VINYL COMPOUNDS IN DIENE SYNTHESIS

COMMUNICATION 4. COMPARATIVE CHARACTERIZATION OF THE DIENOPHILE ACTIVITY OF VINYL AND THIOVINYL ETHERS, AND OPTICAL INVESTIGATION OF THE ADDUCTS OBTAINED

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We have shown earlier the possibility of carrying out a diene synthesis with cyclopentadiene and hexachlorocyclopentadiene using vinyl and thiovinyl ethers containing alkyl and aromatic radicals in the role of dienophile component [1-3]. This allowed the synthesis of a series of derivatives of bicyclo-[2,2,1]hept-5-ene and 1,4,5,8-diendomethylene-1,2,3,4,4a,5,8,8a-octahydronaphthalene of the general structure:



where $R=C_2H_5$ (a); C_4H_9 (b); C_6H_{11} (cycl.) (c); $C_{10}H_{17}$ (β) (d); C_6H_5 (e); $C_6H_4C_4H_9$ (p-tert.) (f); $C_{10}H_7$ (β) (g), and $R_1 = C_2H_5$ (a); C_4H_9 (b); C_6H_5 (c).

Thiovinyl ethers and vinyl esters were considered by Alder [4] as belonging to a group of less active dienophiles having a polar group next to the double bond. Probably, vinyl ethers also belong to this group. However, it was interesting to elucidate their dienophile activity in relation to the structure of the radical, and the nature of the heteroatom. Therefore, to complete our earlier study of vinyl and thiovinyl ethers containing alkyl and aryl groups, in the present communication we discuss the diene synthesis with cyclopentadiene and hexachlorocyclopentadiene using as dienophiles the following ethers containing hydroaromatic radicals: Vinyl cyclohexyl ether, vinyl B-decalyl ether, as well as vinyl ethyl ether and vinyl butyl sulfide. No adduct was isolated when cyclopentadiene was condensed with vinyl ethyl ether, but in the other cases, new derivatives were obtained, viz., of bicycloheptene (Ic, Id, and Vb), octahydronaphthalene (IIc, and Vb), hexachlorobicycloheptene (IIIb, IIIc, and IIId), and dihydraldrene (IVc and IVd). In order to characterize some of the adducts synthesized from cyclopentadiene, we prepared their hydrogenated derivatives, viz., the corresponding norcamphanes, and their condensation products with phenylazide, viz., the corresponding dihydrotriazole derivatives; the latter were also prepared from thioethyl- and thiophenyldiendomethyleneoctahydronaphthalenes.

A comparison between the dienophile activity of vinyl and thiovinyl ethers revealed a noticeable difference in relation to the character of the radical and the heteroatom. It appeared that the most active compounds in diene synthesis with cyclopentadiene and hexachlorocyclopentadiene are vinyl ethers which contain aromatic radicals, ethers with alkyl and hydroaromatic radicals being less reactive. In the latter case the yield of the adduct is lowered because of the thermal decomposition of the starting ether under the conditions of the reaction. The introduction of a heteroatom in a dienophile, and the nature of the heteroatom also influence the reactivity of vinyl ethers in diene synthesis. It is known that ethylene participates in diene synthesis only under conditions of high temperature and pressure [5, 6]. Vinyl alkyl ethers [7, 1] condense with dienes comparatively easier. The diene synthesis with thiovinyl ethers occurs smoothly and with a good yield [2]. These considerations are confirmed by the data of Table 1 which gives the percent conversion of vinyl and thiovinyl ethers into the adducts (I) and (II) upon condensation with cyclopentadiene. In all the reactions we used a two-fold excess of vinyl ether, and the yields are calculated on the basis of the ether which entered the reaction.

