Energies of Alternate Electrocyclic Pathways. Pyrolysis of *cis*-3,4-Dimethylcyclobutene

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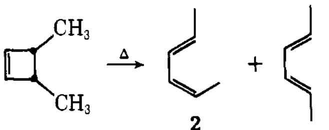
Abstract: Pyrolysis of *cis*-3,4-dimethylcyclobutene yields *ca.* 0.005% of the Woodward-Hoffmann nonallowed product, *trans,trans*-2,4-hexadiene, at 280°. From this and consideration of steric effects it is inferred that the allowed transition state experiences $\geqslant 15$ kcal/mol added electronic stabilization compared to the nonallowed transition state.

The unusual electronic stabilization (empirical resonance energy) exhibited by certain structures, *e.g.*, benzene, has long intrigued chemists, and considerable effort has been expended in exploring both the magnitude and origin of such stabilization. For the most part, these studies have concerned themselves with ground-state molecules such as aromatic hydrocarbons or relatively stable intermediates such as conjugated radicals. It is also possible to evaluate stabilization experienced in certain transition states. In particular, Woodward-Hoffmann[2] "allowed" processes clearly are stabilized relative to other "nonallowed" or possibly stepwise processes. The aromatic nature of these allowed transition states has been pointed out,[3] but there have been few attempts to determine the added stabilization experimentally. Recently, we analyzed cyclobutene ring openings and derived an estimate of $\geqslant 15$ kcal/mol of added stabilization for the allowed process.[4] Doorakian and Freedman[5] attempted to obtain a direct measure by an elegant experiment involving diene equilibration and were able to show $\Delta\Delta G^{\ddagger} \geqslant 7.5$ kcal/mol.

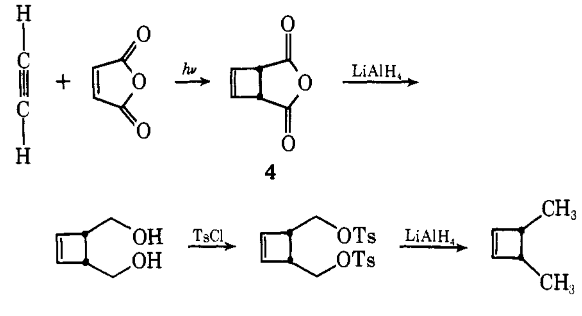
The simplest and most direct method of determining the difference in energy between allowed and nonallowed pathways would be to determine the fraction of nonallowed product. This is, however, a formidable problem since if the estimates are correct the fraction will be very small, and the incursion of other reactions could obscure the nonallowed path. However, such an experiment should provide at the very least a limiting value for the desired energy difference; consequently we have studied the conversion[6,7] of *cis*-3,4-dimethylcyclobutene (**1**) to the 2,4-hexadienes **2** and **3**, eq 1.



1 **2** **3** (1)

Results

Synthesis and Purification. *cis*-3,4-Dimethylcyclobutene (**1**) was prepared essentially as described by Winter,[6] with a modification[8] in the preparation of the anhydride **4**, eq 2. The *cis*-3-,4-dimethylcyclobutene



(2)

was purified by preparative vpc on Apiezon J and silver nitrate columns, providing material which contained less than 1 part in 10^5 of dienes. In order to eliminate the possibility of trans isomer contributing to the nonallowed product, a sample of **1** was purified kinetically by allowing it to react at 175° to *ca.* 50% conversion. As the trans isomer is known to react about seven times faster than the cis,[6] this would have reduced any trans component to less than 1% of its initial concentration. The significance of this experiment is discussed below.

