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Preparation of Some α,β-Unsaturated Aldehydes

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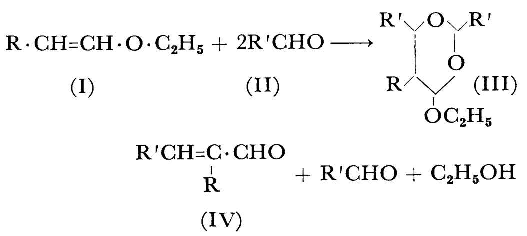
Copenhaver[1] and Hoaglin[2] reported that α,β-unsaturated ethers reacted with saturated aldehydes to form unsaturated aldehydes having two more carbon atoms than the starting aldehydes. However, the works were limited to the reactions of vinyl alkyl ethers with aldehydes except for the reaction of 1-butenyl methyl ether with butyraldehyde. If β-substituted vinyl alkyl ethers were used in addition to vinyl alkyl ethers in these reactions, they could be generalized as a preparative method for α,β-unsaturated aldehydes.

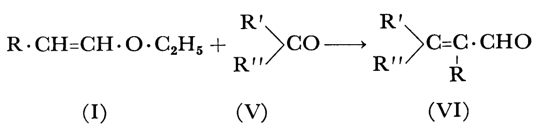


In the present study, 1-propenyl ethyl ether (Ia), 1-butenyl ethyl ether (Ib) and 3-cyano-1-propenyl ethyl ether (Ic) were used as the alkenyl alkyl ether component (I), and acetaldehyde (IIa), propionaldehyde (IIb), butyraldehyde (IIc), benzaldehyde (IId) and β-cyanopropionaldehyde (IIe) were used as the aldehyde component (II). All the reactions of I with II were carried out according to Hoaglin's method, and the results obtained are presented in Table 1.

Hoaglin and Hirsch reported that the intermediate of the reaction was 1,3-dioxane (III), an addition product of one molecule of I and two of II, but gave no experimental details on the isolation and identification of III.[2]

When the catalyst was neutralized with sodium carbonate prior to hydrolysis, a colorless compound was isolated by distillation in a fairly good yield. The analytical values and molecular weight of this compound were very close to those of III, and the IR spectrum exhibited strong doublet peaks in the region 1150—1080 corresponding to those of 1,3-dioxane. This compound was readily converted to the unsaturated aldehyde (IV) by means of hydrolysis with dilute acid. From these facts, it may be concluded that the product is III. The results are summarized in Table 2.

The reaction was also extended to ketones. In a similar manner to that with aldehydes, the reaction of I with acetone (Va) as well as methyl ethyl ketone (Vb) was carried out. Although the yields of VI were lower than those of IV, the expected α,β-unsaturated aldehydes (VI) were also obtained as shown in Table 3. The intermediates were not isolated in this case.



$$R\cdot CH{=}CH\cdot O\cdot C_2H_5 + \underset{R''}{\overset{R'}{>}}CO \longrightarrow \underset{R''}{\overset{R'}{>}}C{=}\underset{R}{C}\cdot CHO$$

The advantage of this method, in comparison with aldol condensation, lies in the preparation of the optional α-substituted-α,β-unsaturated aldehydes and the ease of isolation of the product. Condensation of aldehyde with ketone has a significant limitation. Self-condensation of aldehyde or condensation at the α-carbon atom of ketone takes place and ketone does not condense at the α-carbon atom of aldehyde to form unsaturated aldehyde with simple basic or acid catalysts. Thus, the present reaction to yield VI is regarded as a reaction of wide utility.

Experimental

Materials. 1-Propenyl ethyl ether (Ia) and 1-butenyl ethyl ether (Ib) were obtained by catalytic decomposition of the corresponding aldehyde diethyl acetals.[3]

3-Cyano-1-propenyl ethyl ether (Ic) was prepared from β-cyanopropionaldehyde diethyl acetal.[4]

***α*-Substituted-*α*,*β*-unsaturated Aldehydes (IV).** To a mixture of 0.1 mol of unsaturated ether (I) and 0.3 mol of aldehyde (II), 0.5 g of boron trifluoride etherate in 5 m*l* of diethyl ether was added with good agitation under an anhydrous condition. The temperature of the content was maintained at about 30°C by regulating the rate of addition of catalyst and by external cooling with water. After the mixture was stirred for 4 hr at room temperature, the reaction mixture was directly hydrolyzed by refluxing with 50 m*l* of 10% hydrochloric acid for 6 hr. The oily product was ex-

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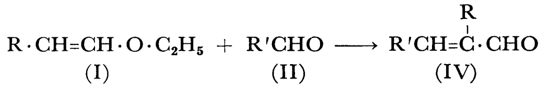
[1] J. W. Copenhaver, U. S. 2543312 (1951).

