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Chemistry of Dienyl Anions. I. Crystalline Dienyl Anions by Direct Reaction of Conjugated and Non-conjugated Dienes with Alkali Metals in the Presence of Et_3N

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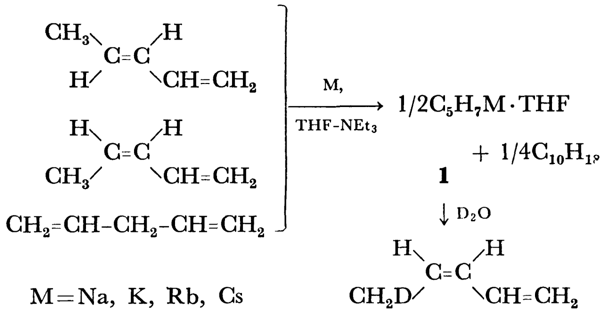
Series of acyclic and cyclic dienyl anions were prepared from both conjugated and non-conjugated dienes by direct metalation with alkali metals (Li, Na, K, Rb, and Cs) in tetrahydrofuran in the presence of triethylamine or *N,N,N′,N′*-tetramethylethylenediamine. Eight different dienyl anions of open chain or cyclic structures were isolated as crystals. All the acyclic potassium dienides of pentadienes, 2-methylpentadienes, 3-methylpentadienes, hexadienes and 2,4-dimethylpentadienes gave the corresponding 1,3-dienes upon hydrolysis, while the potassium cyclic dienide of cycloheptadienes and cyclooctadienes gave 1,4-dienes exclusively. The result of methylation of dienyl anions with methyl iodide agreed with that of hydrolysis. The reaction path for formation of these dienyl anions was studied based on the carbon skeleton and the molar ratio of the reduced diene dimers produced together with the dienyl anions. Selective oxidative coupling of the dienyl anions occurred with CuX or CuX_2 to give linear tetraenes in good yield.

Dienyl anions have been postulated as intermediates in base-catalyzed isomerization of 1,3- and 1,4-dienes[1] or in nucleophilic substitution of aromatics.[2] Their conformational stabilities have recently been studied by simple and extended Hückel MO calculations.[3] The route for preparation of dienyl monoanions has been limited to the metalation of non-conjugated 1,4-dienes with butyllithium[4] in tetrahydrofuran(THF) or with potassium in liquid ammonia.[5] Although conjugated 1,3-dienes[6] are available more readily than the 1,4-dienes, they have not yet been used for this purpose because the well-known "alkali metal catalyzed polymerization[7]" or diene dimer dianion formation[8] occurs preferentially. The only exceptional case is the reaction of cyclopentadiene with sodium to give cyclopentadienyl anion[9] whose cyclopentadienyl group was stabilized by 5π-conjugation. We wish to present here a general method for the preparation of dienyl anions from both conjugated and non-conjugated dienes. All the dienyl anions prepared were isolated as crystals for the first time and their conformation in solution were studied in order to verify the MO prediction. The present method has the advantage of performing the following: 1) preparation of special dienes such as monodeuterated and alkyl-substituted dienes, 2) interconversion reactions between *cis*- and *trans*-dienes, 3) stereoselective synthesis of di- and trisubstituted dienes, 4) selective synthesis of new type of open chain tetraenes which are useful as ligands for transition metals and 5) preparation of other dienyl metal (*e.g.*, Be, Mg, Sn, Si, *etc.*) compounds which serve as reagent for various types of selective organic syntheses.

Results and Discussion

The reaction of 1,3-pentadiene with alkali metals (Na, K, Rb, and Cs) in tetrahydrofuran gave poly-(1,3-pentadiene).[10] However, we found that in the presence of an equimol of aliphatic tertiary amines, it gave pentadienyl anions **1** and reduced pentadiene dimers, $C_{10}H_{18}$, in a 2 : 1 molar ratio. The addition of a tertiary amine inhibits the polymerization completely. Trimethylamine, triethylamine, tripropylamine and *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) were favorable as the tertiary amine over pyridine or 2,2′-bipyridyl with regard to yield. All the pentadiene isomers, *cis*-1,3-pentadiene, *trans*-1,3-pentadiene and 1,4-pentadiene, gave the identical pentadienyl anion $C_5H_7M \cdot THF$ **1** and $C_{10}H_{18}$ quantitatively, irrespective of the alkali metal except for lithium. Based on the molar ratio of **1** to $C_{10}H_{18}$ determined by GC and/or chemical characterization of the hydrolysis products (Tables 1 and 3), the following equation is given for the reaction.



For preparation of the lithium compound, the use of 1,4-pentadiene is pertinent, since 1,3-pentadiene affords lithium pentadienide only in 30—60% yield even in the presence of two moles of TMEDA. Polymerization occurred competitively in this case. A series of pentadienyl anions thus obtained was isolated as yellow needle crystals and their structures were confirmed to be $C_5H_7M \cdot THF$ by GC and chemical characterization of the hydrolysis products (Tables 1 and 2).

The solubility of $C_5H_7M \cdot THF$ in THF decreased in the order Li>Na>K>Rb>Cs with increasing ionic characters of the metal–carbon bond. The THF molecule in $C_5H_7M \cdot THF$ (where M=K, Rb, and Cs) was easily removed by heating at 80—100 °C in a vacuum, while that of Li and Na compounds was strongly coordinated to metals even at 120 °C in a vacuum. This behavior may be explained by Pearson's principle.[11] The affinity of ligands determined by the ligand exchange reaction can also be explained by this principle; *i.e.*, the affinity of ligand to the relatively

Table 1. Characterization of alkali metal pentadienides, $C_5H_7M\cdot THF$ and THF-free C_5H_7M

M	Pentadiene[a] (mol/mol) Found	Calcd	THF[a] (mol/mol) Found	Calcd	M (%) Found	Calcd
Na[b]	1.00	(1.00)	1.00	(1.00)	13.8[d]	(14.2)
K[b]	1.05	(1.00)	0.93	(1.00)	22.0[e]	(21.9)
K[c]	0.98	(1.00)	0.03	(0.00)	35.1[e]	(36.8)
Rb[c]	0.99	(1.00)	0.01	(0.00)	53.2[e]	(55.9)
Cs[c]	1.03	(1.00)	0.00	(0.00)	66.1[e]	(66.3)

a) Determined by GC analysis of the hydrolysis products. b) $C_5H_7M\cdot THF$ system. c) THF-free C_5H_7M system. d) Titration with EDTA. e) Determined by $NaB(C_6H_5)_4$ method.

Table 2. Distribution of hydrolysis products of pentadienyl anions[a]

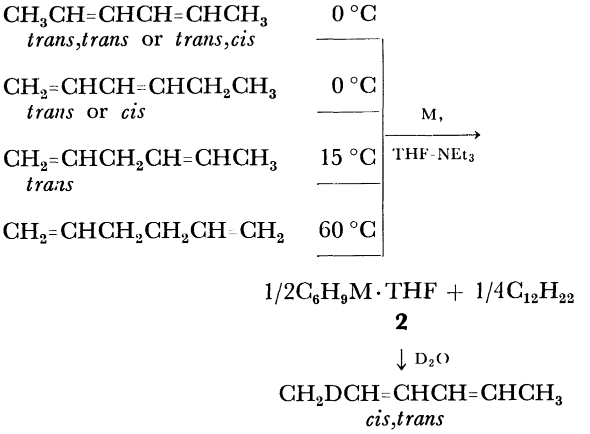
Counter ion	Solvent	1,3-Pentadiene (%) *trans*	*cis*	1,4-Pentadiene (%)
Li	THF	70	20	10
Li	TMEDA	66	22	12
Na	THF	62	38	0
K	THF	2	98	0
K	Isooctane[b]	98	2	0
Rb	THF	2	98	0
Rb	Isooctane	98	2	0
Cs	THF	1	99	0
Cs	Isooctane[b]	100	0	0

a) Hydrolyzed at 0 °C. b) A dispersion of THF-free carbanion was hydrolyzed in 2,2,4-trimethylpentane.

soft lithium compound falls in the order TMEDA> triethylamine>THF, while to the more electropositive K, Rb, and Cs compounds, it is reversed.

The distribution of the hydrolysis products of pentadienyl anions distinctly reflects the nature of their counter cations and the ligands. Potassium, rubidium and caesium pentadienide gave *cis*-1,3-pentadiene stereoselectively upon hydrolysis in THF, but the corresponding THF free anions gave only *trans*-1,3-pentadiene upon hydrolysis in 2,2,4-trimethylpentane or diethyl ether (Table 2). Thus interconversion between *cis*- and *trans*-diene was first accomplished by using the present method. In contrast, the lithium compound gave a mixture of three pentadiene isomers as reported by Bates *et al.*[4] and sodium compound gave a *trans-cis* mixture of 1,3-pentadiene. In the case of the lithium compound, the negative charge of the pentadienyl anion should be delocalized over terminal C_1 and internal C_3 carbon atoms. The following equilibrium is considered. The formation of both *cis*- and *trans*-1,3-pentadiene may be explained by the rotation around the inside C_2–C_3 carbon bond.