Pyrolysis. The pyrolysis of **1** was carried out in a hot tube at 280° using nitrogen as a carrier gas. The temperature profile of the tube was reasonably flat with sharp end regions. A one point, first-order rate constant could be calculated for the isomerization using the extent of conversion measured by vpc and the contact time obtained from the flow rate and heated volume. Agreement within experimental error was obtained with the value of the rate constant calculated from the Arrhenius parameters reported for this isomerization by Srinivasan.[7]

The pyrolysis products were trapped at −80° and analyzed by flame ionization vpc. In addition to unreacted starting material, the products were identified as 99.9% *cis,trans*-2,4-hexadiene (**2**); ~0.005% *trans,trans*-2,4-hexadiene (**3**); and 0.1–0.5% 1,3-hexadiene (**5**). Products were identified by vpc coinjection on two columns. The amount of 1,3-hexadiene increased with increasing contact time; thus its source is undoubtedly a secondary isomerization of **2** by a 1,5 hydrogen shift, eq 3. From the Arrhenius parameters

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[1] (a) Alfred P. Sloan Fellow; (b) NDEA Title IV Fellow, 1967–1969; NIH Predoctoral Fellow, 1969–1970.

[2] R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

[3] H. E. Zimmerman, *J. Amer. Chem. Soc.*, **88**, 1564, 1566 (1965); M. J. S. Dewar, *Tetrahedron, Suppl.*, **8**, 75 (1967).

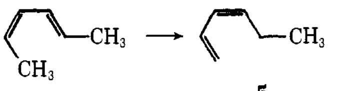
[4] (a) J. I. Brauman and D. M. Golden, *J. Amer. Chem. Soc.*, **90**, 1920 (1968); (b) D. M. Golden and J. I. Brauman, *Trans. Faraday Soc.*, **65**, 464 (1969).

[5] G. A. Doorakian and H. H. Freedman, *J. Amer. Chem. Soc.*, **88**, 5310, 6895 (1968).

[6] R. E. K. Winter, *Tetrahedron Lett.*, 1207 (1965).

[7] R. Srinivasan, *J. Amer. Chem. Soc.*, **91**, 7557 (1969).

[8] G. Koltzenburg, P. G. Fuss, and J. Leitlich, *Tetrahedron Lett.*, 3409 (1966).



2 5 (3)

reported for the reverse reaction[9,10] and an estimate[10] of $\Delta H°$, it can be shown that the extent of conversion is that expected for this reaction.

The product ratio of **3**:**2** was measured directly from areas of the vpc traces multiplied by appropriate attenuation factors. The accuracy of the method was ascertained by analysis of synthetic mixtures of approximately the same composition. Table I shows the results of a number of experiments which include variation of flow rate (contact time in half-lives), added surface area, and kinetic purification. The variations in ratio shown in runs 1–12, which were conducted under identical conditions, are due largely to the analysis procedure itself. Thus, duplicate analyses of the same sample showed variations comparable to those found between different runs. The variation, while apparently large, actually is only about ±3 parts in 10,000. This corresponds to an error in $\Delta\Delta G^{\ddagger}$ of less than ±1 kcal/mol.

Table I. Pyrolysis of *cis*-3,4-Dimethylcyclobutene[a]

No.	Flow rate,[b] ml/sec	Contact time, half-lives[c]	Measured ratio (× 10^5) **3**/**2**
1	1.78	7	3.7
2	1.78	7	3.4
3	1.78	7	2.1
4	1.78	7	2.0
5	1.78	7	6.1
6	1.78	7	8.1
7	1.78	7	12.7
8	1.78	7	7.7
9	1.78	7	5.2
10	1.78	7	5.5
11	1.78	7	8.0
12	1.78	7	8.4
		(Av of 1–12	6.1 ± 3.2)
13[d]	1.78	7	2.2
14	0.42	28	5.2
15	0.83	14	5.8
16	0.83	14	7.5
17	3.57	3.5	2.8
18[e]	0.83		8.9
19[e]	0.83		10.7
20[f]	1.78		8.2

[a] Temperature = 280°. [b] Measured at room temperature. [c] Calculated from[7] $\log k = (13.88 - 34{,}000)/2.303RT$. [d] Kinetically purified starting material. [e] Twofold surface area increase (Pyrex chips). [f] 30-fold surface area increase (glass wool).

Although it is difficult to be certain of the details of a reaction which proceeds to such a minute extent, we believe, for the following reasons, that the measured product ratio is a true reflection of relative homogeneous gas-phase rates.

(a) The ratio of **3** to **2** was found to be insensitive to pretreatment[11] of the tube with silicone oil or Teflon coating and to the surface-to-volume ratio (runs 18–20). Thus, it appears that **3** does not result from a heterogeneous reaction.

