

of the area swept out.¹³ The molecular volumes of the acid and base molecules may be estimated by Edward's method²⁵ as 143 and 124 Å³ mol⁻¹, respectively; treating these as spheres, one obtains radii of 3.2 and 3.1 Å, respectively. Hence we obtain $-\Delta V_f^\ddagger = 12\text{--}13$ cm³ mol⁻¹. The agreement with the experimental value is satisfactory, given the uncertainties in the calculation.

The values of $\Delta V_f^\ddagger_2 (= \Delta V^\circ - \Delta V_f^\ddagger)$, representing the volume change due to electrostriction, do not follow the trend expected from electrostatic theory and shown by Menschutkin reactions,¹⁷ namely, more negative values in the less polar solvents. The electrostatic model is evidently inadequate, as was indeed suggested by the trends in k_f and K at 1 atm.

Conclusion

We conclude that the pressure dependence of the rate constants is consistent with a nearly constant volume of activation in the several solvents, in accordance with the model proposed earlier to account for the large tunneling corrections. The new technique of photosensitized initiation of fast reactions in solution by laser flashes appears promising.

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References and Notes

- (1) Visiting Research Fellow from the Department of Chemistry, University of New Hampshire, Durham, N.H. 03824.
- (2) E. F. Caldin, A. Jarczewski, and K. T. Leffek, *Trans. Faraday Soc.*, **67**, 110 (1971).
- (3) E. F. Caldin and S. Mateo, *J. Chem. Soc., Chem. Commun.*, 854 (1973).
- (4) E. F. Caldin and S. Mateo, *J. Chem. Soc., Faraday Trans. 1*, **71**, 1876 (1975).
- (5) E. F. Caldin and S. Mateo, *J. Chem. Soc., Faraday Trans. 1*, in press.
- (6) R. P. Bell, "The Proton in Chemistry", 2nd ed, Chapman and Hall, London, 1973, Chapter 12.
- (7) E. F. Caldin, *Chem. Rev.*, **69**, 135 (1969).
- (8) R. P. Bell, *Trans. Faraday Soc.*, **55**, 1 (1959).
- (9) R. P. Bell, W. H. Sachs, and R. L. Tranter, *Trans. Faraday Soc.*, **67**, 1995 (1971).
- (10) C. A. Eckert, *Annu. Rev. Phys. Chem.*, **23**, 239 (1972).
- (11) G. Kohnstam, *Prog. React. Kinet.*, **5**, 335 (1970).
- (12) W. J. le Noble, *Prog. Phys. Org. Chem.*, **5**, 207 (1965).
- (13) E. Whalley, *Adv. Phys. Org. Chem.*, **2**, 93 (1964).
- (14) E. F. Caldin, M. W. Grant, B. B. Hasinoff, and P. A. Tregloan, *J. Phys. E*, **6**, 349 (1973).
- (15) E. F. Caldin, M. W. Grant, and B. B. Hasinoff, *J. Chem. Soc., Faraday Trans. 1*, **68**, 2247 (1972).
- (16) E. F. Caldin and M. W. Grant, *J. Chem. Soc., Faraday Trans. 1*, **69**, 1648 (1973).
- (17) H. Hartmann, H. D. Brauer, H. Kelm, and G. Rinck, *Z. Phys. Chem. (Frankfurt am Main)*, **61**, 53 (1968).
- (18) H. Heydtmann, A. P. Schmidt, and H. Hartmann, *Ber. Bunsenges. Phys. Chem.*, **70**, 444 (1966).
- (19) E. Whalley, *J. Chem. Phys.*, **38**, 1400 (1963); J. G. Kirkwood, *ibid.*, **2**, 351 (1934).
- (20) J. F. Skinner, E. L. Cussler, and R. M. Fuoss, *J. Phys. Chem.*, **72**, 1057 (1968).
- (21) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond", Freeman, San Francisco, Calif., 1960, p 291.
- (22) S. N. Vinogradov and R. H. Linnell, "Hydrogen Bonding", Van Nostrand, New York, N.Y., 1971, p 177.
- (23) A. Bondi, *J. Phys. Chem.*, **68**, 441 (1964).
- (24) W. J. Dulmage and W. N. Lipscomb, *Acta Crystallogr.*, **4**, 330 (1951).
- (25) J. T. Edward, *J. Chem. Educ.*, **47**, 261 (1970).

