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Abstract

Full Text

CHEMISTRY

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DIENE SYNTHESIS WITH GLYOXYLIC ACID ESTERS

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Diene syntheses with carbonyl compounds leading to the formation of derivatives of 5,6-dihydro-1,2-pyran have been studied very little. Reactions have been carried out of 2-methylpentadiene with formaldehyde ([1]), of 2,3-dimethylbutadiene, isoprene, and piperylene with chloral ([2]), of 2,3-dimethylbutadiene with chloroacetaldehyde ([3]), and of butadiene and 2,3-dimethylbutadiene with cyanic carbonyl and diethyl mesoxalate ([4]).

We found that 1,3-dienes readily react with glyoxylic acid esters or their hemiacetals to form the corresponding derivatives of 5,6-dihydro-1,2-pyran. In the condensation of butadiene and 2,3-dimethylbutadiene with ethyl glyoxylate and *n*-butyl glyoxylate or their hemiacetals, the corresponding adducts I–IV were obtained:

[structural scheme]

I. $R = H, \quad R' = C_2H_5$
II. $R = H, \quad R' = n\text{-}C_4H_9$
III. $R = CH_3, \quad R' = C_2H_5$
IV. $R = CH_3, \quad R' = n\text{-}C_4H_9$

In the reaction of 1,3-cyclohexadiene with the *n*-butyl hemiacetal of *n*-butyl glyoxylate, adduct V was obtained:

[structural scheme] V

The structure of adducts I–V was established as follows. On acid hydrolysis of adducts I and II* 5,6-dihydro-1,2-pyran-6-carboxylic acid VI was obtained, catalytic hydrogenation of which led to tetrahydropyran-2-carboxylic acid VII. On alkaline hydrolysis of adducts III and IV, 3,4-dimethyl-5,6-dihydro-1,2-pyran-6-carboxylic acid VIII was formed; catalytic reduction of this acid gave 4,5-dimethyltetrahydropyran-2-carboxylic acid IX. Catalytic reduction of adduct V gave the dihydro derivative X, acid hydrolysis of which gave 3,6-endoethylenetetrahydropyran-2-carboxylic acid XI.

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Experimental Part

Condensation of ethyl glyoxylate and *n*-butyl glyoxylate with butadiene

Ethyl ester of 5,6-dihydro-1,2-pyran-6-carboxylic acid (I). A mixture of 14.8 g (0.1 g-mol) of the ethyl hemiacetal of ethyl glyoxylate, 10.8 g (0.2 g-mol) of butadiene, and 0.3 g of hydroquinone was heated in an autoclave at 120—130° for 2.5 h. Obtained 7.2 g (46%) colorless liquid with b.p. 57-58°/2 mm, n_D^{20} 1.4506, d_4^{20} 1.0692. *MR* 39.30. Calculated 39.77.

Found, %:	C 60.26, 60.40;	H 7.92, 7.82
$C_8H_{12}O_3$. Calculated, %:	C 61.52;	H 7.75

5,6-Dihydro-1,2-pyran-6-carboxylic acid (VI). A mixture of 3.12 g (0.02 g-mol) of ester (I), 30 ml of acetic acid, and 12 ml of 2*N* hydrochloric acid was boiled for 1.5 h. This gave 1.85 g (72%) of acid (VI) with b.p. 96-98°/2.5 mm, n_D^{20} 1.4817, d_4^{20} 1.2151. *MR* 30.04. Calculated 30.42. *p*-Bromophenacyl ester: m.p. 126-128° (from ethanol).

Literature data: b.p. 60°/0.005 mm, n_D^{20} 1.4831, d_4^{20} 1.218; m.p. of the *p*-bromophenacyl ester 127-128° (^{4}).

Tetrahydropyran-2-carboxylic acid (VII). 8.5 g (0.066 g-mol) of acid (VI) in 65 ml of ethanol was hydrogenated in the presence of 0.5 g of palladium oxide. This gave 7.0 g (81%) of a colorless liquid with b.p. 76-78°/2 mm, n_D^{20} 1.4595, d_4^{20} 1.1400. *MR* 31.24. Calculated 30.89. *p*-Bromophenacyl ester: m.p. 100-101° (from ethanol).

Literature data: b.p. 110.5°/5 mm, n_D^{20} 1.4665 (^{5}), b.p. 100°/2.3 mm, n_D^{20} 1.4618; m.p. of the *p*-bromophenacyl ester 101-102° (^{4}).

The *n*-butyl ester of 5,6-dihydro-1,2-pyran-6-carboxylic acid (II). Experiment 1. A mixture of 13.0 g (0.1 g-mol) of *n*-butyl glyoxylate, 10.8 g (0.2 g-mol) of butadiene, and 0.5 g of hydroquinone was heated in an autoclave at 120-130° for 3 h. This gave 7.5 g (41%) of a colorless liquid with b.p. 90-91°/2 mm, n_D^{20} 1.4552, d_4^{20} 1.0292. *MR* 48.58. Calculated 49.01.

