

**Table I.** Thermal Decomposition of 2-Chloro-2-azabicyclo[2.2.2]octane (3)

Time, hr	Sodium thiosulfate, 0.0101 N, ml	Unreacted N-chloramine, mmoles
0	33.63	8.50
15	26.16	6.60
31	21.42	5.41
37	20.30	5.12
61	17.20	4.35

acid extracts being added to the bicarbonate solution referred to above. Extraction of the bicarbonate solution with six 10-ml portions of ether gave, after drying and evaporation of the solvent, the desired 1-methyl-3-(2,2-dimethoxyethyl)piperidine. Purification by preparative vapor phase chromatography on a 10-ft column of 10% (4:1) Carbowax 20M-KOH on 60-80 Chromosorb W at 140° gave pure acetal, having the same vpc retention time on Carbowax 20M and infrared spectrum as the material prepared by methylation of 6.

**1-Methyl-3-(2,2-dimethoxyethyl)piperidine (13).** A solution of 62 mg (0.36 mmole) of 6 and 0.050 ml of formalin in 2 ml of methanol was stirred at room temperature for 10 hr. The solution was diluted with 10 ml of methanol and hydrogenated at atmospheric pressure over 200 mg of Adams catalyst. The catalyst was removed by filtration, and the solvent was removed by fractional distillation. Vapor phase chromatography on a 6 ft × 0.5 in. column of 10% (4:1) Carbowax 20M-KOH on 60-80 Chromosorb W at 135° using propiophenone as an internal standard showed the presence of 59 mg (87%) of 1-methyl-3-(2,2-dimethoxyethyl)piperidine (13).

**Table II.** Thermal Decomposition of 6-Chloro-6-azabicyclo[3.2.1]octane (4)

Time, hr	Sodium thiosulfate, 0.101 N, ml	Unreacted N-chloramine, mmoles
0	23.80	2.40
1	20.73	2.09
2	19.40	1.96
4	18.30	1.85
8	14.59	1.47
12	10.86	1.10

Isolation of 13 via vpc on the same column gave an analytical sample,  $n_D^{25} 1.4770$ .

*Anal.* Calcd for  $C_{10}H_{21}NO_2$ : C, 64.13; H, 11.30; N, 7.48. Found: C, 64.03; H, 11.02; N, 7.64.

**Thermal Decomposition of N-Chloramines.** Methanolic solutions of 3 and 4 were prepared as described above with silver nitrate being omitted. The solutions were refluxed in the dark, and the reaction rates were followed by removing 5-ml aliquots. Each aliquot was treated with 2 ml of 1 N sulfuric acid and 5 ml of 5% potassium iodide. The liberated iodine was then titrated with 0.0101 N sodium thiosulfate using a starch indicator. The results are given in Tables I and II.

Product analyses were carried out by vpc on a 5 ft × 1/8 in. column containing 20% (4:1) Apiezon L-KOH on 60-80 Chromosorb P at 118° with diethylaniline as an internal standard.

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## The Thermal Rearrangement of 1,5-Hexadiyne and Related Compounds<sup>1</sup>

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**Abstract:** 1,5-Alkadiynes undergo intramolecular rearrangement at elevated temperatures to give dimethylenecyclobutenes. Thus, at 335° in a flow system, 1,5-hexadiyne rearranges rapidly to 3,4-dimethylenecyclobutene. 1,5-Heptadiyne rearranges somewhat more slowly, giving 1-methyl-3,4-dimethylenecyclobutene at 377°, while 1,2-dimethyl-3,4-dimethylenecyclobutene is formed from 2,6-octadiyne at 410°. Evidence pertinent to the stereochemistry of the reaction was obtained from a study of the rearrangement of the stereoisomeric 3,4-dimethyl-1,5-hexadiynes. Rearrangement of *meso*-3,4-dimethyl-1,5-hexadiyne gives *syn,anti*-3,4-diethylenecyclobutene (13), while *rac*-3,4-dimethyl-1,5-hexadiyne gives a symmetrical cyclic product, believed to be the *anti,anti* isomer 14. Thus the rearrangement involves a conrotatory process. From kinetics data obtained for the rearrangement of 1,5-hexadiyne over the temperature range 210-297° the energy and entropy of activation are calculated to be 34.4 kcal/mole and -9.4 eu, respectively. Two possible mechanisms are presented and the origin of retardation by methyl groups is discussed.

Although there is a wealth of literature on thermal rearrangements of molecules containing olefinic linkages,<sup>3</sup> little has been reported on similar reactions

(1) This work was supported by the National Science Foundation (G25089). Part of the results appeared in a preliminary communication, (W. D. Huntsman and H. J. Wristers, *J. Am. Chem. Soc.*, **85**, 3308 (1963)) and was presented at the 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966.

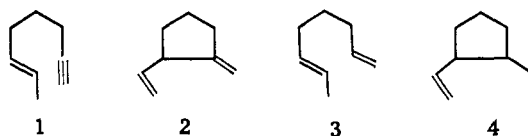
(2) Taken in part from the Ph.D. dissertation of H. J. Wristers, June 1965.

