indicated two products with retention times identical with those of **3b** and **4b** in a ratio of 4:1 respectively. The mixture was concentrated by vacuum distillation with removal of all volatile material with a boiling point less than 60° (3 mm). The residual viscous oil was treated with an equal volume of hexane, filtered from precipitated polymer, and chromatographed on $AgNO_3$–silica gel.[10] The combined fractions rich in **3b** and **4b** were rotary evaporated and collected after passage through the preparative glc using a 1 ft × 0.25 in. 10% OV-17 column at 194°. The viscous yellow oil (42 mg) was dissolved in 200 μl of hot hexane and allowed to crystallize, and the collected crystals were subjected to sublimation at 65° (0.05 mm). The off-white solid had a melting point of 79–82°. A nmr spectrum of this solid (CCl_4) showed the same resonances as the mixtures obtained from the photolysis runs. However, the amount of **4b** remaining in the solid was estimated to be about 5% after the extensive purification.

Thermal Isomerization of 5b to 3b. A sample of **5b** injected into the glc with column B maintained above 170° produced a new peak with retention time identical with that of **3b**. At column temperatures above 225° isomerization of **5b** to **3b** is complete. A mixture of 5 mg of **5b** and 5 ml of undecane (bp 192–194°) when refluxed for 15 hr achieved a 65% isomerization of **5b**. Repeated injections of **5b** onto column B maintained at 228° followed by collection of the effluent yielded 2.6 mg of a compound whose nmr spectrum proved identical with that of **3b**.

Bis(dicyclohexyl-18-crown-6-ether) Complex of Disodium Bengal Red. Bengal Red (Aldrich), 1.0 g (1.0 mmol) in 30 ml of H_2O, was treated with 1.5 ml (9 mmol) of 6 *N* HCl and extracted with three 30-ml portions of methylene chloride, then two 30-ml portions of ether. The combined extracts were washed with 50 ml of H_2O, dried over $MgSO_4$, filtered, and rotary evaporated to yield 730 mg (0.75 mmol) of neutralized Bengal Red. This was dissolved in 50 ml of methanol and filtered, and sodium methoxide (from 1.60 mmol of sodium metal) in 10 ml of methanol added, giving a deep red solution. Dicyclohexyl-18-crown-6-ether (Aldrich, technical), 564 mg (1.48 mmol) in 10 ml of methanol, was added and the solution rotary evaporated 2 hr at 40° to give 1.28 g of dark red mass. This was taken up in 75 ml of methylene chloride, filtered, and added dropwise to 150 ml of stirred ligroin (bp 63–75°), and the resulting precipitate was filtered to yield 300 mg of fine red solid. The filtrate was rotary evaporated, dissolved in 40 ml of methylene chloride, and treated with ligroin to yield a second crop of 784 mg, for a total of 1.084 g (0.62 mmol, 62%). The ir spectrum (KBr) is identical with that of Bengal Red[48] plus absorptions due to the starting dicyclohexyl-18-crown-6-ether. The visible spectrum is similar to that of Bengal Red,[49] having λ_{max} in methylene bromide of 569 nm (ϵ 41,000). *Anal.* Calcd for $C_{60}H_{74}Cl_4I_4O_9Na_2$: C, 40.88; H, 4.23; I, 28.80; Na, 2.61. Found: C, 39.98; H, 4.98; I, 25.34; Na, 2.54.

Acknowledgment. Support of this work by the Robert A. Welch Foundation is appreciated. We thank Mrs. S. T. Weintraub for obtaining the mass spectra. We thank the National Science Foundation for matching funds to purchase the T-60 nmr spectrometer.

[48] Sadtler Standard Infrared Spectrum No. 1573, Philadelphia, Pa.

[49] K. Gollnick, *Advan. Photochem.*, **6**, 14 (1968).

Assessment of the Relative Efficiencies of Syn-Disposed Cyclopropane, Cyclobutane, and Cyclobutene Ring Participation in the Photolysis of Azo Compounds. Kinetic Analysis of a *cis*-Bicyclo[5.2.0]nona-2,5,8-triene to *cis*-Bicyclo[6.1.0]nona-2,4,6-triene Rearrangement

Leo A. Paquette* and Michael J. Epstein

Contribution from the Department of Chemistry, The Ohio State University, Columbus, Ohio 43210. Received May 10, 1973

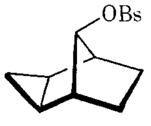
Abstract: The *cis*-bicyclo[5.2.0]nona-2,5,8-triene (**15**) has been synthesized and its thermal (−6 to −25°) rearrangement to the isomeric *cis*-bicyclo[6.1.0]nona-2,4,6-triene (**16**) examined kinetically. The activation parameters, $\Delta H^{\neq} = 13.6$ kcal/mol, $\Delta G^{\neq} = 19.7$ kcal/mol, and $\Delta S^{\neq} = -20.4$ eu, follow directly from the experimentally derived rate constants. The structurally related *cis*-bicyclo[5.2.0]nona-2,5-diene (**22**) was similarly prepared; in contrast to **15**, **22** exhibits no tendency to undergo Cope rearrangement. Access to **15** and **22** was gained by extrusion of nitrogen from azo compounds **14** and **21**. Low-temperature photolysis studies and selected thermal experiments have established that the fused cyclopropane bond in these tetracyclic molecules experiences rupture to the exclusion of similar bonds of the cyclobutene and cyclobutane type. These data lead to the conclusion that strained rings experience cleavage in radical reactions chiefly as a function of their "bent bond" character. In contrast, the direction of equilibria in the [3,3]sigmatropic rearrangement processes is dictated by strain factors.

