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Palladium-catalysed dimerization of isoprene with carbon dioxide in the presence of organotin ethoxide and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU)

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Abstract

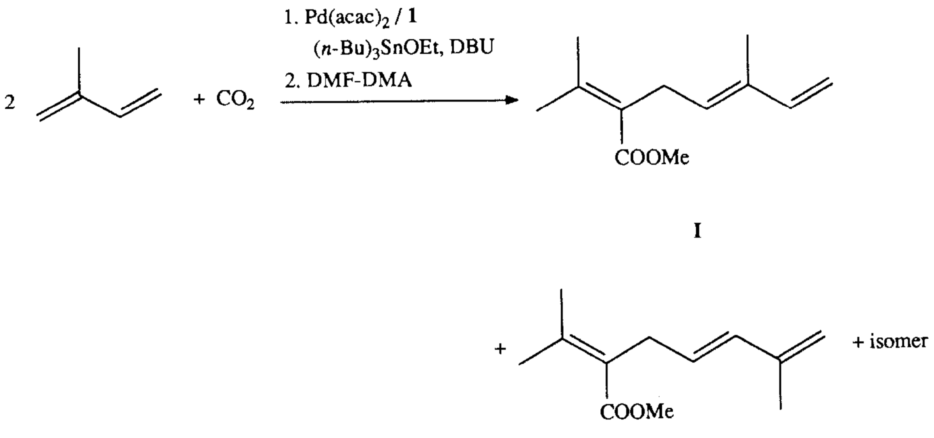
The palladium-catalysed dimerization of isoprene with carbon dioxide is promoted by treatment with tributyltin ethoxide and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU).

The chemistry of carbon dioxide has become of interest in recent years because of its environmental implications. By use of transition metal catalysts, a large number of carbon dioxide fixation reactions have been carried out [1]. In particular the reaction of butadiene and carbon dioxide has been intensively studied [2]. In contrast, the interaction of the less reactive isoprene with carbon dioxide has been little studied. Behr reported that all his attempts to bring about reaction of isoprene with carbon dioxide failed [1c], and Inoue observed formation of only very small amounts of lactones (about 1%) in addition to the isoprene dimers during his studies of the dimerization of isoprene [3]. However, from the standing point of natural product syntheses isoprene dimer compounds are particularly interesting [4].

Tsuji reported that isoprene reacts with isocyanate (a hetero analogue of carbon dioxide) to give divinylpiperidones in high yields in the presence of catalytic amounts of palladium-triphenylphosphine complexes [5]. Intuitively one would expect that by taking advantage of potential activators carbon dioxide could be incorporated effectively into isoprene, and we have now found that a combination of tributyltin ethoxide and DBU does provide effective activation.

Coupling of organotin reagents with π-allyl palladium complexes is well documented [6]. Furthermore, Baba observed a high catalytic activity of organotin halide and Lewis base systems in equimolar and alternate copolymerization of oxetane with carbon dioxide [7].

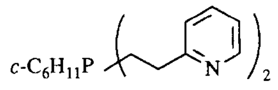
In the present work, a DMF solution of isoprene, Pd(acac)$_2$, ligand **1** [8], and DBU was allowed to react under CO$_2$ pressure in the presence of tributyltin ethoxide. The resulting compounds were esterified. Subsequent GLC analysis re-



I

II

Ligand **1** =



vealed nine peaks, and the mass spectrum indicated the same molecular formula ($C_{10}H_{15}CO_2CH_3$) for all of them. Two of these components were isolated and identified as the head-to-tail dimer I and tail-to-tail dimer II.

Although Inoue obtained five-membered lactones, he could not confirm the formation of the acids corresponding to esters I and II.

It can be seen from Table 1 that both tributyltin ethoxide and DBU separately promote the reaction, but not as effectively as the mixture of both. Davies reported that carbon dioxide reacts readily with tin alkoxide to give tin carbonate, but that carbon dioxide is released when the carbonate is heated [9].

$$R_3SnOR' + CO_2 \rightleftharpoons R_3SnOCO_2R'$$

We think this tin carbonate is an effective carrier of carbon dioxide. The sign of the effect of DBU is obscure. Previously we found that DBU is effective in the oxidative coupling reactions of alkenes with carbon dioxide and Ni^0 to give oxanickela complexes [10], and DBU may activate the π-allyl palladium complex.

Table 1

Palladium-catalysed dimerization of isoprene with carbon dioxide

Catalytic system	Turnover number
Pd(acac)$_2$ + **1** + ^{n}Bu$_3$SnOEt + DBU	21
Pd(acac)$_2$ + **1**	3
Pd(acac)$_2$ + **1** + DBU	8
Pd(acac)$_2$ + **1** + ^{n}Bu$_3$SnOEt	10

Experimental

To a solution of $Pd(acac)_2$ (0.20 g, 0.66 mmol), ligand **1** (0.35 g, 1.07 mmol), DBU (1.66 g, 10.9 mmol) and tributyltin ethoxide (1.82 g, 5.4 mmol) in 100 ml of dry DMF at −40 °C under argon was added an excess of isoprene (20 ml). The mixture was placed in an autoclave and stirred for 84 h at 80 °C under CO_2 pressure (50 bar). After cooling, the solution was concentrated and made basic with 1 *N* sodium hydroxide. The aqueous mixture was washed with ether, acidified with 2 *N* H_2SO_4, and extracted with three portions of ether. The combined extracts were dried over $MgSO_4$ and concentrated. Purification by column chromatography (silica gel) using hexane–EtOAc–AcOH (500 : 10 : 1) afforded 2.4672 g (13.7 mmol, 21 turnover numbers, see Table 1) of carboxylic acids. Treatment of the thus obtained acids with *N*,*N*-dimethylformamidedimethylacetal (DMF-DMA) gave the methyl esters (68%, after purification by silica gel chromatography using 4% EtOAc in hexane) [11]. These were analyzed by GLC (Varian 3700, SE-54 column) and GLC/MS (Varian MAT CH7). A pure sample of ester I or II was isolated by preparative GLC (Gerstel AMPG-60) and was characterized by ^{1}H NMR (Bruker AC 200) and IR (Nicolet 7199 FT-IR) spectroscopy.

