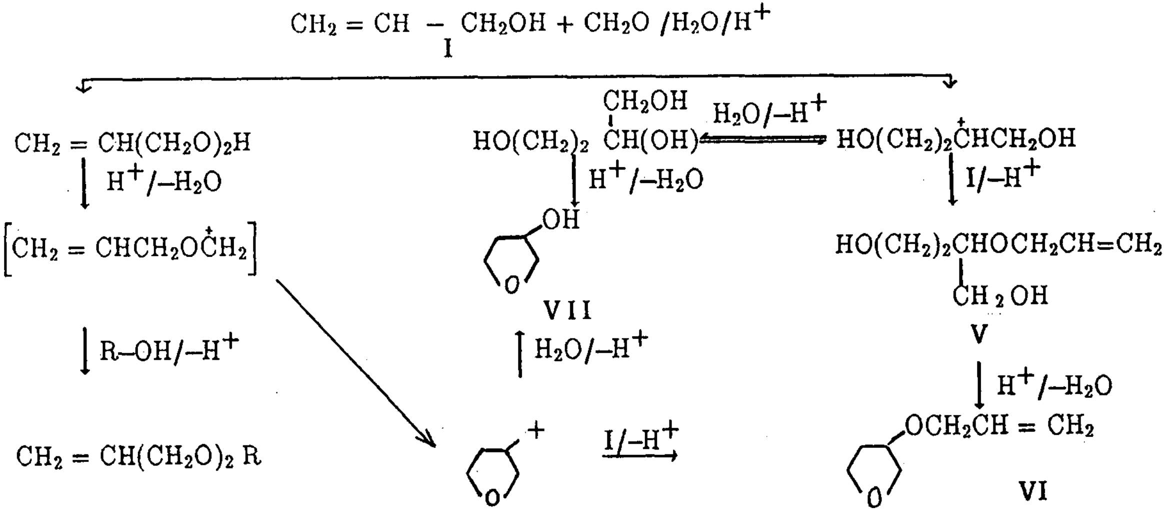
Examination of product distribution (Table III): A sealed ampoule, containing the calculated reagent quantities, was placed into a thermostated bath supplied with a shaker. After the given reaction time, the ampoule was cooled, the mixture was neutralized by Na_2CO_3 and the contents were monitored with GC by the internal standard method.

Discussion

It is known [1,2] that unsaturated alcohols react with formaldehyde to produce compounds with tetrahydrofuran and tetrahydropyran skeletons. Allyl alcohol (I) reacts another way, although there are two directions to produce tetrahydrofurans (Scheme 1).

A more detailed investigation of the reaction showed that the condensation of I and formalin (stabilized by 10–15% MeOH) in the presence of H_2SO_4 produces mainly (stabilized by 10–15 % MeOH) in the presence of H_2SO_4 produces mainly diallylformal II (yield about 40 %) and allylmethylformal III (about 20 %). GC/MS analysis of the reaction mixture showed the presence of

$CH_2{=}CHCH_2(OCH_2)_4OCH_2CH{=}CH_2$ and $CH_2{=}CHCH_2(OCH_2)_4OCH_3$ in traces. Moreover, the GC/MS data demonstrating the presence of V, VI and VII in small quantities in the product mixture support the reality of the reaction pathway shown in Scheme 1. When MeOH was replaced by the more nucleophilic butanol–1, identified products in the reaction mixture included allylbutylformal IV (yield about 50 %) and dibutylformal (about 15 %). Thus the hydroxyl group of I reacts mainly with formaldehyde in aqueous medium, and the structure and ratio of the linear formals formed are determined by the nucleophilicity of the alcohol present.



II : R = $CH_2 = CHCH_2$
III : R = CH_3
IV : R = $(CH_2)_3CH_3$

Scheme I

Table I

Physical and analytical data of the compounds

Compounds	Boiling point K/kPa	n_D^{20}	Formula	Calcd. % C	Calcd. % H	Found % C	Found % H
II	415–429/101,3	1.4266	$C_7H_{12}O_2$	65.61	9.44	66.01	9.12
III	377–382/101,3	1.4066	$C_5H_{10}O_2$	58.80	9.87	60.09	9.76
IV	323–328/1,19	1.4161	$C_8H_{16}O_2$	66.63	11.18	67.06	10.86
VIII	384–486/101,3	1.4138	$C_7H_{12}O_4$	–	–	–	–
IX	–	–	$C_{11}H_{21}ClO_4$	52.28	8.38	51.66	8.59
X + XI (5 : 1)	–	1.4516	$C_7H_{12}O_4$	52.49	7.55	53.01	7.18
XII	–	1.4642	$C_8H_{14}O_3$	60.74	8.92	61.02	8.49
XVI	328–333/0,13	1.4376	$C_8H_{12}O_4$	60.02	7.56	59.91	8.17
XVII	412–414/0,19	1.4425	$C_{13}H_{20}O_8$	51.32	6.58	51.12	7.32