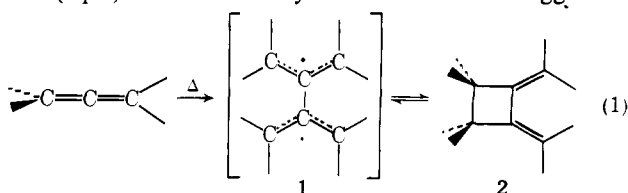
The Mechanism of Allene Cycloaddition. III. Thermal and Photochemical Generation of 2,2'-Bis(1,1-dimethylallyl) Biradical from an Azocyclane Precursor¹

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Abstract: Thermal dimerization of 1,1-dimethylallene in triglyme solution for short times at 151 °C gives 1,2-diisopropylidene-cyclobutane, 1-isopropylidene-2-methylene-3,3-dimethylcyclobutane, and 1,2-dimethylene-3,3,4,4-tetramethylcyclobutane (DMTM) in relative yields of 46, 36, and 18%. Thermal decomposition of 4,5-dimethylene-3,3,6,6-tetramethyl-3,4,5,6-tetrahydropyridazine gives the same products in the same ratio at 151 °C. Extrapolation of the latter thermolysis results at five other temperatures to 35 °C gives a product ratio (53, 33, and 14%, respectively), which is the same as that obtained from direct photolysis at 35 °C of the same compound for short times. The results are interpreted in terms of the title species being a common intermediate for all three reactions. Although accurate product ratios could not be obtained from the triplet sensitized photolysis of the same azo compound, nor from the thermal rearrangement of DMTM, it is proposed that the same intermediate is also involved in these cases.

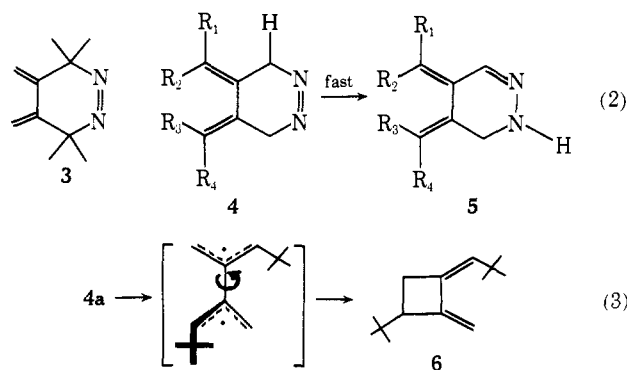
The possible intermediacy of a 2,2'-bisallyl, or tetramethylenecyclobutane, biradical **1** in the thermal dimerization of allenes (eq 1) has been widely debated since the suggestion



was first popularized by Roberts and Sharts in 1962.³ Our own interest in the mechanism of this reaction dates from the same period, when we were using the reaction for synthetic purposes.⁴ The question of the allene cycloaddition mechanism gained considerable currency during the period in which the original series of Woodward-Hoffmann orbital symmetry papers were appearing in 1965. By coincidence, two very convincing and apparently contradictory documents relating to this question were received by one of us (E.F.K.) on the same day: a student research report in

which the stereospecificity of allene cycloaddition was first established⁵ and the second Woodward-Hoffmann paper, in which concerted 2 + 2 thermal cycloaddition was described as forbidden.⁶ At the time our results were finally submitted for publication,⁷ we were still unable to account satisfactorily for the observed stereospecificity, but Hoffmann and Woodward were by then developing an extension of their selection rules which allowed allene cycloaddition to be viewed as a concerted, $\pi 2_s + \pi 2_a$ process.⁸ Previously, a perpendicular or freely rotating biradical **1** had been clearly implicated in the related thermal rearrangement of **2**,⁹ and allene cycloaddition itself was soon shown to be kinetically nonconcerted,¹⁰ implying the intermediacy of **1** in the latter reaction also. However, further proof of the stereospecificity of allene cycloaddition followed,¹¹ which, together with a striking preference for the more sterically crowded products observed in the dimerization of substituted allenes,¹² necessitated the development of a "concerted two-step"¹³ mechanism for allene dimerization. In this view, a bisallyl biradical intermediate either retains its stereochemical integrity throughout its existence (presumably via secondary orbital overlap), or is formed from allene and closed to products in separate but individually stereospecific steps (presumably under steric and orbital symmetry control^{11a}). A series of rather detailed MO calculations on **1** and its interconversion with its various stable valence isomers was carried out,¹⁴ but served only to demonstrate that **1** appears to have no constraining electronic preference as to either molecular geometry or π orbital symmetry.

The question of whether a bisallyl biradical **1** is necessarily an intermediate in allene dimerization and, if so, if it is the same orthogonal or freely rotating species which has been so elegantly circumscribed by the researches of Gajewski and Shih on the thermal rearrangements of dimers **2**^{9a,12d,15a} has proven difficult to answer.¹⁵ In 1969, we set out to generate an authentic bisallyl biradical **1** from an independent source, hoping that a comparison of the ratios of isomeric dimers **2** produced with those obtained from dimerization of the appropriate allene and from thermal rearrangement of the dimers themselves would lead to an unequivocal answer. Although it meant foregoing stereochemical information, we settled on the 1,1-dimethylallene system primarily in order to avoid problems with tautomerization of the desired azo precursor **3** to a conjugated hydrazone, a process expected to be very facile in 4-azoalkenes bearing an α -proton, e.g., **4**.^{15b} Since our results were originally communicated,^{1b} Beetz and Kellogg have succeeded in synthesizing a stereochemically labeled azo compound of type **4** with known geometric configuration (**4a**, $R_1 = R_3 = \text{H}$, $R_2 = R_4 = \text{tert-butyl}$): they confirm that even trace amounts of water catalyze rapid **4** \rightarrow **5** tautomerization.¹⁶ More importantly, Beetz and Kellogg's results on the deazotization of **4a** are in accord with our conclusions,^{1b} that both thermolysis and photolysis of these 4,5-dialkylidene-