(3) Review articles which provide leading references are: S. J. Rhoads in "Molecular Rearrangements," P. de Mayo, Ed., Part 1, Interscience Publishers, Inc., New York, N. Y., 1963; W. von E. Doering and W. R. Roth, *Angew. Chem. Intern. Ed. Engl.*, **2**, 115 (1963).

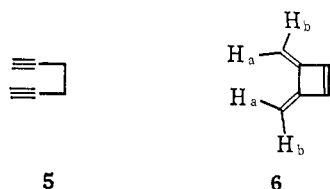
of acetylenic analogs. As a result of the finding that 6-octen-1-yne (1) rearranges to 1-methylene-2-vinylcyclopentane (2) even more rapidly than the olefinic counterpart 3 rearranges to 4,<sup>4</sup> it was decided to study the thermal behavior of other acetylenic derivatives. Results of an investigation of 1,5-hexadiyne (5) and some of its methyl-substituted homologs are presented in this paper.

The behavior of 1,5-hexadiyne was investigated over the temperature ranges 210-232° in a static system and

(4) W. D. Huntsman and R. P. Hall, *J. Org. Chem.*, **27**, 1988 (1962).



278–350° in a flow system. Isomerization occurred over the entire range to give a single product which was readily identified as 3,4-dimethylenecyclobutene (**6**) by comparison of infrared and ultraviolet spectra with those reported for this compound by Blomquist and Maitlis.<sup>5</sup> The nmr spectrum of **6** consists of singlets at  $\tau$  5.43, 5.32, and 3.30 with relative intensities 1:1:1. The signals at  $\tau$  5.43 and 5.32 are assigned to the exocyclic methylene protons, and on the basis of data presented below, they are assigned tentatively to the “inboard” protons  $H_a$  and the “outboard” ones  $H_b$ , respectively.



3,4-Dimethylenecyclobutane is a colorless liquid which is stable for long periods in the absence of air, but polymerizes rapidly upon exposure to air giving a hard, brittle, infusible solid,  $(C_6H_8O_2)_n$ . Samples of partially polymerized material ignite, often with mild detonation, when they are warmed in air or rubbed with a spatula.

A flow system provides the most convenient method for preparing substantial quantities of **6**, but a static system in which the reaction vessel is attached to a conventional high-vacuum line is very useful for small-scale reactions since it is readily adapted to transfer of materials with exclusion of air. In an effort to study the reaction in the liquid phase, a 200-mg sample was sealed in a short section of Pyrex tubing under high vacuum. Shortly after the ampoule, resting in a beaker, was placed in an oven at 280°, a violent detonation occurred which shattered the beaker and raised the oven lid. Liquid-phase experiments were not pursued further.

When carried out in the gas phase, the rearrangement is surprisingly clean-cut. No charring occurs, and virtually quantitative recoveries are possible, particularly when high-vacuum techniques are employed.<sup>6</sup> Over a period of time a slight film of yellow polymeric material deposits on the walls of the exit tube of the flow reactor.

The reaction follows a first-order rate law to beyond 85% completion, and rate constants calculated from data obtained with both the static and flow systems are summarized in Table I. From the slope of the log  $k$  vs.  $1/T$  plot, the energy of activation is calculated to be 34.4 kcal/mole. The large negative entropy of activation,  $-9.4$  eu at 232°, places this rearrangement in the same

**Table I.** First-Order Rate Constants for Isomerization of 1,5-Hexadiyne to 3,4-Dimethylenecyclobutene

Temp, °C	$k \times 10^4$ , sec <sup>-1</sup>
209.5 <sup>a</sup>	$0.762 \pm 0.005$
209.8 <sup>a</sup>	$0.796 \pm 0.004$
218.2 <sup>a</sup>	$1.50 \pm 0.01$
218.7 <sup>a</sup>	$1.42 \pm 0.01$
231.7 <sup>a</sup>	$3.79 \pm 0.04$
232.2 <sup>a</sup>	$3.87 \pm 0.03$
278 <sup>b</sup>	$71.0 \pm 2.0$
297 <sup>b</sup>	$181.0 \pm 2.0$

<sup>a</sup> Reaction studied in static system. <sup>b</sup> Reaction studied in flow system.

category as the Cope and other rearrangements which are believed to possess cyclic transition states.

Rearrangement of 1,5-heptadiyne (**7**) occurs at a rate significantly lower than that of 1,5-hexadiyne to give a product identified as 1-methyl-3,4-dimethylenecyclobutene (**8**) by comparison of the ultraviolet and infrared spectra with those reported for this compound.<sup>7</sup> At 335° and a contact time which resulted in complete rearrangement of 1,5-hexadiyne, only 55% conversion of 1,5-heptadiyne occurred. Complete conversion was realized by raising the temperature to 377°.

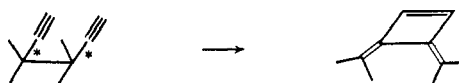


The nmr spectrum of **8** shows a doublet (with further fine splitting) at 8.12 and 8.13, a multiplet at  $\tau$  5.29–5.52, and a multiplet at  $\tau$  3.25–3.35, with relative intensities 3:4:1. The peaks are assigned to methyl, exocyclic methylene, and ring methinyl protons, respectively.

