acid-washed alumina using petroleum ether–benzene as the eluent. The first fraction contained about 20 mg of a gum and the second fraction about 90 mg of a gummy solid. Two recrystallizations of fraction 2 from methanol afforded 60 mg (30%) of the pure keto ester **11** as colorless prisms: mp 102° (lit.[3] mp 102–103°); ultraviolet spectrum λ_{max} 250 mμ (log ϵ 4.11) and 290 mμ (log ϵ 3.33); ir spectrum ν_{max} 1678 and 1724 cm^{-1}.

Anal. Calcd for $C_{17}H_{20}O_3$: C, 75.0; H, 7.4. Found: C, 74.7; H, 7.1.

Elutions with benzene–ether (9:1 to 1:1) gave *ca.* 30 mg of a dark yellow gummy solid (fraction 3) which could not be induced to crystallize and was not investigated further.

D. Preparation of Keto Ester 14.—A solution of ester **13** (300 mg, 1.17 mmol) in 3 ml of acetic acid was oxidized using the above procedure with a solution of 300 mg (3 mmol) of chromium trioxide in 3 ml of acetic acid and 1 ml of water. The resulting crude neutral oxidation product (280 mg) was chromatographed on 15 g acid-washed alumina using petroleum ether–benzene and benzene as the eluent. From the later petroleum ether–benzene and benzene effluents was obtained 180 mg (56.6%) of the keto ester **14**, mp 102–104°. Recrystallization from petroleum ether afforded 165 mg of pure **14**, as colorless needles: mp 109°; ultraviolet spectrum λ_{max} 250 mμ (log ϵ 4.11) and 290 mμ (log ϵ 3.33); infrared spectrum ν_{max} 1678 and 1724 cm^{-1}.

Anal. Calcd for $C_{17}H_{20}O_3$: C, 75.0; H, 7.4. Found: C, 74.6; H, 7.3

Saponification of Esters 10, 13, 16, and 19.—Each of the esters (250 mg) in 4:1 ethanol–water potassium hydroxide (10 ml) was refluxed under a nitrogen atmosphere. The unsaponified ester was repeatedly extracted with ether after dilution with saturated brine (50 ml). After acidification of the alkaline aqueous layer the corresponding acid was isolated by repeated extraction with ether. The product was characterized by melting point, mixture melting point, and its ir spectrum. The results of the comparative study are shown in Table I.

Deuteration of Keto Esters 11, 13, 15, and 17.—Each of the keto esters (5 mg) was treated with 0.5 ml of 4 *N* sodium methoxide in deuterium methoxide.[57] After 3 hr the mixture was diluted with 1 ml of D_2O and the product was extracted with chloroform. Examination of the nmr spectrum showed essentially complete exchange of the C-9 methylene protons.

Preparation of Alcohols 12, 15, 18, and 21.—Each of the acids **1**, **2**, **3**, and **4** (7–40 mg) in 10 ml of dry ether was treated with an excess of lithium aluminum hydride. After standing at room temperature for 6 hr, the excess hydride was decomposed with ethyl acetate and the mixture was shaken with 10 ml of 10% aqueous potassium hydroxide. The ethereal layer was dried over sodium sulfate and evaporated to give essentially a quantitative yield of the alcohol. Alcohol **12** had mp 117–118° but alcohols **15**, **18**, and **21** were colorless oils which could not be induced to crystallize.

Anal. Calcd for $C_{16}H_{22}O$: mol wt, 230. Found: mol wt (mass spectrometry), 230.

Registry No.—**1**, 21995-83-5; **2**, 21995-84-6; **3**, 21995-85-7; **4**, 21995-86-8; **7**, 21995-87-9; **8**, 21995-88-0; **9**, 13936-31-7; **10**, 5708-86-1; **11**, 5708-87-2; **12**, 21995-92-6; **13**, 21995-93-7; **14**, 21995-94-8; **14** (6,6-dideuterio), 21995-72-2; **15**, 21995-95-9; **16**, 21995-96-0; **17**, 21995-97-1; **17** (6,6-dideuterio), 21995-73-3; **18**, 21995-98-2; **19**, 21995-99-3; **20**, 21996-00-9; **21**, 21996-01-0.

Acknowledgment.—The nmr investigation was supported in part by a Public Health Service grant, GM 14533. We thank Mr. Menon Somasekharan, University of Hawaii, for his assistance in the computer analyses of the nmr spectra. Professor P. C. Dutta is gratefully acknowledged for his interest in this work.

[57] Under the reaction conditions no change in the configuration of C-12 occurs.