The capability of three- and four-membered carbocyclic rings to function effectively as neighboring groups when fused in close proximity to developing bridged cationic centers has been recently examined. Not only has the necessity for endo stereochemical orientation of the small ring been convincingly demonstrated, but a parallelism between chemical reactivity and ring size has been noted. For example, whereas the solvolytic rate constant for **1** is merely comparable to that of the 7-norbornyl derivative, tosylate **2** exhibits a 10^{14}-fold rate acceleration.[1] Also, although the cyclobutene ring in **4** is unable to participate in the ionization process,[2] **5** enjoys a relative rate of $10^{5.8}$.[3] Anchimeric assistance by the cyclobutane

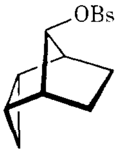
[1] (a) H. Tanida, T. Tsuji, and T. Irie, *J. Amer. Chem. Soc.*, **89**, 1953 (1967); (b) M. A. Battiste, C. L. Deyrup, R. E. Pincock, and J. Haywood-Farmer, *ibid.*, **89**, 1954 (1967); (c) J. Haywood-Farmer and R. E. Pincock, *ibid.*, 91, 3020 (1969).

[2] R. M. Coates and K. Yano, *ibid.*, **95**, 2203 (1973).

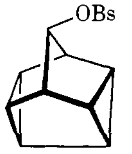
[3] (a) M. Sakai, A. Diaz, and S. Winstein, *ibid.*, **92**, 4452 (1970); (b) M. A. Battiste and J. W. Nebzydoski, *ibid.*, **92**, 4450 (1970).



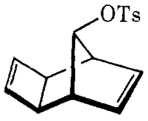
1



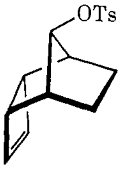
2



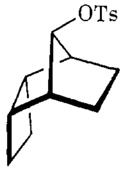
3



4



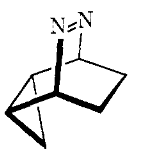
5



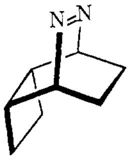
6

ring in **6** amounts to a rate increase of $10^{4.3}$; this latter finding reveals the four-membered ring to be capable of providing only a small fraction of the charge stabilization available from an endo cyclopropyl group.[3] These effects appear not to arise from factors associated with strain release. This conclusion is supported by the behavior of **3** whose large solvolytic rate ($k_{\mathrm{rel}} = 10^{12}$) must be attributed to electronic factors since the major solvolysis product is structurally identical with **3** by virtue of a triply degenerate rearrangement.[4]

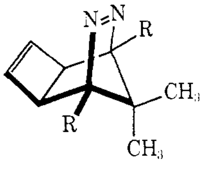
Parallel contributions to the thermal reactivity of structurally related azo compounds have also been encountered. Thus, **7** and **8** suffer loss of nitrogen 10^{17} and 10^{4} times faster, respectively, than 2,3-diazabicyclo[2.2.2]oct-2-ene.[5] In contrast, the exo fused azo compounds **9–11**[6,7] extrude nitrogen at vastly



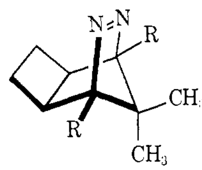
7



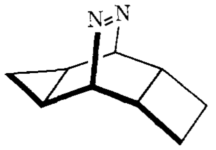
8



9



10



11

slower rates, *e.g.*, $k_7/k_{11} > 10^{14}$. Because the lack of an adequate number of azo compounds from this group has so far precluded an assessment of the relative efficiencies of syn-disposed cyclopropane, cyclobutane, and cyclobutene ring participation during thermolysis or photolysis to be made,[8] we undertook to examine a one-step preparation of a representative polycyclic system which would provide information on this point. In the reasonable expectancy that the three-membered microcycle would again yield most readily to bond cleavage, attention was directed to the synthesis of **14** with the added objective in mind to gain ready access to a derivative of the elusive *cis*-bicyclo[5.2.0]nona-2,5,8-triene system. This goal has been realized and some aspects of the chemical behavior of this little known polyolefinic construct are also described.[9]

Results

In design, the synthetic method is an adaptation of one developed earlier in this laboratory for the preparation of **9**[6] and related substances[10] and consists in the Diels–Alder addition of cyclobutadiene to a heterocycle having a >C=NN=C< part structure. The relative stability of diazanorcaradiene **12** and its convenient preparation either by allylic chlorination–dehydrochlorination of the related diazacycloheptadiene[11] or base-catalyzed condensation of hydrazine with *trans*-1,2-dibenzoylcyclopropane prompted its selection for the present study. When cyclobutadieneiron tricarbonyl (**13**) was oxidized with ceric ammonium nitrate[12] in the presence of **12**, tetracyclic azo compound **14** was obtained in 36% yield. The stereochemistry of **14** is supported by two major lines of evidence. First, saturation of the two-proton singlet at δ 3.56 due to allyl protons H_2 and H_5 resulted in a nuclear Overhauser effect of 5–8% in the integral intensity of the tertiary cyclopropyl protons (H_7 and H_9) located at δ 1.53–1.80. It follows that these pairs of hydrogens must be in mutual spatial proximity. Secondly, lanthanide-induced shifting (LIS) of the nmr spectrum of **14** (0.25 molar equiv of $Eu(dpm)_3$ in $CDCl_3$) produced changes in chemical shift of −0.7 ppm for both sets of tertiary protons, −0.3 ppm for the olefinic pair, and −1.1 ppm for syn H_8. The large LIS for this cyclopropyl hydrogen requires that C_8 be oriented syn to the azo group which serves as the coordination center for the europium complex.