(b) The ratio of **3** to **2** was insensitive to contact time (runs 14–17). This indicates that **3** does not arise from a secondary isomerization of **2**. For example, cyclobutene in run 14 was converted in the first 25% of the tube to the extent to which it was totally converted in runs 1–12. Thus, in run 14 **3** was exposed to the tube for at least three times as long as in runs 1–12. Consequently, **3** appears to be stable to the reaction conditions. As **3** is somewhat more stable than **2** it is exceedingly unlikely that it would undergo decomposition more rapidly than **2**. Furthermore, since the ratio of **3** to **2** is so far from the equilibrium ratio, any simple isomerization reaction would simply have produced more **3**.

(c) The ratio of **3** to **2** was insensitive to kinetic purification of the starting material, run 13. This demonstrates rigorously that *trans*-3,4-dimethylcyclobutene is not the major source of **3**, since if it were, kinetic purification would have reduced **3** to 1% of its initial value.

Consequently, the product ratio **3** to **2** of $6.1 \pm 3.2 \times 10^{-5}$ is almost surely the primary, unimolecular, homogeneous, gas-phase result for the pyrolysis of *cis*-3,4-dimethylcyclobutene at 280°. If the nonallowed component were stepwise and partitioned to produce half-allowed product, the total nonallowed component would be 12×10^{-5} of the allowed. This correction, corresponding to less than 1 kcal/mol, has not been included, as the nature of the nonallowed transition state is not known. It is important to note that even if the nonallowed product arises from a catalyzed pathway, the homogeneous rate would then be lower than that calculated, and the measured ratio thus provides a lower limit on the desired quantity.

Discussion

The ratio of products obtained from competing first-order reactions of a single reactant is equal to the ratio of rate constants for the two reactions. Thus, the ratio of **3** to **2** is also the ratio of rate constants for their formation. The ratio of 6.1×10^{-5} at 280° leads to a difference in activation free energy $\Delta\Delta G^{\ddagger} = 10.7 \pm 0.5$ kcal/mol. The analysis of stabilization energies requires a knowledge of $\Delta\Delta H^{\ddagger}$, and obtaining this number in turn requires a knowledge of $\Delta\Delta S^{\ddagger}$. Examination of the data for all known ring-opening reactions of cyclobutenes, both allowed and nonallowed, suggests that any reasonable mechanism for the nonallowed reaction would have[12] an A factor in the range $10^{13.8}$–$10^{14.4}$. Thus, since the A factor for the allowed reaction[7] is $10^{13.9}$, $\Delta\Delta S^{\ddagger} \cong 0$. Assuming $\Delta\Delta S^{\ddagger} \cong 0$, $\Delta\Delta H^{\ddagger} \cong 10.7$ kcal/mol. If the nonallowed reaction has an A factor at the higher end, $\Delta\Delta S^{\ddagger}$ would be *ca.* 2.3 eu, and $\Delta\Delta H^{\ddagger}$ would be *ca.* 12 kcal/mol. Thus, $\Delta\Delta H^{\ddagger}$ for the observed reaction appears, conservatively, to be 11 ± 1 kcal/mol, taking into account the possible errors arising both from experiment and the estimate of $\Delta\Delta S^{\ddagger}$.

If steric effects played no part in determining the energetics of the relative pathways, then this number

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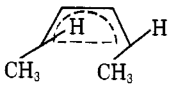
(9) H. M. Frey and B. M. Pope, *J. Chem. Soc. A*, 1701 (1966).

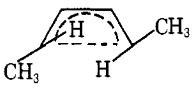
(10) S. W. Benson and H. E. O'Neal, *Nat. Stand. Ref. Data Ser., Nat. Bur. Stand.*, No. 21 (1970).

(11) K. W. Egger and S. W. Benson, *J. Amer. Chem. Soc.*, **87**, 3314 (1965).

