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PLATINUM-METAL CATALYSED FORMATION OF LINEAR OCTADIENES

By S Gardner and D Wright

(Imperial Chemical Industries Limited, Petrochemicals Division,
Research and Development Department, Billingham, Teesside).

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A recent paper[1] 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.

$$RCO_2H + 2\ C_4H_6 \longrightarrow CH_2 = CH(CH_2)_3CH{=}CHCH_2OCOR \qquad (1)$$

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 C_8H_{14} per g atom Pd, and in $> 90\%$ yield based on consumed formic acid. The product was free from other C_8 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

$$2C_4H_6 + HCO_2H \longrightarrow CH_2{=}CH(CH_2)_3CH{=}CHCH_3 + CO_2 \qquad (2)$$

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 esterification[2].

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-triene[3]. 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	$(C_2H_5)_3N$ 0.14	20	50	110	-	99
$Pd(OAc)_2$ 0.09	$(CH_3)_2NCHO$ 0.25	20	40	180	-	99
$[(C_6H_5)_3P]_2\ Pd(OAc)_2$ 0.1	$(CH_3)_2NCHO$ 0.25	5	50	150	33	66
$[n\text{-}Bu_3P]_2Pd(OAc)_2$ 0.1	$(CH_3)_2NCHO$ 0.25	3	100	40	66	33
Li_2PtCl_4 0.1	$(CH_3)_2NCHO$ 0.25	2.5	100	40	80	15
$Pt(C_5H_7O_2)_2$ 0.1	$(CH_3)_2NCHO$ 0.25	3	100	100	40	55

$$CH_2 = CH(CH_2)_3\ CH = CHCH_2OCOH \longrightarrow CH_2 = CH(CH_2)_3\ CH = CHCH_3 + CO_2 \qquad (3)$$

It seems certain therefore that hydride species are formed at an early stage of the reaction and then add directly to a butadiene derived C_8 chain bonded to themetal via two-π-allyl groups[4].

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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