I: ^{1}H NMR (200 MHz, $CDCl_3$, TMS) δ 6.31 (d of d, 1H, $-CH=C(CH_3)C\mathit{H}=CH_2$, $J = 10.7$ and 17.5 Hz), 5.34 (q of t, 1H, $-CH_2C\mathit{H}=C(CH_3)CH=CH_2$, $J = 0.7$ and 7.1 Hz), 5.07 (d, 1H, $=C(CH_3)CH=C\mathit{H}_2$ *cis*, $J = 17.5$ Hz), 4.91 (d, 1H, $=C(CH_3)CH=C\mathit{H}_2$ *trans*, $J = 10.7$ Hz), 3.68 (s, 3H, $-CO_2C\mathit{H}_3$), 3.13 (d, 2H, $=C(CO_2CH_3)C\mathit{H}_2CH=$, $J = 7.1$ Hz) 1.98 (s, 3H, $(C\mathit{H}_3)_2C=$), 1.80 (s, 3H, $(C\mathit{H}_3)_2C=$), 1.76 (d, 3H, $=C(C\mathit{H}_3)CH=CH_2$, $J = 0.7$ Hz). IR 1720 cm^{-1} (C=O), 1220 cm^{-1} (C–O).

II: ^{1}H NMR (200 MHz, $CDCl_3$, TMS) δ 6.12 (d, 1H, $=C\mathit{H}C(CH_3)=CH_2$, $J = 15.8$ Hz), 5.60 (t of d, 1H, $C\mathit{H}=CHC(CH_3)=CH_2$, $J = 6.2$ and 15.8 Hz), 4.85 (2H, $=CHC(CH_3)=C\mathit{H}_2$), 3.73 (s, 3H, $CO_2C\mathit{H}_3$), 3.13 (d, 2H, $-C\mathit{H}_2CH=CHC(CH_3)=CH_2$, $J = 6.2$ Hz), 2.04 (s, 3H, $(C\mathit{H}_3)_2C=C-$), 1.84 (s, 3H, $(C\mathit{H}_3)_2C=C-$), 1.82 (3H, $-CH=CHC(C\mathit{H}_3)=CH_2$). IR 1720 cm^{-1} (C=O), 1200 cm^{-1} (C–O).

References

1 (a) S. Inoue and N. Yamazaki (Eds.), Organic and Bio-organic Chemistry of Carbon Dioxide, Kodansha, Tokyo, 1982; (b) G. Wilkinson, F.G.A. Stone and E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, Vol. 8, Pergamon, New York, 1982, p. 225; (c) A. Behr, Carbon Dioxide Activation by Metal Complexes, VCH, Weinheim, 1988; (d) P. Braunstein, D. Matt and D. Nobel, Chem. Rev., 88 (1988) 747.

2 (a) Y. Inoue,Y. Sasaki and H. Hashimoto, Bull. Chem. Soc. Jpn., (1978) 2375; (b) A. Musco, J. Chem. Soc., Perkin Trans. I, (1980) 693; , (c) A. Behr, K-D. Juszak and W. Keim, Synthesis, 7 (1983) 574; (d) H. Hoberg, S. Gross and A. Milchereit, Angew. Chem., Int. Ed. Engl., 26 (1987) 571.

3 Y. Inoue, S. Sekiya, Y. Sasaki and H. Hashimoto, Yuki Gosei Kagaku Kyokaishi, 36 (1978) 328.

4 (a) M. Hidai, H. Ishiwatari, H. Yagi, E. Tanaka, K. Onozawa and Y. Uchida, J. Chem. Soc., Chem. Commun., (1975) 170; (b) J.P. Neilan, R.M. Laine, N. Cortese and R.F. Heck, J. Org. Chem., 41 (1976) 3455.

5 K. Ohno and J. Tsuji, J. Chem. Soc., Chem. Commun., (1971) 247.

6 J.K. Stille, Angew. Chem., Int. Ed. Engl., 25 (186) 508.

7 A. Baba, H. Meishou and H. Matsuda, Makromol. Chem., Rapid Commun., 5 (1984) 665.

8 Tricyclohexylphosphine was also effective, but the functionalized ligand **1** gave the products in somewhat better yields. **1** was prepared as previously described. See S.D. Toto and J.T. Doi, J. Org. Chem., 52 (187) 4999.

9 (a) A.J. Bloodworth and A.G. Davies, J. Chem. Soc., (1965) 5238; (b) A.G. Davies, P.R. Dalan and S.C. Vasishtha, Chem. Ind. (London), (1967) 229.

10 H. Hoberg, Y. Peres, C. Krüger and Y.-Y. Tsay, Angew. Chem., Int. Ed. Engl., 26 (1987) 771.

11 J.P. Thenot, E.C. Horning, M. Stafford and M.G. Horning, Anal. Lett., 5 (1972) 217.