4. The direction of the catalytic reaction depends on the composition of the complexes and the medium: the cyclic oligomers, 4-vinyl-1-cyclohexene and 1,5-cyclooctadiene, are formed in DMF and pyridine solutions, while the cis- or trans-polybutadienes are formed in ethanol solution.

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DIENE CONDENSATION OF ALLYLACETYLENE AND ALLYLETHYNYLDIMETHYLCARBINOL WITH CYCLOPENTADIENE AND SOME TRANSFORMATIONS OF THE OBTAINED ADDUCTS

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Previously we had shown [1] that allylacetylene (AA) and some of its derivatives enter into the Diels–Alder reaction with cyclic polychlorodienes. In the present paper we studied the diene condensation of AA and allylethynyldimethylcarbinol (AEDMC) with cyclopentadiene (CPD), and also some chemical transformations of the synthesized bicyclic acetylenic compounds.

As the study disclosed, AA and AEDMC condense with CPD, with involvement of the vinyl group, at 150-180°C, i.e., under more drastic conditions than with hexachlorocyclopentadiene and form, in contrast to the latter, not only monoadducts (I) and (III), but also bisadducts (II) and (IV).

The yield of the mono- and bisadducts depends on the mole ratio of the reactants, and also on the reaction time and temperature. At a CPD:AA mole ratio = 1:1 is formed 73% of (I) and 8.5% of (II) in 7 h (150-155°), while at a 2:1 mole ratio of the reactants is formed 20% of (I) and 66.5% of (II) in 16 h. At a CPD:AEDMC mole ratio = 1:1 is formed 76.5% of

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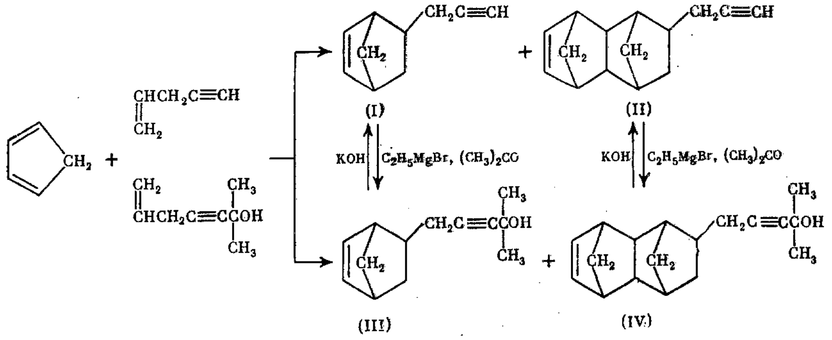
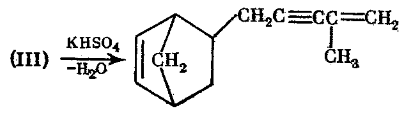


monoadduct (III) and 10% of bisadduct (IV) in 8 h (175-180°), while with a double excess of AEDMC is formed 15% of (III) and 69.5% of (IV) in 20 h.

The structure of the obtained adducts was established on the basis of the IR and PMR spectral data and also chemically, by the cleavage of compounds (III) and (IV) using KOH to (I) and (II), respectively, and also by the conversion of (I) and (II) to (III) and (IV) using EtMgBr and acetone.

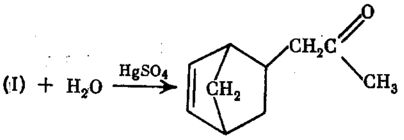
Apparently, adducts (I)-(IV) are mainly the endo isomers [contamination with the exo isomer is distinctly manifest only in the case of (I) via GLC and also by the presence of the signals of the H^5 proton in both the endo and exo regions].

Due to the presence of an OH group, and also of double and triple bonds, the synthesized bi- and tetracyclic acetylenic compounds can undergo various chemical transformations. Thus, alcohol (III) is dehydrated by $KHSO_4$ at 80-85° and gives dienyne (V) in 95% yield.



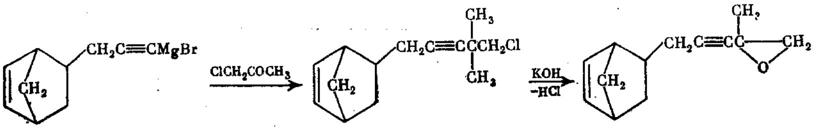
(V)

The hydration of (I) in the presence of $HgSO_4$ leads to the formation of bicyclic ketone (VI) in 96% yield.



