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Preliminary communication

RHODIUM CATALYZED REACTION OF BUTADIENE AND CARBON DIOXIDE

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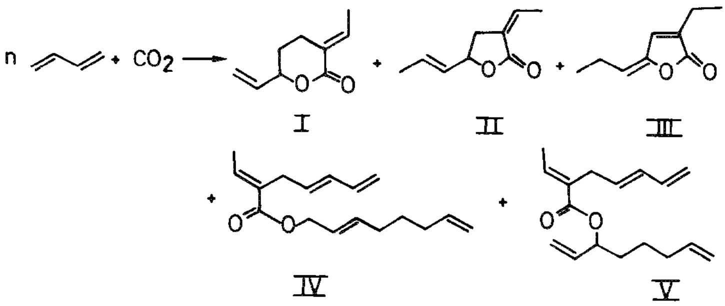
Summary

In the rhodium-catalyzed reaction of butadiene and carbon dioxide the new γ-lactone 2-ethyl-2,4,9-undecatrien-4-olide is formed in a novel combination of three molecules of butadiene with one of CO_2.

The reaction of butadiene and carbon dioxide has been intensively studied in recent years [1—5]. Palladium complexes have been found to be active catalysts, yielding the lactones I—III, formed from one CO_2 and two butadiene molecules, and the esters IV and V, formed from one CO_2 and four butadiene molecules. In these products the carbon atom of CO_2 is linked to a carbon of the hydrocarbon chain formed by the butadiene units.



Rhodium complexes are also known to catalyze C—C-coupling reactions; in both oligomerizations [6—8] and telomerizations [9] use of rhodium compounds as catalysts is well established. Rhodium also catalyzes reactions of unsaturated compounds with carbon dioxide; for example, the reaction of propyne with CO_2

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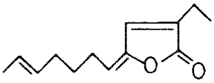
yielding a pyrone [10] and that of ethylene with CO_2 to give propionic acid [11]. In addition, numerous interesting stoichiometric reactions were described recently in which carbon dioxide was activated by rhodium complexes [12—16]. These results encouraged us to extend our investigations of the reaction between butadiene and carbon dioxide to catalysis by rhodium complexes.

Results and discussion

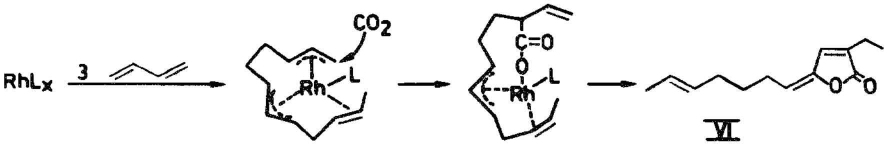
The rhodium-catalyzed reaction of butadiene and carbon dioxide gave the lactones I—III, but the esters IV and V were not formed. In addition to these known products, the new γ-lactone 2-ethyl-2,4,9-undecatrien-4-olide (VI) was obtained, in which three molecules of butadiene are combined with one CO_2.



VI

As shown by GLC analysis, lactone VI exists in four isomeric configurations based on the two double bonds in its hydrocarbon chain. Three further peaks in the gas chromatogram give the same molecular ion as VI ($M^+ = 206$) in the mass spectrum, but a different fragmentation pattern. It can be assumed that these products are C_{13}-δ-lactones; they could not be isolated, however, because they were formed only in trace amounts. The IR spectrum of lactone VI shows a strong absorption at 1770 cm^{-1} which is typical of γ-lactones of this type. Other spectral data are in the Experimental section below.

The best catalyst for the synthesis of lactone VI proved to be rhodium dietheneacetylacetonate which contains ligands which dissociate readily. This complex must be stabilized by the presence of a phosphorus ligand. The addition of a threefold amount of triethylphosphine, a ligand with high basicity and low steric demand, afforded a 5% yield of lactone VI, whereas with bulkier phosphines or phosphites only traces of the product were obtained. At low reaction temperatures (90—100°C) the dimers of butadiene were the main products. The optimum temperature proved to be 120°C; above this, decomposition of the catalyst predominated. The most favourable solvent for the reaction was acetonitrile. In alcohols such as ethanol or isopropanol only small amounts of lactone VI were obtained and n-pentane or acetone deactivated the catalyst. In addition to $[Rh(C_2H_4)_2acac]$, some other rhodium compounds also proved to be active catalyst precursors; for example, the ionic rhodium complexes $[Rh(nbd)(PPh_3)_2]BPh_4$ and $[Rh(cod)(PPh_3)_2]PF_6$ as well as neutral monomeric and dimeric allylrhodium complexes such as $[Rh(C_3H_5)_2acac]$ and $[Rh(C_3H_5)_2(OAc)]_2$. The neutral phenyl- and phenoxy-rhodium phosphine complexes $XRh(PPh_3)_3$ with X = Ph or PhO had no catalytic activity.



