Palladium-Catalyzed Linear Dimerization of Conjugated Dienes

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The dimerization of isoprene in the presence of bis(triphenylphosphine)maleic anhydride palladium(0) occurs in exclusively tail-tail fashion to give 2,7-dimethyl-1,3,7-octatriene (1). 2-Ethyl-1,3-butadiene is dimerized similarly to give the corresponding 2,7-diethyl derivative. Codimerization of isoprene and 1,3-butadiene gives a mixture of codimers consisting of 7-methyl-1,3,7-octatriene (70%) and 2-methyl-1,3,7-octatriene (30%). 2,3-Dimethyl-1,3-butadiene is dimerized in low yield to a mixture of 2,3,6,7-tetramethyl-1,3,7-octatriene and an isomeric triene with a branching methylene group. 1 undergoes typical Diels–Alder cycloadditions with common dienophiles and reacts with formaldehyde to give predominantly a dialkyldihydropyran, **16**. Reaction of 1 with catalytic amounts of potassium *tert*-butoxide–dimethyl sulfoxide gives the conjugated triene, 2,7-dimethyl-2,4,6-octatriene (**23**) and with stoichiometric base gives 1,6,6-trimethyl-1,3-cycloheptadiene (**26**). *n*-Butyllithium reacts with 1 *via* an addition-cyclization mechanism to give the anion of a highly alkylated cyclopentane which is protonolyzed or captured with other electrophilic reagents. The isoprene–butadiene codimer is rearranged by catalytic amounts of base to a single conjugated triene, **33**, or cyclized by stoichiometric base to isomeric dimethylcycloheptadienes.

The linear dimerization of 1,3-butadiene to 1,3,7-octatriene in high conversion and yield under catalysis by certain zero-valent palladium complexes has been reported.[1] In a useful variation on this process, palladium-catalyzed dimerization of 1,3-butadiene or isoprene in the presence of compounds with active hydrogen was shown to give a variety of substituted octadienes. In the case of isoprene, dimerization in the presence of phenol was stated to occur in a fashion which placed the branching methyl groups exclusively at the 3,6 and 3,7 positions on the octadienyl chain.[2a] On the other hand, reaction in the presence of active methylene compounds, *e.g.*, ethyl acetoacetate, placed methyl groups in the 2,7 positions of the octadienyl moiety.[2b] The problem of the influence of alkyl substituents on structural selectivity in diene dimerizations carried out in the absence of nucleophiles or other reactive species had not been investigated when these studies began. After their conclusion, there appeared a report[2c] of the dimerization of isoprene with a palladium(II) complex catalyst describing results that are related to aspects of our own findings. In this paper, the dimerization of isoprene and certain of its homologs by a zero-valent palladium catalyst is described, and aspects of the chemistry of the dimers are discussed.

Results and Discussion

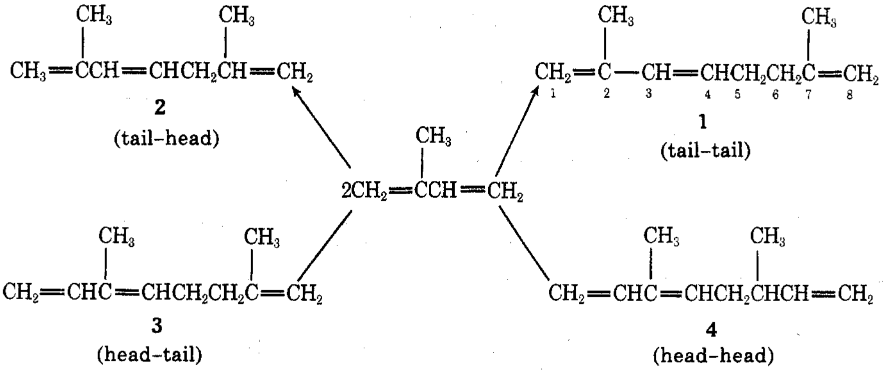
The products of the dimerization of isoprene are especially interesting because of their relationship to naturally occurring diisoprenoid hydrocarbons and other related natural substances. It can be seen that the joining of two isoprene units to give a linear dimer can occur in four distinct ways (Scheme I).

When isoprene was heated in an autoclave under autogenous pressure at 100–110° in acetone solution for 6–8 hr in the presence of bis(triphenylphosphine) maleic anhydride palladium(0),[3] the dimeric product, obtained in 75% yield, was found to consist principally (97–98%) of one isomer along with only trace amounts of other products. From spectroscopic analysis as well as a large body of derivative chemistry, it was shown conclusively that the product was 2,7-dimethyl-1,3,7-octatriene (1), the product of tail-to-tail joining of two isoprene units. This finding presents an interesting contrast with processes of nature, where polyisoprenoid materials are formed virtually exclusively by head-to-tail joining. Nmr spectroscopy was uniquely valuable in distinguishing 1 from 3, which differs only in the location of a methyl group in the diene portion of the molecule. The spectrum of 1 showed singlets at δ 4.80 and 4.69 for the terminal olefinic protons of the diene and monoene group, respectively. The remaining two olefinic protons were seen as an AB multiplet (J_{trans} = 16 Hz) with the lower field component (H_3) appearing as an unsymmetrical doublet and the higher field component (H_4) split further to triplets (J = 6 Hz) by two adjacent protons (H_5). The methyl groups were observed as singlets at δ 1.82 (C_2) and 1.73 (C_7).

The ultraviolet spectrum of 1 showed λ_{max} 229 nm (ϵ 24,600). This spectrum is virtually identical with that of 2-methyl-1,3-pentadiene [λ_{max} 228 nm (ϵ 24,600)],[4] which possesses the same chromophore. Mass spectrometry established the molecular weight of 1 (136).

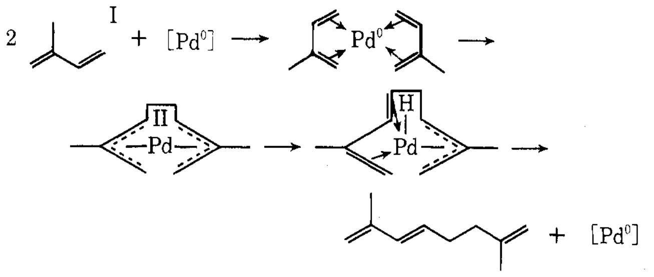
The mechanism of diene dimerization on bis(triphenylphosphine) maleic anhydride palladium(0) is not known with certainty.[1] The remarkable selectivity with isoprene

Scheme I

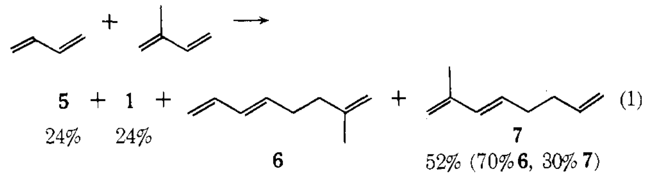


suggests that where alkyl substituents are present, stereochemistry in the catalyst–diene complex may be strongly product determining. It is reasonable that in the first step, two diene units are assembled on the catalyst template through π-complex formation (Scheme II). The ligands maleic anhydride and triphenylphosphine are omitted for clarity, although they are undoubtedly present in the catalyst complex at various stages of reaction. By possibly synchronous processes of oxidative addition of the diene units to palladium and formation of a new carbon–carbon σ bond, the dimer skeleton is formed. Elimination of the elements of a palladium hydride bond from one of the π-allyl units gives a π-alkyl palladium hydride of 3,4-trans stereochemistry. Reductive elimination of the hydrocarbon molecule produces 1 and restores the catalyst for another cycle. The catalyst is quite stable, and after runs involving isoprene:catalyst ratios of *ca.* 700:1, the catalyst residue along with some residual higher diene telomers could be used again with only minor reduction in yield.