In a similar manner, hexadienyl anions having K^+ as a counter cation were prepared from *trans,trans*-2,4-hexadiene, *trans,cis*-2,4-hexadiene, *trans*-1,4-hexadiene, 1,3-hexadiene or 1,5-hexadiene. Conjugated dienes were more reactive than non-conjugated one. The reaction of 2,4-hexadiene occurred at 0 °C while 1,5-hexadiene required higher temperatures (>60 °C). The structures of **2** obtained from the four isomeric hexadienes were identical with each other, as evidenced by GC analysis of dienes obtained upon hydrolysis and the characterization of potassium with Kalignost (sodium tetraphenylborate). The most striking feature of this reaction is that **2** gave *cis,trans*-2,4-hexadiene selectively (94%) upon hydrolysis. The result of deuterolysis of **2** which gave *cis,trans*-2,4-hexadiene-1-*d* is in line with the structure of the *cis*-methylpentadienyl anion prepared from 1,4-hexadiene in liquid ammonia.[5b]


$CH_3CH{=}CHCH{=}CHCH_3$ *trans,trans* or *trans,cis* 0 °C

$CH_2{=}CHCH{=}CHCH_2CH_3$ *trans* or *cis* 0 °C

$CH_2{=}CHCH_2CH{=}CHCH_3$ *trans* 15 °C

$CH_2{=}CHCH_2CH_2CH{=}CH_2$ 60 °C

$$\xrightarrow[\text{THF-NEt}_3]{\text{M,}} \underset{\mathbf{2}}{1/2C_6H_9M\cdot THF} + 1/4C_{12}H_{22}$$

$$\downarrow D_2O$$

$$\underset{cis,trans}{CH_2DCH{=}CHCH{=}CHCH_3}$$

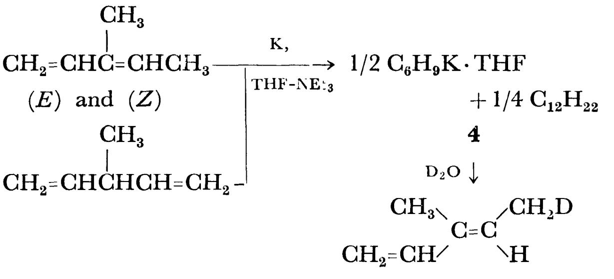
The present method is applicable to the preparation of the octadienyl anion from non-conjugated 1,7-octadiene. A mixture of 1,7-octadiene, potassium and triethylamine (3 : 2 : 2 molar ratio) was heated for 20 h at 70 °C, **3** being precipitated as orange powder in 78% yield by the addition of excess pentane. *cis*-3-Octene (76% yield), 2,6-octadiene (9% yield) and unreacted 1,7-octadiene were obtained from the pentane fraction. Based on the molar ratio, the following equation is given for the reaction.

$$3\,CH_2{=}CH(CH_2)_4CH{=}CH_2 + 2\,K \xrightarrow[\text{THF-NEt}_3]{70\ ^\circ C}$$
$$\underset{\mathbf{3}}{2\,C_8H_{13}K\cdot THF} + CH_3CH_2CH{=}CHCH_2CH_2CH_2CH_3$$

$$\mathbf{3} \xrightarrow{D_2O} CH_2DCH{=}CHCH{=}CHCH_2CH_2CH_3$$
$$+ CH_3CH{=}CHCHDCH{=}CHCH_2CH_3$$

The resulting octadienyl anion **3** gave 2,4-octadiene-1-*d* (90%) and a small amount of 2,5-octadiene-4-*d* (10%) upon deuterolysis. No reduced octadiene dimer was obtained. The yield of 2,6-octadiene became maximum (30 mol% to 1,7-octadiene used) after the mixture had been heated at 70 °C for 8 h, decreasing with continuous heating of the solution with an increase of **3**. This strongly suggests that 1,7-octadiene isomerizes stepwise to 2,4- or 2,5-octadiene to give **3** *via* 2,6-octadiene as postulated by Birch and Phil.[12] Thus, the present method has the advantage to perform the reaction at high temperatures, at which 1,5-, 1,6-, and 1,7-dienes can be converted into 1,3- or 1,4-dienes. Olefines, 1-octene and 2-octene, underwent no reaction under these reaction conditions.

An important feature of the present reaction is that the potassium dienides prepared from trans-conjugated dienes gave thermodynamically unfavorable *cis*-1,3-dienes selectively upon hydrolysis as shown in the hydrolysis of **1** and **2** in THF. The results led us to examine the stereoselective synthesis of di- and trisubstituted dienes by the protonation of anions. Metalation of 3-methyl-1,4-pentadiene with potassium gave 3-methylpentadienyl anion **4** and the reduced dimer, $C_{12}H_{22}$, in 93—95% yields. Deuterolysis of **4** in THF gave (*E*)-3-methyl-1,3-pentadiene-5-*d* selectively (99.5 %) in line with the hydrolysis of the corresponding lithium compound.[13] Differentiation between (*E*) and (*Z*) isomers was done chemically with maleic anhydride according to the method of Bartlett *et al.*[14]



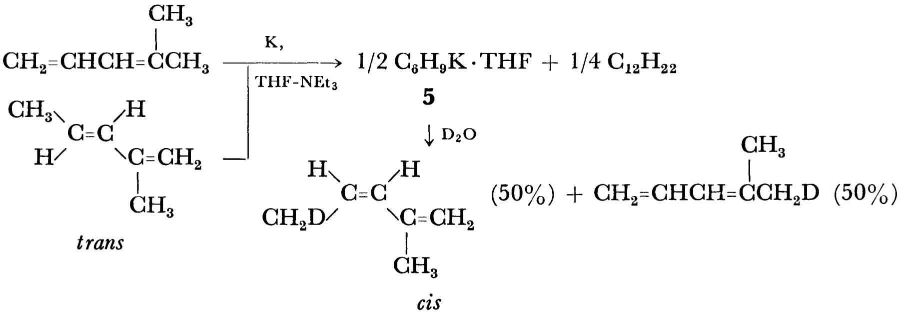
$$CH_2{=}CHC(CH_3){=}CHCH_3\ (E)\text{ and }(Z),\ CH_2{=}CHCH(CH_3)CH{=}CH_2 \xrightarrow[\text{THF-NEt}_3]{\text{K,}} 1/2\ C_6H_9K\cdot THF + 1/4\ C_{12}H_{22}$$

4

$$\xrightarrow{D_2O} (CH_3)(CH_2{=}CH)C{=}C(CH_2D)(H)$$

Thus, substitution with the methyl group on C_3-carbon atom of pentadiene largely effects the geometry of the product. If 3-methyl-1,4-pentadiene behaves similarly to 1,3- or 1,4-pentadiene, the hydrolysis product should be (*Z*)-3-methyl-1,3-pentadiene. This suggests that rotation around the C_2–C_3 carbon bond is inhibited by introducing the methyl group on C_3-carbon atom. A mixture of (*Z*)- and (*E*)-3-methyl-1,3-pentadiene (3 : 7 molar ratio) also gave the same products, but the yield was only 50—60% since the reaction proceeded in competition with polymerization. The substitution of methyl group on the C_3 carbon of pentadiene brings about an increased tendency to promote the polymerization since its chemical structure involves that of isoprene which gives only polymers by the reaction with alkali metals even in the presence of excess tertiary amine.[15]

Both *trans*-2-methyl- and 4-methyl-1,3-pentadiene gave the identical 2-methylpentadienyl anion **5** and reduced dimer, $C_{12}H_{22}$, by metalation with potassium in THF–triethylamine at 0 °C. Hydrolysis of **5** in THF gave *cis*-2-methyl-1,3-pentadiene and 4-methyl-1,3-pentadiene in 1 : 1 ratio. This suggests that the negative charge densities on C_1 and C_5 carbon atoms of **5** are nearly equal. No detectable amount of *trans*-2-methyl-1,3-pentadiene was obtained as evidenced by GC using a capillary column, while the corresponding lithium compound[4] gave *trans*-2-methyl-1,3-pentadiene (45%), 2-methyl-1,4-pentadiene (45%), and 4-methyl-1,3-pentadiene (10%) due to the rapid 1,3-shift present at equilibrium. The yield of **5** from 4-methyl-1,3-pentadiene (92%) is superior to that from *trans*-2-methyl-1,3-pentadiene (60%) since the latter tends to polymerize.

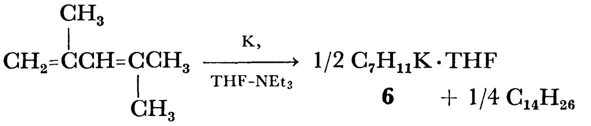


$$CH_2{=}CHCH{=}C(CH_3)CH_3,\ \textit{trans}\text{-}CH_3CH{=}CHC(CH_3){=}CH_2 \xrightarrow[\text{THF-NEt}_3]{\text{K,}} 1/2\ C_6H_9K\cdot THF + 1/4\ C_{12}H_{22}$$

5

$$\xrightarrow{D_2O} \textit{cis}\text{-}CH_2DCH{=}CHC(CH_3){=}CH_2\ (50\%) + CH_2{=}CHCH{=}C(CH_3)CH_2D\ (50\%)$$

A trisubstituted diene, 2,4-dimethyl-1,3-pentadiene, gave 2,4-dimethylpentadienyl anion **6** and $C_{14}H_{26}$ in high yield (85% and 87% respectively) by the reaction with potassium in THF–triethylamine at 10 °C. The anion **6** afforded the starting diene upon hydrolysis quantitatively, no other isomer being detected. In contrast to di- and trisubstituted dienes, a tetrasubstituted diene, 2,5-dimethyl-2,4-hexadiene, was inert to the metalation even at higher temperatures (100—120 °C in a sealed tube). The acidity of its methyl group is probably not so high as to induce the reaction.



$$CH_2{=}C(CH_3)CH{=}C(CH_3)CH_3 \xrightarrow[\text{THF-NEt}_3]{\text{K,}} 1/2\ C_7H_{11}K\cdot THF + 1/4\ C_{14}H_{26}$$

6

The behavior of cyclic dienes markedly differs from that of linear dienes. Although cyclopentadiene is known to give the cyclopentadienyl carbanion by the reaction with potassium or sodium evolving hydrogen,[9] both 1,3- and 1,4-cyclohexadiene gave no cyclohexadienyl anion **7** by the reaction with potassium at 0—50 °C. They isomerized completely to an equal amount of benzene and cyclohexane as was observed in the reaction with butyllithium.[16] Although no detectable amount of potassium was consumed during the course of reaction, the cyclohexadienyl anion can be considered to exist as an intermediate, since **7** was obtained by Kloosterziel and vanDrunen[17] by the reaction with potassium amide in liquid ammonia below −20 °C. At 0 °C, it decomposed thermally to benzene and cyclohexene due to the great electronic stabilization by aromatization.