Studies on Reactions of Isoprenoids. IV.[1] The Reactivity of Myrcene in 1,4-Cycloaddition Reactions

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Cycloaddition reactions of myrcene have been investigated. This 2-substituted 1,3-butadiene is not so reactive as isoprene and failed to give adducts with phenylacetylene, N-*t*-butylpropiolamide, furan, isoprene, and benzoxazole. With cyclopentadiene, it reacted as a dienophile. With stronger dienophiles, adducts were formed in 10–60% yields along with undistillable by-products. The long unsaturated chain appears to contribute in lowering the activity of the diene and in the formation of by-products. However, its regiospecificity in orientation in cycloaddition reactions with acrylonitrile, cyanoacetylene, and chlorocyanoacetylene is the same as the methyl group in isoprene, but it differs in the reaction with thionylaniline.

Although many Diels–Alder reactions of simple 2-substituted butadienes such as isoprene have been reported,[2] little is known about those of 2-substituted butadienes containing a long, functional group. Myrcene (**1**), 7-methyl-3-methylen-1,6-octadiene, belongs to this type. Its 1,4-cycloaddition reactions are expected to afford a class of compounds that might be interesting for model studies on certain biogenetic-like cyclizations[3] and for a possible synthetic route to certain types of terpenes.[4] Diels–Alder reactions of myrcene with maleic anhydride[5] and with acrolein and its analogs[6] have been described, but without any detailed structural elucidation of the cycloadducts. This paper deals with 1,4-cycloaddition re-

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[1] Part III of this series: T. Sasaki and S. Eguchi, *J. Org. Chem.*, **33**, 4386 (1968).

[2] For recent reviews, see (a) J. Sauer, *Angew. Chem.*, **78**, 233 (1966); (b) J. Sauer, *ibid.*, **79**, 76 (1967); (c) J. Hamer, "1,4-Cycloaddition Reactions," Academic Press, New York, N. Y., 1967. For kinetic studies, see (d) M. Charton, *J. Org. Chem.*, **31**, 3745 (1966); (e) S. Seltzer, *Advan. Alicycl. Chem.*, **2**, 1 (1968).

[3] For a recent review, see W. S. Johnson, *Accounts Chem. Res.*, **1**, 1 (1968).

[4] Bisabolene group, for example; see, for a review, P. de Mayo, "Mono- and Sesquiterpenoids," Vol. 2, K. W. Bentley, Ed., Interscience Publishers, New York, N. Y., 1959, pp 180–242.

[5] (a) N. P. Kiryalov, *Dokl. Akad. Nauk SSSR*, **61**, 305 (1948); *Chem. Abstr.*, **43**, 1155*g* (1948); (b) F. Šorm, M. Streibl, V. Jarolin, L. Novotny, L. Dolejs, and V. Herout, *Chem. Listy*, **48**, 575 (1954); (c) G. A. Rudakov and M. M. Shestaeva, *Zh. Prikl. Khim.*, **28**, 1199 (1955); *Chem. Abstr.*, **50**, 9338*c* (1956); (d) M. O. Sutherland and J. W. Wells, *J. Org. Chem.*, **21**, 1272 (1956); (e) M. G.-Schumacher and U. Wicker, *Chem. Ber.*, **93**, 974 (1960).

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TABLE I

1,4 CYCLOADDUCTS OF MYRCENE (1) TO SEVERAL DIENOPHILES

Dienophile	Reaction conditions: Solvent	Reaction conditions: Temp, °C	Reaction conditions: Time, hr	Compd [bp, °C (mm)]	Product n^{25}_D	Yield, %	Formula	C, %: Calcd	C, %: Found	H, %: Calcd	H, %: Found	N, %: Calcd	N, %: Found	Recvd 1, %	Side product, %[a]
Acetylenic															
Cyanoacetylene	None	50–55	96	**2** [90–92 (0.16)]	1.5091	55	$C_{13}H_{17}N$	83.37	83.22	9.15	9.04	7.48	7.67	20	20
Chlorocyano-acetylene	None	50–55	1	**3** [90–92 (0.06)]	1.5385	28	$C_{13}H_{16}ClN$	70.41	70.10	7.29	7.01	6.32	6.15	0	70
		ca. 20	24	**3**		28								30	35
Dimethyl acetylene-dicarboxylate	None	50–55	96	**4** [127–130 (0.15)]	1.5031	56	$C_{16}H_{22}O_4$	69.04	69.22	7.97	7.98			20	20
Phenylacetylene	None	85–90	240			0								25	70
N-*t*-Butylpropiolamide	Benzene	85–90	168			0								40	60
Olefinic															
Acrylonitrile	None	50–55	96	**5** [111–112 (2)]	1.4910	40	$C_{13}H_{19}N$	82.48	82.36	10.12	10.45	7.40	7.18	20	25
p-Benzoquinone	Benzene	85–90	24	**6** [123–125 (0.05)]	1.5319	60	$C_{16}H_{20}O_2$	78.65	78.44	8.25	8.26			20	20
Dicyclopentadiene	None	165–170	48	**7** [80–82 (0.15)]	1.5153	10	$C_{15}H_{22}$	89.04	88.90	10.96	10.70			10	50
				8 [125–129 (0.05)]	1.5158	20	$C_{20}H_{28}$	89.49	89.14	10.51	11.04				
Furan	None	85–90	168	**9** [115–119 (0.1)][b]	1.4988	10	$C_{20}H_{32}$	88.16	87.96	11.84	12.24			40	45
Myrcene (1)	None	130–135	48	**9**		30								30	40
Isoprene	None	130–135[c]	24			0								0	100
Heterodienophiles															
Diethyl azodicarboxylate	Ether	20–25	24	**10** [133–136 (0.5)]	1.4843	55	$C_{16}H_{26}O_4N_2$	61.91	61.73	8.44	8.32	9.03	9.00	0	45
Benzoxazole	None	130–135	38	**9**		20								20	50
Thionylaniline	Benzene	85–90	18	**11** (mp 74–75°)		9	$C_{16}H_{21}ONS$	69.79	70.00	7.69	7.70	5.09	5.10	30	40

