

Synthesis and Chemical Transformations of 9-(2-Propynyl)tetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodec-4-ene

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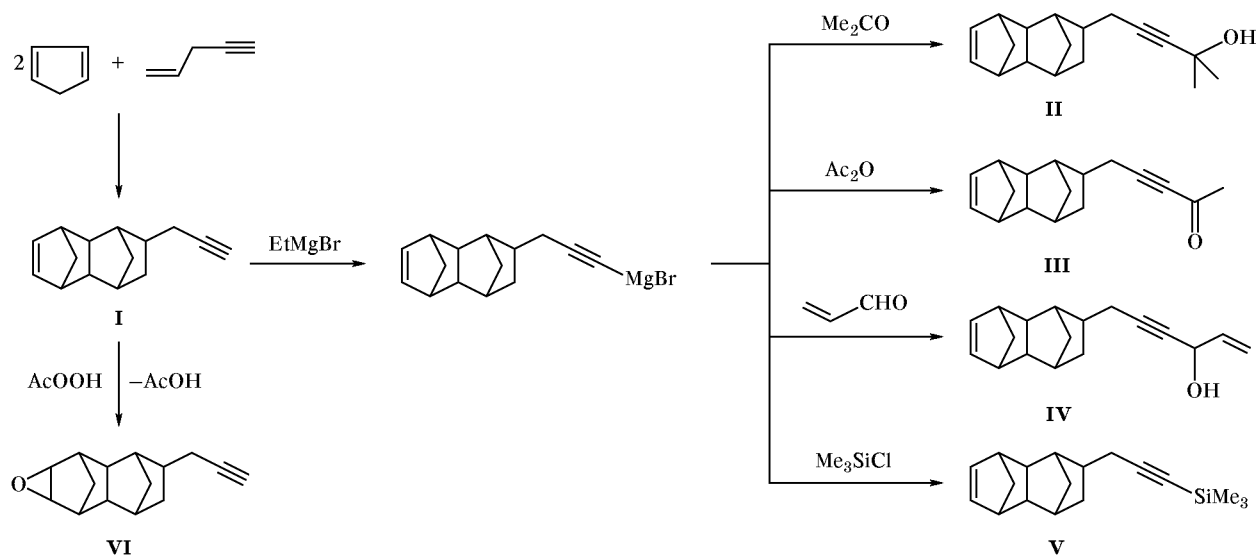
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Abstract—Diels–Alder reaction of allylacetylene with cyclopentadiene involves the double bond of the former to afford 9-(2-propynyl)tetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodec-4-ene. Treatment of the adduct with ethylmagnesium bromide gives the corresponding Iotsitch compound which readily reacts with acetone, acetic anhydride, acrolein, and chlorotrimethylsilane, yielding tetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodec-4-ene derivatives having hydroxy, acetyl, trimethylsilyl, or 1-hydroxypropenyl group in the side chain. Hydrosilylation of 9-(2-propynyl)tetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodec-4-ene over rhodium catalyst occurs in a stereoselective fashion to give only the *trans* adduct.

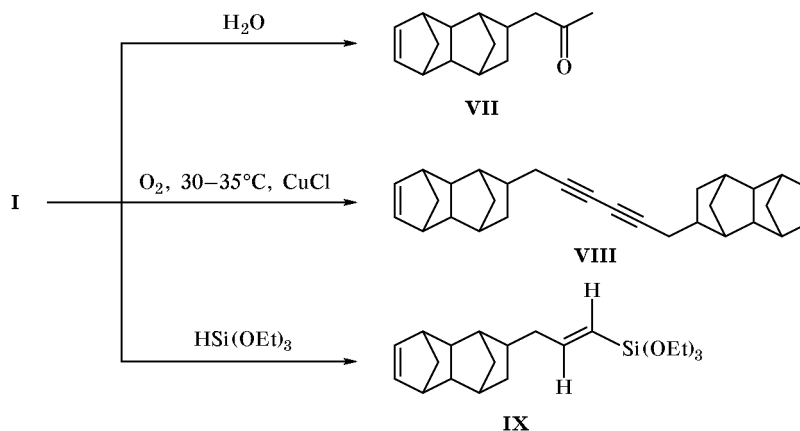
Enyne hydrocarbons are widely used as physiologically active substances and plasticizers; also, they are very important components of fragrant materials [1]. However, there are no published data on the synthesis of acetylene-containing carbo- or heterofunctional compounds of the tetracyclic series. With the goal of preparing such compounds, cyclopentadiene was brought into the Diels–Alder reaction with allylacetylene. As a result, 9-(2-propynyl)tetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodec-4-ene (**I**) was synthesized (Scheme 1). Some chemical transformations of this

