Stepwise Cycloadditions of Pentadienyllithiums to 1,3-Dienes

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Solutions of pentadienyllithium and either furan or toluene in tetrahydrofuran produce cyclic dimers of pentadiene both in the presence and in the absence of added 1,3-pentadiene. A stepwise mechanism is proposed for the dimerization in which the furan and toluene act as proton donors to pentadienyllithium and to 1:1 adducts of pentadienyllithium and 1,3-pentadiene. Reactions of other pentadienyllithiums and 1,3-dienes under similar conditions provide a simple, low-yield route to crossed diene dimers.

Previously we[1] reported that tetrahydrofuran (THF) solutions of pentadienyllithium (**1**) and either furan or toluene produced cyclic pentadiene dimers with and without added 1,3-pentadiene. This paper describes the pentadiene dimerizations in detail and also the formation of similar 1:1 adducts from other pentadienyllithiums and 1,3-dienes.

Results

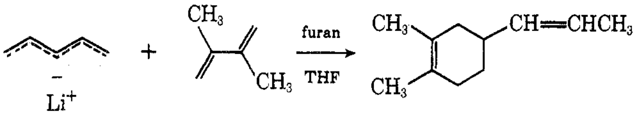
An initially equimolar THF solution of furan and pentadienyllithium (**1**), generated from 1,4-pentadiene and *n*-butyllithium, after 18 hr at 25° contained no **1** by pmr. Addition of excess D_2O to the solution followed by distillation produced furan-2-*d* in 37% yield, and two fractions less volatile than THF in 24 and 10% yields based on 1,4-pentadiene. Glpc analysis showed that the two fractions contained at least four and ten components, respectively. The lower boiling (24%) fraction was separated by preparative glpc into two components which were identified as 3-methyl-5-propenyl- and 3-methyl-4-propenylcyclohexene (**6** and **7**) by elemental analyses and comparison of their glpc retention times, mass spectra, and pmr spectra with those of the thermal dimers of 1,3-pentadiene.[2] Hydrogenation of the lower boiling distillation fraction at 1 atm over Pt produces a mixture of *cis*- and *trans*-1-methyl-3-propylcyclohexane (**8** and **9**) and *trans*- and *cis*-1-methyl-2-propylcyclohexane (**10** and **11**). The components of this saturated hydrocarbon mixture were identified by comparison of their glpc retention times, mass spectra, and pmr spectra with those of independently synthesized **8–11**. In addition to isomers **8–11** a small amount of *n*-decane was detected in the hydrogenated mixture by glpc. Isomers **9** and **10** could not be separated by the glpc conditions employed.

The higher boiling (10%) fraction obtained from reaction of **1** and furan contained two major components which were isolated by preparative glpc and identified as trimers of 1,3-pentadiene by elemental analyses, mass spectra, and pmr spectra. Hydrogenation of the higher boiling fraction over Pt at 1 atm produced a mixture with three major components which were identified as $C_{15}H_{30}$ isomers by mass spectrometry and as saturated hydrocarbons by pmr. Therefore the higher boiling fraction from reaction of **1** and furan consisted of pentadiene trimers containing one ring.

When a solution of **1** and toluene in THF was allowed to react for 48 hr at 70°, hydrolyzed, and analyzed by glpc, not only pentadiene dimers and trimers, but also isomeric phenylhexenes **12–15** were formed. Relative yields under varied conditions follow: **12** (41–68%), **13** (4–7%), **14** (13–28%), and **15** (13–28%). Compounds **12**, **14**, and **15** were isolated by preparative glpc and identified by their mass spectra (M^+ at m/e 160) and their pmr spectra shown in Table I. The two allylic methyl doublets in the pmr spectrum of **12** suggest that it is a mixture of cis and trans isomers. Compounds **14** and **15** could also be mixtures of cis and trans isomers. The structure of **13** is presumed to be isomeric to those of **12**, **14**, and **15** because of its similar glpc retention time.

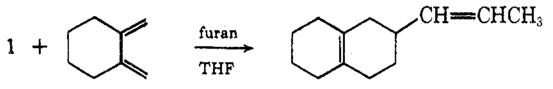
The pentadiene dimers obtained from reaction of **1** and toluene were hydrogenated and then analyzed by glpc. Reactions of **1** and toluene with three different mixtures of *cis*- and *trans*-1,3-pentadiene also were studied. Externally added 1,3-pentadiene caused lower yields (based on **1**) of pentadiene dimers and resulted in somewhat different relative yields of **8–11** after hydrogenation. Results of typical experiments appear in ref 1.

