methylcyclohexylamine (91%) by glpc on a 10 ft × 0.25 in. column of 15% Carbowax 20M and 4% KOH on Chromosorb P 45–60.

The cyclohexene was prepared for mass spectrometric analysis as above. The isotopic composition was calculated from the mass spectrum as follows. Assuming identical ionization efficiencies for isotopic species and statistical loss of hydrogen and deuterium, (P − 1)/P should be identical for deuterated and undeuterated species. Then

$$\%\ d_1 = [((P - 1)/P)_{d_0}/((P - 1)/P)_{d_1}] \times 100$$

In this manner, 94.2% d_1 was found for the cyclohexene. In a control experiment, a known sample of cyclohexene-1-*d* (99% d_1 by nmr) was found to contain 99.1% d_1. The (P + 1)/P ratio was higher for the cyclohexene obtained in this elimination reaction than for either undeuterated cyclohexene or cyclohexene-1-*d*, suggesting the presence of d_2 species. After subtraction of the natural abundance of ^{13}C (6.71%), the intensities of the P + 1 and P peaks indicated 5.0% of $C_6H_8D_2$ and 95.0% of C_6H_9D, in good agreement with the 94.2% d_1 calculated from the (P − 1)/P ratio.

Alternative Electrocyclic Pathways. Photolysis and Thermolysis of Dimethylallene Dimers

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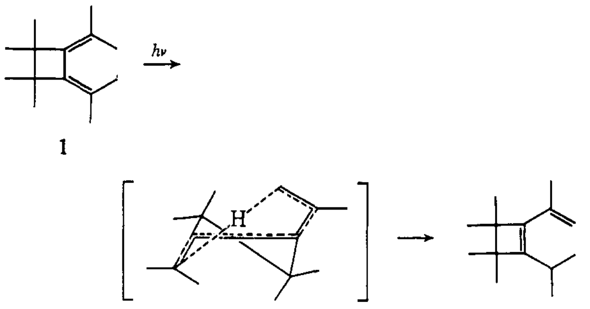
Abstract: The thermal and photochemical isomerizations of 1,2-diisopropylidenecyclobutane and 1-isopropylidene-2-methylene-3,3-dimethylcyclobutane are discussed. The results for both compounds can be interpreted in terms of a concerted 1,5-hydrogen shift, followed in the thermal case by electrocyclic opening of the resulting cyclobutene ring to give a cross-conjugated triene. The relative rates of the thermal and photochemical processes suggest that the initial sigmatropic rearrangement proceeds *via* an antarafacial transition state in the latter case, as predicted by orbital symmetry rules.

In spite of the widespread interest in electrocyclic reactions generated by the Woodward–Hoffmann orbital symmetry rules,[2] certain key points in the general theory have not yet been substantiated.[3] One of these concerns the stereochemistry of sigmatropic rearrangements, in which a σ-bonded substituent migrates from one position in a π-electron system to another.[4] In the absence of an available antisymmetric orbital in the migrating group, only antarafacial transfer is "allowed" for thermal 1,3 and 1,7 and photochemical 1,5 rearrangements (*i.e.*, those rearrangements having π components characterized by antisymmetric frontier orbitals). Among these three possibilities, 1,3 and 1,7 rearrangements are unattractive for testing purposes: concerted antarafacial transfer appears to be sterically impossible for the former and quite possibly preferred on simple steric grounds for the latter in acyclic systems.[5] 1,5 shifts, however, present a meaningful challenge to the theory. The antarafacial transition state in this case clearly must possess significantly higher strain energy than the suprafacial—in fact, the former has been dismissed as effectively "unachievable."[3] A demonstration of its existence would thus carry considerable quantitative significance.

Recently, we reported an exceptionally facile photochemical 1,5-hydrogen shift in tetramethylallene dimer (1), and suggested that steric influences in this compound should strongly favor an antarafacial process.[6]



1

2

(1)

We now wish to describe a study of the thermal and photochemical behavior of dimethylallene dimers 3 and 4 which lends further support to the feasibility of 1,5-antarafacial transition states, as well as presenting a stark contrast to the behavior of unsubstituted allene dimer.[7,8]

Results

Diene 3, the major product from thermal dimerization of 1,1-dimethylallene,[9] displayed unexpected thermal stability; it was recovered essentially unchanged after several hours at 200°. However, at 260–270° it was slowly converted to a single volatile product, with surprisingly little polymer. The 100-MHz nmr spectrum of this product showed only an isopropyl group (τ 8.98, 6 H, d, J = 7 Hz; τ 7.62, 1 H, septet, J = 7 Hz, verified by double resonance), a vinyl methyl group

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[1] National Science Foundation Undergraduate Research Participant, 1966–1967.