[a] Undistillable. [b] Lit.[13] bp 140–150° (3 mm), n^{25}_D 1.5001. [c] Polymerization inhibitor, H and B was used in 10% amount.

actions of **1** with several dienophiles of different reactivity.

Reaction Conditions and Results.—The reactions were carried out in an equimolar ratio of **1** to each dienophile; solvents (if any), reaction time, and temperature are given in Table I together with yields and analyses of the cycloadducts, **2–11**. Since **1** has a strong tendency to polymerize, hydroquinone (H) and/or 2,6-di-*t*-butylphenol (B) were added as polymerization inhibitors to the reaction mixture in *ca.* 5% of the total weight, unless otherwise noted in the table. The formation of undistillable side products was unavoidable even when **1** was recovered. The amount of undistillable side products increased with temperature and time. As may be seen from Table I, the cycloadducts were mostly liquids and were purified by vacuum distillation. The yields ranged from 10 to 60% with stronger dienophiles such as cyanoacetylene, chlorocyanoacetylene, dimethyl acetylenedicarboxylate, acrylonitrile, *p*-benzoquinone, cyclopentadiene, diethyl azodicarboxylate, and thionylaniline. In the presence of weaker dienophiles such as furan and benzoxazole, **1** afforded myrcene dimer **9** as the major distillable product in 10–20% yield, irrespective of the presence of the dienophiles, together with undistillable side products in 20–40% yield. With phenylacetylene, N-*t*-butyl propiolamide, and isoprene, no 1,4 cycloadducts could be isolated.

Structural Elucidation of the Adducts. A. With Acetylenic Dienophiles.—A 1:1 adduct of **1** with cyanoacetylene, **2**, was found to have a 1,4-cyclohexadiene structure with a 4-methyl-3-pentenyl side chain from the spectral data as shown in Table II. The position of the cyano group was determined by chemical conversion to terephthalic acid (**12**) after aromatization with sulfur, followed by alkaline hydrolysis of the cyano group and oxidation of the side chain. The fact that the major distillable product was **2** under the given reaction conditions indicated that the addition occurred mainly in one direction, which was the same direction as observed in the reaction of isoprene with cyanoacetylene.[7]

$$\mathbf{1} \longrightarrow \mathbf{2} \longrightarrow \mathbf{12}$$

In the reaction of **1** with chlorocyanoacetylene at room temperature (*ca.* 20°) or at 50°, the yields of 1:1 adduct **3** were the same (28%) although the amounts of undistillable side product increased and those of recovered **1** decreased on increasing the temperature. The structure of **3** was confirmed as 1-(4-methyl-3-pentenyl)-4-cyano-5-chloro-1,4-cyclohexadiene from its spectrum (Table II) and spontaneous conversion into 2-chloro-4-(4-methyl-3-pentenyl)cyanobenzene (**13**), an aromatization product of **3**. Unlike **2**, **3** was unstable to air oxidation. Redistillation of the sample after 1 month afforded a mixture of **3** and **13**, as demonstrated in the nmr spectrum by the appearance of aromatic protons besides those of **3** (Table II) at τ 2.43 (double d, J = 9.0 and 1.0 Hz, an *ortho* proton to the cyano group), 2.63 (unsymmetrical t, J = *ca.* 1.5 Hz, an *ortho* proton to the chloro group), and 2.82 (double d, J = 9.0 and 1.5 Hz, a *para* proton to the chloro group). These values were in accordance with calculated values

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[7] S. Murahashi, Y. Sudo, and K. Kawasaki, *Nippon Kagaku Zasshi*, **78**, 327 (1957).

