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TWO NEW MONOCYCLIC ALLENE PENTAMERS

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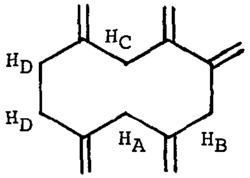
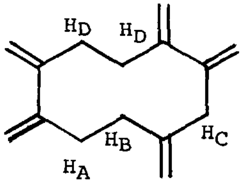
Catalytic cyclo-oligomerization of allene has been observed using some carbonylphosphinenickel(O) complexes to give an oligomer mixture involving trimers and tetramers(1). Previously we reported catalytic regular polymerization of allene catalyzed by low-valent nickel complexes(2). Further investigation of the catalytic reaction, however, has led to a finding of selective pentamerization of allene. Thus, when bis(1,5-cyclooctadiene)nickel was used as a catalyst (ca. 0.2 mole %) under rigorous exclusion of air, a pentamer fraction (I) (bp. 73°/2mm, n_D^{25}: 1.5314) was obtained at 40° or 70° in 50-55% yield, together with a small amount of liquid polymers. Non-polar solvents such as benzene or n-hexane as well as polar ones like tetrahydrofuran, 1,2-dimethoxyethane, acetone or triethylamine may be used. The g.l.c. analysis (capillary columns) of the fraction indicates it to be a single component of at least 98% purity. The elemental analysis(3) and the mass spectrum (M^+ at m/e 200) of I conformed to $C_{15}H_{20}$. The ir spectrum showed strong absorptions at 3080, 2900, 1785, 1630, 1590, and 887 cm^{-1}. The band at 1590 cm^{-1} has been ascribed to the presence of a conjugated double bond system such as $-C(=CH_2)-C(=CH_2)-$(4,5). Consistently, in the ultraviolet region, an absorption maximum at 230 mμ (logε, 4.09) was observed. The presence of conjugation was also supported by preparation of the maleic anhydride adduct, $C_{15}H_{20}\cdot C_4H_2O_3$(6), mp. 151-52°, which lacks the ir band at 1590 cm^{-1}. The nmr spectrum (Table 1) confirmed monocyclic nature of I by the ratio of area due to olefinic protons vs. aliphatic protons (i.e. 1:1). The spectrum showed the presence of three doubly allylic methylenes(7) ($=\overset{|}{C}-CH_2-\overset{|}{C}=$) and two singly allylic methylenes ($=\overset{|}{C}-CH_2-\underset{|}{\overset{|}{C}}-$). The equivalence of the latter methylenes indicates I as

1,2,4,6,9-pentamethylenecyclodecane excluding possibility of the other isomer.

The catalytic reaction apparently involves unstable allene-nickel complexes such as the one previously reported(2). The detail of the isolation and characterization of the complex will be reported separately.

Table 1 Nmr spectra of I and II

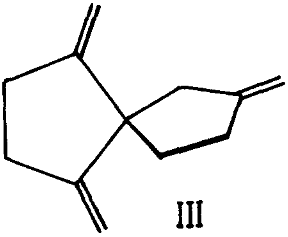
compounds	chem. shift (multiplicity)	coupling const.	rel. int.	assignment
 I	4.85(t)	2 cps	1	exocyclic=CH_2
	5.10(m)		2	
	5.19(s)		2	
	7.00(s)		2	H_B + H_C
	7.22(s)		1	H_A
	7.75(s)^a		2	H_D
 II	4.97 5.03 (double d)	2 cps	1	exocyclic=CH_2
	5.12(s)		2	
	5.25(s)		2	
	7.05(s)		2	H_C
	7.53(s)^a		22	H_D
	7.62(q)^b	7 cps	22	H_A + H_B

The spectra were measured in CCl_4 with TMS as internal reference.

a. sharp singlet, b. A_2B_2 pattern.

Another monocyclic allene pentamer (II) (bp. ∿100°/5mm, n_D^{20}: 1.5370) was obtained through a rhodium complex, $RhCl(C_{15}H_{20})$, which is formed almost quantitatively upon introduction of allene into a benzene solution of $[RhCl(C_2H_4)_2]_2$(8). This complex was treated with 1,2-bis-(diphenylphosphino)ethane at room temperature in benzene to liberate the pentamer(9) in almost quantitative yield. This pentamer II was found to have the structure with two conjugated double bond systems by the mass (M^+ at m/e 200), ir, and nmr spectra (Table 1). The ir spectrum is similar to that of I, the major difference being an increased intensity of the peak at 1596 cm^{-1} consistent with the presence of two conjugated double bond systems. The nmr spectrum indicates the presence of only one doubly allylic methylene group and four singly allylic methylene groups. Thus, II is 1,2,4,7,8-pentamethylenecyclodecane. The arrangement of four double bonds of II can assume a conformation relevant to quadridentate chelation. This is probably the reason why the reaction with allene does not proceed catalytically. The arrangement of double bonds in I, however, is not suitable for quadridentate chelation as the Dreiding model indicates.

It may be added that addition of one or two moles of triphenylphosphine to $[RhCl(C_2H_4)_2]_2$ causes catalytic tetramerization(10) of allene to give 1,4,7-trimethylenespiro[4·4]nonane(III) as also shown by Jones and Lindsey(11).



III

The above-mentioned examples again demonstrate potentiality of low-valent transition metal complexes as catalyst for the synthesis of complicated organic compounds in one step.

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