The Thermal Rearrangement of 1-Alken-5-ynes and 1,2,5-Alkatrienes[1]

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Abstract: 1-Alken-5-ynes undergo a reversible Cope-type rearrangement at 340° to give 1,2,5-alkatrienes which, in turn, undergo cyclization to 3- and 4-methylenecyclopentenes. The effect of methyl substituents is reported, and possible mechanisms are discussed.

Recent studies have revealed interesting thermal rearrangements of certain alkenynes and alkadiynes. For example, 1-methylene-2-vinylcyclopentane (**2**) arises from rearrangement of 6-octen-1-yne (**1**) at 400°, and 3,4-dimethylenecyclobutene (**4a**) is formed from 1,5-hexadiyne (**3a**) at 335°.[2] Methyl-substituted dimethylenecyclobutenes **4b** and **4c** are formed from 1,5-heptadiyne (**3b**) and 2,6-octadiyne (**3c**), respectively. The methyl groups retard the cyclization reactions significantly. Stereospecificity in the rotational motion involved in the formation of the exocyclic groups was demonstrated by the conversion of *meso*-3,4-dimethyl-1,5-hexadiyne (**5**) to **6** and *rac*-3,4-dimethyl-1,5-hexadiyne (**7**) to **8**.[3]

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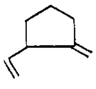

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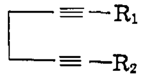

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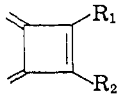
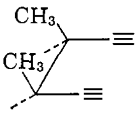


4a, $R_1 = R_2 = H$
b, $R_1 = CH_3$; $R_2 = H$
c, $R_1 = R_2 = CH_3$



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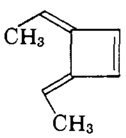

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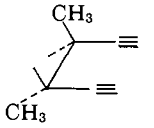

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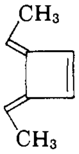

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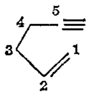
It was of interest to extend these studies to the analogous 1-alken-5-ynes. At the outset, it was anticipated that a simple Cope rearrangement might occur because models indicated a suitable geometry for this type of intramolecular reorganization. The infrared spectrum of the material obtained by heating 1-hexen-5-yne (**9**) at 340° did indeed exhibit absorption characteristic of a terminal allene, but vpc analysis showed the presence of three compounds in addition to starting material. One of these was shown to be the allene **10** by evidence presented below. The proportion of the other compounds in the reaction mixture increased when the contact time was lengthened, or when the reaction temperature was raised to 385°. At the same time, the fraction of **10** passed through a maximum and declined with increasingly drastic conditions.



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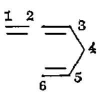

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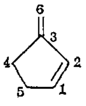

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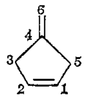

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Separation of the three products was achieved by preparative vpc, and the fractions (i, ii, and iii) were shown to be homogeneous by analytical vpc.

The infrared spectrum of i agreed with that reported for 1,2,5-hexatriene (**10**),[4] and the structure was confirmed by the nmr spectrum, which consisted of a two-proton multiplet at τ 7.25 (H-4), a two-proton multiplet at 5.36 (H-1), a three-proton multiplet at 4.95 (H-3 and H-6), and a one-proton multiplet at 4.12 (H-5). The multiplet at τ 5.36 resembled very closely the signal assigned to the terminal allenic protons in 1,2-pentadiene.[5] Coupling constants obtained by a first-order treatment of the multiplet at τ 4.12 are: $J_{4,5} = 6.4$ cps, $J_{5,6(cis)} = 9.5$ cps, and $J_{5,6(trans)} = 17.5$ cps.

Fraction ii was shown to be 3-methylenecyclopentene (**11**) by comparison of spectral properties with those reported for this compound.[6] Intense absorption occurred in the ultraviolet spectrum at 233 mμ (ε 15,600), and characteristic infrared bands occurred at 6.18, 6.25 (conjugated double bond), and 11.70 μ ($R_2C{=}CH_2$). In the nmr spectrum multiplets appeared at τ 7.52 (H-4, H-5), 3.90 (H-1, H-2), and 5.24 (H-6), with intensities in the ratio 2:1:1. Hydrogenation over platinum oxide gave methylcyclopentane, identified by comparison with an authentic sample.

Fraction iii was identified as 4-methylenecyclopentene (**12**) on the basis of spectroscopic properties and the formation of methylcyclopentane upon hydrogenation. The ultraviolet spectrum showed only end absorption, whereas in the infrared spectrum characteristic bands appeared at 6.04 ($>C{=}C<$), 11.40 ($R_2C{=}CH_2$), and 14.86 μ (*cis*-CH=CH–). The nmr spectrum contained a triplet of triplets at τ 6.98 (H-3, H-5), a pentuplet of triplets at 5.04 (H-6), and a heptuplet at 4.30 (H-1, H-2), with relative intensities 2:1:1. Coupling constants obtained by first-order treatment were $J_{5,6} = 2.5$ cps and $J_{1,6} = J_{1,5} = 0.7$ cps. The distribution of products formed under varying conditions is summarized in Table I.

