

by filtration. This dissolved soluble impurities. They were again dried in the atmosphere and then dissolved in cold methanol and treated with carbon black in the cold for about 10 min. Filtration was repeated four times under suction. Each time meticulously cleaned funnels and flasks were used to ensure complete removal of carbon and insoluble impurities, as well as those adsorbed by the carbon. The clear solutions were poured into petri dishes and allowed to evaporate under the hood. Solids were removed and dried over phosphorus pentoxide in a vacuum desiccator. All nitrophenylhydrazides were deep yellow in color. Other solids took on slight coloration if exposed to the atmosphere too long. This seems to be due to the susceptibility of these substituted hydrazines to slight atmospheric oxidation. Further purification was unnecessary for obtaining correct nitrogen analyses, nor did further purification improve the melting points or optical rotations.

Melting Points.—All melting points were determined by means of a Fisher-Johns melting point apparatus. Corrections were made by the use of several compounds of proper purity and known melting points. A curve was plotted for their measured melting points along with a straight line curve for true melting points, in the usual manner. Substances used were *p*-dichlorobenzene, *m*-dinitrobenzene, benzoic acid, salicylic acid, hippuric acid, and anthracene.

Yields of Arylhydrazides from Listed Reactants.—The reactants and yields for periods of incubation of 0–24 hr (24–48 hr in parentheses) follow (abbreviations for reactants are indicated in Table II; details of the experiments are provided elsewhere in the Experimental Section): HA + P, 0.853 g (0.246 g); BzOC-G + P, 1.370 g (0.223 g); BzOC-L-A + P, 1.576 g (0.0414 g); BzOC-DL-A + P, 1.525 g (0.0203 g); HA + oT, 0.396 g (0.324 g); BzOC-G + oT, 0.821 g (0.314 g); BzOC-L-A + oT, 1.557 g (0.0782 g); BzOC-DL-A + oT, 1.032 g (0.0999 g); HA + mT (see Experimental Section); BzOC-G + mT, 0.619 g (0.105 g); BzOC-L-A + mT, 1.718 g (0.0356 g); BzOC-DL-A + mT, 1.533 g (0.0815 g); HA + pT, 0.654 g (0.223 g); BzOC-G +

pT, 1.256 g (0.247 g); BzOC-L-A + pT, 1.360 g (0.0042 g); BzOC-DL-A + pT, 0.378 g (0.0261 g); HA + oM, 0.674 g (0.254 g); BzOC-G + oM, 0.888 g (0.201 g); BzOC-L-A + oM, 2.067 g (0.0419 g); BzOC-DL-A + oM, 0.864 g (0.0086 g); HA + pM, 0.0523 g (0.0202 g); BzOC-G + pM, 0.209 g (0.0185 g); BzOC-L-A + pM, 0.271 g (0.0312 g); BzOC-DL-A + pM, 0.188 g (0.0467 g); HA + oF, 0.925 g (0.207 g); BzOC-G + oF, 1.495 g (0.160 g); BzOC-L-A + oF, 1.154 g (0.0743 g); BzOC-DL-A + oF, 1.353 g (0.0635 g); HA + mF, 0.363 g (0.143 g); BzOC-G + mF, 0.647 g (0.0769 g); BzOC-L-A + mF, 0.173 g (0.0452 g); BzOC-DL-A + mF, 0.361 g (0.0700 g); HA + pF (see Experimental Section); BzOC-G + pF, 0.163 g (0.0475 g); BzOC-L-A + pF, 0.256 g (0.163 g); HA + oN, 0.132 g (0.000 g); BzOC-G + oN, 0.197 g (0.000 g); BzOC-L-A + oN, 0.205 g (0.000 g); BzOC-DL-A + oN, 0.232 g (0.000 g); HA + mN, 0.293 g (0.0717 g); BzOC-G + mN, 0.518 g (0.0850 g); BzOC-L-A + mN, 0.608 g (0.0558 g); BzOC-DL-A + mN, 0.402 g (0.0658 g); HA + MP, 0.000 g (0.203 g); BzOC-G + MP, 0.206 g (0.198 g); BzOC-L-A MP and BzOC-DL-A + MP (see Experimental Section).

Registry No.—Phenylhydrazine, 100-63-0; *N*-(benzyloxycarbonyl)-DL-alanine, 4132-86-9.

Acknowledgments.—The Research Corp. provided a Frederick Gardner Cottrell grant for purchasing a Rudolph Model 80 high-precision polarimeter and accessories, as well as some chemicals. California State Polytechnic College Institutional Grant No. 233H-264 provided funds for items of equipment, chemicals, and nitrogen analyses. A grant from the Society for the Sigma Xi allowed analyses to be made and chemicals and equipment to be purchased.

Studies on Reactions of Isoprenoids. XIII.¹ The 1,4-Cycloaddition Reactions of Alloocimene with Various Dienophiles

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1,4-Cycloaddition reactions of alloocimene, an isomeric mixture of **1a** and **1b**, with several acetylenic, olefinic, and heterodienophiles were investigated. With cyanoacetylene, alloocimene afforded a 1:1 adduct **2a** and a 1:2 adduct **3**; **3** is regarded as a 1,4 cycloadduct of a 1:1 ene product from **1b** to cyanoacetylene. With dimethyl acetylenedicarboxylate, tetracyanoethylene, *p*-benzoquinone, and 4-phenyl-1,2,4-triazoline-3,5-dione, both **1a** and **1b** gave the corresponding 1,4 adducts, but, with nitrosobenzene, only **1a** reacted to afford two isomeric adducts, **11a** and **12a**, having a different orientation. All the 1,4-cycloaddition reactions proceeded primarily by reaction of **1a** rather than **1b**.