compound were studied. Molecule **I** contains three potential reaction centers: acetylenic hydrogen atom and double and triple bonds, which could give rise to various functional derivatives. Treatment of **I** with ethylmagnesium bromide gave the corresponding Iotsitch compound which readily reacted with acetone, acetic anhydride, acrolein, and chlorotrimethylsilane to afford products **II–V** in more than 70% yield (Scheme 1). Oxidation of **I** with peroxyacetic acid occurs selectively at the double bond, yielding compound **VI**.

Scheme 1.



Scheme 2.



The structure of compounds **II–VI** was determined by IR and ^1H NMR spectroscopy, and their purity was checked by thin-layer and gas–liquid chromatography. In the IR spectra of the products, medium-intensity bands in the regions 1630–1635 and 2240–2245 cm^{-1} unequivocally belong to stretching vibrations of the double and triple carbon–carbon bonds [2], and a broad band with its center at 3460 cm^{-1} in the spectrum of alcohol **II** corresponds to vibrations of associated hydroxy group. Epoxy derivative **VI** shows in the spectrum strong absorption bands at 805, 920, and 3060 cm^{-1} [3], indicating *endo* orientation of the epoxy bridge in keeping with published data [4].

Compound **I** readily undergoes hydrolysis to the corresponding ketone **VII**. Oxidative condensation of **I** in the presence of CuCl gives polycyclic diacetylene derivative **VIII** (Scheme 3). The latter shows in the IR spectrum an absorption band at 2250 cm^{-1} , which belongs to stretching vibrations of disubstituted triple

bond. It was found that addition of triethoxysilane to compound **I** in the presence of (acetylacetonato)(dicarbonyl)rhodium occurs regio- and stereoselectively at the triple bond, yielding *trans* isomer **IX**. The ^1H NMR spectrum of **IX** contained signals from protons of the $\text{SiCH}=\text{CH}$ fragment as doublets of doublets at δ 4.76–5.45 ppm with a coupling constant 3J of 13.2 Hz which indicates *trans* configuration of the double bond.

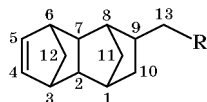
The yields, physical constants, elemental analyses, and IR and ^1H NMR spectra of compounds **I–IX** are given in Tables 1 and 2.

EXPERIMENTAL

The IR spectra were recorded on a Specord-75 spectrometer. The ^1H NMR spectra were obtained on a Tesla BS-487B instrument (80 MHz) using HMDS as internal reference. The purity of the products was

Table 1. Yields, physical constants, elemental analyses, and IR spectra of tetracyclododecene derivatives **I–IX**

