BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 1782—1788 (1970)

Pyrolytic and Photolytic Reactions. I. Thermal Rearrangement of 1-Acetyl- and 1-Isopropenyl-3-methylenecyclobutane[1)]

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(Received October 28, 1969)

1-Acetyl- and 1-isopropenyl-3-methylenecyclobutane (I and II) were prepared and then subjected to pyrolysis. The pyrolysis of I at 304—340°C gave 2-methyl-5-methylene-Δ^2-dihydropyrane, which was then converted to 4-methylenecyclohexanone at this temperature. The pyrolysis of II at 255—340°C gave 1-methyl-4-methylenecyclohexene, which was disproportionated at this temperature to *p*-xylene and 1,4-dimethylcyclohexene. In neither case was fragmentation to olefins observed. These results were interpreted by a two-step biradical mechanism.

There have been ample examples of the thermal fragmentation of a cyclobutane derivative into two molecules of olefins.[3)] For example, cyclobutane is pyrolyzed into two molecules of ethylene, and methylenecyclobutane is likewise pyrolyzed into ethylene and allene. The comparison of these two reactions reveals that the activation energy (63.3 kcal/mol)[4)] required for the pyrolysis of methylenecyclobutane is slightly higher than, or almost equal to, that (61.5—63.2 kcal/mol)[5)] required for

1) a) Taken from the Master of Science thesis of S. O. b) Presented at the 20th Annual Meeting of The Chemical Society of Japan, Tokyo, April, 1967.

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3) See for example, a) R. Breslow, "Molecular Rearrangements," Part I, ed. by P. de Mayo, Interscience Publishers, New York (1963), p. 245; b) H. Kato, *Yuki Gosei Kagaku Kyokai Shi*, **24**, 265 (1966).

4) J. P. Chesick, *J. Phys. Chem.*, **65**, 2170 (1961).

5) R. L. Brandauer, S. Short and S. M. Kellner, *ibid.*, **65**, 2269 (1961); R. W. Vreeland and D. F. Swinehart, *J. Amer. Chem. Soc.*, **85**, 3349 (1963); J. N. Butler and R. B. Ogawa, *ibid.*, **85**, 3346 (1963); C. T. Genaux, F. Kern and W. D. Walters, *ibid.*, **75**, 6196 (1953). A value of 61.2 kcal/mol is reported as the activation energy for the fragmentation of methylcyclobutane: M. N. Das and W. D. Walters, *Z. Phys. Chem.*, **15**, 22 (1958).

cyclobutane. This result may appear contrary to the expectation that the presence of an exocyclic methylene group would reduce the activation energy of pyrolytic fragmentation as a result of the extra strain (*ca.* 2.5 kcal/mol)[6] imposed by the introduction of a methylene group. It was thought of interest to learn if this seemingly anomalous value corresponds, not to the initial ring-cleavage step to give a biradical, but, rather, to the final stage of producing the fragmentation products.[4] Such distinction would be possible by a study of the pyrolysis of deliberately chosen compounds in which a second reaction path exists in preference to, or in competition with, fragmentation.

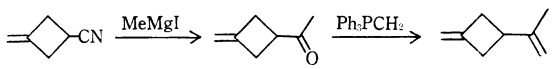
With this in mind, we studied the thermal behavior of 1-acetyl-3-methylenecyclobutane (I) and 1-isopropenyl-3-methylenecyclobutane (II). These compounds will give fragmentation and/or ring-enlargement products depending on the heights of the energy barriers existing in the two reaction paths.

During the course of this investigation, Doering and Gilbert[8] have unequivocally shown with 1,1-dideuteriomethylenecyclobutane that the fragmentation step indeed requires a higher activation energy than that of the initial ring cleavage to a biradical.