	Reaction	Duration of the	Yield of the a	Conversion	
Vinyl ethers	tempera- ture, °C	reaction in hr		A A A A A A A A A A A A A A A A A A A	of the start- ing ether into adducts in %
$CH_2 = CH - O - C_2H_5$	180-195	16	Adduct not	formed	_
$CH_2 = CH - O - C_4H_9$	180190	15	23	10	33
$CH_2 = CH - O - C_6H_{11}$	180-185	15	27	4	31
$CH_2 = CH - O - C_{10}H_{17}$ (β)	180-185	15	15		15
$CH_2 = CH = O = C_6H_5$	165-170	13	76	18	94
$CH_2 = CH - O - C_6H_4C_4H_9(p-tert)$	165-170	13	62	33	95
$CH_2 = CH - O - C_{10}H_7 (\beta)$	165-170	13	72	15	87
$CH_2 = CH - S - C_2H_5$	160-165	12	60	14	74
$CH_2 = CH - S - C_4H_9$	160-165	12	59	13	72
$CH_2 = CH - S - C_6H_5^*$	160-165	12	67	13	80

TABLE 1. Conversion of Vinyl and Thiovinyl Ethers into Adducts

* Because of the lower thermal stability of vinyl phenyl sulfide in comparison with its oxygen analog, it is not possible to recover all the excess of this substance from the reaction products; therefore, the given percent conversion of this ether is lower than the actual amount.

For a more complete characterization of the adducts of vinyl and thiovinyl ethers with cyclopentadiene and hexachlorocyclopentadiene, we carried out their spectroscopic investigation. The infrared and Raman spectra of bicyclo-(2,2,1)heptene and 1,4,5,8-diendomethylene-1,2,3,4,4a,5,8,8a-octahydronaphthalene structures were studied. The frequencies of the absorption bands of infrared spectra and their interpretation for all the compounds investigated are given in Table 2. Some of these spectra (marked in Table 2 with an asterisk) are not complete because of the superposition of the absorption bands of the solvent (chloroform) on the bands of the substance investigated. For the majority of compounds under study, only a few of the absorption bands could be related to definite functional groups and bonds with a sufficient degree of certitude.

The spectra of the majority of compounds show, in the $1620-1560 \text{ cm}^{-1}$ region, the absorption band due to the double bond; the frequency of this band is considerably lower than that of cycloolefins, and this fact, according to the literature [8, 9], is characteristic for a bicycloheptene ring. By taking into consideration the fact that in Raman spectra the valency vibration is reflected better, we recorded these spectra for a series of compounds. The frequencies of the lines of the Raman spectra thus obtained are given in Table 3.

The Raman spectra display intense lines in the frequency region $(1560-1620 \text{ cm}^{-1})$ of the double bond, which are split in some compounds into several components. The magnitude of splitting is equal to $40-50 \text{ cm}^{-1}$. This effect cannot be explained by the occurence of endo-exo isomerism, as Kohlrausch and Seka [10] have shown that substituents in position 2 and 3 cause only a negligible displacement of the double bond frequency of the bicycloheptene ring. Moreover, our measurements of the double bond frequencies of samples of 2-phenoxybicyclo-(2,2,1)hept-5-ene enriched with exo- and endo- isomers show that these frequencies differ only by a few cm⁻¹. An explanation of the splitting of lines only on the basis of Fermi resonance is not very convincing: first, because the frequencies are split not only to two, but to three components; second, because the displacement of frequencies in comparison with samples which do not display splitting of lines is observed only for one of the components. Apparently, the phenomenon of splitting of double bond frequencies is due essentially to a possibility of the existence of sterically isomeric forms of the bicycloheptene ring itself.

Adduct	(IIIg*)	(VIIe*)	(Id)	(IIe*)	(IIb)	(IIg*)	(Ig*)	(VIc*)	(VIa)	(Ib)
, , , , , , , , , , , , , , , , , , , 		706	634 662 683 730	695 718	630 679 706 729	632 661 680		694	744	724
bands (cm ⁻¹)	834 864 894 912	851 867 912	761 787 813 832 853 898	856 882 900	739 755 794 812 844 896 912	836 896	769 832 910	856 900	786 840 904	752 782 844 912
absorption	924 964 1002	971 985 1010	942 970 984	962 984 998	972 984	919 960 994	956 994	962 1008	1012	
Frequencies of <i>i</i>	1105 1125 1179 1214 1256 1359 1396	1028 1065 1096 1154 1278 1448	1028 1083 1117 1152 1260 1352 1454	1024 1076 1088 1120 1152 1166 1364	1111 1159 1249 1318 1360	1043 1120 1178 1215 1250 1362 1394	1040 1068 1120 1176 1258 1365 1396 1445	1024 1064 1088 1128 1140 1322	1042 1250 1318 1352 1448	1272
	1473 1526	1487 1610		1494 1568 1612	1470	1478 1512	1475 1518 1602	1480 1594	1544	

