In equations 3 and 4 are shown the intermediates which seem probable to us for the acid-catalyzed self-condensation of ω -nitroacetophenone. Dehydration might, of course, occur earlier in equation 4, but it would not alter the general nature of the step. It is interesting that a strong acid is required for the reaction. With concentrated sulfuric acid or oxide-free nitric acid, ω -nitroacetophenone gave dibenzoylfurazane oxide, but when concentrated hydrochloric or sirupy phosphoric acids were employed the nitro compound was recovered unchanged.

Support for the conversion of an intermediate such as VI to dibenzoylfurazane oxide is to be found in the observation that the dioxime VII can be converted to dibenzoylfurazane oxide on heating with nitric acid.¹³ Although it is impossible to decide what the actual intermediate is just before ring closure, it can be seen that the dioxime VII is related to the intermediate V by the steps:



Summary

When phenylmethylcarbinol, acetophenone, isonitrosoacetophenone or ω -nitroacetophenone is treated with red fuming nitric acid in boiling glacial acetic acid solution, the principal product is dibenzoylfurazane oxide.



Of the four possible starting materials, only ω -nitroacetophenone will undergo the reaction in the presence of oxide-free nitric acid or concentrated sulfuric acid. It is suggested that all of these reactions involve the intermediate formation of ω -nitroacetophenone and a mechanism is proposed for the transformation.

URBANA, ILLINOIS

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Transetherification Reactions. Preparation and Rearrangement of β -Alloxyacrylates¹

BY W. J. CROXALL AND J. O. VAN HOOK

In a previous paper it was reported that the transetherification of ethyl β -ethoxyacrylate (I) and ethyl β , β -diethoxypropionate (II) with alcohols² produced ethyl β -alkoxyacrylates and alkyl

$$(C_{2}H_{\delta}O)_{2}CHCH_{2}CO_{2}C_{3}H_{\delta}$$

$$II$$

$$C_{2}H_{\delta}OCH=CHCO_{2}C_{2}H_{\delta}$$

$$I$$

$$+ CH_{2}=CH-C$$

 β -alkoxyacrylates. The present paper describes our results when this reaction is applied to allyl type alcohols.

Allyl alcohol and the acrylate (I) or propionate (II) react in the presence of acidic or basic catalysts to give ethyl β -alloxyacrylate (III) and allyl β -alloxyacrylate (IV), respectively. Other allyl type alcohols react in a similar manner. Table I lists the various allyl ether esters which were prepared from these alcohols.

These esters which possess an allyl vinyl ether group³ undergo a Claisen rearrangement on heat-

(1) For the previous paper in this series, see Croxall, Van Hook and Luckenbaugh, THIS JOURNAL, 71, 2741 (1949).

(2) Croxall, Van Hook and Luckenbaugh, *ibid.*, 71, 2736 (1949).
(3) Tarbell, "Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1944, Vol. II, p. 4.

ing. Thus, the alloxyacrylate (III) is converted to ethyl α -formylallylacetate (V). The equation illustrates the transetherification and rearrangement.

$$\begin{array}{c} -C_{2}H_{\delta}OH \\ \hline CH_{2}OH \\ \hline \end{array} \\ CH_{2} - CH_{2} - CH_{2}OCH = CHCO_{2}C_{2}H_{\delta} \\ III \\ \downarrow \\ ibes \\ allyl \\ CH_{2} = CH - CH_{2} \\ CH_{2} = CH_{\delta} \\ CH_{2} = CH_{\delta} \\ V \end{array}$$

In a similar manner ethyl β -crotoxyacrylate (VI) and methallyl β -methalloxyacrylate (VII) were rearranged to ethyl α -formyl-3-methyl-4-pentenoate (VIII) and methallyl α -formylmethallylacetate (IX), respectively.

$$CH_{3}CH=CHCH_{2}OCH=CHCO_{2}H_{5} \longrightarrow H$$

$$VI \qquad O=C-CH-CO_{2}C_{2}H_{5}$$

$$CH_{2}=CH-C-CH_{4}$$

Ĥ



 $\begin{array}{c}
H \\
O = C - CHCO_2C_4H_7 \\
CH_2 = C - CH_2 \\
CH_3 \\
IX
\end{array}$

Although the other β -alloxy esters listed in Table I were converted to rearranged esters as demonstrated by their alkali solubility, the rearranged products in these cases were not isolated as analytically pure compounds and hence were not characterized.