The behavior of 1-hepten-5-yne (**13**) was similar to that of **9**, although the over-all rate of rearrangement

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[1] This work was supported by the National Science Foundation (Grant No. GP4989).

[2] W. D. Huntsman and R. P. Hall, *J. Org. Chem.*, 27, 1988 (1962); W. D. Huntsman and H. J. Wristers, *J. Am. Chem. Soc.*, **85**, 3308 (1963).

[3] W. D. Huntsman and H. J. Wristers, *J. Am. Chem. Soc.*, in press.

[4] G. Peiffer, *Bull. Soc. Chim. France*, 777 (1962); L. Groizeleau-Miginiac, *Compt. Rend.*, **248**, 1190 (1959).

[5] Catalog of Nuclear Magnetic Resonance Spectral Data, Serial No. 467. American Petroleum Institute Research Project 44, Texas A&M University, College Station, Texas.

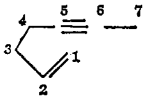
[6] I. N. Narzarov and V. N. Kuznelsov, *J. Gen. Chem. USSR*, **29**, 754 (1959); D. M. Lemal and K. S. Shim, *Tetrahedron Letters*, 3231 (1964).

Table I. Product Distribution from Thermal Rearrangements

Reactant	1-Hexene-5-yne (**9**)				1-Hepten-5-yne (**13**)				2-Methyl-1-hexen-5-yne (**17**)			5-Methyl-1,2-5-hexatriene (**18**)		
Temp, °C	340	340	340	385	340	340	340	385	340	340	340	340	340	340
Contact time, sec	62	130	150	62	63	130	158	63	36	63	158	36	63	158
Product,[a] %														
Alkenyne	29	24	20	10	79	73	63	32	21	22	12	21	19	12
Alkatriene	65	62	50	22	16	16	14	8	67	60	41	66	61	40
Nonconjugated cyclic	2	6	13	30	2	5	10	26	5	8	21	6	9	22
Conjugated cyclic	3	8	17	38	3	6	13	35	7	10	26	8	11	26

[a] Alkenyne refers to 1-alken-5-ynes; alkatriene refers to 1,2,5-hexatrienes; nonconjugated cyclic refers to 4-methylenecyclopentenes; and conjugated cyclic refers to 3-methylenecyclopentenes. Structures of specific products are given in the text. Analyses were made by vpc, and figures cited are the average values of duplicate determinations.

was significantly lower (see Table I). Three products were formed, separated by preparative vpc, and identified as 3-methyl-1,2,5-hexatriene (**14**), 2-methyl-3-methylenecyclopentene (**15**), and 3-methyl-4-methylenecyclopentene (**16**). Assignment of structure **14** rests on the following properties. Absorption bands are present in the infrared spectrum at 5.12 and 11.82 ($>C{=}C{=}CH_2$), and 6.12, 10.10, and 10.98 μ ($RCH{=}CH_2$). The nmr spectrum consists of a triplet (with additional fine splitting) at τ 8.35 (H-7), a multiplet at 7.33 (H-4), a sextuplet at 5.46 (H-1), a multiplet extending from 4.8 to 5.2 (H-6), and a multiplet at 4.20 (H-5), with intensities 3:2:2:2:1. Coupling constants are: $J_{1,7} = J_{1,4} =$ 3.0 cps, $J_{4,5} =$ 6.5 cps, $J_{5,6(cis)} =$ 9.0 cps, and $J_{5,6(trans)} =$ 17.5 cps. Hydrogenation over platinum oxide gave 3-methylhexane, identified by comparison with an authentic sample.



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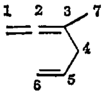

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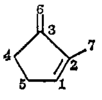

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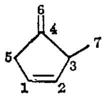

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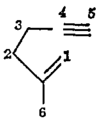
The ultraviolet spectrum of **15** contains a strong absorption band at 238 mμ (ϵ 10,900), and characteristic bands occur in the infrared spectrum at 6.14, 6.18 (conjugated double bond), 7.25 (CH_3), 11.68 ($R_2C{=}CH_2$), and 11.95 μ ($R_2C{=}CHR$). The nmr spectrum exhibits multiplets at τ 8.26 (H-7), 7.52 (H-4, H-5), 5.25 (H-6), and 4.15 (H-1), with relative areas 3:4:2:1. Hydrogenation over platinum oxide gave a mixture o- approximately equal amounts of *cis*- and *trans*-1,2f dimethylcyclopentanes which were separated by preparative vpc and identified by comparison of infrared spectra with the reported spectra.[7]