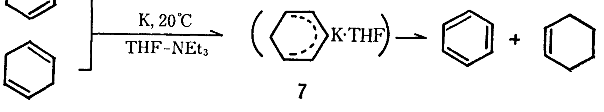


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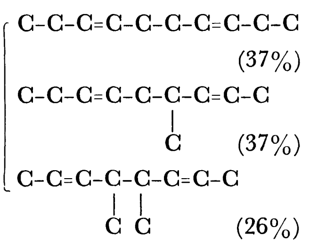
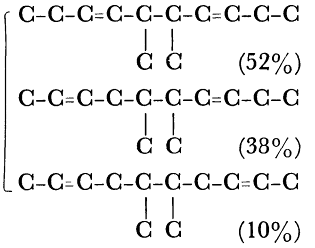
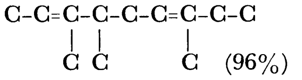
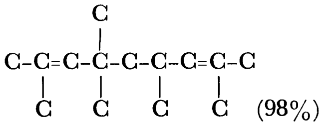
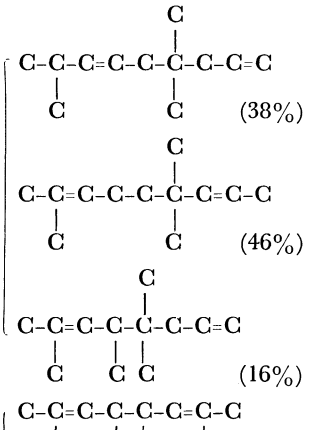
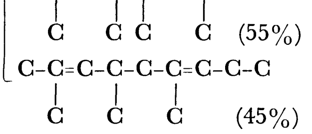
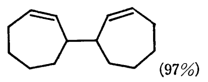
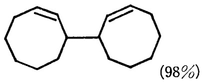
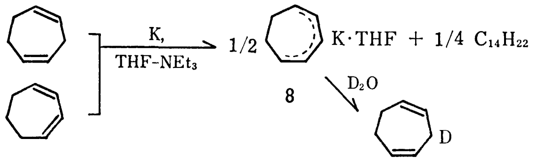
Table 3. Distribution of the reduced diene dimers obtained together with dienyl anions

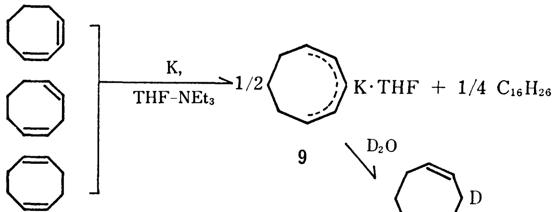
Dienyl anion	Reduced diene dimer	Total yield/%
1	 C-C-C=C-C-C-C=C-C-C (37%) C-C-C=C-C-C-C=C-C (37%) C-C=C-C-C-C=C-C (26%)	98
2	 C-C-C=C-C-C-C=C-C-C (52%) C-C=C-C-C-C-C=C-C-C (38%) C-C=C-C-C-C-C-C=C-C (10%)	95
4	 C-C=C-C-C-C=C-C-C (96%)	92[a)] 60[b)]
6	 C-C=C-C-C-C-C=C-C (98%)	87
5[c)]	 C-C-C=C-C-C-C-C=C (38%) C-C=C-C-C-C-C=C-C (46%) C-C=C-C-C-C-C=C (16%)	92
5[d)]	 C-C=C-C-C-C=C-C (55%) C-C=C-C-C-C=C-C-C (45%)	60
8		99
9		99

a) Reaction of 3-methyl-1,4-pentadiene.
b) Reaction of 3-methyl-1,3-pentadiene.
c) Reaction of 4-methyl-1,3-pentadiene.
d) Reaction of 2-methyl-1,3-pentadiene.

By the present method, however, cycloheptadienes and cyclooctadienes gave the corresponding anions. Both 1,3- and 1,4-cycloheptadienes readily reacted with potassium in THF–triethylamine to produce cycloheptadienyl anion **8** and reduced dimers, $C_{14}H_{22}$, in 96—98% yields. The anion **8** is also prepared by the 1,6-sigmatropic rearrangement of the 1,3,5-heptatrienyl anion.[5d)] The significant difference between **8**, lithium cycloheptadienide and linear dienyl carbanions observed in hydrolysis is that **8** gave a 1,4-diene predominantly (80%) but the latter two gave conjugated 1,3-dienes.

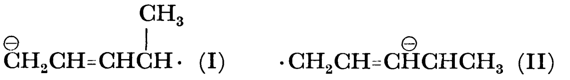


Cyclooctadienyl anion **9** was prepared from 1,3-, 1,4-, and 1,5-cyclooctadienes quantitatively (92—99% yield). Non-conjugated 1,5-cyclooctadiene requires higher temperature (>60 °C) for the completion of the reaction, while 1,3- and 1,4-dienes react with potassium at 10 °C. Cyclooctadienyl anion **9** also gave 1,4-cyclooctadiene exclusively (82%) upon hydrolysis. Thus the negative charge is concluded to be relatively large on the C_3 carbon atom of cyclic dienyl anions as postulated by Hine[18)] The anion **9** is thermally stable as compared to the corresponding lithium compound[19)] which isomerizes irreversibly to *cis*-bicyclo[3.3.0]oct-3-en-2-yl lithium at 35 °C by electrocyclization.[20)] The interconversion to bicyclo[3.3.0]oct-3-en-2-yl anion should be ascribed to the equal sharing of the negative charge to C_1 and C_3 carbons of the cyclooctadienyl anion. The production of an equal amount of 1,3- and 1,4-cyclooctadienes upon the hydrolysis of the lithium compound[21)] at low temperatures supports this conclusion.



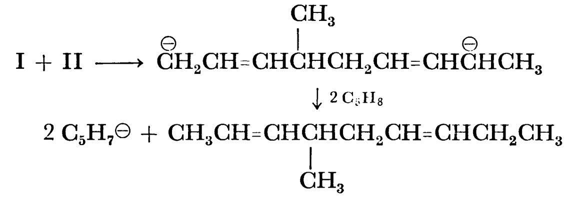
As an extension of the present method, the metalation of *trans,trans,trans*- and *cis,cis,cis*-1,5,9-cyclododecatrienes was examined, 1,3,5-cyclododecatriene being obtained in 40—50% yield together with three isomeric cyclododecatrienes of unknown structures. Quantitative isomerization of these trienes into the conjugated one was unsuccessful.

Process for the Formation of Dienyl Anions. In the preparation of dienyl anions by the present method, reduced diene dimers were obtained. Although 1,3-butadiene, styrene and α-methylstyrene give their dimer[8] or tetramer dianions[22] by the reaction with sodium, no dianions were detected by means of mass spectroscopy of the deuterolysis products. The mass number, (M^+), of reduced pentadiene dimers obtained upon deuterolysis of the reaction mixture is the same as that obtained by hydrolysis with an error of 2%. The reduced pentadiene dimers produced together with **1** are composed of three isomers (Table 3). The carbon skeleton of the dimer strongly suggests that they are formed by the homo or cross coupling of pentadiene radical anions, (I) and/or (II), and by



$$\overset{\ominus}{C}H_2CH{=}CH\overset{\overset{CH_3}{|}}{C}H\cdot\ \text{(I)}\qquad \cdot CH_2CH{=}\overset{\ominus}{C}HCHCH_3\ \text{(II)}$$

the succeeding rapid proton abstraction from free pentadiene with the resulting dianions. As an example, the process for formation of 4-methyl-2,6-nonadiene is expressed by the following equation.



$$\text{I} + \text{II} \longrightarrow \overset{\ominus}{C}H_2CH{=}CH\overset{\overset{CH_3}{|}}{C}HCH_2CH{=}CH\overset{\ominus}{C}HCH_3$$
$$\downarrow 2\,C_5H_8$$
$$2\,C_5H_7^{\ominus} + CH_3CH{=}CH\underset{\underset{CH_3}{|}}{C}HCH_2CH{=}CHCH_2CH_3$$

The production of similar compounds by the reaction of 1,3-pentadiene with lithium naphthalene[23] may also be explained by the same concept. The radical anions corresponding to I and II were reported by Bauld.[24] The carbon skeleton and distribution of the reduced diene dimers (Table 3) strongly suggest that the mode of coupling of the radical anions is the same in principle as that of the allyl radical[25] since both of their dimers formed obey the stability of the aliphatic radical, tertiary>secondary>primary. In agreement with the behavior of pentadienes, hexadienes also gave three isomeric hexadiene dimers in a 11 : 8 : 2 ratio, the ratio being the same irrespective of the four hexadienes used. Both 2-methyl- and 4-methylpentadienes gave two or more isomeric reduced dimers but 3-methyl-1,3-pentadiene and 2,4-dimethyl-1,3-pentadiene gave only one isomer. The process for the formation of these dimers may be explained by the same principle as that described above. Cyclic dienes also gave their reduced dimers regioselectivity; 1,3-cycloheptadiene gave 3-(2-cycloheptenyl)cycloheptene and both 1,3- and 1,5-cyclooctadiene gave 3-(2-cyclooctenyl)cyclooctene. Separation of the meso-isomer from racemate by GC was unsuccessful. The structure of the reduced cyclooctadiene dimer was identical with that obtained with lithium naphthalene.[26]

Alkylation of Dienyl Anions. Alkylation with methyl iodide and *t*-butyl bromide was carried out (Table 4) to know the location of the highest negative charge density on the carbon atoms in the dienyl anions. The result of methylation is in line with that of hydrolysis and of the CNDO-II calculations[3c] of dienyl anions. In the case of the acylic dienyl anions, methylation occurs on C_1 carbon atoms in preference to the C_3 carbon atom, but, occurs exclusively on the C_3 carbon atoms for the cyclic dienyl anions. In contrast, alkylation with *t*-butyl bromide gave reversed result: *i.e.*, alkylation occurred exclusively on the C_3 carbon atom of pentadienyl carbanion. This can be explained not by the steric factor, but by considering the attack of *t*-butyl cation on the free pentadienyl anion since the result is consistent with data of Hückel MO calculations.[3a]

Table 4. Alkylation of dienyl anions on C_1 and C_3 carbon atoms with methyl iodide and *t*-butyl bromide[a)]

Dienyl anion	Methyl iodide		*t*-Butyl bromide	
	C_1 (%)	C_3 (%)	C_1 (%)	C_3 (%)
1	65	35	22	78
2	62[b)] 30	8	8[b)]	92
4	85	15	3	97
5	75	25	4	96
6	42	58	3	95
8	10	90	50	50
9	5	95	47	53

a) Reaction carried out at 20 °C in THF. b) Alkylation on the C_5 carbon atoms.