When irradiated in $CDCl_3$ solution at −60° with a 200-W Hanovia mercury arc, **14** readily lost nitrogen to give exclusively the *cis*-bicyclo[5.2.0]nona-2,5,8-triene (**15**) (Scheme I). Structural assignment to **15** was made on the basis of its nmr spectrum which, in addition to a ten-proton aryl multiplet centered at δ 7.38, gave evidence of a low-field triplet (J = 7 Hz) of area 2 at 6.29, singlets (2 H each) at 6.15 and 4.48, and a multiplet for the doubly allylic methylene group at *ca.* 3.1. In particular, the absence of any cyclopropyl proton absorption was clearly evident. Furthermore, **15** experiences facile [3,3]sigmatropic shift to **16** at temperatures above −25° in a first-order kinetic process. Rate constants determined for this valence isomerization in $CDCl_3$ at −6, −18, and −25° were found experimentally to be 1.38×10^{-3}, 3.83×10^{-4}, and 1.84×10^{-4} sec^{-1}, respectively. These

---

(4) R. M. Coates and J. L. Kirkpatrick, *J. Amer. Chem. Soc.*, **90**, 4162 (1968); **92**, 4883 (1970).

(5) (a) E. L. Allred and J. C. Hinshaw, *Chem. Commun.*, 1021 (1969); (b) E. L. Allred and J. C. Hinshaw, *Tetrahedron Lett.*, 387 (1972); (c) see also L. A. Paquette, *J. Amer. Chem. Soc.*, **92**, 5766 (1970); R. Askani, *Tetrahedron Lett.*, 3349 (1970).

(6) (a) L. A. Paquette and L. M. Leichter, *J. Amer. Chem. Soc.*, **92**, 1765 (1970); **93**, 5128 (1971); (b) *ibid.*, **93**, 4922 (1971).

(7) E. L. Allred and K. J. Voorhees, *ibid.*, **95**, 620 (1973).

(8) In principle, the differing orientations of the two small rings in **11** should permit a somewhat related analysis to be made. Unfortunately, only the pyrolysis of **11** has been studied[7] and the necessarily elevated temperatures required to induce N_2 fragmentation deny the possibility. This is because the resultant hydrocarbon is exceedingly well disposed toward Cope rearrangement, such that thermodynamic equilibration between the valence isomers obtains rapidly under the conditions employed (177–199°).

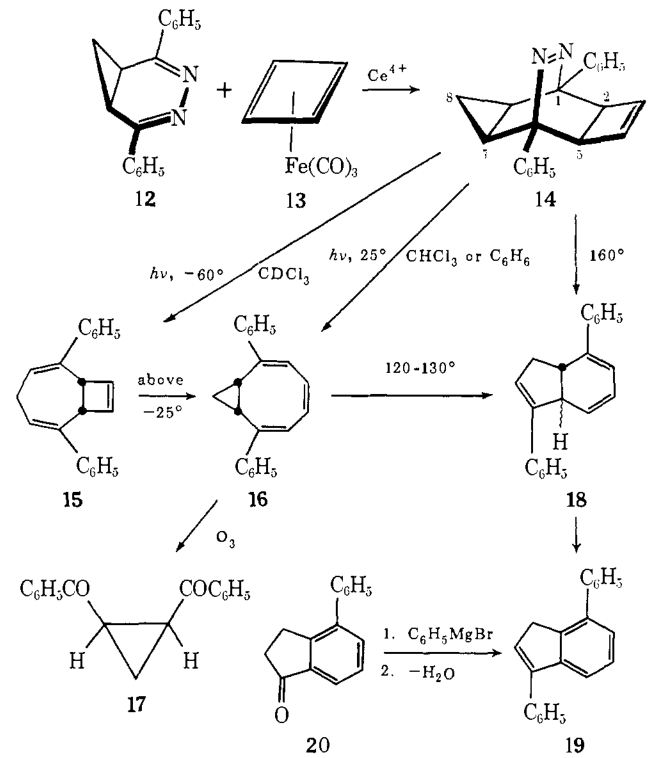
(9) For a preliminary account of this work, consult L. A. Paquette and M. J. Epstein, *J. Amer. Chem. Soc.*, **93**, 5936 (1971).

(10) (a) L. A. Paquette and J. F. Kelly, *Tetrahedron Lett.*, 4509 (1969); (b) L. A. Paquette, M. R. Short, and J. F. Kelly, *J. Amer. Chem. Soc.*, **93**, 7179 (1971).

(11) R. G. Amiet and R. B. Johns, *Aust. J. Chem.*, **21**, 1279 (1968); G. Maier, *Chem. Ber.*, **98**, 2438, 2446 (1965).

(12) L. A. Paquette and L. D. Wise, *J. Amer. Chem. Soc.*, **89**, 6659 (1967); L. Watts, J. D. Fitzpatrick, and R. Pettit, *ibid.*, **87**, 3253 (1965).

