synthesized directly from trimethyl borate (IV) and ammonia.[15]

The identity was established by direct comparison with a synthetic sample.

The reaction of borazine and p-nitroaniline proceeded in the same way as in the case of aniline to give hydrogen and N,N'-bis(p-nitrophenyl)triaminoborine.

It appears that this aminoborinylation of primary amines may be a general reaction. The reaction of borazine and ammonia leads to an unstable product which has not been characterized[14,16]; it is likely that a similar aminoborinylation occurs in this reaction also.

Experimental[17]

N,N'-Diphenyltriaminoborine (III).—Optimum conditions were obtained in runs carried out as follows. To a mixture containing 40.3 g. (0.5 mole) of borazine (I) in 150 ml. of dry benzene was added at room temperature and with agitation a total of 279.4 g. (3.0 moles) of aniline at such a rate that 50° was not exceeded. The reaction was accompanied by the evolution of hydrogen. After refluxing for 4 hr., the mixture was cooled to room temperature. The resulting crystals were vacuum-filtered under nitrogen and washed with pure anhydrous benzene; the yield was 220 g. (69.5%). Upon recrystallization from dry benzene, III was obtained as white stout prisms, m.p. 201–202°. The compound tends to decompose gradually upon storage for extended periods of time.

Anal. Calcd. for $C_{12}H_{14}BN_3$: B, 5.13; N, 19.91. Found: B, 5.39; N, 19.81.

N,N'-Bis(p-nitrophenyl)triaminoborine.—A suspension containing 41.4 g. (0.3 mole) of p-nitroaniline in 240 ml. of dry ether was added gradually to a mixture containing 8.0 g. (0.1 mole) of borazine (I) in 30 ml. of dry ether. An analysis of the gas evolved showed this to be hydrogen; no ammonia was detected. After boiling for 3 hr., ether was removed by distillation, 200 ml. of diglyme was added, and the reaction mixture was boiled again for 4 hr. The contents were allowed to come to room temperature and then filtered. The filtrate yielded N,N'-bis(p-nitrophenyl)triaminoborine as a slightly yellowish solid melting at 244–246°. The yield was 17.5 g. (38.7%).

Anal. Calcd. for $C_{12}H_{12}BN_5O_4$: B, 3.59; N, 23.26. Found: B, 3.78; N, 22.99.

Reaction of N,N'-Diphenyltriaminoborine (III) with Methanol. —Upon adding 6.3 g. (0.3 mole) of III to 15 g. of absolute methanol, an immediate reaction set in which was accompanied by a considerable amount of heat. When the vigorous reaction ceased, the contents were kept boiling for 1 hr., during which time the solid reaction product sublimed into the reflux condenser. The crystalline sublimate was recovered by scraping and was identified as trimethoxyborine–ammonia (V); weight 3.6 g. (100% yield). The product was purified by repeated sublimation and was obtained in the form of fine white needles melting at 75–76°. This melting point was not depressed when a sample of this substance was mixed with authentic samples obtained by methods described below.

Anal. Calcd. for $C_3H_{12}BNO_3$: B, 8.95; N, 11.58. Found: B, 8.83; N, 11.31.

Reaction of Borazine (I) with Methanol.—Inasmuch as there are no experimental details given in the original publication[14] mentioning this reaction for the first time, the reaction conditions used in this laboratory may be summarized as follows. To 4.0 g. (0.05 mole) of borazine (I) was added 30 g. of absolute methanol and the mixture was refluxed for 1.5 hr. During this heating period hydrogen gas was evolved and a white crystalline sublimate was trapped in the reflux condenser. The sublimate was identified as trimethoxyborine–ammonia (V) and was obtained in an amount of 14.8 g. (81.5% yield), m.p. 75–76°. Purification was accomplished by resublimation.

Anal. Calcd. for $C_3H_{12}BNO_3$: B, 8.95; N, 11.58. Found: B, 9.03; N, 11.29.