Found, %:	C 64.28, 64.27;	H 8.78, 8.68
$C_{10}H_{16}O_3$. Calculated, %:	C 65.19;	H 8.75

Experiment 2. A mixture of 15.3 g (0.075 g-mol) of the *n*-butyl hemiacetal of *n*-butyl glyoxylate, 10.8 g (0.2 g-mol) of butadiene, and 0.5 g of hydroquinone

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* We were unable to isolate these adducts in analytically pure form.

was heated in an autoclave at 120–130° for 3 h. This gave 6.5 g (47%) of adduct (II) with b.p. 92–95°/2.5 mm and n_D^{20} 1.4548. Saponification of 14.3 g (0.078 g-mol) of ester (II) with a mixture of acetic acid (100 ml) and $2N$ hydrochloric acid (50 ml) gave 7.5 g (75%) of acid (VI): b.p. 101°/2 mm, n_D^{20} 1.4825, d_4^{20} 1.2137. MR 30.12. Calculated 30.42. *p*-Bromophenacyl ester: m.p. 126–128° (from ethanol).

Condensation of ethyl glyoxylate and *n*-butyl glyoxylate with 2,3-dimethylbutadiene

Ethyl ester of 3,4-dimethyl-5,6-dihydro-1,2-pyran-6-carboxylic acid (III). A mixture of 14.8 g (0.1 g-mol) of the ethyl hemiacetal of ethyl glyoxylate, 10.0 g (0.12 g-mol) of 2,3-dimethylbutadiene, and 0.5 g of hydroquinone was heated in an autoclave at 120–130° for 3 h. This gave 14.2 g (77%) of a colorless liquid with b.p. 102–104°/2 mm, n_D^{20} 1.4662, d_4^{20} 1.0397. MR 49.09. Calculated 49.01.

Found, %:	C 65.07, 65.31;	H 8.70, 8.85
$C_{10}H_{16}O_3$. Calculated, %:	C 65.19;	H 8.75

3,4-Dimethyl-5,6-dihydro-1,2-pyran-6-carboxylic acid (VIII). 3.68 g (0.02 g-mol) of ester (III) was mixed with 15 ml of a 10% ethanolic KOH solution. The precipitated potassium salt was filtered off and dissolved in 10 ml of $2N$ HCl with heating. On cooling the mixture, colorless crystals of acid (VIII) separated, m.p. 86–87° (from CCl_4). Yield 2.38 g (76%). Literature data: m.p. 85–86° (^{4}).

4,5-Dimethyltetrahydropyran-2-carboxylic acid (IX). 9.0 g (0.058 mole) of acid (VIII) in 90 ml of ethanol was reduced in the presence of 0.5 g of platinum oxide. This gave 7.9 g (87%) of a colorless liquid with b.p. 106–107°/3 mm, n_D^{20} 1.4670, d_4^{20} 1.0918. MR 40.20. Calculated 40.12. Literature data: b.p. 137–138°/10 mm, n_D^{20} 1.4650, d_4^{20} 1.091 (4).

n-Butyl ester of 3,4-dimethyl-5,6-dihydro-1,2-pyran-6-carboxylic acid (IV). A mixture of 13.0 g (0.1 mole) of *n*-butyl glyoxylate, 10.0 g (0.12 mole) of 2,3-dimethylbutadiene, and 0.5 g of hydroquinone was heated in an autoclave at 120–130° for 3 hours. This gave 14.9 g (70%) of a colorless liquid with b.p. 100–101°/1 mm, n_D^{20} 1.4660, d_4^{20} 1.0049. MR 58.51. Calculated 58.25.

$C_{12}H_{20}O_3$.	Found, %:	C 67.81, 67.88;	H 9.40, 9.46
	Calculated, %:	C 67.89;	H 9.50

On saponification of 4.24 g (0.02 mole) of ester (IV) with a 10% ethanolic solution of KOH, 2.37 g (76%) of acid (VIII) was obtained, m.p. 86–87° (from CCl_4).

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Condensation of *n*-butyl glyoxylate with 1,3-cyclohexadiene

n-Butyl ester of 2,5-endoethylene-5,6-dihydro-1,2-pyran-6-carboxylic acid (V). A mixture of 20.4 g (0.1 mole) of the *n*-butyl hemiacetal of *n*-butyl glyoxylate and 12.0 g (0.15 mole) of 1,3-cyclohexadiene was heated in a sealed ampoule in the vapors of boiling anisole (b.p. 155°) for 3 hours. This gave 14.5 g (69%) of a colorless liquid with b.p. 105–106°/1 mm, n_D^{20} 1.4750, d_4^{20} 1.0575. *MR* 55.98. Calculated 56.05.

$C_{12}H_{18}O_3$. Found, %: C 68.28, 68.15; H 8.81, 8.79
Calculated, %: C 68.54; H 8.69

n-Butyl ester of 3,6-endoethylenetetrahydropyran-2-carboxylic acid (X). 14.0 g (0.067 mole) of ester (V) in 60 ml of ethanol was hydrogenated in the presence of 0.2 g of platinum oxide. This gave 13.0 g (92%) of a colorless liquid with b.p. 105-107°/2 mm, n_D^{20} 1.4690, d_4^{20} 1.0397. *MR* 56.85. Calculated 56.51.

$C_{12}H_{20}O_3$. Found, %: C 67.53, 67.57; H 9.22, 9.36
Calculated, %: C 67.89; H 9.50

3,6-Endoethylenetetrahydropyran-2-carboxylic acid (XI). A mixture of 10.6 g (0.05 mole) of ester (X), 100 ml of CH_3COOH, and 10 ml of 10% HCl was boiled for 1 hour. This gave 6.9 g (88%) of a colorless liquid with b.p. 119-120°/2 mm, n_D^{20} 1.4950, d_4^{20} 1.2034. *MR* 37.85. Calculated 37.92.

$C_8H_{12}O_3$. Found, %: C 61.50, 61.53; H 7.88, 7.74
Calculated, %: C 61.52; H 7.75

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