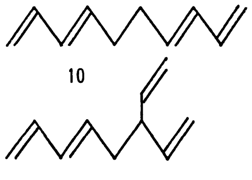
Table 5. Coupling reaction of **1** or **9** with metal halides

Metal halide	Distribution (%)		Total yield/%	Distribution (%)	Total yield/%
	10	**11**		**12**	
$MgBr_2$	0	0	0	0	0
$ZnCl_2$	50	50	98	95	95
$CdCl_2$	68	32	88	90	85
CuCl	99	1	52	100	80
$CuCl_2$	98	2	50	99	73
$NiCl_2$	95	5	18	92	68
$CoCl_2$	97	3	10	91	59

Coupling Reaction of Dienyl Anions. Selective oxidative coupling of dienyl anions is an attractive organic synthesis.[27] Oxidation of alkyl mono- and dianions with metal halides or metal oxides[28] has been reported. We present here the coupling reaction of dienyl anions with a variety of metal halides using **1** as a typical acyclic dienyl anion and **9** as a cyclic dienyl anion (Table 5). The reaction of **1** with a half mol of zinc chloride or cadmium chloride gave quantitatively the tetraene composed of two isomers, **10** and **11**, in a

1 + MCl_2 →

M=Zn, Cd



10 (50%)

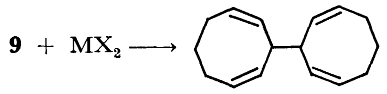
11 (50%)

1 : 1 ratio. Thermally unstable bis(pentadienyl)zinc and bis(pentadienyl)cadmium are considered to be an intermediate in the reaction. The mechanism of these homo and cross couplings should be the same as that of allyl radicals produced by the thermal cracking of bis(allyl)zinc compounds.[29] In order to realize se-

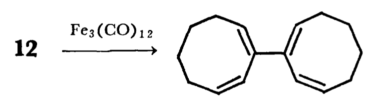
Table 6. Tetraenes obtained by the coupling of **1** with $Br(CH_2)_nBr$

n	Tetranes (%)			Total yield/%
	14	**15**	**16**	
3	20	42	38	96
4	14	50	36	98
5	15	46	39	99

lective coupling, the reaction of **1** with various kinds of metal halides was examined. Copper(I), copper(II), and nickel(II) halides were found to be useful for the selective production of **10**. Pentadienyl metal cluster compounds are the most possible intermediates for the coupling reaction as postulated in the alkyl coupling reaction.[30] The high selectivity should arise from the steric repulsion between the neighboring dienyl groups. The behavior of **9** differs from that of **1** giving 3-(2,7-cyclooctadienyl)-1,4-cyclooctadiene **12** regioselectively even when zinc chloride or cadmium chloride is used as an oxidant. Metal oxides, zinc oxide, and nickel oxide also assist the coupling reaction of **9** effectively. The non-conjugated dimer **12** could be easily converted into conjugated 2-(1,7-cyclooctadienyl)-1,3-cyclooctadiene **13** with a catalytic amount of $Fe_3(CO)_{12}$.

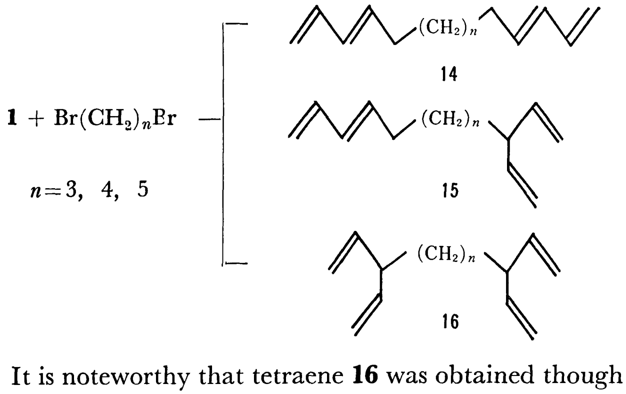


12



13

For the synthesis of the tetraenes separated with a carbon chain, the coupling of **1** with dibromoalkane, $Br(CH_2)_nBr$ (n=1,2,3,4,5), was examined. Coupling of two pentadienyl groups with dibromomethane and 1,2-dibromoethane was not successful since **1** was converted into **10** and **11** in a 7:3 ratio evolving ethylene. However, 1,3-dibromopropane, 1,4-dibromobutane and 1,5-dibromopentane provided the coupling compounds, **14**, **15** and **16** (Table 4).



It is noteworthy that tetraene **16** was obtained though **1** did not give a tetraene with such a branched structure as **16** by the oxidative coupling with metal halides, presumably due to steric repulsion.

Experimental

All the dienes (Aldrich Chem. Inc.) and tertiary amines (Nakarai Chem. Co.) were dried over calcium hydride and distilled before use. Tetrahydrofuran was refluxed over sodium/potassium alloy and distilled under nitrogen. Finely dispersed sodium and potassium were prepared by heating them in toluene and the lithium dispersion in mineral oil. Anhydrous metal halides were prepared by heating the hydrates at prescribed temperatures. 3-Methyl-1,4-pentadiene, 1,4-cycloheptadiene, and 1,4-cyclooctadiene were obtained by the method described in this paper. All the procedures were performed under argon by means of high vacuum technique. GC analysis and separation of the reaction products were carried out with a Hitachi Model K-53 gas chromatograph using a glass capillary column (Silicone OV-101 and HB-2000) and a Varian-Aerograph Model 700 gas chromatograph using a column packed with Silicone DC-550. NMR spectra were taken with a Varian Model A-60 instrument and MS with a Hitachi RMU-7HR spectrometer. IR spectra were recorded on a Hitachi EPI-2 spectrometer. Elemental analysis of the products (bp *ca.*> 120 °C) was carried out with a Yanagimoto Model MT-2 CHN analyzer using a glass ampoule.

Preparation of Pentadienyl Anion 1. To the potassium (3.9 g, 0.1 g-atom) dispersed in a mixture of THF (40 ml, 0.5 mol) and triethylamine (21 ml, 0.15 mol) was added 1,3- or 1,4-pentadiene (20 ml, 0.2 mol) dropwise at 0—5 °C over a 1 h period. Vigorous stirring was necessary in order to avoid explosive reaction and polymerization. After allowing the mixture to attain room temperature in 2—4 h, THF (40 ml) was added and the mixture was heated to 60 °C for completion of the reaction and for dissolution of the suspension of **1**. Orange needle crystals of **1** were precipitated by cooling the solution to 0 °C. Typical yield of **1** was 80% (14.2 g) based on potassium. From the THF soluble fraction, 2.9 g of **1** was further obtained as crystals by addition of hexane (50 ml). The anion **1** was purified by recrystallization in 2:1 THF–hexane. From the hexane soluble fraction, a mixture of reduced pentadiene dimers (described later), $C_{10}H_{18}$, was obtained in 98% yield (6.8 g, 49% conversion based on 1,3-pentadiene). The use of trimethylamine or TMEDA instead of triethylamine also gave **1** in 90—96% yield while the use of pyridine or 2,2′-bipyridyl afforded **1** in 20—30% yield and the polymer in 70—80% yield. Rubidium and caesium compounds were prepared by the same procedure, but crystallization of the sodium compound carried out at -20—-40 °C after addition of hexane (40 ml) to the resulting solution. Yield: 96—99%. Their analytical data are given in Table 1. In the metalation of 1,3-pentadiene (10 ml, 0.1 mol) or 1,4-pentadiene (10 ml, 0.1 mol) with lithium (0.7 g, 0.1 g-atom), TMEDA (30 ml, 0.2 mol) was used instead of triethylamine. The reaction was carried out in THF (20 ml) at 0 °C for 5 h and then at 30 °C for 8 h. After separating the resulting solution from unreacted lithium, hexane (40 ml) was added to the solution and the mixture was cooled to -20 °C to induce the crystallization of $C_5H_7Li\cdot TMEDA$. Yields from 1,3- and 1,4-pentadiene were 52 and 90%, respectively.

THF free alkali metal (K, Rb, Cs) pentadienides were obtained by heating **1** at 90 °C for 1 h in a vacuum (0.05 mmHg). They are explosive in the air and more unstable than the corresponding tetrahydrofuran complexes even in an argon atmosphere. A spontaneous solid state polymerization occurred gradually at room temperature, poly(3-methyl-1-butenylene) being obtained in 90% yield upon hydrolysis by keeping them for 60 days. Deuterolysis of **1** in THF at 0 °C gave *cis*-1,3-pentadiene-5-*d* in 98% yield and that of THF free potassium pentadienide in 1,2,3,4-tetrahydronaphthalene gave *trans*-1,3-pentadiene-5-*d* in 99% yield as evidenced by GC, NMR (position of the deuterium was determined from the peak area ratio), and MS, *m*/*e* 69 (M^+). The purity of the *cis*- and *trans*-1,3-pentadiene-5-*d* was determined to be >97% by reference to the value of M^+ of 1,3-pentadiene.