The nonconjugated isomer **16** shows only end absorption in the ultraviolet region and exhibits infrared bands at 6.03 ($>C{=}C<$), 7.30 (CH_3), 11.39 ($R_2C{=}CH_2$), and 14.24 μ (*cis*-$CH{=}CH$). Present in the nmr spectrum are a doublet at τ 8.88 (H-7), a triplet at 6.93 (H-5) superimposed on a multiplet (H-3), a multiplet at 4.33 (H-1, H-2), and a singlet at 5.07 (H-6). Hydrogenation afforded *cis*- and *trans*-1,2-dimethylcyclopentane in a ratio of approximately 2:1.

Analogous behavior was observed for 2-methyl-1-hexen-5-yne (**17**). The products were identified as 5-methyl-1,2,5-hexatriene (**18**), 5-methyl-3-methylenecyclopentene (**19**), and 1-methyl-4-methylenecyclopentene (**20**).



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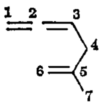

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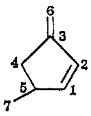

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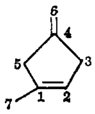

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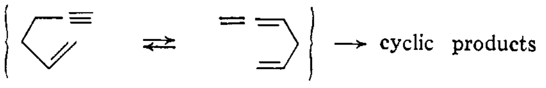
5-Methyl-1,2,5-hexatriene (**18**) was identified by comparison with a sample synthesized by another route. The ultraviolet and infrared spectra of **19** corresponded to those reported for 5-methyl-3-methylenecyclopentene, and confirmation of the structure was provided by the nmr spectrum which contained a doublet at τ 8.95 (H-7), a complex pattern from 7.05 to 8.17 (H-4, H-5), and multiplets at 5.28 (H-6) and 4.01 (H-1, H-2), with relative intensities 3:3:2:2. In the ultraviolet region, **20** shows only end absorption, whereas in the infrared region characteristic absorption occurs at 6.00 and 6.08 ($>C{=}C<$), 7.25 (CH_3), 11.35 ($R_2C{=}CH_2$), and 12.72 μ ($R_2C{=}CHR$). Multiplets are present in the nmr spectrum at τ 8.29 (H-7), 7.03 (H-3, H-5), 5.13 (H-6), and 4.72 (H-2), with intensity ratios 3:4:2:1.

Reversibility of the alkenyne–alkatriene reaction was demonstrated in two cases. 1,2,5-Hexatriene, isolated by preparative vpc from a reaction mixture obtained by thermal rearrangement of 1-hexen-5-yne, was heated briefly at 350° in a static-reaction vessel which was attached to a high-vacuum line. The presence of 1-hexen-5-yne in the product was demonstrated by vpc and infrared spectroscopy.

In the other experiment, pyrolysis of **18** gave a product mixture from which **17** was isolated by preparative vpc and identified by comparison with an authentic sample.

Although it is not established rigorously, it seems highly likely that the cyclization reaction is essentially irreversible. A plot of mole per cent (**11** + **12**) *vs.* per cent reaction (including experiments carried out at 340 and 385°) appears to be headed for 100% conversion to cyclic products.

Thus the reaction may be formulated as a reversible isomerization and a concurrent irreversible cyclization.



There remains the question of whether the alkenyne, or the alkatriene, or both, are precursors of the cyclic products. A plot of per cent cyclic products *vs.* per cent reaction for 1-hepten-5-yne (see Figure 1) approaches the origin with zero, or very nearly zero, slope. This signifies that the formation of cyclic products from 1-hepten-5-yne, if it occurs at all, must be much slower than from 3-methyl-1,2,5-hexatriene. This conclusion is consistent with the behavior observed for other

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(7) Catalog of Infrared Spectral Data, Serial No. 346 and 347, American Petroleum Institute Research Project 44, Texas A&M University, College Station, Texas.

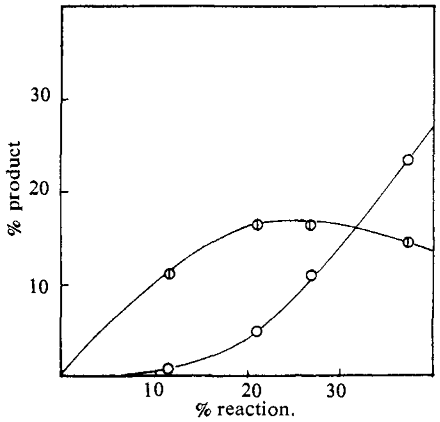
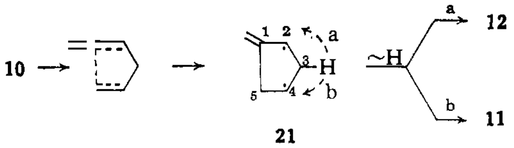


Figure 1. Product distribution from thermal rearrangement of 1-hepten-5-yne at 340°: ⦶, 3-methyl-1,2,5-hexatriene; ○, total cyclic products, 2-methyl-3-methylenecyclopentene and 3-methyl-4-methylenecyclopentene.

allenes.[8,9] Models also indicate that less reorganization is required for cyclization of the alkatrienes than for the alkenynes.