Trimethoxyborine–Ammonia (V) from Trimethyl Borate (IV). —Authentic trimethoxyborine–ammonia (V) was obtained from trimethyl borate and ammonia in anhydrous ether at −80° according to a described method.[15] The substance was obtained in a yield of 83.1%, purified by sublimation, and exhibited a melting point of 75–76°.

Anal. Calcd. for $C_3H_{12}BNO_3$: B, 8.95; N, 11.58. Found: B, 8.93; N, 11.50.

Infrared spectra were recorded with a Perkin-Elmer double-beam spectrophotometer, Model 237. Liquid substances were measured undiluted. To avoid disturbances by absorption bands caused by dispersion media, measurements on solid substances were made in the range of 4000–1350 cm.⁻¹ in "Fluorolube MO-10"[18] and in the range of 1350–625 cm.⁻¹ in Nujol.

(15) J. Goubeau and U. Böhm, Z. anorg. allgem. Chem., **266**, 161 (1951).

(16) A. Stock and E. Pohland, Ber., **59**, 2215 (1926).

(17) Melting points are stated as determined with sealed capillary tubes.

(18) The trade-name "Fluorolube MO-10" has been assigned by the Hooker Chemical Corp., Niagara Falls, N. Y., to an oil being essentially a polymer of chlorotrifluoroethylene.

Synthesis of 1,4-Diolefins[1]

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The thermally initiated reaction of acetylene with olefins containing four to eight carbon atoms was studied in a flow system at 2500 p.s.i. and 350°. The 1:1 addition products obtained were nonconjugated, 1,4-diolefins. For example, butene-1, butene-2, and isobutylene produced 1,4-hexadiene, 3-methyl-1,4-pentadiene, and 2-methyl-1,4-pentadiene, respectively. A large excess of olefin in the reaction mixture was used to facilitate control of temperature and to improve the selectivity of the exothermic reaction. With 10 wt. % acetylene in the feed, the crude effluent from most reactions contained 3–9 wt. % 1,4-diolefins when 50% of the acetylene was converted. This corresponded to an efficiency of about 40% in conversion of both acetylene and olefin feed for the better reactions. The remainder formed heavier liquid products. Most of the diolefin products obtained are in accord with a mechanism involving a pseudo six-membered ring as an intermediate.

The thermally initiated reaction of acetylene with olefins has been studied over a period of many years. Early workers[2] reported the conjugated diolefins, butadiene and isoprene, as reaction products of ethylene

(1) Presented before the Division of Petroleum Chemistry, 148th National Meeting of the American Chemical Society, Chicago, Ill.; Preprints, Vol. 9, No. 3, p. 187 (1964).

(2) Berthelot, Ann. chim. phys., [6] **5**, 136 (1885); Ann. chim., [4] **9**, 469 (1866).

and propylene with acetylene. However, the reactions were done at atmospheric pressure and temperatures up to 500°.

The reaction has now been investigated at higher pressures and lower temperatures. At 2500 p.s.i. and 350°, acetylene reacts with a number of olefins having four to eight carbon atoms to produce nonconjugated 1,4-diolefins as the only 1:1 adduct. Isomerization