The rearranged esters (V, VIII and IX) exhibit a red-violet color with alcoholic ferric chloride. These observations indicate the presence of the enolic forms.

$$\begin{array}{c} \stackrel{H}{\longrightarrow} O = O - CHCO_2 R \xrightarrow{} HOCH = CCO_2 R \\ \stackrel{R'}{\swarrow} R' \\ V, VIII, IX \\ R' = CHCH_2 -, CH_2 = CCH_2 - or CH_2 = CHCH - \\ \stackrel{L}{\longrightarrow} CH_4 \\ \end{array}$$

Furthermore, inspection of the molecular refractions of the rearranged esters (V, VIII and IX) points to the presence of both the enol and alde-The molecular refraction values hyde forms. found for the esters (V, VIII and IX) fall between the calculated values for the aldehyde and enol form. Since the enol (X) values should be higher than the calculated due to exaltation, these results indicate the presence of more aldehyde than enol (X) form. However, the enol esters (X) can exist as hydrogen bonded ring compounds (XI) and the infrared absorption characteristics of such "conjugate chelate" rings⁴ are observed in the spectrum of the ester $V_{.5}^{5}$ The conjugated ester \tilde{C} =O absorption (5.82 μ) is shifted to $\sim 6.0 \,\mu$ with increased intensity and a large shift in hydroxyl absorption from its 2.75 μ "free OH" or 2.9 μ "bonded OH" position is indicated by a very weak, broad band upon which the sharp C-H absorption near 3.5 μ is superposed.



It is logical to expect the ring structure (XI) to be the most stable form. That molecular refractions lead to different conclusions suggests that

(4) Rasmussen, Tunnicliff and Brattain, THIS JOURNAL, **71**, 1068 (1949); Rasmussen and Brattain, *ibid.*, **71**, 1073 (1949).

(5) The authors wish to express their sincere gratitude to Dr. James D. Stroupe for his interpretation of the infrared absorption data.

the unknown effect of chelation on refractivity needs further investigation.⁶

During the preparation of the methalloxyacrylate (VII) using sodium alkoxide as catalyst, it was observed that carbon monoxide was evolved and there was isolated from the reaction, in addition to the methalloxy ester (VII) and the rearranged ester (IX), a lower boiling material which proved to be methallyl methallylacetate (XII). Furthermore, it was found possible to change the course of the reaction so that the major product was the acetate (XII). In a similar manner it was demonstrated that the reaction of allyl alcohol, the acrylate (I) and sodium alloxide catalyst could be directed to give allyl allylacetate (XIII) exclusively. It is apparent that the formation of the unsaturated acetates (XII and XIII) are the result of a reverse Claisen condensation on the α -formyl esters.

Direct application of the reverse Claisen condensation for characterization of one of the rearranged esters was accomplished with the α -formylpentenoate (VIII). This ester in the presence of sodium ethoxide produced what appears to be ethyl 3-methyl-4-pentenoate (XIV) which on hydrogenation yielded ethyl 3-methylpentanoate (XV). These results demonstrate that inversion of the crotyl group has occurred during this rearrangement.³



Determination of the position of the double bond in XIV was not carried out and accordingly it cannot be stated definitely that during this rearrangement a shift in the double bond from the β,γ position to the α,β -position has occurred. However, the proven terminal position of the double bond in the resulting allylacetate (XIII) indicates strongly that a β,γ -shift has occurred in rearrangement of VI to VIII. Furthermore, characterization of the product obtained from the β -methal-

(6) Glasstone, "Textbook of Physical Chemistry," D. Van Nostrand Co., Inc., New York, N. Y., 2nd ed., 1946, p. 531, states that the effect of a hydrogen bond in a ring structure on molecular refraction is not known. loxy ester (VII), methallyl methallylacetate (XII), further substantiates the shift of the double bond for the conversion of VI to VIII. Saponification of the methallylacetate (XII) yielded methallyl alcohol and methallylacetic acid (XVI).⁷ Oxidation of the acid (XVI) with alkaline potassium permanganate produced levulinic acid and therefore definitely established the position of a terminal double bond in XVI. Hydrogenation of XII gave isobutyl isocaproate.

It is interesting to note that in the over-all sequence of reactions employed to obtain the ester (XII), sodium alkoxide was used as catalyst and no migration of the double bond had occurred. Previously it has been shown that α,β - and β,γ olefinic acids and esters are equilibrated to mixtures of the α,β - and β,γ -compounds by alkali or sodium alkoxides.⁸ Our results suggest that five carbon atom terminally unsaturated esters do not equilibrate in this manner.

The application of a transetherification-transesterification reaction to methyl α, α -dimethoxysuccinate using allyl alcohol and sodium alloxide



catalyst gave allyl allylacetate (XIII) and allyl oxalate (XVII). It is evident that during this reaction, allyl alloxymaleate was formed which rearranged to allyl allyloxalacetate and then this ester *via* a reverse Claisen condensation was cleaved to the acetate (XIII) and oxalate (XVII).