Scheme I



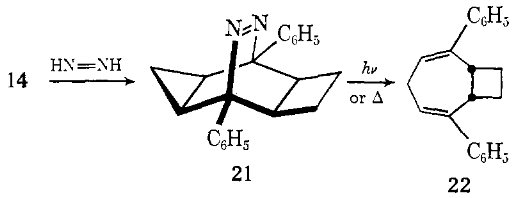
data correspond to $\Delta H^{\ddagger} = 13.6$ kcal/mol, $\Delta G^{\ddagger} = 19.7$ kcal/mol, and $\Delta S^{\ddagger} = -20.4$ eu.

The moderate $\Delta G^{\ddagger}$ of this Cope rearrangement is of some interest. The free energy of activation for **15** is significantly lower than the value measured for *cis*-1,2-divinylcyclobutane (26.6 kcal/mol),[13] although it does not approach those observed for cis-locked divinylcyclopropanes such as octamethylsemibullvalene (6.4 kcal/mol),[14] barbaralane (7.8 kcal/mol),[15] 2,8-pentamethylenesemibullvalene (8.5 kcal/mol),[16] 9-methylenebarbaralane (9.5 kcal/mol),[17] barbaralone (10.5 kcal/mol),[17,18] and bullvalene (12.8 kcal/mol).[19] Rather, the barrier for **15** is roughly comparable to the $\Delta G^{\ddagger}$ for the degenerate rearrangement of 1,3,5,7-tetramethylbicyclo[5.1.0]octa-2,5-diene (13.6 kcal/mol).[20] As with this latter hydrocarbon, **15** is capable of existing in either cisoid or transoid conformations; due to the energetic similarities, rearrangement *via* the less stable folded transition state can be inferred in the two cases. All attempts to obtain nmr verification of this point were not successful. However, the appreciably negative $\Delta S^{\ddagger}$ term does point to a highly ordered transition state.

cis-Bicyclo[6.1.0]nonatriene (**16**) proved to be a highly insoluble white solid which exhibits ultraviolet maxima (in ethanol) at 254 nm (ϵ 24,600) and 299 (9880). Its monomeric nature was revealed by its mass spectral parent ion at *m/e* 270. In addition, ozonolysis gave *cis*-dibenzylcyclopropane (**17**)[21] in 51% yield. Consequently, **16** must contain the indicated cyclopropane ring. Thermal rearrangement of **16** at 120–130° in tetrachloroethylene or pyridine solution resulted in conversion to 8,9-dihydroindene (**18**) which upon treatment with sodio ethylenediamine in ethylenediamine[22] was oxidized to diphenylindene (**19**). Authentic **19** was synthesized by 1,2 addition of phenylmagnesium bromide to indenone **20**[23] and subsequent dehydration. The complexity of the nmr spectrum of **18** unfortunately was not conducive to the assignment of stereochemistry at the ring fusion. Our inability to obtain this oily material in crystalline form may be an indication that both cis and trans isomers were in fact present.

With establishment of the structures of **15** and **16**, attention was turned to the room temperature photochemistry of **14**. When the azo compound was irradiated at 25° in chloroform or benzene solution as previously described or with a 3500 Å light source, **16** was seen to be rapidly deposited. In view of the preceding evidence, we consider **16** to arise mechanistically from initial formation of **15** and its subsequent Cope rearrangement rather than from direct cleavage of the internal cyclobutene bond.

Finally, treatment of **14** with diimide conveniently furnished dihydro derivative **21**. Photolysis of this diazo compound at either −60° or +25° gave **22** as the sole product. In its electronic spectrum (isooctane solution), **22** displays a lone maximum at 243 nm (ϵ 15,000). The nmr spectrum (in $CDCl_3$) consists of an aryl multiplet of area 10 at δ 7.18, a two-proton olefinic triplet ($J = 6.5$ Hz) centered at 6.00, and multiplets at 3.83, 3.04, and 2.02 assignable to the doubly allylic (2 H), allylic (2 H), and cyclobutyl (4 H) protons, respectively.



Thermolysis of **21** in tetrachloroethylene solution at 135° (sealed nmr tubes) was found to proceed readily with an approximate $t_{1/2}$ of 20 min. Again, **22** was produced exclusively. By comparison, the half-life for thermal extrusion of nitrogen from **14** at 132° under comparable conditions was >90 min. An increase in temperature to 160° did result in essentially quantitative conversion to **18** at a convenient rate.

Diene **22** proved to be stable at 135° for at least 1 hr. At 160°, however, slow polymerization was encountered during which time no new nmr signals appeared.

Discussion

Azo Decomposition. It is evident from structural

---

(13) G. S. Hammond and C. D. DeBoer, *J. Amer. Chem. Soc.*, **86**, 899 (1964).

(14) F. A. L. Anet and G. E. Schenck, *Tetrahedron Lett.*, 4237 (1970).

(15) W. von E. Doering, B. M. Ferrier, E. T. Fossel, J. H. Hartenstein, M. Jones, Jr., G. Klumpp, R. M. Rubin, and M. Saunders, *Tetrahedron*, 23, 3943 (1967).

(16) R. K. Russell, L. A. Paquette, L. G. Greifenstein, and J. B. Lambert, *Tetrahedron Lett.*, 2855 (1973).

(17) L. G. Greifenstein, J. B. Lambert, M. J. Broadhurst, and L. A. Paquette, *J. Org. Chem.*, **38**, 1210 (1973).

