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FACILE AND HIGHLY SELECTIVE SYNTHESIS OF 2,2-DIALKYL-1,5-LACTONES BY THE CALBOXYLATION OF PRIMARY,TERTIARY-1,4-DIOLS WITH FORMIC ACID OR COPPER(I)CARBONYLS IN THE PRESENCE OF CONCENTRATED SULFURIC ACID

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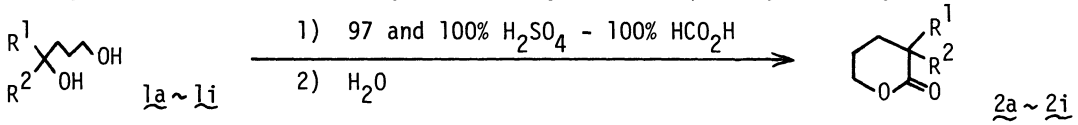
The carboxylation of primary,tertiary-1,4-diols with 100% formic acid or copper(I)carbonyls and carbon monoxide in the presence of 97~100% H_2SO_4 at room temperature and under atmospheric pressure gave 2,2-dialkyl substituted 1,5-lactones in high yields.

The carboxylation of olefins and alcohols with carbon monoxide or formic acid in the presence of a strong acid is an important reaction for the preparation of tertiary-carboxylic acids which is well known as the Koch-Haaf reaction.[1] Diols are considered to be interesting substrates for the synthesis of lactones by the reaction. However, hitherto reported reactions of diols invariably produced a mixture of dicarboxylic acid, hydroxymonocarboxylic acids and other oxygen containing compounds together with lactones.[2-4] We now wish to report a facile and highly selective synthesis of 2,2-dialkyl substituted lactones by the carboxylation of primary,tertiary-1,4-diols.[5]



1a~1i 2a~2i

A mixture of a 1,4-diol (5 mmol) and 100% HCO_2H were added dropwise for 15 min simultaneously stirring to a concentrated sulfuric acid media at 17~23 °C. After additional stirring for 1.0~1.2 h, the reaction mixture was poured on ice (100 gr) and extracted continuously with diethyl ether (100 ml) for 24 h using a liquid-liquid extraction apparatus. The products were obtained by working up in the usual manner. The carboxylation using copper(I)carbonyls of the 1,4-diols was carried out followed by the method referred to in, 6).

The results are summarized in Table.[7] The reaction of 4-methyl-1,4-pentanediol, 1a using 97~100% sulfuric acid took place smoothly to give 2,2-dimethyl-5-pentanolide, 2a exclusively in high yields. In the reaction using 93% sulfuric acid, on the other hand, the formation of 2,2-dimethyloxolane proceeded preferentially with a low yield of 2a. Other products such as 1,4-lactones, hydroxymonocarboxylic acids and dicarboxylic acids were not obtained. The preferential formation of 1,5-lactone, 2a in the presence of sulfuric acid of 97% or higher seems to indicate that the reaction of carbon monoxide with an initially formed carbenium ion having another hydroxyl group which is strongly protonated under the strongly high acidic media, proceeds rapidly to afford a protonated hydroxyacylcarbocation before the occurrence of other reactions such as cyclization, deprotonation and so on.

In the reactions of 1,4-diols, 1b~1i having a long alkyl chain at their 4 position, exclusive formation of corresponding 2,2-dialkyl-1,5-lactones, 2b~2i was observed. This result is interesting for the carboxylation of monols or olefins having long alkyl chain is usually accompanied by their skeletal rearrangement.[8,9]

The present procedure is considered to be a useful and convenient synthetic method for 2,2-dialkyl-1,5-lactones.[10]

Table The Carboxylation of Primary,Tertiary-1,4-Diols, 1a~1i

Substrate			Acid	HCO_2H	React.time	Yield of product (%)[a]	
1,4-Diol	R^1	R^2	(ml)	(ml)	(h)	1,5-Lactone	Others
1a	CH_3	CH_3	20[b]	2.0	1.2	2a, 10	89[i]
1a	CH_3	CH_3	21[c]	2.0	1.3	2a, 94	3[i]
1a	CH_3	CH_3	21[d]	2.0	1.3	2a, ~100	0[j]
1a	CH_3	CH_3	20[e]	1.8	1.3	2a, ~100	0[j]
1a	CH_3	CH_3	40[c]	—[f]	4.4	2a, 68	31[i]
1a	CH_3	CH_3	40[d]	—[f]	6.3	2a, ~100	0[j]
1a	CH_3	CH_3	20[g]	—[h]	2.0	2a, 46	50[i]
1b	$-(CH_2)_4-$		21[c]	0.6	1.0	2b, 86	0[j]
1c	$-(CH_2)_5-$		20[c]	0.5	1.1	2c, 88	0[j]
1d	CH_3	C_2H_5	21[c]	1.9	1.3	2d, 92	0[j]
1e	CH_3	n-C_3H_7	21[c]	2.0	1.4	2e, 95	0[j]
1f	CH_3	n-C_4H_9	21[c]	2.9	1.2	2f, 96	0[j]
1g	CH_3	n-C_5H_{11}	21[d]	3.2	1.2	2g, 95	trace[j]
1h	CH_3	n-C_6H_{13}	21[d]	4.5	1.3	2h, 87	trace[j]
1i	CH_3	n-C_8H_{17}	20[d]	4.2	1.2	2i, 72	trace[j]

a) Based on 1,4-diols (5 mmol) employed. b) 93% H_2SO_4. c) 97% H_2SO_4. d) 100% H_2SO_4. e) 5% SO_3-H_2SO_4. f) Cu_2O, 5 mmol; CO, 1 atm; 1,4-diol, 10 mmol; react.temp., ~25 °C. g) BF_3-H_2O(1:1 molar ratio). h) Cu_2O, 2.5 mmol; CO, 1 atm. i) 2,2-Dimethyloxolane. j) 1,4-Lactones.

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