When 2,3-dimethyl-1,3-butadiene (**16**) was added slowly to a mixture of **1** and furan in THF at 25°, a mixture of isomeric crossed dimers (**17**) of pentadiene and **16** was isolated by preparative glpc. The yield of **17** depended on reactant and furan concentrations and addition and reaction times as shown in Table II. Structural assignment of mixture **17** is based on mass, pmr, and ir spectra and elemental analysis.



1 **16** **17**

Similarly, addition of 1,2-dimethylenecyclohexane (**18**) to **1** and furan at 25° gave a 6% yield of crossed adduct **19** (presumably a mixture of isomers). The structural assignment of **19** is based on its pmr and mass spectra and elemental analysis.

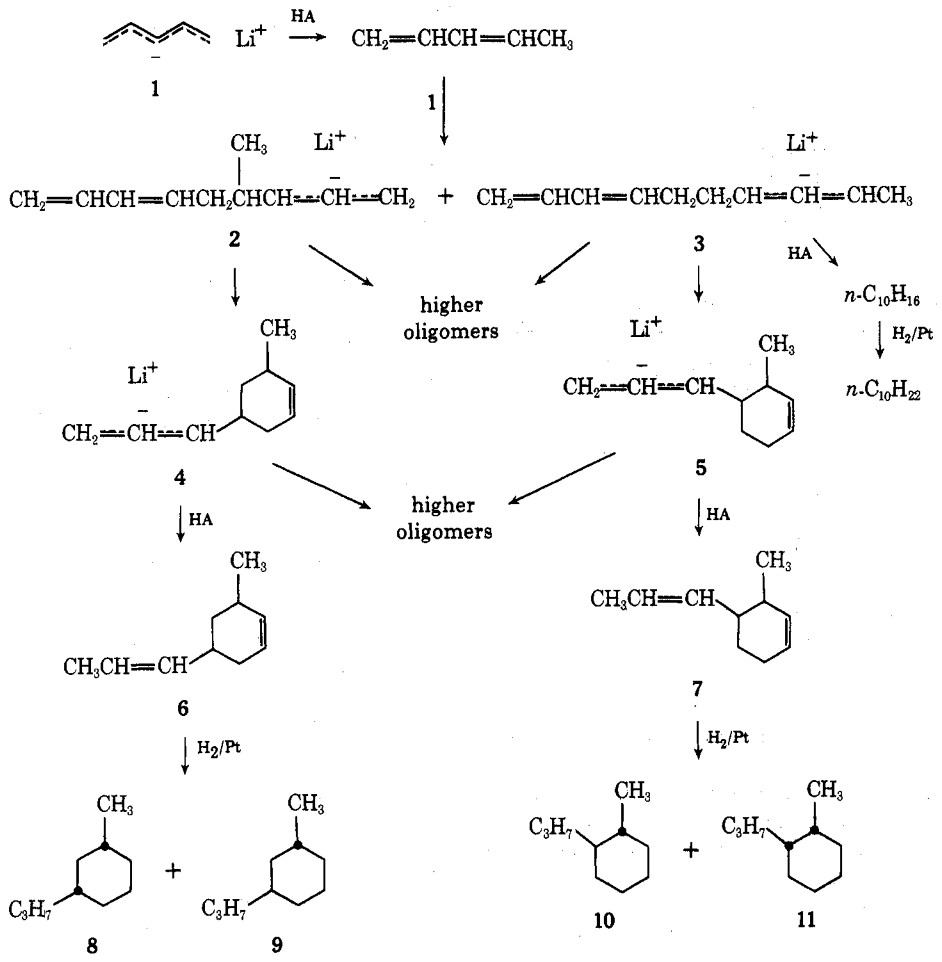


18 **19**

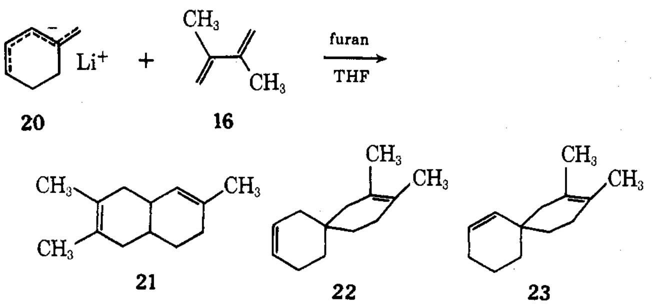
Both 1,3-butadiene and 1,3-cyclohexadiene gave small yields of possible 1:1 adducts with pentadiene when treated with **1** and furan in THF, but the products were not analyzed. 2,5-Dimethyl-2,4-hexadiene and **1** did not appear to react under conditions which produced adducts with other dienes. 4-Methyl-1,3-pentadiene formed only products of higher molecular weight under conditions which produced 1:1 adducts from **1** and **16**.