(18) J. B. Lambert, *Tetrahedron Lett.*, 1901 (1963).

(19) A. Allerhand and H. S. Gutowsky, *J. Amer. Chem. Soc.*, **87**, 4092 (1965).

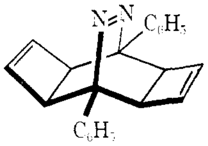
(20) L. Birladeanu, D. Harris, and S. Winstein, *ibid.*, **92**, 6387 (1970).

(21) G. W. Griffin, E. J. O'Connell, and H. A. Hammond, *ibid.*, **85**, 1001 (1963). We thank Professor Griffin for an authentic sample which permitted direct comparison with 17 to be made.

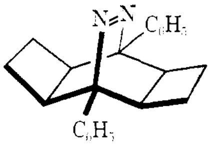
(22) L. Reggel, S. Friedman, and I. Wender, *J. Org. Chem.*, **23**, 1136 (1958).

(23) J. W. Cook, G. T. Dickson, J. Jack, J. D. London, J. McKeown, J. Macmillan, and W. F. Williamson, *J. Chem. Soc.*, 139 (1950).

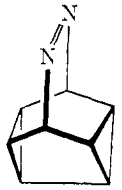
considerations that exo fusion of the small rings in **14** and **21** does not permit favorable orientation of the bent bonds for overlap as C–N cleavage begins. Irrespective of whether loss of nitrogen from these molecules proceeds by the fragmentation of one or both C–N bonds in the rate-determining step, the relevant orbitals are seen to be orthogonally aligned to the developing radical center(s) such that little or no overlap operates at this kinetically important stage of reaction. Nor, as previously commented upon by Allred and Voorhees,[7] is inward rotation of such bonds a likely possibility because of the rapid incursion of severe angle strain as a result of incipient *trans,trans*-diene production. Not unexpectedly, **14** and **21** parallel closely in their reactivity the chemical behavior of homologs **23** and **24** which likewise thermally extrude nitrogen at reasonable rates only above 150.°[10b] Of major relevance in the present work is the fact that **14** and **21** are unsymmetrically constructed with flanking



23



24

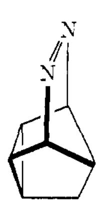


25

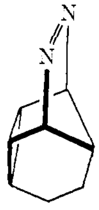
exo rings of differing size. However, the mere presence of an exo cyclopropane ring is seen not to facilitate greatly the fragmentation process. In this connection, the mismatch in reactivity between **14** and **21** on the one hand and **25** is very striking. Although lacking bridgehead phenyl substituents to stabilize any possible radical intermediate (should a nonconcerted process operate), **25** decomposes so rapidly below 0° that its isolation has been precluded to date.[5c,24,25]

Despite the experimentally demonstrated inability of the cyclopropane ring in **14** and **21** to promote marked acceleration of the loss of nitrogen, the data require that the central cyclopropyl bond rupture in high preference to those of the cyclobutene or cyclobutane rings under both thermal and photochemical conditions. The question of whether the photodecompositions occur from the $n \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$ manifolds has not been examined. Notwithstanding the multifaceted mechanistic possibilities that could operate upon irradiation,[26] that adjacent C–C linkage endowed with the greatest "bent-bond" character is observed to cleave exclusively within the limit of experimental detectability. The calculations of Coulson and Goodwin[27] establish that the degree of "bent bonding" for cyclopropane is approximately three times that for cyclobutane. Thus, despite the geometrically enforced inoperability of synchronous reactions in exo-fused systems, the relative efficiencies of strained bond cleavage reactions appear to be dictated chiefly by differences in bond hybridization.

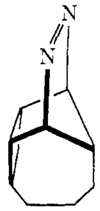
The observed reactivity features are not correlatable with varying levels of strain which are selectively released in the transition state. In contradistinction to our results the most recent strain estimates available[28] show cyclobutene (30.6 kcal/mol) to be 2.5 kcal/mol more strained than cyclopropene (28.1 kcal/mol), and cyclobutane (26.9 kcal/mol) to be relatively less congested than either of the first two. Rather, indications are that these contributions are of lesser importance than electronic influences. A similar conclusion in support of the controlling effect of hybridization factors has recently been arrived at from a study of the behavior of azo compounds **26–28**.[29]



26



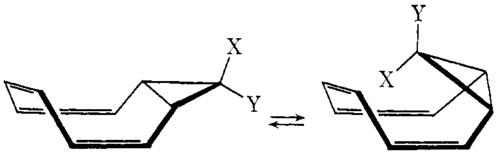
27



28

The respective relative decomposition rates of 9.2, 5.2×10^6, and 1.9×10^{11} convincingly demonstrate that alterations of the dihedral angle between the cyclopropane ring and the departing azo group (with attendant changes in "bent bond" character) exert profound alterations in reactivity.