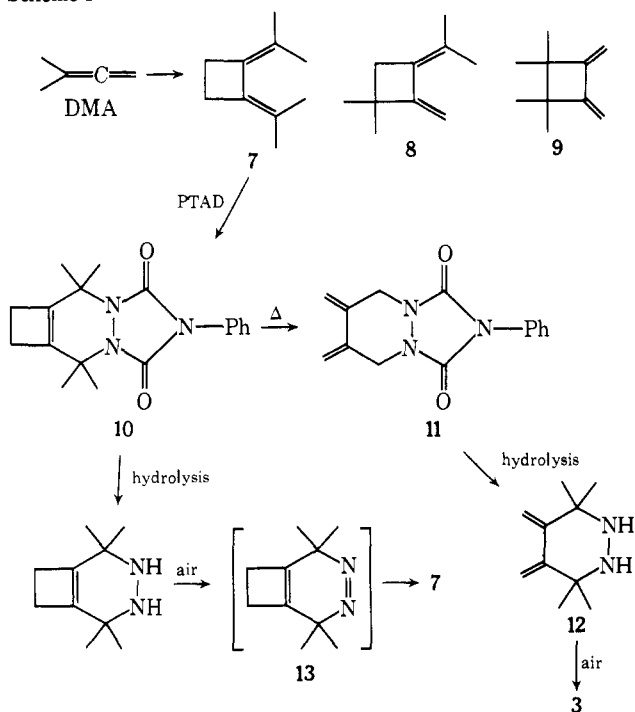


3,4,5,6-tetrahydropyridazines yield the same, effectively orthogonal 2,2'-bisallyl biradical. In their case, the torsional strains induced by the bulky *tert*-butyl groups apparently control the direction of ring closure to such a degree that only one of the four orbital symmetry-allowed^{15a} cyclobutane products (**6**) is initially formed, i.e., the one which appears to have the least hindered transition state for closure. The striking equivalence of thermal and photochemical results in their case (and in ours) further suggests that the common intermediate (**1**) has become thermally equilibrated before closure, since any residual excess vibrational or rotational energy resulting from the exothermic loss of N_2 from ground and/or excited electronic states might be expected to lead to observable differences in product composition.¹⁷ This point enables one to assert with reasonable confidence that if the same 2,2'-bisallyl species (**1**) is involved in allene dimerization, it is a true biradical intermediate, i.e., a free rotor, as suggested by theory,¹⁴ rather than a shallow energy minimum in an orbitally concerted process.¹³

Results

Synthesis of Azo Compounds. The known 1,2-diisopropylidene-cyclobutane²⁰ (**7**), the major thermal dimer of 1,1-dimethylallene, was itself used as a precursor for the desired azo compound **3**. Addition of 4-phenyl-1,2,4-triazoline-3,5-dione²¹ (PTAD) to the terminally tetrasubstituted diene occurs rapidly at room temperature to give the Diels-Alder adduct **10**, which thermally isomerizes cleanly to diene **11**.²² Hydrolysis of this hindered urazole requires high temperature and very concentrated base, but proceeds satisfactorily; the resulting hydrazine **12** is slowly oxidized to **3** in a stream of air at room temperature. For comparative purposes, adduct **10** was also hydrolyzed to the hydrazine, air oxidation of which caused immediate evolution of N_2 and gave a quantitative yield of dimer **7**, presumably via azo compound **13**. The synthetic reactions are summarized in Scheme I.

Scheme I



Dimerization of 1,1-Dimethylallene (DMA). For analytical purposes, the thermal dimerization of 1,1-dimethylal-

Table I. Product Distribution from Dimerization of 1,1-Dimethylallene in Triglyme (151°), Sealed Pyrex Tubes (%)

Reaction time, h	7	8	9
4	48.4	(34.4)	17.2
1	47.5	(35.0)	17.5
0.3	46.5	(35.6)	17.8
0 ^a	46 ± 1	(36 ± 4) ^b	18 ± 1

^a Extrapolated. ^b A trace impurity present in DMA appeared as a shoulder on the GLC peak due to **8**. Figures for **8** are based on an estimated **8:9** ratio of 2 (±0.2):1. The **8:9** ratios in duplicate samples of pure DMA heated *without solvent* for 1 h were 2.07 and 2.10.

lene is best carried out below 150 °C, since higher temperatures favor the sigmatropic rearrangement of **8**.^{20a} At 140–145 °C, the reaction requires several days for completion, and the ratio of dimers **7**, **8**, and **9** reported²⁰ have invariably been in the range (64 ± 4):(34 ± 4):(3 ± 1%). Although 100% of dimers **7** and **8** and 80% of **9** were recoverable after reheating for 120 h at 145 °C in dilute benzene solutions, both **8** and **9** are apparently somewhat unstable during the dimerization reaction itself; we have observed that the dimer ratio is time as well as temperature dependent, longer reaction times producing higher proportions of **7** at the expense of **8** and **9**. The effect is much less pronounced than that observed by Gajewski and Shih in the dimerization of methylallene,^{12d} which may be due to the lower temperature employed in our work.