Results and Discussion

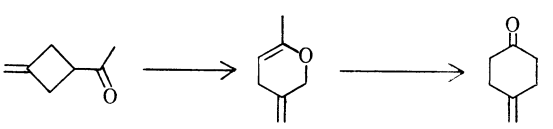
The reaction of 3-methylenecyclobutanecarbonitrile[9] and methylmagnesium iodide, followed by hydrolysis, gave 1-acetyl-3-methylenecyclobutane (I). The NMR spectrum of I, in complete agreement with the assigned structure, showed a three-proton singlet at τ 8.05 for the acetyl group, a four-proton multiplet and a one-proton multiplet at τ 7.27 and 7.25 for the two methylene and the methine groups, and a two-proton pentuplet (J=2.5 Hz) for the exocyclic methylene group. Its infrared spectrum confirmed the presence of the acetyl (1720, 1370 cm^{-1}) and the exocyclic methylene (3080, 1680, 1410, 880 cm^{-1}) groups. The mass spectrum of I showed a parent peak at *m/e* 110, in accord with the molecular formula of $C_7H_{10}O$, and major fragment peaks at *m/e* 95 $(P-Me)^+$, 67 $(P-Ac)^+$, and 43 $(Ac)^+$.

The treatment of I with methylenetriphenylphosphorane afforded 1-isopropenyl-3-methylenecyclobutane (II), the structure of which was established by the spectral data described below. The NMR spectrum of II consisted of three poorly-resolved multiplets at τ 8.32 (3H), 7.30 (5H), and 5.33 (4H), corresponding to the methyl group on the double bond, the ring protons, and the two terminal methylene groups respectively. The infrared spectrum of II had bands of the terminal methylene groups at 3100, 1680, 1650, 1420, 1380, 885, and 875 cm^{-1}.



I II

Pyrolysis of 1-Acetyl-3-methylenecyclobutane. The pyrolysis of 1-acetyl-3-methylenecyclobutane (I), as a neat liquid or as a toluene solution and in a sealed tube at 304 and 340°C, gave two products besides the starting material, which were considered as 2-methyl-5-methylene-Δ^2-dihydropyrane (III) and 4-methylenecyclohexanone (IV) on the basis of the following spectral data.



I III IV

The NMR spectrum of III consisted of a three-proton singlet (with fine splittings) at τ 8.35 corresponding to the methyl group on the double bond, a two-proton multiplet at τ 7.35 corresponding to the methylene group between the two double bonds, a two-proton singlet (with fine splittings) at τ 5.80 corresponding to the methylene group between the double bond and the oxygen atom, a one-proton triplet (J=5 Hz, with fine splittings) at τ 5.69 corresponding to the proton on the double bond, and a two-proton singlet (with fine splittings) at τ 5.10 corresponding to the terminal methylene protons. Its infrared spectrum showed bands of a terminal methylene and olefinic groups at 3100, 1680, 1430, and 900 cm^{-1} and characteristic bands of a vinyl ether at 1240 and 1050 cm^{-1}. Its mass spectrum showed a parent peak at *m/e* 110 and prominent framgent peaks at 95 $(P-Me)^+$, 67 $(P-Ac)^+$, 43 $(Ac)^+$, and 39 $(CH_2-C\equiv CH\ ?)^+$.

The NMR spectrum of the ketone IV displayed only two broad peaks, at τ 7.60 (8H) and 5.15 (2H), which are attributable to the ring protons and the exocyclic methylene groups respectively. The infrared spectrum of IV supported the presence of the exocyclic methylene (3080, 1650, 1430 and 900 cm^{-1}) and the carbonyl (1710 cm^{-1}) groups. Further support for structure IV was provided by its mass spectrum which, in addition to a parent peak at *m/e* 110, showed a fragment peak at 82 (P—

6) R. B. Turner, "Theoretical Organic Chemistry—Papers Presented to the Kekulé Symposium," Butterworths Sci. Pub., London (1959), p. 67. This value may now be regarded as an overestimation.[7]

7) R. B. Turner, P. Goebel, B. J. Mallon, W. von E. Doering, J. F. Coburn, Jr., and M. Pomerantz, *J. Amer. Chem. Soc.*, **90**, 4315 (1968).

8) W. von E. Doering and J. C. Gilbert, *Tetrahedron*, Supplement No. 7, 397 (1966).

9) H. N. Cripps, J. K. Williams and W. H. Sharkey, *J. Amer. Chem. Soc.*, **80**, 751 (1958).