***cis*-Bicyclo[5.2.0]- to *cis*-Bicyclo[6.1.0]nonatriene Rearrangement.** The mechanisms by which *cis*-bicyclo[6.1.0]nona-2,4,6-trienes (**29**) undergo thermal rearrangement to 8,9-dihydroindenes have recently received much intensive investigation.[30] The observed mechanistic dichotomies are postulated to arise because of a high level of dependence upon reactant conformation. In those derivatives where the X substituent is sufficiently large to deter attainment of folded conformation **29b**, bond relocation proceeds *via* **29a** along a series of steps to afford ultimately *trans*-8,9-dihydroindene products.[30–32] In contrast, when the X substituent is not sterically demanding, rearrangement *via* **29b** is kinetically preferred ($\Delta\Delta G^{\ddagger} \approx 4$ kcal/mol).[33] In these examples, *cis*-8,9-dihydroindenes are produced and the structural reorganization is seemingly mediated by *cis,cis,trans,cis*-cyclononatetraenes.[34] Several groups have recently considered the possibility that access to such medium-ring polyolefins is gained in certain instances by initial [3,3]sigmatropic rear-



29a **29b**

---

(24) (a) R. M. Moriarty, C.-L. Yeh, and N. Ishibi, *J. Amer. Chem. Soc.*, **93**, 3085 (1971); (b) J. P. Snyder, L. Lee, V. T. Bandurco, C. Y. Yu, and R. J. Boyd, *ibid.*, **94**, 3260 (1972).

(25) The same high level of reactivity has been noted in annelated derivatives of this ring system: L. A. Paquette, R. E. Wingard, Jr., and R. K. Russell, *ibid.*, **94**, 4739 (1972).

(26) J. A. Berson and S. S. Olin, *ibid.*, **92**, 1086 (1970), and relevant references cited therein.

(27) C. A. Coulson and T. H. Goodwin, *J. Chem. Soc.*, 2851 (1962); 3161 (1963).

(28) P. v. R. Schleyer, J. E. Williams, and K. L. Blanchard, *J. Amer. Chem. Soc.*, **92**, 2377 (1970).

(29) E. L. Allred and A. L. Johnson, *ibid.*, **93**, 1300 (1971).

(30) An excellent leading review of this problem is available: S. W. Staley, *Intra-Sci. Chem. Rep.*, **5**, 149 (1971).

(31) S. W. Staley and T. J. Henry, *J. Amer. Chem. Soc.*, **91**, 1239, 7787 (1969).

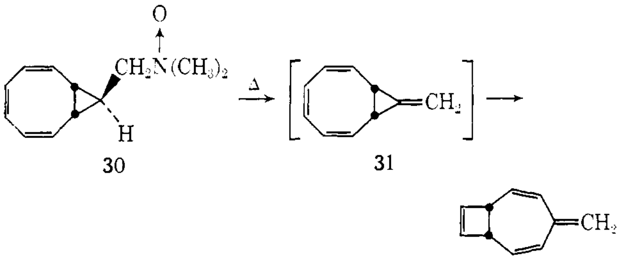
(32) A. G. Anastassiou and R. C. Griffith, *ibid.*, **95**, 2379 (1973).

(33) A. G. Anastassiou and R. C. Griffith, *J. Chem. Soc. D*, 1301 (1971); 399 (1972).

(34) A. G. Anastassiou and R. C. Griffith, *J. Amer. Chem. Soc.*, **93**, 3083 (1971).

rangement of **29b** to *cis*-bicyclo[5.2.0]nona-2,5,8-trienes.[34,35] However, confirmation of this suggestion is presently lacking.

The only previous evidence that the bicyclo[6.1.0]nonatriene system may be capable of kinetically controlled Cope rearrangement to a [5.2.0]bicyclic counterpart is found in the behavior of **31** (not interceptable).[36] However, this particular example is very likely atypical because of the destabilization accorded **31** by the exocyclic methylene group. Unquestionably, the 11.1 kcal/mol strain energy difference between methylenecyclopropane (41.7 kcal/mol)[28] and cyclobutene will appreciably destabilize **31** relative to **32**. Prior to this work, **32** represented the only known derivative of this ring system.

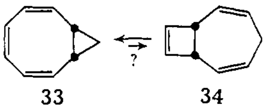


30

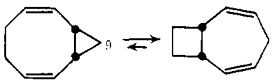
31

32

The presence of the two phenyl substituents in **15** and **16** may be too great a complication of the parent systems to permit the present data to contribute directly toward the mechanistic solution of the bicyclo[6.1.0]nonatriene to 8,9-dihydroindene rearrangement. Unfortunately, the inherent instability of lesser substituted 3,4-diazanorcaradienes[37] has precluded their utilization in the synthetic sequence. Notwithstanding, the propensity of **15** for valence isomerization parallels in direction what is expected of hydrocarbon **33** if strain factors exert the dominant influence on the direction of equilibrium ($\mathrm{SE}_{◫} - \mathrm{SE}_{\triangle} = 2.5$ kcal/mol). This latter conclusion is supported by the tendency of **35** to rearrange unidirectionally to **36** at 40° (folded conformation necessary)[38] since in this instance the [5.2.0]bicyclic is now less strained ($\mathrm{SE}_{\triangle} - \mathrm{SE}_{\square} = 1.2$ kcal/mol). That **35** and **36** are more nearly isoenergetic than **33** and **34** is evident from the work of Grimme[38b] who has found it possible to directly observe equilibria between these two isomers (nmr methods) by introducing methyl groups at C_9 (in **35**) for the purpose of stabilizing the cyclopropane ring (0.7–2.5 kcal/mol per methyl group).[39]