(VI)

The Grignard reagent of adduct (I) reacts with monochloroacetone to give chlorohydrin (VII), which in the presence of KOH is dehydrochlorinated to epoxide (VIII).



(VII) (VIII)

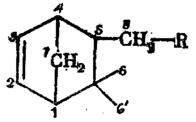
The structure of the obtained compounds (V)-(VIII) was also confirmed by the IR and PMR spectra (see Table 1).

EXPERIMENTAL

The IR spectra of the compounds were obtained on a UR-20 spectrophotometer; the PMR spectra were obtained on a Tesla B-487B spectrometer (80 MHz) using HMDS as the internal standard. The purity of the obtained compounds was checked by TLC on Al_2O_3 (II activity) in the system: 3:1 benzene—ether, and using iodine as the developer.

The GLC analysis was run on a Chrom-3 chromatograph using a column packed with 3% SE-30 deposited on Chromaton W, a programming of the temperature from 80-100 to 220°, a rate of temperature rise of 8 deg/min, and nitrogen as the carrier gas.

TABLE 1.* PMR Spectral Data for Bicyclic Adducts



Compound	δ, ppm							
	H^1+H^4	H^2+H^3	H^5	H^6	$H^{6'}$	$H^7+H^{7'}$	H^8	R
(I)	2,6–2,95 m	5,8–6,15 m	2,1 m	0,6 m	1,8 m	1,1–1,5 m	1,54–1,9 m	1,54–1,9 m
(III)	2,65–2,95 m	5,9–6,15 m	2,15 m	0,56 m	1,6–2,0 m	1,1–1,5 m	1,9 m	1,0–1,5 m (CH_3) and 3,0 s (OH)
(V)	2,5–2,9 m	5,8–6,1 m	3,3 m	1,1 m	2,2 m	1,15–1,35 m	1,95 m	1,8 m (CH_3) and 5,0 m (CH_2)
(VI)	2,7 m	5,7–6,1 m	2,8 m	1,3 m	2,8 m	1,5–2,2 m	2,0–2,2 m	1,98 s ($COCH_3$)
(VII)	2,7–3,1 m	5,9–6,4 m	3,7–4,0 m	0,7 m	1,8–2,5 m	1,3–1,8 m	1,8–2,5 m	3,65m (CH_2Cl), 1,3–1,8 m (CH_3) and 3,0 s (OH)
(VIII)	2,46–2,9 m	5,8–6,05 m	2,1 m	0,55 m	1,8 m	1,1–1,4 m	1,1–1,4 m	1,1–1,4 m (CH_3) and 2,4–2,9 m (CH_2)

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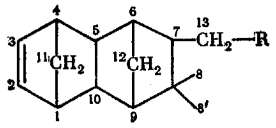
*m = multiplet (the positions of the center or the intervals between the extreme signals are given); s = singlet.

TABLE 2. PMR Spectral Data for Tetracyclic Adducts



Compound	δ, ppm									
	H^1+H^4	H^2+H^3	H^5+H^{10}	H^6	H^7	H^8	$H^{8'}$	H^9	$H^{11}+H^{11'}+H^{12}+$ $+H^{12'}$	H^{13}	R
(II)	2,7–3,0 m	5,85 m	1,7–2,3 m	1,7–2,3 m	2,4 m	0,9 m	2,0 m	1,6–2,0 m	1,1–1,35 m	2,2 m	1,85 s
(IV)	2,7–2,3 m	5,95–6,15 m	2,0–2,4 m	1,5–2,5 m	2,5 m	0,7 m	2,5 m	2,7–3,0 m	1,1–2,0 m	2,2 m	1,1–2,0 m $(CH_3)_2$ and 3,5 s (OH)

TABLE 3. Physicochemical Characteristics of Synthesized Compounds

Compound	Yield, %	bp, °C (p, mm Hg)	n_D^{20}	d_4^{20}	Found/calc., %		Empirical formula	IR spectrum, ν, cm^{-1}
					C	H		
(I)	73	140–141	0,4894	0,9221	90,96/90,91	9,18/9,09	$C_{10}H_{12}$	725, 1640, 2130, 3300
(II)	66,5	87–88 (27)	1,5326	1,0224	90,88/90,91	9,12/9,09	$C_{15}H_{18}$	730, 1650, 2130, 3300
(III)	76,5	86,5–87,5 (1)	1,5020	0,9788	82,17/82,10	9,34/9,47	$C_{13}H_{18}O$	720, 1635, 2240, 3400
(IV)	69,5	121–122 (1)	1,5284	1,0189	84,14/84,37	9,62/9,75	$C_{18}H_{24}O$	725, 1645, 2240, 3400
(V)	95	73–74 (1)	1,5154	0,9488	90,78/90,70	9,22/9,30	$C_{13}H_{16}$	730, 1615, 2235, 3100
(VI)	96	106–107 (30)	1,4818	0,9815	80,3/80,00	9,39/9,33	$C_{10}H_{14}$	725, 1635, 1710
(VII)	89,5	116–117 (2)	1,5118	1,0801	69,48/69,44	7,54 */7,57	$C_{14}H_{19}Cl$	725, 1630, 2245, 3400
(VIII)	94	88–89 (1,5)	1,5072	0,9904	82,88/82,97	8,60/8,51	$C_{13}H_{16}O$	725, 1630, 1265, 920, 895, 830