Additions of two substituted pentadienyllithiums to 1,3-dienes were explored. Solutions of **20** (generated from 4-methylenecyclohexene and *n*-butyllithium), **16**, and furan in THF at 25° produced mixtures of 1:1 adducts. Two fractions, formed in 1–3 and 8–9% yields under varied conditions, were separated by preparative glpc. The second fraction was shown to contain at least two components by analysis on a different glpc column. By glpc–mass spectrometry the first fraction and both components

Scheme I
Mechanism of Anionic Dimerization of 1,3-Pentadiene



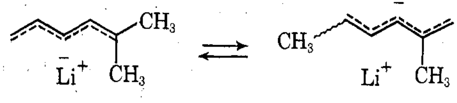
of the second fraction had molecular ions at m/e 176, which fits $C_{13}H_{20}$ isomers. Hydrogenations of the crude product mixture over Pt at 1 atm and 25° and over Raney nickel at 100 atm and 150° both gave three saturated compounds which were separated by preparative glpc and analyzed by mass spectrometry. One had M^+ at m/e 182 ($C_{13}H_{26}$), corresponding to an alkylated cyclohexane. The other two saturated compounds, formed in nearly equal amounts, both had M^+ at m/e 180 ($C_{13}H_{24}$), corresponding to two rings. Independent hydrogenation of the second (8–9%) fraction of the original reaction mixture gave the two m/e 180 compounds. From our proposed mechanism for pentadiene dimerization (Scheme I) and these mass spectral results, we tentatively assign structures 21–23 to



the major components of the original reaction mixture. A pmr spectrum of the 8–9% fraction had a 1.5:18.5 ratio of olefinic to aliphatic protons, which might correspond to approximately a 1:1 mixture of 21 and either 22 or 23.

Solutions of **20**, furan, and 1,3-butadiene in THF at 25° formed 1:1 hydrocarbon adducts in up to 13% yield. At least seven compounds were present in the product mixture, all of which had mass spectra with M^+ at m/e 148. Hydrogenation of the mixture over Pt at 1 atm produced a mixture containing at least six compounds, of which the four major ones had M^+ at m/e 154 ($C_{11}H_{22}$, one ring) and the two minor ones had M^+ at m/e 152 ($C_{11}H_{20}$, two rings). No further analysis of this mixture was attempted.

Treatment of 5-methyl-1,4-hexadiene with n-butyllithium in THF produces 1,1-dimethylpentadienyllithium (24).[3] Although 24 isomerizes to approximately at 1:1 mixture of 24 and 25 rapidly at 50°, it can be held for hours at 0° in THF with little conversion to 25.[3]



24 25

A solution of 24, furan, and 1,3-butadiene in THF at 0° for 12 hr (≤12% of 24 could have isomerized) produced at least two 1:1 adducts, both in ca. 2% yield, and at least three 1:2 adducts of 24 and butadiene in 14% total yield. The adduct mixtures had mass spectra with M^+ at m/e 150 and 204, respectively, but no further attempts were made to characterize them.

Discussion

Four methods now are available for dimerization of 1,3-pentadiene. Photolysis[4] and Ni catalysis[5] produce mainly divinylcyclobutanes and 1,5-cyclooctadienes.

Table I
Pmr Spectra of Phenylhexenes[a]

	Chemical shift, δ					
	a	b	c	d	e	f
$C_6H_5CH_2^{a}\overset{CH_3^{c}}{CH^{b}}CH^{d}{=}CH^{e}CH_3^{f}$ (**12**)	2.6 (m)	2.6 (m)	0.9 (d, J = 6 Hz)	——5.3 (m)——		1.5 (two doublets)
$C_6H_5CH_2^{a}CH_2^{b}CH^{c}{=}CH^{d}CH_2^{e}CH_3^{f}$ (**14**)	2.6 (m)	1.8–2.5 (m)	——5.4 (m)——		1.8–2.5 (m)	0.9 (m)
$C_6H_5CH_2^{a}CH_2^{b}CH_2^{c}CH^{d}{=}CH^{e}CH_3^{f}$ (**15**)	2.6 (t)	——1.6–2.0 (m)——		——5.4 (m)——		1.6–2.0 (m)

[a] Spectra were obtained with dilute CCl_4 solutions. Integrated areas of signals support the assignments.