Preparation of Hexadienyl Anion ***2***. In essentially the same way as described above, the reaction of 1,3-hexadiene (5:3 *trans-cis* mixture), *trans,trans*-2,4-hexadiene, *trans,cis*-2,4-hexadiene, or *trans*-1,4-hexadiene (5.7 ml, 50 mmol) with potassium (1 g, 25 mg-atom) was carried out in a mixture of THF (9 ml) and triethylamine (5 ml) at 5—10 °C for 10 h, while that of 1,5-hexadiene was carried out at 60 °C for 20 h. After the completion of the reaction by heating the resulting suspension to 65 °C for 2 h, excess hexane (20 ml) was added and cooled to −20 °C in order to precipitate **2** as orange powder. Yield: 94% (4.5 g) for 2,4- and 1,4-hexadiene; 84% (4.0 g) for 1,3-hexadiene. The anion **2** thus obtained was washed with two portions of 20 ml hexane and then recrystallized in THF–hexane at 0 °C. Hydrolysis of **2** in 2,2,4-trimethylpentane, Found: hexadiene 43.7%; THF, 37.8% (by GC); K, 18.5% by $NaB(C_6H_5)_4$. Calcd for $C_6H_9K \cdot C_4H_8O$: hexadiene, 42.2%; THF, 37.5%; K, 20.3%. Distributions of the hydrolysis products of **2** prepared from the above four isomers were identical with each other; *trans,cis*-2,4-hexadiene (94%), *trans,trans*-2,4-hexadiene (3%) and *cis,cis*-2,4-hexadiene (3%). Purity of the deuterolysis products, *cis,trans*-2,4-hexadiene-1-*d* (or *trans, cis*-isomer), was >98% by MS. From the hexane soluble fraction, reduced hexadiene dimers were obtained by distillation (1.9 g, 95% yield).

Preparation of Dienyl Anions ***4—9***. The reaction of 3-methyl-1,3-pentadiene, 3-methyl-1,4-pentadiene, *trans*-2-methyl-1,3-pentadiene, 4-methyl-1,3-pentadiene, 2,4-dimethyl-1,3-pentadiene, 1,3-cycloheptadiene, 1,4-cycloheptadiene, 1,3-cyclooctadiene, or 1,4-cyclooctadiene with potassium (2:1 ratio) was carried out in the same manner as in the preparation of **2**, since the solubility of their carbanions in THF is larger than that of **1**. Addition of 3-methyl-1,3-pentadiene and 2-methyl-1,3-pentadiene was made over a period of 3 h. The resulting crude crystals were recrystallized in THF–hexane at −40—0 °C. Characterization of **4—9** was carried out in the same way as described for **1** and **2**. Analysis of K by $NaB(C_6H_5)_4$ method, Found: 19.2, 18.8, 18.1, 17.3, and 17.8% for **4**, **5**, **6**, **8** and **9**. Calcd: 20.3, 20.3, 18.9, 19.1, and 17.9% respectively. GC analysis of dienes obtained by the hydrolysis of **4—9** is in line with the calculated values with errors of 2%. These dienes were identified with GC, NMR, and IR using commercial authentics amples (Aldrich Chemicals and Tokyo Kasei Co.) except for the following dienes.

*(*E*)-3-Methyl-1,3-pentadiene*: IR (neat) 1645, 1601 (C=C), 990, 894 (CH_2=CH), 764, 747 cm^{-1} (CH=CH); PMR ($CDCl_3$) δ 6.40 (d of d, 1, CH), 5.53 (q, 1, CH), 5.02 (m, 2, CH_2), 1.79 (s, 3, CH_3), 1.73 (d, 3, CH_3); MS, Found: 82 (M^+) for C_6H_{10} and 83 (M^+) for the deuterolysis product, (*E*)-3-methyl-1,3-pentadiene-5-*d* (97% purity).

cis*-2-Methyl-1,3-pentadiene*: IR (neat) 1645, 1601 (C=C), 895 (CH_2=C), 749 cm^{-1} (*cis* CH=CH); PMR ($CDCl_3$) δ 5.90 (d, 1, J=11.9, CH), 5.57 (d, of q, 1, J=11.9, CH), 4.92 (d, 2, CH_2), 1.90 (d, 3, CH_3), 1.86 (s, 3, CH_3); MS, Found: 82 (M^+) for C_6H_{10} and 83 (M^+) for the deuterolysis product, *cis*-2-methyl-1,3-pentadiene-5-*d*.

1,4-Cycloheptadiene: IR (neat) 1630 (C=C), 850, 772, 760, 711 cm^{-1} (CH=CH); PMR ($CDCl_3$) δ 5.54 (m, 4, CH), 2.79 (t, 2, CH_2), 2.23 (m, 4, CH_2); MS, Found: 94 (M^+) for C_7H_{10} and 95 (M^+) for 1,4-cycloheptadiene-3-*d*.

1,4-Cyclooctadiene: IR (neat) 1646 (C=C), 810, 790, 762, 716 cm^{-1} (CH=CH); PMR ($CDCl_3$) δ 5.73 (d of q, 2, J=6.3, CH), 5.56 (d of t, 2, J=6.3, CH), 2.77 (t, 2, CH_2), 2.23 (m, 4, CH_2), 1.46 (m, 2, CH_2); MS, Found: 108 (M^+) for C_8H_{12} and 109 (M^+) for 1,4-cyclooctadiene-3-*d*. Deuteration occurred in 98% purity.

Preparation of Octadienyl Anion ***3***. 1,7-Octadiene (22 ml, 0.15 mol) was added to potassium (3.9 g, 0.1 g-atom) dispersed in a mixture of THF (40 ml, 0.5 mol) and triethylamine (21 ml, 0.15 mol). The mixture was allowed to react at 70 °C for 20 h and the resulting solution was concentrated by distillation. The anion **3** was precipitated by the addition of pentane (60 ml) to the residue. Yield: 78% (8.5 g, 52% conversion based on 1,7-octadiene). The position of deuterium in the following deuterolysis products of **3** was determined from the PMR peak area ratio by reference to the corresponding hydrolysis products.

*2,5-Octadiene-4-*d: IR (neat) 1658 (C=C), 963, 900, 719 cm^{-1} (CH=CH); PMR (CCl_4) δ 5.02 (m, 2, J=7.5, CH), 5.00 (m, 2, J=7.9, CH), 2.24 (m, 1, CHD), 1.59 (m, 2, CH_2), 1.22 (d, 3, CH_3), 0.53 (t, 3, CH_3); MS, Found: *m*/*e* 111. Calcd for $C_8H_{13}D$: M, 111.

*2,4-Octadiene-1-*d: IR (neat) 1650 (C=C), 945, 926, 816 cm^{-1} (CH=CH); PMR (CCl_4) δ 5.60 (d of d, 1, J=13.0, CH), 5.35 (d of d, 1, J=7.2, CH), 4.98 (m, 2, CH), 1.70 (d of t, 2, CH_2), 1.28 (d, 2, CH_2D), 1.06 (m, 2, CH_2), 0.57 (t, 3, CH_3); MS, Found: *m*/*e* 111. Calcd for $C_8H_{13}D$: M, 111.

3-Octene (76% yield, 25% conversion based on 1,7-octadiene), 2,6-octadiene (9% yield), and unreacted 1,7-octadiene (15%) were obtained from the distillate and pentane extract and characterized after isolation by GC.

3-Octene: IR (neat) 1658 (C=C), 964 (CH=CH); PMR (CCl_4) δ 5.00 (m, 2, J=7.9, CH), 1.60 (m, 4, CH_2), 0.95, 0.93 (m, 4, CH_2), 0.57 (t, 3, CH_3), 0.53 (t, 3, CH_3); MS, Found: *m*/*e* 112 (M^+). Calcd for C_8H_{16}: M, 112.

2,6-Octadiene: IR (neat) 1660 (C=C), 962, 898, 720 (CH=CH); PMR (CCl_4) δ 4.98 (m, 4, CH), 1.58 (bs, 4, CH_2), 1.16 (d, 6, CH_3); MS, Found: *m*/*e* 110. Calcd for C_8H_{14}: M, 110.

Reaction of Cyclohexadienes with Potassium. The reaction of 1,3-cyclohexadiene (2.4 ml, 25 mmol) or 1,4-cyclohexadiene (2.4 ml, 25 mmol) with potassium (1 g, 25 mg-atom) in a mixture of THF (10 ml) and triethylamine (5 ml) was carried out at 50 °C for 20 h. Both 1,3- and 1,4-hexadiene were converted into benzene (1.1 ml, 99%) and cyclohexene (1.2 ml, 98%), 98% of potassium used being recovered.

Alkylation of ***1***, ***2***, ***4***, ***5***, ***6***, ***8***, *and* ***9***. A typical experiment is as follows: To potassium cyclooctadienide **9** (4.1 g, 20 mmol) in THF (20 ml) was added a THF solution (10 ml) of methyl iodide (1.3 ml, 21 mmol) at 0 °C over a 20 min period. The mixture was stirred at 0 °C for 3 h, then heated up to 50 °C for 2 h and concentrated by evaporation. The products were extracted with pentane and distilled. Yield, 99% by GC; isolated yield, 2 g (80%). Alkylation with *t*-butyl bromide was carried out under the same reaction conditions. All the alkyl-substituted dienes were obtained in 95—99% yield as evidenced by GC and separated into their respective isomers by preparative GC to determine the structure by PMR, IR, and MS. Relative ratio of the products (Table 4) was determined by a high sensitive GC using glass capillary column (Silicone OV-101). For the isolation of low boiling methyl-substituted compounds of **1—5**, diethylene glycol dimethyl ether was used as a solvent instead of THF since the peaks of the products and THF overlapped each other in preparative GC.