CO)$^{\cdot+}$, characteristic of a cyclic ketone, and peaks at 81 (P−CO−H)$^+$, 67 (P−Ac)$^+$, 54 ($\overline{CH_2CH_2C}$=CH_2 or $\overline{CH}$=$CH\overline{C}$=O ?)$^{\cdot+}$, and 39 (CH_2–C≡CH ?)$^+$.

The results of a kinetic study of this rearrangment are shown in Fig. 1. The figure clearly shows that III is the initial product of the pyrolysis of I and that III rearranges further to IV at the reaction temperature.

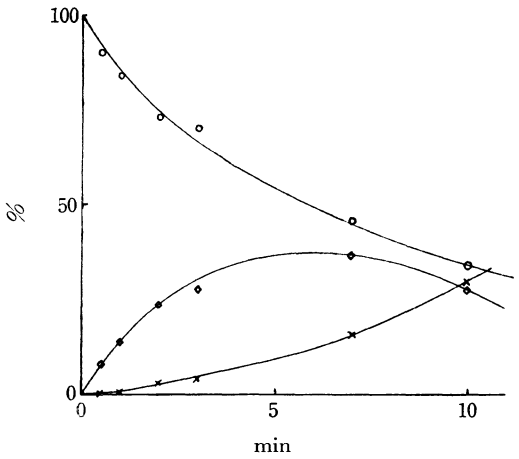
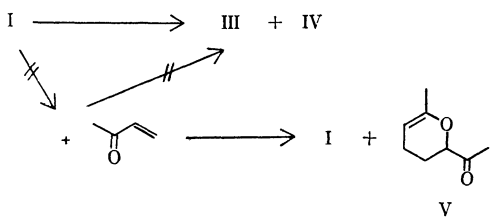


Fig. 1. Pyrolysis of 1-acetyl-3-methylenecyclobutane.
○—○ 1-Acetyl-3-methylenecyclobutane
◇—◇ 2-Methyl-5-methylene-Δ^2-dihydropyrane
×—× 4-Methylenecyclohexanone

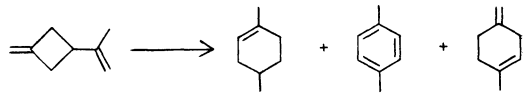
Neither allene nor methyl vinyl ketone, which is the expected fragmentation product of I, was found to be formed by the pyrolysis of I. However, it may be reasonable to assume that the observed product, III, was formed by the cycloaddition reaction of the fragmentation products. To check on this possibility, a mixture of allene and methyl vinyl ketone was heated to 220°C for two hours in an autoclave. A resinous product resulted, and from it a small amount of a distillable component could be isolated. The distillate consisted of I (1 part) and a compound (20 parts) tentatively thought to be 2-methyl-6-acetyl-Δ^2-dihydropyrane (V), a dimer of methyl vinyl ketone but neither III nor IV could be detected. This must mean that the pyrolysis of I does not proceed through the fragmentation-recombination pathway considered earlier.



V

The assignment of structure V to the addition product follows from the NMR spectrum, which showed a three-proton doublet (J=1.5 Hz) and a three-proton singlet at τ 8.25 and 7.75 for the two methyl groups, a four-proton broad multiplet centered at τ 8.10 for the ring methylene protons, a one-proton multiplet at τ 5.87 for the proton between the acetyl group and the oxygen atom, and a one-proton multiplet at τ 5.55 for the proton on the double bond. Its infrared spectrum, showing bands of an acetyl group at 1720 and 1360 cm^{-1}, and bands of a vinyl ether at 1238 and 1070 cm^{-1}, is consistent with the indicated structure.