Comparison of product distribution from 1-hepten-5-yne (**13**) with that from 1-hexen-5-yne (**9**) (Table I) reveals an interesting effect brought about by the methyl group in **13**: whereas formation of alkatriene is retarded, the rate of formation of cyclic products is increased significantly. Retardation in the first step is most likely steric in origin, although stabilization of the ground state due to electron release to the more electronegative sp-hydridized carbon may also be a factor. In any event, it appears that this step proceeds by a concerted mechanism with a transition state having little radical character. Enhancement of cyclization, on the other hand, is rationalized most readily as being due to radical stabilization by the methyl group. The mechanism illustrated in the following scheme embodies this feature, and is also consistent with the finding that preferential attack occurs at the central allenic carbon in thermal reactions.[8,9] In the case of 1-hepten-5-yne,



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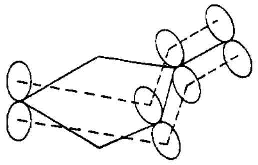
a methyl group, present at position 2 in **21**, would increase the stability of the radical, and presumably the transition state leading to this intermediate.

A number of rotational motions must occur during cyclization, of which one of the most conspicuous is that of the exocyclic carbon, where a net rotation of 90° is required. Allylic stabilization should become significant as this rotation progresses, and extended delocalization as depicted in **22** may also be significant.



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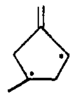
In the case of **17**, since the methyl group is removed from the reaction site and the hybridization of the carbon at position 2 is not significantly different in the ground state and the transition state, the rearrangement of **17** to **18** should not be retarded by the methyl group. This is borne out by the experimental results summarized in Table I, where it is seen that the isomerization of **17** is even somewhat faster than that of 1-hexen-5-yne itself. In fact, the close correspondence between the composition of products from **17** and those from **18**, even at very short contact times, points to a very rapid interconversion of **17** and **18**.

The diradical **23** formed from **18** should be stabilized



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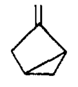
by the methyl group, and an enhanced rate of cyclization would be anticipated. Results presented in Table I confirm this expectation.

In each case the amount of conjugated cyclic diene formed exceeded the nonconjugated isomer, the ratio being in the range 1.2–1.4 for the various compounds. From the standpoint of product stabilities, one would expect the smallest ratio in the case of **19** and **20**, and this appears to be the case, but the differences are too small to permit a definite conclusion.

Absence of high-field absorption in the nmr spectra of the products indicated the absence of products with the bicyclo[2.1.0]pentane skeleton, *e.g.*, **24**. This is



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not unexpected since it has been shown that bicyclopentane rearranges to cyclopentene at a significant rate at 291°.[10] Compounds with this skeleton, if formed, would have a short lifetime at the temperatures employed in this study. Furthermore, it is doubtful whether the diradical **21** can undergo ring closure, even at lower temperatures. Calculations indicate that ring closure of the trimethylene diradical should occur in a conrotatory sense.[11] This type of closure is not possible in **21** without disruption of the C_5 ring.

Experimental Section[12]

Starting Materials. 1-Hexen-5-yne. The procedure of Sondheimer, *et al.*,[13] was followed except that an excess of sodium

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[8] L. Skattebøl and S. Solomon, *J. Am. Chem. Soc.*, **87**, 4506 (1965).

[9] K. G. Untch and D. J. Martin, *ibid.*, **87**, 4501 (1965).

[10] M. L. Halberstadt and J. P. Chesick, *ibid.*, **84**, 2688 (1962).

[11] R. Hoffmann, Abstract of Papers presented at the 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966, p 109-K.