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*Found Cl 15.89%, Calculated Cl 15.81%.

The starting allylethynyldimethylcarbinol (AEDMC) was obtained as described in [2].

The physicochemical constants and elemental analysis data for the compounds are given in Table 3.

5-(Propyn-2-yl)bicyclo[2.2.1]-2-heptene (I). a) A mixture of 6.6 g (0.1 mole) of AA, 6.6 g (0.1 mole) of CPD, and 0.05 g of hydroquinone was heated in a sealed ampul for 7 h at 150-155°. Fractional distillation in vacuo gave 9.53 g (73%) of (I) and 1.12 g (8.5%) of (II).

b) Into a Claisen flask were charged 9.5 g (0.05 mole) of (III) and 0.7 g of powdered KOH and the mixture was subjected to fractional distillation in vacuo. We obtained 6.2 g (94%) of (I).

7-(Propyn-2-yl)tetracyclo[2.2.2.1.1]-2-dodecene (II). a) A mixture of 13.2 g (0.2 mole) of AA, 6.6 g (0.1 mole) of CPD, and 0.5 g of hydroquinone was heated at 150-155° for 16 h. Fractional distillation in vacuo gave 2.64 g (20%) of (I) and 8.79 g (66.5%) of (II).

b) A mixture of 6.5 g (0.025 mole) of (IV) and 0.5 g of powdered KOH was heated. Fractional distillation in vacuo gave 4.54 g (90.5%) of (II).

5-(4-Methyl-4-hydroxypentyn-2-yl)bicyclo[2.2.1]-2-heptene (III). a) A mixture of 12.4 g (0.1 mole) of AEDMC, 6.6 g (0.1 mole) of CPD, and 0.05 g of hydroquinone was heated in a sealed ampul for 8 h at 175-180°. Fractional distillation in vacuo gave 14.5 g (76.5%) of (III) and 1.9 g (10%) of (IV).

b) A mixture of 2 g (0.083 g-atom) of Mg, 10 g (0.091 mole) of EtBr, and 11.2 g (0.085 mole) of (I) in abs. ether was refluxed for 2 h. With ice cooling, 5.2 g (0.09 mole) of acetone was added to the reaction mixture, which was refluxed for another 5 h, decomposed with water, extracted with ether, and dried over $MgSO_4$. After distilling off the ether the residue was fractionally distilled in vacuo to give 15.08 g (94%) of (III).

7-(4-Methyl-4-hydroxypentyn-2-yl)tetracyclo[2.2.2.1.1]-2-dodecene (IV). a) A mixture of 24.8 g (0.2 mole) of AEDMC, 6.6 g (0.1 mole) of CPD, and 0.05 g of hydroquinone was heated in a sealed ampul for 20 h at 175-180°. Fractional distillation in vacuo gave 2.85 g (15%) of (III) and 13.2 g (69.5%) of (IV).

b) A mixture of 2 g (0.083 g-atom) of Mg, 10 g (0.091 mole) of EtBr, and 16.83 g (0.085 mole) of (II) in abs. ether was refluxed for 2 h, cooled with ice, and 5.2 g (0.09 mole) of acetone was added. The reaction mixture was refluxed for another 5 h, decomposed with water, extracted with ether, and dried over $MgSO_4$. After distilling off the ether the residue was fractionally distilled in vacuo to give 19.42 g (89%) of (IV).

5-(4-Methylpenten-4-yn-2-yl)bicyclo[2.2.1]-2-heptene (V). With vigorous stirring, a mixture of 10 g (0.53 mole) of (IV), 13.5 g (0.1 mole) of $KHSO_4$, and 0.02 g of hydroquinone in 15 ml of abs. toluene was heated at 80-85° for 10 h. Then the mixture was extracted with ether, washed with water, and dried over $MgSO_4$. After distilling off the ether the residue was fractionally distilled in vacuo to give 8.60 g (95%) of (V).