TABLE II

SPECTRAL PROPERTIES OF 1,4-CYCLOADDUCTS OF MYRCENE (1) WITH ACETYLENIC DIENOPHILES

	Nmr ($CDCl_3$), τ, ppm[a]						
	In 1,4-cyclohexadiene ring			In 4-methyl-3-pentenyl side chain			Others
Compd	CH=CCN	CH=C	CH_2	CH=C	CH_2CH_2	$C=C(CH_3)_2$	$COOCH_3$
2	3.40 (m)	4.56 (br s)	7.18 (s)	4.93 (br s)	7.97 (a s)	8.30 (s), 8.38 (s)	
3		4.55 (br s)	6.98 (s)	4.90 (br s)	7.93 (a s)	8.32 (s), 8.40 (s)	
4		4.59 (br s)	7.10 (s)	4.90 (br s)	7.98 (a s)	8.30 (s), 8.37 (s)	6.28 (s)

Compd	Ir (neat), cm^{-1}
2	2256 (CN), 1670 (C=CH), 1638 (C=CCN), 845–800 (complex, C=CH)
3	2275 (CN), 1675 (C=CH), 1620 (C=CCN)
4	1750 (CO), 1650 (C=CH), 1236 ($COOCH_3$)

[a] In the nmr data, br s = broad singlet, a s = asymmetrical singlets.

using Smith's parameters[8] and provided good evidence that the addition had occurred in the same direction as in the reaction with cyanoacetylene described above. Similar phenomena have been observed in the 1,3-dipolar cycloaddition reactions of cyanoacetylene and chlorocyanoacetylene with several 1,3-dipoles.[9,10] Comparison of the nonaromatized with the corresponding aromatized protons indicated that the mixture consisted *ca.* 70% **3** and 30% **13**.

$\mathbf{1} \longrightarrow \mathbf{3} \longrightarrow \mathbf{13}$

Structural elucidation of the 1:1 adduct of **1** with dimethyl acetylenedicarboxylate, **4**, was carried out similarly (Tables I and II), and **4** was concluded to be 1-(4-methyl-3-pentenyl)-4,5-dimethoxycarbonyl-1,4-cyclohexadiene. Compound **4** also had a tendency to aromatize spontaneously on standing in air at room temperature, which was demonstrated in the nmr spectrum by the appearance of aromatic protons at τ 2.75 (q, J = 8.0 and 1.0 Hz, C-2 H), 2.36 (d, J = 8.0 Hz, C-3 H), and 2.55 (d, J = 1.0 Hz, C-6 H).

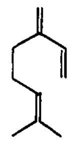
$\mathbf{1} \longrightarrow \mathbf{4}$

B. With Olefinic Dienophiles.—The 1:1 adduct of **1** with acrylonitrile, **5**, was demonstrated to have the 1-cyclohexene structure with a 4-methyl-3-pentenyl side chain from the analytical (Table I) and spectral data (Table III). Compound **5** was treated with N-bromosuccinimide (NBS) and the brominated product was directly aromatized and hydrolyzed with alkali. The resulting aromatized mixture was again directly oxidized with aqueous potassium permanganate to afford terephthalic acid, indicating that the cyano group was located at C-4 in **5**. The direction of addition is the same as the above-described addition of cyanoacetylene, providing a good indication that the 1,4 cycloaddition under the given reaction conditions is more influenced by steric factors than by the polar effect of the dienophiles used.

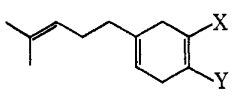
$\mathbf{1} \longrightarrow \mathbf{5} \longrightarrow \mathbf{12}$

The 1,4 cycloadduct of **1** with *p*-benzoquinone, **6**, was shown to be 7-(4-methyl-3-pentenyl)-5,8,9,10-tetrahydro-1,4-napthoquinone on the basis of the analytical (Table I) and spectral data (Table III).

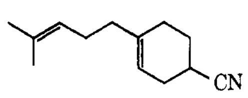
The 1,4 cycloaddition of **1** to dicyclopentadiene proceeded with some difficulty (see the reaction conditions given in Table I) and afforded two products, **7** and **8**.



1



2, X = H; Y = CN
3, X = Cl; Y = CN
4, X = Y = COOCH$_3$



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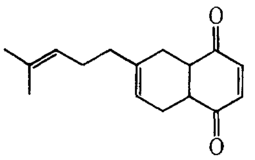

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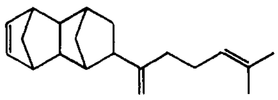

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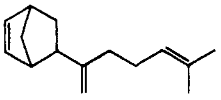

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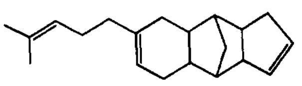

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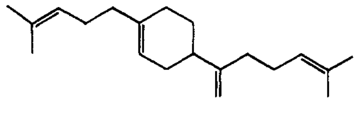