Comp. no.	Yield, %	bp, °C (<i>p</i> , mm)	n_{D}^{20}	d_4^{20}	Found, %		Formula	Calculated, %		IR spectrum, cm^{-1}
					C	H		C	H	
I	93.3	87–88 (27)	1.5328	1.0224	90.88	9.12	$\text{C}_{15}\text{H}_{18}$	90.91	9.09	730, 1650, 2130, 3300
II	72.5	121–122 (1)	1.5284	1.0189	84.14	9.62	$\text{C}_{18}\text{H}_{24}\text{O}$	84.32	9.43	720, 1670, 2230, 3460
III	76.3	125–127 (1)	1.5102	1.0599	84.55	8.44	$\text{C}_{17}\text{H}_{20}\text{O}$	84.95	8.39	730, 1650, 1740, 2230
IV	85.6	151–152 (5)	1.5366	1.0436	84.95	8.80	$\text{C}_{18}\text{H}_{22}\text{O}$	84.99	8.71	720, 1590, 1660, 2240, 3420
V	86.5	141–142 (3)	1.5301	0.9876	79.61	9.48	$\text{C}_{18}\text{H}_{26}\text{Si}$	79.92	9.69	735, 1255, 1665, 2195
VI	70.5	66–67 (10)	1.5093	1.0532	84.32	8.59	$\text{C}_{15}\text{H}_{18}\text{O}$	84.06	8.47	805, 920, 2235, 3060
VII	92.5	116–117 (3)	1.5272	1.0576	83.54	9.09	$\text{C}_{15}\text{H}_{20}\text{O}$	83.28	9.31	730, 1660, 1740, 2235
VIII	96.0	mp 94°C	–	–	91.14	8.86	$\text{C}_{30}\text{H}_{34}$	91.31	8.68	725, 1600, 2230
IX	76.7	158–159 (1)	1.4872	1.0172	69.60	9.54	$\text{C}_{21}\text{H}_{34}\text{O}_3\text{Si}$	69.56	9.45	1250, 1610, 1640

Table 2. ^1H NMR spectra^a (chemical shifts δ , ppm) of tetracyclododecene derivatives **I–VII** and **IX**

Comp. no.	1-H, m	2-H, 7-H, m	3-H, 6-H, m	4-H, 5-H, m	8-H, m	9-H, m	10-H _A , m	10-H _B , m	11-H, 12-H, m	13-H, m
I	1.7–2.1	1.7–2.3	2.7–3.0	5.8–5.9	1.7–2.3	2.4	0.9	2.1	1.1–1.35	2.2
II	2.7–3.0	2.0–2.4	2.7–2.9	5.9–6.1	1.5–2.5	2.5	0.7	2.5	1.1–2.0	2.2
III	2.8–3.1	2.1–2.3	2.7–2.9	5.7–6.1	1.6–2.5	2.6	0.9	2.5	1.1–2.1	2.0–2.2
IV	2.7–3.2	3.4	2.6–2.8	5.6–6.1	1.3–1.5	2.2	0.8	2.4	1.2–2.4	1.9
V	2.7–2.9	2.1–2.3	2.7–3.1	5.7–6.0	1.6–2.2	2.3	0.9	2.5	1.1–1.9	2.1
VI	2.6–3.1	1.9–2.2	2.7–2.9	2.7	1.2–1.4	2.3	0.9	2.3	1.1–1.4	2.2
VII	2.7–3.2	3.3	2.6–2.8	5.8–6.2	1.1–1.3	2.2	0.8	2.6	1.1–2.3	1.9
IX	2.6–3.3	2.3	2.6–2.7	5.6–6.1	1.2–1.4	2.4	0.9	2.5	1.2–2.1	2.1

^a Other signals, δ , ppm: **I**: 1.85 s (C \equiv CH); **II**: 1.1–2.0 m (CH₃), 3.5 s (OH); **III**: 1.96 s (COCH₃); **IV**: 3.5 s (OH), 5.8 (=CH), 5.00–5.25 m (=CH₂); **V**: 0.2 s (SiMe₃); **VI**: 1.85 s (C \equiv CH); **VII**: 1.95 s (COCH₃); **IX**: 5.1 m and 5.4 m (SiCH=CH), 3.55 q (OCH₂), 1.05 t (OCH₂CH₃).

checked by TLC on Silufol plates and by GLC on a Chrom chromatograph (30% of SF-30 on Chromaton N-AW-DMCS).