Although 1,4-cycloaddition reactions of alloocimene, 2,6-dimethyl-2,4,6-octatriene, with maleic anhydride² and dialkyl azodicarboxylate³ have been studied extensively, those with other dienophiles have apparently not yet been investigated. As an extension of our study on the 1,4-cycloaddition reactions of myrcene,^{1,4} this paper deals with the reactions of alloocimene with several acetylenic, olefinic, and heterodienophiles of unsymmetrical structure such as cyanoacetylene and nitrosobenzene. Regiospecific properties of the cycloadditions are discussed.

(1) Part XII of this series: T. Sasaki, S. Eguchi, T. Ishii, and H. Yamada, *J. Org. Chem.*, **35**, 4273 (1970).

(2) (a) J. E. Milks and J. E. Lancaster, *ibid.*, **30**, 888 (1965); (b) E. K. von Gustorf and J. Leitich, *Tetrahedron Lett.*, 4689 (1968), and references cited therein.

(3) E. K. von Gustorf, *ibid.*, 4693 (1968).

(4) T. Sasaki, S. Eguchi, and T. Ishii, *J. Org. Chem.*, **34**, 3749 (1969).

Results and Discussion

Reaction Conditions.—The alloocimene used in all the reactions was an isomeric mixture of **1a** and **1b**⁵ in a 57:43 ratio, since the interconversion of **1a** and **1b** by dienophiles has been reported^{2b} and since the separation of **1a** and **1b** requires considerable effort. Reaction conditions, product distribution, and yields as well as the isomer ratios of the recovered alloocimene and the products are summarized in Table I. Reaction temperatures were chosen so as to give the adducts under as mild conditions as possible. The polymerization of alloocimene was not serious under the employed conditions and no polymerization inhibitor was used.

In reactions with acetylenic dienophiles, such as

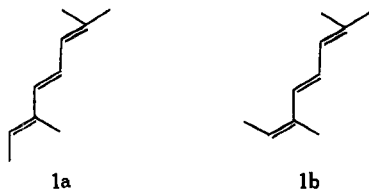
(5) For nomenclature of the two geometrical isomers, **1a** and **1b**, see K. J. Crowley, *ibid.*, **33**, 3679 (1968).

TABLE I
 1,4-CYCLOADDITION REACTIONS OF ALLOOCIMENE (1a AND 1b) WITH VARIOUS DIENOPHILES

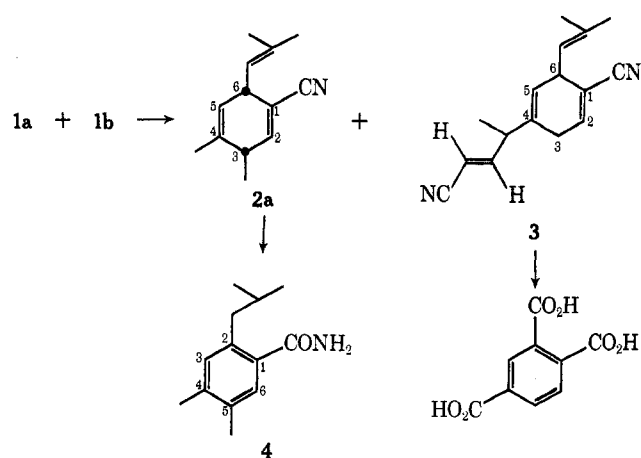
Dienophile ^a (solvent)	Reaction		Products (yield, %) ^b	Ratio of a series to b series ^c	Ratio of recovered 1a to 1b ^d
	Temp, °C	Time, days			
Cyanoacetylene (benzene)	55-60	4	2a (56) + 3 (15)	100:0 ^e	0:100
Dimethyl acetylenedicarboxylate (benzene)	55-60	4	5a + 5b (66)	89:11	0:100
Tetracyanoethylene (benzene)	20-25	1	8a + 8b (87)	60:40 (61:39) ^f	No recovery
<i>p</i> -Benzoquinone (benzene)	Reflux	0.3	9a + 9b (14)	67:33 ^g (72:28) ^f	No recovery
Nitrosobenzene ^h (benzene)	20-25	3	11a (32) + 12a (16)	100:0 ⁱ	23:77
4-Phenyl-1,2,4-triazoline-3,5-dione (<i>p</i> -dioxane)	20-25	1	13a + 13b (79)	75:25 (76:24) ^f	No recovery

^a Equimolar amounts of dienophile and alloocimene were used. ^b Products isolated as a mixture of a and b series. All of the a series were isolable from the mixture. ^c Glpc analysis at 150°. ^d Glpc analysis at 100°. ^e For the 1:1 adduct. ^f Nmr analysis. ^g Glpc at 200° was accompanied by some decomposition. ^h The molar ratio of nitrosobenzene to alloocimene was 1:2. ⁱ For both 11a and 12a.

cyanoacetylene and dimethyl acetylenedicarboxylate, alloocimene gave 71 and 66% yields of the adducts, respectively. With chlorocyanoacetylene, however, it afforded only black polymers even under mild conditions (20–25° for 5 days and 0–5° for 2 weeks). With stronger dienophiles, such as tetracyanoethylene and 4-phenyl-1,2,4-triazoline-3,5-dione, alloocimene gave the corresponding adducts in excellent yields even at 20–25°. By contrast, *p*-benzoquinone afforded only a low yield of adduct which was accompanied by unavoidable side products, for example, considerable amounts of quinhydrone. Only 1a reacted with nitrosobenzene at 20–25° to afford a mixture of adducts which differed in orientation.