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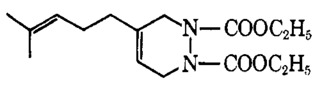

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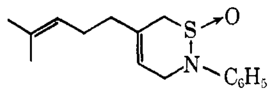

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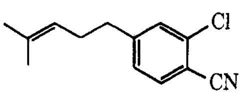

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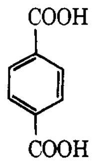

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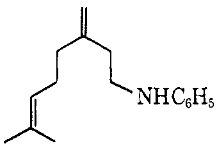

14

When freshly distilled cyclopentadiene was used in the reaction at *ca.* 20°, rapid dimerization gave only dicyclopentadiene. Therefore, the reaction was carried out at higher temperature, at which dicyclopentadiene is known to decompose to cyclopentadiene. Microanalysis and mass spectral data showed that the lower boiling fraction was a 1:1 adduct of **1** and cyclopentadiene, which had the structure of 5-(1-methylene-5-methyl-4-hexenyl)bicyclo[2.2.1]heptene-2, **7**. The nmr

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[8] G. W. Smith, *J. Mol. Spectrosc.*, **12**, 146 (1964).

[9] T. Sasaki, S. Eguchi, and A. Kojima, *J. Heterocycl. Chem.*, **5**, 243 (1968).

[10] T. Sasaki, K. Kanematsu, and Y. Yukimoto, *J. Chem. Soc., C*, in press (1969).

TABLE III

SPECTRAL PROPERTIES OF 1,4 CYCLOADDUCTS OF MYRCENE (**1**) WITH OLEFINIC DIENOPHILES

	Nmr ($CDCl_3$), τ, ppm[a]							
	In 1-cyclohexenyl ring				In 4-methyl-3-pentenyl side chain			Others
Compd	CH=C	CHCN	C=CCH_2	CH_2	C=CH	CH_2CH_2	C=$C(CH_3)_2$	COCH=CHCO
5	4.61 (br s)	7.30 (s)	7.50–8.20[c]	*b*	4.90 (br s)	7.50–8.20 (a br s)[c]	8.23 (s), 8.36 (s)	
		COCH						
6	4.69 (br s)	6.86 (s)	7.65 (s)		5.01 (br s)	8.03 (a s)	8.38 (s), 8.45 (s)	3.45 (s)
					Ir (neat), cm^{-1}			
5			2270 (CN), 1688, and 828 (C=CH)					
6			1685 (CO), 1603 (CH=CCO)					

[a] In the nmr data, br s = broad singlet, a s = asymmetrical singlet. [b] The signal was superimposed with the signals owing to C=$C(CH_2)_2$. [c] This range overlapped.

spectrum ($CDCl_3$) had signals at τ 3.93 (d split to t, 1 H, J = 12.0 and 1.8 Hz, one of vinyl protons of norbornene ring), 4.28–4.62 (broad m, 3 H, another of vinyl protons of norbornene ring and C=CH_2), 4.90 [broad s, 1 H, -CH=$C(CH_3)_2$], 7.25 (broad s, 2 H, two bridgehead protons of norbornene ring), 8.32 and 8.42 [each s, 6 H, C=$C(CH_3)_2$], 8.65–9.20 (complex m, *ca.* 2 H, one of two methylene protons of norbornene ring), and 7.50–8.25 (complex m, *ca.* 7 H, the other methylene and methine protons). In the mass spectrum, the molecular ion peak appeared at m/e 202 (rel intensity 42.3); other main fragment ions were at m/e (rel intensity, ion) 187 (14.6, M − CH_3), 159 (26.9, M − C_3H_7), 136 (11.0, M − C_5H_6), 133 (26.9, M − C_5H_9), 93 (42.3, C_7H_9), 91 (63.5, C_7H_7), 69 (49.5, C_5H_9), 66 (100, C_5H_6), and 41 (30.7, C_3H_5). Two ion peaks at m/e 66 due to cyclopentadiene and at m/e 136 due to mycene in the fragmentations probably originated from a retro Diels–Alder reaction of **7**. This result indicates that myrcene reacted as a dienophile at the *end* vinyl group with cyclopentadiene as a diene. Similar reactions of cyclopentadiene with isoprene have been reported.[11] The stereochemistry of **7** remains unsolved. Application of the *endo*-addition rule to this addition seems improper, since this rule is generally applicable to the addition of cyclic dienophiles to cyclic dienes but not always to that of open-chain dienophiles to cyclic dienes.[12] The higher boiling fraction was tentatively concluded to be a mixture of **8**, a 1:1 adduct of **1** to dicyclopentadiene, and a myrcene dimer **9** on the basis of analytical and spectral data. In its mass spectrum, the presence of two characteristic peaks at m/e 272 (rel intensity 14.4 to a base peak at m/e 69) and at m/e 268 (rel intensity 15.0), corresponding to the molecular ions for **9** and **8**, respectively, supports this conclusion.