[2] For a recent survey, see R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, 1, 17 (1968).

[3] J. A. Berson, *ibid.*, 1, 152 (1968).

[4] R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, **87**, 2511 (1965).

[5] J. L. M. A. Schlatmann, J. Pot, and E. Havinga, *Rec. Trav. Chim. Pays-Bas*, **83**, 1173 (1964).

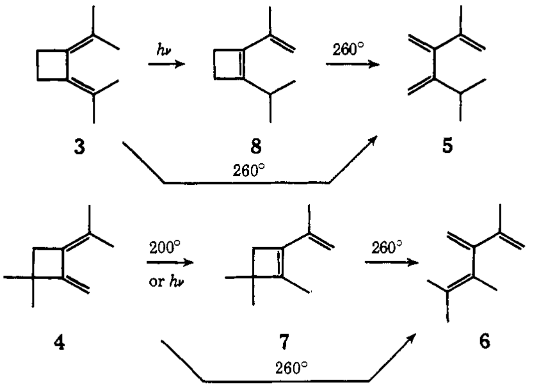
[6] E. F. Kiefer and J. Y. Fukunaga, *Tetrahedron Lett.*, 773 (1969).

[7] (a) J. J. Gajewski and C. N. Shih, *J. Amer. Chem. Soc.*, **89**, 4532 (1967); (b) W. von E. Doering and W. R. Dolbier, Jr., *ibid.*, **89**, 4534 (1967).

[8] G. J. Fonken, Annual Report of the Robert A. Welch Foundation, 1965–1966, p 81, and private communication.

[9] (a) S. V. Lebedev, *J. Russ. Phys. Chem. Soc.*, **45**, 1357 (1913); (b) J. McClenon, Ph.D. Thesis, University of California at Los Angeles, 1964; *Dissertation Abstr.*, **25**, 101 (1964).

(τ 8.12, 3 H, t, $J = 1$ Hz), and six vinyl protons (τ 4.9–5.4, 6 H, m), which, along with the ultraviolet [λ_{max} 227 nm (broad, unsymmetrical) (ϵ 14,000)] and mass spectra (M^+ 136, $C_{10}H_{16}$) establish the structure **5**. The infrared spectrum shows that all of the vinyl protons are present as methylene groups.



Thermolysis of diene **4** proceeded at least 20 times faster than that of **3** at 260°, and also gave at this temperature a single volatile product, though in this case polymerization was more extensive. The nmr spectrum of the product revealed four vinyl methyl groups (τ 8.13, 3 H, t, $J = 1$ Hz; τ 8.31, 6 H, s; τ 8.49, 3 H, s) and four weakly coupled vinyl protons (τ 4.94, 1 H; τ 5.15, 2 H; τ 5.27, 1 H), leading to the assigned structure **6**. The ultraviolet spectrum of **6** also shows an unsymmetrical maximum at 227 nm, with a weak shoulder at 234 nm, which is consistent with an acyclic, cross-conjugated triene bearing the indicated substituents.

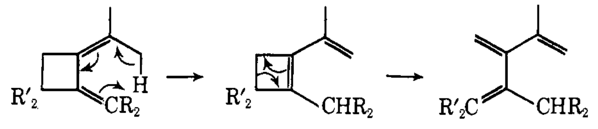
When thermolysis of diene **4** was carried out at 170–200°, an intermediate could be isolated, which was converted to triene **6** on more vigorous heating. The nmr spectrum of this compound was strikingly similar to that of **4**, showing two equivalent quaternary methyl groups (τ 8.90, s), two nonequivalent vinyl methyl groups (τ 8.29, 8.11, t), two equivalent cyclobutyl protons (τ 7.87, q), and two weakly coupled vinyl protons (τ 5.37, m). Spin decoupling experiments established that only one of the vinyl methyl groups was coupled to the cyclobutyl protons ($J = 2$ Hz), and the other to the vinyl protons ($J = 1$ Hz), permitting structure **7** to be assigned. The ultraviolet spectrum of **7** showed a maximum at 242 nm (ϵ 19,000) with shoulders at 235 and 251 nm.

Photolysis of diene **3** proceeded analogously to that of **1**, though at least an order of magnitude more slowly. The major (86%) initial product showed an isopropyl group, an isopropenyl group, and a four-proton cyclobutyl singlet at τ 7.72 in the nmr spectrum, and was assigned the structure **8**. The ultraviolet spectrum was essentially indistinguishable from that of **7**. Diene **8** was quantitatively converted to triene **5** on heating to 260° in a sealed capillary, or on passage through a gas chromatograph injector block heated to 350°, thus providing further support for the assigned structures.

