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A Cleavage of a Furan Derivative Observed during the Curtius Reaction

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It is well known that furfuryl alcohol derivatives are easily attacked by acidic reagents to afford γ-diketones, γ-ketoacids, or γ-lactones. In this paper a conversion of a furfuryl alcohol derivative to a γ-valerolactone derivative in the absence of acidic reagent during the Curtius reaction is reported.

Furfuryl alcohol (I) was converted to 2-hydroxymethylfuran-3,4-dicarboxylic acid dimethylester (II) by the Alder-Rickert reaction.[1] 2-Acetoxymethylfuran-3,4-dicarboxylic acid (IV), which was obtained by alkaline hydrolysis of dimethylester (II) followed by acetylation with acetic anhydride-pyridine, was treated with thionyl chloride to give 2-acetoxymethylfuran-3, 4-dicarbonylchloride (V). Diacyl azide (VI), which was prepared from the reaction of acyl chloride (V) with sodium azide, was subjected to the Curtius reaction in ethanol or benzyl alcohol-benzene solution.

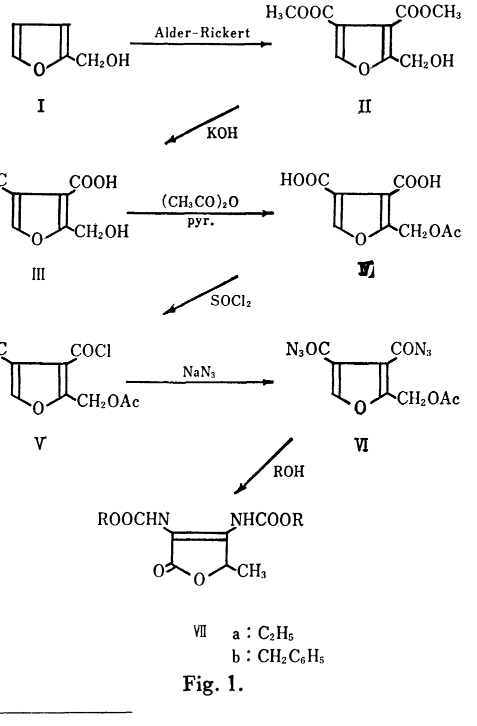

Fig. 1.

The structures of the products separated by means of silica gel column chromatography were elucidated from IR, NMR, and UV spectroscopic studies. When diacyl azide (VI) was heated in ethanol, the product showed the absorption at 1780, 1690, 1190 cm^{-1} in IR spectrum which indicated the presence of α,β-unsaturated γ-lactone. In NMR spectrum signals of a three proton doublet at δ1.55 (J=6.5 Hz) and one proton quartet at δ 5.70 (J=6.5 Hz) appeared. This showed the presence of structure of $\rangle$CH-CH$_3$ in the molecule. UV spectrum also showed $\lambda_{\max}$ at 267.5 mμ (ε, 15.500). From these results as well as from elemental analysis and molecular weight measurement, the structure of the product was confirmed to be α,β-dehydro-α,β-dicarbethoxyamino-γ-valerolactone (VII, a). When benzyl alcohol was used on the Curtius reaction, the product which showed similar spectra to those of VIIa in IR and NMR was confirmed to have the structure of α,β-dehydro-α,β-dicarbobenzyloxyamino-γ-valerolactone (VII, b).

Experimental

All melting points are uncorrected. IR, NMR, and UV were measured by use of Jasco IR-S, Varian A-60, and Hitachi EPS-3 spectrometers, respectively.

2-Hydroxymethylfuran-3,4-dicarboxylic Acid Dimethylester (II). A mixture of furfuryl alcohol (1) (4.9g, 0.05 mol), acetylenedicarboxylic acid dimethylester (7.2 g, 0.05 mol) and anhydrous dioxane (20m*l*) was heated under reflux for 5 hr. After dioxane was removed, the residue was dissolved in ethyl acetate (50m*l*). The solution was subjected to hydrogenation with 10% palladium on charcoal under atmospheric pressure at room temperature. When one equivalent (0.05mol) of hydrogen was absorbed, the catalyst was filtered off and the filtrate was evaporated to remove ethyl acetate. The residue was heated to 200°C under reduced pressure of about 100 mmHg until the generation of ethylene stopped. Subsequent distillation at 2 mmHg afforded 2-hydroxymethylfuran-3,4-dicarboxylic acid dimethylester (II) (9.0 g, 84%), bp 140—141°C/2 mmHg. IR (neat): 3450, 1730, 1600, 1200, 1080, 770 cm^{-1}. NMR (CDCl$_3$): δ 3.83, 3.87 (7H, s-s), 4.73 (2H, s), 7.87 (1H, s).

Found: C, 49.80; H, 4.74%. Calcd for $C_9H_{10}O_6$: C, 50.47; H, 4.71%.

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[1] K. Alder and H. F. Rickert, *Ber.*, **70**, 1354 (1937); K. Hofmann, *J. Amer. Chem. Soc.*, **67**, 421, 738 (1945).

2-Hydroxymethylfuran-3,4-dicarboxylic Acid (III). 2-Hydroxymethylfuran-3,4-dicarboxylic acid dimethylester (II) (12.9 g, 0.06 mol) was dissolved in methanol (60 m*l*). To this solution sodium hydroxide aqueous solution (8.4 g in 20 m*l*) was added dropwise with cooling, and the reaction mixture was allowed to stand for 18 hr at room temperature. After evaporating methanol under reduced pressure, the residual solution was acidified with concentrated hydrochloric acid (14.5 m*l*). Precipitated crystals were collected on a funnel and washed with a small amount of cold water. Recrystallization from water gave 2-hydroxymethylfuran-3,4-dicarboxylic acid (III) (7.7 g, 16%), mp 173°C (dec). IR (Nujol): 3300, 1720, 1620, 1015, 765 cm^{-1}.