The retardation of rearrangement brought about by the methyl group in 1,5-heptadiyne is magnified even more by the introduction of a second methyl group. Thus, even at 410°, incomplete rearrangement of 2,6-octadiyne (**9**) occurred in two passes through the flow reactor. The product was identified as 1,2-dimethyl-3,4-dimethylenecyclobutene (**10**) by comparison of spectral properties with those reported by Griffin and Peterson.<sup>8</sup> The infrared spectrum of the tetracyanoethylene adduct also agreed with that reported by these authors.



On the basis of the results presented to this point it is possible to formulate the rearrangement in the following manner.



A net rotation of 90° must occur about the bonds marked with an asterisk, and to gain information on the sense of this motion, the rearrangement of *rac*-(**11**) and *meso*-3,4-dimethyl-1,5-hexadiyne (**12**) was studied. 3,4-Diethylidenecyclobutene, the product expected from the

(7) J. K. Williams and W. H. Sharkey, *J. Am. Chem. Soc.*, **81**, 4269 (1959).

(8) G. W. Griffin and L. I. Peterson, *ibid.*, **85**, 2268 (1963).

(5) A. T. Blomquist and P. M. Maitlis, *Proc. Chem. Soc.*, 332 (1961).

(6) M. L. Heffernan and A. J. Jones, *Chem. Commun.*, 120 (1966), have reported that fulvene and benzene are also formed when the rearrangement is carried out at 380°, with much longer contact times than were used in the present study. Gas chromatography, infrared, and nmr spectroscopy failed to reveal the presence of these compounds in any reactions carried out in the present study, so apparently they arise only under conditions considerably more drastic than employed by us.

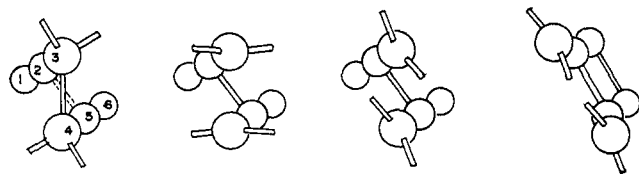
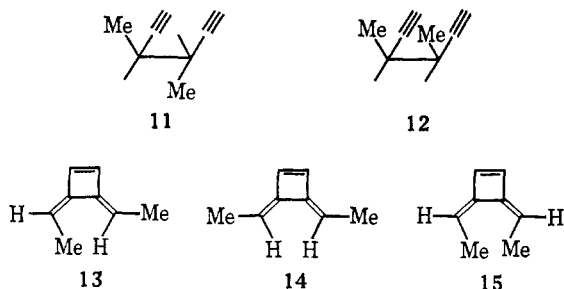


Figure 1. Possible sequence in the rearrangement of 1,5-hexadiyne.

rearrangement, can exist in three stereoisomeric forms **13**, **14**, and **15**, which will be designated as *syn,anti*, *anti,anti*, and *syn,syn*, respectively. The terms *syn* and *anti* refer to the orientation of the methyl groups relative to the 3-4 ring bond.



The products from rearrangement of **11** and **12** are less stable and more sensitive to polymerization upon contact with air than those described above. Substantial amounts of high-boiling material are formed during the reactions. The monomeric products showed single glpc peaks with slightly different retention times. The spectra of the products are in agreement with their formulation as diethylenecyclobutenes. The product from the *meso*-diyne **12** showed infrared absorption at 5.82, 5.95, 6.08, 12.3, and 13.4  $\mu$ , and that from the *rac*-diyne **11** at 5.82, 6.09, 12.25, and 13.3  $\mu$ . Both products exhibit patterns in their ultraviolet spectra which are typical of dialkylidenecyclobutenes. Bands are present at 254 (log  $\epsilon$  3.65), 220 (sh, log  $\epsilon$  4.32), and 212  $m\mu$  (log  $\epsilon$  4.45) for the product from **12** and at 254 (log  $\epsilon$  3.73) and 212  $m\mu$  (log  $\epsilon$  4.48) for that from **11**.

The nmr spectrum ( $\tau$ ) of the product from the *rac*-diyne exhibits a doublet centered at 8.29 ( $\text{CH}_3$ ) ( $J$  = 7 cps), a quartet at 5.00 (exocyclic  $=\text{CH}$ ), and a singlet at 3.10 (ring protons) with intensity ratios of 3:1:1. The unsymmetrical *syn,anti* structure, **13**, may be eliminated, but a definite decision cannot be made between the *anti,anti* **14** and the *syn,syn* **15** structures. Both stereoisomers could arise by conrotatory motions,<sup>9</sup> but the former is preferred on steric grounds. Substantial interaction between the methyl groups would be anticipated in the transition state leading to **15**.

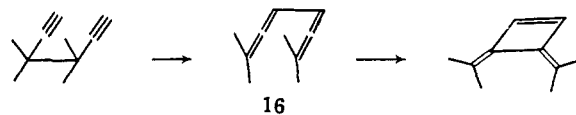
The nmr spectrum of the product from the *meso*-diyne shows two overlapping doublets for the methyl protons, two overlapping quartets for the exocyclic protons, and a typical AB pattern for the ring protons. This splitting pattern excludes the symmetrical structures **14** and **15**, and is in agreement with the *syn,anti* structure, **13**. As with the *rac* isomer, the formation of this product involves a conrotatory process.

