Nickel Complex-catalysed Telomerization of Butadiene with Alcohols

By T. C. SHIELDS* and W. E. WALKER

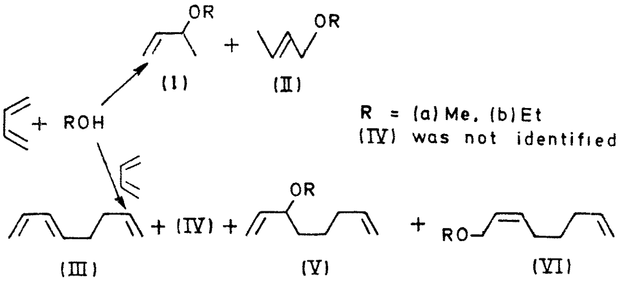
(*Research and Development Department, Union Carbide Corporation, Chemicals and Plastics, South Charleston, West Virginia 25303*)

Summary Nickel complex catalysts are used with butadiene and alcohols to give octa-2,7-dienyl ethers as the major products.

ZERO-VALENT nickel complexes are known to catalyse the dimerization and trimerization of butadiene.[1,2] If active hydrogen compounds are added to the reaction, a variety of products is formed, but all are hydrocarbon oligomers.[2] In one instance a low yield of octadienylated amine was reported[3] in a nickel complex-catalysed oligomerization of butadiene in the presence of amine.

When palladium complex catalysts are used with butadiene in the presence of active hydrogen compounds, the major products are telomers rather than hydrocarbon oligomers. Much recent work has dealt with the novel synthesis of octa-2,7-dienyl derivatives by the palladium-catalysed telomerizations of butadiene with alcohols,[4,5] carboxylic acids,[6,7] amines,[6] active methylene compounds,[8] and water.[9] Palladium-catalysed telomerization of butadiene with aldehydes[10,11] gave mainly cyclic structures of the divinyltetrahydropyran type. We now report the telomerization of butadiene with alcohols catalysed by nickel complexes.

For example, nickel acetylacetonate (0·25 mmol), phenyldi-isopropoxyphosphine (0·375 mmol), and sodium borohydride (4 mg) were added to oxygen-free methanol (10 ml) and the mixture agitated. This mixture, together with butadiene (50 m mol) was charged to a pressure tube and heated at 100° for 2 h. The mixture was found to contain six products. The two shortest retained peaks (Ia, IIa) were isolated by preparative vapour–liquid chromatography.† The n.m.r. spectrum of (Ia) consisted of a characteristic vinyl pattern between δ 5·80 and 4·80 (3H, m, *J ca.* 6·5 Hz) and δ 3·60 (1H, allylic, oxygen geminal), 3·18 (3H, methoxy), and 1·18 (3H, d, methyl, *J ca.* 6·5 Hz). That of (IIa) had δ 5·47 (2H, m, olefin), 3·73 (2H, m, allylic oxygen geminal), 3·16 (3H, methoxy), and 1·67 (3H, m, allylic). These data together with g.l.p.c. and n.m.r. comparisons with authentic samples established five products arising from the reaction. These products with their respective yields were: 27·4% 3-methoxybut-1-ene (Ia), 6·7% 1-methoxybut-2-ene (IIa), 17·8% octa-1,3,7-triene (IIIa), 9·5% 3-methoxyocta-1,7-diene (Va), and 31·3% 1-methoxyocta-2,7-diene (VIa).



R = (a) Me, (b) Et
(IV) was not identified

The use of other alcohols gave varying results. Ethanol gave a more efficient formation of octadienyl ethers but with lower conversion of butadiene. Isopropyl alcohol gave a complex mixture of hydrocarbon oligomers with cyclo-octa-1,5-diene being a main product. No reaction was observed with t-butyl alcohol or phenol. Phenol, however, did react in the presence of a catalytic amount of phenoxide ion, with 1-phenoxyocta-2,7-diene being a major product.

---

† Isolation was performed on a 0·5 in. × 6 ft. 30% SE-30 silicone gum rubber column at 65°.

The use of arylalkoxyphosphines as ligands is necessary for this nickel-catalysed telomerization Thus, in addition to the previously mentioned phenyldi-isopropoxyphosphine, diphenylethoxyphosphine could be used as the ligand, but all attempts with triphenylphosphine, triphenyl phosphite, or tri-isopropyl phosphite proved unsuccessful These experimental results are probably related to the known[12] ability of aryldialkoxyphosphines to reduce nickel(II) salts readily to nickel(0) species

(*Received, November 23rd*, 1970, *Com* 2018)

[1] G Wilke, *Angew Chem Internat Edn* , 1963, **2**, 105
[2] J Feldman, O Frampton, B Saffer, and M Thomas, *Amer Chem Soc , Div Petrol Chem , Preprints*, 1963, **9** (4), A55
[3] P Heimbach, *Angew Chem* , 1968, **80**, 967
[4] E J Smutney, *J Amer Chem Soc* , 1967, **89**, 6793
[5] S Takahashi, T Shibano, and N Hagihara, *Tetrahedron Letters*, 1967, 2451
[6] S Takahashi, T Shibano, and N Hagihara, *Bull Chem Soc Japan*, 1968, **41**, 454
[7] W E Walker, R M Manyik, K E Atkins, and M L Farmer, *Tetrahedron Letters*, 1970, 3817
[8] G Hata, K Takahashi, and A Miyake, *Chem and Ind* , 1969, 1836
[9] K E Atkins W E Walker, and R M Manyik, submitted for publication in *Chem Comm*
[10] P Haynes, *Tetrahedron Letters*, 1970, 3687
[11] R M Manyik, W E Walker, K E Atkins, and E S Hammack, *Tetrahedron Letters*, 1970, 3813.
[12] A A Orio, B B Chastain and H B Gray, *Inorg Chim Acta*, 1969, **3** (1), 8