[2] R. I. Hoaglin and D. H. Hirsh, *ibid.* 2628257 (1953).

[3] W. Rottig and O. Liethen, German 1019090 (1957).

[4] S. Satsumabayashi and S. Motoki, This Bulletin, **41**, 2538 (1968).

Table 1.

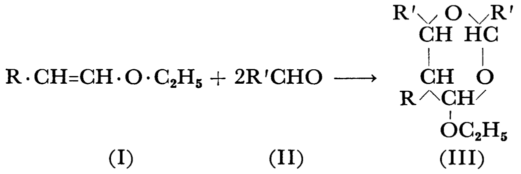


$$\underset{\text{(I)}}{R\cdot CH{=}CH\cdot O\cdot C_2H_5} + \underset{\text{(II)}}{R'CHO} \longrightarrow \underset{\text{(IV)}}{R'CH{=}\overset{R}{\overset{|}{C}}\cdot CHO}$$

Ether	Aldehyde	R	R′	Product
Ia	IIa	CH_3	CH_3	IVa: 2-methyl-2-butenal-(1)
Ia	IIb	CH_3	C_2H_5	IVb: 2-methyl-2-pentenal-(1)
Ia	IIc	CH_3	n-C_3H_7	IVc: 2-methyl-2-hexenal-(1)
Ia	IId	CH_3	C_6H_5	IVd: 2-methyl-3-phenyl-2-propenal-(1)
Ia	IIe	CH_3	$NC\cdot CH_2CH_2$	IVe: 5-cyano-2-methyl-2-pentenal-(1)
Ib	IIa	C_2H_5	CH_3	IVf: 2-ethyl-2-butenal-(1)
Ib	IIb	C_2H_5	C_2H_5	IVg: 2-ethyl-2-pentenal-(1)
Ib	IIc	C_2H_5	n-C_3H_7	IVh: 2-ethyl-2-hexenal-(1)
Ib	IId	C_2H_5	C_6H_5	IVi: 2-ethyl-3-phenyl-2-propenal-(1)
Ib	IIe	C_2H_5	$NC\cdot CH_2CH_2$	IVj: 5-cyano-2-ethyl-2-pentenal-(1)
Ic	IIa	$NC\cdot CH_2$	CH_3	IVk: 2-cyanomethyl-2-butenal-(1)
Ic	IIb	$NC\cdot CH_2$	C_2H_5	IVl: 2-cyanomethyl-2-pentenal-(1)

	Bp (°C/mmHg)	Yield (%)	IR(cm^{-1})		Analysis			
					Calcd		Found	
			-CHO	C=C	C%	H%	C%	H%
IVa	117—118	50.5	2725, 1692	1645	71.39	9.59	71.10	9.82
IVb	51— 52/4	91.5	2720, 1685	1640	73.43	10.27	73.35	10.47
IVc	55— 57/11	67.5	2710, 1680	1639	74.95	10.78	75.11	10.57
IVd	97— 99/4	52.8	2725, 1685	1629	82.16	6.90	81.98	7.13
IVe	118—120/5	29.0	2730, 1692	1641	68.27	7.37	68.20	7.62
IVf	57— 59/55	55.1	2725, 1692	1648	73.43	10.27	73.21	9.99
IVg	58— 59/25	67.9	2700, 1680	1637	74.95	10.78	74.79	10.93
IVh	54— 55/7	54.9	2710, 1682	1640	76.14	11.18	75.85	11.24
IVi	102—104/3	64.1	2730, 1690	1635	82.46	7.55	82.39	7.80
IVj	122—123/4	33.4	2725, 1679	1639	70.04	8.08	69.78	8.31
IVk	87— 89/4	30.8	2720, 1681	1650	66.03	6.47	65.81	6.70
IVl	115—117/4	25.0	2710, 1688	1645	68.27	7.37	67.99	7.45

Table 2.