Table II

Spectral data of the compounds

Compounds	^{1}H–NMR (δ,ppm)	MS (m/2)
II	3.9 m (4H, $C\underline{H}_2CH$); 4.5 m (2 H, $OC\underline{H}_2$); 4.9–5.3 m (4H, $CH{=}C\underline{H}_2$); 5.8 m (2H, $C\underline{H}{=}CH_2$)	M–H$^+$ (0.07)(100).
III	as above and 3.2s (3H, $OC\underline{H}_3$)	M$^+$(0.01), M–H$^+$(0.35), 57(100)
IV	0.9t (3II,$C\underline{H}_3$), 1.4 m (4H, $C\underline{H}_2C\underline{H}_2$; 3.4 m (2H, $C\underline{H}_2O$); 3.9 m (2H, $CHC\underline{H}_2O$); 4.5 q (2H, $OC\underline{H}_2O$); 5.1 m (2H, $C\underline{H}_2{=}CH$); 5.7 m (1H, $CH_2{=}C\underline{H}$)	–
VIII	1.5 s (3H, $C\underline{H}_3$); 3.5 m (2H, $C\underline{H}_2O$) 4.2 m (4H, $OC\underline{H}_2O$); 4.6 m (2H, $C\underline{H}_2{=}CH$); 5.3 m (1H, $CH_2{=}C\underline{H}$)	–
IX	1.3–2.0 m (7H, $C\underline{H}_3$, $C\underline{H}_2$); 3.2 s (1H, OH); 3.3–4.1 m (8H, $C\underline{H}Cl$, $C\underline{H}_2O$, $C\underline{H}OH$, $CHC\underline{H}_2O$); 4.6 m (2H, $OC\underline{H}_2O$); 5.0 m (2H, $C\underline{H}_2CH$); 5.8 m (1H, $CH_2C\underline{H}$)	–
X	1.4–2.0 m (2H,$C\underline{H}_2$); 2.0 s (3H, $C\underline{H}_3$); 3.4–3.9 m (5H,$C\underline{H}_2O$, $C\underline{H}O$); 4.7 q (2H, $OC\underline{H}_2O$)	M–H$^+$(0.4), 100(17.2), 87(55.5), 73(5.3), 72(7.0), 57(16.6), 45(24.4), 43(100), 42(13.5), 45(6.1)
XI	as above	M–H$^+$(1.4), 87(4.7), 73(23.8), 71(10.1), 70(59.7), 54(7.6), 45(16.3), 44(51.1), 43(100), 42(14.4), 41(6.6)
XII	1.4–1.9 m (2H, $C\underline{H}_2$); 3.0–4.0(7H,$C\underline{H}_2O$, $C\underline{H}O$); 4.7 q (2H, $OC\underline{H}_2O$); 5.1 m (2H, $C\underline{H}_2$, CH); 5.7 m (1H, $CH_2C\underline{H}$)	–
XVI	2.0 s (6H, $COOC\underline{H}_3$); 3.8 m (4H, $C\underline{H}_2O$); 5.2 m (2H, $C\underline{H}C\underline{H}$)	70(39.1), 43(100)
XVII	2.0 s (12H, $COOC\underline{H}_3$); 1.9–2.0 m (1H, $C\underline{H}$); 4.0 m (6H, $C\underline{H}_2O$); 5.1 m (1H, $C\underline{H}O$)	159(8.1), 117(13.7), 99(11.7), 70(11.4), 43(100)

Table III

The dependence of the product distribution on the conditions in the reaction of allylacetate (XIII) and formaldehyde[a]

	Reaction				Yield (%)		
No	Temp.(K)	Time (h)	H_2SO_4[b]	[XIII]:[CH_2O]	XIV	XV	XVI
1.	323	0.5	0.5	1:4	16.5	16.9	36.3
2.	323	0.5	10.0	1:4	1.2	–	4.9
3.	323	0.5	10.0	4:1	1.1	–	2.1
4.	323	3.5	0.5	4:1	1.6	14.2	27.9
5.	323	3.5	10.0	1:4	–	3.7	–
6.	323	3.5	10.0	4:1	0.6	3.2	6.8
7.	363	0.5	0.5	1:4	25.1	7.6	–
8.	363	0.5	10.0	1:4	0.3	2.9	8.9
9.	363	3.5	0.5	1:4	2.4	34.0	38.0
10.	363	3.5	10.0	1:4	–	4.6	2.0
11.	363	13.5	10.0	4:1	2.8	–	–
12.	343	2.0	5.3	1:1	–	5.2	8.7
13.	343	2.5	5.8	1:2	1.2	8.4	12.0
14.	343	3.0	6.3	1:3	10.2	22.8	38.1
15.	343	3.5	6.8	1:4	25.8	43.0	26.9
16.	343	3.5	7.3	1:4	14.8	37.1	20.4
17.	343	3.5	7.8	1:4	4.7	10.8	5.2
18.	343	3.5	8.3	1:4	11.0	18.8	13.2