TABLE 2. Infrared Spectra of Adducts of Vinyl and Thiovinyl Ethers

In the spectra of the majority of substances possessing either a bicycloheptene or a diendomethyleneoctahydronaphthalene structure, we observed intense absorption lines in the region of 710-740 cm⁻¹ (14-13.5 μ); this is in good agreement with published data [11-13]. The infrared spectra, as well as Raman spectra, displayed a frequency in the region of 895-910 cm⁻¹. According to Aleksanyan and Sterin [8], this frequency must be ascribed to the pulsational vibration of the five-membered ring. We noticed that the infrared spectra of the substances under investigation have an intense absorption band in the region of 990-1010 cm⁻¹. Apparently, this band must be ascribed to a deformation vibration of the GH group in the neighborhood of the double bond. A comparison with the spectra of cycloolefins shows that this region of the frequency of the given vibration is rather specific for the bicycloheptene structure.

EXPERIMENTAL

Condensation of Vinyl Ethers Containing Hydroaromatic Radicals with Cyclopentadiene

<u>Vinyl β -decalyl ether</u>. Cyclopentadiene (6.6 g, 0.1 mole) and vinyl ether (36.2 g, 0.2 mole) were heated together in an autoclave at 175-180° for 15 hr. The reaction mixture was steam-distilled, and two fractions were obtained. Fraction I boiling at 104-118° (5 mm) consisted of a mixture of the starting ether (21.1 g) and β -decalol. Fraction II (15 g) boiling at 130-200° (4 mm) gave, after heating with 2% H₂SO₄ for removing acetal, 6.5 g of 2- β -decaloxybicyclo-(2,2,1)-hept-5-ene (Id) which appeared as a colorless liquid with a camphane smell, b. p. 162-164° (4 mm); $n^{20}D$ 1.5125; d^{20}_{4} 1.043; found MR 72.76. $C_{17}H_{25}O \models$. calculated MR 73.08. Found: C 83.08, 83.00; H 10.51, 10.40%. Calculated: C 82.87; H 10.64%.

TABLE 2 (continued)

	(Id))			
(Ic)	(Va)	(II _f *)	(If*)	exo-	endo-	Functional group or bond
724	712 732	692		706 724	695	\bigcirc
752 782 844	764 808 882	841 891	828	752 800 824 852 880	857 885	
906	906	903		908	906	Pulsational vibration of the five-membered ring
952 1000	942 992	992	992	949 968 984 996	964 994	CH
1090 1180 1272 1368	1048 1096 1132 1184 1220 1264 1322 1376 1452	1008 1030 1082 1114 1186 1300 1318 1368 1398	1042 1052 1068 1116 1152 1184 1292 1408	1044 1074 1096 1118 1170 1244 1300 1344 1364 1465	1041 1075 1115 1154 1176 1230 1288 1341 1362	ĊH
<u> </u>		1475	1475		1	CH ₃
		1580	1521 1581	1504 1603	1501 1602	C=C

Yield of the adduct, 15% of the theoretical, based on the ether which entered the reaction (22.1 g). For its spectrum, see Table 2.