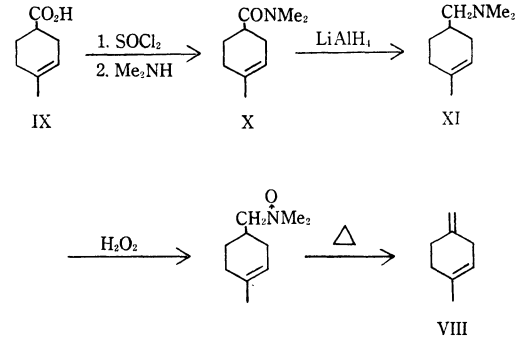
Pyrolysis of 1-Isopropenyl-3-methylenecyclobutane. The pyrolysis of 1-isopropenyl-3-methylenecyclobutane (II) as a neat liquid or as a toluene solution, at 255—340°C and in a sealed tube, gave 1,4-dimethylcyclohexene (VI),[10] *p*-xylene (VII), and 1-methyl-4-methylenecyclohexene (VIII).



II VI VII VIII

The NMR spectrum of VIII had a three-proton singlet (with fine splittings) at τ 8.38 for the methyl group on the double bond, two overlapping two-proton multiplets at τ 7.90 and 7.78 for the two methylene groups adjacent to a double bond, a two-proton multiplet at τ 7.35 for the methylene group between the two double bonds, a slightly-broadened two-proton singlet at τ 5.38 for the terminal methylene group, and a one-proton multiplet at τ 4.75 for the hydrogen atom on the double bond. Its infrared spectrum exhibited bands of a terminal methylene group and an olefinic group at 3075, 1655, 1445, 1435, and 884 cm^{-1}. Conclusive evidence for the structure assignment could be obtained by an independent synthesis of VIII by the route to be described below.

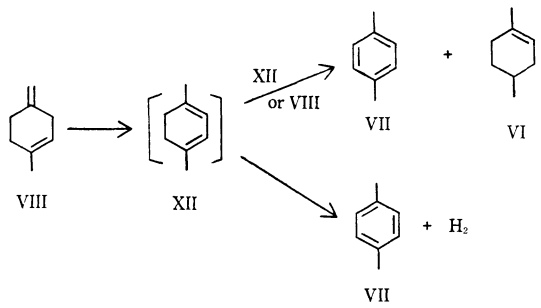
1-Methylcyclohexene-4-carboxylic acid (IX)[11]



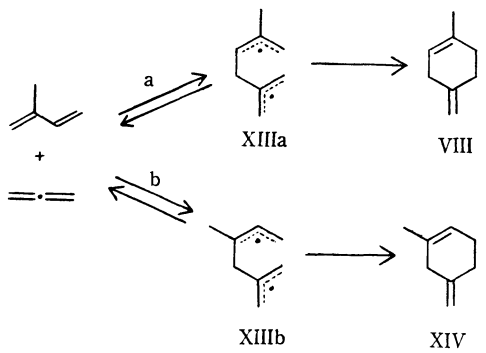
10) J. -F. Sauvage, R. H. Baker and A. S. Hussey, *J. Amer. Chem. Soc.*, **82**, 6090 (1960).
11) E. Lehmann and W. Paasche, *Ber.*, **68**, 1068 (1935).

was converted to the corresponding dimethylamide, X, through its acid chloride. The amide X was then reduced with lithium aluminum hydride to 1-methyl-(4-dimethylaminomethyl)cyclohexene (XI), which was subsequently converted to the corresponding *N*-oxide with hydrogen peroxide. The pyrolysis of the *N*-oxide afforded 1-methyl-4-methylenecyclohexene (VIII), which proved identical with the sample obtained by the pyrolysis of II.

When 1-methyl-4-methylenecyclohexene (VIII) was heated at 340°C in a sealed tube, three new products were formed in a vpc peak area ratio of 3:1:10, of which the two major products were identified as 1,4-dimethylcyclohexene (VI) (3 parts) and *p*-xylene (10 parts) respectively by comparison with authentic samples. Such a conversion of VIII may be considered to proceed through an initial isomerization to 1,4-dimethylcyclohexa-1,3-diene (XII) and its intermolecular hydrogen transfer and, in part, dehydrogenation.[12]



It was observed that no fragmentation product, allene or isoprene, was formed by the pyrolysis of II. In this case, the possibility of the fragmentation of II and recombination to VIII should also be considered. If the addition of allene and isoprene proceeds by a stepwise radical mechanism, then the reaction may be expected to proceed through pathway b to give a slightly more stabilized biradical intermediate, XIIIb, than the biradical XIIIa.



