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Abstract

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ON SOME PROPERTIES OF SPIRO-(2,4)-HEPTADIENE-1,3

Spiro-(2,4)-heptadiene-1,3 (I) was first synthesized in 1955 by Levin and co-workers ([1]) by the interaction of one mole of ethylene bromide, two gram-atoms of sodium, and one mole of cyclopentadiene in liquid ammonia:

$$\text{cyclopentadiene} \xrightarrow[\text{BrCH}_2-\text{CH}_2\text{Br}]{\text{Na/NH}_3} \text{spiro-(2,4)-heptadiene-1,3} \qquad (I)$$

In this work, and also in later investigations by other authors ([2,3]), the hydrogenation of this hydrocarbon was studied; depending on the conditions, it affects either the double bonds or the three-membered ring:

$$\text{spiro-(2,4)-heptadiene-1,3} \xrightarrow[\text{skeleton Ni}]{2\text{H}_2} \text{partially hydrogenated spiro compound;} \qquad \text{spiro-(2,4)-heptadiene-1,3}$$

$$\text{spiro-(2,4)-heptadiene-1,3} \xrightarrow{\text{Na/NH}_3} \text{ethyl-substituted cyclopentadiene isomers}$$

as well as certain reactions confirming the diene character of (I) ([1,2]).

The presence in (I), adjacent to a three-membered ring, of the system of double bonds of the cyclopentadiene ring makes it possible to suppose that this compound possesses a number of interesting properties worthy of further study. In such a system one may expect coupling of the distinctive "π-cloud" of the three-membered ring with the double bonds ([4]) and the formation of a quasi-aromatic system in the event that this "π-cloud" is capable of closing the system of π-electrons of the five-membered ring.

$$\text{spiro-(2,4)-heptadiene-1,3} \longrightarrow \text{bicyclic adduct with a cyclic anhydride fragment}$$

In order to introduce some clarity into the question of the nature of the mutual influence of the cyclopentadiene and three-membered rings, we decided to study

the spectral characteristics and certain transformations of this hydrocarbon. For comparison, another hydrocarbon was studied—spiro-(4,4)-nonadiene-1,3 (II), in which, as in (I), the double bonds are fixed owing to substitution of both hydrogen atoms of one of the carbons of the pentadiene ring; however, the substituent is not a three-membered ring but a five-membered one, possessing ordinary σ-bonds, i.e., incapable of interaction with the system of double bonds:

spiro-(4,4)-nonadiene-1,3 (II)

Both hydrocarbons (I) and (II) were synthesized by the procedures described in the papers of Levin and co-workers ([1,5]).

Examination of the vibrational spectra of the substances obtained and comparison of them with the spectra of other cyclopentadienes studied in ([6]) first of all made it possible to establish that the structure of the hydrocarbons indeed corresponds to formulas (I) and (II). In fact, the frequencies, intensities, and polarization of the lines in the region of $C{=}C$ in the combination-scattering spectra of both hydrocarbons indicate the presence in their molecules of a cyclopentadiene ring (see Table 1).

The frequency of the symmetric vibration of the double bonds in the spectra of both compounds lies lower than in the case of cyclopentadienes substituted at the double bond by alkyl substituents. The band of the antisymmetric vibration of $C{=}C$ appears only in the infrared absorption spectra, which is usually the case in the absence of substituents or with symmetrical substitution of the ring. In the spectra of substance (I) there are no lines of stretching vibrations

CH_2- and CH_3-groups of the usual type (region 2850-2970), while at the same time the lines of stretching vibrations of the CH_2-groups of the three-membered ring appear in them. On prolonged storage or heating to 200°, (I) and (II) dimerize; moreover, judging from the spectra, dimers are formed with unsubstituted double bonds in bicyclo(2,2,1)-heptene and cyclopentene rings (lines at 1570 and 1605 cm^{-1} in the spectrum of the dimer of (I), and lines at 1574 and 1614 cm^{-1} in the spectrum of the dimer of (II)). A certain increase in the intensity of the line of the cyclopentene ring in the spectrum of the dimer of (I) indicates the proximity of the double bond to the three-membered ring.