1,3-Hexadiene from ***1***: IR (neat) 1655, 1606 (C=C), 1002, 898 ($CH=CH_2$), 950, 776, 756 cm^{-1} (CH=CH); PMR ($CDCl_3$) δ 5.30—4.89 (m, 5, CH and CH_2), 2.20 (d of q, 2, CH_2), 1.02 (t, 3, CH_3).

3-Methyl-1,4-pentadiene from ***1***: IR (neat) 1641 (C=C), 997, 910 cm^{-1} ($CH=CH_2$); PMR ($CDCl_3$) δ 5.63 (m, 2, CH), 4.87 (m, 4, CH_2), 2.77 (m, 1, CH), 1.03 (d, 3, CH_3); MS, Found: M$^+$, 82.

2,4-Heptadiene from ***2***: IR (neat) 1650, 1610 (C=C), 817, 765, 720 cm^{-1} (CH=CH); PMR ($CDCl_3$) δ 5.30—6.30 (m, 4, CH), 2.20 (d of q, 2, CH_2), 1.78 (d, 3, CH_3), 1.02 (t, 3, J=7.2, CH_3); MS, Found: M$^+$, 96.

5-Methyl-1,3-hexadiene from ***2***: IR (neat) 1655, 1605 (C=C), 1002, 898 cm^{-1} ($CH=CH_2$); PMR ($CDCl_3$) δ 6.17 (m, 1, CH), 5.80 (m, 2, J=8.6, CH), 5.38 (m, 2, CH_2), 2.15 (m, 1, CH), 0.90 (d, 6, CH_3); MS, Found: M$^+$, 96.

3-Methyl-1,4-hexadiene from ***2***: IR (neat) 1636 (C=C), 958, 913 ($CH=CH_2$), 800, 730 cm^{-1} (CH=CH); PMR ($CDCl_3$) δ 5.64 (m, 1, CH), 5.50 (d of d, 1, J=6.9, *cis* CH), 5.31 (d of q, 1, CH), 4.89 (m, 2, CH_2), 2.76 (m, 1, CH), 1.74 (d, 3, CH_3), 0.99 (d, 3, CH_3); MS, Found: M$^+$, 96.

3-Methyl-1,3-hexadiene from ***4***: IR (neat) 1646, 1609 (C=C), 999, 915, 892 cm^{-1} ($CH=CH_2$); PMR ($CDCl_3$) δ 6.41 (m, 1, CH), 5.53 (t, 1, J=7.0, CH), 5.06 (m, 2, CH_2), 2.17 (d of q, 2, CH_2), 1.76 (s, 3, CH_3), 1.02 (t, 3, J=7.6, CH_3); MS, Found: M$^+$, 96.

3,3-Dimethyl-1,4-pentadiene from ***4***: IR (neat) 1642 (C=C), 995, 912 cm^{-1} ($CH=CH_2$); PMR ($CDCl_3$) δ 5.85 (m, 2, CH), 5.00 (m, 4, CH_2), 1.03 (bs, 6, CH_3).

4-Methyl-1,3-hexadiene from ***5***: IR (neat) 1650, 1610 (C=C), 984, 964, 895 cm^{-1} (CH=CH, $CH=CH_2$); PMR ($CDCl_3$) δ 6.60 (m, 1, CH), 5.96 (d, 1, CH), 4.98 (m, 2, CH_2), 2.15 (q, 2, J=7.8, CH_2), 1.75 (s, 3, CH_3), 1.00 (t, 3, J=7.8, CH_3); MS, Found: M$^+$, 96.

2,3-Dimethyl-1,4-pentadiene from ***5***: IR (neat) 1641 (C=C), 995, 915, 805 cm^{-1} (CH=CH, $CH=CH_2$); PMR ($CDCl_3$) δ 5.71 (m, 1, CH), 4.93 (m, 2, CH_2), 4.73 (bs, 2, CH_2), 2.86 (d of q, 1, CH), 1.78 (s, 3, CH_3), 1.35 (d, 3, CH_3).

2,4-Dimethyl-1,3-hexadiene from ***6***: IR (neat) 1645, 1635 (C=C), 889, 850, 800 cm^{-1} (CH=CH, $CH=CH_2$); PMR ($CDCl_3$) δ 5.83 (s, 1, CH), 5.02 (d, 2, J=7.0, CH_2), 2.44 (q, 2, J=7.6, CH_2), 1.95—1.97 (two-s, 6, CH_3), 1.21 (t, 3, J=7.6, CH_3); MS, Found: M$^+$, 110.

2,3,4-Trimethyl-1,4-pentadiene from ***6***: IR (neat) 1645 (C=C), 890 cm^{-1} ($CH=CH_2$); PMR ($CDCl_3$) δ 5.06 (bs, 4, CH_2), 3.04 (q, 1, J=7.0, CH), 1.89 (bs, 6, CH_3), 1.40 (d, 3, J=7.0, CH_3).

3-Methyl-1,4-cycloheptadiene from ***8***: IR (neat) 1638 (C=C), 763, 715 cm^{-1} (CH=CH); PMR ($CDCl_3$) δ 5.62 (m, 2, CH), 5.41 (d of d, 2, J=11.5, CH), 3.30 (m, 1, CH), 2.21 (m, 4, CH_2), 1.14 (d, 3, J=7.2, CH_3); MS, Found: M$^+$, 108.

3-Methyl-1,4-cyclooctadiene from ***9***: IR (neat) 1645 (C=C), 800, 763, 732, 717 cm^{-1} (CH=CH); PMR ($CDCl_3$) δ 5.33 (m, 2, CH), 5.09 (d of d, 2, J=10.7, CH), 2.88 (d of q, 1, CH), 1.97 (d of t, 4, CH_2), 1.19 (m, 2, CH_2), 0.85 (d, 3, CH_3); MS, Found: M$^+$, 122.

6,6-Dimethyl-1,3-heptadiene from ***1***: IR (neat) 1655, 1602 (C=C), 1002, 896 ($CH=CH_2$), 760 cm^{-1} (CH=CH); PMR ($CDCl_3$) δ 6.05 (m, 1, CH), 5.81 (m, 2, CH), 4.89 (m, 2, CH_2), 1.85 (d, 2, CH_2), 0.79 (bs, 9, CH_3); MS, Found: *m/e* 124. Calcd for C_9H_{16}: M, 124.

*3-*t*-Butyl-1,4-pentadiene from* ***1***: IR (neat) 1642 (C=C), 997, 912 ($CH=CH_2$), 780 cm^{-1} (CH=CH); PMR ($CDCl_3$) δ 6.11 (d of d of d, 2, CH), 4.94 (m, 4, CH_2), 2.78 (t, 1, CH), 0.92 (bs, 9, CH_3); MS, Found: M$^+$, 124.

5,6,6-Trimethyl-1,3-heptadiene from ***2***: IR (neat) 1652, 1603 (C=C), 1000, 950, 899, 758 (CH=CH, $CH=CH_2$); PMR ($CDCl_3$) δ 5.82—6.03 (m, 3, CH_2), 4.88 (m, 2, CH_2), 2.15 (d of q, 1, CH), 0.90 (d, 3, CH_3), 0.81 (bs, 9, CH_3); MS, Found *m/e* 138. Calcd for $C_{10}H_{18}$: M, 138.

3-Butyl-1,4-hexadiene from ***2***: IR (neat) 1640 (C=C), 995, 910 ($CH=CH_2$), 968, 788, 715, 703 cm^{-1} (CH=CH); PMR ($CDCl_3$) δ 5.79 (m, 1, CH), 5.39 (m, 2, CH), 5.00 (m, 2, CH_2), 2.75 (t, 1, CH), 1.67 (d, 3, CH_3), 0.83 (bs, 9, CH_3); MS, Found: M$^+$, 138.

*3-Methyl-3-*t*-butyl-1,4-pentadiene from* ***4***: IR (neat) 1641 (C=C), 996, 911, 785 cm^{-1} ($CH=CH_2$); PMR ($CDCl_3$) δ 6.12 (m, 2, CH), 4.99 (m, 4, CH_2), 1.07 (s, 3, CH_3), 0.90 (bs, 9, CH_3); MS, Found: *m/e* 138. Calcd for $C_{10}H_{18}$: M, 138.

*2-Methyl-3-*t*-butyl-1,4-pentadiene from* ***5***: IR (neat) 1645 (C=C), 968, 910, 890, 789 cm^{-1} (CH=CH, $CH=CH_2$); PMR ($CDCl_3$) δ 5.93 (m, 1, CH), 5.07 (bs, 2, CH_2), 4.80 (m, 2, CH_2), 2.42 (d, 1, J=10.0, CH), 1.78 (s, 3, CH_3), 0.90 (s, 9, CH_3); MS, Found: 138. Calcd for $C_{10}H_{18}$: M, 138.

*2,4-Dimethyl-3-*t*-butyl-1,4-pentadiene from* ***6***: IR (neat) 1643 (C=C), 890 cm^{-1} ($C=CH_2$); PMR ($CDCl_3$) δ 4.99 (m, 4, CH_2), 1.07 (bs, 6, CH_3), 0.90 (s, 9, CH_3); Found: C, 86.52; H, 13.45%; M$^+$, 152. Calcd for $C_{11}H_{20}$: C, 86.76; H, 13.24%; M, 152.

*3-*t*-Butyl-1,4-cycloheptadiene from* ***8***: IR (neat) 1638 (C=C), 807, 760, 715 cm^{-1} (CH=CH); PMR δ 5.79 (d of d, 2, J=7.0, CH), 5.73 (m, 2, CH), 3.00 (m, 1, CH), 2.27 (m, 4, CH_2), 0.89 (s, 9, CH_3); Found: C, 87.35; H, 12.29%; M$^+$, 150. Calcd for $C_{11}H_{18}$: C, 87.92; H, 12.08%; M, 150.