33 34



35 36

Like **36**, **22** gives no evidence for equilibration with its *cis*-bicyclo[6.1.0]nona-2,6-diene valence tautomer. Since the electronic features in **15** and **22** are essentially comparable, the exclusive overt tendency of **15** for rearrangement to cyclopropyl form **16** must have its origins principally in the strain imbalance generated by the presence of the otherwise insulated cyclobutene double bond. The C_4–C_5 double bond in **16** probably also contributes to triene stabilization; however, the structurally enforced nonplanarity of the cyclooctatriene part structure is recognized to minimize π-overlap interaction to a marked degree.[40]

Experimental Section

Infrared spectra were obtained with a Perkin-Elmer Model 137 infracord spectrometer. The nmr spectra were determined on Varian A-60A and HA-100 instruments and apparent splittings are cited. Mass spectra were measured with an AEI MS-9 mass spectrometer at an ionizing energy of 70 eV. Microanalyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

2,5-Diphenyl-3,4-diazabicyclo[4.1.0]hepta-2,4-diene (12). A. To each of five flasks containing a solution of 1.0 g (4.0 mmol) of 3,7-diphenyl-1,2-diazacyclohepta-2,7-diene[41] in 10 ml of chloroform was added 0.5 g (3.75 mmol) of *N*-chlorosuccinimide (NCS). Each flask was then swirled in hot water (*ca.* 65°) until the NCS reacted, as evidenced by bubbling and dissolution of the latter reagent. The contents were then poured into a saturated aqueous sodium bicarbonate solution contained in a separatory funnel. When all five reactions were completed, the funnel was vigorously shaken for several minutes. The yellow organic phase was dried and evaporated at 25°. The residue was chromatographed on 40 ml (dry volume) of alumina. Elution with benzene and then chloroform gave a yellow solid which after washing briefly with ethyl acetate left 3.06 g (66%) of fine yellow prisms, mp 203–210° dec (lit.[11] mp 195–196° dec). Decomposition ranges of 210–215° could be obtained by recrystallization from ethyl acetate and isooctane. However, the material prepared by the above procedure was stable to storage for more than 6 months and was pure on the basis of nmr analysis: $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 7.9–8.3 (m, 10, aryl), 2.4–2.7 (m, 2, H_1 and H_6), 1.8–2.2 (m, 1, cyclopropyl), and 0.1–0.4 (q, 1, cyclopropyl).

B. A mixture of 3.0 g (12.0 mmol) of *trans*-1,2-dibenzoylcyclopropane,[21] 4.1 g (62 mmol) of potassium hydroxide, 0.75 ml (23.7 mmol) of 97% hydrazine, and 500 ml of methanol was placed in a stoppered flask and swirled occasionally during 5 days. Small pieces of solid carbon dioxide were introduced to neutralize the solution. The solvent was removed on a rotary evaporator and the residue was partitioned between water and chloroform. The organic phase was dried and evaporated and the residue was chromatographed as above to give 1.16 g (40%) of **12**, mp 200–211° dec.

1,6-Diphenyl-10,11-diazatetracyclo[4.3.2.0^{2,5}.0^{7,9}]undeca-3,10-diene (14). A mixture of 5.05 g (20.5 mmol) of **12**, 3.81 g (19.9 mmol) of cyclobutadieneiron tricarbonyl,[12] and 75 ml of acetone was stirred in an ice bath under nitrogen while 33.6 g (61.4 mmol) of ceric ammonium nitrate was added in 1-g portions during 3 hr. The resulting dark suspension was added to a mixture of 3 ml of 2-propanol, 600 ml of ether, and 400 ml of water, and stirred for 20 min. The ether layer was dried and evaporated, and the residue was chromatographed on 30 ml (dry volume) of alumina; elution with dichloromethane afforded 2.37 g of white solid. This material was percolated briefly with 70 ml of isooctane and cooled to give 2.20 g (36%) of small white crystals: mp 170–172°; nmr $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 7.3–8.0 (m, 10, aryl), 7.07 (s, 2, vinyl), 3.57 (s, 2, allyl), 1.67 (q, 2, cyclopropyl), and 0.1–0.7 (m, 2, cyclopropyl), decoupling of the ABX_2 cyclopropyl pattern revealed $\delta_A = 0.31$, $\delta_B = 0.47$, $|J_{AB}| = 7$ Hz, $|J_{AX}| = 7$ Hz; ir ($CHCl_3$) 2959, 1603, 1490, 1441, 1312, 1289, 1266, 1131, 1053, 1027, 952, and 887 cm^{-1}.

Anal. Calcd for $C_{21}H_{18}N_2$: C, 84.52; H, 6.08. Found: C, 84.50; H, 6.20.

Low-Temperature Photolysis of 14. A solution of 30 mg of **14** in *ca.* 0.3 ml of $CDCl_3$ contained in an nmr tube was irradiated at

---

(35) (a) P. Radlick and W. Fenical, *J. Amer. Chem. Soc.*, **91**, 1560 (1969); (b) J. E. Baldwin, A. H. Andrist, and R. K. Pinschmidt, Jr., *ibid.*, **94**, 5845 (1972).

(36) P. Radlick, W. Fenical, and G. Alford, *Tetrahedron Lett.*, 2707 (1970).

(37) (a) G. Maier and T. Sayrac, *Angew. Chem.*, **78**, 981 (1966); (b) G. Maier, *ibid.*, **79**, 446 (1967).

(38) (a) M. S. Baird and C. B. Reese, *J. Chem. Soc. D*, 1519 (1970); (b) W. Grimme, *J. Amer. Chem. Soc.*, **95**, 2381 (1973).

