# PREPARATION OF BUTADIENE CYCLOTETRAMERS ON COMPLEX NICKEL CATALYSTS

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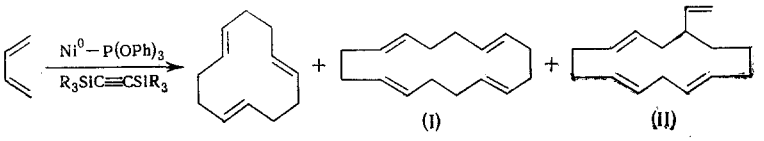
We found that butadiene on the catalytic system: $Ni(acac)_2$—$P(OPh)_3$—$Al(C_2H_5)_3$, 1:1:3 (4) (60°C, 3 h), in the presence of bis(trimethylsilyl)acetylene, is converted in 90% yield to a mixture of cyclic oligomers that consists of trans,trans,trans-1,5,9-cyclododecatriene (I), trans-1,5,9,13-cyclohexadecatetraene (II), and vinyl-trans-1,7,10-cyclotetradecatriene (III) in an 80:15:5 ratio. The mixture of cyclotetramers is easily isolated by fractional distillation through a column. After separation by preparative GLC the hydrocarbons had the following constants:

Hydrocarbon (II), bp 103° (1 mm); $n_D^{20}$ 1.5058. Infrared spectrum ($\nu$, $cm^{-1}$): 975, 3030, (trans-CH=CH—). NMR spectrum ($\delta$, ppm): 1.9 s (16H, —$CH_2$—), 5.1 s (8H, —CH=CH—), m/e 216.

Hydrocarbon (III), bp 126° (0.8 mm); $n_D^{20}$ 1.5138. Infrared spectrum ($\nu$, $cm^{-1}$): 920, 1000, 3085 (—$C=CH_2$), 975, 3030 (trans-CH=CH—). NMR spectrum ($\delta$, ppm): 1.5 m (10H, —$CH_2$—), 1.92 (8H, =C—$CH_2$—), 2.3 (1H, $C_4$—H), 5.1 (2H, —$C=CH_2$), 6.0 (1H, H—C=C), m/e 216.




(I) (II)

Only succinic acid is obtained by the ozonolysis of (II), while the ozonolysis of (III) gives succinic acid and 3-carboxypimelic acid.

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