Structure Elucidation of Adducts.—Reaction of alloocimene with cyanoacetylene afforded two products which were separated by distillation. The more abundant of them was a 1:1 adduct on the basis of analysis and mass spectrum and was assigned structure 2a. In the nmr spectrum, a doublet of doublets ($J_{2,3} = 4.5$, $J_{2,6} = 1.5$ Hz) at τ 3.40 assignable to $\text{CH}=\text{C}(\text{CN})$ supported the postulated mode of the 1,4 cycloaddition, since the reverse orientation would have led to a coupling between C_1 H and C_5 H in addition to those between C_1 H and C_6 H, and C_1 H and C_3 H. Treatment of 2a with potassium *tert*-butoxide–dimethyl sulfoxide followed by catalytic hydrogenation afforded 2-isobutyl-4,5-dimethylbenzamide (4). The nmr spectrum of 4 at 100 MHz exhibited singlets of two aromatic protons at τ 2.82 and 3.06, indicating a *para* relationship between them.⁶ Since 2a revealed only single peak on glpc and since 1a is more reactive than 1b in 1,4 cycloadditions due to steric inhibition in the *s*-cis form of 1b,^{2b} the C_3 and C_6 substituents of 2a were assumed to be *cis* to each other. However, since the homoallylic coupling constants could not be determined readily, the



conformation of the 1,4-cyclohexadiene system of 2a is not known at present.⁷

The second compound was a 1:2 adduct of the formula $\text{C}_{16}\text{H}_{18}\text{N}_2$. In the nmr spectrum (100 MHz), signals characteristic of a 1,4-cyclohexadiene substituted with cyano, isobutenyl, and 1-methyl-3-cyano-2-propenyl groups at C_1 , C_6 , and C_4 , respectively, appeared at τ 3.44, 4.65, 6.24, and 7.30. Ir absorptions at 1660 and 970 cm^{-1} and the value of $J_{2,3} = 16$ Hz permitted assignment of the *trans* configuration to the 1-methyl-3-cyano-2-propenyl group. The relative position of the substituents was determined by conversion of this isomer to trimellitic acid. Hence its structure was 3.

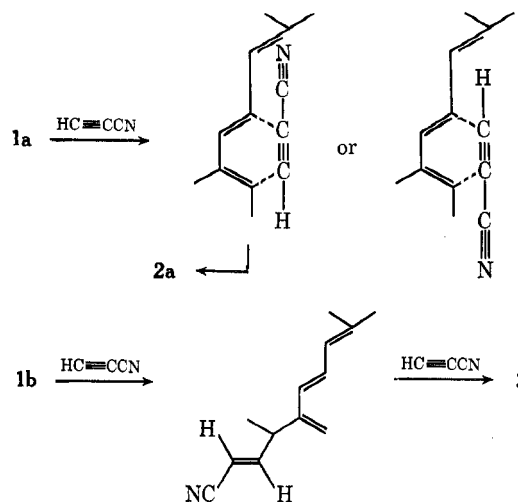
The formation of 3 indicates that 1b reacted initially as an ene component⁸ with a molecule of cyanoacetylene as an enophile to give 1-cyano-3,8-dimethyl-4-methylenenona-1,5,7-triene which reacted further as a diene with a second molecule of cyanoacetylene as a dienophile.

The product of alloocimene and dimethyl acetylenedicarboxylate was a 1:1 adduct whose nmr spectrum was compatible with that of a 1,4 cycloadduct, although the C_6 H signal at τ 6.13 overlapped those of the carbomethoxy protons at τ 6.19 and 6.23, and the C_3 H signal at τ 7.05 appeared as a very broad multiplet which made it difficult to assign stereochemistry. Examination of the recovered alloocimene and the ad-

(6) L. M. Jackman and S. Sternhell, "Application of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed, Pergamon Press, New York, N. Y., 1969, p 306.

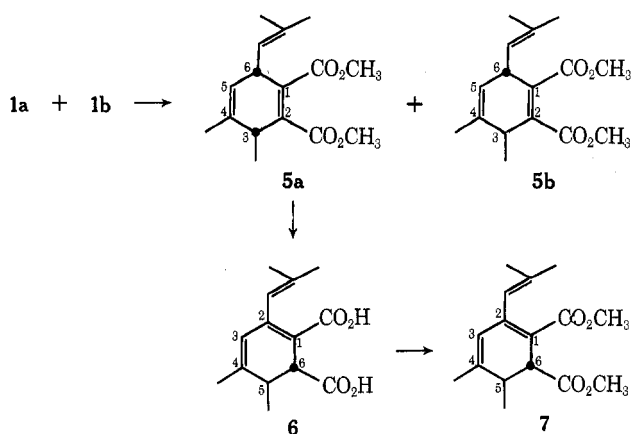
(7) Some conflicting results have recently been reported for simply substituted 1,4-cyclohexadienes. For example, see J. L. Marshall, K. C. Erickson, and T. K. Folsom, *J. Org. Chem.*, **35**, 2038 (1970).

(8) For a review on the ene reaction, see H. M. R. Hoffman, *Angew. Chem. Int. Ed. Engl.*, **8**, 556 (1969).



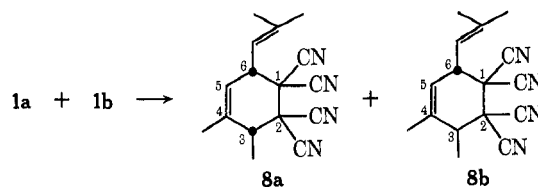
duct revealed that **1b** had remained unreacted, and that the product was a 89:11 mixture of the cis-trans isomers **5a** and **5b**. Pure **5a**, the nmr spectrum of which was practically the same as that of the mixture, was isolated by fractional distillation.

