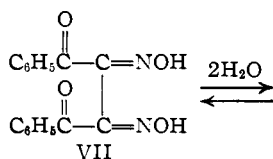
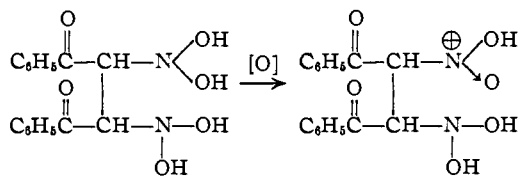


In equations 3 and 4 are shown the intermediates which seem probable to us for the acid-catalyzed self-condensation of  $\omega$ -nitroacetophenone. Dehydration might, of course, occur earlier in equation 4, but it would not alter the general nature of the step. It is interesting that a strong acid is required for the reaction. With concentrated sulfuric acid or oxide-free nitric acid,  $\omega$ -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.<sup>13</sup> 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:

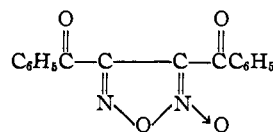


(13) Angeli, *Ber.*, **26**, 528 (1893).



### Summary

When phenylmethylcarbinol, acetophenone, isonitrosoacetophenone or  $\omega$ -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  $\omega$ -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  $\omega$ -nitroacetophenone and a mechanism is proposed for the transformation.

URBANA, ILLINOIS

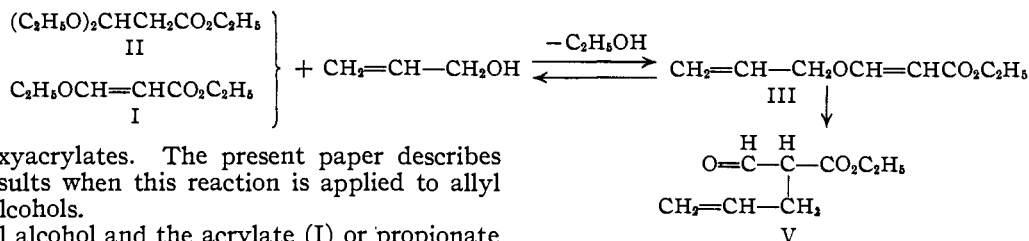
RECEIVED JULY 20, 1949

[CONTRIBUTION FROM ROHM & HAAS COMPANY]

## Transetherification Reactions. Preparation and Rearrangement of $\beta$ -Alloxyacrylates<sup>1</sup>

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

In a previous paper it was reported that the transesterification of ethyl  $\beta$ -ethoxyacrylate (I) and ethyl  $\beta,\beta$ -diethoxypropionate (II) with alcohols<sup>2</sup> produced ethyl  $\beta$ -alkoxyacrylates and alkyl



$\beta$ -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  $\beta$ -alloxyacrylate (III) and allyl  $\beta$ -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 group<sup>3</sup> 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  $\alpha$ -formylallylacetate (V). The equation illustrates the transesterification and rearrangement.

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

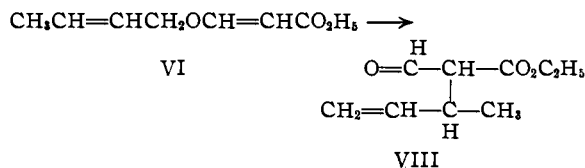






TABLE I  
 $\beta$ -ALLOXYACRYLATES, R'OCH=CHCO<sub>2</sub>R

R	R'	Catalyst	Yield, %	B. p., °C.	Mm.	$n_D^{20}$	$d_4^{20}$
1 CH <sub>3</sub> —	CH <sub>2</sub> =CH—CH <sub>2</sub> —	NaHSO <sub>4</sub>	30	57–63	3	1.4675	1.054
2 C <sub>2</sub> H <sub>5</sub> —	CH <sub>2</sub> =CH—CH <sub>2</sub> —	NaHSO <sub>4</sub>	71	73	3	1.4640	1.005
3 C <sub>2</sub> H <sub>5</sub> —	CH <sub>3</sub> —CH=CH—CH <sub>2</sub> —	NaHSO <sub>4</sub>	40	71	0.9	1.4619	0.976
4 C <sub>2</sub> H <sub>5</sub> —	CH <sub>2</sub> =CCl—CH <sub>2</sub> —	NaHSO <sub>4</sub>	53	80–87	1	1.4800	1.180
5 CH <sub>2</sub> =CH—CH <sub>2</sub> —	CH <sub>2</sub> =CH—CH <sub>2</sub> —	NaHSO <sub>4</sub>	<sup>b</sup>	83–89	1	1.4715	1.010
6 CH <sub>2</sub> =CCH <sub>3</sub> —CH <sub>2</sub> —	CH <sub>2</sub> =CCH <sub>3</sub> —CH <sub>2</sub> —	NaOC <sub>4</sub> H <sub>7</sub>	21	91–92	3	1.4721	0.9901