[12] Microanalyses were performed by Mrs. J. De Boer of this department, or by Galbraith Laboratories, Knoxville, Tenn. Infrared spectra were determined with a Perkin-Elmer 237G spectrophotometer. Lists of absorption bands for compounds include those of moderate or greater intensity when measured as a liquid film in a 0.03-mm cell. Ultraviolet spectra were measured with a Cary Model 14 spectrophotometer, and nmr spectra were determined with a Varian A-60 spectrometer with carbon tetrachloride as solvent, and tetramethylsilane as internal standard. Analytical vpc determinations were performed on an F and M 720 chromatograph using these columns: No. 1, 3 m, 20% LAC-446 on Chromosorb WAW; No. 2, 3 m, 40% β,β'-oxydipropionitrile on Columpak; No. 3, 6 m, 30% LAC-728 on Diatoport W; No. 4, 4 m, 30% Apiezon L on Diatoport W. Preparative scale separations were performed on a Wilkens–Anderson A700 Autoprep with these columns: No. 5, 3 m, 40% β,β'-oxydipropionitrile on Celite; No. 6, 3 m, 30%

amide was avoided. This precaution minimized the formation of 3-hexen-1-yne which these authors observed. The product was purified by preparative vpc on column 6 at 80°, and had these properties: bp 68.0–68.5°, $n^{25}\mathrm{D}$ 1.4167 (lit.[13] bp 70–71°, $n^{27}\mathrm{D}$ 1.4180). Infrared bands coincided with reported values; nmr: multiplets at τ 8.15 (1 H), 7.79 (4 H), 4.97 (2 H), and 4.03 (1 H); $J_{2,3} = 6$ cps, $J_{1,2cis} = 9.5$ cps, and $J_{1,2trans} = 17.5$ cps.

1-Hepten-5-yne. Following the procedure described for the preparation of 1-hexen-5-yne, 60.5 g (0.25 mole) of 1,2-dibromo-5-hexene was treated with sodium amide in liquid ammonia prepared from 19.6 g of sodium (0.85 g-atom) and 500 ml of liquid ammonia. The mixture was stirred for 1 hr at $-33°$ and then cooled with a Dry Ice–acetone bath. Methyl iodide, 54.0 g (0.38 mole), was added dropwise during 45 min, the bath was removed, and the mixture was stirred 2 hr. The mixture was allowed to stand overnight, during which time the ammonia evaporated. Ether, 200 ml, was added followed by the dropwise addition of 200 ml of ice water, and the layers were separated. The aqueous layer was washed with three 75-ml portions of ether, and the combined extracts were washed successively with 25-ml portions of 5% sulfuric acid, water, 5% sodium bicarbonate, water, and saturated salt solution. The ether solution was dried over magnesium sulfate, and the ether was removed by distillation through a 50-cm Fenske column. The residue was distilled under reduced pressure into a trap cooled in Dry Ice–acetone, and the distillate (12.1 g, 51.5% yield) was purified by preparative vpc on column 6 at 105°. The material exhibited these properties: bp 109–110°; $n^{25}\mathrm{D}$ 1.4373; infrared λ_{max} 3.28, 3.39, 3.46, 3.53, 6.11, 6.97, 7.08, 7.52, 8.01, 10.11, and 11.00 μ; nmr multiplets at τ 8.28 (3 H), 7.83 (4 H), 5.02 (2 H), and 4.22 (1 H); $J_{2,3} = 6.0$ cps, $J_{1,2cis} = 9.5$ cps, and $J_{1,2trans} = 17.5$ cps.

5-Methyl-1,2,5-hexatriene. Propargylmagnesium bromide was prepared by the dropwise addition of 23.0 g (0.19 mole) of propargyl bromide in 25 ml of anhydrous ether to 4.6 g (0.19 g-atom) of magnesium in 75 ml of anhydrous ether, and activated with 0.1 g of mercuric chloride. The reaction mixture was maintained at 5° during this addition and the following one. Stirring was continued for 1 hr after the addition was complete. Cuprous chloride (0.1 g) was added, followed by the dropwise addition over a period of 1 hr of 18.0 g (0.20 mole) of β-methylallyl chloride in 30 ml of anhydrous ether. Stirring was continued, and the temperature was maintained at 5° for 2 hr after the addition was complete.[14] The mixture was allowed to stand overnight at room temperature and then was refluxed for 1 hr and poured into a solution of 11 g of ammonium chloride in 50 ml of water. The aqueous layer was acidified and extracted with ether, and the combined ether solution was washed with water, 5% sodium bicarbonate, and saturated sodium chloride. The solution was dried over calcium sulfate and the ether removed through a 50-cm Fenske column. The residue was distilled under reduced pressure and purified by preparative vpc on column 8 at 98°. The hydrocarbon obtained, 10.5 g (58% yield), had $n^{25}\mathrm{D}$ 1.4540 and exhibited infrared bands at 3.26, 3.38, 3.41, 3.45, 5.12, 6.05, 6.95, 7.27, 7.88, 8.18, 9.72, 10.04, 11.20, and 11.85 μ. Multiplets were present in the nmr spectrum at τ 8.28 (3 H), 7.33 (2 H), 5.52–5.33 (4 H), and 4.97 (1 H).

Anal. Calcd for C_7H_{10}: C, 89.29; H, 10.71. Found: C, 89.13; H, 10.68.