In order to facilitate comparison with the very much faster decomposition of **3** (below), dimerization of DMA was carried out in a high-boiling solvent (triglyme) at the lowest temperature and shortest times commensurate with reasonably accurate gas chromatographic analysis and extrapolated to zero time. The results, shown in Table I, are for DMA conversion of less than 1%.

Thermolysis of Azo Compound 3. The product distributions from the thermal decomposition of **3** at different temperatures are shown in Table II. The low-temperature reactions were for purposes of comparison with the photochemical reaction described below. The combined yield of **7**, **8**, and **9** at all temperatures was essentially quantitative. The single sample pyrolyzed at 220 °C in hexafluorobenzene solvent was originally intended for comparison with the thermal rearrangement of **9**, which was unsuccessful (see below). Although the results shown for this temperature are highly approximate, they do support the trend indicated by the more precise GLC results at lower temperatures.

Photolysis of Azo Compound 3. Direct irradiation of **3** was carried out under conditions as similar as possible to those for thermolysis, i.e., ca. 5% solutions in triglyme, degassed and sealed in 5-mm Pyrex tubes, at 35 °C, a temperature at which **3** is thermally stable for at least 2 weeks. A Corning 0-54 filter (cut-off >300 nm) was used with a high-pressure (550-W) mercury lamp in order to assure light absorption by only the azo chromophore (λ_{\max} 385 nm). Under these conditions, the concentration of **3** decreased linearly with time, reaching zero after 12.5 h. Compounds **7**, **8**, and **9** accounted for >99% of the product after short photolysis times; however, despite the care taken to exclude light of the wavelength range corresponding to the absorption spectra of these products,^{20a} some further photochemistry did occur, necessitating yet another extrapolation, again to zero time. Table III shows the distribution of DMA dimers produced, with reaction times corrected to show the actual (average) time of photolysis of the products themselves.

The photochemistry of the individual dimers **7**, **8**, and **9** under these conditions was not explored, so it cannot be

Table II. Product Distribution from Thermolysis of Azo Compound 3 in Triglyme, Sealed Pyrex Tubes (%)^a

Bath temp, °C	Reaction time, h	7	8	9
(220) ^b	0.02	(40) ^b	(40) ^b	(20) ^b
151	0.3	46.7	36.0	17.3
121	0.5	49	34.3	16.7
102	0.5	47.3	36.4	16.3
83	5	50.6	34.4	15.0
46	1000	52.2	33.6	14.2
35 ^c		~53	~33	~14

^a Duplicate GLC analyses except as noted. ^b Hexafluorobenzene solvent, analysis by NMR integration. Values are approximate. ^c Extrapolated.

Table III. Product Distribution from Direct Photolysis of **3** in Triglyme, 300-nm Filter, 34.5 °C (%)

Reaction time, h		7	8	9
Actual	Cor ^a			
19.25	13.0	58.5	32.4	9.1
16.5	10.25	57.2	31.1	11.7
12.5	6.25	55.8	32.0	12.2
	0 ^b	~53	~32	~15

^a Corrected for **3**, $t_{1/2} = 6.25$ h; see text. ^b Extrapolated.

stated whether the apparent photorearrangement of **9** to **7** suggested by the data of Table III actually occurs. In fact, up to 1.5% of dimethylallene, plus four other volatile trace products are produced, suggesting that **9** and probably also **8** are simply disappearing via an unrelated photodecomposition, leaving an apparent increase in the proportion of **7**. Gajewski and coworkers noted the disappearance of methylallene dimers structurally analogous to **9** on prolonged irradiation in solution^{18a} and identified all three possible ring-cleavage products from the low-pressure vapor-phase photolysis of 1,2-dimethylenecyclobutane;^{18b} in addition, **7** appears to be much less reactive than **8** and **9** toward sensitized photolysis (see below).