Table 1

Substance	$\nu^{s}_{C=C}$	$I^{\mu *}$	ρ	$\nu^{as}_{C=C}$
[[structural formula: spiro compound with a cyclopropane ring and a cyclopentadiene ring]]	1481 1494	1450	0.07	1632 (IR)
[[structural formula: spiro compound with cyclopentadiene and cyclobutene rings]]	1515	1200	0.09	1643 (IR)
[[structural formula: bicyclic diene; first isomer]]	$1532^{(10)**}$			$1631^{(3)}$
[[structural formula: bicyclic diene; second isomer]]	$1555^{(10)**}$			–***
[[structural formula: substituted cyclopentadiene]]	$1534^{(10)**}$			$1634^{(4)}$
[[structural formula: cyclopentadiene]]	$1562^{(10)**}$			–***

* Molar integral intensities.
** Intensities on a ten-point visual scale.
*** Not observed in the Raman spectrum; IR-spectrum data are absent.

As is known, the proximity of a double bond and a three-membered ring leads to an approximately twofold increase in the integral intensity of the double-bond lines in the Raman spectrum of a substance[7]. Further study of the spectral data obtained in the present work showed that this effect is absent in the case of hydrocarbon (I): the intensities of the double-bond lines in compounds (I) and (II) are close to one another. From this, however, one cannot conclude that conjugation is absent in (I), since the structural features of this hydrocarbon, mentioned above, make it possible to explain the observed phenomenon in another way. The point is that two effects that may occur in (I)—conjugation of the double bonds with the three-membered ring and enhancement of the aromatic properties of the five-membered ring (i.e., an increase in the degree of closure of its electron shell)—have opposite influences on the magnitude of the intensity of the double-bond lines. Superposition of these two influences may thus lead to compensation of the effects.

We have repeatedly had occasion to observe that cyclopropane derivatives in which the three-membered ring is conjugated with an unsaturated grouping are capable, in the cold, of adding hydrogen in the presence of palladium, with cleavage of the C—C bond of the ring adjacent to the substituent[8–12]. In accordance with this, we studied the hydrogenation of hydrocarbon (I) and found that, in the presence of palladium black in an alcoholic solution at room temperature, addition of three moles of hydrogen to (I) takes place according to the scheme:

[[structural formula of (I)]] $\xrightarrow[20^\circ]{\text{Pd; } 3H_2}$ [[structural formula: ethylcyclopentane, $-CH_2-CH_3$ substituent]]

The fact that the sole reaction product, identified from the constants and by gas-liquid chromatography, is ethylcyclopentane can serve as direct confirmation of the presence of conjugation between the three-membered ring and the double bonds in hydrocarbon (I). As was found by analysis of the catalysts from incomplete hydrogenation of (I), hydrogen addition occurs nonselectively.

We have already mentioned the propensity of hydrocarbons (I) and (II) toward dimerization when they are heated to 200°. If hydrocarbon (II) is heated at 200-250° for one hour, however, it is isomerized into tetrahydroindane with double bonds in the five-membered ring.

(reaction scheme)

(III) (IV) (V)

Fig. 1

Figure 1: Fig. 1

Judging from the spectral data, isomer (IV) predominates substantially in the mixture. A reaction of this type may be represented as analogous to the previously described isomerization reaction of alkylcyclopentadienes ([6]). Of great interest is the fact that hydrocarbon (I) is not isomerized under the same conditions, i.e., it exhibits greater stability than (II), which is possibly connected with its quasi-aromatic character.

The investigations carried out make it possible to supplement the characterization of the spiro-(2,4)-heptadiene-1,3 hydrocarbon, in which, as has been shown, the mutual influence of the cyclopentadiene and three-membered rings is markedly manifested.

Experimental Part

1. Hydrocarbons. Spiro-(2,4)-heptadiene-1,3 (I) was synthesized in 24% of the theoretical yield by method ([1]). After distillation in a nitrogen atmosphere on a vacuum column with an efficiency of 30 theoretical plates, (I) had the following constants: b.p. 57.0°/100 mm, n_D^{20} 1.5081, d_4^{20} 0.8992. Literature data: b.p. 57.0°/100 mm, n_D^{20} 1.5078, d_4^{20} 0.8999 ([1]).

Raman spectrum $\Delta\nu$ (cm^{-1}): 171(105, sh), 256(60,sh), 307(40), 336(10), 513(15, sh, f), 529(520, p), 568(16, sh), 664(5), 711(5), 734(58), 796(7), 814(130, sh), 870(65,p), 905(50, sh), 936(10), 961(350), 996(42), 987(150), 1056(9), 1092(215), 1114(6), 1174(10), 1248(5), 1269(95, p), 1330(10), 1392(180), 1429(80), 1448(170, p), 1481(390), 1494(170, f), 3016(220, sh), 3082(340, sh), 3128(80, p). IR spectrum $\Delta\nu$ (cm^{-1}): 671, 731, 757, 787, 812, 833, 857, 870, 905, 920, 933, 961, 992, 1024, 1053, 1074, 1122, 1135, 1188, 1247, 1269, 1297, 1331, 1381, 1391, 1432, 1447, 1481, 1533, 1632, 1821 (Fig. 1).