The β -alloxyacrylate (I) upon heating in the presence of acetic anhydride is simultaneously rearranged and acetylated to ethyl β -acetoxy- α -allylacrylate (XVIII). Rearrangement of the β alloxy ester (I) in the presence of propionic and butyric anhydrides produced the corresponding β -propionoxy and β -butyroxyacrylates, respectively.

$$CH_{2}=CH-CH_{2}OCH=CHCO_{2}C_{2}H_{5} + (RCO)_{2}O \longrightarrow$$

$$III$$

$$RCO_{2}CH=C-CO_{2}C_{2}H_{5} + RCO_{2}H$$

$$\downarrow$$

$$CH_{2}-CH=CH_{2}$$

$$CH_{2}-CH=CH_{2}$$

$$R = CH_3, C_2H_5 \text{ or } C_3H$$

Table II lists the yields and physical constants of the resulting β -acyloxy esters. Saponification

(7) Jones and Tattersall, J. Chem. Soc., 85, 1691 (1904), have reported that in their preparation of this acid, decomposition and polymerization occurred on distillation under reduced pressure. Our acid (XVI) did not have behave in this manner. It could be distilled without polymerization or decomposition.

(8) Baker, "Tautomerism," D. Van Nostrand Co., Inc., New York, N. Y. 1934, pp. 156, 157.

of the β -acetoxy ester (XVIII) gave the corresponding acid which was not isolated but decarboxylated to allylacetaldehyde (XIX).



The β -acetoxy ester (XVIII) undergoes alcoholysis in the presence of an acid catalyst to yield alkyl β -alkoxy- α -allylacrylates.

 $CH_{3}CO_{2}CH = CCO_{2}C_{2}H_{5} + 2ROH \longrightarrow$

$$CH_{2}CH=CH_{2}$$

$$XVIII$$

$$ROCH=CCO_{2}R + CH_{3}CO_{2}C_{2}H_{5} + H_{2}O$$

$$\downarrow$$

$$CH_{2}-CH=CH_{2}$$

The resulting ether esters obtained from ethanol, cyclohexanol and 2-ethylhexanol are listed in Table II.

Application of the alcoholysis reaction to the β -acetoxy ester (XVIII) with allyl alcohol presumably gave allyl β -alloxy- α -allylacrylate (XX) which, however, upon distillation rearranged so that it was impossible to obtain pure XX. Accordingly, the resulting alcoholysis product, XX, contaminated with its

rearranged product was completely converted by heating to the final rearranged ester, namely, allyl diallylmalonaldehydate (XXI).

$$CH_{2}=CH-CH_{2}OCH=C-CO_{2}C_{4}H_{5} \longrightarrow$$

$$CH_{2}CH=CH_{2}$$

$$XX$$

$$CH_{2}-CH=CH_{2}$$

$$H$$

$$O=C-C-CO_{2}C_{5}H_{5}$$

$$CH_{2}CH=CH_{2}$$

$$XI$$

The malonaldehydate (XXI) on treatment with cold aqueous potassium hydroxide was cleaved to potassium formate and allyl diallylacetate (XXII).⁹



⁽⁹⁾ Blaize and Marcilly, Bull. soc. chim., [3] 31, 160 (1904), report a similar cleavage of ethyl α -formylisobutyrate by barium hydroxide to barium formate, ethyl isobutyrate and isobutyric acid.

TABLE I

	R	R'
1	CH3-	$CH_2 = CH - CH_2 - CH_2$
2	C_2H_5 —	$CH_2 = CH - CH_2 - CH_2$
3	C ₂ H ₅ —	CH ₂ —CH=CH—CH ₂ —
4	C_2H_5 —	$CH_2 = CCl - CH_2 - CH_2$
5	$CH_2 = CH - CH_2 - CH_2$	$CH_2 = CH - CH_2 - CH_2$
6	CH2=CCH3-CH2-	CH2=CCH3-CH2-

Characterization of the diallylacetate (XXII) was accomplished by saponification to diallylacetic acid (XXIII).

Acknowledgment.—The analyses were carried out under the direction of Dr. E. L. Stanley and Mr. C. W. Nash. Mr. C. Gianotti and Mrs. R. Albert prepared a number of the compounds.

Experimental

Both the acid and basic catalyzed transetherification reactions when applied to allyl type alcohols required certain modifications which were not necessary for transetherification reactions with saturated alcohols.² The following two procedures utilizing an acidic and a basic catalyst are therefore reported to illustrate these reactions with the allyl alcohols.