Photolysis of **4** similarly gave rise to **7**, though at a rate still slower than that of **3** by about two orders of magnitude.

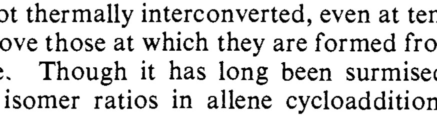
Discussion

Although there is, as usual, no direct evidence that any of the above reactions is concerted, the relatively low temperatures employed and high specificity observed suggest that both **3** and **4** undergo consecutive electrocyclic reactions, involving a 1,5-hydrogen shift and subsequent ring opening (eq 2). There is ample precedent for both types of reaction.[10,11] Ring opening of cyclobutene **8** would be expected to be significantly faster than that of **7**,[11a] and it is not surprising that **8** could not be detected as an intermediate in the thermolysis of **3**.



(2)

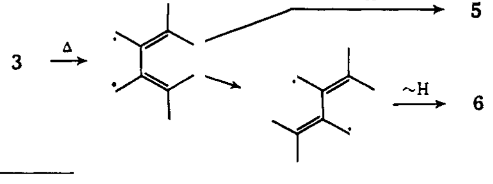
Among several noteworthy features of these results, the following should be mentioned. (a) Dienes **3** and **4** are not thermally interconverted, even at temperatures well above those at which they are formed from dimethylallene. Though it has long been surmised that observed isomer ratios in allene cycloaddition were the result of kinetic control,[12] this is apparently the first conclusive demonstration of the fact. In the analog of **3** with deuterium atoms in place of methyl groups, thermal equilibration of isomers is observed at 250–300° (the temperature normally required for dimerization of allene), apparently *via* the expected tetramethyleneethane biradical, which does not dissociate into monomeric allene at those temperatures.[7] The failure of **3** and **4** to display similar behavior was unexpected. Unfortunately, the third dimethylallene dimer, **9**, is produced only in trace amounts, and could not be isolated in sufficient quantity for study. The photolysis of **9** would also have been of interest, because of the possibility of rearrangement to **3** *via* a bicyclohexene[8] (eq 3). Although **9** was not detected among the photolysis products of **3**, the possibility of an unfavorable photoequilibrium makes it impossible to comment on the relative importance of cyclization and sigmatropic rearrangement in this case. An attempt to synthesize **9** independently *via* thermal or photochemical dimerization of β-methylcrotononitrile failed.



(3)

9

(b) No triene **5** is formed from **4**, nor triene **6** from **3**. Presumably the biradical intermediate which would result from initial thermal ring fission of **3** or **4** could also produce **5** and **6** by intramolecular disproportionation, but the observed results would then require that this biradical be prevented from rotating about its central single bond (eq 4). Such a rigid planarity, at the



(4)

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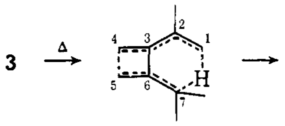
[10] J. Wolinsky, B. Chollar, and M. D. Baird, *J. Amer. Chem. Soc.*, **84**, 2775 (1962).

[11] (a) H. M. Frey, B. M. Pope, and R. F. Skinner, *Discussions Faraday Soc.*, **63**, 1166 (1967), and references cited therein; (b) K. J. Crowley, *Tetrahedron*, **21**, 1001 (1965).

[12] J. D. Roberts and C. M. Sharts, *Org. Reactions*, **12**, 1 (1962).

temperatures involved, would be in accord with neither theoretical expectations nor with the results of Gajewski and Shih.[7a] There remains the possibility that hydrogen transfer and ring opening are entirely concerted in the thermal rearrangement of **3** (eq 5). The fact that these processes are clearly consecutive in the case of **4** is not a very convincing counterargument, since the steric situations in **3** and **4** are quite different. Molecular orbital calculations indicate that the existence of a 3,6 bond in an over-all 1,7-sigmatropic shift does not alter the requirement that the hydrogen atom be transferred antarafacially, a requirement which should actually facilitate the (conrotatory) cleavage of the 4,5 bond. However, in the absence of positive evidence or established precedent, such a mechanism must remain entirely speculative, and for the purposes of further discussion, it will be assumed that **3** and **4** react by the same mechanism (eq 2).