Table II
Products from Reaction of Pentadienyllithium (1) and 2,3-Dimethyl-1,3-butadiene (16) in THF at 25°

Concn			Addn	Reaction	Yield,[a] %	
1, M	**16**, M	furan, M	time, hr	time, hr	**17**	**6 + 7**
0.35	0.71		0.8	5	3.5	0
0.29	0.60	0.60	0.3	0.9	9.4	0
0.22	0.88	0.88	1.0	4.8	14.3	0
0.22	0.88	0.88	0.3	4	9	0
0.19	0.19	1.9	0.8	9	5.7	2.9
0.19	0.38	1.9	0.7	9	10.3	2.2
0.20	0.80	2.0	0.8	17	13	*b*

[a] Yields based on **1** were determined by comparison of glpc peak areas to an internal standard, dodecane. [b] No yield was determined.

Thermolysis produces 50–90% 3-methyl-4-propenylcyclohexenes (**7**),[2] while our anionic route produces more **6** than **7**.

The mechanism in Scheme I explains production of pentadiene dimers from pentadienyllithium and furan or toluene in THF. (Some isomeric denotations have been omitted for brevity). Our mechanism for additions of pentadienyllithiums to 1,3-dienes is based on the Ziegler[6] mechanism for initiation and propagation of anionic diene polymerization. Formations of other simple 1:1 adducts and small oligomers from strong nucleophiles and 1,3-dienes proceed by similar mechanisms. Allyllithiums have been prepared by addition of alkyllithiums to 1,3-dienes and examined by pmr spectroscopy.[7] 1-(*N,N*-Dialkylamino)-2-butenes have been prepared from alkyllithiums, dialkylamines, and 1,3-dienes.[8] Phenylhexenes similar to the ones we isolated from **1** and toluene have been prepared from toluene and isoprene with an organosodium initiator.[9] Polymerization of 1,3,6,8-nonatetraene with a coordination-type catalyst gives a polymer with repeating 5-propenyl-$\Delta^{1,2}$-cyclohexen-3-yl units[10] by a cyclization analogous to formation of our **6**.

In Scheme I the carbon acid HA participates in the reaction in two ways, donation of a proton to **1** to produce 1,3-pentadiene and donation of a proton to the anionic dimers **3**, **4**, and **5** to produce **6**, **7**, and decatrienes. In principle cycloaddition of **1** and 1,3-pentadiene could be concerted, but the presence of *n*-decane in the hydrogenated dimers indicates strongly that the cyclic dimers arise *via* closure of the decatrienyl anions **2** and **3**.

The difference in reaction temperatures required for furan and toluene to promote pentadiene dimerization shows that toluene is a weaker acid kinetically than furan. This conclusion also is supported by an experiment in which an equimolar mixture of **1** and toluene in THF still showed some **1** in its pmr spectrum after 10 days at 25°.

Production of all possible isomers **8–11** in the cyclodimerized mixture after hydrogenation and production of phenylhexene isomers **12–15** indicate that there is no strong preference for addition of either pentadienyllithium or benzyllithium to either the 1 or the 4 position of 1,3-pentadiene.[11]

The dependence of diene dimer yields on carbon acid concentration is best illustrated by comparison of the first and third lines of data in Table II. In the absence of furan less dimer and more higher oligomers are formed. The last three lines of Table II show that more efficient use of the pentadienyllithium in cycloaddition is attained when the diene is used in excess.

The yields of our 1,3-diene dimerizations are low. In brief experiments aimed at finding another carbon acid to improve the yields, we tried diphenylmethane in place of furan and obtained even less **17** from **1** and **16**. Inclusion of hexamethylphosphoramide in the reaction mixture did not help either. The utility of our method appears to be limited to single-step preparation of cyclohexenes not readily available by other routes. Formations of an octahydronaphthalene from **1** and **18** and a spiro[5.5]undecadiene from **20** and **16** are illustrations of its potential.