Hydrolysis of **5a** gave a crystalline dicarboxylic acid characterized as **6** by analytical and spectral data; its uv absorption [$\lambda_{\text{max}}^{\text{EtOH}}$ 220 and 303 nm (ϵ 8280 and 6480)] was similar to that of 1,6-dicarboxy-4-methyl-1,3-cyclohexadiene ($\lambda_{\text{max}}^{\text{EtOH}}$ 296 nm).⁹ Brief treatment of **6** with excess diazomethane gave the corresponding dimethyl ester **7** which had nmr signals at τ 7.30 (double q, $J = 7.5$ and 1.5 Hz) and 6.25 (d, $J = 1.5$ Hz) due to C_5 H and C_6 H, respectively. The magnitude of $J_{5,6} = 1.5$ Hz permitted the deduction that the C_5 -methyl group was trans to the C_6 -carboxyl group.¹⁰ Double bond isomerization of 1,2-dicarboxy-1,4-cyclohexadiene to 1,6-dicarboxy-1,3-cyclohexadiene under hydrolysis conditions has been reported.¹¹ Hence structure **5a** could be assigned to the original 1:1 adduct.

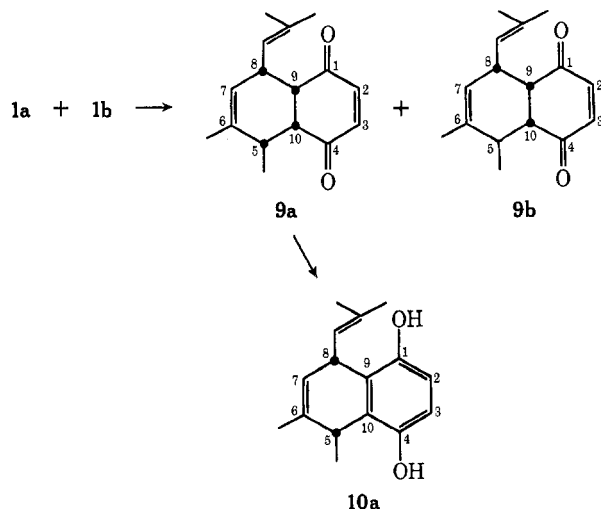


The reaction of alloocimene with tetracyanoethylene proceeded very smoothly even under mild conditions; no alloocimene was recovered. Since glpc analysis revealed the presence of two peaks in a 61:39 ratio and the nmr spectrum had a pair of doublets at τ 8.37 and 8.46 (C_3 methyl) in a ratio of 6:4, the adduct was a

mixture of **8a** and **8b**. The main isomer was isolated in solid form and assigned structure **8a** on the basis of analytical and spectral data (see Experimental Section).



The product from alloocimene and *p*-benzoquinone, $\text{C}_{16}\text{H}_{20}\text{O}_2$, had ir absorptions at 1680, 1650 sh, and 1600 cm^{-1} which suggested the presence of an enedione moiety. The uv spectrum [$\lambda_{\text{max}}^{\text{EtOH}}$ 203 and 286 nm (ϵ 20,800 and 897)] was indicative of the presence of a homocisoid type enedione chromophore.¹² The nmr spectrum of the adduct was very similar to that reported for the maleic anhydride adduct of alloocimene,² but the appearance of the C_5 -methyl protons signals as a pair of doublets at τ 8.80 and 8.88 ($J = 7.5$ Hz) suggested that the adduct was a mixture of **9a** and **9b** in *ca.* 7:3 ratio. Glpc analysis supported this conclusion. The major isomer was isolated in crystalline form and characterized as **9a** on spectral evidence and by its conversion to **10a**. Chromatography of **9a** on an alumina column resulted in the aromatization of the 1,4-cyclohexadiene ring and formation of **10a** which exhibited strong hydroxyl stretching frequency at 3600–3000 cm^{-1} and uv absorption at 285 nm (ϵ 3460) similar to that of hydroquinone.¹³ The nmr spectrum exhibited only one doublet due to the C_5 -methyl protons at τ 8.67, thus supporting the purity of **10a**.



In the reaction with nitrosobenzene, the ratio of recovered **1a** to **1b** was 23:77, *i.e.*, considerably enriched in **1b** compared with the original 57:43 composition, thus indicating that **1a** reacted selectively with the dienophile. Distillation and chromatography resulted in isolation of **11a** and **12a** as oils. Both products were 1:1 adducts. The nmr spectrum of one isomer contained a broad singlet at τ 4.71 and a broad quartet at τ 6.24 attributable to H_6 and H_3 , respectively, since in

(9) (a) G. F. Hennion, J. J. Sheehan, and D. E. Maloney, *J. Amer. Chem. Soc.*, **72**, 3542 (1950); (b) V. F. Kucherov and N. Ya. Grigor'eva, *Dokl. Akad. Nauk SSSR*, **128**, 547 (1959); *Chem. Abstr.*, **54**, 7583d (1960).

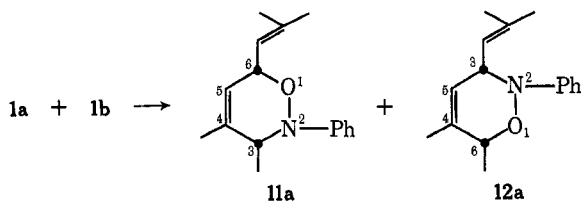
(10) For example, see ref 6, p 281.

(11) N. Ya. Grigor'eva and V. F. Kucherov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 2196 (1962); *Chem. Abstr.*, **58**, 11234h (1963).