Myrcene dimer **9** has been reported as a side product in the reaction of **1** with formaldehyde,[13] but no decisive evidence for the structure has been given. The nmr spectrum ($CDCl_3$) showed signals due to the 1-cyclohexenyl ring at τ 4.72 (s, 1 H, a cyclic olefin proton), and 7.30–8.22 (broad m with strong signals at τ 7.98 and 8.07, *ca.* 13 H, allylic methylene and methine protons of the ring superimposed with the signals due to allylic methylene protons of the side chain), and the signal of the other ring methylene protons was superimposed with the signals due to four allylic methyl protons at τ 8.36 and 8.43 (s, 14 H). Vinyl protons of the side chain appeared at τ 4.95 (broad s, 2 H, -CH=C) and 5.27 (s, 2 H, C=CH_2). The mass spectrum showed the parent ion peak at m/e 272 (rel intensity 54.2, M^+) and the base peak at m/e 69 (C_5H_9). Other characteristic fragment ions appeared at m/e (rel intensity, ion) 257 (10.8, M − CH_3), 229 (30.5, M − C_3H_7), 203 (24.0 M − C_5H_9), and 136 (5.2, $C_{10}H_{16}$, the retro Diels–Alder fragmentation). Ion peaks at m/e (rel intensity, ion) 83 (8.3, C_6H_{11}), 109 (26.0, C_8H_{13}), and 121 (21.7, C_9H_{13}) may be correlated with ion peaks at m/e (rel intensity) 189 (8.7) and 187 (15.2), 161 (17.4) and 159 (9.0), and 149 (6.8) and 147 (17.4). Other fragmentations are very similar to those of myrcene itself.[14] However, these data do not allow a decision between the two possible structures, 1- or 2-(4-methyl-3-pentenyl)-4-(1-methylene-5-methyl-4-hexenyl)-1-cyclohexene. Chemical conversion of **9** to terephthalic acid permitted a decision in favor of the former structure.

$$\mathbf{1} \longrightarrow \mathbf{9} \longrightarrow \mathbf{12}$$

In the reaction of **1** with isoprene under the similar reaction conditions, only nondistillable materials were obtained; this formation was not suppressed even by increasing of the amounts of H or B up to 10% from 5%.

C. With Heterodienophiles.—The structure of the 1:1 cycloadduct of **1** with diethyl azodicarboxylate **10** was characterized as 1,2-diethoxycarbonyl-4-(4-methyl-3-pentenyl)-3,6-dihydropyridazine on the basis of the analytical and nmr data. The nmr spectrum ($CDCl_3$) had signals at τ 4.41 (m, 1 H, C=CH), 4.86 (m, 1 H, C=CH), 5.74 (q, 4 H, J = 6.6 Hz, CH_2CH_3), 5.62 and 6.27 (AB q, 4 H, J = 18.0 Hz, NCH_2C=C), 7.89 (s, 4 H, =$CHCH_2CH_2C$=), 8.25 and 8.34 [each s, 6 H, C=$C(CH_3)_2$], and 8.69 (t, 6 H, J = 6.6 Hz, CH_2CH_3). The formation of fairly large amounts of nondistillable side product was unavoidable even at room temperature.

Since the C=N bond of benzoxazole is known to react with butadiene to give the corresponding Diels–Alder adduct in 50–70% yields,[15] a similar reaction was attempted with **1**. However, benzoxazole did not react at all with **1** even on heating at 130–135° for 38 hr, and only myrcene dimer **9** could be isolated in a low yield. The lower diene reactivity of **1** was also demonstrated by the reaction with thionylaniline, which is known to react with butadiene, isoprene, and 2,3-dimethylbutadiene to give the corresponding cyclo-

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[11] A. F. Plate and N. A. Belikova, *Zh. Obshch. Khim.*, **30**, 3953 (1960); *Chem. Abstr.*, **55**, 22254*a* (1961).

[12] R. Huisgen, R. Grashey, and J. Sauer, "The Chemistry of Alkenes," S. Patai, Ed., Interscience Publishers, New York, N. Y., 1964, p 911.

[13] S. Watanabe and K. Suga, *Bull. Chem. Soc. Jap.*, **36**, 1495 (1963).

[14] (a) For the mass spectrum of myrcene, see J. H. Beynon, R. A. Saunders, and A. E. Williams, "The Mass Spectra of Organic Molecules," Elsvier Publishing Co., New York, N. Y., 1968, p 113, and references cited therein. (b) For the isomerization process before the rupture of terpene molecules, see D. S. Weinberg and C. Djerassi, *J. Org. Chem.*, **31**, 115 (1966).