Ethyl β-Morpholinocrotonate. This compound was prepared in 77% yield by the procedure previously reported,[15] bp 109–114 (<0.5 mm), $n^{25}\mathrm{D}$ 1.5316 (lit.[15] bp 120–124 (0.5 mm), $n^{23.5}\mathrm{D}$ 1.5162).

Anal. Calcd for $C_{10}H_{17}O_3N$: C, 60.28, H, 8.60; N, 7.03. Found: C, 60.36; H, 8.34; N, 7.25.

The infrared spectrum of this compound contains these bands (in CCl_4): 3.38, 3.44, 3.47, 3.51, 5.91, 6.30, 6.93, 7.12, 7.30, 7.47, 7.65, 7.85, 8.00, 8.75, 8.97, 9.13, 9.45, 9.79, and 10.00 μ; the nmr spectrum contains a triplet at τ 7.97 (3 H, $J = 7.0$ cps), a singlet at 7.67 (3 H), an A_2B_2 pattern at 6.60 (8 H), and a quartet at 5.32 (1 H).

Ethyl Propargylacetoacetate. This ester was obtained in 65% yield by the alkylation of ethyl β-morpholinocrotonate with propargyl bromide, according to the general procedure of Eglington and Whiting.[16] The product had bp 56–59° (<0.5 mm), $n^{25}\mathrm{D}$ 1.4439 (lit.[16] bp 48–49 (0.05 mm), $n^{24}\mathrm{D}$ 1.4450).

5-Hexyn-2-one. From 87.0 g of ethyl propargylacetoacetate, treated according to the procedure described,[17] there was obtained 32 g (65% yield) of 5-hexyn-2-one, bp 85–86° (85 mm), $n^{25}\mathrm{D}$ 1.4332 (lit.[17] bp 149 (760), $n^{20}\mathrm{D}$ 1.4366).

2-Methyl-1-hexen-5-yne. A Wittig reagent was prepared from 35.7 g (0.1 mole) of methyltriphenylphosphonium bromide and 65 ml of 1.46 *N* butyllithium in ether according to the procedure described.[18] To this was added 9.6 g (0.1 mole) of 5-hexyne-2-one, and the product was processed in the customary manner.[18] Analysis by vpc revealed that the product was contaminated with a substantial amount of benzene. Removal of the benzene was accomplished, with considerable loss of product, by preparative vpc on column 9 at 120°, and there was obtained 0.5 g of 2-methyl-1-hexen-5-yne, $n^{25}\mathrm{D}$ 1.4290; infrared bands at 3.05, 3.27, 3.38, 3.43, 3.45, 3.52, 4.72, 6.07, 6.92, 7.27, 7.46, 7.83, 7.99. 8.19, 11.20, and 15.5 μ. The nmr spectrum consisted of a distorted triplet at τ 8.27 (3 H), a multiplet at 8.18 (1 H), a broad singlet at 7.77 (4 H), and a multiplet at 5.27 (2 H).

Anal. Calcd for C_7H_{10}: C, 89.29; H, 10.71. Found: C, 89.07; H, 10.94.

Thermal Rearrangement Reactions. Apparatus. The thermal rearrangements were conducted in a flow system of the type described previously.[3] The vaporizing chamber was constructed of Pyrex tubing 1.5 cm i.d. × 25 cm long. The reaction chamber was constructed of Pyrex tubing 2.5 cm i.d. × 44 cm long with a 1.0 × 29 cm inlet tube and a 1.0 × 30 cm outlet tube. The reactor volume was 145 ml. A thermocouple well extended axially to a depth of 96 cm, and the temperature was continuously monitored by iron–constantan thermocouples at depths of 28, 31, 54, and 76 cm and recorded by a Honeywell-Brown Electronik multipoint recorder. "Pre-purified" nitrogen (Matheson) was used as the carrier gas, and the contact time was adjusted by regulating the nitrogen flow rate, which was measured with a soap-film flowmeter.

Reactants were added to the vaporizer by a constant-rate, motor-driven syringe. The vaporizer temperature was maintained at 125–150°. A trap attached to the outlet tube from the reactor and immersed in a Dry–Ice acetone bath served as product receiver.

Typical experiments which were conducted for the purpose of isolating products are described in the text that follows. Additional experiments are summarized in Table I.

1-Hexen-5-yne. Preliminary experiments demonstrated the formation of three products for 1-hexen-5-yne over the temperature range 350–385°. Gas chromatographic analysis indicated that the formation of two of the products (designated fractions ii and iii below) was optimized by using long contact times whereas the third one (designated fraction i) was favored by short times. For preparative experiments designed for isolation of ii and iii, the reactions were carried out at 385° with a nitrogen flow of 30 ml/min; for those designed for isolation of i, the flow rate was increased to 77 ml/min. Preparative vpc separations were performed on column 8 at 77°.