*5-*t*-Butyl-1,3-cycloheptadiene from* ***8***: IR (neat) 1639, 1600 (C=C), 764, 715 cm^{-1} (CH=CH); PMR ($CDCl_3$) δ 5.73 (m, 4, CH), 2.43 (m, 1, CH), 1.92 (m, 2, CH_2), 1.50 (m, 2, CH_2), 0.98 (s, 9, CH_3); MS, Found: M$^+$, 150.

*3-*t*-Butyl-1,4-cyclooctadiene from* ***9***: IR (neat) 1660 (C=C), 790, 745, 716 cm^{-1} (CH=CH); PMR ($CDCl_3$) δ 5.50 (m, 4, J=6.8, CH), 2.91 (t, 1, CH), 2.00 (m, 4, CH_2), 1.31 (m, 2, CH_2), 0.87 (s, 9, CH_3); Found: C, 87.70; H, 12.52%; M$^+$, 164. Calcd for $C_{12}H_{20}$: C, 87.73; H, 12.27%; M, 164.

*5-*t*-Butyl-1,3-cyclooctadiene from* ***9***: IR (neat) 1650 (C=C), 815, 790, 758 cm^{-1} (CH=CH); PMR (CCl_3) δ 5.48 (m, 4, CH), 2.35 (m, 1, CH), 2.13 (m, 2, CH_2), 1.29 (m, 4, CH_2), 0.78 (s, 9, CH_3); MS, Found: M$^+$, 164.

Characterization of Reduced Diene Dimers. Excess pentane (50 ml) was added to the reaction solution of dienes (0.2 mol) and potassium (3.9 g, 0.1 g-atom) in order to precipitate dienyl anions. Reduced diene dimer compounds obtained from the pentane soluble fraction were separated into their respective isomers by preparative GC after distillation. Yields and distribution of the products determined by GC are given in Table 3. Isolated yields by preparative GC, 40—70% of the distillate.

3,7-Decadiene from 1,3-Pentadiene: IR (neat) 1661 (C=C), 963, 719 cm^{-1} (CH=CH); PMR (CCl_4) δ 5.36 (m, 4, CH), 1.96 (m, 8, CH_2), 0.99 (t, 6, CH_3); Found: C, 86.53; H, 13.22%; M$^+$, 138. Calcd for $C_{10}H_{18}$: C, 86.88; H, 13.12%; M, 138.

4-Methyl-2,6-nonadiene from 1,3-Pentadiene: IR (neat) 1660 (C=C), 718 cm^{-1} (CH=CH); PMR (CCl_4) δ 5.09 (m, 4, CH), 2.11 (m, 1, CH), 1.65 (m, 4, CH_2), 1.17 (d, 3, CH_3), 0.60 (t, 3, CH_3), 0.58 (d, 3, CH_3); Found: C, 86.50; H, 13.30%; M$^+$, 138.

4,5-Dimethyl-2,6-octadiene from 1,3-Pentadiene: IR (neat) 1611 (C=C), 964, 718 cm^{-1} (CH=CH). PMR (CCl_4) δ 5.00 (m, 4, CH), 1.95 (m, 2, CH), 1.23 (d, 6, CH_3), 0.52 (d, 6, CH_3). Found: C, 86.68; H, 13.08%; M$^+$, 138, The above three isomers were also obtained from 1,4-pentadiene by the reaction with potassium (see Table 3) in the same ratio with an error of 5%.

5,6-Dimethyl-3,7-decadiene from 1,4-Hexadiene: IR (neat) 1660 (C=C), 965, 900, 738 cm^{-1} (CH=CH); PMR (CCl_4) δ 5.03 (m, 4, CH), 1.90 (m, 2, CH), 1.72 (m, 4, CH_2), 0.72 (d, 6, CH_3), 0.68 (t, 6, CH_3); MS, Found: *m/e* 166. Calcd for $C_{12}H_{22}$: M, 166.

5,6-Dimethyl-2,7-decadiene from 1,4-Hexadiene: IR (neat) 1688 (C=C), 963, 736 cm^{-1} (CH=CH); PMR (CCl_4) δ 5.10 (d of q, 1, J=6.2, CH), 5.07 (d of t, 1, J=6.2, CH), 5.08 (m, 2, CH), 1.85 (m, 2, CH), 1.70 (m, 4, CH_2), 1.32 (d, 3, CH_3), 0.64 (t, 3, CH_3), 0.62 (d, 6, CH_3); MS, Found: *m/e*, 166. Calcd for $C_{12}H_{22}$: M, 166.

5,6-Dimethyl-2,8-decadiene from 1,4-Hexadiene: IR (neat) 1655 (C=C), 964 cm^{-1} (CH=CH); PMR (CCl_4) δ 5.25 (d of q, 2, J=6.3, CH), 5.23 (d of t, 2, J=6.3, CH), 1.88 (m, 6, CH_2C=C and CH), 1.38 (d, 6, CH_3), 0.75 (d, 6, CH_3); MS, Found: M^+, 166.

The structure and relative ratio of reduced hexadiene dimers, $C_{12}H_{22}$, obtained from 1,5- and 2,4-hexadienes were identical with those obtained from 1,4-hexadiene.

3,4,7-Trimethyl-2,6-nonadiene from 3-Methyl-1,3-pentadiene: IR (neat) 1655 (C=C), 965, 832 cm^{-1} (CH=C); PMR ($CDCl_3$) δ 5.10 (m, 2, CH), 2.46 (t of q, 1, CH), 1.88 (m, 4, CH_2), 1.51 (s, 6, CH_3), 1.49 (d, 3, CH_3), 0.87 (d, 3, CH_3), 0.85 (t, 3, CH_3); Found: C, 86.59; H, 13.40%; M^+, 166. Calcd for $C_{12}H_{22}$: C, 86.66; H, 13.34%; M, 166.

2,4,5,7-Tetramethyl-2,6-octadiene from 2-Methyl-1,3-pentadiene: IR (neat) 1669 (C=C), 908, 842 cm^{-1} (CH=CH); PMR ($CDCl_3$) δ 4.96 (bd, 2, CH), 2.19 (m, 2, CH), 1.61 (bs, 12, CH_3), 0.83(d, 6, CH_3); Found: C, 86.20; H, 13.68%; M^+, 166. Calcd for $C_{12}H_{22}$: C, 86.66; H, 13.34%; M, 166.

2,4,6-Trimethyl-2,6-nonadiene from 2-Methyl-1,3-pentadiene: IR (neat) 1670 (C=C), 835, 735 cm^{-1} (CH=CH); PMR ($CDCl_3$) δ 5.25 (t, 1, CH), 4.93(d, 1, CH), 2.52(m, 1, CH), 2.01(m, 2, CH_2), 1.89(d, 2, CH_2), 1.62(bs, 9, CH_3), 0.91 (t, 3, CH_3), 0.87(d, 3, CH_3); MS, Found: M^+, 166.

4,4,8-Trimethyl-2,6-nonadiene from 4-Methyl-1,3-pentadiene: IR (neat) 1655 (C=C), 970, 885 cm^{-1} (CH=CH); PMR ($CDCl_3$) δ 5.34 (m, 4, CH), 2.20 (m, 1, CH), 1.89 (two-d, 2, CH_2), 1.61(d, 3, CH_3), 0.95(d, 6, CH_3), 0.89(s, 6, CH_3); Found: C, 86.58; H, 13.37%; M^+, 166. Calcd for $C_{12}H_{22}$: C, 86.66; H, 13.34%; M, 166.

2,6,6-Trimethyl-2,7-nonadiene from 4-Methyl-1,3-pentadiene: IR (neat) 1670 (C=C), 972, 832 cm^{-1} (CH=CH); PMR ($CDCl_3$) δ=5.34 (m, 2, CH), 5.10 (t, 1, CH), 1.90 (m, 2, CH_2), 1.62(m, 9, CH_3), 1.24 (m, 2, CH_2), 0.93 (s, 6, CH_3); MS, Found: M^+, 166.

2,4,5,5-Teramethyl-2,6-octadiene from 4-Methyl-1,3-pentadiene: IR (neat) 1670, 1650 (C=C), 970, 884, 830, 713 cm^{-1} (CH=CH); PMR ($CDCl_3$) δ 5.33 (m, 2, CH), 5.12 (d, 1, CH), 1.96(m, 1, CH), 1.63(bs, 6, CH_3), 1.61(d, 3, CH_3), 1.09 (s, 6, CH_3), 0.92 (d, 3, CH_3); MS, Found: M^+, 166.

2,4,4,6,8-Pentamethyl-2,7-nonadiene from 2,4-Dimethyl-1,3-pentadiene: IR (neat) 1670, 1655 (C=C), 965, 832 cm^{-1} (CH=CH); PMR ($CDCl_3$) δ 5.10 (m, 2, CH), 2.43 (m, 1, CH), 1.61 (m, 12, CH_3), 1.24 (d, 2, CH_2), 1.04 (s, 6, CH_3), 0.86 (d, 3, CH_3); Found: C, 86.10; H, 13.75%; M^+, 194. Calcd for $C_{14}H_{26}$: C, 86.51; H, 13.49%; M, 194.

3-(2-Cycloheptenyl)cycloheptene from 1,3-Cyloheptadiene: IR (neat) 1650 (C=C), 786, 684 cm^{-1} (CH=CH); PMR ($CDCl_3$) δ 5.73 (m, 4, CH), 2.38 (m, 2, CH), 2.16 (m, 4, CH_2), 1.35—1.65 (m, 12, CH_2); Found: C, 88.20; H, 11.59%; M^+, 190. Calcd for $C_{14}H_{22}$: C, 88.35; H, 11.65%; M, 190.