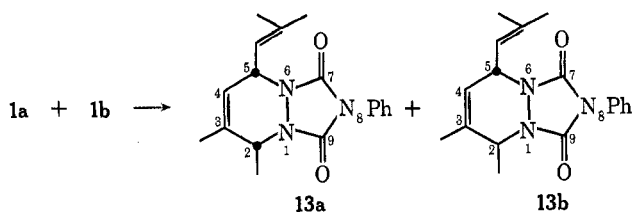
(12) The maximum of 5,6-dimethyl-5,6-dialkylcyclohex-2-ene-1,4-dione appears at 224 nm. The apparent maximum at 203 nm in the spectrum of the adduct is possibly attributable to overlap with an isolated double bond absorption; see A. I. Scott, *Int. Ser. Monogr. Org. Chem.*, **7**, 61 (1964).

(13) $\lambda_{\text{max}}^{\text{EtOH}}$ 295 nm (ϵ 3100): G. L. Schmur, L. A. Cohen, and B. Witkop, *J. Amer. Chem. Soc.*, **81**, 2228 (1959).

the 3,6-dihydro-1,2-oxazine ring system H_6 appears generally at the lower field than H_8 .¹⁴ Hence this isomer was **11a**. The other isomer exhibited a broad quartet at τ 6.25 and a broad singlet at τ 5.12, which were assignable to C_6H and C_3H respectively. In view of the fact that cycloaddition of *p*-chloronitrosobenzene to 1,4-disubstituted 1,3-diene produces predominantly their adduct having a more bulky group at the C_6 position,¹⁵ this isomer was assigned formula **12a**.



No alloocimene was recovered from the reaction of alloocimene with 4-phenyl-1,2,4-triazoline-3,5-dione (Table I). From the product, a mixture of **13a** and **13b** by nmr and glpc analysis, one isomer was isolated after repeated recrystallization and assigned formula **13a** because its nmr spectrum exhibited no signal at τ 8.68 expected from the C_2 -methyl protons of **13b**.



These results indicate clearly that **1a** is a more reactive diene than **1b** where considerable steric hindrance in the *s-cis* form indispensable to 1,4-cycloaddition reaction exists. It should also be noted that **1b** reacted as an ene rather than as a diene with cyanoacetylene to afford an ene adduct which then reacted with a second molecule of cyanoacetylene to give finally the 1:2 adduct **3**.

The formation of **2a** in the 1,4 cycloaddition of **1a** and cyanoacetylene is an interesting example of a reaction where a symmetry-allowed second-order interaction¹⁶ governs the direction of cycloaddition, because the secondary orbital interaction between the 2,3 double bond of **1a** and the cyano group is possible at the transition state to **2a**.

Experimental Section¹⁷

General Procedure for 1,4-Cycloaddition Reactions of Alloocimene.—An equimolar mixture of freshly distilled alloocimene, bp 83–85° (22 mm), n_D^{20} 1.5382, and a dienophile was allowed to

react under conditions given in Table I. Dienophiles such as cyanoacetylene,¹⁸ chlorocycloacetylene,¹⁹ nitrosobenzene,²⁰ and 4-phenyl-1,2,4-triazoline-3,5-dione²¹ were prepared by known methods and others were commercially available.

1-Cyano-3,4-dimethyl-6-isobutenyl-1,4-cyclohexadiene (2a) and 1-Cyano-4-(1-methyl-3-cyano-2-propenyl)-6-isobutenyl-1,4-cyclohexadiene (3).—A mixture of 13.6 g (0.100 mol) of alloocimene and 5.50 g (0.108 mol) of cyanoacetylene in 100 ml of benzene was heated in a sealed tube at 55–60° for 4 days. Products were purified by distillation under reduced pressure to give 10.5 g (56%) of **2a** and 3.47 g (15%) of **3** both as colorless oils. **2a**: bp 92–93° (0.35 mm); n_D^{20} 1.5032; ir (neat) 2924, 2230, 1660, 1630, 1450, 1380, and 835 cm^{-1} ; nmr ($CDCl_3$) τ 3.40 (d, d, $J_{2,3} = 4.5$ Hz, $J_{2,6} = 1.5$ Hz, 1, C_2H), 4.65 (m, 1, C_6H), 5.10 (br d, $J = 12.0$ Hz, 1, $C=CH$), 6.20 (br m, 1, C_6H), 7.33 (br m, 1, C_8H), 8.18 (s, 9, C_4CH_3 and $C(CH_3)_2$), and 8.81 (d, $J = 7.5$ Hz, 3, C_3CH_3); mass spectrum m/e (rel intensity) 187 (0.7), 186 (5.7), 185 (29.5), 171 (84.2), 158 (20.0), 157 (32.0), 146 (21.6), 145 (87.0), 144 (51.0), 131 (100.0), 119 (31.8), 116 (30.7), 91 (19.3), 77 (26.1), and 55 (28.4).

Anal. Calcd for $C_{13}H_{17}N$: C, 83.37; H, 9.15; N, 7.48. Found: C, 83.54; H, 9.29; N, 7.17.

3: bp 175–178° (0.08 mm); n_D^{20} 1.5409; ir (neat) 2924, 2230, 1660, 1628, 970, 860, and 827 cm^{-1} ; nmr ($CDCl_3$, 100 MHz) τ 3.38 (d, d, $J = 6.5$ and 16.0 Hz, 1, $C(CN)=CH$), 3.44 (m, 1, C_2H), 4.65 (m, 1, C_6H), 4.68 (d, d, $J = 16.0$ and 1.5 Hz, 1, $CH(CN)=C$), 5.17 (d, $J = 10.0$ Hz, 1, $C=CH$), 6.24 (m, 1, C_6H), 7.05 (quintet, $J = 6.5$ Hz, 1, CH), 7.30 (m, 2, C_8H), 8.24 (s, 6, $C(CH_3)_2$), and 8.82 (d, $J = 6.5$ Hz, 3, CH_3); mass spectrum m/e (rel intensity) 238 (8.5), 237 (40.0), 236 (28.0), 235 (39.0), 223 (41.0), 195 (58.5), 158 (62.2), 116 (100.0), 91 (23.7), and 53 (65.9).