<u>Vinyl cyclohexyl ether.</u> A mixture of cyclopentadiene (6.6 g, 0.1 mole) and vinyl ether (25.4 g, 0.2 mole) was heated in an autoclave under analogous conditions. After vacuum distillation of the reaction mixture, and the removal of the acetal by hydrolysis, 10.5 g of the starting ether and 6.1 g of 2-cyclohexoxybicyclo-(2.2,1)hept-5-ene (Ic) was isolated. (Ic) had b, p. 95-98° (2 mm); $n^{20}D$ 1.5060; d^{20}_{4} 1.0052; foundMR57.15. $C_{13}H_{20}O \vdash$. Calculated MR 57.91. Found: C 81.30, 81.22; H 10.47, 10.43%. $C_{13}H_{20}O$. Calculated: C 81.10; H 10.56%.

Yield of the adduct, 27% of the theoretical. Spectra data in Tables 2 and 3.

A fraction boiling at 148-150° (2.5 mm) (1.3 g, 4.3% of the theoretical) was also obtained. It consisted of 1,4,5,8-diendomethylene-2-cyclohexoxy-1,2,3,4,4a,5,8,8a-octahydronaphthalene (IIc), $n^{20}D$ 1.5190; d^{20}_4 1.0492; found MR 74.76. $C_{13}H_{26}O \vdash$. Calculated MR 75.50. Its crystalline addition product with phenylazide (yield, 68% of the theoretical) melted at 185-187.5° (dec.). Found: N 11.51, 11.67%. $C_{24}H_{31}N_3O$. Calculated: N 11.13%.

Vinyl butyl sulfide. A mixture of dicyclopentadiene (6.6 g, 0.05 mole) and vinyl sulfide (23.2 g, 0.2 mole) was heated in an autoclave for 12 hr at 160-165°. Vacuum distillation of the reaction product gave 12.0 g of the starting thioether, 10.3 g (58.6% of the theoretical, calculated on the basis of 11.2 g of thioether which has reacted)

of 2-thiobutylbicyclo-(2,2,1)hept-5-ene (Vb), b. p. 94-94.8° (4 mm); $n^{20}D$ 1.5076; $d_{.4}^{20}$ 0.9693; found MR 56.04. C₁₁H₁₈SL. Calculated MR 56.12. Found: C 72.56, 72.72; H 9.83, 9.94; S 17.29, 17.27%. Calculated: C 72.46; H 9.95; S 17.59%, and 3.0 g of 1,4,5,8-diendomethylene-2-thiobutyl-1,2,3,4,4a,5,8,8a-octahydronaphthalene (VIb), (12.5% of the theoretical calculated on the basis of 11.2 g of thioether which has reacted), b. p. 160-160.5° (4.5 mm); $n^{20}D$ 1.5345; $d_{.4}^{20}$ 1.0392; found MR 74.46. C₁₆H₂₄SL. Calculated MR 74.82. Found: C 77.50, 77.55; H 9.92, 9.83; S 13,15, 13.32%. Calculated: C 77.36; H 9.73; S 12,90%.

A mixture of dicyclopentadiene (3.3 g, 0.025 mole) and vinyl ethyl sulfide (8.8 g, 0.1 mole) was heated in an autoclave at 160-165° for 12 hr.* The yield of 2-thioethylbicyclo-(2,2,1)hept-5-ene (Va) was 4.1 g (60% of the theoretical, calculated on the basis of the 3.8 g of sulfide which entered the reaction). (Va) had b. p. 60-60.5° (3 mm), and $n^{20}D$ 1.5158. It was accompanied by 1.3 g (14% of the theoretical, calculated w.r. to the 3.8 g of sulfide which had reacted) of 1,4,5,8-diendomethylene-2-thioethyl-1,2,3,4,4a,5,8,8a-octahydronaphthalene (VIa), b. p. 135.5-137° (5 mm); $n^{20}D$ 1.5462.

Under analogous conditions, 3.3 g (0.025 mole) of dicyclopentadiene and 13.6 g (0.1 mole) of vinyl phenyl sulfide gave 6.5 g (66.3% of the theoretical, based on 6.5 g of the sulfide which had reacted) of 2-thiophenylbicyclo-(2,2,1) hept-5-ene (Vc), b. p. 143-144° (6 mm); n^{20} D 1.5925, and 1.6 g (12.5% of the theoretical w.r. to the 6.5 g of the sulfide which had reacted) of 1,4,5,8-diendomethylene-2-thiophenyl-1,2,3,4,4a,5,8,8a-octahydronaphthalene (VIc), b. p. 200-201° (4 mm).