Experimental Section

General. All temperatures are uncorrected. Pmr spectra were run on Varian A-60A, A-56/60, or T-60 spectrometers. Mass spectra were run on a Varian-MAT CH-5 mass spectrometer. Glpc-mass spectra were run on a Varian-MAT CH-7 or GNOM-111 mass spectrometer and a Varian 2700 series chromatograph. Ir and uv spectra were run on Perkin-Elmer Models 521, 237B, and 202 spectrophotometers. Analytical glpc was run on a Hewlett-Packard Model 700 chromatograph with thermal conductivity detection, and preparative glpc was run on a Varian Model A-90-P chromatograph. Glpc yields were not corrected with thermal conductivity response factors, but these corrections should be slight for isomeric compounds. All reactions with organometallic compounds were run under nitrogen or argon in dry glassware. THF was distilled from sodium naphthalenide or CaH_2. Furan was distilled from CaH_2. Toluene was distilled and stored over sodium wire.

Glpc columns were as follows: A, 0.125 in. × 10 ft, 20% Apiezon L on 60/80 Chromosorb P; B, 0.25 in. × 10 ft, 20% Apiezon L on 60/80 Chromosorb W; C, 0.125 in. × 4 ft, 20% Apiezon L on 60/80 Chromosorb W; D, 0.25 in. × 6 ft, 30% of a solution of 26% $AgNO_3$ in ethylene glycol on 60/80 firebrick; E, 0.375 in. × 10 ft, 20% Carbowax 20M on 60/80 Chromosorb W; (F) 0.125 in. × 21 ft, 10% DEGS on 60/80 Chromosorb W; and (G) 0.25 in. × 6 ft, 20% Apiezon L on 60–80 Chromosorb W.

Dienes. 1,3-Butadiene (Matheson) and 5-methyl-1,4-hexadiene (Chemical Samples) were used without further purification. 1,4-Pentadiene[12] was >96% pure by glpc (C, 45°), bp 24–26.5° (lit.[12] bp 26–27.5°). 4-Methyl-1,3-pentadiene[13] was isolated 99% pure by preparative glpc (E, 85°). 2,3-Dimethyl-1,3-butadiene (**16**)[14] was pure by pmr. 1,2-Dimethylenecyclohexane (**18**)[15] was purified by preparative glpc (E, 105°). A commercial mixture of 1,3-pentadienes (Aldrich) was distilled from CaH_2 and contained by glpc (D, 23°) 26% *trans*- and 61% *cis*-1,3-pentadiene and 13% cyclopentene. *cis*-1,3-Pentadiene[16] contained 81% *cis*-1,3-pentadiene and 19% cyclopentene by glpc (D), and *trans*-1,3-pentadiene[16] contained 75% *trans*- and 13% *cis*-1,3-pentadiene and 12% cyclopentene by glpc (D). 4-Methylenecyclohexene was synthesized by a method similar to that of Gosselink.[17]

Reactions of Pentadienyllithiums with Dienes. General. Solutions of pentadienyllithiums **1**, **20**, and **24** were generated by treatment of appropriate 1,4-dienes with *n*-butyllithium in THF[18] and aged for 8–16 hr to destroy excess *n*-BuLi.[19] A solution of the 1,3-diene, furan or toluene, and glpc standard (if employed) in THF was added with stirring. After varying periods, the reaction was terminated by addition of water. Products were dissolved in ether, washed with water and saturated aqueous NaCl solution, dried, and either distilled or freed of ether and analyzed by glpc.

Reaction of 1 with Furan. To a solution of 0.147 mol of 1 (from 10.0 g 1,4-pentadiene) in THF was added 10.1 g (0.149 mol) of furan at 25°. Disappearance of 1 was followed by pmr of a small sample. After 18 hr, 1 could not be detected, and excess furan was distilled. A sample removed from the reaction flask showed the pmr spectrum of 2-lithiofuran: δ 7.8 (d, 1 H), 6.3 (d, 1 H), 6.1 (d of d, 1 H, J_{34} = 3.0, J_{45} = 1.5 Hz). The reaction mixture was quenched with excess D_2O and distilled to yield 3.7 g (37% by glpc, F, 50°) of furan-*2-d* in a mixture with hydrocarbons and THF. Pmr of the distillate (CCl_4) showed 1.0 atom D at the 2 position. After hydrolysis and extraction with ether, distillation of the products gave fractions of 2.40 [24%, bp 55–75° (28 Torr)] and 1.05 g [10%, bp 63–83° (0.1 Torr)]. An oily residue and solid (6.1 g, 61%) did not distil. The lower boiling fraction contained at least four compounds by glpc (A, 136°), and had the following spectral properties: uv (hexane) end absorption at 205 nm (ϵ 1400); mass spectrum (70 eV) *m/e* 136 (M^+); pmr ($CDCl_3$) δ 5.0–5.8 (m, 4 H), 0.8–2.8 (m, 12 H). A mixture of the major components of the lower boiling fraction (6 and 7) was purified by preparative glpc (B, 165°).