3-(2-Cyclooctenyl)cyclooctene from 1,3-Cyclooctadiene: IR (neat) 1650 (C=C), 762, 710, 662 cm^{-1} (CH=CH); PMR ($CDCl_3$) δ 5.42 (m, 4, J=6.3, CH), 2.42 (m, 2, CH), 2.05 (m, 4, CH_2), 1.51 (m, 16, CH_2); Found: C, 87.75; H, 11.90; M^+, 218. Calcd for $C_{16}H_{26}$: C, 88.00; H, 12.00; M, 218. The same compound was obtained also from 1,4- and 1,5-cyclooctadienes in 99 and 92% yield, respectively.

*Coupling Reaction of **1** and **9** with Metal Halides.* A solution of **1** (8.9 g, 50 mmol) in THF (120 ml) was added with use of a syringe to the vigorously stirred suspension of anhydrous copper(I) chloride (5.9 g, 60 mmol in THF (50 ml) at 0 °C over 30 min period. The resulting solution was quenched with water (7 ml), filtered quickly (contact of THF to the air for a long time should be avoided in order to prevent the formation of thermally unstable peroxide) and concentrated by vacuum distillation at temperatures below 30 °C after adding 1,4-benzenediol (0.18 g) to the filtrate to inhibit the radical polymerization of the tetraene. The products were separated by LCG using a column (30×3 cm) packed with silica gel (Wako gel C-200) and using pentane as elution solvent. Separation by LCG is preferable to distillation since 10—40% of tetraenes is polymerized by heating to 150 °C. When zinc chloride or cadmium chloride was used as a coupling reagent, the resulting mixture was heated to 80 °C for 1 h in order to induce thermal cracking after **1** (50 mmol) had been added to the THF solution of the metal halide (30 mmol) at 0 °C.

1,3,7,9-Decatetraene: Bp 108 °C/48 mmHg. IR (neat) 1650, 1604 (C=C), 1004, 968, 951, 900 cm^{-1} (CH=CH_2, CH=CH); PMR ($CDCl_3$) δ 6.13 (m, 2, CH), 5.50—5.93 (m, 4, CH), 5.07 (m, 4, CH_2), 2.05 (t, 4, CH_2); Found: C, 89.10; H, 10.50%; M^+, 134. Calcd for $C_{10}H_{14}$: C, 89.49; H, 10.51%; M, 134.

6-Vinyl-1,3,7-octatriene: Bp 103 °C/49 mmHg. IR (neat) 1645, 1635, 1600 (C=C), 1000, 950, 915, 900, 833 cm^{-1} (CH=CH_2, CH=CH); PMR ($CDCl_3$) δ 5.71—6.21 (m, 5, CH), 5.01, 5.03 (m, 6, CH_2), 2.77 (t of t, 1, CH), 2.15 (t, 2, CH_2); Found: C, 89.44; H, 10.50%; M^+, 134. Calcd for $C_{10}H_{14}$: C, 89.49; H, 10.51%; M, 134.

In essentially the same way, **9** (10.9 g, 50 mmol) in THF (150 ml) was allowed to react with copper(I) chloride (5.9 g, 60 mmol) in THF (50 ml) at 0 °C for 2 h, the products being separated by LCG. Yield, 8.7 g (80%). Results of the coupling reaction with the other metal halides are given in Table 5. Zinc oxide and nickel oxide also gave **12** in 50—60% yield under the same reaction conditions.

3-(2,7-Cyclooctadienyl)-1,4-cyclooctadiene: Bp 101 °C/0.5 mmHg. IR (neat) 1640 (C=C), 718, 679 cm^{-1} (CH=CH); PMR ($CDCl_3$) δ 5.55 (m, 8, CH), 3.30 (bs, 2, CH), 3.23 (d of t, 8, CH_2), 1.52 (m, 4, CH_2); Found: C, 89.65; H, 10.20%; M^+, 214. Calcd for $C_{16}H_{22}$: C, 89.65; H, 10.53%; M, 214. Isomerization to the following conjugated tetraene occurred by keeping the compound at 180—200 °C for 3 h in 35% conversion. Complete isomerization was proceeded by the addition of $Fe_3(CO)_{12}$ (5 mol %) and heating the mixture at 170 °C for 15 h. Conversion, 97%.

2-(1,7-Cyclooctadienyl)-1,3-cyclooctadiene: Bp 103 °C/1 mmHg. IR (neat) 1642, 1697 (C=C), 920, 845, 800, 765, 690 cm^{-1} (CH=CH); PMR ($CDCl_3$) δ=5.49—5.86 (m, 6, CH), 2.15—2.35 (m, 8, CH_2), 1.50 (bs, 8, CH_2); Found: C, 89.48; H, 10.30%; M^+, 214. Calcd for $C_{16}H_{22}$: C, 89.65; H, 10.35%; M, 214.

*Tetraenes Obtained by the Reaction of **1** with Dibromoalkanes.* A solution of 1,3-dibromopropane (1.0 ml, 10 mmol) in THF (30 ml) was added to a solution of **1** (3.6 g, 20 mmol) in THF (60 ml) with stirring at 0 °C. The mixture was heated at 40 °C for 1 h, quenched with water (2 ml) and then filtered. The resulting teraenes were separated with GC into their individual isomers. The reactions of 1,4-dibromobutane and 1,5-dibromopentane were carried out under the same conditions.

1,3,10,12-Tridecatetraene: IR (neat) 1640, 1603 (C=C), 988, 947, 894, 830, 784, 735 cm^{-1} (CH=CH_2, CH=CH); PMR ($CDCl_3$) δ 5.60—6.30 (m, 6, CH), 5.03, 4.88 (m, 4, CH_2), 2.17 (m, 4, CH_2), 1.44 (m, 6, CH_2); Found: C, 87.99; H, 11.42%; M^+, 176. Calcd for $C_{13}H_{20}$: C, 88.56; H, 11.44%; M, 176.

9-Vinyl-1,3,10-undecatriene: IR (neat) 1640, 1604 (C=C), 995, 912 (CH=CH_2), 949, 830, 785, 731 cm^{-1} (CH=CH); PMR ($CDCl_3$) δ 6.30 (m, 1, CH), 5.73(d of q, 2, CH), 5.64 (m, 2, CH), 5.05, 5.01, 4.87(m, 6, CH_2), 2.68(t of t, 1, CH), 2.12(m, 2, CH_2), 1.35(m, 6, CH_2); MS, Found: M^+, 176.

3,7-Divinyl-1,8-nonadiene: IR (neat) 1637(C=C), 994, 912 cm^{-1} (CH=CH_2); PMR ($CDCl_3$) δ 5.71 (d of q, 4, CH), 5.04, 4.86 (m, 8, CH_2), 2.67 (t of t, 2, CH), 1.31 (m, 6, CH_2); MS, Found: M^+, 176.

1,3,11,13-Tetradecatetraene: IR (neat) 1640, 1603 (C=C), 1000, 987, 907 (CH=CH_2), 967, 947, 830, 783 cm^{-1} (CH=CH); PMR ($CDCl_3$) δ 5.61—6.31 (m, 6, CH), 5.08, 4.87 (m, 4, CH_2), 2.11 (d of t, 4, CH_2), 1.33 (m, 8, CH_2); Found: C, 88.30; H, 11.60%; M^+, 190. Calcd for $C_{14}H_{22}$: C, 88.35; H, 11.65%; M, 190.

10-Vinyl-1,3,11-dodecatriene: IR (neat) 1642, 1637, 1604 (C=C), 1000, 995, 912 (CH=CH_2), 949, 831, 783, 729 cm^{-1} (CH=CH); PMR ($CDCl_3$) δ 5.60—6.30 (m, 3, CH), 5.73 (d of q, 2, CH), 5.07, 4.85(m, 6, CH_2), 2.70(t of t, 1, CH), 2.12(d of t, 2, CH_2), 1.31(m, 8, CH_2); MS, Found: M^+, 190.

3,8-Divinyl-1,9-decadiene: IR (neat) 1636 (C=C), 990, 914 cm^{-1} (CH=CH_2); PMR ($CDCl_3$) δ 5.71 (d of q, 4, CH), 5.06, 4.84 (m, 8, CH_2), 2.67 (t of t, 2, CH), 1.29(s, 8, CH_2); MS, Found: M^+, 190.

1,3,12,14-pentadecatetraene: IR (neat) 1638, 1602 (C=C), 987, 910(CH=CH_2), 945, 840, 785, 764, 737 cm^{-1} (CH=CH); PMR ($CDCl_3$) δ 5.60—6.32 (m, 6, CH), 5.08, 4.88 (m, 4, CH_2), 2.08 (m, 4, CH_2), 1.33 (bs, 10, CH_2); Found: C, 88.65; H, 12.25%; M^+, 204. Calcd for $C_{15}H_{24}$: C, 88.16; H, 11.84%; M, 204.

11-Vinyl-1,3,12-tridecatriene: IR (neat) 1635, 1602 (C=C), 989 912 (CH=CH_2), 945, 785, 764, 737 cm^{-1} (CH=CH); PMR ($CDCl_3$) δ 5.60—6.32 (m, 3, CH), 5.74 (d of q, 2, CH), 5.10, 4.88 (m, 6, CH_2), 2.69 (t of t, 1, CH), 2.12 (bt, 2, CH_2), 1.34(bs, 10, CH_2); MS, Found: M^+, 204.

3,9-Divinyl-1,10-undecadiene: IR (neat) 1636 (C=C), 995, 912 cm^{-1} (CH=CH_2); PMR ($CDCl_3$) δ 5.74 (d of q, 4, CH), 5.08, 4.86 (m, 8, CH_2), 2.68 (bt, 2, CH), 1.30 (bs, 10, CH_2); MS, Found: M^+, 204.

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