Scheme II



The efficient dimerization of both butadiene and isoprene suggested a study of their codimerization. Reaction of equimolar amounts of the dienes under standard conditions gave a dimeric product which was shown by glc to consist of butadiene dimer (1,3,7-octatriene, **5**), **1**, and a codimer in near statistical ratio, 1:1:2.2 (eq 1). The codimer behaved as a single compound on distillation and glc analysis. However, nmr studies revealed that the product was, in fact, a mixture of the isomeric codimers 7-methyl-1,*trans*-3,7-octatriene (**6**) and 2-methyl-1,*trans*-3,7-octatriene (**7**) in the ratio 70:30, respectively. The isomers were differentiated by chemical shifts of the side-chain methyl groups (7-CH_3, δ 1.70; 2-CH_3, δ 1.80) whose subtly different electronic environments had already been observed in the spectrum of **1**. The codimer mixture was further characterized by its uv spectrum [λ_{max} 226 nm (ϵ 23,300)] and mass spectrum (mol wt 122).



6 7 (1)

The distinct preference for **6** over **7** in codimer formation may be explained plausibly by assuming that the step in which a palladium hydride bond is formed, as in Scheme I, will occur in the manner which produces the more stable remaining π-allyl-metal bond, in this case that in which the π-allyl groups bear the electron-releasing methyl substituent. In this way, the sequence which incorporates butadiene as the dienic part of the codimer (*i.e.*, **6**) is energetically favored over the alternative. This proposal can be tested experimentally by noting the way in which codimer isomer ratios vary as a function of the electronic character of the substituent on the starting diene. Such studies are now in progress.

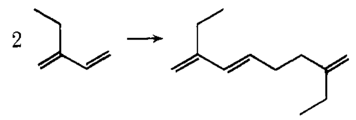
Table I
Effect of Diene Ratio on Dimer Composition

Isoprene: butadiene, mol/mol	Glc peak area 5	6 + 7	1
1:1	1	2.2	1
2:1	1	3.7	2.63
4:1	1	5.15	6.15

A brief study was made of the effect of diene ratio on product composition (Table I).

Dimerization reactions were carried out with a variety of readily available dienes.

2-Ethyl-1,3-butadiene. Not surprisingly, this simple diene reacts in the manner of isoprene to give in 75% yield 2,7-diethyl-1,3,7-octatriene (**8**).



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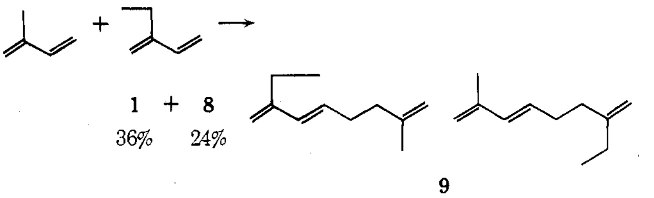
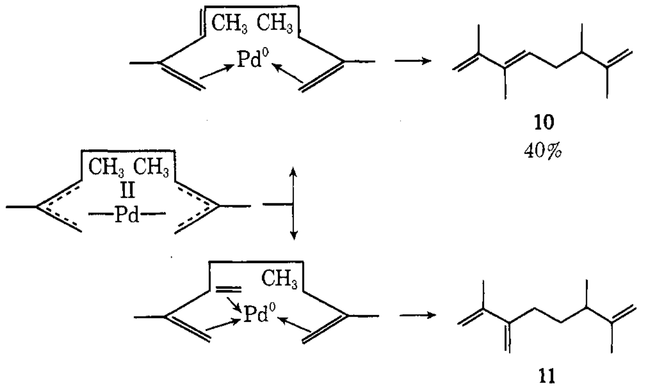
Isoprene and 2-Ethyl-1,3-butadiene. Codimerization of equimolar amounts of these structurally similar dienes gave, in 37% conversion, a product consisting of **1**, **8**, and a new C_{11} codimer, **9**, as shown below. Quantitative analysis by nmr of the isomer distribution in **9** was hindered by severely overlapping resonances, but indications are that neither is markedly preferred.



9
40%

2,3-Dimethyl-1,3-butadiene. The sensitivity of the dimerization reaction to diene structure is well illustrated by the low conversion (*ca.* 10%) noted in this case. In addition, a new type of product bearing a branching methylene group was observed. Both observations may be related to the existence of an intermediate according to Scheme II, *viz.*

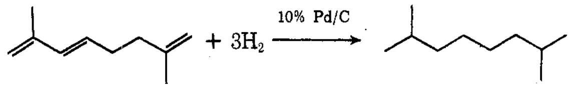


10
40%

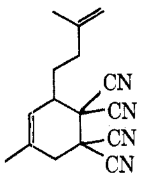
11
60%

Clearly, two methyl groups not only suffer extreme compression, thereby hindering formation of the dimer skeleton, but also offer an alternative path involving a methyl group for β elimination of a palladium hydride bond. The new C-12 trienes **10** and **11** are obtained in 75% yield in the indicated ratio.

Isoprene dimer (**1**) and the butadiene–isoprene codimer (**6** + **7**) were selected for further studies, which have verified the assigned structures and revealed a broad and intriguing derivative chemistry. Catalytic hydrogenation of **1** over 10% Pd/C gave 2,7-dimethyloctane (**12**) as the sole product in high yield, and thereby established the carbon skeleton of the dimer. Reaction of **1** with TCNE gave the expected [2 + 4] cycloadduct **13**. Cycloadditions also occurred readily with acrolein and acrylic acid to yield **14** and **15**, whose structures were assigned from nmr spectra and by analogy with similar reactions described elsewhere.[5]



1 **12**



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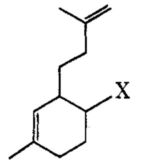
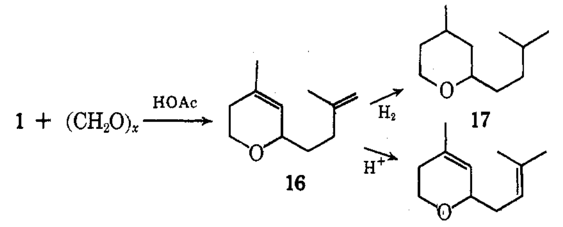


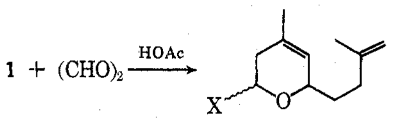
14, X = CHO
15, X = CO_2H

The reaction of **1** with paraformaldehyde in boiling acetic acid took an unexpected course, in that the carbonyl group functioned as the dienophile in a [2 + 4] cycloaddition to give the dihydropyran **16** as the predominant product (49%). A complex, high-boiling fraction appeared to contain the usual array of Prins-type products whose separation was not pursued. **16** was hydrogenated easily to a mixture of cis and trans isomers, **17**. Treatment of **16** with acid failed to cause cyclization, but led instead to the isomeric ether **18**.



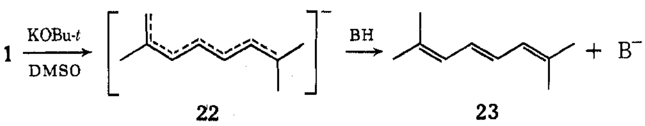
16 **17** **18**

In a similar way, **1** reacted with glyoxal to give the formyl dihydropyran **19** as a mixture (60:40) of conformational isomers (32%). Cycloadditions of this type involving highly electrophilic carbonyl compounds (*e.g.*, chloral) have been reported previously.[6] **19** was converted by conventional techniques to the carbinol **20** ($NaBH_4$) and the carboxylic acid **21** (Ag_2O).



