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SELECTIVE CATALYTIC ACTIVITY OF METAL COMPLEXES TOWARDS ACETYLENES: CYCLISATION OF 2-METHYLBUT-3-YN-2-OL TO 1,2,4-TRIS(1-HYDROXY-1-METHYLETHYL) BENZENE

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In the course of our studies on the reactivity of 2-methylbut-3-yn-2-ol(I) in the presence of some nickel and platinum complexes we have found that this acetylene derivative is linearly polymerised in the presence of the complex cis-$(Ph_3P)_2PtCl_2$ (1) (medium length of the polymeric chain about 20 monomeric units) and that the same acetylenic alcohol is trimerised to 1,3,5-tris(1-hydroxy-1-methylethyl) benzene in the presence of the complex $(nBu_3P)_2NiBr_2$ (yield about 90%) (2).

Now we have found that in the presence of the complex $(Ph_3P)_2NiI_2$ (II) I is converted in very high yield to 1,2,4-tris(1-hydroxy-1-methylethyl) benzene.

The complexes previously proposed for the cyclisation of I gave normally mixtures of cyclisation and polymerisation products from which pure compounds were obtained in lower yields (3-4). A typical experiment is given below: to 5 ml (4.34 g) of I in 15 ml of benzene 0.418 g of II are added. The reaction mixture is refluxed for about 1 hour. In the course of the reaction a crystalline mass separates. After cooling the solid product is filtered off and recrystallised from benzene-CH_3OH (1:1) (yield 3.67 g - 85%) m.p. 186-87°C; U.V. max 262 nm in CH_3OH log ε 2.35; I.R. 1608(mw) 1555(mw) cm^{-1}; N.M.R. in DMSO (δ values referred to TMS): H aromatic 7.30 s (1H), 7.09 s (2H); -OH 6.93 s (1H), 6.90 s (1H), 4.71 s (1H); $-CH_3$ 1.56 s (12H) 1.38 s (6H); mw osmometric

254 (calc. 252); mass spectrum (70 eV - m/e values, ions, relative intensities, m^* = metastable ions): 237 $(M-CH_3)^+$ (10); 235 $(M-OH)^+$ (0.1)(252 $\xrightarrow{-OH}$ 235) m^*= 219.15; 220 $(M-CH_3OH)^{\cdot+}$ (19); 219 $(M-CH_3-H_2O)^+$ (100) (237 $\xrightarrow{-H_2O}$ 219) m^* = 202.37; 204 $(M-2CH_3-H_2O)^{\cdot+}$ (7) (219 $\xrightarrow{-CH_3}$ 204) m^* = 190.03; 201 $(M-CH_3-2H_2O)^+$ (4) (219 $\xrightarrow{-H_2O}$ 201) m^* = 184.48; 161 (12); 159 (6); 143 (5); 92 (8); 77 $(C_6H_5)^+$ (3); 59 $(C(CH_3)_2OH)^+$ (19); 43 $(C(CH_3)_2H)^+$ or $(COCH_3)^+$ (68); 41 $(CH_2=C-CH_3)^+$ (6); 31 $(OCH_3)^+$ (5); 28 $(CO)^{\cdot+}$ (5); 18 $(H_2O)^{+\cdot}$ (37).

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