Anal. Calcd for $C_{16}H_{19}N_2$: C, 80.63; H, 7.61; N, 11.76. Found: C, 80.90; H, 7.60; N, 11.33.

2-Isobutyl-4,5-dimethylbenzamide (4) from 2a.—A mixture of 1.87 g (10.0 mmol) of **2a** and 1.70 g (15.0 mmol) of potassium *tert*-butoxide in 10 ml of dry dimethyl sulfoxide was stirred for 2 weeks at room temperature under nitrogen. The mixture was diluted with water, neutralized with 10% hydrochloric acid, and extracted with ether (five 30-ml portions). The ether extract was washed with 10% aqueous sodium hydroxide and water successively and dried (Na_2SO_4). Removal of ether gave solid residue which was purified on a silica gel column to afford an amide derivative (105 mg). Catalytic hydrogenation of the amide with 10% palladium on charcoal in ethanol gave **4** (95 mg) as crystals from *n*-hexane-dichloromethane: mp 127–128°; ir (KBr) 3375, 3190, 2920, 1645, 1452, 1380, 1230, and 880 cm^{-1} ; nmr ($CDCl_3$, 100 MHz) τ 2.82 (s, 1, C_6H), 3.06 (s, 1, C_3H), 3.76–4.74 (br m, 2, $CONH_2$), 7.36 (d, $J = 7.5$ Hz, 2, Ar CH_2), 7.79 (s, 6, C_4CH_3 and C_5CH_3), 8.14 (m, 1, $CH_2CH(CH_3)_2$), and 9.14 (d, $J = 7.0$ Hz, 6, $CH(CH_3)_2$).

Anal. Calcd for $C_{13}H_{19}NO \cdot \frac{1}{2}H_2O$: C, 72.86; H, 9.41; N, 6.54. Found: C, 72.78; H, 9.55; N, 6.48.

Trimellitic Acid from 3.—A mixture of 0.950 g (3.99 mmol) of **3** and 0.430 g (13.4 mg-atom) of sulfur was heated for 0.5 hr at 205–215°. The resulted dark brown oil was refluxed with 50 ml of 10% aqueous sodium hydroxide for 4 hr. Heating was continued for another 20 hr; during this time 4.00 g (25.3 mmol) of potassium permanganate was added. After decomposition of the excess permanganate with ethanol, the mixture was filtered while still hot. The filtrate was neutralized with concentrated hydrochloric acid and extracted with ether (five 200-ml portions). Work-up gave 0.450 g (53%) of trimellitic acid identified with the superimposable ir spectrum on that of an authentic sample.

1,2-Dimethoxycarbonyl-3,4-dimethyl-6-isobutenyl-1,4-cyclohexadiene (5a).—The reaction of 13.6 g (0.100 mol) of alloocimene with 14.2 g (0.100 mol) of dimethyl acetylenedicarboxylate in 100 ml of benzene gave 18.3 g (66%) of a 89:11 mixture of **5a** and **5b** as an oil, bp 140–142° (0.4 mm), n_D^{20} 1.5040. Redistillation afforded pure **5a**: bp 141–142°; n_D^{20} 1.5041; ir (neat) 2975, 1720, 1642, 1450, 1380, 1265, and 835 cm^{-1} ; uv max (EtOH) 206 and 234 nm inflection (ϵ 18,800 and 7370); nmr ($CDCl_3$) τ 4.65 (m, 1, C_6H), 5.20 (br d, $J = 11.0$ Hz, 1, $C=CH$),

(18) See footnote 18 in ref 4.

(19) See footnote 19 in ref 4.

(20) G. H. Coleman, C. M. McCloskey, and F. A. Stuart, "Organic Syntheses," Collect. Vol. III, Wiley, New York, N. Y., 1955, p 668.

(21) R. C. Cookson, S. S. H. Gilani, and I. D. R. Stevens, *J. Chem. Soc. C*, 1905 (1967).

(14) (a) G. Kresze and J. Firl, *Tetrahedron*, **24**, 1043 (1968); (b) see also ref 1.

(15) G. Kresze and J. Firl, *Tetrahedron Lett.*, 1163 (1965).

(16) R. Hoffmann and R. B. Woodward, *J. Amer. Chem. Soc.*, **87**, 4388 (1965).

(17) Microanalyses were performed with a Perkin-Elmer 240 elemental analyzer. Melting points were determined with a Yanagimoto hot-stage type melting point apparatus and are uncorrected; boiling points are also uncorrected. Ir spectra were obtained with a JASCO IR-S spectrometer and uv spectra with a JASCO ORD/UV5 spectrometer. Nmr spectra were taken with Varian A-60 and/or HA-100 spectrometers using TMS as internal standard, and mass spectra with a JEOL JMS-018G spectrometer at 70 eV. Glpc analyses were performed with a K-23 Hitachi gas chromatograph using a 2-m column packed with silicone SE-30 and/or Apiezon L.

6.13 (br m, 1, C₆ H), 6.19 and 6.23 (s, each 3, 2COOCH₃), 7.05 (br m, 1, C₈ H), 8.27 (s, 9, C₄ CH₃ and C(CH₃)₂), and 8.70 (d, *J* = 7.5 Hz, 3, C₃ CH₃); mass spectrum *m/e* (rel intensity) 278 (39.3), 263 (36.9), 231 (100.0), 219 (30.3), 199 (25.4), 187 (44.3), 159 (48.4), 149 (36.9), 105 (35.2), and 91 (38.5).

Anal. Calcd for C₁₆H₂₂O₄: C, 69.04; H, 7.97. Found: C, 68.77; H, 7.81.