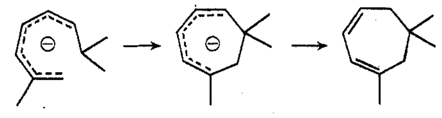
19, X = CHO
20, X = CH_2OH
21, X = CO_2H

Reactions with Strong Bases. The unusual acidities of octatrienes and related hydrocarbons toward typical strong bases have been attributed to stabilization of the resulting carbanions through extensive charge delocalization.[7] In the case of **1**, reaction with a catalytic amount of potassium *tert*-butoxide in dimethyl sulfoxide[8] at 25° for short periods gave 2,7-dimethyl-2,4,6-octatriene (**23**) in 70% yield. It is likely that an intermediate in this isomerization is the heptatrienide anion, **22**, which, under these conditions, is rapidly protonated to give the isomeric, fully conjugated triene. **23** is a crystalline (mp 30°), highly oxygen-sensitive hydrocarbon that has been cursorily mentioned as the product of a laborious synthesis and incompletely characterized.[9] Its unique reactivity is the subject of a separate report.



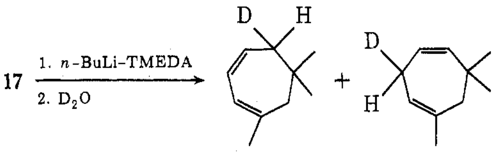
22 **23**

Theoretical studies[10] have indicated that the energetically most favored conformation of an anion such as **22** is the "sickle" form, **24**, which strongly favors cyclization to the new anion, **25**. In fact, treatment of **1** (or **23**) with a stoichiometric amount of potassium *tert*-butoxide in DMSO led, after protonation, to the new hydrocarbon, 1,6,6-trimethyl-1,3-cycloheptadiene (**26**), in 93% yield.

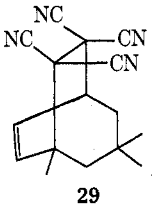


24 **25** **26**

Reaction of **23** with a catalytic amount of metallic sodium also gave **26** (75%) after long reaction times (*ca.* 40 hr) under an argon atmosphere.[11] On the other hand, cyclization of **23** with the *n*-butyllithium–tetramethylethylenediamine (TMEDA) complex followed by hydrolysis with D_2O gave a mixture (75%) consisting principally of the conjugated and nonconjugated monodeuterated dienes **27** and **28** in the ratio 9:1. The structure of **26** was established by its nmr, uv [λ_{max} 251 nm (ϵ 7630)], and mass spectra (mol wt, 136). Diels–Alder cycloaddition of TCNE occurred slowly but gave 94% of the bicyclononene derivative **29**.



27 (90%) **28** (10%)



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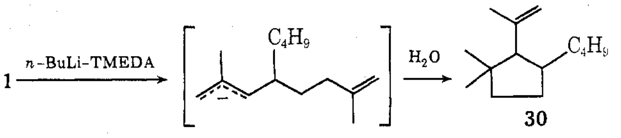
An attempt to effect the reaction **1** → **26** with the *n*-butyllithium-TMEDA complex led instead to addition of an *n*-butyl group to the diene chromophore and cyclization of the resulting carbanion to the highly alkylated cyclopentane **30**. The yield is moderately sensitive to temperature (25°, 49%; −30°, 57%). The structure of **30** was clearly established by its 220-MHz nmr and mass spectra (mol wt, 194). Deuterolysis of the reaction mixture led exclusively to **31** and treatment with paraformaldehyde gave the carbinol **32** as a mixture of two conformers of undetermined stereochemistry in the ratio 42:58. The use of al-



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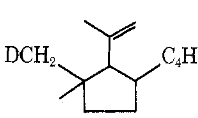

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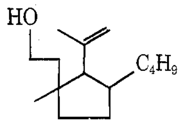

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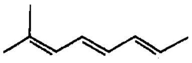
kyllithium reagents to cause polymerization of conjugated dienes is well known,[11] and the mechanism appears to involve addition of the alkyl carbanion to the diene in the manner shown above.[12] In some instances, 1:1 adducts have been identified in solution by spectroscopic techniques.[12] The transformation **1** → **30** is unique in combining addition and cyclization in a way that is preparatively useful.

The cyclization of butadiene–isoprene codimer (**6** + **7**) with a stoichiometric amount of potassium *tert*-butoxide in DMSO showed surprising structural selectivity. After a lengthy (12 hr) reaction period, the hydrocarbon product was obtained in 67.5% yield as a mixture of three components in the ratio 60:32:8. The minor component (8%) was shown to be 2-methyl-2,4,6-octatriene (**33**), the product of rearrangement of the codimer. The major components were isolated and separately characterized as 6,6-dimethyl-1,3-cycloheptadiene (**34**, 60%) and 1,3-dimethyl-1,3-cycloheptadiene (**35**, 32%) by their uv and nmr spectra as well as their reactions with TCNE to give the isomeric bicyclononene derivatives **36** and **37**, respectively.



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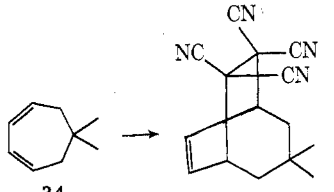
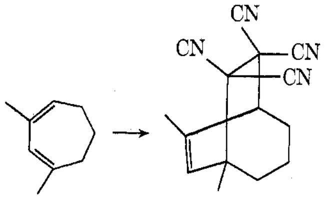


34 **36**



35 **37**

The conjugated triene **33** could be made the major product (49% yield) by the use of only a catalytic amount of base for a short period (15 min). Even under these mild conditions, appreciable cyclization occurred so that the total hydrocarbon product consisted of **33**, **34**, and **35** in the ratio 60:37:3.

Experimental Section

Nmr spectra were obtained on Varian A-60, HA-100, or HR-220 spectrometers, ultraviolet spectra on a Cary 14 spectrometer, and mass spectra on a Du Pont 21-103C spectrometer. Gas chromatographic analyses were run on a Varian Aerograph 1700 instrument with a 0.25 in. × 12 ft 10% XE-60 on Chromosorb T column (tc detector, helium flow rate 60 ml/min). Boiling points and melting points are uncorrected.

2,7-Dimethyl-1,3,7-octatriene (1). Dimerization of Isoprene. A 2-l., stirred autoclave was charged with 500 g (735 ml) of isoprene, 520 ml of acetone, and 8 g of bis(triphenylphosphine) maleic anhydride palladium(0). The mixture was stirred at 105° for 10 hr, cooled to 25°, and vented, and the product was collected. The pale yellow solution contained a small amount of black palladium metal. Examination by glc (186°) showed significant unreacted isoprene as well as one major new product with a retention time of 1.8 min. Two trace impurities (retention times, 1.6 and 20 min) were noted along with several barely discernible materials of longer retention times.

By water-pump distillation, 45 g (9%) of isoprene was recovered, indicating conversion of *ca.* 90%. After removal of acetone, isoprene dimer was collected at 12–15 mm using a hot-water bath. There was obtained 332 g (75%) of 2,7-dimethyl-1,3,7-octatriene which was 97–98% pure by glc. Redistillation gave an analytical sample: bp 70° (25 mm); nmr ($CDCl_3$) δ 1.70 (s, 3 H, 7-CH_3), 1.78 (s, 3 H, 2-CH_3), 2.12 (broad s, 4 H, $-CH_2-$), 4.69 (s, 2 H, C_8-vinyl), 4.80 (s, 2 H, C_1-vinyl) AB q (J = 6 Hz) 5.65 center (d of t, J = 6 Hz, 1 H, C_4-vinyl), 6.15 center (1 H, C_3-vinyl); uv max (isooctane) 229 nm (ϵ 24,600), sh 224 nm; mass spectrum mol wt 136 (calcd for $C_{10}H_{26}$, 136).