12) A similar disproportionation reaction has recently been reported with cyclohexa-1,3-diene: S. W. Benson and R. Shaw, *J. Amer. Chem. Soc.*, **89**, 5351 (1967).

The reaction of allene and isoprene at 300°C in an autoclave afforded, besides a large quantity of unreacted starting materials and polymeric substances, a small quantity of distillable products, which consisted of five components in a ratio of 7.5:4:8:1:1.5 (in the increasing order of their retention times). The vpc retention times of none of these components corresponded to *p*-xylene. The vpc retention time of the component with the shortest retention time was identical with that of VIII, and its infrared and NMR spectra were very similar to those of VIII except that the multiplet at τ 7.78 of VIII was shifted to a slightly higher magnetic field to give a poorly-resolved four-proton multiplet centered at τ 7.85. When it was subjected to the same pyrolysis conditions as those for VIII described earlier, it was converted to two products in a ratio of 1:1.3, though much more sluggishly than VIII. This isomerization could be effectively accelerated by the addition of a catalytic amount of alumina. The major product of the isomerization was identified as *m*-xylene by comparison with an authentic sample. From the above experiment, it may now be concluded that allene and isoprene react regiospecifically to give 1-methyl-5-methylenecyclohexene (XIV). This fact, as well as the absence of XIII and *m*-xylene in the pyrolysis products of II, gives conclusive evidence that no fragmentation occurred in the pyrolysis of 1-isopropenyl-3-methylenecyclobutane (II).

Interpretation of the Results. An arresting feature of the pyrolyses of I and II described above is that no fragmentation products could thus be detected. The pyrolysis of acetylcyclobutane gives ethylene and methyl vinyl ketone,[13] while the pyrolysis of isopropenylcyclobutane gives ethylene, isoprene, and 1-methylcyclohexene.[14] The activation energies of these reactions (54.5 kcal/mol and 51.0 kcal/mol respectively) clearly demonstrate the contribution of allylic resonance at the ring-cleavage step.

For steric reasons, the ring-enlargement reaction of II cannot proceed concertedly through a transition state similar to that of the Cope rearrangement,[15] to which it bears a formal analogy, nor can it be regarded as a concerted sigmatropic rearrangement.[16] The same holds true of the ring-enlargement reaction of I. Thus, it appears most reasonable to assume that the reaction proceeds by a stepwise biradical mechanism. The seem-

13) L. G. Daignault and W. D. Walters, *ibid.*, **80**, 541 (1958).

14) R. J. Ellis and H. M. Frey, *Trans. Faraday Soc.*, **59**, 2076 (1963).

15) W. von E. Doering and W. R. Roth, *Tetrahedron*, **18**, 67 (1962).

16) R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, **87**, 2511 (1965); R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968).

ingly anomalous rearrangements of I and II can, then, readily be explained on the basis of the results of the degenerate rearrangement of methylenecyclobutane, elegantly studied by Doering and Gilbert.[8]

The pyrolysis of II (or I) gives a biradical intermediate, XIIIc, in which a full delocalization of the two radical sites have been attained (Chart 1). The biradical XIIIc may regenerate II (or I) *via* a transition state, XIIId, in which one allylic delocalization is completely, and the other, partially, retained,[17] but in order for the biradical XIIIc to give fragmentation products, one of the allylic stabilizations have to be nearly completely lost at the transition state XIIIe, since the two planes occupied by the two H–C–H groups in the allyl group should be almost perpendicular to each other.

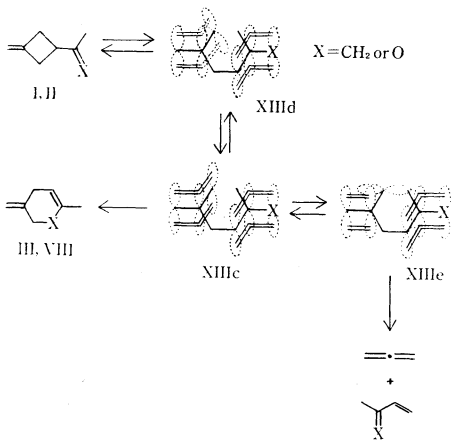


Chart 1. Pyrolytic path of 1-acetyl- and 1-isopropenyl-3-methylenecyclobutane.