Photolysis of **3** in the presence of a triplet sensitizer (thioxanthone) in hexafluorobenzene–benzene resulted in deazotization at a rate similar to that of the direct photolysis described above. However, a number of unidentified products were produced in addition to **7**, **8**, and **9**, and the isomer distribution of the DMA dimers produced consisted of >90% of **7** and <10% of **8** + **9**. Subsequently, thioxanthone-sensitized photolysis of the product mixture obtained from direct irradiation of **3** in hexafluorobenzene–benzene (**7:8:9** ratio ≈ 56:32:12) rapidly led to this same distribution of products. Since both **8** and **9** were being destroyed considerably faster than they were formed from **3**, further attempts to obtain an accurate initial DMA dimer ratio from sensitized photolysis were abandoned, and no information bearing on the multiplicity of **1** was obtained.¹⁹

Thermolysis of DMA Dimers. The thermal and photochemical isomerizations of DMA dimers **7** and **8** have been described previously;^{20a} a similar study of **9** was, in fact, the earliest goal of the present work.^{1a} The low yields (2–4%) of **9** obtained from DMA dimerization under preparative conditions make it more difficult to study (two alternative approaches to the preparation of **9** were no more successful in our hands^{20d}); nonetheless, its inability to undergo the 1,5-hydrogen migrations characteristic of **7** and **8** made an attempt worthwhile. Unfortunately, however, **9** does not react appreciably below 200 °C, a temperature at which expected product **8** and its further rearrangement products are unstable.^{20a} At least nine compounds were produced by heating **9**

at 210 °C, only one of which (7) was positively identified. Isomer 8 was absent. In view of Gajewski and Shih's results on the structurally analogous methylallene dimers,^{12d,15a} it seems reasonable to assume that 8 was a primary product; however, our inability to measure accurate primary ratios of 7 and 8, produced thermally from 9 for comparison with DMA dimerization (see above), led to abandonment of this goal also.

Discussion

The data of Tables of I and II indicate that the dimerization of DMA and the decomposition of 3 at 151 °C in triglyme solution both produce dienes 7, 8, and 9 in yields of 46–47, 35–36, and 17–18%, respectively. Data from Tables II and III further show that thermolysis and direct photolysis of 3 in triglyme solution at 35 °C also produce the same ratios of 7, 8, and 9 at this temperature, ~53, 32–33, and 14–15%, respectively. Barring an extraordinary coincidence,²³ we believe these data establish a common intermediate for all three reactions and that the known behavior of these reaction types must erase any remaining doubt that the intermediate is a 2,2'-bis(1,1-dimethylallyl) biradical.

Regardless of the mechanistic details of nitrogen expulsion from 3,²⁴ the presence of 8 in the product mixture is sufficient to establish rotation about the 2–2' bond, precluding a concerted ring closure. As discussed above in connection with the equivalent results of Beetz and Kellogg,¹⁶ the identity of the thermal and photochemical product ratios from 3 formed under kinetic control virtually requires that the biradical intermediate be thermally equilibrated prior to ring closure, i.e., that ring closure is slow compared to 2–2' bond rotation. The production of larger proportions of the minor isomers 8 and 9 from 3 at higher temperatures, noted in Table II, is a clear-cut manifestation of this fact and, in addition, suggests (but does not require) that 1 has a small but significant energy minimum at or near the perpendicular (D_{2d}) geometry, rather than a freely rotating 2–2' bond. This is in line with expectations based on extended Hückel calculations¹⁴ and with current terminology, which describes 1 as "effectively orthogonal".^{15,16}

Although our attempts to obtain a primary product distribution from triplet-sensitized photodecomposition of 3 failed because of product instability (see above), our superstition is that this experiment, if successful, would have been doomed to give the same distribution as the others reported herein. The triplet is either the ground state of 1 or lies very close to it,¹⁹ and all that would be required to guarantee the above result is that intersystem crossing between these states of very similar energy¹⁴ be fast compared to ring closure—a virtual certainty, given the slowness of the latter process indicated by the present results. Since each allyl moiety would be expected to maintain its own geometric integrity in either state, orbital interaction between the two allyl radicals need only be reestablished during the act of symmetry-controlled closure of singlet 1 in order to accommodate the known stereospecificity of formation and rearrangement of 2.^{9–12}

Experimental Section

General. Melting points were determined with a Hershberg apparatus or with a Fisher-Johns melting point block and are uncorrected. Ultraviolet absorption spectra were recorded with a Cary-14 double-beam recording spectrophotometer using 1-cm silica cells. Infrared spectra were obtained on a Perkin-Elmer Model 700 spectrophotometer or a Beckman Model IR-10 spectrophotometer. Bands are designated as strong (S), medium (M), or weak (W). Nuclear magnetic resonance spectra were obtained on Varian A-60 or HA-100 spectrometers using 5–10% solutions in CCl₄ unless otherwise noted. Chemical shifts are recorded in parts per mil-

lion downfield from internal Me₄Si as δ values. Signal multiplicities are designated as singlet (s), doublet (d), triplet (t), quartet (q), and multiplet (m). Mass spectra were recorded by Sr. Mary Roger (Brennan) on a Hitachi Perkin-Elmer RMU-6D single focusing mass spectrometer using a direct inlet system and operating at 70 eV. Analytical and preparative gas-liquid chromatography (GLC) was performed on Perkin-Elmer F-11 and Varian Aerograph A-90P instruments, respectively.