Anal. Calcd for $C_{10}H_{16}$: C, 88.2; H, 11.9. Found: C, 88.3; H, 11.6.

7-Methyl- and 2-Methyl-1,3,7-octatriene (6 and 7). Codimerization of Butadiene and Isoprene. A. Isoprene:Butadiene Ratio 1:1. A 2-l. stirred autoclave was charged with 136 g (2 mol) of isoprene, 108 g (2 mol) of 1,3-butadiene, 300 ml of reagent grade acetone, and 2.0 g of bis(triphenylphosphine) maleic anhydride palladium(0). The mixture was stirred and heated at 105° for 8 hr under autogenous pressure, cooled, and vented. The light brown solution was stripped of solvent and unreacted dienes at water-pump pressure, and the mixture of dimers was collected in one fraction by rapid distillation using a warm-water bath. Examination of the product by glc showed three peaks in the approximate ratio 1:2.2:1. These are due, respectively, to 1,3,7-octatriene (butadiene dimer), the butadiene–isoprene codimers, and 2,7-dimethyl-1,3,7-octatriene (isoprene dimer).

Separation was accomplished by fractional distillation at 40–50 mm through an 18-in. spinning band column. Thirteen fractions were collected: fractions 1–4, bp 45–54° (47 mm), 13.3 g (butadiene dimer with traces of codimers); fractions 5–6, bp 59–63° (45 mm), 3.76 g (butadiene dimer and codimers, *ca.* 1:1); fractions 7–11, bp 67° (43 mm), 33.84 g (codimers with traces of impurities); fraction 12, bp 80–81° (38 mm), 6.10 g (codimers and isoprene dimer, 1:2); fraction 13, bp 70–75° (25 mm), 16.41 g (isoprene dimer with traces of impurities). Redistillation of fractions 7–11 gave codimers with bp 70° (50 mm). Glc (185°) showed one peak with a retention time of 1.5 min; nmr ($CDCl_3$) δ 1.70 (s, 7-CH_3, 64%), 1.80 (s, 2-CH_3, 36%) (total 3 H), 2.12 (br s, 4 H, $-CH_2-$), 4.50–5.50 (m, 4 H, terminal vinyl), 5.50–7.00 (m, 3 H, internal vinyl); uv max (isooctane) 226 nm (ϵ 23,300); mass spectrum mol wt 122 (calcd for C_9H_{14}, 122).

Anal. Calcd for C_9H_{14}: C, 88.5; H, 11.5. Found: C, 88.3; H, 11.0.

B. Isoprene:Butadiene Ratio 2:1. In the early stages of the reaction, the ratio of codimers to butadiene dimer was *ca.* 3 and gradually increased as the reaction progressed. Final glc peak area ratios were 1:3.7:2.63 for butadiene dimer:codimers:isoprene dimer.

C. Isoprene:Butadiene Ratio 4:1. Final glc peak area ratios were 1:5.15:6.15 for butadiene dimer:codimers:isoprene dimer.

2,7-Diethyl-1,3,7-octatriene (8). A solution of 41 g (0.5 mol) of 2-ethyl-1,3-butadiene, 1.0 g of bis(triphenylphosphine) maleic anhydride palladium(0), and 40 ml of reagent grade acetone was heated in a 200-ml stainless steel rocker bomb for 9 hr at 110° under autogenous pressure. After cooling to 25°, the product was collected as a pale yellow solution with only a trace of metallic palladium present. Examination of the crude product by glc (186°) showed one major new peak with a retention time of 3.5 min and two trace impurities at 2.9 and 4.0 min. A minor amount of unconverted 2-ethyl-1,3-butadiene was also indicated. The solvent was removed by distillation under water-pump vacuum, and the residual hydrocarbon fraction was distilled at reduced pressure. There was obtained 30.3 g (75%) of material: bp 44–46° (0.75 mm); nmr ($CDCl_3$) δ 1.08 (t, J = 7 Hz, 3 H, CH_3 of C_7 C_2H_5), 1.13 (t, J = 7 Hz, 3 H, CH_3 of C_2 C_2H_5), 1.50–2.70 (m, 8 H, $-CH_2-$), 5.02 (m, 2 H, C_8 vinyl), 5.13 (m, 2 H, C_1 vinyl), 5.40–6.60 (m, 2 H, $C_{3,4}$ vinyl).

Anal. Calcd for $C_{12}H_{20}$: C, 87.7; H, 12.3. Found: C, 87.5; H, 12.0.

Codimerization of Isoprene and 2-Ethyl-1,3-butadiene (9). A 300 ml stainless steel autoclave was charged with 25 g (0.3 mol) of 2-ethyl-1,3-butadiene, 21 g (0.3 mol) of isoprene, 40 ml of reagent acetone, and 1.0 g of bis(triphenylphosphine) maleic anhydride palladium(0). The mixture was stirred rapidly and heated at 105° under autogenous pressure for 7 hr. Periodic monitoring of the reaction mixture by glc (180°) showed that homodimers of isoprene and 2-ethyl-1,3-butadiene (retention times 2.5 and 5.2 min, respectively) were present. In addition, a new component consisting of two poorly resolved peaks was observed at 3.5 min and attributed to the two isomeric codimers. At the end of the reaction period, the reaction product was concentrated to remove acetone, and crude dimeric produce was collected in one fraction by rapid distillation at reduced pressure. On redistillation through a 16-in. spinning band column, there was obtained 5.25 g (0.039 mol) of **1**, 4.90 g (0.03 mol) of **8**, and 6.63 g (0.045 mol) of **9**, bp 75–85° (14 mm); nmr ($CDCl_3$) δ 4.72 (s, 2 H, monoene terminal vinyl), 4.83 (s, 2 H, diene terminal vinyl), 5.20–6.40 (m, 2 H, internal vinyl). Analysis of the aliphatic region δ 0.85–2.50, was hindered by overlapping multiplets but suggested that 2-ethyl-7-methyl- and 2-methyl-7-ethyl-1,3,7-octatriene were present in about equal amounts.

Anal. Calcd for $C_{11}H_{18}$: C, 87.9; H, 12.1. Found: C, 87.6; H, 12.0.

Dimerization of 2,3-Dimethyl-1,3-butadiene (10 + 11). A solution of 51 g (0.62 mol) of 2,3-dimethyl-1,3-butadiene (DMBD) and 1.0 g of bis(triphenylphosphine) maleic anhydride palladium(0) in 75 ml of reagent grade acetone was heated for 8 hr at 105° in a 300-ml stirred autoclave under autogenous pressure. Periodic examination of the reaction mixture by glc (150°) showed the slow growth of two new peaks with retention times of 6.6 and 7.9 min. The ratio of peak areas was *ca.* 3:2, respectively. After 8 hr, much unreacted DMBD remained, and the reaction was terminated. After cooling to 25°, solvent and unreacted DMBD were removed by distillation at water pump pressure, and the residue was fractionally distilled: fraction 1, bp 65–70° (10 mm), 0.83 g; fraction 2, bp 70–72° (10 mm), 0.95 g; fraction 3, bp 73–74° (10 mm), 1.54 g; fraction 4, bp 75–80° (10 mm), 0.52 g.