The nmr spectrum of **13** consists of these signals ( $\tau$ ): methyl doublets centered at 8.21 ( $J$  = 7 cps) and at 8.27 ( $J$  = 7 cps); *exo* proton quartets at 4.74 and 5.02;

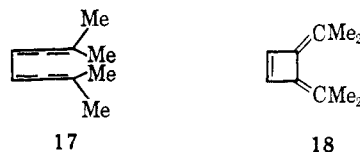
ring proton doublets at 3.13 and 3.30 ( $J$  = 2 cps). If one assumes that the product from the racemic diyne is the *anti,anti* isomer **14**, then the *exo* proton signals in **13** can be identified. The protons in **14**, which are "inboard," absorb at  $\tau$  5.00; thus in **13**, the signal at  $\tau$  5.02 may be assigned to the "inboard" proton and the one at  $\tau$  4.72 to the "outboard" proton.

One would expect this same relationship to prevail in other dimethylenecyclobutenes, *i.e.*, the "inboard" protons will be more strongly shielded than the "outboard" ones. This is the basis of the assignments described previously for 3,4-dimethylenecyclobutene itself.

A number of pathways for the reaction are conceivable. One that comes to mind immediately, and which has been suggested,<sup>10</sup> is a two-step process involving first a Cope-type rearrangement to the tetraene **16** which undergoes the internal counterpart of the dimerization reaction characteristic of allenes. Conrotation would be predicted in this scheme in agreement with the findings. In support of this scheme is the finding that **17** cyclizes to **18** rapidly at 250°. Allenes were not detected in the reaction products, but of course they would not be if the second step were substantially



faster than the first.



However, one feature of this mechanism does seem incongruous, *viz.*, carbons 1 and 6 in 1,5-hexadiyne appear to be too far removed to allow appreciable bonding without significant rupture of the central 3-4 bond. On the other hand, positions 2 and 5 are reasonably close together, and models indicate the possibility of interaction between the  $\pi$  clouds at these positions. It is difficult to see how the allene could arise without passing through a transition state where bonding exists between positions 2 and 5. This bond would have to be broken in passing to the allene, and then re-formed in the transition state of the second step. One wonders what is gained by the stopover at the allene stage.

It is possible to formulate a one-step mechanism in which bonding arises between positions 2 and 5 concomitant with rupture of the 3-4 bond. If this interaction is initiated from a skew conformation (see Figure 1), then it is easy to see why conrotation occurs about the 2-3 and 4-5 bonds. As bonding develops between 2 and 5, p orbitals will arise with axes perpendicular to the 2-5 bond. These are oriented properly for significant overlap with the incipient p orbitals at positions 3 and 4, and clockwise rotation of both groups would lead to increasing overlap. As the 3-4 rupture proceeds, rotation about the 2-5 bond permits positions 1 and 6 to come within bonding range.

The origin of the retardation produced by the methyl groups in 1,5-heptadiyne and 2,6-octadiyne is not cer-

(9) R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 395 (1965).

(10) L. Skattebøl and S. Solomon, *ibid.*, **87**, 4506 (1965).

tain. Results from experiments in progress indicate that the effect may be general for reactions in which a methyl group is attached to a carbon undergoing change from  $sp$  hybridization to  $sp^2$  hybridization. Perhaps it is due to ground-state stabilization resulting from electron release by methyl to the more electronegative  $sp$ -hybridized carbon. It is also possible that steric factors are responsible for the retardation. If this is the case, then in terms of the concerted mechanism, the transition state must have a configuration in which positions 1 and 6 are reasonably close together. This matter is being studied further.

## Experimental Section<sup>11</sup>

**Materials. 1,5-Hexadiyne.** Treatment of 1,2,5,6-tetrabromohexane with sodium amide in liquid ammonia by the procedure of Raphael and Sondheimer<sup>12</sup> gave 1,5-hexadiyne, which was fractionally distilled through a 90-cm column packed with glass helices, bp 85–86° (lit.<sup>12</sup> bp 86°).

**1,5-Heptadiyne.** Alkylation of 18.0 g of 1,5-hexadiyne with 38.7 g of methyl iodide in liquid ammonia by the procedure described for 1,5-octadiyne<sup>13</sup> gave 12.5 g of 1,5-heptadiyne, bp 65.5° (90 mm),  $n_D^{25}$  1.4542 (lit.<sup>13</sup> bp 26–27° (30 mm),  $n_D^{25}$  1.4521). Analysis by glpc showed a single peak, and the material exhibited infrared absorption at: 3.03, 3.42, 3.50, 4.72, 6.96, 7.23, 7.45, 7.54, 7.91, 8.73, 8.9, 9.08, 10.91, and ca. 15.5  $\mu$ .

*Anal.* Calcd for  $C_7H_8$ : C, 91.25; H, 8.75. Found: C, 91.08; H, 8.90.