Anal. Calcd for $C_{10}H_{16}$: C, 88.16; H, 11.84. Found: C, 88.12; H, 11.68.

The higher boiling fraction contained at least ten compounds by glpc (B, 247°). The two major components were isolated by preparative glpc (B, 247°). They had similar spectral properties: mass spectrum (70 eV) *m/e* 204 (M^+); pmr (CCl_4) δ 4.8–6.2 (6 H), 0.9–3.0 (18 H).

Anal. (a mixture of two major components). Calcd for $C_{15}H_{24}$: C, 88.16; H, 11.84. Found: C, 88.04; H, 11.74.

Hydrogenation of the higher boiling fraction by the method used for 6 and 7 produced a mixture containing three major components, separated by preparative glpc (B, 250°). The mass spectrum (18 eV) for each showed M^+ at *m/e* 210.

Hydrogenation of 6 and 7. A 0.5-g sample of the lower boiling fraction obtained from reaction of 1 with furan was hydrogenated in 10 ml of ethanol at 1 atm for 12 hr over Pt generated from chloroplatinic acid.[20] In the product mixture four components were resolved by glpc (A, 136°, relative areas 4:40:46:10). The three major components were isolated by preparative glpc (B, 165°) and shown to be **8**, a mixture of **9** and **10**, and **11**, respectively, by identity of their glpc retention times and mass and pmr spectra with those of authentic samples. The first (4%) component was shown to be *n*-decane by comparison of its glpc (A) retention time with that of an authentic sample. In an independent experiment **11** isomerized ($\leq$3%) to the more stable **10** under the above hydrogenation conditions.

***trans*- and *cis*-1-Methyl-2-propylcyclohexane (10 and 11).** The crude product from a Grignard reaction of 0.1 mol of 2-methylcyclohexanone (Aldrich) and *n*-propylmagnesium bromide was distilled from 10 drops of H_2SO_4 to give 4.36 g (bp 145–175°) of a mixture which contained 10% 2-methylcyclohexanone and at least three other components by glpc (B, 140°).

A 1.0-g sample of the mixture was hydrogenated (5 ml of hexane, 150 mg of Raney Ni, 100 atm, 150°, 6 hr) to two major products, present in a 34:66 ratio by glpc (A, 136°). Samples of these were collected by preparative glpc (B, 138°). The first (34%) compound was **10**: mass spectrum (70 eV) *m/e* 140 (M^+); pmr (CCl_4) complex pattern at δ 0.6–2.0 with singlets at δ 0.90 and 0.95. The second (66%) compound was **11**: mass spectrum (70 eV) *m/e* 140 (M^+); pmr (CCl_4) δ 0.83 (d, *J* = 6–7 Hz), 1.21 (s), 1.39 (s, shoulder at 1.43), 1.60 (broad s), 1.88 (m); the ratio of areas of the methyl signals (δ 0.8–0.9) to other signals was 6:14.

Assignment of isomeric structures **10** and **11** was verified by two methods. (1) Their pmr spectra are strikingly similar to those of *trans-* and *cis*-1,2-dimethylcyclohexane, which have been analyzed in detail.[21] (2) Equilibrations of pure samples of **10** and **11** over 5% Pd/C[22] at 241 ± 2° for 99 hr each gave a mixture of 75% **10** and 25% **11** (glpc, A, 136°), confirming that **10** is the more stable trans isomer.