[a] [HOAc] : [CH_2O] = 2 : 1

[b] Mass % to HOAc

The reaction of I and formaldehyde in aqueous HOAc results in the formation of VIII:

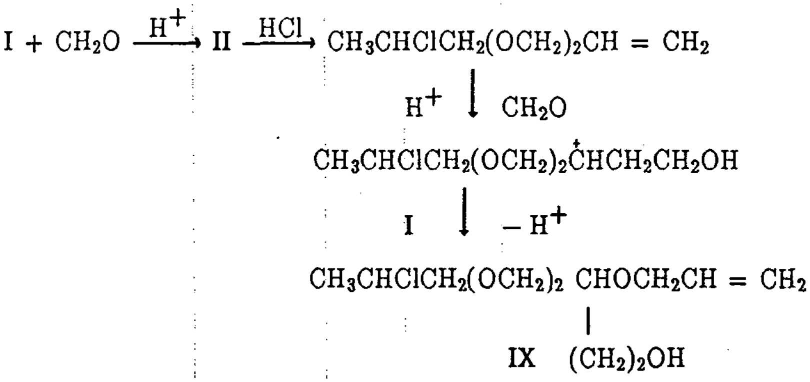
$$\mathrm{I} + CH_2O + HOAc \xrightarrow[H_2O]{H^+} CH_2 = CHCH_2(OHCH_2)_2\ OAc$$

VIII

The condensation in $CHCl_3$ in the presence of $AlCl_3$ resulted in II, and the GC/MS spectra also revealed a by–product (about 4 %) resulting from the addition of HCl to II:

$$\mathrm{I} + (CH_2O)_x \xrightarrow[CHCl_3]{AlCl_3} \mathrm{II} + CH_2 = CH(CH_2O)_2CH_2CHClCH_3$$

The reaction in HCl solution resulted the formation of IX:

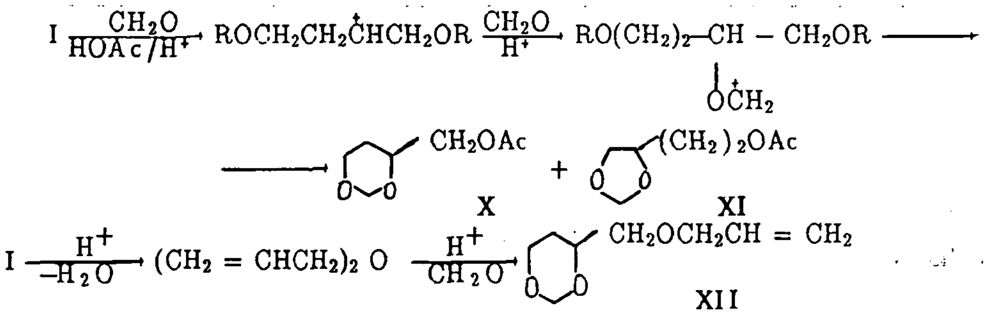


$$\begin{array}{l} \mathrm{I} + CH_2O \xrightarrow{H^+} \mathrm{II} \xrightarrow{HCl} CH_3CHClCH_2(OCH_2)_2CH = CH_2 \\ \qquad\qquad\qquad\qquad\qquad H^+ \downarrow CH_2O \\ \qquad\qquad\qquad\quad CH_3CHClCH_2(OCH_2)_2\overset{+}{C}HCH_2CH_2OH \\ \qquad\qquad\qquad\qquad\qquad \mathrm{I} \downarrow -H^+ \\ \qquad\qquad\qquad\quad CH_3CHClCH_2(OCH_2)_2\ \underset{\displaystyle (CH_2)_2OH}{\underset{|}{C}H}OCH_2CH = CH_2 \end{array}$$

IX

The main products of the condensation in anhydrous HOAc were the linear formals II and VIII, and allyl acetate. X, XI and XII were identified in negligible quantities. These are formed according to the following scheme (R = H or Ac):