Found: C, 44.98; H, 3.19%. Calcd for $C_7H_6O_6$: C, 45.17; H, 3.25%.

2-Acetoxymethylfuran-3,4-dicarboxylic Acid (IV). A mixture of 2-hydroxymethylfuran-3,4-dicarboxylic acid (20 g, 0.11 mol), acetic anhydride (40 m*l*) and pyridine (80 m*l*) was stirred for 10 min until disolution was complete. After the increase in temperature of the solution stopped, the solution was gradually heated and kept at about 100°C for 4 hr. The crystalline product obtained after the reaction mixture had been cooled was collected and dissolved in water (100 m*l*). The solution was acidified with concentrated hydrochloric acid to precipitate crude product. Recrystallization from ethyl acetate gave 2-acetoxymethylfuran-3,4-dicarboxylic acid (IV) (12.5 g, 51%), mp 156.5—157°C. IR (Nujol): 1725, 1200, 1050, 770 cm^{-1}.

Found: C, 47.22; H, 3.53%. Calcd for $C_9H_8O_7$: C, 47.38; H, 3.53%.

2-Acetoxymethylfuran-3,4-dicarbonyl Chloride (V). A mixture of 2-acetoxymethylfuran-3,4-dicarboxylic acid (IV) (4 g, 0.018 mol) and thionyl chloride (10 m*l*) was heated under reflux for 1 hr. After evaporating excess of thionyl chloride, distillation of the residual oil afforded 2-acetoxymethylfuran-3,4-dicarbonyl chloride (V) (4.4 g, 95%) bp 128°C/1 mmHg. IR (neat): 1750—1790, 1600, 1220, 750 cm^{-1}.

Found: Cl, 25.77%. Calcd for $C_9H_6O_5Cl_2$: Cl, 26.75%.

α,β-Dehydro-α,β-dicarbethoxyamino-γ-valerolactone (VII,a). To a solution of sodium azide (2.2 g, 0.034 mol) in water (10 m*l*), which was cooled with ice-salt bath, was added a solution of 2-acetoxymethylfuran-3,4-dicarbonyl chloride (V) (4.4 g, 0.017 mol) in anhydrous ether (20 m*l*) during 30 min with vigorous stirring. The reaction mixture was then stirred for an additional 3 hr at below 0°C. The ethereal layer was washed well with cooled saturated sodium bicarbonate solution and cooled water, and dried over anhydrous magnesium sulfate. Ether was removed under reduced pressure at room temperature. Crude acyl azide (VI) (5.3 g) thus obtained was dissolved in ethanol (20 m*l*), and the ethanol solution was heated gradually under nitrogen atmosphere. After the first vigorous evolution of gas ceased, the reaction mixture was refluxed for an additional 2 hr. Ethanol was removed under reduced pressure and residual oil was subjected to column chromatography on silica gel (Kieselgel, 0.02—0.5 mm, 50 g). The fraction eluted with carbon tetrachloride-chloroform (1:1, 600 m*l*) afforded 1.3 g of crude product. Recrystallization from methanol gave α,β-dehydro-α,β-dicarbethoxyamino-γ-valerolactone (VII,a) (710 mg, 16%) mp 120—121°C. IR (Nujol): 3350, 3100, 1780, 1740, 1690, 1570, 1270, 1190, 1050 cm^{-1}. NMR ($CDCl_3$): δ 1.30 (6H, t), 1.55 (3H, d, J=6.5 Hz), 4.21, 4.23 (4H, q, q), 5.70 (1H, q, J=6.5 Hz) UV: $\lambda_{\max}^{\text{EtOH}}$ 267.5 mμ (ε=15.500).

Found: C, 48.45; H, 5.85; N, 10.26%; mol wt (Rast), 268. Calcd for $C_{11}H_{16}O_6N_2$: C, 48.52; H, 5.92; N, 10.29%; mol wt, 272.

α,β-Dehydro-α,β-dicarbobenzyloxyamino-γ-valerolactone (VII,b).

The crude acyl azide (VI), prepared from 2-acetoxye methylfuran-3,4-dicarboxylic acid (4.5 g, 0.017 mol) by the same procedure as described above, was heated under reflux with benzyl alcohol (3.9 g, 0.036 mol) in benzene (20 m*l*) for 2.5 hr. After evaporating benzene, the residual oil was subjected to column chromatography on silica gel (Kieselgel, 0.02—0.5 mm, 50 g). The fraction eluted with chloroform-carbon tetrachloride (1:1, 300 m*l*) afforded α,β-dehydro-α,β-dicarbobenzyloxyamino-γ-valerolactone (VII, b) (770 mg, 11%) mp 115—116°C (recrystallized from methanol). IR (Nujol): 3350, 1750, 1735, 1700, 1570, 1270, 1190, 1030 cm^{-1}. NMR ($CDCl_3$): δ 1.50 (3H, d, J=6 Hz), 5.17 (4H, s), 5.70 (1H, d, J=6 Hz), 7.35 (10H, s).

Found: C, 63.71; H, 5.14; N, 7.08%. Calcd for $C_{21}H_{20}O_6N_2$: C, 63.63; H, 5.09; N, 7.07%.