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Preliminary communication

Reaction of active methylene compounds with butadiene catalysed by nickel complexes

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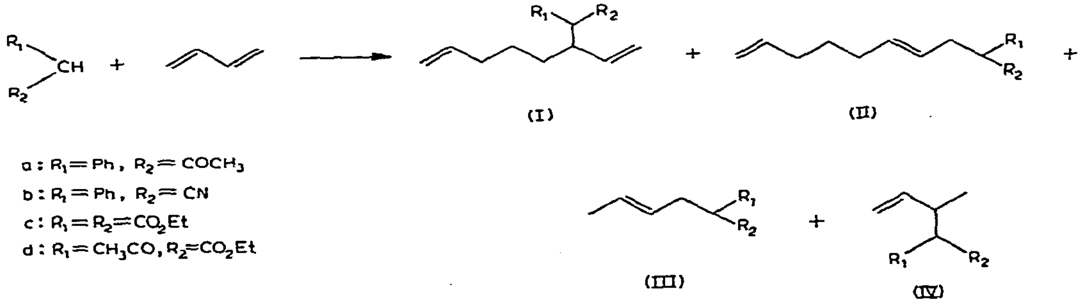
Reactions of active hydrogen compounds with 1,3-butadiene have been reported with catalysis by both nickel and palladium complexes. Palladium(0) complexes have been shown to catalyse the reaction of butadiene with alcohols[1], amines[2], carboxylic acids[2,3] and active methylene and methyne compounds[4]. Although telomerisation of methanol with butadiene in the presence of a Ni^0 complex has been reported[5], the reaction is, by no means, general for all alcohols. Furthermore, whilst the presence of amines has been reported to facilitate the dimerisation of butadiene catalysed by a Ni^0–triethyl phosphite complex[6], alkylation of amines by butadiene has been shown to be catalysed by a Ni^0-complex prepared from a dialkoxy phosphine[7]. In the present communication we report that no direct extrapolation can be made from the reactions of active methylene compounds with butadiene catalysed by Pd^0 complexes to equivalent reactions involving Ni^0 catalysts. Whereas compounds such as benzyl methyl ketone and benzyl cyanide react readily with butadiene in the presence of catalytic amounts of a Ni^0 complex, diethyl malonate and ethyl acetoacetate require higher concentrations of catalyst.

Benzyl methyl ketone (0.05 *M*), butadiene (0.15 *M*), $Ni(acac)_2$ (0.75 mmole), phenyldiisopropoxyphosphine (1.13 mmole), sodium borohydride (0.3 mmole) and sodium phenoxide (1.4 mmole) were heated at 75° for 16 hours to give a 93% conversion to a mixture of Ia (5%), IIa (8.1%), IIIa (8%) and IVa (6%). The structures of the products

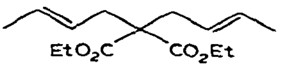


(I) (II) (III) (IV)

a : R_1 = Ph, R_2 = $COCH_3$
b : R_1 = Ph, R_2 = CN
c : R_1 = R_2 = CO_2Et
d : R_1 = CH_3CO, R_2 = CO_2Et