It is known [3,4] that the main products of the reaction between allyl acetate (XIII) and formaldehyde in HOAc are 4–acetoxymethyl–1,3–dioxane (X), the

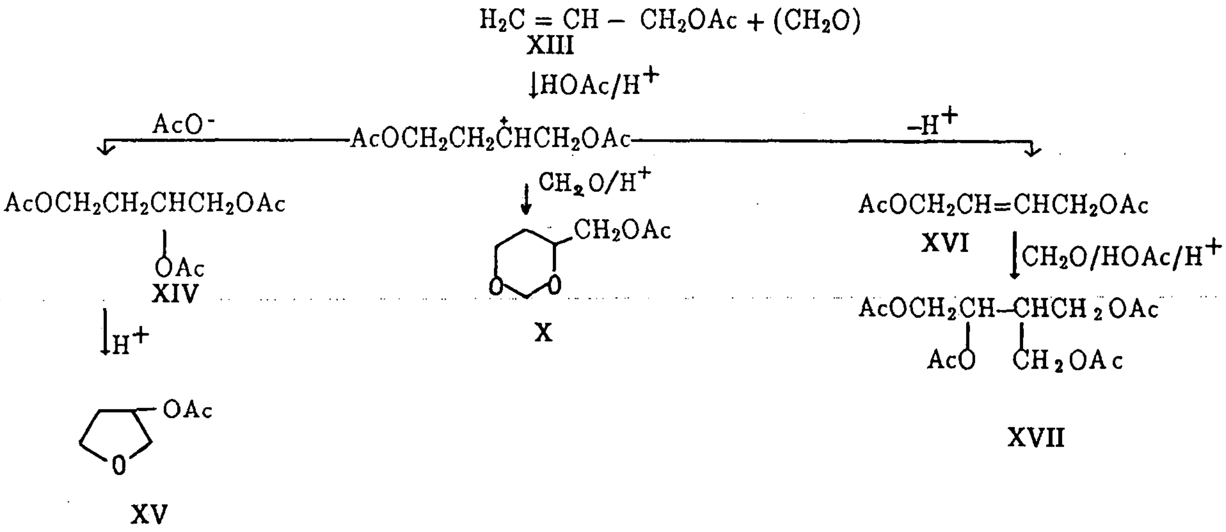


triacetate of 1,2,4–butanetriole (XIV) and 3–acetoxytetrahydrofuran (XV). In the product of our experiments we identified large quantities of *trans*–1,4–diacetoxy–butene–2 (XVI) [1], 1,2,4–triacetoxy–3–acetoxymethylbutane (XVII) and 1,2–diacetoxybutane as an addition product of HOAc to the double bond of XIII (Scheme 2). It has been found [5] that, in the Prins reaction, the presence of an aqueous organic medium facilitates the formation of 1,3–diols and 1,3–dioxanes, where as anhydrous organic solvents, such as HOAc, facilitate the formation of unsaturated alcohols. In an attempt to increase the yield of XVI, we changed the reaction conditions (Table III), but failed to achieve a selective formation of XVI. This is clearly connected with the fact that the energy barrier of the reaction between allyl acetate and formaldehyde is higher that of a secondary Prins reaction between XVI and CH_2O. It was earlier reported [6] that the presence of more strongly electrondonating substituents facilitates the reaction between a double bound and formaldehyde.

References

[1] *Hanschke, E.:* Chem. Ber. *88*, 1053 (1955).

[2] *Gelin, R., R. Henry, S. Gelin:* C. R. Acad. Sci., Ser. C. *275*, 957 (1972).


H₂C = CH – CH₂OAc + (CH₂O)
XIII
HOAc/H+
AcO-
AcOCH₂CH₂ĊHCH₂OAc
-H+
AcOCH₂CH₂CHCH₂OAc
OAc
XIV
H+
OAc
O
XV
CH₂O/H+
CH₂OAc
O
O
X
AcOCH₂CH=CHCH₂OAc
XVI
CH₂O/HOAc/H+
AcOCH₂CH–CHCH₂OAc
AcO
CH₂OAc
XVII

Scheme II

[3] *Olsen, S.:* Acta Chem. Scand. *4*, 462 (1950).

[4] *Setinen, K., V. Blazek, M. Kraus, Z. Zitny:* Chem. Prum. *28*, 415 (1978); C. A. *89*, 215140 n (1978).

[5] *Stapp, P. R., J. C. Randall:* J. Org. Chem. *35*, 2948 (1970).

[6] *Tanaka, T., Y. Nishimura:* Mem. Fac. Eng., Kyushu Univ. *28*, 1 (1968); C. A. *70*, 37740 (1969).