Thus, the energetically most preferred path for the biradical XIIIc is ring enlargement, because, in this case, the biradical XIIIc can give a ring-enlargement product simply by rotation about a single bond, which can rotate freely with virtually no loss of stabilization energy.

In the cases of 1-acetyl- and 1-isopropenylcyclobutane, there is no such conformational preference of the biradical intermediates to warrant one of the two reaction paths (ring enlargement *vs.* fragmentation), and in the case of methylenecyclobutane, only a recombination to the starting material or fragmentation is possible.

17) It has been established that the ring-opening of (and thus recombination to) methylenecyclobutane is markedly assisted by allylic delocalization. For further discussion on the transition states and intermediates of this system, see Ref. 8.

Experimental[18]

1-Acetyl-3-methylenecyclobutane (I). A solution of 20 g (0.26 mol) of 3-methylenecyclobutanecarbonitrile[9] in 30 m*l* of ether was added, with cooling and stirring, to a solution of methymagnesium iodide, prepared from 8.7 g (0.36 g atom) of magnesium and 51.1 g (0.36 mol) of methyl iodide, in 50 m*l* of ether. The mixture was stirred for three hours at room temperature and was then hydrolyzed by the addition of dilute sulfuric acid; the organic layer was separated, and the aqueous layer was extracted repeatedly with ether. The ether extract was washed with aqueous sodium bicarbonate and then with water, and dried over sodium sulfate. Distillation gave 16.3 g (60% yield) of I boiling at 53—54°C/14 mmHg. n_D^{25} 1.4543.

Found: C, 76.45; H, 9.15%. Calcd for $C_7H_{10}O$: C, 76.32; H, 9.15%.

Semicarbazone of I: mp 146—148°C.

Found: C, 57.33; H, 7.81%. Calcd for $C_8H_{13}N_3O$: C, 57.46; H, 7.84%.

2,4-Dinitrophenylhydrazone of I: mp 142—143°C.

Found: C, 53.86; H, 5.10; N, 19.54%. Calcd for $C_{13}H_{14}N_4O_4$: C, 53.79; H, 4.86; N, 19.30%.

1-Isopropenyl-3-methylenecyclobutane (II). A solution of 8 g (0.07 mol) of 1-acetyl-3-methylenecyclobutane in 20 m*l* of ether was added, under an atmosphere of nitrogen and with cooling and stirring, to a solution of methylenetriphenylphosphorane in 300 m*l* of ether, prepared *in situ* from 35.7 g (0.1 mol) of triphenylmethylphosphonium bromide and *n*-butyllithium, and the resulting mixture was refluxed for ten hours. The precipitate was then filtered off, and the filtrate was dried over calcium chloride. The fraction distilling between 80—130°C and consisting of II and benzene was collected and subsequently purified by vpc (Carbowax 20M on Diasolid A). Bp 98—100°C, n_D^{25} 1.4531.

Found: C, 88.64; H, 10.44%. Calcd for C_8H_{12}: C, 88.82; H, 11.18%.[19]

Thermal Rearrangement of I. Samples of I (10—100 μl) were sealed in Pyrex tubes under an atmosphere of nitrogen, and were placed in an atmosphere of refluxing acetanilide (bp 304°C) or anthracene (bp 340°C) for periods of time, and then quenched by immersion in an ice bath. Vpc analysis showed the presence of three components, which were fractionated by vpc (Carbowax 20M on Diazolid A) to afford I, 2-methyl-5-methylene-Δ^2-dihydropyrane (III), and 4-methylenecyclohexanone (IV).

18) The melting points were determined on a micro hot stage, and all melting and boiling points are not corrected. The infrared spectra were recorded on a Hitachi model EPI-SII spectrophotmeter as neat liquid. The NMR spectra were determined using a Jeolco C-60 model (60MHz) spectrometer on solutions of carbon tetrachloride and the chemical shifts are represented by τ values. The vpc analyses were performed with a Shimadzu model GC-1B chromatograph. The spectral data discussed in the text are not reproduced in this section.

