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CARBOXYLATION OF γ-BUTYROLACTONES WITH CARBON MONOXIDE USING HF-SbF_5 SUPER ACID

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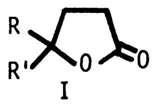
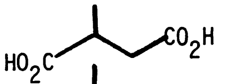
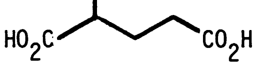
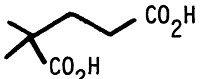
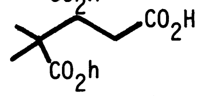
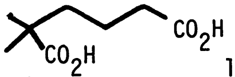
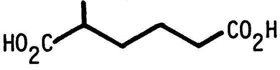
γ-Butyrolactones react with carbon monoxide at -20 to 30 °C and at atmospheric pressure in HF-SbF_5 super acid media containing an excess of SbF_5 to give dicarboxylic acids in good yields.

Although diols and lactones are considered to be useful substrates for the preparation of dicarboxylic acids by the reaction with carbon monoxide in strong acid media, diprimary, primary-secondary, and disecondary diols with small carbon numbers are known to be quite difficult to undergo the reaction in usual strong acids such as H_2SO_4 and BF_3-H_2O.1) Previously we reported that the carboxylation of these diols proceeds smoothly in HF-SbF_5.2) However, in spite of high conversion of substrates under such conditions, lactones were main products, paticularly in the reaction of diols having the structures that favor five or six membered lactone formation, the reason of which should be that five or six membered lactones once formed are stable and do not form dicarboxylic acids by the further reaction with carbon monoxide. In order to overcome this difficulty, we examined the carboxylation of lactones and found that γ-butyrolactones are readily carboxylated with carbon monoxide in HF-SbF_5 containing an excess of SbF_5 to give corresponding dicarboxylic acids in good yields.

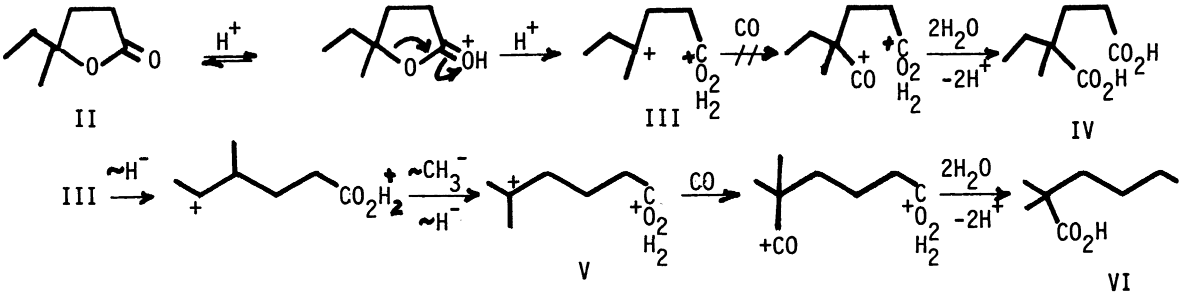
A solution of HF-SbF_5 (ca. 20 cm^3) was placed in a three-necked 100 cm^3 Kel-F reaction vessel under sufficient stirring at a given temperature. Then a lactone (10 mmol) was added dropwise for 45 min into the acid solution with the introduction of carbom monoxide. The reaction mixture was hydrolyzed with ice-water and the products were extracted with ether. Dicarboxylic acids thus formed were esterified with diazomethane and then analyzed by VPC. Some of the results are listed in Table 1.

Judging from the products, the carbon-oxygen bonds of γ-butyrolactones with γ-alkyl or γ,γ'-dialkyl groups are cleaved readily by the protonation of oxygen atom in the super acid solution to give corresponding carbenium ions such as III, which react with carbon monoxide and then with water to yield dicarboxylic acids, as shown in Scheme. γ-Butyrolactone itself gives the primary carbenium ion in the initial stage of reaction. This unstable cation would isomerize to the more stable secondary carbenium ion preferentially. Consequently, γ-butyrolactone does not give pentanedioic acid but produces 2-methylbutanedioic acid exclusively. The yield was not good under the conditions described in Table 1 (32%), but it increased in the prolonged reaction (63% at 3 h). γ-Alkyl- or γ,γ'-dialkylbutyrolactones react more readily with carbon monoxide under the similar conditions giving corresponding dicarboxylic acids in almost quantitative yields, because these lactones form stable secondary or tertiary carbenium ions as depicted in Scheme.

Table 1. Carboxylation[a)] of γ-Butyrolactones (I)

 I R	 R'	Reaction temperature (°C)	Molar ratio of SbF_5/lactone	Molar ratio of HF/SbF_5	Product[b)] and yield (%)[c)]
H	H	30	6.1	1.7	 32
CH_3	H	30	5.0	2.3	 100
CH_3	H	0	4.9	2.2	 100
CH_3	CH_3	0	4.9	2.5	 100
CH_3	CH_3	0	2.9	5.5	 100
CH_3	CH_3CH_2	-20	2.9	5.3	 100
H	CH_3CH_2	0	5.0	5.5	 96

a) Reaction conditions; CO, 1 atm; reaction time, 1 h; lactone, 10 mmol. b) All products exhibited analytical data and spectra in accordance with structures of authentic samples prepared. c) Determined as methyl esters by VPC and based on the lactones used.



Scheme

Interestingly, γ-ethyl-γ-methyl-γ-butyrolactone (II) did not give 2-ethyl-2-methylpentanedioic acid (IV) but 2,2-dimethylhexanedioic acid (VI) in a quantitative yield. The tertiary carbenium ion (III) initially formed may be unstable because of the protonated carboxylic group closely located. Consequently, it isomerizes to the cation (V), which then gives VI. The same type of result was observed in the reaction of γ-ethylbutyrolactone giving 2-methylhexanedioic acid exclusively. The present procedure provides a facile dicarboxylic acid synthesis from lactones.

References

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