**2,6-Octadiyne.** In a 5-l., round-bottomed flask, fitted with a mechanical stirrer and a reflux condenser with a calcium chloride drying tube, was prepared 6.25 moles of sodium amide in 2500 ml of liquid ammonia. To this mixture, a solution of 355 g (0.894 mole) of 1,2,5,6-tetrabromohexane in 920 ml of anhydrous ether was added dropwise during a period of 2 hr. The mixture was stirred while the flask was immersed in a Dry Ice-acetone bath for 3 hr. A solution of 378 g (2.68 moles) of methyl iodide in 750 ml of anhydrous ether was added dropwise during a period of 1.5 hr. The cooling bath was removed, and the reaction mixture was allowed to stand for 36 hr to permit the ammonia to evaporate. The flask was cooled to  $-10^\circ$ , and 500 ml of ether was added to the brown residue, and then 700 ml of ice water was added dropwise. Stirring was begun as soon as it was possible. The ether layer was separated, and the aqueous solution was extracted with four 50-ml portions of ether. The ethereal solutions were washed with 5% sulfuric acid until the washings were acidic, and then with 5% sodium bicarbonate until the washings were basic to litmus paper. The ether solution was dried over anhydrous magnesium sulfate, and after the solvent was removed, the residue was distilled through a Fenske column to yield 42.3 g of crude 2,6-octadiyne, bp 80–85° (45 mm). This material contained ~10% impurity according to glpc analysis. Fractionation of this product with a spinning-band column gave 30 ml of liquid, bp 82–83.5° (45 mm), which showed less than 2% impurity by glpc. Redistillation through the spinning-band column gave a product with bp 81.5–82.0° (47 mm), mp 31° (lit.<sup>13</sup> bp 62° (19 mm), mp 26.5–27°). Final purification was accomplished by preparative-scale glpc.

*Anal.* Calcd for  $C_8H_8$ : C, 90.51; H, 9.49. Found: C, 90.69; H, 9.25.

The infrared spectrum of a liquid film showed absorption bands at: 3.42, 3.51, 3.65, 4.48, 6.91, 6.96, 7.23, 7.44, 7.53, 7.91, 8.71, and 9.70  $\mu$ .

**3,4-Dimethyl-1,5-hexadiyne.** From 128 g of magnesium turnings, and 260 g of 3-bromo-1-butyne in 500 ml of tetrahydrofuran, treated according to the procedure of Sondheimer and Ben-Efraim,<sup>14</sup> there was obtained 5.55 g of a hydrocarbon mixture, bp 70–71° (165 mm),  $n_D^{25}$  1.4432 (lit.<sup>14</sup> bp 50–52° (80 mm),  $n_D^{25}$  1.4405). This material was shown by glpc to consist of three components,

two of which were found to be *meso*- and *rac*-3,4-dimethyl-1,5-hexadiyne, and the third was not positively identified, but the evidence suggested it might be 3-methyl-4,5-heptadien-1-yne.

Separation was accomplished by preparative-scale glpc on a 6-m decyl phthalate column at 82°, and three fractions (i, ii, and iii) were isolated in approximately equal amounts.

A 0.532-g sample of fraction i was treated with a solution of 3.22 g of potassium permanganate in 250 ml of water and allowed to stand for 24 hr at room temperature. The manganese dioxide was removed by filtration, and the water was evaporated from the filtrate on a rotary evaporator. Acidification of the residue gave *meso*-2,3-dimethylsuccinic acid, mp 194.5° (lit.<sup>15</sup> mp 195°). The infrared spectrum of this material was identical with the reported spectrum of *meso*-2,3-dimethylsuccinic acid.<sup>16</sup>

The infrared spectrum of *meso*-3,4-dimethyl-1,5-hexadiyne (in  $CCl_4$ ) showed bands at: 3.03, 3.36, 3.41, 3.47, 3.48, 4.72, 6.86, 7.25, 7.47, 7.71, 7.95, 8.05, 8.88, 8.98, 9.18, 9.40, 9.70, 10.15, and 10.26  $\mu$ .

Fraction ii was shown to be *rac*-3,4-dimethyl-1,5-hexadiyne by oxidation of a sample by the same procedure as described for fraction i. The crude acid obtained, mp 114°, was identified as *rac*-2,3-dimethylsuccinic acid by infrared spectroscopy. The amount of acid was too small to permit recrystallization for comparison with the reported melting point, 123°, but correspondence of the infrared spectrum with the published spectrum<sup>16</sup> left no doubt of identity.

The infrared spectrum of *rac*-3,4-dimethyl-1,5-hexadiyne (in  $CCl_4$ ) showed absorption at: 3.03, 3.37, 3.41, 3.47, 3.48, 3.54, 4.72, 6.83, 6.88, 7.24, 7.42, 7.58, 7.83, 7.88, 8.60, 8.90, 9.30, 9.70, 9.78, 10.08, 10.18, and 10.38  $\mu$ .

**Thermal Rearrangement Reactions. Apparatus.** The general features of the flow system have been described previously.<sup>17</sup> It is important that the hydrocarbon be vaporized before it enters the reaction tube, since it generally ignites if the liquid is dropped directly into the hot reaction zone. This difficulty is not experienced if the hydrocarbon is vaporized and swept through the reaction tube with "prepurified" nitrogen (Matheson).