Ethyl β -Alloxyacrylate (III).—A mixture of 114 g. (1.0 mole) of ethyl β -ethoxyacrylate, 174 g. (3.0 moles) of allyl alcohol and 0.1 g. of sodium bisulfate was fractionated through a four foot packed column to give 41 g. of ethanol, b. p. 78-79° and 21 g. of an ethanol-allyl alcohol mixture, b. p. 80-94° (maximum still pot temperature 125°). The excess allyl alcohol was removed under reduced pressure. Continued fractionation gave 111 g. of a fraction consisting of a mixture of the ester (III) and ethyl α -formylallylacetate (V), b. p. 51-65° (2 mm.); n^{20} p 1.4528-1.4640. There was 17 g. of higher boiling material, b. p. 65-77° (2 mm.); n^{20} p 1.4650-1.4751.

The above ester fraction was washed with two 100-ml. portions of cold aqueous 10% sodium hydroxide, the organic layer separated and dried over anhyd. potassium carbonate. Distillation from a Claisen flask gave the pure ester (III).

Methallyl β -Methalloxyacrylate (VII).—In a similar experiment, fractionation of a mixture consisting of 144 g. (1.0 mole) of ethyl β -ethoxyacrylate, 170 g. (2.4 moles) of methallyl alcohol which contained 5 g. of dissolved sodium and 200 g. of toluene gave 140 g. of a toluene–ethanol mixture, b. p. 76–85° (maximum still pot temperature 125°). The distillation residue was cooled, acidified with aqueous acetic acid, washed with a saturated sodium chloride solution and dried over anhyd. potassium carbonate. Distillation gave 134 g. of material, b. p. 40–140° (1 mm.). The distillate was washed with aqueous 10% sodium hydroxide solution, the organic layer separated and dried over anhyd. potassium carbonate. Fractionation gave (a) 12 g. of material, b. p. 32–40° (1 mm.), (b) 42 g. of crude ester (VII), b. p. 40–85° (1 mm.) and (c) 27 g. of higher boiling material, b. p. 85–90° (1 mm.); n^{20} 1.4558.

Redistillation of fraction b gave the pure ester (VII).

Ethyl α -Formylallylacetate (V).—Ethyl β -alloxyacrylate (III) (156 g., 1.0 mole) and 5 g. of β -naphthol (used as a polymerization inhibitor) was stirred at 145–155° for one hour, cooled and extracted with 250 ml. of 4 N sodium hydroxide solution. The organic layer was separated and distilled to give 47 g. of the unchanged acrylate (III). Acidification of the aqueous layer gave an oil which was

Acidification of the aqueous layer gave an oil which was taken up in ether, dried over anhydrous calcium sulfate and distilled. There was obtained 87 g. (71%) of the α -formylacetate (V), b. p. $45-47^{\circ}$ (1 mm.); n^{20} D 1.4565; d^{20}_{20} 1.040. Anal. Calcd. for $C_8H_{12}O_2$: C, 61.51; H,

β -Alloxyacrylates, R'OCH=CHCO ₂ R										
R'	Catalyst	Vield, %	°C. ^{B. 1}	р., Мт.	n ²⁰ D	d 20 20				
CH—CH₂—	NaHSO₄	30	57-63	3	1.4675	1.054				
CH—CH2—	NaHSO4	71	73	3	1.4640	1.005				
H=CH-CH2-	$NaHSO_4$	40	71	0.9	1.4619	0.976				
$Cl-CH_2-$	$NaHSO_4$	53	80-87	1	1.4800	1.180				
$H-CH_2-$	$NaHSO_4$	Ъ	83-89	1	1.4715	1.010				
CH3-CH2-	NaOC ₄ H7	21	91-92	3	1.4721	0.9901				

7.74; *MR* for aldehyde, 40.33; *MR* for enol, 41.39. Found: C, 61.83; H, 7.85; *MR*, 40.86.

Ethyl α -Formyl-3-methyl-4-pentenoate (VIII).—In a similar manner ethyl β -crotoxyacrylate was rearranged to the pentenoate (VIII); yield 68%; b. p. 60-68° (1 mm.); $n^{20}D$ 1.4490; d^{20}_{20} 0.995. Anal. Calcd. for C₉H₁₄O₃: C, 63.51; H, 8.28; MR for aldehyde, 44.86; MR for enol, 46.01. Found: C, 63.47; H, 8.31; MR, 45.89. Methallyl α -Formylmethallylacetate (IX).—This ester

Methallyl α -Formylmethallylacetate (IX).—This ester was obtained by acidification of the aqueous caustic extract obtained during the preparation of the methalloxy ester (VII), b. p. 64-66° (1 mm.), n^{20} D.14651, d^{20}_{10} O.995, yield 10 g. (5%). Anal. Calcd. for C₁₁H₁₆O₃: C, 67.33; H, 8.22; MR for aldehyde, 53.72; MR for enol, 54.78. Found: C, 66.39; H, 8.49; MR, 54.65. Methallyl Methallylacetate (XII).—Redistillation of fraction c, obtained during the propagation of the meth

Methallyl Methallylacetate (XII).—Redistillation of fraction *a* obtained during the preparation of the methalloxyacrylate (VII) gave the pure acetate (XII), b. p. 80° (9 mm.), n^{30} D 1.4438, d^{30}_{20} 0.9103, *MR* 49.08. *Anal.* Calcd. for C₁₀H₁₆O₂: C, 71.40; H, 9.59; sapon. equiv., 167; *MR*, 49.10. Found: C, 71.18; H, 9.66; sapon. equiv., 169.