5-(Propanoyl-2-bicyclo[2.2.1]-2-heptene (VI). A mixture of 0.4 g of $HgSO_4$ and 0.7 ml of H_2SO_4 in 20 ml of distilled water was heated for 1 h at 60°, after which the temperature was raised to 80° and, with vigorous stirring, 5.8 g (0.04 mole) of (I) was added in drops, and the stirring was continued for another 4-5 h. The next day the mixture was filtered, the precipitate was washed with ether, and the filtrate was washed with satd. NaCl solution until neutral and then dried over $MgSO_4$. After distilling off the ether the residue was fractionally distilled in vacuo to give 6.32 g (96%) of (VI).

5-(4-Chloromethyl-4-hydroxypentyn-2-yl)bicyclo[2.2.1]-2-heptene (VII). To a solution of EtMgBr (from 2 g of Mg and 10 g of EtBr) in abs. ether was added 9 g (0.085 mole) of (I), the mixture was refluxed for 2 h and then, with ice cooling, 7 g (0.071 mole) of chloroacetone was added. The mixture was refluxed for another 4 h, decomposed with water, the ether layer was separated, the aqueous layer was extracted with ether, and the combined ether layers were dried over $MgSO_4$. After distilling off the ether the residue was fractionally distilled in vacuo to give 13.68 g (89.5%) of (VII).

5-(4-Methyl-4,5-oxidopentyn-2-yl)bicyclo[2.2.1]-2-heptene (VIII). With shaking, to a solution of 4.5 g (0.02 mole) of (VII) in 50 ml of abs. ether was gradually added 6 g of KOH powder, after which the stirred mixture was refluxed for 7 h, cooled, and filtered. After distilling off the ether from the filtrate the residue was fractionally distilled in vacuo to give 3.13 g (94%) of (VIII).

CONCLUSIONS

The diene condensation of allylacetylene and allylethynyldimethylcarbinol with cyclopentadiene proceeds, as in the case of hexachlorocyclopentadiene, with involvement of the vinyl group, but under more drastic conditions and with the formation of both the mono- and the bisadducts.

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Ag$^+$-CATALYZED OXIDATION OF ALKANONE CYANOHYDRINS BY PEROXYDISULFATE IONS: GENERATION AND REACTIONS OF 1-CYANOALKOXYL RADICALS*

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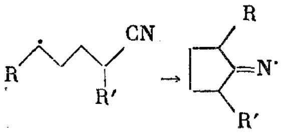
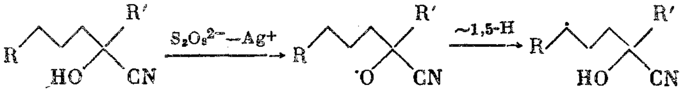
The Ag$^+$-catalyzed oxidation of cyanohydrins was not used previously. The reason for our undertaking a study of this reaction was the observation that 4-cyanoalkyl radicals exhibit an unusually high ability to undergo intramolecular addition to the C≡N bond [2, 3].



In the present paper, in order to make a more extensive study of this property of cyanoalkyl radicals and the subsequent transformations of the cyclic iminyl radicals, we studied the possibility of obtaining hydroxy-substituted 4-cyanoalkyl radicals by a scheme analogous to the scheme for the formation of 4-hydroxyalkyl radicals from alkanols [4].



(Ia—e) (A) (B)

R'=CH$_3$, R=H (a); R=R'=CH$_3$ (b); R'=CH$_3$, R=n-C$_3$H$_7$ (c); R' = CH$_3$, R=n-C$_4$H$_9$ (d); R' = n-C$_4$H$_9$, R = CH$_3$ (e).

As the study objects we selected the cyanohydrins (CH) of acetone, 2-pentanone (Ia), 2-hexanone (Ib), 2-octanone (Ic), 2-nonanone (Id), 5-nonanone (Ie), and 3-methyl-2-heptanone (If). The reason for selecting these CH was to study the effect of the structure and molecular weight of alkanone cyanohydrins (ACH) on the character and rate of their reaction with the system $S_2O_8^{2-}$—Ag^+, and also the effect of the structure of the thus generated 1-cyanoalkoxyl radicals on their transformations.

The reaction of the ACH with the indicated system was run at 60°C in aqueous solutions, using in most experiments 150 mole % of $Na_2S_2O_8$ and 10-15 mole % of $AgNO_3$. The reactivity

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*See [1] for preliminary communication.

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