Hydrocarbon was fed to the vaporizer by means of a motor-driven syringe, and the contact time was regulated by controlling the nitrogen flow rate. The flow rate was measured with a soap-film flowmeter which was attached to the outlet of the product receiver. In the initial experiments, the reaction tube was packed with glass helices, but later it was found that this is unnecessary, and actually the contact time can be estimated and controlled more readily if an unpacked tube is used. A convenient sized reactor is made from a section of 22-mm o.d. Pyrex tubing, 44 cm long, with the entrance and exit tubes constructed from 12-mm o.d. tubing. The entrance tube serves as a preheater section. A thermocouple, well mounted axially, permits temperature monitoring along the entire reactor. The temperature gradient at the ends of the reactor is minimized by the use of end heaters, and it is possible to maintain a gradient of less than 2° along the 44-cm section.

A 1-l. flask surrounded by a heating mantle and attached to a conventional high-vacuum system was used as a static reaction vessel for some experiments. Conventional high-vacuum techniques were used for degassing samples and transferring reactants and products. This system is very convenient for carrying out studies on 0.05–0.15-g samples.

**1,5-Hexadiyne.** In a typical experiment, 1,5-hexadiyne was added to the vaporizer at a rate of 5.4 ml/hr, and a nitrogen flow of approximately 150 cc/min was used. The reactor was maintained at 345°. A total of 1 ml of 1,5-hexadiyne was added, and the product, which was distilled directly into a calibrated receiver on the vacuum line, amounted to 0.95 ml. The glpc tracing showed that complete conversion of 1,5-hexadiyne had occurred, and a single peak appeared for the product. The infrared spectrum of this material agreed with that reported for 3,4-dimethylenecyclobutene.<sup>5</sup> Ultraviolet maxima (EtOH) appeared at 245  $m\mu$  (log  $\epsilon$  4.3) and 211  $m\mu$  (log  $\epsilon$  5.0) (lit.<sup>5</sup>  $\lambda_{max}$  248  $m\mu$  (log  $\epsilon$  4.3) and 211.5  $m\mu$  (log  $\epsilon$  5.0)). In the nmr spectrum, singlets appeared at  $\tau$  5.43, 5.32, and 3.30 with intensity ratios of 1:1:1. Evidence of long-range coupling appeared when the spectrum was expanded.

A number of experiments were conducted to ascertain the temperature range over which significant rearrangement occurs. At

(11) Microanalyses were performed by the Galbraith Laboratories, Knoxville, Tenn. Infrared spectra were obtained with a Perkin-Elmer 237-G spectrophotometer. Nuclear magnetic resonance spectra were measured with a Varian A-60 spectrometer, using TMS as internal standard.

(12) R. A. Raphael and F. Sondheimer, *J. Chem. Soc.*, 120 (1950).

(13) M. Urion, *Compt. Rend.*, **185**, 1286 (1927).

(14) F. Sondheimer and D. A. Ben-Efraim, *J. Am. Chem. Soc.*, **85**, 52 (1963).

(15) E. H. Farmer and A. T. Healy, *J. Chem. Soc.*, 1067 (1927).

(16) L. Schotte and A. Rosenberg, *Arkiv Kemi*, **7**, 479 (1955).

(17) W. D. Huntsman and T. H. Curry, *J. Am. Chem. Soc.*, **80**, 2252 (1958).

Table II

Temp, °C	Contact time, sec	% dimethylenecyclobutene
278	26	12
278	50	22
278	83	48
297	20	24
297	42	47
297	96	80

260°, a hydrocarbon feed rate of 2.7 ml/hr, and a nitrogen flow of 35 cc/min, ~14% conversion to **6** occurred. Other typical results are summarized in Table II.

**1,5-Heptadiyne.** At 377°, a nitrogen flow of 35 cc/min, and a hydrocarbon feed rate of 5.4 ml/hr, 1,5-heptadiyne gave a product which was identified as 1-methyl-3,4-dimethylenecyclobutene by comparison of the infrared spectrum with that reported for this compound.<sup>7</sup> The glpc tracing showed a single peak, and indicated that complete conversion of 1,5-heptadiyne had occurred. Maxima in the ultraviolet spectrum appeared at 244 and 210 m $\mu$ . (Due to an error in measuring out the sample, extinction coefficients could not be calculated; lit.<sup>7</sup>  $\lambda_{\text{max}}^{\text{EtOH}}$  245 m $\mu$  (log  $\epsilon$  3.76) and 210 m $\mu$  (log  $\epsilon$  4.49).)

The nmr spectrum of **8** shows a doublet (with further fine splitting) at  $\tau$  8.12 and 8.13, a multiplet at 5.29–5.52, and a multiplet at 3.25–3.35 with relative intensities 3:4:1.

Studies of the reaction at different temperatures with a nitrogen flow of 35 cc/min and hydrocarbon feed of 5.4 ml/hr gave results as follows for the per cent conversion to **8**: 250°, 1%; 260°, 3%; 316°, 24%; 350°, 75%.

**2,6-Octadiyne.** When this diyne was heated at 370°, incomplete rearrangement occurred, and although raising the temperature to 450° resulted in a greater percentage of rearranged product, a substantial amount of decomposition occurred at this temperature. Recycling of the product at 410° was found to be the most effective means for effecting rearrangement. A 4.0-ml sample of 2,6-octadiyne was passed through the reaction tube at a rate of 5.4 ml/hr. The product was collected and recycled two more times under the same conditions. The product was checked after each cycle by glpc to indicate 33, 63, and 83% conversion. Decomposition occurred to the point that further recycling was deemed unwise. Distillation of the pyrolysate did not effect significant separation of the mixture but gave a single fraction, bp 135–140°, for which the glpc tracing was identical with the pyrolysate before distillation.