(12) S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968. Concerted cyclobutene isomerizations have A factors at the low end; about $10^{13.9}$. Cyclobutane ring openings have[10] A factors of about $10^{14.6}$; a biradical nonallowed ring opening would probably have a lower A factor due to its resonance stabilization. The bicyclic cyclobutenes (nonallowed reactions) have A factors of about $10^{14.2}$.

would correspond to the difference in stabilization between the two pathways. However, it is apparent that the methyl groups introduce a complication. For example, *trans*-3,4-dimethylcyclobutenes appear to have E_a for ring opening about 4 kcal/mol lower than the cis compounds.[7,13,14] In general, trans compounds are accelerated and cis compounds inhibited relative to the unsubstituted ones. This effect must be due at least partially to developing interactions in the formation of the *s-cis*-butadiene. It is difficult to evaluate completely this effect of moving a methyl group "in" as opposed to "out," but data of Frey and his coworkers suggest an added increment of 5–10 kcal/mol.[15] Since the allowed reaction requires moving a methyl "in" whereas the nonallowed reaction does not, we can estimate that the allowed transition state is sterically destabilized by 7 ± 3 kcal/mol relative to the nonallowed one. Thus, the allowed transition state must experience electronic stabilization of at least 15 kcal/mol compared with the alternate pathway. If $\Delta S^{\ddagger}$ is greater for the nonallowed path, the estimate can only be corrected upward. The analysis can be refined by considering various models such as a biradical one[4b,12] and correcting for substituent effects; essentially identical conclusions are derived from these analyses.

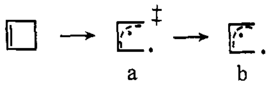




The derived difference of ⩾15 kcal/mol between allowed and nonallowed reactions corresponds quite closely to that obtained previously from an analysis of ring opening in bicyclic systems.[4] Consideration of the thermochemical analysis suggests that this must indeed be the case, since the assumptions cannot be greatly in error.[17] The recent observations of Baldwin and Andrist indicating[18] that bicyclo[2.1.0]pent-2-enes may isomerize *via* an alternative pathway do not vitiate these thermochemical arguments which produce only limiting values. Thus, even if intervention of new alternate pathways occurs, a lower estimate for stabilization can still be obtained.

It is of interest to compare the value of ⩾15 kcal/mol for cyclobutene isomerizations with that found in the Diels–Alder reaction. From the data of Bartlett and Schueller[19] on the relative amounts of vinylcyclobutene and cyclohexene formed from the reaction of ethylene and butadiene, one can estimate an upper limit for the difference in pathways (presumably concerted *vs.* biradical) of *ca.* 7.6 kcal/mol. It is not readily apparent why the intermolecular reaction should have only about half of the enhanced stabilization experienced by the intramolecular reaction, although differences in overlap as well as intrinsic electronic effects must be involved.

The nature of the nonallowed transition state is also a matter of some importance. While it is difficult, if not impossible, to ascertain experimentally whether the nonallowed reaction is biradical or concerted, it is possible to estimate the minimum energy that a biradical transition state might be expected to have and to compare it with the observed energy. Alkyl substituents have a small stabilizing effect on concerted reactions and would be expected to exert a similar effect on stepwise ones. Since the thermochemical quantities are well known for the unsubstituted case, we consider it here. At worst, we might expect a biradical transition state, a, to have no interaction between the 3 and 4 carbons and the 2 and 3 carbons, *viz.*



This is precisely the structure one might consider for a diene isomerization transition state, and its energy can be adequately estimated[12] by subtracting one π bond from butadiene and adding the allyl resonance.[20] Thus, we estimate the energy of the biradical, b, at about 53 kcal/mol above butadiene or 41.5 kcal/mol above cyclobutene.[21] Typically,[12] small ring biradicals require an activation energy for rotation or closure, four-membered rings usually in the neighborhood of 5 kcal/mol. Therefore, the biradical transition state, a, would probably have an energy of about 47 kcal/mol relative to cyclobutene.

