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PALLADIUM CATALYZED REACTION OF BUTADIENE MONOXIDE WITH CARBON DIOXIDE

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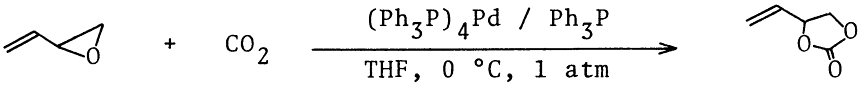
Carbon dioxide readily reacts with 1,3-butadiene monoxide in the presence of a catalytic amount of tetrakis(triphenylphosphine)-palladium under ordinary pressure at 0 °C to afford vinylethylene carbonate in a quantitative yield.

The catalytic process for synthesis of cyclic carbonates from epoxides and CO_2 have been always operated under high pressure at elevated temperature.[1)] Although some catalyst systems composed of metal halides and Lewis bases were found to be active under normal conditions, even the most effective catalyst system among them needed very long reaction time.[2)] Vinylethylene carbonate described herein has also synthesized under severe conditions of temperature and pressure.[3)] In this communication, we wish to report the very facile reaction of CO_2 with 1,3-butadiene monoxide 1 catalyzed by a low valent palladium complex under mild conditions.



1 2

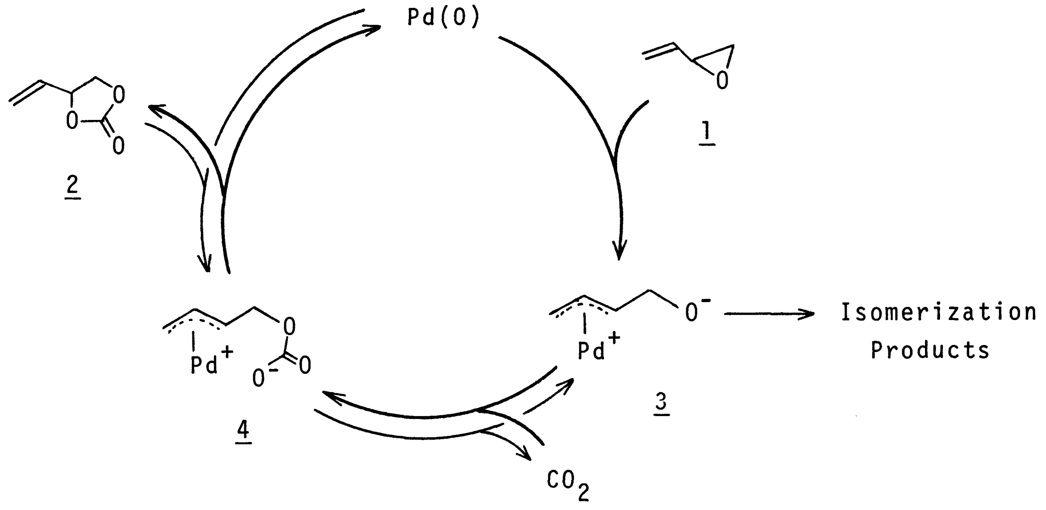
A solution of 1 (1.4 g, 20 mmol), $(Ph_3P)_4Pd$ (0.12 g, 0.1 mmol), and triphenylhposphine (0.03 g, 0.1 mmol) in THF (10 cm^3) was stirred under nitrogen atmosphere and cooled in an ice bath. Then a excess amount of CO_2 (ca. 600 cm^3) was introduced into the solution under ordinary pressure during 5 min. After stirring was continued under CO_2 atmosphere for 15 min at 0 °C or room temperature, the quantitative formation of vinylethylene carbonate 2 was observed in ^{1}H-NMR and IR spectra.[5)] The yield of 2 determined by GLC was 96%.

Since the reaction was exothermic, a rapid introduction of CO_2 without cooling resulted in a loss in the yield of 2 to 62%. When the reaction mixture was refluxed for 2 h, 2 was completely converted to the decarboxylated isomerization products, 3-butenal and an unidentified viscous material which had no absorption band of cyclic carbonate in the IR spectrum.

It has been recently reported that diene monoxides undergo the palladium mediated reactions such as isomerization or allylic alkylation with nucleophiles.[6)] These reactions have been commonly considered to proceed via π-allyl complexes generated by oxidative addition of diene monoxides to palladium(0) species. According to these mechanistic aspects and our experimental observations mentioned above, the present reaction may be explained by the following scheme.

The oxidative addition product, π-allyl intermediate 3, from 1 and palladium (0) species reacts with electrophilic CO_2. Then the resulting carbonate complex 4 should undergo the intramolecular nucleophilic attack on the inner π-allylic carbon atom to give 2 and palladium(0) species. The isomerization products at risen temperature may be formed by the side reactions involving the reverse process from 2 and palladium(0) species.7)

From isoprene monoxide, 4-methyl-4-vinylethylene carbonate was also formed in 92 % yield by the same procedure. Further works related to the palladium catalyzed reactions using other diene monoxides and other heteroallenes instead of CO_2 are in progress.



References

1) Some recent examples: R. J. De Pasquale, J. Chem. Soc., Chem. Commun., 1973, 157; H. Matsuda, A. Ninagawa, R. Nomura, and T. Tsuchida, Chem. Lett., 1979, 573; H. Matsuda, A. Ninagawa, and R. Nomura, ibid., 1979, 1261; R. Nomura, A. Ninagawa, and H. Matsuda, J. Org. Chem., 45, 3735 (1980).

2) M. Ratzedhofer and H. Kisch, Angew. Chem., Int. Ed. Engl., 19, 317 (1980).

3) Reported catalysts and conditions (temperature, pressure) are as follows: ethylbutylpyrrolidinium carbonate (120-150 °C, 35 atm)4a); NaI/Al_2O_3 (150-200 °C, 80-40 atm)4b); $MnCl_2\cdot 4H_2O/Ph_3P$ (190 °C, ca. 120-60 atm)4c); tricyclohexylphosphine (210 °C, ca. 130-60 atm)4d)

4) a) P. P. McClellan, U. S. Patent 2873282 (1959); Chem. Abstr., 53, 15987i (1959); b) W. Muenster and E. Dreher, Ger. Patent, 1169459 (1964); Chem. Abstr., 61, 4218d (1964); c) Y. Fujita, T. Morimoto, and T. Nakano, Japan Kokai 72-26786 (1972); Chem. Abstr., 77, 139451f (1972); d) Y. Fujita, T. Morimoto, and T. Nakano, Japan Kokai, 73-22702 (1973); Chem. Abstr., 79, 146007 (1973).

5) 2: bp 43-45 °C/13 Pa, IR ($CHCl_3$) 1804 cm^{-1} (C=O), ^1H-NMR ($CDCl_3$) δ 4.13 (1H, dd, J=8.4 and 7.2 Hz, OCH_2), 4.59 (1H, dd, J=8.4 and 7.7 Hz, OCH_2), 4.95-5.31 (1H, m, OCH), 5.27-6.21 (3H, m, $CH=CH_2$).

6) M. Suzuki, Y. Oda, and R. Noyori, J. Am. Chem. Soc., 101, 1623 (1979); J. Tsuji, H. Kataoka, and Y. Kobayashi, Tetrahedron Lett., 22, 2573 (1981); B. M. Trost and G. A. Molander, J. Am. Chem. Soc., 103, 5969 (1981).

7) Supporting the reverse process, vinylethylene carbonate 2 reacted with nucleophiles in the presence of $(Ph_3P)_4Pd$ to produce hydroxybutenyl derivatives through the oxidative addition of 2 to palladium(0) species to form 4. The details will appear in another article.

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