From 0.85 g of hexenyne (385°, 77 cc of N_2/min) there was obtained 0.65 g of product which, by analytical vpc, contained 32% of fraction i. This fraction was isolated; $n^{25}\mathrm{D}$ 1.4487. The infrared spectrum agreed with that of 1,2,5-hexatriene, and the nmr consisted of multiplets at τ 7.25 (2 H), 5.36 (2 H), 4.95 (3 H), and 4.12 (1 H).

From 1.20 g of 1-hexen-5-yne (385°, 30 cc of N_2/min) there was obtained 1.00 g of product which contained 45% fraction ii and 36% fraction iii.

Fraction ii, identified as 3-methylenecyclopentene, exhibited these properties: $n^{25}\mathrm{D}$ 1.4802; λ_{max} (isooctane) 233 mμ (ϵ 15,600); infrared bands at 3.28, 3.31, 3.39, 3.47, 3.50, 3.55, 6.18, 6.25, 6.93, 7.03, 7.49, 7.72, 8.13, 8.79, 9.16, 9.95, 10.08, 10.62, 11.10, 11.70, 12.26, 13.01, and 15.17 μ; nmr multiplets at τ 7.52 (2 H), 5.24 (1 H), and 3.90 (1 H). Upon hydrogenation over PtO_2 in acetic acid, a 0.214-g sample absorbed 4.32×10^{-3} mole of hydrogen. The vpc retention time and infrared spectrum of the saturated product coincided with those of methylcyclopentane.

Fraction iii, identified as 4-methylenecyclopentene, had $n^{25}\mathrm{D}$ 1.4498; λ_{max} (isooctane): only end absorption; infrared λ_{max} at 3.29, 3.38, 3.49, 3.57, 6.04, 6.21, 7.04, 7.43, 7.94, 8.64, 10.29,

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LAC-446 on Chromosorb P; No. 7, 3 m, 30% Carbowax 750 on Chromosorb P; No. 8, 3m, 30% Apiezon L on Diatoport W; and No. 9, 6 m, 30% silicone rubber on Chromosorb P

(13) F. Sondheimer, D. A. Ben-Efraim, and R. Wolovsky, *J. Am. Chem. Soc.*, **83**, 1675 (1961).

(14) If the flask is not cooled in an ice bath during the addition of β-methylallyl chloride, the yield of **18** drops to 34%, and a small amount of **17** is formed.

(15) J. F. Tinker and T. E. Whatmough, *J. Am. Chem. Soc.*, **74**, 5235 (1952).

(16) G. Eglington and M. C. Whiting, *J. Chem. Soc.*, 3052 (1953).

(17) J. Colonge and R. Gelin, *Bull. Soc. Chim. France*, 208 (1954).

(18) G. Wittig and U. Schuellkopf, *Org. Syn.*, 40, 66 (1960).

11.00, 11.40, and 14.86 μ; nmr absorption: a triplet of triplets at τ 6.98 (2 H), a pentuplet of triplets at 5.04 (1 H), and a heptuplet at 4.30 (1 H). A 0.167-g sample absorbed 3.36×10^{-3} mole of hydrogen, and the saturated product had a retention time identical with that of methylcyclopentane on column 4.

Isomerization of 4-methylenecyclopentene occurred during vpc on certain columns containing untreated Chromosorb P as the solid support.

1-Hepten-5-yne. As with 1-hexen-5-yne, preliminary experiments with 1-hepten-5-yne showed the formation of three products, one of which (iv) was formed in largest yield at short contact times, and the other two (v and vi) were formed in largest yield at longer contact times.

From 3.65 g of 1-hepten-5-yne at 385° and a nitrogen flow of 150 cc/min, there was obtained 3.45 g of product which contained 15% of iv. This fraction was isolated by preparative vpc on column 5 at 70°, followed by an additional separation on column 7 at 55°. Infrared absorption bands for this fraction were present at 3.27, 3.38, 3.45, 3.55, 5.12, 6.12, 7.00, 7.10, 7.31, 7.65, 7.76, 7.92, 8.58, 8.70, 10.10, 10.98 and 11.82 μ, and nmr signals were present as follows: a triplet with further fine splitting at τ 8.35 (3 H), a multiplet at 7.33 (2 H), a sextuplet at 5.46 (2 H), multiplets at 5.12 and 5.00 (2 H), and a multiplet at 4.20 (1 H). A 0.0578-g sample absorbed 1.18×10^{-3} mole of hydrogen over PtO$_2$, and the infrared spectrum of the saturated product was identical with that of 3-methylhexane. These properties characterize fraction iv as 3-methyl-1,2,5-hexatriene.