Fraction 1. Glc peak area ratios 6.6 (77%), 7.9 min (16%); nmr ($CDCl_3$) δ 1.00 (d, $J = 7$ Hz, 3 H), 1.65 (s, 3 H), 1.85 (s, 3 H), 1.50–2.50 (m, 5 H), 4.68 (s, 2 H), 4.90 (s, 2 H); 5.00 (s, 2 H). Minor resonances due to the presence of another isomer were seen. This spectrum establishes the identity of the major component in this fraction as **11**.

Fraction 4. Glc peak area ratios 6.6 (14%), 7.9 min (86%); nmr ($CDCl_3$) δ 1.04 (d, $J = 7$ Hz, 3 H), 1.50–2.40 (m, 12 H), 4.60–4.75 (m, 2 H), 4.75–5.10 (m, 2 H), 5.30–5.85 (m, 1 H). Other minor resonances were noted. This spectrum establishes the identity of the major component as **10**.

Hydrogenation of 1. A mixture of 13.6 g (0.1 mol) of **1**, 80 ml of methanol, and 0.5 g of 10% Pd/C was hydrogenated in a Parr apparatus until hydrogen uptake stopped. Glc (180°) showed the complete disappearance of **1** and the appearance of one new component with the retention time (1.2 min) of authentic 2,7-dimethyloctane. On distillation at atmospheric pressure, the hydrocarbon (bp 160°) was removed as an azeotrope (bp 65°) with methanol. The distillate was diluted with water and the hydrocarbon layer was removed to give 11.3 g (83%) of 2,7-dimethyloctane (**12**), nmr ($CDCl_3$) δ 1.86 (d, $J = 7$ Hz, 12 H, CH_3), 1.10–2.00 (m, 10 H).

Anal. Calcd for $C_{10}H_{22}$: C, 84.4; H, 15.6. Found: C, 84.5; H, 15.2.

On interruption of the hydrogenation at *ca.* 75% completion, it was found that the mixture contained of 60% of **12** along with *ca.* 40% of 2,7-dimethyl-2-octene, indicating that reduction of the 1,3-diene unit is accomplished *via* initial 1,4 addition of hydrogen.

Reaction of 1 with TCNE (13). A solution of 5.73 g (0.045 mol) of TCNE in 35 ml of anhydrous tetrahydrofuran was chilled in an ice bath and 6.2 g (0.045 mol) of isoprene dimer was added in one portion. A deep red color formed but vanished in seconds as the solution became light brown-yellow. The solution was stirred cold for 0.5 hr, then at 25° for 1 hr. Glc analysis indicated complete consumption of isoprene dimer. Removal of the solvent gave a light tan crystalline solid which was recrystallized from hexane to give 8.81 g (79%) of colorless prisms of **13**: mp 81.5–82.5°; nmr ($CDCl_3$) δ 1.70–2.50 (m, 10 H, alkyl), 3.00 (br s, 3 H, singlet H adjacent to CN), 4.82–4.90 (m, 2 H, terminal vinyl), 5.56 (sl br s, 1 H, ring vinyl).

Anal. Calcd for $C_{16}H_{16}N_4$: C, 72.7; H, 6.10; N, 21.2. Found: C, 72.8; H, 6.08; N, 21.5.

Reaction of 1 with Acrolein (14). A solution of 33.3 ml (28 g, 0.5 mol) of freshly distilled acrolein and 68 g (0.5 mol) of isoprene dimer in 125 ml of glacial acetic acid was heated at reflux in a nitrogen atmosphere. After 30 min, glc showed that the starting materials had been consumed and that two new components were present in the ratio 1:1. Acetic acid was removed at reduced pressure, and the residue was fractionally distilled to give 68.7 g (75%) of the unsaturated aldehyde **14** as a 1:1 mixture of isomers: bp 80° (0.05 mm); 100-MHz nmr ($CDCl_3$) δ 1.50–2.70 (m, 16 H), 4.65 (s, 2 H, terminal vinyl), 5.39 and 5.45 (sl br s, ratio 1:1, total 1 H, ring vinyl of epimers), 9.63 and 9.67 (d, $J = 2$ Hz, ratio 1:1, total 1 H, aldehyde H).

Anal. Calcd for $C_{13}H_{20}O$: C, 81.2; H, 10.5. Found: C, 81.4; H, 10.2.

Reaction of 1 with Acrylic Acid (15). A solution of 71.4 g (0.525 mol) of **1** and 36 g (0.5 mol) of glacial acrylic acid in 100 ml of acetic acid was heated at reflux for 3 hr. The pale yellow solution was cooled and poured into a mixture of ice and water. The mixture was extracted twice with 150 ml of methylene chloride, and the extract was washed twice with water and dried over anhydrous sodium sulfate. After removal of the solvent, the residue was heated at 70° under vacuum (0.1 mm) for 1 hr to remove traces of acetic acid. The yield of clear, straw-colored carboxylic acid **15** was 87 g (84%): nmr ($CDCl_3$) δ 1.30–3.00 (m, 16 H, alkyl), 4.72 (s, 2 H, terminal vinyl), 5.25 and 5.65 (sl br s, ratio 1:2, total 1 H, ring vinyl of epimers) 11.8 (s, 1 H, CO_2H). The analytical sample distilled at 121° (0.25 mm).

Anal. Calcd for $C_{13}H_{20}O_2$: C, 75.0; H, 9.68. Found: C, 75.3; H, 9.68.

Reaction of 1 with Paraformaldehyde (16). A mixture of 33 g (1.1 mol) of paraformaldehyde, 136 g (1.0 mol) of isoprene dimer, and 250 ml of glacial acetic acid was heated at reflux for 1.5 hr. The clear, light yellow solution was cooled in ice water and poured into a mixture of 200 ml of water and 150 ml of ether. The aqueous layer was drawn off, and the organic layer was washed successively with three portions of 250 ml of water, once with 250 ml of saturated sodium bicarbonate solution, and once with 250 ml of water. After drying over magnesium sulfate and evaporation of the solvent, the residue was fractionally distilled at reduced pressure. After collection of 13.73 g (10%) of unconverted hydrocarbon, there was obtained 72.73 g (48.7%) of colorless, pleasant-smelling dihydropyran **16**: bp 96–100° (18 mm); nmr ($CDCl_3$) 1.20–2.50 (m, 12 H, alkyl), 3.20–4.15 (m, 3 H, ether α H), 4.67 (broad s, 2 H, terminal vinyl), 5.30 (br s, 1 H, internal vinyl).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.5; H, 10.9. Found: C, 79.6; H, 11.0.

Hydrogenation of 16 (17). A mixture of 8.3 g (0.05 mol) of the dihydropyran, 3.5 ml of methanol, and 0.1 g of 10% palladium on carbon was hydrogenated in a Parr hydrogenation apparatus until absorption of hydrogen was complete. Distillation at reduced pressure gave 4.22 g (51%) of material, bp 85–88° (18 mm), which was shown by glc to consist of 85% of 4.9-min and 15% of 6.0-min material. The nmr spectrum shows the absence of any olefinic protons and indicates that the products are probably cis and trans isomers of 2-isoamyl-4-methyltetrahydropyran (**17**), nmr ($CDCl_3$) δ 0.50–2.20 (m, 19 H, alkyl), 2.90–4.30 (m, 3 H, ether α H).

Anal. Calcd for $C_{11}H_{22}O$: C, 77.1; H, 12.9. Found: C, 76.9; H, 12.6.

