

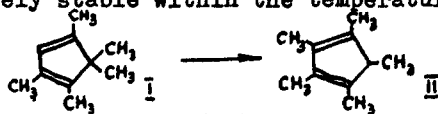
CYCLIC UNSATURATED COMPOUNDS. XXX. THE THERMAL ISOMERIZATION OF 1,2,4,5,5-PENTAMETHYLCYCLOPENTADIENE INTO 1,2,3,4,5-PENTAMETHYLCYCLOPENTADIENE I)

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Earlier we have found ²⁾ that under relatively mild conditions a number of substituted cyclopentadienes undergo the intramolecular 1,2-shift of hydrogen. Thus 5-substituted cyclopentadienes isomerize almost completely into more stable dienes with a free methylene group. 5,5-Disubstituted cyclopentadienes (including spiro-dienes) were assumed to be more unstable thermodynamically ^{2c)}. Actually, heating of such dienes results in the formation of the structures having free methylene group due to the supposed 1,2-migration of alkyl group ³⁾. This paper presents the first example of 1,3-migration of an alkyl group in cyclopentadiene series.

The thermal transformation of 1,2,4,5,5-pentamethylcyclopentadiene(I) ⁴⁾ has been now investigated. It was found that on passing through the quartz tube packed with the crushed quartz at 450-490° the diene (I) undergoes readily the isomerization into 1,2,3,4,5-pentamethylcyclopentadiene (II). The latter appears to be completely stable within the temperature range mentioned.

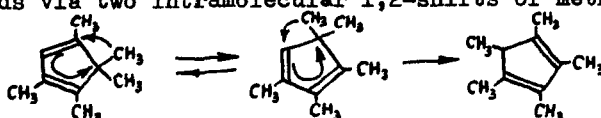


According to g.l.c. the diene (II) may be obtained at 475° with the optimum yield about 56% (74% taking into account the diene (I) recovered). The reaction under these conditions may be used as a convenient method of diene (II) preparation ^{5,6)}.

The by-products of this reaction are: tetramethylcyclopentadiene-6-8% (equilibrium mixture of three isomers ^{2d)}), 1,2,3,5,5-pentamethylcyclopentadiene (III) - 7-II% and nonidentified hydrocarbons - 0-4%. Tetramethylcyclo-

pentadiene formation proceeds to a considerable extent at the temperature above 480°. However there is no hexamethylcyclopentadiene production even at high temperatures. On this basis the observed 1,3-migration of methyl group is assumed to be intramolecular.

The ratio of diene (III) to diene (II) drops markedly with increase of temperature (from 1:0.73 at 400° to 1:8.1 at 500°). Therefore one may suppose that diene (III) is an intermediate product in I → II conversion and this reaction proceeds via two intramolecular 1,2-shifts of methyl group:



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2. See for example: V.A.Mironov, E.V.Sobolev, A.N.Elizarova (a) Dokl.Akad.Nauk, SSSR, 143, III2(1962); (b) Izv.Akad.Nauk, SSSR, Ser.Khim. (1963), I607; (c) Tetrahedron, 19, I939(1963); (d) V.A.Mironov, T.M.Fadeeva, E.V.Sobolev, A.N.Elizarova, Zh.Obshch.Khim., 33, 84(1963).
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4. The methylation of easily preparable tetramethylcyclopentadiene 2d) in liquid ammonia gives 60% yield of diene (I). The used sample of diene (I) was at least 99,9% pure by g.l.c.: b.p. 50,4-50,5° (23 mm), n_D^{20} 1,4630, d_4^{20} 0,8195, $\lambda_{max}^{256 m\mu}$, ϵ 3780 (in heptane). Found: C 88.3; H 11.8%. $C_{10}H_{16}$ requires: C 88.2; H 11.8%. The diene (I) - maleic anhydride adduct: m.p. 177,5-178,5° (from hexane). Found: C 71.8; H 7.8%. $C_{14}H_{18}O_3$ requires: C 71.8; H 7,7%.
5. Pure (> 99,9%) diene (II) has b.p. 70,5-70,6° (23 mm), n_D^{20} 1,4740, d_4^{20} 0,8395, $\lambda_{max}^{267 m\mu}$, ϵ 2760 (in heptane). Found: C 82.2; H 11.6%. $C_{10}H_{16}$ requires: C 88,2; H 11.8%. The main adduct (apparently 7-syn-isomer, see V.A.Mironov, T.M.Fadeeva, A.A.Akhrom, Dokl.Akad.Nauk, SSSR, 174, 852(1967) of diene (II) and maleic anhydride: m.p. 136,5-138° (from benzene-hexane mixture). Found: C 71.9; H 7.8%. $C_{14}H_{18}O_3$ requires: C 71.8; H 7.7%.
6. For the preparative purpose it is reasonable to use the crude mixture of tetramethylcyclopentadiene methylation products, containing 87.5, 12 and 0.5% diene (I), (II) and (III) respectively.^{I)} Repeated pyrolysis of the light fraction from diene (II) separation (diene (I) mainly) allows to increase the total yield of diene (II) to about 70%.