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CYCLIC UNSATURATED COMPOUNDS.XXXVIII.
THE THERMAL REARRANGEMENTS OF SPIRO[4,4]NONA-1,3-DIENE [1].

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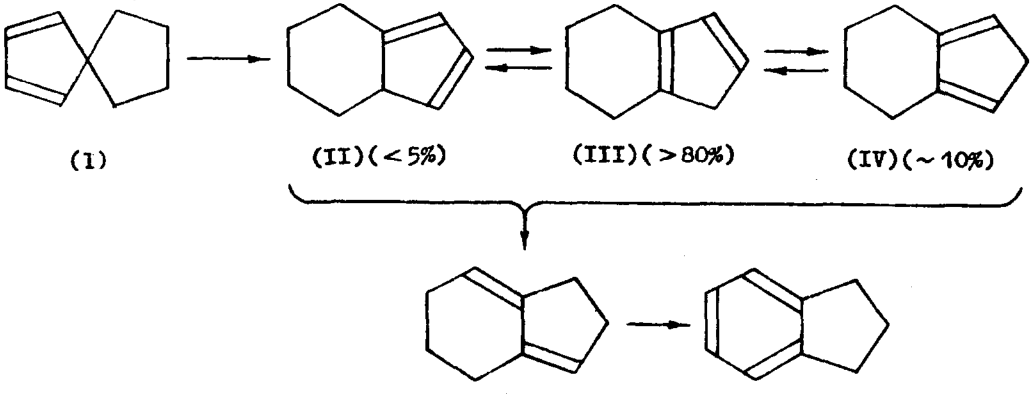
It is well known [2] that 5,5-disubstituted cyclopentadienes are thermodynamically less stable than the corresponding cyclopentadienes with a free methylene group. At 300-400° the former dienes undergo irreversible structural isomerization to the latter as a result of intramolecular 1,5-shift of an alkyl group accompanied by 1,5-shifts of hydrogen [2a]. Spiro-cyclopentadienes may be considered as bicyclic analogues of 5,5-disubstituted dienes and have been predicted [2a] to undergo such an isomerization. In the present paper we report on the thermal behaviour of spiro[4,4]nona-1,3-diene (I) [3].

It was found that when spiro[4,4]nona-1,3-diene (I) is passed through a quartz tube packed with crushed quartz with a contact time of about 8 sec over the temperature range 200-500° three types of consecutive transformation of diene (I) take place as indicated in the scheme:



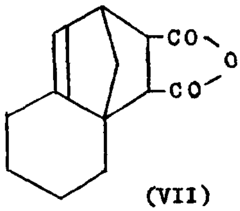
(I) (II)(<5%) (III)(>80%) (IV)(~10%)

(V) (VI)

Type 1. At 250-320° under the conditions mentioned diene (I) undergoes ready isomerization to the equilibrium mixture of bicyclo[4,3,0]nonadienes (II)-(IV): b.p. 42.5-43° (7 mm), n_D^{20} 1.5103, d_4^{20} 0.9544. C_9H_{12} [5]. The optimum yield (89%) of the mixture (II)-(IV) can be obtained at 320°. No other products can be detected in this mixture by v.p.c. analysis. When the mixture is passed over Pd/C (10%) at 300° it is dehydrogenated to give indane (VI) in 93% yield. The bicyclo[4,3,0]nonadiene structures, with two double bonds in the five-membered ring, for the mixture are supported by UV (λ_{max} 254 nm, ε 3860) [6], IR (ν 1531, 1559, 1605 and 1629 cm^{-1}) and Raman ($\Delta\nu$ 1528(10), 1556(0-1) and 1630(3)cm^{-1}) spectra data (see ref.2a).

The composition of the mixture of isomer (II)-(IV) was established by comparison of intensities of double bond stretching frequencies in the vibrational spectra of the mixture. On previously found criteria [2a], the frequencies 1528 and 1630 cm^{-1} may be ascribed to the in-phase (ν^{s}) and out-of-phase (ν^{as}) C=C stretching modes of bicyclo[4,3,0]nona-1(6), 8-diene (III) and the frequencies 1556 and 1605 cm^{-1} to the $\nu^{s}_{C=C}$ and $\nu^{as}_{C=C}$ of bicyclo [4,3,0] nona-6,9-diene (IV), respectively. Therefore by Raman and IR spectra data the dienes mixture contains at least 80% of isomer (III) and on the order of 10% of isomer (IV).

The absence of a $\nu^{s}_{C=C}$ of lower frequency than those quoted in the Raman spectrum shows that the mixture contains no substantial amount of isomer (II) (with monosubstituted double bond system, see ref.2a).



(VII)

This conclusion is supported by the finding that the diene mixture (II)-(IV) reacts with maleic anhydride to give adduct (VII) of diene (III) in 64% yield: m.p. 105-106° (from benzene-hexane mixture). $C_{13}H_{14}O_3$ [5]. The structure of adduct (VII) is proved by IR ($\nu_{C=C}$ 1621 cm^{-1}, $\nu_{=C-H}$ 3050 cm^{-1}) [8] and NMR [9] (δ 5.70 p.p.m., 1H) spectra data.

The observed skeletal isomerization may be well explained by intramolecular thermal 1,5-shift of the substituent producing initially diene (II). Under the experimental conditions 1,5-shifts of hydrogen would occur immediately to convert diene (II) to equilibrium mixture of double bond isomers (II)-(IV).

Type 2. At 350-450° diene (I) is found to undergo isomerization to give bicyclo[4,3,0]nona-1,6-diene (V). This isomerization over the 390-420° temperature range produces in 78% yield the hydrocarbon mixture consisting (by v.p.c.) of 68% (II+III+IV) and 32% (V). Pure (at least 99.5% by v.p.c.) diene (V) was separated from this mixture by distillation with a 100 t.p. column: b.p. 38.2-38.4° (3 mm), n_D^{20} 1.5314, d_4^{20} 0.9367. C_9H_{12} [5]. Diene (V) was dehydrogenated to give indane (VI) (220°; 6 sec over 10% Pd/C; yield: 92%). The structure of this diene is established by UV (λ_{max} 245 mm, ε 12710), Raman ($\Delta\nu$ 1653 (7), 1622 (1-2) cm^{-1}), IR(ν 1655 and 1628 cm^{-1} in the inverse ratio of intensities) and NMR (δ 3.05 (10H) and 4.64 (2H) p.p.m.) spectral data [10].

Under the same conditions transformation of diene mixture (II)-(IV) to diene (V) occurs more readily than that of diene (I). Hence, one may suppose that the diene equilibrium mixture (II)-(IV) is an intermediate in (I) $\rightarrow$ (V) conversion. This isomerization may proceed in diene (IV) by 1,3-shift of hydrogen. The (II+III+IV) $\rightarrow$ (V) conversion is found to be irreversible.

Type 3. At 470-500° indane (VI) (12% at 500° by v.p.c.) is detected in products of pyrolysis of diene (I). The physical properties and IR spectrum of the sample of indane separated from the pyrolysis products were quite similar to those of an authentic sample. The rate of conversion to indane rises markedly in the order of (I)$<$(II+III+IV)$<$(V). Therefore diene (V) is assumed to be the starting material of indane formation. Apparently, the thermal dehydrogenation of bicyclo[4,3,0]nonadienes is similar to that observed in the cyclohexadiene series [11].

The experimental details will be published [12]. Finally, it may be noted that thermal isomerization of diene (I) is a novel and convenient route to compounds of the tetrahydroindene series.

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9. NMR spectra were determined with Varian DA-60-IL instrument employing TMS as the internal reference.
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