Materials. Solvents were reagent grade, dried over molecular sieves, and used without further purification. **1,1-Dimethylallene** (DMA, 3-methyl-1,2-butadiene) was obtained from Chemical Samples Co. and contained <0.1% of an unknown impurity. **1,2-Diisopropylidene-cyclobutane** (7)²⁰ was prepared in 65% yield on a preparative scale by heating ca. 25% (w/w) benzene solutions of DMA in sealed 20 × 150 mm Pyrex tubes at 210 ± 3 °C for 3 days and separated by distillation through a 60-cm Nester-Faust Teflon spinning-band column; bp 70–71 °C (25 mm). **4-Phenyl-1,2,4-triazoline-3,5-dione** (PTAD) was prepared by the procedure of Cookson, Gilani, and Stevens.²¹

Diels-Alder Addition of PTAD to Dimer 7. To a solution of 2.57 g (0.014 mol) of freshly sublimed PTAD in 50 ml of acetone at –77 °C was added 2.0 g (0.015 mol) of 7. On warming to room temperature, the red color of PTAD was slowly discharged. After removal of the acetone in vacuo, the residue was chromatographed on a 2 × 90 cm silica gel column with benzene as eluent, yielding 3.6 g (78%) of urazole 10. Recrystallization from hexane gave long white needles: mp 137.5–138 °C; NMR δ 1.50 (s, 12 H), 2.43 (s, 4 H), 7.26 (m, 5 H); ir (KBr) 1710 (s) and 1765 cm⁻¹ (s); mass spectrum m/e 311 (M⁺) and 135 (100%). For comparison, the Diels-Alder adduct of PTAD and dimer 9 was prepared similarly:²² mp 158–162 °C; NMR δ 1.15 (s, 12 H), 3.99 (s, 4 H), 7.39 (m, 5 H). The adduct of PTAD and 8 (mp 116.5–118.5°) showed NMR lines at δ 1.20 (2, 6 H), 1.50 (s, 6 H), 2.25 (t, J = 3.0 Hz, 2 H), 3.85 (t, J = 3.0 Hz, 2 H), and 7.25 (m, 5 H).

Thermal Ring Opening of Adduct 10. A solution of 3.6 g of 10 in 15 ml of *p*-xylene was sealed in a 15 × 200 mm Pyrex tube and heated at 180–185 °C for 12 h. After removal of the solvent in vacuo (hot water bath), the residue was recrystallized from hexane, yielding 2.9 g (80%) of 11 as small white needles: mp 131.5–133 °C; NMR δ 1.62 (s, 12 H), 4.90 (d, J = 1.0 Hz, 2 H), 5.07 (d, J = 1.0 Hz, 2 H), 7.23 (m, 5 H); ir (KBr) 915 (m), 3050 cm⁻¹ (m); uv λ_{max} 218 nm (ϵ 25 740); mass spectrum m/e 311 (M⁺, 100%). The temperature-dependent NMR spectrum of the corresponding product derived from 9 has been described.²²

Hydrolysis and Oxidation of Urazole 11 to Azocyclane 3. Urazole 11 (4 g, 0.0128 mol), potassium hydroxide (64.6 g, 1.152 mol), 30 ml of water, and 30 ml of ethylene glycol were placed in a 500-ml round-bottomed flask equipped with a gas inlet, magnetic stirring bar, Claisen distilling head, condenser, and distillation receiver. The system was flushed with argon for 1 h, and a slow stream of argon was maintained as the solution was heated for 1.5 h at 160–170 °C.²⁵ The solution was then cooled to room temperature and opened to the atmosphere, and the combined receiver and pot residues were diluted with 30 ml of water. The aqueous layer was extracted with five 25-ml portions of ether, and the combined extracts were washed with 20 ml of cold saturated sodium chloride solution, dried over anhydrous sodium sulfate, and carefully concentrated under reduced pressure, keeping the bath temperature below 30 °C. Flash distillation in vacuo yielded ca. 3 g of a 1:1 mixture of aniline and hydrazine 12 as a pale-yellow oil: NMR (neat) δ 1.12 (s, 12 H), 3.65 (broad s, 4 H), 4.60 (d, J = 1.5 Hz, 2 H), 4.73 (d, J = 1.5 Hz, 2 H), 6.6 (m, 5 H). This mixture was dissolved in 100 ml of ether and a slow stream of air was passed through the stirred solution for 4 days at room temperature. After drying (Na₂SO₄) and careful removal of the solvent below room temperature, the pale-yellow, oily residue of 3 + aniline was taken up in a minimum amount of pentane and chromatographed on a 3 × 60 cm Florisil column eluted with pentane. Rechromatography of the volatile azo compound under the same conditions, followed by careful distillation of the pentane eluent below 25 °C, produced ca. 1 g (ca. 47% yield from 11) of azocyclane 3 of >99% purity as judged by its NMR spectrum: δ 1.38 (s, 12 H), 4.68 (d, J = 1.3 Hz, 2 H), 4.84 (d, J = 1.3 Hz, 2 H).