This ester was also obtained directly as follows: A mixture of 720 g. (5.0 moles) of ethyl β -ethoxyacrylate and 734 g. (10.2 moles) of methallyl alcohol which contained 4 g. of dissolved sodium was fractionated. During the fractionation additional sodium (4 g. dissolved in 40 g. of ethanol) was added. A total of 590 g. of ethanol was removed (maximum still pot temperature 175°) during which time 66.51. of carbon monoxide was evolved. Continued distillation gave 735 g. of a liquid, b. p. 38-125° (1 mm.). There was 101 g. of residue. Refractionation gave 77 g. of a forerun, b. p. 51-94° (20 mm.), n^{20} D.1.4242 and 595 g. (69%) of the methallylacetate (XII), b. p. 93° (10 mm.) to 57° (1 mm.), n^{20} D.1.4440.

Allyl Allylacetate (XIII).—In a similar experiment there was obtained from 432 g. (3.0 moles) of ethyl β -ethoxyacrylate, 360 g. (6.2 moles) of allyl alcohol and 4 g. of sodium which was dissolved in 100 g. of allyl alcohol and added during the fractionation, 424 g. of an ethyl alcoholallyl alcohol mixture, 28.45 1. of carbon monoxide and 285 g. of crude ester (XIII), b. p. 163–168° (maximum still pot temperature 206°). Refractionation of the crude ester (XIII) produced 258 g: (61%) of pure XIII, b. p. 59° (10 mm.), n^{20} p 1.4344, d^{20}_{00} 0.9318, sapon. equiv. 138 (calcd. 140), MR 39.27 (calcd. 39.86).¹⁰ Allylacetic Acid.—Saponification of 47 g. (0.33 mole) of

Allylacetic Acid.—Saponification of 47 g. (0.33 mole) of the ester (XIII) with 200 ml. of aqueous 15% sodium hydroxide solution yielded 10 g. (52%) of allyl alcohol, b. p. $95-97^{\circ}$, n^{20} D 1.4116, and 22 g. (66%) of the acid, b. p. $83-84^{\circ}$ (12 mm.), n^{20} D 1.4280, d^{20}_{20} 0.9877, MR 26.14 (calcd. 26.36).¹¹

Ethyl 3-Methyl-4-pentenoate (XIV).—A mixture of 30 g. (0.18 mole) of ethyl α -formyl-3-methyl-4-pentenoate (VIII) and 1 g. of sodium ethoxide was stirred and heated in an oil-bath maintained at 150–173° for two hours. There was evolved 2 l. of carbon monoxide. To the cooled mixture water was added, the organic material taken up in ether and dried over anhyd. potassium carbonate.

(10) McElvain, Anthes and Shapiro, THIS JOURNAL, 64, 2525
 (1942) report b. p. 48-50° (8 mm.); n²⁵D 1.4198; d²⁵, 0.8808;
 saponification equivalent, 141.

(11) Linstead and Rydon, J. Chem. Sec., 580 (1933).

				<i></i>					
		MR		Ca	lcd.	Found		Sapn. equiv.	
	Calcd.	Obs.	Formula	С	н	С	н	Calcd.	Found
1	36.89	37.43	C7H10O3					142	145
2	41.51	42.84	C8H12O8	61.51	7.75	61.00	7.73	156	157
3	46.13	47.92	$C_{9}H_{14}O_{3}$	63.51	8.28	63.75	8.45	170	172
4	46.37	45.89	C8H11O3C1	50.39	5.82	50.12	5.99ª		
5	45.73	46.58	C ₉ H ₁₂ O ₃	64.27	7.19	63.60	7.47	168	168
6	54.89	55.49	$C_{11}H_{16}O_3$	67.33	8.22	66.76	8.57	196	191
~ .			and the second sec				/	- \	

TABLE I (Continued)

" Calcd.: Cl, 18.82. Found: Cl, 18.65. ^b Obtained as a by-product in preparation of (III).