Acid-Catalyzed Rearrangement of 16 (18). A solution of 8.3 g (0.05 mol) of **16** and 0.1 g of *p*-toluenesulfonic acid in 100 ml of benzene was heated at reflux for 18 hr. During this period the color of the solution became pale yellow and then quite dark, although glc (180°) showed no apparent change in the composition of the solution. An additional 0.1 g of *p*-toluenesulfonic acid was added, and reflux was continued for 7 hr.

The solution was cooled and washed with saturated sodium bicarbonate solution and water before drying over magnesium sulfate. Distillation of the product gave 5.78 g (70%) of material, bp 90–95° (18 mm). Glc analysis of the product showed that its retention time (7.2 min) was identical with that of starting material. However, analysis of the olefinic proton region of the nmr spectrum showed that the product consisted of 87.5% rearranged dihydropyran **18** and 12.5% **16**.

Anal. Found: C, 79.7; H, 10.6.

Reaction of 1 with Glyoxal (19). A mixture of 81.6 g (0.6 mol) of isoprene dimer and 43.5 g (0.6 mol) of glyoxal monohydrate in 300 ml of acetic acid was refluxed for 1.5 hr, cooled, and poured into a mixture of ice water and ether. The aqueous layer was removed, and the organic layer was washed successively with three portions of 250 ml of water, twice with 250 ml of saturated sodium bicarbonate solution, and once with 250 ml of water. After drying over magnesium sulfate and evaporation of the solvent, the residue was fractionally distilled at reduced pressure. After a foreshot (10.77 g, 13.5%) consisting chiefly of unconverted low-boiling [to 6° (0.7 mm)] hydrocarbon, the product was collected at 80–85° (0.15 mm). There was obtained 32.14 g (31.8%) of the aldehyde **19**.

Glc analysis showed that the product consisted of two components, probably cis-trans isomers, in the ratio 60:40 (retention times 11.9 and 13.8 min with a temperature program of 180-225°, 10°/min): nmr ($CDCl_3$) δ 1.50–2.50 (m, 12 H, alkyl), 3.80–4.50 (m, 2 H, ether α H), 4.73 (s, 2 H, terminal vinyl), 5.40 (br s, 1 H, ring vinyl), 9.68 (d, $J = 2$ Hz, 1 H, aldehyde H).

Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.2; H, 9.31. Found: C, 74.0; H, 9.65.

Sodium Borohydride Reduction of 19 (20). A solution of 4.05 g (0.11 mol) of sodium borohydride in 150 ml of absolute ethanol was stirred at 25–30° while 41.2 g (0.212 mol) of the aldehyde in 150 ml of absolute ethanol was added dropwise during 1.5 hr. Stirring was continued after the addition for 2 hr, and 10 ml of water was cautiously added. After 0.5 hr, the mixture was concentrated by vacuum distillation, and the residue was added to 250 ml of ether. The ether layer was extracted with three 75-ml portions of water and dried over magnesium sulfate. Removal of solvent and distillation under reduced pressure gave 30.53 g (73.2%) of slightly viscous carbinol, bp 70–80° (0.3 mm). Glc analysis (225°) showed the product to consist of two components with retention times of 13.7 (39%) and 16.8 min (61%). This composition reflects the isomer content of the starting aldehyde which contained two components at 12.3 (40%) and 14.0 min (60%). These are probably cis-trans isomers: nmr ($CDCl_3$) δ 1.30–2.32 (m, 12 H, alkyl), 3.59–3.98 (m, 5 H, $-OCH_2-$, $-OH$), 4.70 (s, 2 H, terminal vinyl), 5.34 (s, 1 H, internal vinyl).

Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.4; H, 10.3. Found: C, 73.6; H, 10.3.

Silver Oxide Oxidation of 19 (21). A solution of 35.4 g (0.207 mol) of silver nitrate in 70 ml of distilled water was added to a solution of 16.5 g (0.41 mol) of sodium hydroxide in 70 ml of distilled water. The dark silver oxide was stirred vigorously and chilled in an ice bath while 19.4 g (0.1 mol) of the aldehyde was added in portions during 25 min. The internal temperature was 20–23° throughout the addition. After 30 min, the mixture was filtered through Celite, and the clear, dark brown filtrate was acidified with 12 *N* hydrochloric acid, extracted twice with water, and dried over magnesium sulfate. Exhaustive evaporation of the solvent left a viscous, clear, light brown oil: 18.0 g (86%); nmr ($CDCl_3$) δ 1.75–2.50 (m, 12 H, alkyl), 4.00–4.60 (m, 2 H, ether α H), 4.70 (s, 2 H, terminal vinyl), 5.39 (br s, 1 H, ring vinyl), 11.15 (s, 1 H, CO_2H).

2,7-Dimethyl-2,4,6-octatriene (23) from Base-Catalyzed Rearrangement of 1. One liter of reagent grade dimethyl sulfoxide was deaerated with a stream of dry argon for 15 min. **1** (150 g, 1.1 mol) was added and followed with 5 ml of 0.94 *M* potassium *tert*-butoxide in dimethyl sulfoxide under argon. After 15–20 min at 50°, glc showed that a small amount of the conjugated triene was present but that most of **1** remained unchanged. The solution was cooled and 15 ml of the potassium *tert*-butoxide solution was added. The dark solution was stirred for 1 hr, during which glc monitoring showed a dramatic increase in conjugated triene. Five milliliters of water was added, and stirring was continued for an additional 1 hr. A short-path still was attached to the reaction vessel, and distillate was collected at 3–5 mm until the heat temperature was 70°. Water was added to the distillate and the hydrocarbon layer which separated crystallized on cooling in ice. The product was taken up in equal volume of petroleum ether (bp 30–60°), washed once with water, and dried over magnesium sulfate. Distillation at reduced pressure gave 105.4 g (70%) of pure 2,7-dimethyl-2,4,6-octatriene: bp 90–92° (25 mm); mp 30°; nmr ($CDCl_3$) δ 1.80 (br s, 12 H, CH_3), 4.50–5.50 (m, 4 H, vinyl), uv max (isooctane) 291 nm (ϵ 36,300), 279 (46,250), 269 (34,300); mass spectrum mol wt, 136 (calcd, 136).

Anal. Calcd for $C_{10}H_{16}$: C, 88.2; H, 11.9. Found: C, 88.3; H, 12.1.

A sample of **23** was readily hydrogenated to give as the sole product 2,7-dimethyloctane (**12**), with bp 44° (13 mm), in 77% yield.

1,6,6-Trimethyl-1,3-cycloheptadiene (26). A. From Base-Catalyzed Cyclization of 1. A solution of 0.25 lb of potassium *tert*-butoxide in 1 l. of dimethyl sulfoxide was deaerated with a stream of dry argon for 10 min. Isoprene dimer (136 g, 1 mol) was added in one portion under an argon atmosphere. Glc analysis indicated that the dimer was completely consumed in minutes. The dark blue-green solution was heated at 70–75° with stirring for 30 min. A modified Claisen stillhead was then attached, and the pressure was reduced to 6–8 mm with an aspirator. The temperature of the mixture was maintained at 75–80°, and distillate was collected until the head temperature was 70°. Argon was introduced into the system, the stillhead was removed, and water was added to the distillate. The upper hydrocarbon layer was removed and shown by glc to be pure 1,6,6-trimethyl-1,3-cycloheptadiene. The yield was 126 g (93%). A second charge of 68 g of isoprene dimer was added to the distillate residue, and the above process was repeated. A third charge of 36 g of isoprene dimer was treated similarly. Distillation of the product from a total of 240 g (1.76 mol) of isoprene dimer gave 200.5 g (83.5%) of 1,6,6-trimethyl-1,3-cycloheptadiene: bp 64–66° (25 mm); nmr ($CDCl_3$) δ 1.98 (s, 6 H, gem-CH_3), 1.81 (s, 3 H, C-1 CH_3), 2.00 (s, 4 H, $-CH_2-$), 3.68 (br s, 3 H, vinyl); uv max (isooctane) 251 nm (ϵ 7630); mass spectrum mol wt 136 (calcd, 136).