Thermolysis of 3. A stock solution of 3 in triglyme (ca. 4% w/w) was divided in equal volumes of ca. 0.2 ml into clean 5 × 200-mm Pyrex tubes, which were degassed by four to five freeze-pump-

thaw cycles, sealed under vacuum, and stored at 6 °C until needed. Tubes were immersed in an insulated, stirred UCON oil bath preheated to the temperatures shown in Table II ($\pm 1^\circ$). Progress of the reaction at the lower temperatures was monitored by NMR spectroscopy. When **3** could no longer be detected, the tubes were opened and the contents analyzed by GLC using a 200-ft capillary column packed with UCON LB-550-X and operated at 100 °C. Relative amounts of **7**, **8**, and **9** (retention times ca. 12, 8, and 7 min, respectively) were determined by paper weight for duplicate injections.

Dimerization of DMA. The experimental procedure for the formation and analysis of dimers **7**, **8**, and **9** from DMA was identical with that described above for **3**, except that the DMA concentration was 50% w/w in triglyme, and the volumes of solution used were ca. 0.5 ml.

Photolysis of 3. The procedure for direct photolysis of **3** in triglyme solution was identical with that described above for thermolysis, except that the bath was maintained at $34.5 \pm 0.5^\circ$ and contained a Hanovia 550-W Hg lamp inside a water-cooled Pyrex immersion well, shielded from the reactant tubes by a Corning 0-54 glass filter. Analytical procedures were identical with those described above. Direct photolysis of a 1% (w/w) solution of **3** in hexafluorobenzene containing a few percent benzene was also carried out, using the same experimental setup described. Analysis by NMR revealed that a ratio of **7**, **8**, and **9** similar to that observed in triglyme solution was formed initially, but that rapid subsequent reactions of **7** and **8** occurred. The procedure used for sensitized photolysis of **3** was identical (1% solution of **3** in $C_6F_6 + C_6H_6$; analysis by NMR) except that the solution was saturated (ca. 3-4% w/w) with thioxanthone (E_T , 65.5 kcal/mol).²⁶ Results of these photochemical experiments are described in the text.