TABLE I
OLEFINS TREATED WITH ACETYLENE TO PRODUCE 1,4-DIOLEFINS

Olefin	Diolefins in effluent, wt. %	Diolefin	Isomer as % of diolefins	B.p., °C.
Butene-1	2.8	1,cis-4-Hexadiene	42	64[a]
		1,trans-4-Hexadiene	58	64[a]
cis-Butene-2	0.9	3-Methyl-1,4-pentadiene	100	55[b]
trans-Butene-2	2.3	3-Methyl-1,4-pentadiene	100	...
Isobutylene	4.8	2-Methyl-1,4-pentadiene[c]	100	56[d]
Pentene-2	4.0	3-Methyl-1,4-hexadiene[c]	72	...
		3-Ethyl-1,4-pentadiene[c]	28	79
2-Methylbutene-1	8.0	4-Methyl-1,cis-4-hexadiene[c]	31	91
		4-Methyl-1,trans-4-hexadiene[c]	31	93
		2-Ethyl-1,4-pentadiene[c]	38	87
3-Methylbutene-1	3.0	5-Methyl-1,4-hexadiene[c]	100	92
2-Methylbutene-2	7.8	5-Methyl-1,4-hexadiene[c]	15	...
		2,3-Dimethyl-1,4-pentadiene[c]	77	79
		3,3-Dimethyl-1,4-pentadiene	8	70[e]
Cyclohexene	3.6	3-Vinylcyclohexene[c]	100	128
4-Methylpentene-1	5.0	6-Methyl-1,4-heptadiene[c]	100	109
trans-4-Methylpentene-2	6.1	3,5-Dimethyl-1,4-hexadiene[c]	75	106
		3-Isopropyl-1,4-pentadiene	25	103
2,3-Dimethylbutene-1	7.0	4,5-Dimethyl-1,4-hexadiene[c]	44	117
		2-Isopropyl-1,4-pentadiene	56	105
2,3-Dimethylbutene-2	7.3	4,5-Dimethyl-1,4-hexadiene[c]	26	...
		2,3,3-Trimethyl-1,4-pentadiene[c]	74	102
2,4,4-Trimethylpentene-1	9.0	2-Neopentyl-1,4-pentadiene	49	145
		4,6,6-Trimethyl-1,4-heptadiene	18	145
		I (2,6,6-trimethyl-1,4-heptadiene or 2-t-butyl-1,4-hexadiene)	33	144

[a] Ref. 3 reports 65°. [b] Calcd. from g.l.c. data. Ref. 3 reports 55°. [c] Isolated in 96–100% purity. [d] Ref. 3 reports 56°. [e] R. Ciola and R. L. Burwell, Jr. [*J. Org. Chem.*, **23**, 1063 (1958)] reports 70.2°.

to conjugated diolefins evidently does not take place under these reaction conditions, since none were detected as 1:1 addition products.

Since the addition of olefin to acetylene is exothermic, the reactions were studied with a large excess of olefin to facilitate temperature control, improve selectivity and minimize hazards of high concentrations of acetylene. An olefin–acetylene feed containing approximately 10 wt. % acetylene was suitable.

Experimental

Procedure and Results.—The reactions were carried out in a simple flow system which included a feed cylinder, pump, preheater, 0.5-in.-i.d. stainless steel reactor 29 in. long, pressure-control valve, and product collection system. The olefins used were Phillips Pure Grade. Acetylene was obtained from a commercial welding supply cylinder and was purified only by partial removal of acetone in an ice-cooled trap.

In a typical experiment, the olefin was transferred to the feed cylinder and acetylene was added through an induction line until the solution was saturated at an acetylene partial pressure of about 100 p.s.i. This was usually adjusted to give an analyzed acetylene content of 10 wt. %. The feed was pumped at a rate of 3 liquid volumes of feed per hour per volume of the reactor (3 LHSV) through the reactor maintained at 2500 p.s.i. and at a temperature near 350° adjusted to give about 50% conversion of acetylene. The effluent, reduced to atmospheric pressure, was passed through suitable traps and a Dry Ice cooled scrubber column to recover liquid products. Vapor samples were analyzed as needed to determine acetylene conversion.

The liquid product was fractionated under nitrogen in a Podbielniak Hyper-Cal column to separate the 1:1 addition product either as substantially pure 1,4-diolefins or as simple mixtures of isomers suitable for identification. Where the 1:1 addition product consisted of more than one structural isomer, distribution among the isomers was determined by gas–liquid chromatography.

The reactions of a total of 14 different olefins with acetylene were studied, and these, along with the diolefins obtained as products, are listed in Table I. The weight per cent of diolefins in the effluent product, the per cent of each isomer in the total diolefins, and the boiling point of each isomer are given, and those isomers separated in substantially pure form are indicated.