1,6-Dicarboxy-2-isobutenyl-4,5-dimethyl-1,3-cyclohexadiene (6) and Its Dimethyl Ester (7) from 5a.—A suspension of 1.00 g (3.60 mmol) of **5a** in 50 ml of 20% aqueous sodium hydroxide was refluxed for 1 day. The cooled mixture was washed twice with ether and neutralized with 5% sulfuric acid to afford a turbid solution which was extracted with ether (five 100-ml portions). The ether extract was dried (Na₂SO₄) and evaporated to give an oily residue which on crystallization from chloroform-ether afforded 0.370 g (36%) of **6** as colorless prisms: mp 178–181° dec; ir (KBr) 3000–2800, 1665, 1440, 1415, 1380, and 840 cm⁻¹; nmr ((CD₃)₂SO) τ -2.00–0.00 (br m, 2, disappeared on deuteration, 2COOH), 3.61 (m, 1, C₈ H), 4.33 (d, *J* = 1.7 Hz, 1, C=CH), 6.58 (br s, 1, C₆ H), 7.37 (br q, *J* = 7.5 Hz, 1, C₅ H), 8.19 (m, 6, C(CH₃)₂), 8.38 (s, 3, C₄ CH₃), and 9.03 (d, *J* = 7.5 Hz, 3, C₃ CH₃); mass spectrum *m/e* (rel intensity) 250 (38.1), 191 (30.2), 189 (14.3), 187 (23.8), 173 (25.4), 119 (25.4), and 73 (100.0).

Anal. Calcd for C₁₄H₁₈O·2H₂O: C, 58.73; H, 7.75. Found: C, 59.01; H, 8.05.

Treatment of **6** with excess diazomethane in ether at 0–10° for several minutes afforded quantitatively the dimethyl ester **7** as an oil: *n*_D²⁰ 1.5241; ir (neat) 2960, 1715, 1700, 1685 sh, 1635 sh, 1565, 1434, 1378, 1280, 1225, and 873 cm⁻¹; uv max (EtOH) 204 and 295 nm (ϵ 11,300 and 5900); nmr (CDCl₃) τ 3.67 (br s, 1, C₈ H), 4.36 (m, 1, C=CH), 6.25 (d, *J* = 1.5 Hz, 1, C₆ H), 6.31 and 6.41 (s, each 3, 2COOCH₃), 7.30 (d, q, *J* = 1.5 and 7.5 Hz, 1, C₅ H), 8.16 (d, *J* = 1.5 Hz, 6, C(CH₃)₂), 8.35 (s, 3, C₄ CH₃), and 8.98 (d, *J* = 7.5 Hz, C₃ CH₃).

Anal. Calcd for C₁₆H₂₂O₄: C, 69.04; H, 7.97. Found: C, 69.12; H, 7.89.

1,1,2,2-Tetracyano-3,4-dimethyl-6-isobutenyl-4-cyclohexene (8a).—The reaction product from 1.36 g (10.0 mmol) of alloocimene and 1.28 g (10.0 mmol) of tetracyanoethylene was purified by chromatography on a silica gel column eluting with 5% methanol-benzene to give 2.30 g (87%) of a 60:40 mixture of **8a** and **8b** as an oil which solidified on standing. Recrystallization from *n*-hexane-dichloromethane gave **8a** as prisms: mp 67–69°; ir (KBr) 2980, 2920, 2260, 1658, 1445, 1388, and 848 cm⁻¹; nmr (CDCl₃) τ 4.63 (br s, 1, C₆ H), 4.77 (br d, *J* = 10.0 Hz, 1, C=CH), 6.07 (br d, *J* = 10.0 Hz, 1, C₆ H), 6.95 (br, q, *J* = 7.5 Hz, 1, C₅ H), 8.13 (s, 9, C₄ CH₃ and C(CH₃)₂), and 8.37 (d, *J* = 7.5 Hz, 3, C₃ CH₃).

Anal. Calcd for C₁₈H₁₈N₄: C, 72.70; H, 6.10; N, 21.20. Found: C, 72.39; H, 6.12; N, 21.49.

5,6-Dimethyl-8-isobutenyl-5,8,9,10-tetrahydro-1,4-naphthoquinone (9a) and 1,4-Dihydroxy-5,6-dimethyl-8-isobutenyl-5,8-dihydronaphthalene (10a).—The reaction product from 13.6 g (0.100 mol) of alloocimene and 10.8 g (0.100 mol) of *p*-benzoquinone was treated with *n*-hexane in order to remove insoluble quinhydrone and polymers. The soluble portion in *n*-hexane was purified by distillation to give a fraction of bp 150–168° (0.15 mm) which was chromatographed on a silica gel column eluting with chloroform to afford 3.41 g (14%) of ca. 7:3 mixture of **9a** and **9b** as an oil. Recrystallization of the solidified mixture from *n*-hexane-dichloromethane gave **9a** as pale green crystals: mp 81–84°; ir (KBr) 2924, 1680, 1650, 1600, 1443, and 1372 cm⁻¹; nmr (CDCl₃) τ 3.33 (s, 2, C₂ H and C₃ H), 4.72 (br s, 1, C₇ H), 4.84 (m, 1, C=CH), 6.58 (br m, 3, C₈ H, C₉ H, and C₁₀ H), 7.53

(br m, 1, C₅ H), 8.22, 8.34 (s, 6, C(CH₃)₂), 8.43 (d, *J* = 2.0 Hz, 3, C₆ CH₃), and 8.80 (d, *J* = 7.5 Hz, 3, C₅ CH₃).

Anal. Calcd for C₁₆H₂₀O₂: C, 78.65; H, 8.25. Found: C, 78.49; H, 8.18.