References and Notes

- (1) Taken in part from the Ph.D. Thesis of T. J. Levek, University of Hawaii, May 1972. (b) Presented in brief at the 164th National Meeting of the American Chemical Society, New York, N.Y., Aug 30, 1972, Abstracts ORGN-88. The photochemical part is not described in the abstract. (c) Supported in part by the Petroleum Research Fund, administered by The American Chemical Society.
- (2) American Chemical Society-Petroleum Research Fund Fellow, 1969-70.
- (3) J. D. Roberts and C. M. Sharts, *Org. React.*, **12**, 1 (1962).
- (4) E. F. Kiefer and J. D. Roberts, *J. Am. Chem. Soc.*, **84**, 784 (1962).
- (5) "This indicates that there is little or no free rotation in the transition state, and lends strong support to a concerted mechanism; in any case, a mechanism involving a stable, true biradical intermediate can be ruled out": M. Y. Okamura, B.A. (Honors) Thesis, University of Hawaii, June 8, 1965, p 13.
- (6) "It must be concluded that those cycloadditions which do occur in cases prohibited by our selection rules for concerted reactions must proceed through multistep mechanisms (e.g., formation of cyclobutane derivatives by dimerization of allenes and ketenes, ...)": R. Hoffmann and R. B. Woodward, *J. Am. Chem. Soc.*, **87**, 2046 (1965).
- (7) E. F. Kiefer and M. Y. Okamura, *J. Am. Chem. Soc.*, **90**, 4187 (1968).
- (8) The stereochemistry of cycloaddition was first treated briefly by R. Hoffman and R. B. Woodward, *Acc. Chem. Res.*, **1**, 17 (1968), then formalized and elaborated by Professor Hoffmann at the 21st Organic Chemistry Symposium, Salt Lake City, Utah, June 1969.
- (9) (a) J. J. Gajewski and C. N. Shih, *J. Am. Chem. Soc.*, **89**, 4532 (1967); (b) W. v. E. Doering and W. R. Dolbier, *ibid.*, **89**, 4534 (1967).
- (10) (a) W. R. Dolbier, Jr., and S.-H. Dai, *J. Am. Chem. Soc.*, **90**, 5028 (1968); **92**, 1774 (1970); *Tetrahedron Lett.*, 4645 (1970); S.-H. Dai and W. R. Dolbier, Jr., *J. Am. Chem. Soc.*, **94**, 3946 (1972); (b) W. R. Moore, P. D. Mogolesko, and D. D. Traficante, *ibid.*, **94**, 4754 (1972).
- (11) (a) W. R. Moore, R. D. Bach, and T. M. Ozretich, *J. Am. Chem. Soc.*, **91**, 5918 (1969); (b) J. E. Baldwin and U. V. Roy, *Chem. Commun.*, 1225 (1969); (c) J. J. Gajewski and W. A. Black, *Tetrahedron Lett.*, 899 (1970).
- (12) (a) O. J. Muscio, Jr., and T. L. Jacobs, *Tetrahedron Lett.*, 2867 (1969); (b) T. L. Jacobs and O. J. Muscio, Jr., *ibid.*, 4829 (1970); (c) T. L. Jacobs, J. R. McClenon, and O. J. Muscio, Jr., *J. Am. Chem. Soc.*, **91**, 6038 (1969); (d) J. J. Gajewski and C. N. Shih, *ibid.*, **91**, 5900 (1969); *J. Org. Chem.*, **37**, 64 (1972).
- (13) (a) J. E. Baldwin, presented at the 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969, Abstract ORGN-003; (b) J. E. Baldwin and R. H. Fleming, *Fortschr. Chem. Forsch.*, **15**, 281 (1970).
- (14) B. G. Odell, R. Hoffmann, and A. Imamura, *J. Chem. Soc. B*, 1675 (1970).
- (15) (a) J. J. Gajewski and C. N. Shih [*J. Am. Chem. Soc.*, **94**, 1675 (1972)] provide the most thorough and incisive recent discussion of this question. (b) J. J. Gajewski, personal communications.
- (16) T. Beetz and R. M. Kellogg, *J. Am. Chem. Soc.*, **95**, 7925 (1973).
- (17) This conclusion follows only because the product composition in each case is demonstrably under kinetic control. Gajewski and co-workers¹⁸ were able to show that a 2,2'-bisallyl biradical was most probably involved in the degenerate photorearrangement of deuterium-labeled **2**, but the statistical distribution of labeled product precluded any concrete conclusions regarding the possible identity of the thermal and photochemical bisallyl intermediates. In a parallel study of the photolysis of *cis*- and *trans*-3,4-dimethyl-2,¹⁸ the product distribution differed somewhat from the corresponding thermal reaction, but this could be ascribed to structural isomerization of a vibrationally excited diene prior to ring opening to **1**.
- (18) (a) J. J. Gajewski and C. N. Shih, *J. Am. Chem. Soc.*, **92**, 4457 (1970); (b) P. A. Kelso, A. Yeshurun, C. N. Shih, and J. J. Gajewski, *ibid.*, **97**, 1513 (1975).
- (19) P. Dowd, *J. Am. Chem. Soc.*, **92**, 1066 (1970).
- (20) (a) E. F. Kiefer and C. H. Tanna, *J. Am. Chem. Soc.*, **91**, 4478 (1969); (b) S. V. Lebedev, *J. Russ. Phys.-Chem. Soc.*, **43**, 1735 (1911); (c) J. R. McClenon, Ph.D. Thesis, University of California, Los Angeles, 1964; *Diss. Abstr.*, **25**, 101 (1964); (d) C. H. Tanna, B.S. (Honors) Thesis, University of Hawaii, 1968.
- (21) R. C. Cookson, S. S. H. Gilani, and I. D. R. Stevens, *J. Chem. Soc. C*, 1905 (1967).
- (22) E. F. Kiefer, T. J. Levek, and T. T. Bopp, *J. Am. Chem. Soc.*, **94**, 4751 (1972). The other two dimers of 1,1-dimethylallene also form PTAD adducts which ring-open thermally to the corresponding dienes. In the adduct from **8**, the ring opening is followed by a facile thermal 1,5-hydrogen shift.^{20a}
- (23) Some support for this possibility might be obtained by examining, for example, the ratios of methylallene dimers of structural types **7**, **8**, and **9** obtained by Gajewski and Shih:^{12d}

$$CH_2CH=C=CH_2 \xrightarrow[20 \text{ hr}]{150^\circ} \begin{matrix} \text{CH}_3 \\ | \\ \text{C} \\ / \quad \backslash \\ \text{C} \quad \text{C} \\ | \quad | \\ \text{CH}_3 \quad \text{CH}_3 \end{matrix} + \begin{matrix} \text{CH}_3 \\ | \\ \text{C} \\ / \quad \backslash \\ \text{C} \quad \text{C} \\ | \quad | \\ \text{CH}_3 \quad \text{CH}_3 \end{matrix} + \begin{matrix} \text{CH}_3 \\ | \\ \text{C} \\ / \quad \backslash \\ \text{C} \quad \text{C} \\ | \quad | \\ \text{CH}_3 \quad \text{CH}_3 \end{matrix}$$

16% 55% 29%
63.5% 32% 4.5%
- (24) For relevant discussion, see (a) R. J. Crawford and A. Mishra, *J. Am. Chem. Soc.*, **88**, 3963 (1966); (b) R. G. Bergman and W. L. Carter, *ibid.*, **91**, 7411 (1969); (c) R. C. Neuman, Jr., and E. W. Ertley, *ibid.*, **97**, 3130 (1975).
- (25) L. A. Paquette, *J. Am. Chem. Soc.*, **92**, 5765 (1970). This hydrolysis was unsuccessful if lower base concentrations, lower temperatures, or less rigid exclusion of oxygen were employed.
- (26) P. S. Engel [*J. Am. Chem. Soc.*, **89**, 5731 (1967)] found that thioxanthone was the lowest-energy triplet sensitizer which would efficiently transfer triplet energy to a rigid cyclic azo compound.