CYCLOTETRAMERIZATION OF BUTADIENE

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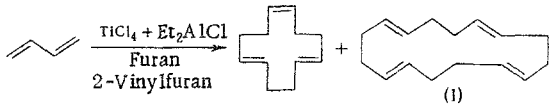
UDC 541.64:547.315.2

The cyclooligomerization of butadiene in the presence of the catalyst $(\pi\text{-}C_3H_5)_2Ni + (\pi\text{-}C_3H_5NiCl)_2$ was described recently, which leads to a complex mixture of cyclooligomers, from which the tetramers and pentamers could be isolated in low yield [1].

We were the first to develop a convenient method for the preparation of trans-1,5,9,13-cyclohexadecatetraene (I) by contacting a benzene solution of butadiene with the catalyst $TiCl_4$–$(C_2H_5)_2AlCl$ at 50°C. A necessary condition is the addition of a modifier (furan or 2-vinylfuran) in a ratio of 5-6 moles to the $TiCl_4$. Under these



conditions a mixture of trans,trans,cis-1,5 9-cyclododecatriene and (I) is formed in 80% yield in a 7:3 ratio. Cyclotetramer (I), isolated by distillation, has 100° (1 mm), mp 18-20°, n_D^{20} 1.5058. Found: C 88.7; H 11.2%. $C_{16}H_{24}$. Calculated: C 88.9; H 11.1%. Infrared spectrum (ν, cm^{-1}): 980, 3030 (trans-CH=CH–); NMR spectrum (δ, ppm): 1.92 (16 H), 5.1 (8H). The mass spectrum contains intense peaks that correspond to the fragments $(M-55)^+$ and $(M-107)^+$, which corresponds to the loss of the groupings $C_4H_7^{\cdot}$ and $C_8H_{11}^{\cdot}$ by the molecular ion. The high intensity of the peak of the molecular ion (70%) indicates the cyclic structure. The hydrogenation of (I) on Pd/C goes with the absorption of 4 moles of H_2 and leads to cyclohexadecane, mp 60°. Found: C 85.6; H 14.2%. Calculated: C 85.7; H 14.3%. The ozonolysis of (I) gives only succinic acid. The bromination of (I) in ether gives the octabromide with mp 156-157° (decompn.). Found: C 22.3; H 2.5; Br 74.5%. Calculated: C 22.4; H 2.8; Br 74.8%.

Institute of Chemistry, Bashkir Branch of the Academy of Sciences of the USSR, Ufa. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 2, p. 487, February, 1975. Original article submitted October 23, 1974.