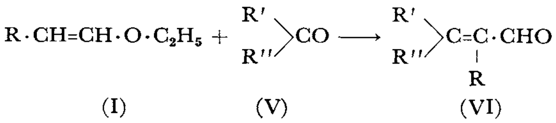


$$\underset{\text{(I)}}{R\cdot CH{=}CH\cdot O\cdot C_2H_5} + \underset{\text{(II)}}{2R'CHO} \longrightarrow \text{(III)}$$

Ether	Aldehyde	R	R′	Product
Ib	IIa	C_2H_5	CH_3	IIIa: 4-ethoxy-5-ethyl-2,6-dimethyl-1,3-dioxane
Ib	IIc	C_2H_5	n-C_3H_7	IIIb: 4-ethoxy-5-ethyl-2,6-dipropyl-1,3-dioxane
Ib	IId	C_2H_5	C_6H_5	IIIc: 4-ethoxy-5-ethyl-2,6-diphenyl-1,3-dioxane

	Bp (°C/mmHg)	Yield (%)	IR(cm^{-1}) -C-O-C-O-C-	Analysis Calcd (%)	Analysis Found (%)	Molecular weight Calcd	Molecular weight Found
IIIa	64- 65/6	57.2	1145, 1105	C: 63.79 H: 10.71	63.57 10.99	188.3	183.2
IIIb	127-129/2	58·8	1145, 1100	C: 68.81 H: 11.55	68.64 11.81	244.4	238.5
IIIc	175-177/2	70.1	1130, 1090	C: 76.89 H: 7.74	76.78 7.53	312.4	320.2

TABLE 3.



$$\underset{\text{(I)}}{R\cdot CH{=}CH\cdot O\cdot C_2H_5} + \underset{\text{(V)}}{\begin{matrix}R'\\R''\end{matrix}\!\!>\!CO} \longrightarrow \underset{\text{(VI)}}{\begin{matrix}R'\\R''\end{matrix}\!\!>\!C{=}\underset{\displaystyle R}{\underset{|}{C}}\cdot CHO}$$

Ether	Ketone	R	R′	R″	Product
Ia	Va	CH_2	CH_3	CH_3	VIa: 2, 3-dimethyl-2-butenal-(1)
Ia	Vb	CH_3	CH_3	C_2H_5	VIb: 2, 3-dimethyl-2-pentenal-(1)
Ib	Va	C_2H_5	CH_3	CH_3	VIc: 2-ethyl-3-methyl-2-butenal-(1)
Ib	Vb	C_2H_5	CH_3	C_2H_5	VId: 2-ethyl-3-methyl-2-pentenal-(1)

	Bp	Yield	IR(cm^{-1})		Analysis			
					Calcd		Found	
	(°C/mmHg)	(%)	-CHO	C=C	C%	H%	C%	H%
VIa	43-45/16	36.8	2705, 1693	1637	73.43	10·27	73.61	10.55
VIb	84-86/30	33.0	2702, 1690	1636	74·95	10·78	74·73	10·84
VIc	55-57/14	27.7	2710, 1692	1640	74·95	10.78	74.68	11.01
VId	64-65/14	29·4	2705, 1692	1638	76·14	11.18	75·91	11.46

tracted with ether and dried over anhydrous sodium sulfate. Distillation of the extract gave the results shown in Table 1.

In the case of the use of acetaldehyde, the reaction temperature was maintained at about 10°C on account of the low boiling point of the aldehyde.

1,3-Dioxane Derivatives (III). After stirring the reaction mixture of I and II for 4 hr as in the preceding experiment, 5 g of powdered anhydrous sodium carbonate was added to the mixture in order to neutralyze the catalyst. The mixture was well agitated for 3 hr and then filtered. Fractional distillation of the filtrate gave III. The results are summarized in Table 2.

Hydrolysis of III with 10% hydrochloric acid gave IV, yield *ca.* 90%.

2-Ethyl-2-butenal-(1) (IVf) was obtained from IIIa. bp 55—56°C/50 mmHg. Found: C, 73.14; H, 10.31%, Calcd for $C_6H_{10}O$: C, 73.43; H, 10.27%.

2-Ethyl-2-hexenal-(1) (IVh) from IIIb, bp 54—56°C/7 mmHg. Found: C, 76.28; H, 11.10%. Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18%.

2-Ethyl-3-phenyl-2-propenal-(1) (IVi) from IIIc, bp 102—104°C/3 mmHg. Found: C, 82.20; H, 7.78%. Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.55%.

α-Substituted-α,β-unsaturated Aldehydes (VI). A mixture of 0.1 mol of I and 0.3 mol of the ketone (V) was treated with boron trifluoride in the same manner as for IV. After stirring for 6 hr, the mixture was hydrolyzed for 10 hr. The results are summarized in Table 3.

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