From 3.85 g of 1-hepten-5-yne at 385° and a nitrogen flow of 30 cc/min, there was obtained 3.50 g of product. Preparative vpc on column 5 at 70° afforded vi in a pure state, but gave incomplete separation of iv and v. Separation of these two was accomplished with column 7 at 55°.

Fraction v, identified as 3-methyl-4-methylenecyclopentene, possessed these properties: $n^{25}\text{D}$ 1.4470; infrared $\lambda_{\max}$ at 3.28, 3.39, 3.43, 3.47, 3.51, 3.56, 6.03, 6.90, 7.00, 7.11, 7.30, 7.42, 7.94, 9.01, 9.37, 9.86, 10.47, 10.73, 11.39, 12.71, 12.85, 13.00, and 14.24 μ; only end absorption in the ultraviolet region; nmr absorption: a doublet at τ 8.88 (3 H), a triplet at 6.93 superimposed on a multiplet (3 H), a multiplet at 5.07 (2 H), and a singlet at 4.33 (2 H). A 0.214-g sample absorbed 4.01×10^{-3} mole of hydrogen over PtO$_2$, and the saturated product was identified as a mixture of *cis*- and *trans*-1,2-dimethylcyclopentane by comparison of the infrared spectrum and vpc retention times with the corresponding product described under fraction vi.

Fraction vi was identified as 2-methyl-3-methylenecyclopentene on the basis of these properties: $n^{25}\text{D}$ 1.4803; $\lambda_{\max}$ (isooctane) 238 mμ (ϵ 10,900); infrared $\lambda_{\max}$ at 3.27, 3.31, 3.39, 3.45, 3.49, 3.52, 6.14, 6.18, 6.90, 7.00, 7.25, 7.72, 8.80, 8.94, 9.80, 9.95, 10.94, 11.11, 11.68, 11.95, and 12.70 μ; nmr multiplets at τ 8.26 (3 H), 7.52 (4 H), 5.25 (2 H), and 4.15 (1 H). Quantitative hydrogenation with a Brown[2] Hydro-Analyzer gave an unsaturation number of 2.1. Another sample was hydrogenated, and the saturated products, separated by preparative vpc on column 5, were identified as *cis*- and *trans*- 1,2-dimethylcyclopentane by comparison of their infrared spectra with the recorded spectra.

In one experiment in which the vaporizer stopped functioning during an experiment and the liquid hydrocarbon ran into the reactor, an additional peak appeared in the vpc tracing. This did not occur in any other experiments, and the identity, or explanation of formation, of this isomer is not known.

5-Methyl-1,2,5-hexatriene. A 3.00-g sample was passed through the reactor at 385° with a nitrogen flow of 90 cc/min. Analysis of the product (2.65 g) by vpc showed three components in addition to starting material, and separation was accomplished with column 8 at 90°.

One component was identified as 2-methyl-1-hexen-5-yne by comparison with an authentic sample. The second component possessed properties in agreement with those reported for 3-methylene-5-methylcyclopentene: $n^{25}\text{D}$ 1.4690; $\lambda_{\max}$ (isooctane) 234 mμ (ϵ 14,500); infrared $\lambda_{\max}$ at 3.25, 3.28, 3.40, 3.43, 3.50, 6.14, 6.88, 6.98, 7.28, 7.45, 7.64, 8.98, 9.22, 9.33, 9.70, 10.49, 10.60, 11.65, 12.55, and 14.72 μ; nmr: doublet (with further fine splitting) at τ 8.95 (3 H), multiplets from 7.05 to 8.17 (3 H), a multiplet at 5.28 (2 H), and a multiplet at 4.01 (2 H) (lit.[19] $n^{20}\text{D}$ 1.4621; $\lambda_{\max}$ (heptane) 234.5 (ϵ 14,700)).

The third component, identified as 2-methyl-4-methylenecyclopentene, possessed these properties: $n^{25}\text{D}$ 1.4559; only end absorption in the ultraviolet region; infrared $\lambda_{\max}$ at 3.27, 3.30, 3.39, 3.43, 3.45, 3.45, 3.49, 3.57, 6.00, 6.08, 6.92, 7.03, 7.25, 7.57, 7.85, 8.63, 9.85, 10.39, 10.89, 11.35, and 12.72 μ; nmr: multiplets at τ 8.29 (3 H), 7.03 (4 H), 5.13 (2 H), and 4.72 (1 H).

2-Methyl-1-hexen-5-yne. Pyrolysis of this hydrocarbon gave the same products, in essentially the same proportions, as obtained from 5-methyl-1,2,5-hexatriene. The results are summarized in Table I.

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(19) V. H. Mironov, M. W. Mavrou, and A. N. Elizarova, *J. Gen. Chem. USSR*, **32**, 2608 (1962).