***cis*- and *trans*-1-Methyl-3-propylcyclohexane (8 and 9).** From 3-methylcyclohexananone (Aldrich) by the method given above for **10** and **11** a 67:33 mixture (glpc, A, 136°) of **8** and **9** was prepared and separated (preparative glpc, B, 135°). The component of shorter retention time was **8**: mass spectrum (70 eV) *m/e* 140 (M^+); pmr (CCl_4) δ 0.88 (d, *J* = 2 Hz), 0.89 (t, *J* = 3.5 Hz), 1.18 (broad d, *J* = 2 Hz), 1.60 (s), 1.77 (s). The component of longer retention time was **9**: mass spectrum (70 eV) *m/e* 140 (M^+); pmr (CCl_4) δ 0.88 (m), 1.2 (m), 1.4 (m); relative areas of the δ 0.88 and lower field signals were 6:14. The structures of **8** and **9** were verified by (1) comparison with the pmr spectra of *cis-* and *trans*-1,3-dimethylcyclohexane[21] and (2) equilibration over 5% Pd/C[22] to a 79:21 mixture of **8**:**9**, confirming **8** as the more stable cis isomer.

Reaction of 1 and Toluene. A THF solution of 0.7 *M* 1 and 4 *M* toluene was stirred for 48 hr at 70°. Products were isolated by the general method and analyzed by glpc (C, 120°) to contain a 17% yield (based on 1) of pentadiene dimers and a 12% yield (based on 1) of a mixture of phenylhexenes (in order of increasing retention time) **12**:**13**:**14**:**15** in relative yields of 54:6:17:24. Samples of **12**, **14**, and **15** were isolated for mass and pmr spectra by preparative glpc (B, 210°).

Reactions of 1 and 1,3-pentadiene were carried out by the general method. In the absence of a proton donor (furan or toluene) no pentadiene dimers were found by glpc. In the presence of toluene at many reactant concentrations and reaction times, some of which are in ref 1, varied yields (after hydrogenation) of *n*-decane and **8–11** were determined by comparison of glpc (A) peak areas to those of mixed *cis-* and *trans*-decalin (internal standard). Small amounts of 4-methylnonane would not be detected by this glpc analysis.

Reactions of 1 and 2,3-dimethyl-1,3-butadiene (16) were carried out by the general method. A mixture of the cis and trans isomers of 1,2-dimethyl-4-(1-propenyl)cyclohexene (**17**) was isolated by preparative glpc (G, 190°): pmr (CCl_4) 4.7–5.6 (m), 2.4–2.6 (m), 1.8–2.3 (m), 1.66 (s), 1.56 (s), 1.1–1.4 (m); ratio of olefinic/aliphatic areas was 2:16; mass spectrum (70 eV) *m/e* 150 (M^+).

Anal. Calcd for $C_{11}H_{18}$: C, 87.93; H, 12.07. Found: C, 88.00; H, 11.97.

Reaction of 1 and 1,2-Dimethylenecyclohexane (18). A solution of 1 (17 mmol) and 11.4 g (170 mmol) of furan in 110 ml of THF was stirred at 25° while a solution of 1.4 g (13 mmol) of **18** in 100 ml of THF was added dropwise over 2 hr. The solution was stirred for an additional 2 hr and worked up by the general method. Distillation (after addition of 1 ml of hexadecane) gave 0.56 g [bp 40–50° (30 Torr)] of **18** and 1.30 g [bp 90–140° (7 Torr)] of a mixture containing 10% **19** (0.13 g, 0.68 mmol, 6%) and 90% hexadecane by glpc (B, 204°). Purification of **19** by preparative glpc (B, 200°), gave material with the following spectra: pmr ($CDCl_3$) δ 5.0–5.5 (m, 2 H), 1.0–2.3 (m, 18 H); mass spectrum (70 eV) *m/e* 176 (M^+).

Anal. Calcd for $C_{13}H_{20}$: C, 88.64; H, 11.36. Found: C, 88.35; H, 11.50.

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Registry No. 1, 42806-72-4; **6**, 1611-23-0; **7**, 1611-25-2; **8**, 42806-75-7; **9**, 34522-19-5; **10**, 42806-77-9; **11**, 4926-71-0; **12**, 42806-79-1; **14**, 35008-86-7; **15**, 23086-43-3; **16**, 513-81-5; *cis*-**17**, 42806-82-6; *trans*-**17**, 42806-83-7; **18**, 2819-48-9; **19**, 42806-85-9; furan, 110-00-9; 2-lithiofuran, 2786-02-9; 2-methylcyclohexanone, 583-60-8; 3-methylcyclohexanone, 591-24-2; toluene, 108-88-3; *cis*-1,3-pentadiene, 1574-41-0; *trans*-1,3-pentadiene, 2004-70-8.