TABLE II

ETHYL α-ALLYL-β-ACYLOXYACRYLATES RC-OCH=CCO₂C₂H

					C_3H_6								
	Vield.	В. р.				MR			Calcd., %		Found, %		
R	%	°C.	Mm.	n ²⁰ D	$d^{20}20}$	Calcd.	Obs.	Formula	С	H	C	H	
CH₃	82	75	1	1.4600	1.056	50.76	51.41	$C_{10}H_{14}O_{4}$	60.59	7.06	59.86	7.73	
C ₂ H ₅	61	92 - 94	0.5	1.4597	1.029	55.37	56.46	$C_{11}H_{16}O_{4}$	62.25	7.61	62.18	7.54	
C₃H7	52	95-102	0.4	1.4571	1.018	59.98	60.55	$C_{12}H_{18}O_4$	63.68	8.04	63.79	8.07	

Alkyl α -Allyl- β -alkoxyacrylates ROCH=C-CO₂R

C₂H₅	73	65-70	0.4	1.4644	0.988	50.74	51.43	C10H16O3	65.20	8.76	65.46	8.72
$C_{6}H_{11}^{a}$	49	140–144	0.2	1.5025	1.039	83.29	83.06	$C_{18}H_{28}O_{3}^{\circ}$				
C8H17	42	158-176	0.5	1.4658	0.919	106.2	106.2	$C_{22}H_{40}O_3$	74.95	11.44	74.58	11.25

^a Cyclohexyl. ^b 2-Ethylhexyl. ^c Saponification equivalent 307 (calcd. 292).

Distillation gave, after removal of ether, 10 g. of the pen-tenoate (XIV), b. p. 44-47° (8 mm.), n^{20} D 1.4168, d^{20}_{20} 0.883, *MR* 40.47 (calcd. 40.47). *Anal.* Calcd. for C₈-H₁₄O₂: C, 67.58; H, 9.91; sapon. equiv., 142. Found: C, 67.32; H, 9.92; sapon. equiv., 143. Ethyl 3-Methylpentanoate (XV).—Hydrogenation of 6.5 g. (0.05 mole) of the pentenoate (XIV) over Raney nickel at 1300 p. s. i. and room temperature gave 3 g. (46%) of

at 1300 p. s. i. and room temperature gave 3 g. (46%) of the saturated ester (XV), b. p. 156-158°, n^{20} D 1.4068, d²⁰20 0.863

An anilide was prepared according to the method of Hardy¹² m. p. 84-86° (from pet. ether, b. p. 80-100°). A mixture of this anilide and one prepared from an authentic sample of 3-methylpentanoic acid melted at 87°.¹⁸ The anilide of caproic acid¹³ was prepared and a mix-

ture of this anilide and the anilide obtained from the pentenoate (XVI) melted at 70-80°.

Isobutyl Isocaproate.-The methallylacetate (XII) (95 so but is to apply a second s

(calcd. 112), n^{20} R 50.15 (calcd. 50.03). Saponification of 52 g. (0.3 mole) of the ester gave 15 g. (68%) of isobutyl alcohol, b. p. 104–107°, $n^{10.5}$ D 1.3968, d^{20}_{20} 0.805, and 22.4 g. (65%) of isocaproic acid, b. p. 195–198°, n^{20} D 1.4146, d^{20}_{20} 0.9192, neut. equiv., 120 (calcd. 116).¹⁴

Methallylacetic Acid (XVI) .-- Saponification of 50 g. (0.3 mole) of the methallylacetate (XII) yielded 10 g. (47%) of methallylacehol, b. p. 104–110°, n^{20} D 1.4239 and 22 g. (65%) of acid, b. p. 76–82° (2 mm.), m. p. -3° , n^{20} D 1.4380, d^{20} , 0.9863, neutral equivalent 117 (calcd. 114), MR found 30.48 (calcd. 30.48).

Levulinic Acid.—A stirred solution consisting of 11.4 g. (0.1 mole) of methallylacetic acid, 300 ml. of water and 6 g. of potassium hydroxide was treated at 20-35° with 60 g. (0.38 mole) of potassium permanganate. The permanganate was added in small portions over a half-hour period

after which the mixture was allowed to stir until the violet color was discharged. Dilute sulfuric acid (0.25 mole) was added, the mixture digested for fifteen minutes at 80° filtered, the filtrate adjusted to pH 2 with dilute suffuric acid and exhaustively extracted with ether. Distillation gave, after removal of ether, 2.5 g. (22%) of the acid, b. p. 96-104° (1 mm.), n^{20} D 1.437.¹⁵