Fig. 1

Band frequencies in the region of ~ 2000 cm^{-1} are not reported, since this region of the spectrum was studied at low resolution (NaCl prism).

Spiro-(4,4)-nonadiene-1,3 (II) was synthesized in 20% of the theoretical yield by method ([5]). The tetramethylenedibromide required for carrying out the synthesis was obtained in 80% yield by the action of hydrobromic and sulfuric acids on tetrahydrofuran. After distillation on a vacuum column in a stream of nitrogen, (II) had the following constants: b.p. 50.7°/26 mm, n_D^{20} 1.4880, d_4^{20} 0.8990. Literature data ([5,13]): b.p. 52.0°/10 mm, n_D^{20} 1.4790, d_4^{20} 0.8849, b.p. 44–46°/22 mm, n_D^{20} 1.4817.

Raman spectrum $\Delta\nu$ (cm^{-1}): 150(215, sh, f), 238(48, sh), 360(26), 431(70, sh), 516(3, sh), 560(5, sh), 590(1), 633(2, sh), 677(9, sh), 721(3), 738(5), 792(12),

Fig. 2

Figure 2: Fig. 2

805(11), 847(62,p), 885(42), 922(44), 973(110), 1008(32), 1033(23), 1064(55,f), 1076(52,f), 1093(55),

1132(16), 1159(9), 1213(12), 1277(8), 1304(10), 1317(12), 1372(80, p), 1445(50), 1455(55), 1481(15), 1515(390), 2862(80), 2874(100), 2922(80, ph), 2946(220, ph), 2961(240, sh, ph), 3063(100), 3086(130), 3161(15, p). IR spectrum $\Delta\nu$ (cm^{-1}): 522, 663, 733, 759, 802, 891, 914, 939, 972, 994, 1030, 1062, 1074, 1091, 1129, 1235, 1280, 1304, 1318, 1335, 1372, 1450, 1515, 1643, 1835, 2863, 2872, 2913, 2955, 3048, 3065, 3081, 3105 (Fig. 2).

Fig. 2

2. **Hydrogenation** was carried out in a duck-shaped vessel at a temperature of 20°, as described earlier ([8,11]).

a) Hydrogenation of (I) in the presence of palladium black: 2.63 g (0.028 mole) of (I), 0.1 g of Pd black, and 20 ml of ethyl alcohol were taken. In 90 min, 1950 ml of hydrogen was absorbed. The theoretical amount corresponding to the addition of three moles of hydrogen is 1920 ml. 2.2 g of catalyzate was isolated, n_D^{20} 1.4197, d_4^{20} 0.7669. The constants of ethylcyclopentane ([14]) are n_D^{20} 1.4198, d_4^{20} 0.7665. Analysis by gas-liquid chromatography showed that the catalyzate is ethylcyclopentane.

b) Incomplete hydrogenation of (I) in the presence of palladium black. 6.00 g (0.065 mole) of (I), 0.15 g of Pd black, and 25 ml of ethyl alcohol were taken. After absorption of 1460 ml of hydrogen (the amount corresponding to the addition of one mole of hydrogen), the hydrogenation was stopped. 5.6 g of catalyzate was isolated. Judging from the Raman spectra, in the catalyzate, in addition to unchanged (I), one may assume the presence of ethylcyclopentane, ethylcyclopentene, and spiroheptene with different positions of the double bond in the five-membered ring. Ethylcyclopentadiene is absent from the catalyzate.

3. **Isomerization** (II). 6 ml of hydrocarbon (II) were heated for two hours at a temperature of 200-250° in a sealed standard cuvette used for obtaining Raman spectra. Examination of the spectrum of the sample revealed the appearance of new lines in comparison with the spectrum of the starting (II) and its dimer. Brief storage of this sample led to its almost complete dimerization. When the dimer was heated to 250-300° with continuous distillation, it was possible to convert it to a considerable extent into an equilibrium mixture of tetrahydroindane monomers (III), (IV), and (V).

The method of preparation and the study of spectra have been described earlier ([15–16]). Raman spectra were obtained on a standard ISP-51 spectrograph. IR

absorption spectra were obtained on double-beam IKS-15 spectrometers (LiF and KBr prisms) and Leitz (NaCl prism).

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Note: Figure translations are in progress. See original paper for figures.