Infrared and nmr data agreed with the data reported for 1,2-dimethyl-3,4-dimethylenecyclobutene.<sup>8</sup> The infrared spectrum of the pyrolysate (homogeneous liquid) exhibited absorption due to the 1,2-dimethyl-3,4-dimethylenecyclobutene at: 3.24, 3.38, 3.41, 3.42, 3.50, 5.89, 6.07, 6.22, 6.30, 6.96, 7.57, 9.10, 9.45, 9.90, 11.15, 11.71, 12.20, and 14.70  $\mu$ , and absorption due to unreacted 2,6-octadiyne at: 3.41, 3.42, 3.50, 6.94, 7.23, 7.44, 7.57, 7.91, and 9.69  $\mu$ .

The mixture (2 g) containing 83% of rearranged material was treated with 2.42 g of tetracyanoethylene in 10 ml of *t*-butyl alcohol and 45 ml of dry tetrahydrofuran. The mixture was stirred under a nitrogen atmosphere at room temperature for 12 hr. The solvents were removed under reduced pressure, and part of the purple residue was recrystallized twice from 1:3 benzene–ligroin (bp 66–75°) to yield white crystals, mp 145–150° dec.

Anal. Calcd for C<sub>14</sub>H<sub>10</sub>N<sub>4</sub>: C, 71.78; H, 4.30; N, 23.92. Found: C, 71.76; H, 4.40; N, 23.67.

The infrared spectrum (KBr disk) was identical with the spectrum reported for the TCNE adduct of 1,2-dimethyl-3,4-dimethylenecyclobutene,<sup>8</sup> and the ultraviolet spectrum determined in 95% ethanol agreed with the reported spectrum:  $\lambda_{\text{max}}$  226 m $\mu$  (log  $\epsilon$  3.98) (lit.<sup>8</sup>  $\lambda_{\text{max}}$  227 m $\mu$  (log  $\epsilon$  4.09)).

**meso-3,4-Dimethyl-1,5-hexadiyne.** A 0.100-g sample of this hydrocarbon was heated at 350° for 15 min in the static system. A single peak appeared in the glpc tracing of the product, at a time which was different from the retention time of the starting compound, and the infrared spectrum, measured in CCl<sub>4</sub> and in CS<sub>2</sub>, showed bands at: 3.22, 3.29, 3.34, 3.37, 3.40, 3.42, 3.47, 3.50, 5.40, 5.55, 5.82, 5.95, 6.08, 6.88, 6.93, 7.23, 7.45, 7.55, 9.23, 9.18, 10.49, 11.11, 12.26, 13.39, and 14.07  $\mu$ . The ultraviolet spectrum showed  $\lambda_{\text{max}}^{\text{EtOH}}$  254 m $\mu$  (log  $\epsilon$  3.65), 220 m $\mu$  (log  $\epsilon$  4.32), and 212 m $\mu$  (log  $\epsilon$  4.45). In the nmr spectrum, these peaks were observed: methyl doublets

centered at  $\tau$  8.21 ( $J$  = 7 cps) and at  $\tau$  8.27 ( $J$  = 7 cps); two overlapping quartets centered at  $\tau$  4.74 and 5.02 for the exocyclic protons; and an AB pattern at  $\tau$  3.13 and 3.30 ( $J$  = 2 cps) for the ring protons.

**rac-3,4-Dimethyl-1,5-hexadiyne.** Heating a 0.138-g sample of *rac*-3,4-dimethyl-1,5-hexadiyne in the static system at 350° for 15 min resulted in complete disappearance of the starting material, and the glpc tracing showed a single peak. The infrared spectrum, measured in CCl<sub>4</sub> and in CS<sub>2</sub>, showed bands at: 3.23, 3.29, 3.35, 3.42, 3.43, 3.47, 3.51, 5.40, 5.58, 5.82, 6.09, 6.89, 6.94, 7.22, 7.24, 7.34, 7.42, 7.60, 9.10, 9.23, 9.64, 10.20, 10.35, 12.07, 12.25, and 13.30  $\mu$ . The ultraviolet spectrum showed  $\lambda_{\text{max}}^{\text{EtOH}}$  254 m $\mu$  (log  $\epsilon$  3.73) and 212 m $\mu$  (log  $\epsilon$  4.48). The nmr spectrum consisted of a methyl doublet centered at  $\tau$  8.29 ( $J$  = 7 cps), a quartet at  $\tau$  5.00, and a singlet at  $\tau$  3.10 with intensity ratios 3:1:1.

## Kinetic Experiments

**Flow System.** The furnace and feed system described above were used. The exit line from the reactor led, through a three-way stopcock (no. 1), to two traps in series, each cooled in Dry Ice–acetone. The outlet line from the second trap was connected, through a three-way stopcock (no. 2), to a high-vacuum line, or to a soap-film flowmeter. During an experiment, stopcock no. 2 was turned to connect the outlet of the trap to the flowmeter. At the end of the experiment, the traps were isolated from the reactor by turning stopcock no. 1, and were connected to the vacuum line by turning stopcock no. 2. The product was distilled into a detachable trap on the vacuum line, and when all the product had been collected, the trap was transferred to a glove bag without exposing the product to air. The glove bag was flushed thoroughly with nitrogen, the trap was opened, and samples of product were withdrawn by micro syringe for glpc analysis.