Condensation of Vinyl Ethers with Hexachlorocyclopentadiene

<u>Vinyl butyl ether</u>. A mixture of the ether (3 g, 0.03 mole), and of the diene (8.1 g, 0.03 mole) was heated in a flask fitted with a reflux condenser for 3 hr at 85-95° in the presence of hydroquinone. After removal of unreacted diene 4.2 g, 3.5 g (66% of the theoretical based on the diene which has reacted) of 2-butoxy-1,4,5,6,7,7hexachlorobicyclo-(2,2,1)hept-5-ene (IIIb) was obtained as a pale yellow liquid with a characteristic unpleasant smell, b. p. 140-141° (2 mm); n^{20} D 1.5250, d^{20}_{4} 1.4552; found MR 78.68. C₁₁ H₁₂Cl₆O \downarrow . Calculated MR 79.00. Found: C 35.08, 35.17; H 3.19, 3.10; Cl 56.94, 56.57%. Calculated: C 35.42; H 3.24; Cl 57.05%.

<u>Vinyl cyclohexyl ether.</u> The ester (5.2 g, 0.04 mole) and the diene (5.4 g, 0.02 mole) gave, under analogous conditions, 14.5 g (70% of the theorectical w.r. to the 4.4 g of the diene which entered the reaction) of 2-cyclohexoxy-1,4,5,6,7,7-hexachlorobicyclo-(2,2,1)hept-5-ene (IIIc), b. p. 104-105° ($8 \cdot 10^{-5}$ mm); n²⁰D 1.5495. Found: C 39.35, 39.57; H 3.63, 3.49; Cl 52.73, 52.86%. C₁₃H₁₄Cl₆O. Calculated: C 39.12; H 3.54; Cl 53.30%.

<u>Vinyl β -decalyl ether</u>. Under the same conditions, 10.8 g (0.06 mole) of the ether and 8.1 g (0.03 mole) of the diene gave 3.6 g (42% of the theoretical calculated on the basis of the 5.1 g of the diene which had reacted) of 2- β -decaloxy-1,4,5,6,7,7-hexachlorobicyclo-(2,2,1)hept-5-ene (IIId), as a thermally poorly stable, very viscous product with an unpleasant smell, b. p. 138-140° ($5 \cdot 10^{-3}$ mm). Found: C 44.78, 44.56; H 4.86, 4.75; Cl 46.57; 46.72%. C₁₇H₂₀Cl₆O. Calculated: C 44.95; H 4.44; Cl 46.85%.

Reaction of the Bicycloheptenes with Hexachlorocyclopentadiene

a) The diene (2.7 g, 0.01 mole) and 1.94 g (0.01 mole) of 2-cyclohexoxybicycloheptene (Ic) were heated together for 9 hr at 125-130° in a flask fitted with a reflux condenser. After removal of the portion of starting materials which did not react (containing 0.7 g of the diene), 2.2 g (65% of the theoretical) of 1,4,5,8-diendomethylene-2cyclohexoxy-5,6,7,8,9,9-hexachloro-1,2,3,4,4a,5,8,8a-octahydronaphthalene (IVc) was obtained as a very viscous pale yellow product, b. p. 208-210° (1 mm). Found: C 46.63, 46.56; H 4.03, 4.14; Cl 45.99, 46.30%. $C_{18}H_{20}Cl_6O$. Calculated: C 46.48; H 4.33; Cl 45.74.

b) Under analogous conditions, 2.7 g (0.01 mole) of the diene and 1.8 g (0.01 mole) of 2- β -decaloxybicycloheptene (Id) gave 0.6 g of recovered diene, and 1.9 g (45% of the theoretical) of 1,4,5,8-diendomethylene-2- β decaloxy-5,6,7,8,9,9-hexachloro-1,2,3,4,4a,5,8,8a-octahydronaphthalene (IVd), b. p. 184-185.5° (2 · 10⁻² mm). (IVd) appeared as a very viscous,thermally poorly stable compound. Found: C 50.73, 50.81; H 4.80, 4.77%. C₁₇H₂₀Cl₆O. Calculated: C 50.84; H 4.55%.