Reaction Variables.—The exothermic heat of reaction in the addition of olefins to acetylene caused ome difficulty in control of temperature at the desired level, especially with high concentrations of acetylene in the feed. In the reaction of isobutylene with acetylene to produce 2-methyl-1,4-pentadiene, hot spots in the reactor developed readily at temperatures above 355° or with acetylene concentrations above 10 wt. % of the feed. These hot spots resulted in formation of larger amounts of heavy liquid products and deposition of carbon in the reactor. Some data on the effect of acetylene concentration on the reaction with isobutylene are given in Table II, showing a sharp increase in acetylene conversion and formation of heavy liquids at 14 wt. % acetylene in the feed, and a correspondingly lower efficiency to diolefin. Reduction in pressure from 2500 to 1800 p.s.i. reduced the content of 2-methyl-1,4-pentadiene in the total effluent from 4.7 to 3.0 wt. %, in reactions carried out at the same temperature and acetylene conversion.

TABLE II
REACTION OF ISOBUTYLENE WITH ACETYLENE[a]

Acetylene concn., wt. % of feed	Acetylene conversion, %	Acetylene efficiency to diolefins, %	Content of effluent, wt. %	
			Diolefin	Heavies
7.4	39	31	2.7	5
9.8	38	43	4.7	5
14.0	74	15	4.4	15

[a] 355°, 2500 p.s.i., 3 LHSV.

Reactions of the other olefins studied were carried out at 2500 p.s.i. with approximately 10 wt. % acetylene in the feed. Temperature was varied from 340 to 370° as required to give about