Our experiments suggest that the nonallowed transition state actually lies at least 15 kcal/mol above the allowed one, setting its energy at ≥48 kcal/mol relative to cyclobutene. Thus, the biradical model is close in energy to the observed transition state. If the nonallowed reaction has a concerted component, it is probably not exclusive. Although the nonallowed transition state may be biradical in nature, it has not been possible to stabilize it sufficiently with phenyl substitution to allow competition with the allowed pathway, since phenyls appear also to stabilize the allowed transition state.[22]

Finally, knowledge of the energetics of the allowed and nonallowed pathways provides pertinent information regarding the mechanism of diene isomerizations. While it may appear reasonable that dienes, like olefins, should isomerize through simple bond rotation *via* a biradical, it is apparent from examination of the above energetics that, for example, in the case of *cis*- → *trans*-1-deuteriobutadiene, isomerization *via* 3-deuteriocyclobutene is about 10 kcal/mol preferred. Isomerizations *via* cyclobutenes are well established in some cases.[5,16] Except for the intervention of steric effects which destabilize cyclobutene ring opening and closing transition states, the cyclobutene pathway appears as the attractive general mechanism. Clearly on an electronic basis alone, it is substantially preferred.

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(13) G. R. Branton, H. M. Frey, and R. F. Skinner, *Trans. Faraday Soc.*, **62**, 1546 (1966).

(14) H. M. Frey, B. M. Pope, and R. F. Skinner, *ibid.*, **63**, 1166 (1967).

(15) When 3-methylcyclobutene was pyrolyzed at 235°, less than 0.2% of *cis*-1,3-pentadiene could be found.[14] Recent work[16] on diene isomerizations gives a direct measure of 5–10 kcal/mol depending on the compound.

(16) H. M. Frey, A. M. Lamont, and R. Walsh, *J. Chem. Soc. D*, 1583 (1970).

(17) However, see E. C. Lupton, Jr., *Tetrahedron Lett.*, 4209 (1968).

(18) J. E. Baldwin and A. H. Andrist, *J. Chem. Soc. D*, 1561 (1970).

(19) P. D. Bartlett and K. E. Schueller, *J. Amer. Chem. Soc.*, **90**, 6071 (1968).

(20) D. M. Golden, A. S. Rodgers, and S. W. Benson, *ibid.*, **88**, 3194 (1966); K. W. Egger, D. M. Golden, and S. W. Benson, *ibid.*, **86**, 5420 (1964).

(21) The energy difference between butadiene and cyclobutene is 11.5 kcal/mol: K. B. Wiberg and R. A. Fenoglio, *ibid.*, **90**, 3395 (1968).

(22) J. I. Brauman and W. C. Archie, Jr., *Tetrahedron*, **27**, 1275 (1971).

Experimental Section[23]

cis-**3,4-Cyclobutenedicarboxylic acid anhydride** (**4**) was prepared[8] by photolysis (medium-pressure 550-W Hg arc) in acetone solvent (*ca.* 500 ml) of maleic anhydride (60 g, 0.61 mol) and acetylene sensitized by 20 g of benzophenone. The reaction was maintained at −80° and acetylene (dried by bubbling through sulfuric acid) was added slowly for *ca.* 40 hr at which point *ca.* 80% of the maleic anhydride had reacted (by vpc). The solution was concentrated to one-third of the original volume on a rotary evaporator, and a small amount of side product[8] which precipitated was removed by filtration. The crude product obtained by further concentration was purified by short-path distillation (100–125°, <0.1 Torr), and recrystallization (1:1 benzene–cyclohexane) to give **4**, 25.3 g (50% based on maleic anhydride), mp 88–92° (lit.[8] mp 90°).

cis-**3,4-Dimethylcyclobutene** (**1**). The anhydride **4** was treated with lithium aluminum hydride in ether to give a clear oil (91.5%) with an nmr spectrum acceptable for *cis*-**3,4-di(hydroxymethyl)cyclobutene.** This diol was treated with *p*-toluenesulfonyl chloride in pyridine at 0°. The product was filtered and dried to give 78% of *cis*-**3,4-di(hydroxymethyl)cyclobutene ditosylate,** mp 65–67° (lit.[6] mp 66–67°). The ditosylate was added to a slurry of lithium aluminum hydride in glyme. The product was flash distilled at room temperature and pump pressure and trapped at liquid nitrogen temperature. Analysis by vpc showed two impurities (5–10%) which were removed by preparative vpc (12 ft × $^{1}/_{4}$ in., 15% ethylene glycol saturated with silver nitrate, 80–100 mesh Chromosorb). Only the second half of the peak was collected. The nmr spectrum of the *cis*-3,4-dimethylcyclobutene was consistent with that previously reported.[24] Samples for pyrolysis were analyzed for dienes and contained less than one part in 10^5.