References and Notes

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Halogenated Ketenes. XXV. Cycloadditions with Allenes[1]

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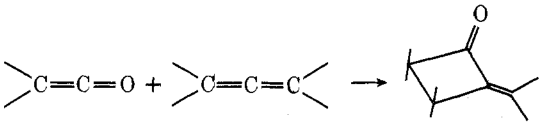
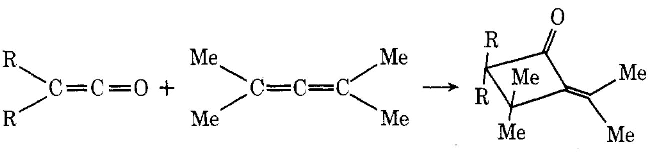
The cycloaddition of variously substituted ketenes with tetramethylallene, 1,2-cyclononadiene, and 1-methyl-1,2-cyclononadiene to give α,β-unsaturated cyclobutanones is described. Tetramethylallene and 1,2-cyclononadiene exhibit unusual reactivity in such cycloadditions. Several other allenes investigated were very unreactive.

Allenes undergo cycloaddition reactions with ketenes to yield α,β-unsaturated cyclobutanones. Tetramethylallene exhibited unexpected reactivity in cycloadditions with dimethyl- and diphenylketenes as reported by Hasek and coworkers in 1965.[2] Moore and coworkers have reported the cycloaddition of *tert*-butylcyanoketene and 1,2-cyclononadiene and revealed that, when the diene is partially resolved, both epimers show appreciable optical activity.[3] This type of stereospecificity has also been reported for the cycloaddition of dimethylketene with 1,3-dimethylallene and 1,2-cyclononadiene.[4,5] We now report on an investigation into the general nature of the cycloaddition of ketenes and allenes with particular emphasis on halogenated ketenes.



The reaction of ketenes with tetramethylallene is a 1,2-cycloaddition reaction and can be generally represented as follows.



The α,β-unsaturated cyclobutanones and the yields of the preparations are shown in Table I. The infrared spectra of the cycloadducts revealed the carbonyl absorptions at 1740–1760 cm^{-1} and the C=C absorptions at 1660 cm^{-1}.

The cycloadditions of the halogenated ketenes and tetramethylallene were effected whereby the ketene was generated in the presence of the diene. This was accomplished by the triethylamine dehydrohalogenation of an appropriately substituted acid halide in refluxing hexane containing tetramethylallene. The order of addition of acid halide and amine was very critical. If the acid halide is added to a refluxing solution of hexane, tetramethylallene, and triethylamine, in some cases no cycloadduct can be isolated and in others a very small amount. This is the result of the amine reacting with the cycloadduct as it is formed. Conversely, the addition of triethylamine to the acid halide, hexane, and the diene results in a much improved yield in spite of the fact that this order of addition is desirable for the formation of α-halovinyl esters.[6] Unfortunately, some of the α-halovinyl ester is produced and is difficult to separate from the cycloadduct.

The cycloadducts of phenylmethyl- and phenylethylketenes with tetramethylallene were prepared by combining tion of the amine at −78° prior to the addition of the allene. Subsequent warming to room temperature produces a 25% yield of the cycloadduct.

The cycloadducts of phenylmethyl- and phenylethylketenes with tetramethylallene were prepared by combining equimolar amounts of the insolable ketene and the allene at room temperature.

The nmr data for the tetramethylallene cycloadducts are recorded in Table II. The two methyl groups of the isopropylidene substituent are in different environments and thus are revealed as two singlets in the spectra (δ 1.7–1.9 and 1.95–2.1). The methyl protons closest to the carbonyl are expected to be further downfield. The two methyl groups attached to the 3 carbon of the cyclobutanone are above and below the plane of the ring and will be in identical environments only when the substituents on the ketene are identical (a symmetrical ketene). This is evident in the dichloroketene (IV) and bromochloroketene (V) cycloadducts in that IV shows only one singlet at δ 1.5 for the two methyl groups and V reveals two singlets at δ 1.5 and 1.6; yet it is interesting to note that, in the ethylchloroketene adduct (III), these methyl groups occur at identical chemical shifts. The spectrum of the methylbromoketene adduct (II) revealed five singlets with equivalent areas as expected. However, the methylchloroketene adduct (I) revealed only four singlets in a ratio of 2:1:1:1. Apparently, the methyl of the ketene functionality and the methyl trans to the chloro substituent overlap at δ 1.4.