Chromatography of **9a** on an alumina column eluting with benzene gave **10a** in 95% yield as needles from *n*-hexane-dichloromethane: mp 104.5–105.5° dec; ir (KBr) 3320, 2970, 2920, 1622, 1487, 1375, 903, 795, and 740 cm⁻¹; nmr (CDCl₃) τ 3.39 (s, 2, C₂ H and C₃ H), 4.42 (br m, 2, 2OH), 4.58 (br d, *J* = 5.0 Hz, 1, C₇ H), 4.99 (br d, *J* = 12.0 Hz, 1, C=CH), 5.77 (br m, 1, C₈ H), 6.55 (br q, *J* = 7.0 Hz, 1, C₅ H), 8.08 (m, 6, C(CH₃)₂), 8.23 (s, 3, C₆ CH₃), and 8.67 (d, *J* = 7.0 Hz, 3, C₅ CH₃).

Anal. Calcd for C₁₆H₂₀O₂: C, 78.65; H, 8.25. Found: C, 78.48; H, 8.20.

2-Phenyl-3,4-dimethyl-6-isobutenyl-3,6-dihydro-1,2-oxazine (11a) and 2-Phenyl-3-isobutenyl-5,6-dimethyl-3,6-dihydro-1,2-oxazine (12a).—The product from 9.20 g (66.7 mmol) of alloocimene and 3.60 g (33.3 mmol) of nitrosobenzene was distilled to give 4.67 g of an oil, bp 86–90° (0.05 mm), which was chromatographed on an alumina (Woelm, neutral, grade I) column eluting with *n*-hexane-benzene to give 2.63 g (32%) of **11a** and 1.31 g (16%) of **12a** both as oils successively. **11a**: *n*_D²⁰ 1.5465; ir (neat) 3030, 2980, 2924, 1660, 1600, 1495, 1372, 755, and 690 cm⁻¹; nmr (CCl₄) τ 2.99 (br m, 5, C₆H₅), 4.71 (br s, 1, C₆ H), 4.93 (br s, 2, C=CH and C₅ H), 6.24 (br q, *J* = 7.0 Hz, 1, C₅H), 8.24 (s, 9, C₄ CH₃ and C(CH₃)₂), and 8.92 (d, *J* = 7.0 Hz, 3, C₃ CH₃); mass spectrum *m/e* (rel intensity) 243 (86.1), 198 (32.8), 137 (98.0), 136 (68.0), 122 (100.0), 121 (59.8), 119 (39.3), 118 (43.4), 107 (67.2), 105 (96.5), 79 (91.8), 77 (75.4), 65 (53.3), 55 (87.7), and 53 (66.4).

Anal. Calcd for C₁₈H₂₁NO: C, 78.97; H, 8.70; N, 5.76. Found: C, 78.49; H, 8.47; N, 6.10.

12a: *n*_D²⁰ 1.5565; ir (neat) 3030, 2980, 2924, 1659, 1600, 1495, 1371, 857, 755, and 690 cm⁻¹; nmr (CCl₄) τ 3.02 (br m, 5, C₆H₅), 4.65 (br s, 2, C=CH and C₄ H), 5.12 (br m, 1, C₃ H), 6.25 (br q, *J* = 7.0 Hz, 1, C₆ H), 8.28 (m, 9, C₄ CH₃ and C(CH₃)₂), and 8.95 (d, *J* = 7.0 Hz, 3, C₃ CH₃); mass spectrum *m/e* (rel intensity) 243 (26.4), 137 (23.6), 136 (92.7), 122 (21.8), 121 (100.0), and 77 (37.3).

Anal. Calcd for C₁₈H₂₁NO: C, 78.97; H, 8.59; N, 5.76. Found: C, 78.73; H, 8.59; N, 5.58.

2,3-Dimethyl-5-isobutenyl-8-phenyl-1,6,8-triazabicyclo[4.3.0]-non-3-ene-7,9-dione (13a).—The product from 2.04 g (15.0 mmol) of alloocimene and 3.50 g (20.0 mmol) of 4-phenyl-1,2,4-triazoline-3,5-dione was purified by chromatography on a silica gel column eluting with chloroform to give 3.68 g (79%) of a 75:25 mixture of **13a** and **13b** as an oil which solidified on standing. Recrystallization from *n*-hexane-dichloromethane afforded **13a** as colorless crystals: mp 100–102.5°; ir (KBr) 3020, 2924, 1767, 1706, 1600, 1505, 1420, 1380, 724, and 685 cm⁻¹; nmr (CDCl₃) τ 2.56 (br m, 5, C₆H₅), 4.66 (s, 1, C₆ H), 4.94 (br s, 2, C=CH and C₄ H), 5.68 (br q, *J* = 7.0 Hz, 1, C₂ H), 8.20 (s, 9, C(CH₃)₂ and C₃ CH₃), and 8.52 (d, *J* = 7.0 Hz, 3, C₂CH₃); mass spectrum *m/e* (rel intensity) 311 (2.1), 168 (43.8), 154 (41.1), 153 (31.5), 149 (24.7), 73 (100.0), and 57 (32.9).

Anal. Calcd for C₁₈H₂₁N₃O₂: C, 69.43; H, 6.80; N, 13.50. Found: C, 69.21; H, 6.75; N, 13.24.

Registry No.—**1a**, 3016-19-1; **1b**, 7216-56-0; **2a**, 28875-58-3; **3**, 28875-59-4; **4**, 28957-66-6; **5a**, 28875-60-7; **6**, 28875-61-8; **7**, 28875-62-9; **8a**, 28875-63-0; **9a**, 28875-64-1; **10a**, 28875-65-2; **11a**, 28875-66-3; **12a**, 28875-67-4; **13a**, 28875-68-5.