A semicarbazone was prepared, m. p. 183-183.5°, which when mixed with the semicarbazone of an authentic sample melted at 182°. A p-bromophenacyl ester melted at 81-83° and gave a mixed m. p. 81-83°. Allyl Oxalate (XVII) and Allyl Allylacetate (XIII).—A

mixture of 206 g. (1 mole) of methyl α , α -dimethoxysuccinate and 174 g. (3.0 moles) of allyl alcohol was fractionated through a two-foot packed column while a solution of 4 g. of sodium dissolved in 116 g. (2.0 moles) of allyl alcohol was added. There was obtained 100 g. (3.1 moles) of methanol, b. p. $67-70^{\circ}$, and 60 g. of material, b. p. $70-97^{\circ}$, which was a mixture of methanol and allyl alcohol. The residue was acidified with 25 ml. of glacial acetic acid and poured into 200 ml. of water. The organic layer was taken up in ether, dried over Drierite, and the ether retaken up in ether, dried over Drierite, and the ether fe-moved on the steam-bath. Fractionation gave (a) 81 g. (58%) of allyl allylacetate (XIII), b. p. 57–59° (10 mm.), n^{20} D 1.4344; (b) 19 g. of an intermediate fraction, b. p. 59–70° (8–11 mm.); and (c) 76 g. (54%) of allyl oxalate (XVII), b. p. 70–71° (1 mm.), n^{20} D 1.4455, d^{20}_{20} 1.109, *MR* 41.34 (calcd. 41.51), saponification equivalent 87 (cold 45) 87 (calcd. 85).

Ethyl β -Acetoxy- α -allylacrylate (XVIII).—A mixture of 105 g. (0.67 mole) of ethyl β -alloxyacrylate (I) and 153 g. (1.5 moles) of acetic anhydride was fractionated through a four-foot packed column to give 45 g. of acetic acid, b. p. 113-125°, and 6 g. of an acetic acid-acetic anhydride mixture, b. p. 125-136°. Continued fractionation through a two-foot packed column under reduced pressure gave, after removal of excess acetic anhydride, 109 g. (82%) of

the acetoxyacrylate (XVIII). Allylacetaldehyde (XIX).—A mixture of 99 g. (0.5 mole) of the β -acetoxyacrylate (XVIII) and an aqueous solu-

(15) Sah and Ma, THIS JOURNAL, 52, 4880 (1930).

⁽¹²⁾ Hardy, J. Chem. Soc., 398 (1936).

⁽¹³⁾ Schwartz and Johnson, THIS JOURNAL, 53, 1065 (1931).

⁽¹⁴⁾ M. Hammelen, Bull. soc. chim. Belg., 42, 243 (1933).

tion of sodium hydroxide (50 g. in 250 ml.) was refluxed for five minutes, cooled, extracted with ether and acidified with concd. hydrochloric acid. The resulting organic material was removed by extraction with ether and dis-tilled to give 44 g. of material, b. p. $20-56^{\circ}$ (1 mm.). The distillate (35 g.) was distilled from a Claisen flask with the evolution of carbon dioxide to give 16 g. of liquid, n^{20} D 1.4190–1.420. Redistillation of 6 g. of this material gave 4 g. of the aldehyde (XIX), b. p. $103-109^{\circ}$, $n^{20}D$ 1.4163, d^{29}_{20} 0.863.

A 2,4-dinitrophenylhydrazone was prepared and after two recrystallizations from ethanol melted at 116–117.5°.16

Anal. Calcd. for $C_{11}H_{22}N_4O_4$: C, 50.19; H, 4.59. Found: C, 50.21; H, 4.38.

Ethyl β -Ethoxy- α -allylacrylate.—A mixture of 104 g. (0.53 mole) of the β -acetoxyacrylate (XVIII), 150 g. (3.26 moles) of anhyd. ethanol and 1 g. of p-toluenesulfonic acid was fractionated through a four-foot packed column to give 120 g. of a mixture consisting of ethanol, ethyl acetate and water; b. p. 70-80°, n²⁰D 1.3642. The residue was fractionated through a one-foot packed column to give 71 g. (73%) of the β -ethoxyacrylate.

Allyl Diallylmalonaldehydate (XXI).-Fractionation of 99 g. (0.5 mole) of the β -acetoxyacrylate (XVIII), 116 g. (2 moles) of allyl alcohol, 1 g. of *p*-toluenesulfonic acid and 2 g. of β -naphthol (polymerization inhibitor) gave 81.5 g. of a mixture consisting of allyl alcohol, allyl acetate and g. of a mixture consisting of allyl alcohol, allyl acetate and water. The residue was taken up in ether and washed with water. The ether was removed on the steam-bath and the oily residue was heated at 200-220° for one and a half hours. Distillation from a Claisen flask gave 75 g. (72%) of the malonaldehydate (XXI), b. p. 71-72° (0.3 mm.), n^{30} D 1.4539, d^{30}_{20} 0.997, MR 56.33 (calcd. 57.98), sapon. equiv., 105 (calcd. as a dibasic acid 104). A 2,4-dinitrophenylhydrazone was prepared and re-crystallized from ethanol; m. p. 96-97°. Anal. Calcd. for C₁₈H₂₀N₄O₈: N, 14.42. Found: N, 14.65. Allyl Diallylacetate (XXII).—A mixture of 34 g. (0.17 mole) of the malonaldehydate (XXI) and 17 g. (0.3 mole) of potassium hydroxide dissolved in 20 ml. of water was