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

**Ethyl  $\beta$ -Alloxyacrylate (III).**—A mixture of 114 g. (1.0 mole) of ethyl  $\beta$ -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  $\alpha$ -formylallylacetate (V), b. p. 51–65° (2 mm.);  $n_D^{20}$  1.4528–1.4640. There was 17 g. of higher boiling material, b. p. 65–77° (2 mm.);  $n_D^{20}$  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  $\beta$ -Methalloxyacrylate (VII).**—In a similar experiment, fractionation of a mixture consisting of 144 g. (1.0 mole) of ethyl  $\beta$ -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.);  $n_D^{20}$  1.4558.

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

**Ethyl  $\alpha$ -Formylallylacetate (V).**—Ethyl  $\beta$ -alloxyacrylate (III) (156 g., 1.0 mole) and 5 g. of  $\beta$ -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 taken up in ether, dried over anhydrous calcium sulfate and distilled. There was obtained 87 g. (71%) of the  $\alpha$ -formylacetate (V), b. p. 45–47° (1 mm.);  $n_D^{20}$  1.4565;  $d_4^{20}$  1.040. *Anal.* Calcd. for C<sub>8</sub>H<sub>12</sub>O<sub>2</sub>: C, 61.51; H,

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

**Ethyl  $\alpha$ -Formyl-3-methyl-4-pentenoate (VIII).**—In a similar manner ethyl  $\beta$ -crotyoxyacrylate was rearranged to the pentenoate (VIII); yield 68%; b. p. 60–63° (1 mm.);  $n_D^{20}$  1.4490;  $d_4^{20}$  0.995. *Anal.* Calcd. for C<sub>9</sub>H<sub>14</sub>O<sub>2</sub>: 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  $\alpha$ -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.),  $n_D^{20}$  1.4651,  $d_4^{20}$  0.995, yield 10 g. (5%). *Anal.* Calcd. for C<sub>11</sub>H<sub>16</sub>O<sub>2</sub>: 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 a obtained during the preparation of the methalloxyacrylate (VII) gave the pure acetate (XII), b. p. 80° (9 mm.),  $n_D^{20}$  1.4438,  $d_4^{20}$  0.9103, *MR* 49.08. *Anal.* Calcd. for C<sub>10</sub>H<sub>16</sub>O<sub>2</sub>: 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  $\beta$ -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 66.5 l. 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.),  $n_D^{20}$  1.4242 and 595 g. (69%) of the methallylacetate (XII), b. p. 93° (10 mm.) to 57° (1 mm.),  $n_D^{20}$  1.4440.

**Allyl Acrylate (XIII).**—In a similar experiment there was obtained from 432 g. (3.0 moles) of ethyl  $\beta$ -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 alcohol-allyl alcohol mixture, 28.45 l. 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.),  $n_D^{20}$  1.4344,  $d_4^{20}$  0.9318, sapon. equiv. 138 (calcd. 140), *MR* 39.27 (calcd. 39.86).<sup>10</sup>

**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°,  $n_D^{20}$  1.4116, and 22 g. (66%) of the acid, b. p. 83–84° (12 mm.),  $n_D^{20}$  1.4280,  $d_4^{20}$  0.9877, *MR* 26.14 (calcd. 26.36).<sup>11</sup>

**Ethyl 3-Methyl-4-pentenoate (XIV).**—A mixture of 30 g. (0.18 mole) of ethyl  $\alpha$ -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.);  $n_D^{20}$  1.4198;  $d_4^{20}$  0.8808; saponification equivalent, 141.