TABLE III

N.M.R. SPECTRA OF DIOLEFINS

Diolefin	Molecular formula	Chemical shift (multiplicity, relative intensity)[a]
1-cis-4-Hexadiene	C_6H_{10}	4.42 (m, 1), 4.57 (m, 2), 4.98 (m, 1), 5.00 (m, 1), 7.28 (m, 2), 8.40 (m, 3)
1-trans-4-Hexadiene	C_6H_{10}	4.35 (m, 1), 4.58 (m, 2), 5.00 (m, 1), 5.00 (m, 1), 7.32 (m, 2), 8.40 (m, 3)
2-Methyl-1,4-pentadiene	C_6H_{10}	4.27 (m, 1), 4.90 (m, 1), 4.92 (m, 1), 5.27 (s, 2), 7.28 (d, 2), 8.32 (s, 3)
3-Methyl-1,4-hexadiene	C_7H_{12}	4.38 (m, 1), 4.63 (m, 2), 5.05 (m, 1), 5.13 (m, 1), 7.27 (m, 1), 8.38 (m, 3), 8.97 (d, 3)
4-Methyl-1-cis-4-hexadiene	C_7H_{12}	4.35 (m, 1), 4.75 (m, 1), 5.00 (m, 1), 5.02 (m, 1), 7.28 (d, 2), 8.38 (s, d, 6)
4-Methyl-1-trans-4-hexadiene	C_7H_{12}	4.33 (m, 1), 4.75 (m, 1), 4.98 (m, 1), 5.00 (m, 1), 7.32 (d, 2), 8.45 (s, d, 6)
5-Methyl-1,4-hexadiene	C_7H_{12}	4.30 (m, 1), 4.90 (m, 1), 5.02 (m, 1), 5.03 (m, 1), 7.28 (t, 2), 8.40 (s, 3), 8.30 (s, 3)
2-Ethyl-1,4-pentadiene	C_7H_{12}	4.30 (m, 1), 4.95 (m, 1), 4.97 (m, 1), 5.27 (s, 2), 7.27 (d, 2), 7.98 (q, 2), 9.00 (t, 3)
3-Ethyl-1,4-pentadiene	C_7H_{12}	4.42 (m, 2), 4.97 (m, 2), 4.98 (m, 2), 7.43 (m, 1), 8.57 (m, 2), 9.12 (t, 3)
2,3-Dimethyl-1,4-pentadiene	C_7H_{12}	4.35 (m, 1), 5.00 (m, 1), 5.02 (m, 1), 5.27 (s, 2), 7.23 (m, 1), 8.35 (s, 3) 8.90 (d, 3)
3-Vinylcyclohexene	C_8H_{12}	4.37 (m, 1), 4.42 (m, 2), 5.00 (m, 1), 5.03 (m, 1), 7.25 (m, 1), 8.08 (m, 2), 8.37 (m, 4)
6-Methyl-1,4-heptadiene	C_8H_{14}	4.28 (m, 1), 4.67 (m, 2), 5.00 (m, 1), 5.02 (m, 1), 7.30 (t, 2), 7.78 (m, 1), 9.04 (d, 6)
3,5-Dimethyl-1,4-hexadiene	C_8H_{14}	4.35 (m, 1), 5.05 (m, 1), 5.08 (m, 1), 7.00 (m, 1), 8.40 (s, 3), 8.33 (s, 3), 9.00 (d, 3)
4,5-Dimethyl-1,4-hexadiene	C_8H_{14}	4.42 (m, 1), 5.07 (m, 1); 5.10 (m, 1), 7.27 (d, 2), 8.38 (s, 9)
2-Isopropyl-1,4-pentadiene	C_8H_{14}	4.30 (m, 1), 4.97 (m, 1), 5.00 (m, 1), 5.23 (m, 2), 7.25 (d, 1), 7.78 (m, 2), 8.98 (d, 6)
2,3,3-Trimethyl-1,4-pentadiene	C_8H_{14}	4.28 (m, 1), 5.17 (m, 1), 5.18 (m, 1), 5.23 (s, 2), 8.32 (s, 3), 8.88 (s, 6)
2-Neopentyl-1,4-pentadiene[b]	$C_{10}H_{18}$	4.5–5.4, 7.28 (q, 2), 8.08 (s, 2), 9.08 (s, 9)
4,6,6-Trimethyl-1,4-heptadiene[b]	$C_{10}H_{18}$	4.5–5.4, 7.25 (d, 2), 8.38 (q. 3), 8.93 (s, 9)
2,6,6-Trimethyl-1,4-heptadiene[b] or 2-t-butyl-1,4-hexadiene	$C_{10}H_{18}$	4.5–5.4, 7.42 (d, 2), 8.37 (s, 3), 9.02 (s, 9)

[a] s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Numbers in parentheses are relative intensities, taking the smallest as unity. [b] These compounds were identified in a mixture containing all three. Exact shifts for olefinic protons could not be obtained because of overlapping resonances.

50% conversion of acetylene. In the case of 2,4,4-trimethyl-pentene-1, complete conversion of acetylene was observed at 340° and this reaction also gave the highest content of diolefins in the effluent product.

Product Separation and Identification.—The products were readily separated by fractionation from components other than the 1,4-diolefins obtained by 1:1 addition, and in most cases diolefins of 96–100% purity were prepared. Preparative g.l.c. was used in a few cases and gave good separations.

cis–trans isomers were the most difficult to separate. The first fractions collected in fractionation of 1,4-hexadiene produced from butene-1 were enriched in the trans isomer, indicating that it has a slightly lower boiling point, and a sample containing 90% of this isomer was isolated by preparative g.l.c. In this case the isomers were easily identified by the infrared spectra. The cis–trans isomers of 3-methyl-1,4-hexadiene, 4-methyl-1,4-hexadiene, and 6-methyl-1,4-heptadiene were difficult to separate by distillation, although the isomers of 4-methyl-1,4-hexadiene were separated readily by preparative g.l.c.

The diolefins produced from trans-4-methylpentene-2 and from 2,3-dimethylbutene-1 each consisted of two isomers, one of which was separated in pure form as shown in Table I. The structure of the other isomer was established on the basis of the infrared and/or n.m.r. spectra of a mixture of the two.