19) Some compounds, especially low boiling liquid, did not give satisfactory analytical values although they were proved homogeneous by vpc, and showed quite satisfactory spectra.

Samples of I containing 20% of toluene as an internal standard were heated at the refluxing temperature (340°C) of anthracene, and the concentration of the components, I, III, and IV, as evaluated by the ratio of their vpc peak areas to those of toluene, were plotted against the time. The results are shown in Fig. 1.

Reaction of Allene and Methyl Vinyl Ketone. A solution of 5 g (0.07 mol) of methyl vinyl ketone, 5 m*l* (*ca.* 0.08 mol) of allene, and 0.5 g of hydroquinone in 50 m*l* of toluene was heated at 220°C for two hours in a 100-m*l* autoclave under autogeneous pressure (20 atm). The reddish-brown product was concentrated and distilled under reduced pressure to give 0.9 g of a colorless liquid boiling at 88—90°C/50 mmHg. The residue of the distillation consisted of a large amount of a polymeric material. The distillate was separated into two components (A and B) in a ratio of 1 : 20 (Carbowax 20M on Diasolid A).

Component A had the same infrared spectrum and vpc retention time as those of an authentic sample of I.

The spectral data of component B are given in the text above.

Thermal Rearrangement of II. Samples of II were heated as has been described above at the refluxing temperature of biphenyl (bp 255°C), acetanilide or anthracene, and the product mixture was separated by vpc (Silicone DC 550 on Shimalite) giving II, *p*-xylene, 1-methyl-4-methylenecyclohexene (VIII), and a component with identical vpc retention times with those of an authentic sample of 1,4-dimethylcyclohexene (VI).[10] The infrared spectra and the vpc retention times of VIII and *p*-xylene were identical with those of authentic samples of VIII and *p*-xylene respectively.

1-Methylcyclohexene-4-carbodimethylamide (X). Into an ice-cooled, saturated solution of dimethylamine in 100 m*l* of ether, there was added with stirring, 31.7 g (0.2 mol) of 1-methylcyclohexene-4-carbonyl chloride,[11] and the resulting mixture was allowed to stand overnight at room temperature. The mixture was washed with water and then with a saturated aqueous solution of sodium chloride, and was dried over magnesium sulfate. Distillation afforded 24 g (72% yield) of X boiling at 147—153°C/23 mmHg.

Found: C, 71.70; H, 10.31; N, 8.57%. Calcd for $C_{10}H_{17}NO$: C, 71.81; H, 10.25; N, 8.38%.

1-Methyl-4-dimethylaminomethylcyclohexene (XI). Into a suspension of 5 g (0.14 mol) of lithium aluminum hydride in 100 m*l* of ether, 19 g (0.11 mol) of 1-methylcyclohexene-4-carbodimethylamide (X) was slowly added with stirring, after which the mixture was stirred for another three hours at room temperature. The excess hydride was decomposed by the addition of 5% aqueous sodium hydroxide, and the organic layer was separated, washed with aqueous sodium chloride, and dried over sodium sulfate. Distillation gave 14.2 g (80% yield) of 1-methyl-4-dimethylaminomethylcyclohexene boiling at 74—76°C/11 mmHg, n_D^{25} 1.4628.

This product was characterized by conversion to its methiodide; mp 209—210°C.

Found: C, 45.03; H, 7.58; N, 4.99%. Calcd for $C_{11}H_{22}NI$: C, 44.76; H, 7.51; N, 4.74%.

1-Methyl-4-dimethylaminomethylcyclohexene *N*-Oxide. Compound XI (10 g, 0.034 mol) was slowly added to a stirred and cooled solution of 50 m*l* of 10% aqueous hydrogen peroxide. The mixture was then stirred at room temperature for twenty hours, and the excess peroxide was decomposed by catalase. The mixture was subsequently filtered, and the water was removed under reduced pressure, and the yellow, viscous residue which remained was used for the pyrolysis reaction without further purification.