^{*} The condensation of vinyl phenyl sulfide and vinyl ethyl sulfide with cyclopentadiene was carried out by us earlier [2] with equimolecular amounts of the starting materials. To compare the diene activity of vinyl ethers and thioethers, we give the results of experiments carried out with a two-fold excess of sulfide.

Hydrogenation of the Adducts of the Diene Synthesis

A hydrogenation flask was charged with 4.6 g of 2-cyclohexoxybicyclo-(2.2.1)hept-5-ene (Ic) in 20 ml of methanol. Hydrogenation was carried out over platinum oxide prepared according to Adams, or over Raney nickel. Absorption of hydrogen occurred rapidly at room temperature (417 ml of hydrogen were required; volume actually absorbed, 398 ml). The yield of 2-cyclohexoxynorcamphane thus obtained was 4.2 g (89% of the theoretical). Data concerning the hydrogenation of the substances under study are given in Table 4.

Com-	(1110)	(1/2)	(Tc)	(Ib) (Ie)		(IIb)	0	le)
pound			(10)				endo	exo-
Frequencies (cm ⁻¹); intensities on a ten-point scale are indicated between brackets	$\begin{array}{c} 152 & (2) \\ 172 & (2) \\ 265 & (0) \\ 282 & (0) \\ 299 & (1) \\ 486 & (0) \\ 504 & (0) \\ 529 & (1) \\ 553 & (0) \\ 673 & (4) \\ 702 & (2sh) \\ 732 & (0) \\ 812 & (1) \\ 887 & (2) \\ 913 & (2)$	$\begin{array}{ccccc} 153 & (3) \\ 168 & (2) \\ 275 & (2 {\rm sh}) \\ 297 & (2 {\rm sh}) \\ 469 & (1) \\ 487 & (0) \\ 651 & (0) \\ 672 & (4) \\ 703 & (2 {\rm sh}) \\ 703 & (2 {\rm sh}) \\ 728 & (0) \\ 811 & (1) \\ 888 & (1) \\ 912 & (2) \\ 914 & (4) \\ 943 & (0) \\ 970 & (0) \\ 985 & (0) \\ 1003 & (1) \\ 1051 & (1) \\ 1068 & (1) \\ 1051 & (1) \\ 1068 & (1) \\ 1169 & (1) \\ 1163 & (0) \\ 1189 & (1) \\ 1289 & (0) \\ 1388 & (0) \\ 1428 & (0) \\ 1428 & (0) \\ 1428 & (0) \\ 1428 & (0) \\ 1428 & (0) \\ 1454 & (1 {\rm sh}) \\ 1576 & (6) \\ \end{array}$	788 (0) 839 (1) 900 (1sh) 945 (1sh) 989 (0) 1023 (2) 1043 (6) 1063 (0) 1089 (2) 1114 (0) 1152 (0) 1218 (0) 1252 (0) 1373 (1) 1437 (2 sh) 1566 (6) 1616 (0)	675 (0) 750 (1) 775 (0) 835 (1sh) 943 (2) 960 (0) 1020 (2) 1091 (4) 1116 (0) 1238 (0) 1265 (0) 1289 (1) 1375 (1) 1444 (3/d) 1567 (6) 1615 (0)	$\begin{array}{c} 150 & (1)\\ 175 & (1)\\ 243 & (2)\\ 274 & (2)\\ 621 & (2)\\ 755 & (2)\\ 775 & (0)\\ 809 & (4)\\ 857 & (0)\\ 912 & (2)\\ 932 & (0)\\ 912 & (2)\\ 932 & (0)\\ 912 & (2)\\ 932 & (0)\\ 912 & (2)\\ 932 & (0)\\ 912 & (2)\\ 932 & (0)\\ 912 & (2)\\ 932 & (0)\\ 912 & (2)\\ 932 & (0)\\ 912 & (2)\\ 932 & (0)\\ 912 & (2)\\ 912 $	624 (0) 802 (0) 845 (0) 902 (1) 905 (2sh) 1035 (3) 1102 (3,d) 1138 (1) 1159 (0) 1190 (0) 1244 (2) 1302 (1) 1316 (1) 1354 (0) 1388 (0) 1478 (1) 1571 (4) 1618 (2) 1657 (0)	1452 (0) 1489 (1) 1509 (1) 1543 (1) 1589 (2) 1602 (0)	1438 (0) 1452 (0) 1520 (0) 1579 (4) 1609 (1)