Reaction products of 2,4,4-trimethylpentene-1 were separated only partially by distillation. The lowest boiling component I having the structure either 2,6,6-trimethyl-1,4-heptadiene or 2-t-butyl-1,4-hexadiene separated from the other two components by g.l.c. using a polypropylene glycol column. Identification was done on the basis of the infrared and n.m.r. spectra of a sample which contained 55% of I, 35% of 2-neopentyl-1,4-pentadiene, and 10% of 4,6,6-trimethyl-1,4-heptadiene, determined by g.l.c. and from n.m.r. data, and a second sample containing 8, 61, and 31%, respectively, of the same components. Evidently, 2-neopentyl-1,4-pentadiene has a slightly lower boiling point than does 4,6,6-trimethyl-1,4-heptadiene.

The identity of 3-methyl-1,4-pentadiene as the reaction product of either cis- or trans-butene-2 and acetylene was established entirely by gas chromatography data. A single peak corresponding to a 1:1 addition product appeared when either reaction mixture was analyzed. Product peaks from the two reactions had identical retention times on two different columns. A plot of retention time vs. boiling point using 2-methyl-1,4-pentadiene (b.p. 56°) and 1,4-hexadiene (b.p. 65°) for comparison gave a value of 55° for the boiling point. This boiling point and non-identity with the other two C_6 diolefins showed the structure to be that of 3-methyl-1,4-pentadiene.[3]

Carbon–hydrogen analyses were done on all diolefins, either as pure components or as mixtures of isomers. Results obtained were within 0.2% of theory for hydrogen and within 0.3% of theory for carbon, with a few exceptions where deviation was 0.5% of theory for carbon.

As already indicated, individual diolefins were identified by a combination of infrared and n.m.r. spectroscopy. The infrared spectra of terminal olefins have strong absorption bands characteristic of vinyl or branched vinyl groups. No conjugated diolefins were detected. The n.m.r. spectra were obtained on the liquid samples to which a small amount of tetramethylsilane was added as an internal standard. A Varian A-60 spectrometer was used.

Table III lists the chemical shift, multiplicity, and relative intensity for each resonance observed in the n.m.r. spectrum of each compound. The chemical shifts are given in τ-units and were measured from the center of gravity of the resonances. Unresolved fine structure arising from long-range coupling was generally ignored in assigning multiplicity to the resonances.

As can be seen from the table, the n.m.r. spectra had many resonances in common. Most, for example, showed the characteristic ABC pattern of the vinyl group near τ 4.35, 5.00, and 5.05. Most had a resonance near τ 7.3 from protons allylic to both double bonds; only the 3,3-disubstituted compounds lacked this resonance. Most showed a resonance near τ 8.4 from a methyl group attached to a double bond. By making use of the chemical shifts, multiplicities, and intensities, an unambiguous selection of structures from the various possibilities was possible for most of the compounds. A close examination of the table shows that, except for cis–trans isomers, the n.m.r. spectra were distinctive for each compound.

As an example, we can take the data for 2,3-dimethyl-1,4-pentadiene. The τ 4.35, 5.00, and 5.02 resonances show a vinyl group, while the 5.27 resonance, equivalent to two protons, is evidently a methylene group. The τ 7.23 resonance, equivalent to one proton, shows a CH group allylic to both double bonds. The τ 8.35 and 8.90 resonances are evidently methyl groups. The first is at a position expected for a methyl group on a double bond. The second, at a higher field, must be further removed from the double bond and is attached to a CH group, since it occurs as a doublet. Only one structure can be written which completely satisfies the n.m.r. data.

(3) F. D. Rossini, K. S. Pitzer, R. L. Arnett, R. M. Braun, and G. C. Pimetel, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pittsburgh, Pa., 1953, Table 11a.