Repeated reinjection of the cyclobutene and collection of the second half of the peak had no effect on results. However, when the entire initial cyclobutene peak was collected, the pyrolysis results were erratic, suggesting the presence of an impurity which produced a product with the retention time of **3**. The impurity could not have been *trans*-3,4-dimethylcyclobutene, since kinetic purification did not change the results. Samples of *cis*-3,4-dimethylcyclobutene prepared in ether and purified by preparative vpc on the silver nitrate column and on a 10 ft × $^{1}/_{4}$ in. 10% Apiezon J, 80–100 mesh Chromosorb P column did not give erratic results.

Pyrolysis. The pyrolysis apparatus consisted of an 8-mm o.d. Pyrex tube wrapped in aluminum foil and asbestos and wound with Nichrome heating wire. Auxiliary heaters were placed on each end to ensure a flat temperature profile. The tube was *ca.* 35 cm long, the heated region was *ca.* 22 cm with a rise and fall (25–280°) of about 4 cm on each end. A trap at the end cooled to −80° served to recover the pyrolysis products. The temperature characteristics were determined under conditions of gas flow, using a glass-encased thermocouple. Flow rate measurements were made at the outlet, at room temperature, using a soap bubble flow meter. After allowing the heated tube with gas flowing to equilibrate for an hour or more, the flow rate was determined and a 30–75-μl sample of the cyclobutene was introduced into an inlet system. The gas was directed over the sample and swept through the tube. At the end of the pyrolysis run, the trap was removed and capped tightly prior to sample analysis by vpc.

Analysis. Quantitative vpc measurements were carried out on a Hewlett-Packard F and M Model 700 chromatograph fitted with a dual-flame ionization detector. An 18 ft × $^{1}/_{4}$ in. 15% 1,2,3-tris(2-cyanoethoxy)propane Chromosorb P (acid-washed and DMCS) 60–80 mesh column was used for analysis. The major peak (>99%) corresponded to *cis,trans*-2,4-hexadiene, previously identified by Winter.[6] 1,3-Hexadiene was identified as one of the products by comparison of its vpc retention time (coinjection) to that of an authentic sample (Chemical Samples Co.). The column did not separate the cis and trans isomers of 1,3-hexadiene, so isomeric purity was not determined. The other pyrolysis product was identified as *trans,trans*-2,4-hexadiene by comparison of its retention time (coinjection) to that of an authentic sample (Columbia Organics) on both the above column and on a 15% β,β′-oxydipropionitrile column.

The ratio of isomers was determined by measuring the peak areas corresponding to the major and minor products and multiplying by the appropriate attenuation factor. Thus, the ratio was determined directly and not by relative comparison with internal or external standards. In order to ensure the reliability and accuracy of the method, calibrations were performed. The vpc electronics were shown to be linear within 1%. Then, a mixture was made of 75 μl of authentic *trans,trans*-diene in 10 ml of acetonitrile, and equal volumes of this mixture (*ca.* 1×10^{-4} in diene) and the reaction products were mixed, and analyzed (acetonitrile is not eluted from these columns under our conditions). The mixture was found to be enriched in the *trans,trans*-diene (peak enhanced) by the appropriate amount, about three times compared with the pure reaction mixture. Thus, the absolute amount of *trans,trans*-diene must be *ca.* 6×10^{-5} compared with the *cis,trans*-diene.

Acknowledgment. We thank the National Science Foundation (GP-10621, GP-27532) for support of this work, and Drs. D. M. Golden and L. M. Stephenson for helpful discussions.

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(23) Nmr spectra were obtained with a Varian A-60 or T-60 spectrometer. Melting points are uncorrected.

(24) R. Srinivasan, *J. Amer. Chem. Soc.*, **90**, 4498 (1968).