n-Hexadecatetraene prepared by Tetramerization of Butadiene on a Nickel Atom

By NOBORU YAMAZAKI* and SHOJI MURAI

(Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo, Japan)

DURING studies on the synthesis of metal–olefin complexes by means of electrolytic reduction, we have prepared *trans,trans,trans*-n-hexadecatetraene, a partially hydrogenated linear tetramer of butadiene, recovered from its nickel metal complex. It was produced by electrolytic reduction at the platinum cathode of the solution containing (tetrakispyridine)nickel diperchlorate or nickel dichloride and butadiene in ethanol or dimethoxyethane, using tetrabutylammonium perchlorate as an electrolyte.

On electrolysis, the blue colour of $Ni^{2+}(py)_4$ solution changed to brown-red around the cathode. The solvent of the cathodic solution was evaporated off and a brown-red compound was extracted from the supporting electrolyte with diethyl ether; it was composed of nickel and hydrocarbons, exclusive of pyridine and chlorine. This olefin complex is soluble in alcohols, ethers, and benzene, but it becomes an insoluble product on removing the solvent, of which the structure is unknown. Therefore, the complex is difficult to isolate.

The complex as well as its adduct were decomposed by dilute H_2SO_4 or pyrolysed above 150° *in vacuo*, liberating olefin. The organic materials collected in these reactions were distilled and the main product (about 59%) was identified as *trans,trans,trans*-n-hexadecatetraene.

The hydrogenation of the olefin with the Raney nickel catalyst produced n-hexadecane consuming 3·7 moles of hydrogen per mole of the olefin. Examination of the u.v. spectra, suggested that the hydrogenation occurred preferably on the double bond of the third carbon atom, as the amount of conjugated double bond estimated was less than the expected value.

In the i.r. spectrum of the tetramer, there were absorption bands at 960 and 1635 cm.$^{-1}$ due to out-of-plane C-H deformation and C-H stretching vibration of CH=CH *trans*-groups, and at 985 cm.$^{-1}$ due to out-of-plane C–H deformation of the vinyl groups. The structure of the tetramer as hexadeca-1,6,10,14-tetraene was confirmed by the n.m.r. spectrum, where the area ratio of peaks was close to that of the calculated value.

When the electrolysis was performed with bistriphenylphosphinenickel dichloride instead of (tetrakispyridine)nickel dichloride, octa-1,3,7-triene was obtained.

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[1] B. Bogdanovic, M. Kröner, and G. Wilke, *Annalen,* 1966, **699**, 1.