Anal. Calcd for $C_{10}H_{16}$: C, 88.2; H, 11.8. Found: C, 88.3; H, 11.2.

B. From 23 by Reaction with Potassium *tert* Butoxide. A solution of 5 g of **23** in 25 ml of 0.94 *M* potassium *tert*-butoxide in DMSO was stirred at 60° for 30 min. Glc showed the complete disappearance of **23** and the appearance of **26** at the sole detectable product. After the usual work-up, 1.51 g (30%) of **26** was obtained.

C. From 23 by Reaction with Sodium. A small piece (*ca.* 0.01 g) of clean, dry sodium metal was added to a solution of 13.6 g (0.1 mol) of 2,7-dimethyl-2,4,6-octatriene in 100 ml of dry ethylene glycol dimethyl ether, and the solution was heated to reflux under an argon atmosphere. The sodium dissolved slowly (*ca.* 4 hr) to produce a pale yellow solution. Examination of the mixture by glc showed no cyclization product. Evidently adventitious moisture or oxygen caused consumption of sodium in unprofitable side reactions. A second 0.01-g sample of sodium was added, and refluxing was continued for 11 hr. At this point the solution was deep red in color, and glc showed cyclized product in addition to unconverted starting material in the ratio of 2.3:1.0. A third 0.01-g sample of sodium was added, and refluxing was continued for 24 hr. Isopropyl alcohol (2 ml) was added to decompose metal compounds. The solvent was removed by distillation, and the product was collected at 44–45° (7 mm). There was obtained 10 g (74.5%) of **26**.

D. From 23 by Reaction with *n*-Butyllithium–TMEDA Complex. Freshly distilled *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) (6.75 g, 0.058 mol) was added to 36.3 ml (0.059 mol) of a 1.6 *M* hexane solution of *n*-butyllithium under argon with water-bath cooling. The complex is ready for further reaction when the addition is complete. A solution of 7.9 g (0.058 mol) of 2,7-dimethyl-2,4,6-octatriene in 20 ml of cyclohexane was added dropwise during 1 hr. The initial pale yellow color changed during the addition to a clear, dark red. The solution was stirred at 25° for 3.25 hr, when analysis of an aliquot by glc showed that the starting triene had disappeared. After hydrolysis with 5 ml of D_2O, the organic layer was separated. After TMEDA was removed by washing with 1 *N* HCl solution, the organic layer was washed with saturated sodium bicarbonate solution and dried over magnesium sulfate. The solvent was removed and the residual oil was distilled at reduced pressure to give fractions totaling 5.90 g (74.5%) of isomeric monodeuterated trimethylcycloheptadienes, bp 64–65° (25 mm). The product consisted principally of 1,6,6-trimethyl-1,3-cycloheptadiene-*5-d* (**27**), which was identified by its nmr spectrum. In addition, the product contained 10–12% of another isomer identified by nmr as 1,6,6-trimethyl-1,4-cycloheptadiene-*3-d* (**28**), nmr ($CDCl_3$) δ 2.18 (s, C_3 H), 5.25 (s, unconjugated vinyl.

Reaction of 26 with TCNE (29). A solution of 2.56 g (0.02 mol) of TCNE in 25 ml of anhydrous tetrahydrofuran was stirred at 25°, and 2.72 g (0.02 mol) of **26** was added in one portion. A deep red color was formed and faded only very slowly over a period of 2 days. The pale tan solution was evaporated to give 5.05 g (95.5%) of light brown, crystalline solid, mp 133–134°. Recrystallization of an analytical sample from ethanol gave thick, colorless prisms of **29**: mp 145°; nmr ($CDCl_3$) δ 1.05, 1.11 (s, 3 H each, gem-CH_3), 1.60–2.50 (m, 4 H, ring CH_2), 1.68 (s, 3 H, bridgehead CH_3), 3.50 (m, 1 H, bridgehead H), 6.00–6.60 (m, 2 H, vinyl H).

Anal. Calcd for $C_{16}H_{16}N_4$: C, 72.7; H, 6.10; N, 21.2. Found: C, 72.9; H, 6.00; N, 21.5.

Reaction of 1 with *n*-Butyllithium–TMEDA Complex (30). A solution of 79 g (0.58 mol) of **1** in 150 ml of dry cyclohexane was added under argon during 2.25 hr to *n*-butyllithium–TMEDA complex prepared from 67.5 g (0.58 mol) of freshly distilled TMEDA and 363 ml (0.58 mol) of 1.6 *M* *n*-butyllithium in hexane. The mixture was initially orange in color, then in the later stages of the addition, bright red. After an additional 1 hr, a sample of the mixture was hydrolyzed and examined by glc (173°). In addition to small amounts of starting material, a large, highly symmetrical new peak at 5.8 min was observed. Smaller peaks appeared at 5.0, 7.4, and 8.1 min. The mixture was stirred for 16 hr and hydrolyzed with H_2O. The organic layer was washed with 1 *N* HCl solution to remove TMEDA, then with saturated sodium bicarbonate solution, and dried over magnesium sulfate. Removal of the solvent left a clear, pale straw liquid shown by glc to consist of 75% 5.8-min material, 12% 7.4- and 8.1-min material, and 13% recovered starting material, 2.0–2.7 min.

Distillation at reduced pressure gave 55.32 g (49.4%) of material: bp 105–115° (25 mm) with major portion boiling at 114–115°; nmr ($CDCl_3$) δ 0.60–2.20 (m, 24 H, alkyl), 4.69 (m, 1 H, terminal vinyl), 4.91 (m, 1 H, terminal vinyl). The 220-MHz spectrum included the following features: δ 175 (s, 3 H, gem-CH_3), 218 (s, 3 H, gem-CH_3), 190 (t, J = 7 Hz, 3 H, CH_3 of *n*-butyl), 372 (s, 3 H, $CH_3C{=}C$), 369 Hz (d, J = 7 Hz, 1 H, allylic H on ring); mass spectrum mol wt 194 (calcd for $C_{14}H_{26}$, 194). The relatively intense (11.3%) molecular ion peak suggests a cyclic structure.

Anal. Calcd for $C_{14}H_{26}$: C, 86.5; H, 13.5. Found: C, 86.2; H, 13.2.

Addition of **1** at −25 to −30° raises the yield of **30** to 57.2%. From the light-colored distillation residue, there could be isolated 6 g of material, bp 60° (0.2 mm), glc retention time (173°) 8.2 min. The mass spectrum of this fraction gave molecular ions at *m/e* 192 and 194, and the fragmentation pattern suggested a branched, acyclic hydrocarbon whose structure has not been determined.

Reaction of Paraformaldehyde with the Adduct of 1 and *n*-Butyllithium (32). A solution of 39.5 g (0.29 mol) in 75 ml of dry cyclohexane was added during 1 hr to a solution of 0.29 mol of *n*-butyllithium–TMEDA complex at −250°. After an additional 15 min at this temperature, the mixture was warmed in an ice water bath for 1 hr. Solid paraformaldehyde, 11 g (0.37 mol), was added to the bright red suspension during 20 min at 0°, and stirring was continued for 0.5 hr. The ice bath was removed, and the mixture was allowed to warm slowly. As the temperature neared 20°, an exothermic reaction occurred, and the mixture became a pale yellow, clear solution. After 30 min, 30 ml of water was added, and after brief stirring, the organic layer was transferred to a separatory funnel, washed several times with water, and dried over magnesium sulfate. After removal of solvent and distillation of the residue, there was obtained 34 g (52%) of the colorless, slightly viscous alcohol, **32**, bp 98° (0.3 mm). Gc analysis with temperature programming (180–225°, 10°/min) showed the presence of two components in the proportion of 42.2 (18.3 min) and 57.8% (20.8 min), which are probably geometrical isomers differing in the conformation of the hydroxyl-bearing side chain.

