

PALLADIUM CATALYZED REACTION OF ETHYLENE, γ -BUTYROLACTONE AND CUPRIC CHLORIDE

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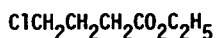
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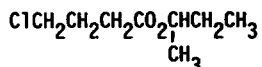
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There have been published numerous papers describing various reactions of olefins in the presence of palladium catalyst.

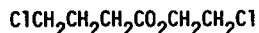
The present communication reports the reaction of ethylene, γ -butyrolactone and CuCl_2 in the presence of Pd metal or PdCl_2 as catalyst. The following three esters of 4-chlorobutyric acid were formed.



I



II



III

Among these three esters, 2-chloroethyl 4-chlorobutyrate (III) is quite specific for the three components reaction by palladium catalyst. The other two esters, I and II, are produced in the two components reaction between ethylene and γ -butyrolactone by palladium catalyst.

In a 50 ml stainless steel tube 3 ml (3.9 mmoles) of γ -butyrolactone and 5.3 g (3.9 mmoles) of CuCl_2 were placed, to which ethylene was compressed up to 55 kg/cm² at room temperature. The tube was closed and was heated in an oil bath at the desired temperature. Then the reaction mixture was freed from the insoluble catalyst residue and was subjected to gas chromatography analysis. Only the three esters besides γ -butyrolactone were detected, which were isolated by preparative gas chromatography and were identified by nmr and infrared spectra and by the comparison of the retention time of gas chromatography with the authentic samples. The structure of III rests on its infrared and nmr spectra. In the infrared spectrum, the bands at 1740 and 1175 cm⁻¹ were assigned to the ester group. The nmr spectrum showed a triplet at τ 5.76 (2H, $-\text{OCH}_2-$), two overlapping triplets at τ 6.47 and 6.43 (4H, two ClCH_2- groups), a diffused triplet at τ 7.52 (2H, $-\text{CH}_2\text{CO}_2-$), and a multiplet at τ 7.90 (2H, $-\text{C}-\text{CH}_2-\text{C}-$).

The results are shown in the following table. In these reaction, neither stirring nor shaking was applied. Consequently, much improved yields of products may be expected for the reaction with stirring. The combined yields of I, II and III are not so high. Unreacted γ -butyrolactone was recovered, whose amount well counterbalanced the amount of the reacted one.

TABLE I. Reaction of Ethylene, γ -Butyrolactone and Cupric Chloride by Palladium Catalyst.^{a)}

Catalyst (mole %) ^{b)}	Reaction temp. (°C)	Yields of Products (%) ^{c)}		
		I	II	III
PdCl ₂ (10)	120	1.4	3.2	7.1
PdCl ₂ (1)	80	0.1	0.4	5.5
"	120	3.0	0.8	9.0
"	160	0.7	0.2	9.0
Pd (10)	80	0.6	0.2	4.8
Pd (1)	120	2.5	0.5	9.4
"	160	0.6	0.1	7.7
No catalyst ^{d)}	80	no product		
Two Components Reaction of Ethylene and γ -Butyrolactone				
PdCl ₂ (50)	120	0.1	2.1	0
PdCl ₂ (10)	80	trace	1.3	0
HCl (44)				

a) To a mixture of 3 ml of γ -butyrolactone, 5.3 g of CuCl₂ and catalyst, in a pressure tube, ethylene was compressed up to 55 kg/cm² at room temperature. The reaction tube was closed and heated at the indicated temperature for 20 hrs.

b) The amounts of catalysts are based on γ -butyrolactone.

c) The yields of products are based on γ -butyrolactone.

d) The three components reaction without palladium catalyst.

The ester (III) is formed in the three components reaction of ethylene, γ -butyrolactone, and CuCl_2 in the presence of PdCl_2 or Pd metal as catalyst. In the absence of palladium catalyst, no reaction was observed. Furthermore, the reaction of ethylene, γ -butyrolactone and CuCl instead of CuCl_2 in the presence of PdCl_2 produced only I and II in quite small yields. The two components reaction of ethylene and γ -butyrolactone by PdCl_2 catalyst yielded small amounts of I and II. Even a fairly large amount of PdCl_2 was employed, III was not formed in the two components reaction.

In the formation of III, CuCl_2 plays an essential role. When the amount of CuCl_2 was increased, the yield of III was increased. For example, the relative peak area of III in gas chromatography analysis was 0.14, 1.0 and 2.1, respectively, when the amount of CuCl_2 was 50, 100 and 200 mole % to γ -butyrolactone in the reaction with 10 mole % PdCl_2 at 80°C .

It might be assumed as one of the possible mechanisms that the ring opening of γ -butyrolactone with hydrochloric acid occurred first to produce 4-chlorobutyric acid which was a precursor of each of three esters, I, II and III. The additions of ethylene and butene-2 to 4-chlorobutyric acid would give I and II, respectively. As to the formation of III, the addition of vinyl chloride to 4-chlorobutyric acid might be assumed. A patent¹⁾ has claimed the treatment of ethylene with PdCl_2 and cupric halide to prepare vinyl halide. However, the direction of the acid catalyzed addition of vinyl chloride²⁾ is opposite to that leading to III, and III may be formed by another reaction path. Further studies are required to elucidate the mechanism of the three components reaction. These results may be interestingly compared with the formation of vinyl or alkenyl ester in the reaction of carboxylic acid with olefin by palladium catalyst in the presence of base.³⁾

REFERENCES

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