could be assigned unambiguously from their NMR spectra (CCl_4)★; IIa, δ, 1.4 (m, 2H, methylene), 1.8–2.0 (m, 4H, allylic), 1.95 (s, 3H, methyl), 2.6 (m, 2H, methylene), 3.7 (t, 1H,–CHCO–), 4.7–5.1 (m, 2H, terminal olefin), 5.15–6.1 (m, 3H, vinylic), and 7.2 (s, 5H, aromatic) ppm; Ia, δ, 1.4 (m, 4H, methylene), 2.0 (s, 3H, methyl), 1.9–2.1 (m, 2H, allylic), 3.45 (d, 1H, α-phenyl, J 10Hz), 2.5–2.9 (m, 1H, allylic), 4.7–5.15 (m, 4H, terminal olefinic), 5.3–5.9 (m, 2H, vinylic) and 7.2 (s, 5H, aromatic) ppm. The structures of IIIa and IVa were also clearly differentiated. In IVa the methyl absorption appeared as two doublets due to the presence of two diastereoisomers arising from two chiral centres in this molecule. Similarly, a 55% conversion of benzyl cyanide to Ib (10%), IIb (70%), IIIb (7%) and IVb (13%) was found in 16 h at 100°. Under the same conditions no reaction was found with diethyl malonate. When the concentration of nickel salt and phosphine was increased, however, reaction was observed. For example, with the ratio of diethyl malonate/$Ni(acac)_2$/phosphine, 1/0.06/0.06, 96% reaction was observed at 100° for 16 h. A mixture of Ic (4%), IIc (15%), IIIc (33%), IVc (38%), V (4%) and VI (6%) was obtained. Similar results were found with ethyl acetoacetate but no reaction was found with acetyl acetone even under conditions with a stoichiometric amount of nickel salt and phosphine.

The reactions depend upon the ability of the dialkoxy phosphine to reduce the Ni^{II} salt to a Ni^0 species[8]. For the octadienyl products I and II, dimerisation of the diene to yield intermediate VII is followed by reaction with the methylene compound at either the 1- or 3-position of one of π-allyl groups. Reaction probably involves initial coordination of the methylene compound onto the nickel atom and subsequent formation of the carbon–carbon bond; intermediate VII can also give rise to 1,3,7-octatriene or vinylcyclohexene★★. Formation of the butenyl products can be envisaged as arising from an intermediate associated with only one molecule of butadiene with the diene acting as a two π-electron ligand VIII. Some complexing of diethyl malonate to the nickel species explains the lack of reaction at low nickel salt concentration. This hypothesis finds support in the absence of reaction with acetyl acetone. The ability of diethyl malonate to act as a chelating



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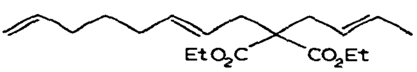

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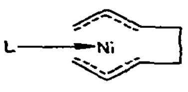

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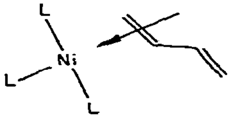


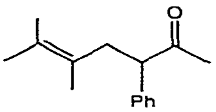
(VIII)

★Separation of the products was achieved by fractional distillation and GLC. The other physical data were fully consistent with the assigned structures. The omission of sodium phenoxide from the reaction results in a rate decrease.

★★These products are formed in varying amounts in all these reactions from excess diene.

ligand, thus preventing coordination of a further molecule of butadiene, is reflected in the distribution of the products. Butenyl derivatives are predominant in the diethyl malonate reaction, compared with the preferred formation of octadienyl derivatives with benzyl methyl ketone. In this connection, we have observed that the addition of small amounts of acetyl acetone to a mixture of benzyl methyl ketone and butadiene effectively prevents the reaction between the monoketone and diene. It would appear that the differences in chelation between the intermediates of these reactions involving diesters, keto-esters and diketones is one of degree, and governs the course of reaction.

Benzyl methyl ketone also reacts with isoprene and 2,3-dimethylbutadiene but the extent of reaction, under similar conditions, decreases in the order butadiene > isoprene > 2,3-dimethylbutadiene. Furthermore, the ratio of products varies so that the amount of butenyl derivative formed increases with substitution on the diene. For example, the major product obtained from 2,3-dimethylbutadiene is IX and isoprene yields a mixture of X (21%), XI (56%), XII (4%) and XIII (19%).



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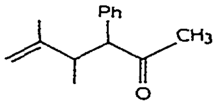

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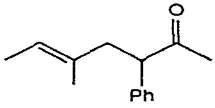

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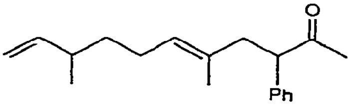

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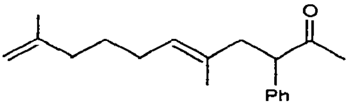

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