[15] Reference 2c, p 5.

adducts in excellent yields.[16] Similar treatment of **1** with thionylaniline afforded the 1:1 adduct **11** in only 9% yield. Since yields are also low in the reaction of thionylaniline with 1,3-hexadiene and 1-substituted butadienes,[16a] the 9% yield might be ascribed similarly to the presence of a long substituent at the 2 position of butadiene. The structure of **11** was confirmed as 2-phenyl-5-(4-methyl-3-pentenyl)-3,6-dihydro-1,2-thiazine-1-oxide on the basis of analytical and spectral data, and hydrolysis to 1-anilino-3-methylene-7-methyloctene-6 (**14**). This direction of the addition was the reverse from that of the reaction with isoprene.[16a,b]

$$\mathbf{1} \longrightarrow \mathbf{11} \longrightarrow \mathbf{14}$$

Experimental Section[17]

General Procedure for 1,4-Cycloaddition Reactions.—An equimolar mixture of freshly distilled myrcene and a dienophile was heated in the presence of hydroquinone and/or 2,6-di-*t*-butylphenol (*ca.* 5% of the total weight) in a sealed tube flashed by nitrogen under the reaction conditions given in Table I. The products were purified by fractional distillation under vacuum. These results are summarized in Table I. Cyanoacetylene,[18] chlorocyanoacetylene,[19] N-*t*-butylpropiolamide,[20] diethyl azodicarboxylate,[21] and thionylaniline[22] were prepared by the reported methods; other dienophiles were commercially available.

Conversion of 1-(4-Methyl-3-pentenyl)-4-cyano-1,4-cyclohexadiene (2) into Terephthalic Acid (12).—A mixture of **2** (1.87 g) and sulfur powder (0.8 g) was heated without solvent at 200–210° for 1 hr. The resulting dark brown oil was directly refluxed in 50 ml of 10% sodium hydroxide for 3 hr. The alkaline solution, after washing with benzene, was refluxed overnight with 10 g of potassium permanganate in 50 ml of water. The resulting precipitates were filtered and washed with 100 ml of hot water. The filtrate and washings were combined and acidified with 10% sulfuric acid to result in precipitation of crude terephthalic acid (1.65 g). The pure acid 12 was obtained by two recrystallization from hot alcohol. The infrared spectrum was completely superimposable on that of an authentic specimen.

Aromatization of 1-(4-Methyl-3-pentenyl)-4-cyano-5-chloro-1,4-cyclohexadiene (3).—A mixture of 2.2 g of **3** and 0.35 g of sulfur powder was heated at 210° for 5 min in a nitrogen stream. The resulting brownish mixture was promptly distilled to give crude aromatized compound (1.2 g) which was redistilled to give 0.9 g of **13**, bp 118–121° (0.7 mm). An analytical sample was obtained after chromatography on alumina (Merck, grade I) by eluting with *n*-hexane–benzene: $n^{20}\text{D}$ 1.4895; ir (neat) 2279 ($C{=}N$), 1650 ($C{=}C$), 1600, 870, and 828 cm^{-1} (phenyl); nmr ($CDCl_3$) τ 2.38 (double d, 1 H, J = 9.0 and 1.0 Hz, a *para* proton to Cl), 2.59 and 2.78 (2 H, unsymmetrical t with J = *ca.* 1.5 Hz, and double d with J = 9.0 and 1.5 Hz, each an *ortho* proton to Cl and CN, respectively), 4.83 (broad s, *ca.* 1 H, $CH{=}C$), 7.0–8.0 (m, 4 H, allylic and benzylic methylene protons), 8.22 and 8.35 [s, 6 H, $C{=}C(CH_3)_2$]. Although very weak signals at τ 5.22 (s) and around 8.7 were observed, further purification on a silica gel column was not effective for removal of these signals, indicating that **13** might be contaminated with small amounts of the double-bond isomer of the type with an *end* methylene structure.

Anal. Calcd for $C_{13}H_{14}ClN$: C, 71.06; H, 6.42; N, 6.37. Found: C, 71.17; H, 6.43; N, 6.77.

Conversion of 1-(4-Methyl-3-pentenyl)-4-cyano-1-cyclohexene (5) into Terephthalic Acid (12).—A mixture of **5** (0.95 g), NBS (7.1 g), and benzoyl peroxide (0.05 g) in 100 ml of dry carbon tetrachloride was refluxed for 0.5 hr. After cooling, the precipitates were filtered and the filtrate was evaporated to dryness *in vacuo* to give crude bromide (1.25 g). Then 10% sodium hydroxide (100 ml) was added and the mixture was refluxed for 5 hr. After cooling, the mixture was washed with benzene (two 50-ml portions) and the alkaline solution was oxidized with potassium permanganate (10 g in 50 ml of water) by heating at 95° for 3 hr. The precipitates were filtered and washed with hot water. The combined filtrate and washings were acidified with 20% sulfuric acid to give crude **12** (0.1 g), whose infrared spectrum was superimposable on that of an authentic sample.