The nitrogen flow rate was checked frequently during each experiment. The temperature at the inlet, center, and outlet of the reactor was measured by thermocouples fixed at each of these points. Temperature fluctuation during an experiment was less than 0.3°.

The composition of products was determined by gas chromatographic analysis, using a 3.8-m column with a LAC-446 liquid phase (F & M Scientific), at 90° and He flow of 60 cc/min. Relative areas of the two peaks were computed by triangulation; values calculated in this way agreed well with those obtained by measurement with a planimeter. Analyses of a mixture by gas chromatography and by nmr spectroscopy gave values within 3% of each other.

In computing the contact time it was assumed that the hydrocarbon vapor and nitrogen obey the ideal gas law at the temperatures employed.

At each temperature, nine experiments were carried out at flow rates ranging from 20 to 96 sec at 297°, with conversions ranging from 24 to 80%, and 26 to 96 sec at 278°, which gave conversions in the range of 12 to 43%. Rate constants were computed by a least-squares treatment of the data, and are summarized in Table I.

**Static System.** A 1-l. flask thermostated in a well-insulated, circulating air bath served as the reaction vessel. Temperature control was provided by an F & M Model 220 power proportioning temperature controller, and the temperature was monitored frequently during an experiment by means of a thermocouple in a well extending to the center of the flask. During an

experiment, the temperature fluctuation was less than 0.2°, and temperature settings could be duplicated to within 0.5°.

The flask was attached to a high-vacuum line which permitted introduction of reactant and periodic sampling of the reaction mixture. Sampling was accomplished by means of a hollow-plug, high-vacuum stopcock attached to the flask through a short length of capillary tubing. A hole in the plug in addition to the one provided for evacuation permitted withdrawal of a sample with volume equal to that of the hollow core of the plug and transfer of the sample through a gas-sampling valve to a gas chromatography column. The sample volume was ~8 ml. A 2-m column packed with 1,2,3-triscyanoethoxypropane (25% on Chromosorb) and operated at 110° with He flow of 40 cc/min was used for the analyses.

A 0.25–0.30-ml sample of 1,5-hexadiyne was introduced into the vacuum line and thoroughly degassed. The reaction flask was thoroughly evacuated, and after temperature equilibrium was established, the diyne was distilled rapidly into the flask, the inlet stopcock was closed, and timing was started. Samples were removed for analysis at 12–15-min intervals by means of the hollow-plug stopcock. The rate at which a high vacuum could be reestablished after removal of a sample limited the sampling frequency. Reactions at 210° were carried to 72% of completion, and those at 218 and 232° were carried to 88% of completion. Plots of log (1/fraction of 1,5-hexadiyne unchanged) were linear. A slight upward curvature was observed at points beyond 92% of completion. First-order rate constants were computed by a least-squares treatment of the data, and are presented in Table I.

## Optical Rotary Dispersion Studies. CIX.<sup>1</sup> An Octant Rule for the Azide Chromophore<sup>2</sup>

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**Abstract:** An analysis of the relevant orbitals involved in the 280–290-m $\mu$  transition of azides has led to the development of an octant rule, which may prove useful in conformational studies of optically active azides. The optical rotatory dispersion and circular dichroism properties of 34 steroidal azides have been measured and analysis of some of the data in terms of the newly developed octant rule has been attempted. Difficulties associated with the potentially free rotation of the chromophore in the steroidal azides are noted and discussed.

For the purpose of correlating optical activity with molecular structure some chromophores have been designated as "inherently symmetric."<sup>3</sup> The term is meant to signify that the local symmetry, *i.e.*, the symmetry of the isolated chromophore, is sufficiently high to preclude optically active chromophoric transitions. Only when the chromophore is placed in a dissymmetric molecular environment will its transitions manifest optical activity, and the signed magnitude of this activity will depend upon the detailed nature and geometry of the extrachromophoric environment. For this reason, an inherently symmetric chromophore can be useful as a molecular probe with which to explore molecular geometries.

The most extensive application of the above concept has been made in connection with the carbonyl group of saturated ketones,<sup>4</sup> for which an "octant rule" could

be formulated.<sup>5</sup> However, it has been emphasized<sup>6</sup> that any inherently symmetric chromophore whose transitions are readily accessible can be used in an analogous manner; one need only ascertain the nature of the orbitals involved in the pertinent transition so as to be able to specify the shape of the sign determining regions in space. This latter task, of course, may not be a trivial one.

In the present work, we shall be concerned with the inherently symmetric azide chromophore which in alkyl azides exhibits a weak transition ( $\epsilon \sim 30$ ) in the vicinity of 280–290 m $\mu$ . Closson and Gray<sup>7</sup> and Lieber, *et al.*,<sup>8</sup> have discussed the pertinent orbitals. The former<sup>7</sup> attribute the transition roughly to the promotion of an electron from a nonbonding 2p<sub>y</sub> orbital, situated mainly on the nitrogen atom N<sub>1</sub> con-

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