TABLE 3. Raman Spectra

TABLE 4. Description of the Hydrogenated Adducts of Vinyl Ethers with Cyclopentadiene

	в.р., °С			M	R	Foun	d,%	Calc	i. %	Yield ゆ of the
Formula	(pressure ' in mm)	n _D ²⁰	d_D^{20}	found	calc .	с	н	с	н	theo- retical)
OC _n H _u (cyclo)	94 (3)	1,4880	0,9903	56,74	67,24	$ 80,46 \\ 80,64 $	11,32 11,46	80,32	11,48	89
V OC 10 H11 (8)	165 (2)	1,5085	1,0052	73,13	73,55	82,38 82,42	10,90 10,72	82,19	11,30	88
OC.H.	145 (6)	1,4907	0,9892	68,32	68,93	81,90 81,70	11,10 11,05	82,00	11,19	91

Preparation of Trihydrotriazole Derivatives by Reaction with Phenylazide

A mixture of 1.9 g (0.01 mole) of 2-cyclohexoxybicyclo-(2,2,1)hept-5-ene (Ic) and 2.4 g (0.02 mole) of phenylazide was left to stand at room temperature for 3 days. The white crystalline precipitate thus obtained (1.4 g) was filtered off and washed with diethyl ether. The description of this product, and of other compounds similarly prepared is given in Table 5.

Spectroscopic Study of the Adducts Obtained

Infrared spectra were obtained in the region of 700-2,000 cm⁻¹ with the help of a one-beam infrared spectrometer IKS-11. The accuracy of frequency measurements of absorption bands was $\pm 5 + 10$ cm⁻¹. Raman spectra were recorded with the help of a three-prism spectrograph ISP-67 with a f = 500 mm chamber. The accuracy of the frequency determinations of the Raman spectra lines was ± 1 cm⁻¹.

Starting bicyclo-	M. p., (°C) of the dihydrotriazole	N% in the dihydrotriazole derivative				
neptene	derivative	found	calculated			
(Ic) (VIa) (VI c)	with 134—136 decomp. 165—168 decomp. 200—202 decomp.	13,45; 13,65 12,50: 12,65 10,93; 11,03	13,49 12,37 10,85			

TABLE 5. Description of the Condensation Products of the Adducts with Phenylazide

SUMMARY

1. The reactivity of vinyl ethers containing hydroaromatic radicals in the diene synthesis with cyclopentadiene and hexachlorocyclopentadiene was investigated. A comparison between the diene activity of vinyl ethers with radicals of different structures showed that vinyl aryl ethers are more reactive in diene synthesis than their hydroaromatic analogs.

2. Introduction of a heteroatom in the α -position to the double bond leads to a considerable increase of the dienophile activity of vinyl derivatives in this reaction; in this respect, sulfur has a greater effect than oxygen.

3. The presence of a bicycloheptene structure in diene synthesis adducts of vinyl ethers with cyclopentadiene and hexachlorocyclopentadiene was confirmed by spectroscopic methods. In addition to the already known absorption bands, a new band was found in the region of 990-1010 cm⁻¹; it appears to be characteristic for the given structure. The splitting of the double bond frequencies in the Raman spectra is apparently due to the existence of sterically isomeric forms of the bicycloheptene ring.

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