VI

The formation of the new lactone VI can be accounted for in terms of the mechanistic pathway shown in Scheme 1; this includes some intermediates so far unknown in rhodium catalysis. The initial rhodium complex is suggested to react with three molecules of butadiene, which combine with formation of a C_{12}-chain η^3,η^3,η^2-bound to the rhodium. Analogous transition metal complexes with a C_{12}-chain have previously been described. Wilke and coworkers isolated a similar complex in the nickel-catalyzed trimerization of butadiene [17], and the related ruthenium compound $[Ru(C_{12}H_{24})Cl_2]$ was prepared from $RuCl_3$ and butadiene [18]. Insertion of carbon dioxide into the terminal allyl group of the proposed rhodium-C_{12} chain complex gives a C_{13}-carboxylate complex, which yields lactone VI.

Alongside lactone VI, the C_9-lactones I—III are also formed by rhodium catalysis. It can be assumed that in a parallel reaction path a C_8-chain rhodium complex is formed, yielding the lactones I—III, as in palladium catalysis [1].

Experimental

A solution of $[Rh(C_2H_4)_2acac]$ (0.65 mmol) and PEt_3 (1.95 mmol) in 30 ml of acetonitrile was placed in a 75 ml steel autoclave and 0.2 mol of butadiene and 0.4 mol of carbon dioxide were added. The solution was stirred for 24 h at 120°C After cooling the mixture was concentrated and analyzed by GLC (Carlo Erba 2900 S) and GLC/MS (Varian MAT 112 S). A pure sample of lactone VI was isolated by preparative GLC (Hupe APG 402), and was characterized by ^{1}H NMR (Varian EM 390), ^{13}C NMR (Bruker CXP 200) and IR (Perkin—Elmer 577) spectroscopy.

^{1}H NMR (90 MHz, $CDCl_3$, TMS): δ 6.95 (s, 1H, $=C\mathit{CH}{=}$); 5.38 (m, 2H, $CH_3\mathit{CH}{=}\mathit{CH}CH_2$); 5.1 (t, 1H, $CH_2\mathit{CH}{=}C$); 2.35 (m, 4H, $HC{=}C\mathit{CH}_2CH_3$ and $CH_2\mathit{CH}_2CH{=}C$); 2.0 (m, 2H, $CH_3HC{=}CH\mathit{CH}_2CH_2$); 1.7—1.3 (m, 5H, $\mathit{CH}_3CH{=}CHCH_2\mathit{CH}_2CH_2$); 1.17 (t, 3H, $CH_2\mathit{CH}_3$) ppm.

^{13}C NMR (200 MHz, $CDCl_3$): δ 170.6 ($\mathit{C}{=}O$); 148.5 ($HC{=}\mathit{C}O$); 136.2 ($=C\mathit{C}H{=}C$); 134.9 ($HC{=}\mathit{C}C{=}O$); 130.4 ($CH_3\mathit{C}H{=}CHCH_2$); 125.4 ($CH_3CH{=}\mathit{C}HCH_2$); 114.4 ($CH_2CH_2\mathit{C}H{=}C$); 32.1 ($CH_2\mathit{C}H_2CH{=}C$); 28.9 ($CH_3CH{=}CH\mathit{C}H_2CH_2$); 25.6 ($CH_2\mathit{C}H_2CH_2$); 18.4 ($HC{=}C\mathit{C}H_2CH_3$); 17.8 ($\mathit{C}H_3CH{=}CHCH_2$); 11.8 ($\mathit{C}H_3CH_2$) ppm.

IR: ν 3005, 2985, 2935, 2880, 2860, 1770, 1675, 1615, 1460, 1440, 1230, 1075, 1035, 965 cm^{-1}.

Mass spectrum: m/e = 206 (M^+, 29%); 191 (2,3); 178 (6); 177 (24,2); 165 (12,5); 150 (25); 138 (30); 137 (22,8); 125 (46,5); 110 (55); 96 (16,3); 95 (25); 83 (21); 82 (53); 81 (27); 79 (22); 77 (18); 67 (55); 55 (100); 41 (79); 39 (44).

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