9-(2-Propynyl)tetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodec-4-ene (I). A mixture of 9.9 g (0.15 mol) of allylacetylene, 19.9 g (0.3 mol) of freshly distilled cyclopentadiene, and 0.06 g of hydroquinone was heated in a sealed ampule for 15 h at 160°C. Vacuum distillation gave 21.8 g of compound **I**.

9-(4-Hydroxy-4-methyl-2-pentynyl)tetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodec-2-ene (II). Compound **I**, 19.8 g (0.1 mol), was added to a solution of ethylmagnesium bromide, prepared from 2.3 g of magnesium and 10.9 g of ethyl bromide in anhydrous ether. The mixture was stirred for 5 h under reflux and cooled to 5°C, and 5.8 g (0.1 mol) of acetone in 50 ml of ether was added. After appropriate treatment, vacuum distillation gave 14.8 g of compound **II**.

9-(4-Oxo-2-pentynyl)tetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodec-4-ene (III) was synthesized as described above for alcohol **II** from 15.8 g of compound **I** and 8.2 g (0.8 mol) of acetic anhydride. The mixture was stirred for 6 h at room temperature and was then decomposed with water. After appropriate treatment, vacuum distillation gave 15.1 g of ketone **III**.

9-(4-Hydroxy-5-hexen-2-ynyl)tetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodec-4-ene (IV). A solution of 2.8 g (0.05 mol) of acrolein in dry ether was slowly added with stirring and cooling to the Iotsitch compound

prepared from compound **I**. The mixture was heated at 30–35°C and was then treated with a dilute acid. The solvent was removed, and the residue was distilled under reduced pressure to obtain 10.8 g of product **IV**.

9-[3-(Trimethylsilyl)-2-propynyl]tetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodec-4-ene (V) was synthesized as described above for compound **II** from 5.9 g of enyne **I** and 3.3 g (0.03 mol) of chlorotrimethylsilane. The mixture was stirred for 3 h at 25°C and for 6 h under reflux. After appropriate treatment, vacuum distillation gave 7.0 g of compound **V**.

4,5-Epoxy-9-(2-propynyl)tetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodecane (VI). Compound **I**, 7.9 g (0.04 mol), was dissolved in ether, and 10.1 ml of 85% peroxyacetic acid was added at 20°C under vigorous stirring. The mixture was stirred for 6 h and neutralized with a 10% solution of sodium carbonate. After appropriate treatment, vacuum distillation gave 6.1 g of epoxy derivative **VI**.

9-(2-Hydroxypropyl)tetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodec-4-ene (VII). A mixture of 0.2 g of Hg(SO₄)₂ and 0.4 ml of H₂SO₄ in 10 ml of distilled water was heated for 1.5 h at 65°C; the temperature was then raised to 85°C, 3.96 g (0.02 mol) of compound **I** was added dropwise under vigorous stirring, and the mixture was stirred for 6 h and was left overnight. The precipitate was filtered off and washed with ether, and the filtrate was washed with a saturated solution of NaCl until neutral reaction and dried over calcined

MgSO₄. The solvent was removed, and the residue was distilled under reduced pressure to obtain 4.0 g of compound **VII**.

1,6-Bis(tetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodec-9-en-4-yl)-2,4-hexadiyne (VIII). Air was bubbled over a period of 8 h at 35°C through a mixture of 12.0 g (0.06 mol) of compound **I**, 8 g of CuCl, 60 ml of methanol, and 100 ml of pyridine. The mixture was then poured into a saturated solution of ammonium chloride and extracted with ether. The extract was washed with hydrochloric acid and dried over K₂SO₃. The solvent was distilled off, and the residue was recrystallized from hexane. Yield of **VIII** 11.4 g.

9-[3-Triethoxysilyl]-2-propenyl[tetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodec-4-ene (IX). A mixture of 8.2 g (0.05 mol) of triethoxysilane, 9.9 g (0.05 mol) of

compound **I**, and 0.003 g of (acetylacetonato)(dicarbonyl)rhodium in 50 ml of dry benzene was refluxed for 12 h. Vacuum distillation gave 13.7 g of **IX**.

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