32 had nmr ($CDCl_3$) δ 0.70–2.50 (n, 23 H, alkyl), 3.25 (s, 1 H, OH, disappears with D_2O), 3.72 (t, J = 7 Hz, 2 H, $-OCH_2-$), 4.85 (s, 1 H, vinyl), 4.99 (s, 1 H, vinyl).

Anal. Calcd for $C_{15}H_{28}O$: C, 80.3; H, 12.6. Found: C, 80.3; H, 12.2.

2-Methyl-2,4,6-octatriene (33) from Base-Catalyzed Rearrangement of 6 and 7. A solution of 20 g (0.164 mol) of butadiene–isoprene codimer in 300 ml of dimethyl sulfoxide was stirred at 25° under a nitrogen atmosphere, and 5 ml of a solution of 0.3 g of potassium *tert*-butoxide in 25 ml of dimethyl sulfoxide was added. The mixture became dark green. After 15 min, glc analysis showed the codimer to be virtually gone, and three new materials were seen with retention times of 2.1 and 2.5 (**34** and **35**, respectively, total 25 area %) and 3.4 min (**33**, 75 area %). An additional 5 ml of potassium *tert*-butoxide solution was added. The color of the solution was now deep blue. After 15 min, glc showed an increase in 2.1-min material (33 area %), no change in 2.5-min material (7 area %), and a decrease in 3.4-min material (60 area %). Water (50 ml) was added to quench the reaction, a short distillation column was attached to the flask, and distillate was collected in a chilled receiver (−78°) until the stillhead temperature was 60° (9 mm). Water was added to the distillate, and the hydrocarbon layer was taken up in 60–75 ml of petroleum ether. **33** is easily air oxidized, and the work-up was conducted under a nitrogen atmosphere. After drying and removal of the petroleum ether, the crude product was fractionally distilled. The yield of **33, 34,** and **35,** expressed as per cent of total product, was 60, 37, and 3%, respectively. The net yield of **33** was 49%. A fraction with bp 76° (23 mm) was selected for analysis: nmr ($CDCl_3$) δ 1.72 (s, br, 9 H, $C{=}CCH_3$), 5.20–6.80 (m, 5 H, vinyl); uv max (isooctane) 228 nm (ϵ 37,200), 271 (46,800), 262 (35,600).

Anal. Calcd for C_9H_{14}: C, 88.5; H, 11.5. Found: C, 88.9; H, 11.3.

Cyclization of 6 and 7 with Stoichiometric Potassium *tert*-Butoxide–DMSO. Potassium *tert*-butoxide (300 ml, 0.94 *M*) in dimethyl sulfoxide (0.28 mol) was stirred at 25° under an argon atmosphere, and 25% (0.205 mol) of a 2:1 mixture of 7- and 2-methyl-1,3,7-octatrienes was added in one portion. The reaction was slightly exothermic (35–40°), and a very deep magenta color was produced. After 12 hr, glc analysis (182°) showed three components at 2.0 (60 area %), 2.4 (32 area %), and 3.2 min (8 area %) which are, respectively, **34, 35,** and **33.** The deep bluish-purple mixture was poured into water and extracted twice with 150-ml portions of petroleum ether. The hydrocarbon layer was washed several times with water and dried over magnesium sulfate. Evaporation of the solvent and distillation of the residue gave 20.83 g (83.5%) of C_9 hydrocarbons.

A fraction with bp 60° (35 mm), 7.49 g, was pure **34:** nmr ($CDCl_3$) δ 0.95 (s, 3 H, gem-CH_3), 1.02 (s, 3 H, gem-CH_3), 1.40–D.50 (m, 4 H, allylic H), 5.40–6.00 (m, 4 H, vinyl); uv max (isooctane) 248 nm (ϵ 8380), 241 (7960).

Anal. Calcd for C_9H_{14}: C, 88.5; H, 11.5. Found: C, 88.8; H, 11.8.

Reaction of 2.44 g (0.02 mol) of **34** with 2.56 g (0.02 mol) of TCNE in dry THF produced a deep red solution. After 16 hr removal of solvent and recrystallization of the adduct from hexane–benzene gave 3.56 g (71%) of **36** as colorless needles: mp 181°; nmr ($CDCl_3$) δ 1.90–2.50 (m, 4 H, ring CH_2), 3.40–3.60 (m, 2 H, bridgehead H), 6.52 (center of AB q, 2 H, vinyl).

Anal. Calcd for $C_{15}H_{14}N_4$: C, 72.0; H, 5.63; N, 22.4. Found: C, 72.0; H, 5.68; N, 22.6.

A fraction with bp 72° (35 mm), 1.06 g, was shown by glc to be **35** of greater than 94% purity: nmr ($CDCl_3$) δ 0.97 (s, 2 H, nonallylic ring CH_2), 1.50–2.50 (m, 10 H, allylic H), 5.30–5.80 (m, 2 H, vinyl); uv max (isooctane) 248 nm (ϵ 7550).

Reaction of 2.44 g (0.02 mol) of **35** with TCNE as described above gave 1.77 g (35%) of pale yellow prisms, mp 180–181°. A sample crystallized twice from ethanol had mp 196°; nmr ($CDCl_3$) δ 1.70–2.20 (m, 9 H, $C{=}CCH_3$, ring CH_2), 3.21 (t, J = 4 Hz, 1 H, bridgehead H), 5.73 (q, J = 1.5 Hz, 1 H, vinyl).

Anal. Calcd for $C_{15}H_{14}N_4$: C, 72.0; H, 5.63; N, 22.4. Found: C, 71.6; H, 5.72; N, 22.4.

Registry No. 1, 36638-38-7; **6,** 36638-61-6; **7,** 36638-62-7; **8,** 36638-39-8; **9** (2-ethyl-7-methyl isomer), 36663-08-8; **9** (2-methyl-7-ethyl isomer), 36638-42-3; **10,** 36638-41-2; **11,** 42915-58-2; **12,** 1072-16-8; **13,** 42915-59-3; *cis*-**14,** 42915-60-6; *trans*-**14,** 42915-61-7; **15,** 42915-62-8; **16,** 42915-63-9; *cis*-**17,** 42915-64-0; *trans*-**17,** 42915-65-1; **18,** 42915-66-2; *cis*-**19,** 42915-67-3; *trans*-**19,** 42915-68-4; *cis*-**20,** 42915-69-5; *trans*-**20,** 42915-70-8; **21,** 42915-71-9; **23,** 38086-92-9; **26,** 42915-72-0; **29,** 42915-73-1; **30,** 42915-74-2; **32,** 42915-75-3; **33,** 42915-76-4; **34,** 25866-61-9; **35,** 40391-65-9; **36,** 42915-79-7; **37,** 42915-80-0; isoprene, 78-79-5; 1,3-butadiene, 106-99-0; 2-ethyl-1,3-butadiene, 3404-63-5; 2,3-dimethyl-1,3-butadiene, 513-81-5; TCNE, 670-54-2; acrolein, 107-02-8; acrylic acid, 79-10-7; paraformaldehyde, 30525-89-4; glyoxal, 107-22-2.

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