of potassium hydroxide dissolved in 20 ml. of water was stirred at room temperature for three hours and extracted with ether. The extracts were dried over anhydrous magnesium sulfate and distilled to give, after removal of

(16) Hurd and Pollack, THIS JOURNAL, 60, 1905 (1938) report m. p. 120°.

The aqueous portion from above was acidified and dis-tilled to give a distillate, b. p. 90–100°, which had a sharp odor and reduced mercuric oxide and accordingly indicates the presence of formic acid.

Diallylacetic Acid (XXIII).—A mixture of 9 g. (0.05 mole) of the acetate (XXII) and 4 g. of sodium hydroxide dissolved in 30 ml. of water was refluxed and stirred for thirty minutes. Acidification of the aqueous solution gave an oil which was taken up in ether and dried over anhydrous magnesium sulfate. Distillation gave, after re-moval of ether, 6 g. (86%) of the acid (XXIII), b. p. 115–120° (3 mm.), n^{20} D 1.4510, d^{20}_{20} 0.9532, neut. equiv., 140 (calcd. 140).¹⁷

Summary

1. Allyl type alcohols transetherify with ethyl β -ethoxyacrylate (I) and ethyl β , β -diethoxypropionate (II) to give the corresponding β -alloxyacrylates.

2. The β -alloxyacrylates undergo a Claisen rearrangement to α -formylpentenoates.

3. A method for the preparation of allyl allylacetate (XIII) and methallyl methallylacetate (XII) is presented.

4. Methyl α, α -dimethoxysuccinate with allyl alcohol in the presence of a sodium alkoxide catalyst has been found to yield allyl oxalate (XVII) and allyl allylacetate (XIII).

5. Ethyl β -alloxyacrylate (III) rearranges in the presence of acid anhydrides to give ethyl β $acyloxy-\alpha$ -allylacrylates.

6. The β -acyloxyacrylates undergo alcoholysis to yield alkyl β -alkoxy- α -allylacrylates.

7. Application of this reaction to allyl alcohol produced allyl diallylmalonaldehydate (XXI).

(17) V. Auwers and Moosbrugger, Ann., 387, 167 (1912).

PHILADELPHIA, PA.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WASHINGTON UNIVERSITY]

The Condensation of Nitromethane with D-Erythrose and 2,4-Benzylidene-Dervthrose¹

By John C. Sowden

Since the introduction five years ago² of the aldehyde-nitromethane condensation reaction as a synthetic tool in the carbohydrate series, this method of lengthening the sugar chain has been applied to various pentoses, both unsubstituted and as the benzylidene derivatives, as well as to D-glucose and 4,6-benzylidene-D-glucose. Carbohydrate C-nitroalcohols have been prepared from D- and L-arabinose,³ 3,5-benzylidene-D-arabinose,² 2,4-benzylidene-L-xylose⁴ and 4,6-benzylidene-D-

(1) A preliminary communication outlining the main features of this work appeared in THIS JOURNAL, 71, 1897 (1949).

(2) Sowden and Fischer, ibid., 66, 1313 (1944).

(3) Sowden and Fischer, ibid., 69, 1963 (1947); Sowden, Science, 109, 2827 (1949); J. Biol. Chem., 180, 55 (1949).

glucose.⁵ Acetylated carbohydrate C-nitroölefins have been prepared from D- and L-arabinose,3 Dand L-xylose,6 D-ribose6 and D-glucose.6 In general, it has been found that the yields of the nitro compounds are higher from the pentose series than from the hexose series.7 This agrees with previous observations that the condensation reaction gives decreasing yields with increasing complexity or

(5) Sowden and Fischer, ibid., 68, 1511 (1946).

(6) Sowden and Fischer, ibid., 69, 1048 (1947).

(7) Carbohydrate C-nitroalcohols have recently been prepared in this Laboratory by Mr. Robert Schaffer from D-mannose and Dgalactose. In each instance the yields are considerably higher than for D-glucose but somewhat lower than the average yield from the pentoses listed above. Experimental details will be reported in the near future.

⁽⁴⁾ Sowden and Fischer, THIS JOURNAL, 67, 1713 (1945).