

PLATINUM-METAL CATALYSED FORMATION OF LINEAR OCTADIENES

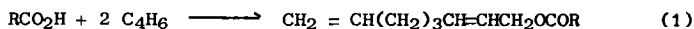
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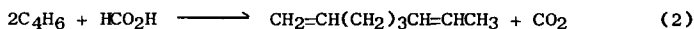
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A recent paper¹ describes the formation of octa-2,7-dienyl esters from butadiene and carboxylic acids (equation 1) in the presence of organic bases and catalysed by palladium salts.



We find that in the case of formic acid, the reaction takes a different course leading very specifically to the formation of octa-1,6-diene. For example, when a mixture of formic acid and triethylamine was autoclaved at 50°C with butadiene using diacetatopalladium(II) as catalyst the 1,6-diene was produced with an efficiency of 1,000 moles C₈H₁₄ per g atom Pd, and in > 90% yield based on consumed formic acid. The product was free from other C₈ olefins and formate ester was produced in only trace amounts. Carbon dioxide is released during the reaction and the stoichiometry is as follows (2). The constitution



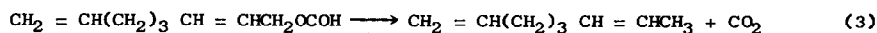
of the octadiene was established by spectroscopic techniques and by its absorption of 2 moles of hydrogen to afford n-octane.

Weaker bases such as dimethylformamide (Table I) were also effective in forming highly pure octa-1,6-diene but if undiluted formic acid were used a very complicated product was produced of the composition expected from an acid catalysed diene esterification².

Of the various possible mechanisms for this reaction we have shown that the octadiene does not arise by a specific hydrogenation of primarily formed octa-1,3,7-triene³. The intermediacy of octa-2,7-dienyl formate is also ruled out since although a solution of octa-2,7-dienyl formate in dimethylformamide readily affords octa-1,6-diene(3) in the presence of diacetato-palladium(II) no decomposition occurred in the presence of a high concentration of butadiene.

TABLE I OCTADIENE FORMATION FROM BUTADIENE (0.6 moles) AND FORMIC ACID (0.26 moles)

CATALYST m moles	BASE moles	DURATION hr	TEMP °C	OCTADIENE		
				m moles	% 1,7-Diene	% 1,6-Diene
Pd(OAc) ₂ 0.1	(C ₂ H ₅) ₃ N 0.14	20	50	110	-	99
Pd(OAc) ₂ 0.09	(CH ₃) ₂ NCHO 0.25	20	40	180	-	99
[(C ₆ H ₅) ₃ P] ₂ Pd(OAc) ₂ 0.1	(CH ₃) ₂ NCHO 0.25	5	50	150	33	66
[n-Bu ₃ P] ₂ Pd(OAc) ₂ 0.1	(CH ₃) ₂ NCHO 0.25	3	100	40	66	33
Li ₂ PtCl ₄ 0.1	(CH ₃) ₂ NCHO 0.25	2.5	100	40	80	15
Pt(C ₅ H ₇ O ₂) ₂ 0.1	(CH ₃) ₂ NCHO 0.25	3	100	100	40	55



It seems certain therefore that hydride species are formed at an early stage of the reaction and then add directly to a butadiene derived C₈ chain bonded to the metal via two- π -allyl groups⁴.

In contrast to the reactions using palladium catalysts, reactions using platinum salts afforded octa-1,7-diene in addition to the 1,6-diene. Using lithium tetrachloroplatinate(II) in the formic acid-dimethylformamide system the 1,7-diene made up 80% of the product. Mixtures of octa-1,7- and 1,6-diene were similarly obtained when palladium catalysts complexed with phosphines were used, and the ratio of the olefins depended on the particular phosphine employed.

References

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