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

TABLE I (Continued)

	MR		Formula	Analyses, %				Sapn. equiv.	
	Calcd.	Obs.		Calcd.	H	Found	H	Calcd.	Found
1	36.89	37.43	C <sub>7</sub> H <sub>10</sub> O <sub>3</sub>					142	145
2	41.51	42.84	C <sub>8</sub> H <sub>12</sub> O <sub>3</sub>	61.51	7.75	61.00	7.73	156	157
3	46.13	47.92	C <sub>9</sub> H <sub>14</sub> O <sub>3</sub>	63.51	8.28	63.75	8.45	170	172
4	46.37	45.89	C <sub>8</sub> H <sub>11</sub> O <sub>3</sub> Cl	50.39	5.82	50.12	5.99 <sup>a</sup>		
5	45.73	46.58	C <sub>9</sub> H <sub>12</sub> O <sub>3</sub>	64.27	7.19	63.60	7.47	168	168
6	54.89	55.49	C <sub>11</sub> H <sub>16</sub> O <sub>3</sub>	67.33	8.22	66.76	8.57	196	191

<sup>a</sup> Calcd.: Cl, 18.82. Found: Cl, 18.65. <sup>b</sup> Obtained as a by-product in preparation of (III).

TABLE II

R	Yield, %	B. p. °C.	Mm.	$n_D^{20}$	$d_4^{20}$	MR		Formula	Calcd., %		Found, %	
						Calcd.	Obs.		C	H	C	H
CH <sub>3</sub>	82	75	1	1.4600	1.056	50.76	51.41	C <sub>10</sub> H <sub>14</sub> O <sub>4</sub>	60.59	7.06	59.86	7.73
C <sub>2</sub> H <sub>5</sub>	61	92-94	0.5	1.4597	1.029	55.37	56.46	C <sub>11</sub> H <sub>16</sub> O <sub>4</sub>	62.25	7.61	62.18	7.54
C <sub>3</sub> H <sub>7</sub>	52	95-102	0.4	1.4571	1.018	59.98	60.55	C <sub>12</sub> H <sub>18</sub> O <sub>4</sub>	63.68	8.04	63.79	8.07

R	Yield, %	B. p. °C.	Mm.	$n_D^{20}$	$d_4^{20}$	MR		Formula	Calcd., %		Found, %	
						Calcd.	Obs.		C	H	C	H
C <sub>2</sub> H <sub>5</sub>	73	65-70	0.4	1.4644	0.988	50.74	51.43	C <sub>10</sub> H <sub>16</sub> O <sub>3</sub>	65.20	8.76	65.46	8.72
C <sub>6</sub> H <sub>11</sub> <sup>a</sup>	49	140-144	0.2	1.5025	1.039	83.29	83.06	C <sub>18</sub> H <sub>28</sub> O <sub>3</sub> <sup>c</sup>				
C <sub>8</sub> H <sub>17</sub> <sup>b</sup>	42	158-176	0.5	1.4658	0.919	106.2	106.2	C <sub>22</sub> H <sub>40</sub> O <sub>3</sub>	74.95	11.44	74.58	11.25

<sup>a</sup> Cyclohexyl. <sup>b</sup> 2-Ethylhexyl. <sup>c</sup> Saponification equivalent 307 (calcd. 292).

Distillation gave, after removal of ether, 10 g. of the pentenoate (XIV), b. p. 44-47° (8 mm.),  $n_D^{20}$  1.4168,  $d_4^{20}$  0.883, MR 40.47 (calcd. 40.47). Anal. Calcd. for C<sub>8</sub>H<sub>14</sub>O<sub>2</sub>: 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 the saturated ester (XV), b. p. 156-158°,  $n_D^{20}$  1.4068,  $d_4^{20}$  0.863.

An anilide was prepared according to the method of Hardy<sup>12</sup> 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°.<sup>13</sup>

The anilide of caproic acid<sup>13</sup> was prepared and a mixture of this anilide and the anilide obtained from the pentenoate (XVI) melted at 70-80°.

**Isobutyl Isocaproate.**—The methylacetate (XII) (95 g., 0.56 mole) was hydrogenated over Raney nickel at 50° and 1500 p. s. i. to yield 75 g. of ester, b. p. 76-77° (10-12 mm.),  $n_D^{20}$  1.4135,  $d_4^{20}$  0.8551; sapon. equiv., 171 (calcd. 172), MR 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°,  $n_D^{20}$  1.3968,  $d_4^{20}$  0.805, and 22.4 g. (65%) of isocaproic acid, b. p. 195-198°,  $n_D^{20}$  1.4146,  $d_4^{20}$  0.9192, neut. equiv., 120 (calcd. 116).<sup>14</sup>

**Methylacetic Acid (XVI).**—Saponification of 50 g. (0.3 mole) of the methylacetate (XII) yielded 10 g. (47%) of methylalcohol, b. p. 104-110°,  $n_D^{20}$  1.4239 and 22 g. (65%) of acid, b. p. 76-82° (2 mm.), m. p. -3°,  $n_D^{20}$  1.4380,  $d_4^{20}$  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 methylacetic 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 sulfuric 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.),  $n_D^{20}$  1.437.<sup>15</sup>

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 (XVIII).**—A mixture of 206 g. (1 mole) of methyl  $\alpha,\alpha$ -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°, and 60 g. of material, b. p. 70-97°, 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 removed on the steam-bath. Fractionation gave (a) 81 g. (58%) of allyl allylacetate (XVIII), b. p. 57-59° (10 mm.),  $n_D^{20}$  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.),  $n_D^{20}$  1.4455,  $d_4^{20}$  1.109, MR 41.34 (calcd. 41.51), saponification equivalent 87 (calcd. 85).