(5)

(c) The order of hydrogen shift reactivity of dienes **1**, **3**, and **4** was reversed in the photochemical and thermal processes (photochemical: $\mathbf{1} > \mathbf{3} > \mathbf{4}$; thermal: $\mathbf{4} > \mathbf{3}, \mathbf{1}$[13]). These rate orders are precisely what one would expect on the basis of steric effects if 1,5-hydrogen transfer occurs antarafacially in the excited state and suprafacially in the ground state, as predicted by the Woodward–Hoffmann rules. Comparison of the photolysis rates of **1** and **3** is particularly instructive, since these compounds have the same substituted chromophore and virtually identical ultraviolet spectra [$\lambda_{\max}$ 253 nm (ϵ 16,000 ± 2000)]. The importance of conformational factors in electrocyclic photoreactions is well documented,[11] and it is tempting to propose[15] that the observed rate order results from the tendency of **1** to spend more time in a puckered, axisymmetric conformation (**2**, eq 1) due to vicinal methyl–methyl interactions on the ring.[6] One would predict that **1** would undergo thermal(suprafacial) 1,5-hydrogen transfer more slowly than **3**, provided ring cleavage did not occur first. Diene **4**, which lacks the all-important "*endo–endo*" vinyl methyl–methyl interaction, is not particularly strained in the planar conformation, and would thus be expected to achieve a suprafacial transition state with relative ease, but have a low probability of attaining the twisted geometry necessary for an antarafacial process. Although these results of course do not constitute proof of stereochemistry, they are suggestive enough to encourage continuation of the search for an authentic 1,5-antarafacial migration.

Experimental Section

Materials. 1,2-Diisopropylidenecyclobutane (**3**) and 1-isopropylidene-2-methylene-3,3-dimethylcyclobutane (**4**) were obtained in approximately 2:1 ratio, along with traces of 1,2-dimethylene-3,3,4,4-tetramethylcyclobutane (**9**), from the dimerization of 3-methyl-1,2-butadiene (Chemical Samples Co.) at 145°,[9] and purified by glpc (see below). Their physical properties agreed with those reported by McClenon.[9b]

Thermolyses. The thermal reactions were conducted in sealed Pyrex tubes in order to keep the temperature as low as possible and permit a more direct comparison with the conditions usually employed for allene dimerization, even though the danger of extensive polymerization was thereby increased. Exploratory runs were carried out in benzene solution in 5-mm tubes, and monitored by nmr. After glpc retention times for known products had been established, most thermolyses were done on a micro scale in sealed melting point capillaries. Relative rates in an open system were also examined, using the injector block of a Wilkins gas chromatograph as a reaction chamber for temperatures in the 250–400° range.[10]

Photolyses. All photochemical reactions were carried out in dilute, degassed, anhydrous ether solutions in sealed Vycor tubes, using a Rayonet chamber reactor with 16 low-pressure mercury lamps as a 2537-Å light source. Dienes **1**, **3**, and **4** all have maxima very near 2537 Å, with the same extinction coefficient at this wavelength within a factor of 50% at most. Thus the photolysis rates, which differed by factors of 20–100, are likely to have relative significance, though they were not measured actinometrically.[15]

Product Analyses. This entire research project proved to be largely an exercise in gas chromatographic column construction. No single column was found which would cleanly separate all of the seven isomeric compounds described herein. The most useful analytical columns employed were two 200-ft capillary columns packed with UCON LB-550-X and triscyanoethoxypropane (TCEP), respectively. The latter column was necessary for distinguishing **6** and **7**. Preparative separations were effected, after distillation at 25 mm to remove polymer, with the following packed columns, all containing approximately 25% stationary phase on 60–80 mesh Chromosorb P: 20 ft × $^3/_8$ in. and 5 ft × 0.25 in. silicone SE-30 (separation of **3** from **4** + **9**, **3** from **5**, and **3** from **8**), 10 ft × 0.25 in. UCON 50-HB-280-X (**4** from **9** and **4** from **6** + **7**), and 20 ft × 0.25 in. TCEP (**6** from **7**). Nmr and uv spectra were measured in carbon tetrachloride and cyclohexane solutions, respectively.

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[13] The thermolysis of **1** was not studied; however, it can be placed relative to **4** by the fact that it was found to be stable for at least 90 hr at 170°.[14]

[14] E. F. Kiefer and M. Y. Okamura, *J. Amer. Chem. Soc.*, **90**, 4187 (1968); M. Y. Okamura, B.S. Honors Thesis, University of Hawaii, 1965.

[15] The possibility cannot be entirely discounted that the apparent rates of rearrangement result from inverse substituent effects on competing excited-state processes, such as internal conversion.