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FORMATION OF A LINEAR DIMER OF ISOPRENE ON THE COMPLEX CATALYST $(\text{iso-}C_4H_9)_3Al + TiCl_4$

(Presented by Academician I. L. Knunyants on 18 XII 1959)

Thermal dimerization of isoprene leads exclusively to cyclic compounds, as was convincingly shown by I. N. Nazarov and co-workers (⁀1), and later confirmed by American investigators (⁀2). The possibility of linear dimerization of isoprene has been discussed repeatedly (${}^{3-}$6); however, up to the present time, apparently in no case have linear dimers been isolated in individual form, nor has their structure been determined.

Thus, in work (⁀5) it is stated that isoprene in the presence of an aluminosilicate catalyst gives, in negligible yield, a linear dimer which was not isolated by the authors in pure form (it contained an admixture of a dihydrodimer) and did not form an adduct with maleic anhydride. In work (⁀6), during dimerization of isoprene under the action of sulfuric and phosphoric acids, a mixture of dimeric products was obtained, in which the presence of a linear dimer was proved by isolation, after hydrogenation of the mixture over a platinum catalyst at 180°, of 2,6-dimethyloctane. The same work notes the formation of trimeric compounds, but says nothing about their structure. Recently (⁀7) it has been shown that isoprene, under the action of a complex catalyst, polymerizes to cis-1,4-polyisoprene, close in its properties to natural rubber.

In the present work we have found that, on this same catalyst, under changed reaction conditions, isoprene forms mainly dimeric, trimeric, and tetrameric products, and only to a slight extent a polymer. The reaction was carried out by us in toluene solution at a temperature of 75–85° with a catalyst prepared at molar ratios of $(\text{iso-}C_4H_9)_3Al$ to $TiCl_4$ equal to 2.25–3.25 to 1. Under these conditions the reaction proceeds rapidly, and isoprene enters into reaction practically completely. Lowering the reaction temperature or decreasing the ratio of $(\text{iso-}C_4H_9)_3Al$ to $TiCl_4$ increases the amount of copolymer. When the ratio of $(\text{iso-}C_4H_9)_3Al$ to $TiCl_4$ is increased, the reaction rate is greatly slowed, or the reaction does not begin at all. This indicates that the reaction is indeed catalyzed by a complex catalyst. Dimeric and trimeric products are formed in approximately equal amounts; less than 10% polymer is obtained.

Thus, 136 g (200 ml) of carefully dried isoprene were added over 2 hours, with stirring at 75–80°, to 100 ml of toluene containing a catalyst prepared from 5.2 g of (iso-$C_4H_9)_3Al$ and 1.8 g of $TiCl_4$. On distillation of the reaction products, 55 g of a mixture of dimers, 49 g of a mixture of trimers, 12 g of a mixture of tetramers, and, in the residue, 12 g of polymer were obtained. In the present work we investigated mainly the dimeric compounds. Upon fractionation of the dimer mixture on a column, the following were isolated:

1) "Lebedev hydrocarbon" –2,4-dimethyl-4-ethenyl-1-cyclohexene, with b.p. 48–48.5° at 14 mm, n_D^{20} 1.4646, d_4^{20} 0.8321 (literature data (ˆ8): b.p. 44° at 9 mm, n_D^{20} 1.4658, d_4^{20} 0.8331).

2) As the main product, a linear dimer of isoprene, to which, on the basis of its reactions, we assign the structure 2,6-dimethyloctatriene-1,3,6,

$$CH_2 = C(CH_3)CH = CH—CH_2—C(CH_3) = CH—CH_3,$$

with b.p. 57–58° at 12 mm, n_D^{20} 1.4794; d_4^{20} 0.7966.

Found, %: C 88.22; 88.10; H 11.80; 11.85
$C_{10}H_{16}$. Calculated, %: C 88.23; H 11.76

3) A small amount, apparently, of octacyclic dimers with b.p. 66–68° at 12 mm, n_D^{20} 1.4880 (literature data (1): b.p. 83–83.5° at 26 mm, n_D^{20} 1.4885).

The linear dimer of isoprene obtained by us differs from the known natural linear dimers: myrcene and ocimene. On hydrogenation of the linear dimer over a Pd/$BaSO_4$ catalyst at room temperature, 3 moles of hydrogen are absorbed per 1 mole of dimer and 2,6-dimethyloctane is obtained, with b.p. 158–159°; n_D^{20} 1.4103; d_4^{20} 0.7289 (literature data (9): b.p. 158–159.5°, n_D^{20} 1.4100; d_0^{20} 0.7287). On reduction of the dimer with sodium in alcohol, a dihydro compound $C_{10}H_{18}$ is formed, with b.p. 162.5–163.5°; n_D^{20} 1.4458; d_4^{20} 0.7795; MR found 47.44, calculated 47.45.

Found, %: C 86.74; 86.76; H 12.91; 12.89
$C_{10}H_{18}$. Calculated, %: C 88.95; H 13.04

The dihydro compound is apparently 2,6-dimethyloctadiene-2,6; it is readily oxidized in air. The linear dimer reacts vigorously with maleic anhydride, giving, in high yield, an adduct with b.p. 167–168° at 5 mm; n_D^{20} 1.5050.

Found, %: C 71.83; 71.74; H 7.78; 7.65
$C_{14}H_{18}O_3$. Calculated, %: C 71.79; H 7.69

On alkaline hydrolysis of the adduct, a dicarboxylic acid was obtained with m.p. 137-138° (from acetonitrile).

Found, %:	C 66.58; 66.45;	H 8.00; 8.07
$C_{14}H_{20}O_4$. Calculated, %:	C 66.66;	H 7.98

On hydrogenation of the obtained dicarboxylic acid over $Pd/BaSO_4$ at room temperature, 2 moles of hydrogen are absorbed per 1 mole of acid. On ozonization of the linear dimer followed by treatment with hydrogen peroxide, formic and acetic acids were obtained, which indicates the presence in the dimer of $CH_3CH = C <$ and $CH_2 = C <$ groupings. On ozonization of the adduct of the dimer with maleic anhydride, followed by reduction of the ozonide with zinc, acetaldehyde was obtained. This result indicates that the conjugated system of double bonds in the dimer is located on the side of the methylene group,

$$CH_2 = C—C = C <.$$

All the data obtained establish sufficiently convincingly the structure of the dimer as 2,6-dimethyloctatriene-1,3,6.

A preliminary study of the mixture of trimeric compounds also shows that they consist of both linear and cyclic products, but their structure has not yet been established by us. From the mixture, for example, a fraction was isolated with b.p. 117-118° at 8 mm; n_D^{20} 1.4908; d_4^{20} 0.8454; MR found 69.86, calculated 69.60 (for aliphatic sesquiterpene), MR calculated 67.87 (for monocyclic sesquiterpene).

Found, %:	C 88.14; 88.14;	H 11.62; 11.58
$C_{15}H_{24}$. Calculated, %:	C 88.23;	H 11.76

However, this fraction is not a pure aliphatic trimer, since on hydrogenation it absorbs somewhat less hydrogen than follows from the calculation for four double bonds. With maleic anhydride it forms an adduct of composition $C_{19}H_{26}O_3$, with b.p. 193-195° at 5 mm; n_D^{20} 1.5121.

Found, %: C 75.31; 75.29; H 8.50; 8.48
$C_{19}H_{26}O_3$. Calculated, %: C 75.49; H 8.60

On hydrogenation of the adduct, 3 moles of hydrogen are absorbed per 1 mole of adduct. The study of the structure of the trimeric and tetrameric compounds will be continued.

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