**Ethyl  $\beta$ -Acetoxy- $\alpha$ -allylacetate (XVIII).**—A mixture of 105 g. (0.67 mole) of ethyl  $\beta$ -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).

**Allylacetalddehyde (XIX).**—A mixture of 99 g. (0.5 mole) of the  $\beta$ -acetoxyacrylate (XVIII) and an aqueous solu-

(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).

(15) Sah and Ma, *This Journal*, **52**, 4880 (1930).

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 distilled to give 44 g. of material, b. p. 20–56° (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°,  $n_{20}^D$  1.4163,  $d_{20}^{20}$  0.863.

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

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

**Ethyl  $\beta$ -Ethoxy- $\alpha$ -allylacrylate.**—A mixture of 104 g. (0.53 mole) of the  $\beta$ -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°,  $n_{20}^D$  1.3642. The residue was fractionated through a one-foot packed column to give 71 g. (73%) of the  $\beta$ -ethoxyacrylate.

**Allyl Diallylmalonaldehyde (XXI).**—Fractionation of 99 g. (0.5 mole) of the  $\beta$ -acetoxyacrylate (XVIII), 116 g. (2 moles) of allyl alcohol, 1 g. of *p*-toluenesulfonic acid and 2 g. of  $\beta$ -naphthol (polymerization inhibitor) gave 81.5 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 malonaldehyde (XXI), b. p. 71–72° (0.3 mm.),  $n_{20}^D$  1.4539,  $d_{20}^{20}$  0.997, *MR* 56.33 (calcd. 57.98), sapon. equiv., 105 (calcd. as a dibasic acid 104).

A 2,4-dinitrophenylhydrazone was prepared and recrystallized from ethanol; m. p. 96–97°. *Anal.* Calcd. for  $C_{18}H_{20}N_4O_6$ : N, 14.42. Found: N, 14.65.

**Allyl Diallylacetate (XXII).**—A mixture of 34 g. (0.17 mole) of the malonaldehyde (XXI) and 17 g. (0.3 mole) 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

ether, 19 g. (62%) of the acetate (XXII), b. p. 52–58 (2 mm.),  $n_{20}^D$  1.4440,  $d_{20}^{20}$  0.904, *MR* 52.54 (calcd. 53.25), sapon. equiv. 172 (calcd. 180).

The aqueous portion from above was acidified and distilled 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 removal 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).<sup>17</sup>

### Summary

1. Allyl type alcohols transesterify with ethyl  $\beta$ -ethoxyacrylate (I) and ethyl  $\beta,\beta$ -diethoxypropionate (II) to give the corresponding  $\beta$ -alloxyacrylates.

2. The  $\beta$ -alloxyacrylates undergo a Claisen rearrangement to  $\alpha$ -formylpentenoates.

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

4. Methyl  $\alpha,\alpha$ -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  $\beta$ -alloxyacrylate (III) rearranges in the presence of acid anhydrides to give ethyl  $\beta$ -acyloxy- $\alpha$ -allylacrylates.

6. The  $\beta$ -acyloxyacrylates undergo alcoholysis to yield alkyl  $\beta$ -alkoxy- $\alpha$ -allylacrylates.

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

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

PHILADELPHIA, PA.

RECEIVED JUNE 8, 1949

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WASHINGTON UNIVERSITY]

## The Condensation of Nitromethane with D-Erythrose and 2,4-Benzylidene-D-erythrose<sup>1</sup>

BY JOHN C. SOWDEN

Since the introduction five years ago<sup>2</sup> 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,<sup>3</sup> 3,5-benzylidene-D-arabinose,<sup>2</sup> 2,4-benzylidene-L-xylose<sup>4</sup> and 4,6-benzylidene-D-

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

(5) Sowden and Fischer, *ibid.*, **68**, 1511 (1948).

(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 D-galactose. 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.

(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).

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