Conversion of 1-(4-Methyl-3-pentenyl)-4-(1-methylene-5-methyl-4-hexenyl)-1-cyclohexene (9) into Terephthalic Acid (12).—A mixture of **9** (1.2 g), NBS (8.9 g), and benzoyl peroxide(0.05 g) in 100 ml of dry carbon tetrachloride was refluxed for 1 hr. The mixture was cooled, and removal of the precipitates by filtration and drying up of the filtrate *in vacuo* afforded crude bromide as a brownish oil (2.11 g). The oil was heated with 10% potassium hydroxide (200 ml) and ethanol (100 ml) at 90° for 10 hr. After concentration to *ca.* 100 ml, the mixture was diluted with water (100 ml) and treated with potassium permanganate (10 g) as above, except for the use of pyridine (30 ml) and the prolonged reaction time (24 hr at 90°), to afford finally 0.08 g of **12**, which was identified with an authentic sample by comparison of the ir spectra.

2-Phenyl-5-(4-methyl-3-pentenyl)-3,6-dihydro-1,2-thiazine 1-Oxide (11) and Its Hydrolysis.—A mixture of thionylaniline (2.8 g, 0.20 mol) and myrcene (2.7 g, 0.20 mol) in 5 ml of benzene was heated at 85–90° for 18 hr in a sealed tube, and the product was purified on a silica gel column eluting with benzene to give white solids which afforded 0.5 g (9%) of white plates of **11** on recrystallization from *n*-hexane (Table I): ir (KBr) 1605, 757 and 698 (phenyl), and 1069 cm^{-1} (SO); nmr ($CDCl_3$) τ 2.75 (m, 5 H, C_6H_5), 4.18 (m, 1 H, $C{=}CH$), 4.85 (broad s, 1 H, $C{=}CH$), 5.69 and 6.30 (AB q, 2 H, J = 18.0 Hz, $SOCH_2C{=}C$), 6.28 and 6.82 (AB q, 2 H, J = 15.0 Hz, $NCH_2C{=}C$), 7.80 and 7.85 (each s, 4 H, CH_2CH_2), and 8.23 and 8.30 [each, s, 6 H, $C(CH_3)_2$].

A mixture of **11** (0.6 g) and 5% sulfuric acid (5 ml) was left standing at room temperature for 1 month and the resulting dark brown oil was taken in benzene (10 ml) after neutralization with 10% sodium hydroxide. The benzene solution was dried (Na_2SO_4) and was passed through an alumina (Merck, neutral, grade I) column to give pure 1-anilino-3-methylene-7-methyloctene-6 (**14**) as an oil: ir (neat) 3450 (NH), 1675 ($C{=}CH$), 1640 and 890 ($C{=}CH_2$), 1601, 750, and 690 (phenyl) cm^{-1}; nmr ($CDCl_3$) τ 2.70–3.60 (m, 5 H, phenyl protons), 4.86 (broad s, 1 H, $CH{=}C$), 5.15 (s, 2 H, $C{=}CH_2$), 6.49 (broad s, 1 H, NH), 6.75 (t, 2 H, J = 7.5 Hz, $CH_2\mathbf{CH_2}N$), 7.60 (t, *ca.* 2 H, J = 7.5 Hz, $C{=}C{-}\mathbf{CH}CH_2N$), 7.95 (unsymmetrical s, *ca.* 4 H, $C{=}CCH_2CH_2C{=}C$), 8.25 and 8.35 [s, 6 H, $C(CH_3)_2$].

Anal. Calcd for $C_{16}H_{23}N$: C, 83.78; H, 10.11; N, 6.11. Found: C, 83.91; H, 10.00; N, 5.74.

Registry No.—**1,** 123-35-3; **2,** 21690-40-4; **3,** 21690-41-5; **4,** 21690-42-6; **5,** 21690-43-7; **6,** 21690-44-8; **7,** 21690-45-9; **9,** 532-87-6; **10,** 21690-47-1; **11,** 21690-48-2; **13,** 21690-49-3; **14,** 21690-50-6.

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(17) Microanalyses were carried out on a Yanagimoto C. H. N. Corder, Model MT-1. Melting points determined on a Yanagimoto micromelting point apparatus and boiling points are uncorrected. Infrared spectra were recorded on a Jasco Model IR-S infrared spectrometer. Nmr spectra were obtained with Varian A-60 and Hitachi H-6013 spectrometers and are reported in τ values relative to TMS as an internal standard. Broad or complex signals are designated as br or m, singlet signals as s, doublet as d, triplet as t, quartet as q, etc. Mass spectra were taken with a Hitach high-resolution mass spectrometer, Model RMU-7HR, at 70 eV.

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