1-Methyl-4-methylenecyclohexene (VIII). The crude *N*-oxide prepared by the above-described method was decomposed at 200°C on an oil bath under reduced pressure; the distillate was collected in a trap which was cooled by a Dry Ice - acetone bath. The condensate was dissolved in 40 m*l* of ether, washed successively with dilute hydrochloric acid, water, and a saturated aqueous solution of sodium chloride, and dried over sodium sulfate. Distillation gave 2.5 g of VIII boiling at 113—114°C. The infrared spectrum and the vpc retention times of this material were identical with those of the sample of VIII isolated from the pyrolysis of II, n_D^{25} 1.4690.

Found: C, 87.97; H, 10.87%. Calcd for C_8H_{12}: C, 88.82; H, 11.18%.[19]

Thermal Rearrangement of 1-Methyl-4-methylenecyclohexene (VIII). Compound VIII (100 μl) was sealed in a Pyrex tube under an atmosphere of nitrogen and heated at 340°C for seven minutes. The product consisted of three components in a vpc peak area ratio of 3 : 1 : 10, of which the two major components (C and D) were collected by vpc (Carbowax 20M on Diasolid A).

Component C had the same infrared spectrum and vpc retention times as those of an authentic sample of 1,4-dimethylcyclohexene (VI).[10]

Component D had the same NMR and infrared spectra and vpc retention times as those of *p*-xylene.

The Reaction of Allene and Isoprene. A mixture of 5 g (0.07 mol) of isoprene, 5 m*l* (*ca.* 0.08 mol) of allene, 0.5 g of hydroquinone, and 50 m*l* of *n*-hexane was slowly heated to 300°C for seven hours in an autoclave and under autogeneous pressure (maximum, 50 atm). The product was distilled to give 1.5 g of a product boiling at 78—80°C/40 mmHg. Considerable amounts of allene and isoprene were recovered, and a transparent polymeric material was formed on the wall of the autoclave. The distillate consisted of five components in a vpc peak area ratio of 7.5 : 4 : 8 : 1 : 1.5 (Carbowax 20M on Diasolid A), none of which had the same vpc retention time as that of *p*-xylene. The first three major components (E, F, G) were collected by vpc.

Component E (1-Methyl-5-methylenecyclohexene, XIV): NMR: 8.35 (3H, s), 7.85 (4H, m), 7.38 (2H, m), 5.34 (2H, s) and 4.75 (1H, m). IR: 3075, 1660, 1445, 1440 and 885 cm^{-1}. Its vpc retention times (Carbowax 20M and Silicone DC 550) were identical with those of 1-methyl-4-methylenecyclohexene (VIII).

Component F was found to be a mixture of 1,4-dimethyl-4-vinylcyclohexene and 2,4-dimethyl-4-vinylcyclohexene by comparison of its NMR and infrared spectra with the reported values.[20]

Component G was identified as 1-methyl-5-isopropenylcyclohexene by comparison of its infrared spectrum with a previously reported chart.[21] NMR: 8.39 (3H, s), 8.29 (3H, s), 8.08 (7H, m), 5.35 (2H, s)

20) G. S. Hammond, N. J. Turro and R. S. H. Liu, *J. Org. Chem.*, **28**, 3297 (1963).

21) J. I. Binder, K. C. Eberly and G. E. P. Smith, Jr., *J. Polym. Sci.*, **38**, 229 (1959).

and 4.68 (1H, m).

Thermal Rearrangement of 1-Methyl-5-methylenecyclohexene (XIV). Compound XIV was sealed, under an atmosphere of nitrogen, in a Pyrex tube in the presence of a small amount of alumina, and then heated at 540°C for one hour. The product consisted of two components in a vpc area ratio of 1 : 1.3; the latter, major component was collected by vpc (Carbowax 20M on Diasolid A) and identified as *m*-xylene by a comparison of its NMR and infrared spectra and vpc retention times.

We are indebted to Miss Mizuko Yoshida for the measurement of NMR spectra, to the staffs of microanalysis in this laboratory for the elemental analyses, and to Takeda Chemical Industries, Ltd, for the measurement of mass spectra.