Discussion

Most of the 1:1 addition products obtained from these reactions may be explained by a mechanism involving formation of a pseudo six-membered ring intermediate. Allylic hydrogen from the olefin is transferred to acetylene, and allylic rearrangement of the double bond in the olefin takes place as shown by the addition of 3-methylbutene-1 to acetylene to produce 5-methyl-1,4-hexadiene.
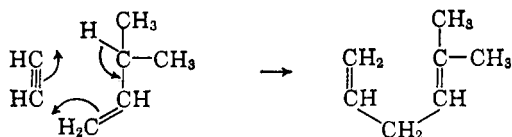
In the addition of 2-methylbutene-2 to acetylene, two products can be formed by this mechanism, depending upon whether addition to acetylene takes place at C-2 (path a) or C-3 (path b) of 2-methylbutene-2. Ex-

3,3-dimethyl-1,4-pentadiene

2,3-dimethyl-1,4-pentadiene
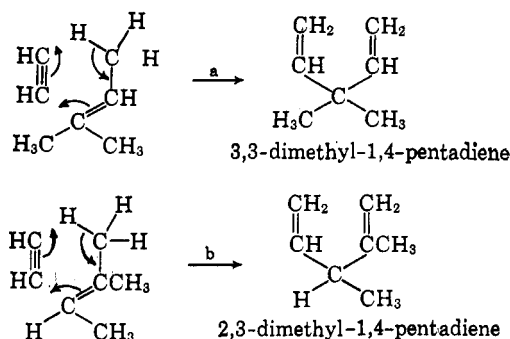
perimentally, it was found that 3,3-dimethyl-1,4-penta-diene, 2,3-dimethyl-1,4-pentadiene, and 5-methyl-1,4-hexadiene are produced in the ratio 0.1:1.0:0.2.

In the reaction of 2,3-dimethylbutene-2 with acety-lene, 2,3,3-trimethyl-1,4-pentadiene can be formed by a cyclic mechanism. This diolefin and 4,5-dimethyl-1,4-hexadiene are obtained. In the reaction of 2,4,4-trimethylpentene-1 with acetylene, 2-neopentyl-1,4-pentadiene and 4,6,6-trimethyl-1,4-heptadiene can be formed by a cyclic mechanism. The three products listed in Table I are obtained.

In reactions where the six-membered cyclic transition state is the actual pathway of the reaction, groups which interfere with the formation of a planar six-membered ring would be expected to have an inhibiting effect upon the reaction. The simplest case is that of

cis-butene-2. The formation of a six-membered ring is severely hindered by a methyl group. Experimentally, it was found that trans-butene-2 produced 2.5 times as much 3-methyl-1,4-pentadiene as did the cis isomer.
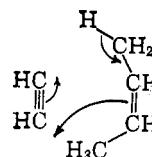
Steric effects also will influence the orientation of branched and internal olefins in the transition state. Some values for allylic hydrogen transfer determined by the ratio of diolefins produced are given in Table IV.

TABLE IV
Per Cent of Allylic Hydrogen Transferred in Reaction
with Acetylene to Produce 1,4-Diolefins

CH_3 (38)

$H_2C=C-CH_2CH_3$
(62)

$H_3CCH=CHCH_2CH_3$
(28)   (72)

     1 2   3 4
$(H_3C)_2C=CHCH_3$
(77)   (8)

CH_3 (56)

$H_2C=C-C(CH_3)_2$
               H
              (44)

$H_3CCH=CHC$ $(CH_3)_2$
(25) | (75)
               H

CH_3 (49)
$H_2C=CCH_2C(CH_3)_3$
(18)

In the case of 2-methylbutene-1, 62% of the reaction occurs by transfer of secondary hydrogen to yield 4-methyl-1,4-hexadiene as the major product. In the case of 2,3-dimethylbutene-1, only 44% of reaction occurs by transfer of tertiary hydrogen, compared to 56% transfer of primary hydrogen of the methyl group with formation of a terminal double bond and production of 2-isopropyl-1,4-pentadiene as the major product.

In the case of 2-methylbutene-2, hydrogen on different methyl groups reacts at different rates. Allowing for a statistical effect of two, hydrogen on C-1 undergoes transfer five times as fast as hydrogen on C-4.