(39) J. C. Barborak, S. Chari, and P. v. R. Schleyer, *ibid.*, **93**, 5275 (1971).

(40) See, for example, L. A. Paquette and K. A. Henzel, *ibid.*, **95**, 2724, 2726 (1973).

(41) C. G. Overberger and J. J. Monagle, *ibid.*, **78**, 4470 (1956).

−60° with a 200-W Hanovia lamp housed in a water-cooled Pyrex well. Periodic examination of the nmr spectrum was made at temperatures below −40°. After 60 min, no **14** remained and the following spectral features (CH_2Cl_2 as internal standard, δ 5.35) consistent with **15** were observed: $\delta_{TMS}^{CDCl_3}$ 7.38 (m, 10, aryl), 6.29 (t, $|J|$ = 7 Hz, 2, vinyl), 6.15 (s, 2, cyclobutenyl), 4.48 (br s, 2, tertiary bisallyl), and 3.09 (m, 2, bisallyl). A white precipitate of **16** (identical by melting point and ir with the product isolated below) formed quickly as the sample was allowed to warm above −20°. However, the insolubility of this latter hydrocarbon in this medium precluded obtention of its nmr spectrum.

The kinetics of the **15** → **16** rearrangement was studied by means of low-temperature nmr. Samples consisting of 50 mg of **14**, 0.3 ml of $CDCl_3$, and an integration standard (6 mg of dichloromethane and/or 1.2 mg of cyclohexane) were wax-sealed in nmr tubes and photolyzed in a Dry Ice–2-propanol filled, unmirrored Pyrex dewar flask with light from a 200-W Hanovia lamp in a standard Pyrex cooling jacket. For a kinetic run, a tube was removed from the dewar and quickly (*ca.* 10 sec) placed in the precooled nmr probe; then the region from *ca.* δ 6 to *ca.* 3 was integrated at measured time intervals. The ratio of the peak at δ 4.48 for **15** to the absorption of the standard used was measured as a function of time (Table I).

Table I. Rates of Thermal Rearrangement of **15** in $CDCl_3$ Solution at Several Temperatures

Run no.	Temp, °C	k, sec^{-1}	
1	−6	1.381×10^{-3}	
2	−6	1.385×10^{-3}	Av $k = 1.386 \times 10^{-3}$
3	−6	1.392×10^{-3}	
4	−18	3.511×10^{-4}	
5	−18	4.132×10^{-4}	Av $k = 3.834 \times 10^{-4}$
6	−18	3.860×10^{-4}	
7	−25	1.651×10^{-4}	
8	−25	2.025×10^{-4}	Av $k = 1.838 \times 10^{-4}$

2,7-Diphenylbicyclo[6.1.0]nona-2,4,6-diene (16). A solution of 113 mg (0.420 mmol) of **14** in 8 ml of benzene contained in a quartz tube was irradiated in a Rayonet reactor fitted with 3500 Å lamps for 2 hr. Thin-layer chromatography (silica gel, benzene) at that time indicated the absence of **14**. The mixture was evaporated under vacuum and chromatographed on 30 ml (dry volume) of alumina; elution with 10% benzene–90% petroleum ether and recrystallization from dichloromethane–isooctane afforded 66 mg (64%) of **16** as white crystals: mp 161–163°; $\lambda_{max}^{isooctane}$ 254 nm (ϵ 24,600) and 299 (9880); ir (KBr) 2985, 1587, 1475, 1425, 1153, 1065, 1033, 1025, 983, 969, 879, 843, 779, 759, 718, and 692 cm^{-1}; *m/e* 279.

Anal. Calcd for $C_{21}H_{18}$: C, 93.29; H, 6.71. Found: C, 93.14; H, 6.74.

Ozonolysis of 16. A solution of 94 mg (0.348 mmol) of **16** in 7 ml of methanol and 200 ml of dichloromethane was cooled in a Dry Ice–2-propanol bath while oxygen was bubbled through the solution. When the solution was judged to be near −78° the Welsbach ozone generator through which the oxygen passed was activated (100 V, 1 SLCFM, 7 psi) until the solution turned blue (about 90 sec). The solution was flushed with oxygen while it was allowed to warm to 10°. The colorless solution was added to 400 ml of distilled water containing three drops of acetic acid, heated with stirring to remove the dichloromethane, and percolated for 30 min to ensure hydrolysis of the ozonide. The cooled mixture was extracted with dichloromethane and the organic phases were dried and evaporated under vacuum to leave 86 mg of almost white solid. Chromatography of this material on 20 ml (dry volume) of silica gel gave 44 mg (51%) of **17** as fine white needles: mp 121–123° (lit.[21] mp 123–124°); $\delta_{TMS}^{CDCl_3}$ 7.8–8.1 and 7.1–7.6 (m, 10, aryl), 3.1 (q, 2), 2.1 (m, 1), and 1.5 (sextet, 1); ir (KBr) 1675 cm^{-1}. This diketone was identical in all respects with an authentic sample.

Preparative Scale Pyrolysis of 14. In an evacuated glass tube was sealed 351 mg of **14** and 0.35 ml of tetrachloroethylene and the solution was heated at 160° for 65 min. There was obtained a clear greenish solution which was subjected to preparative thick-layer chromatography on silica gel plates. The yellow band of greatest R_f corresponded to 60% of the theoretical amount of $C_{21}H_{18}$ obtainable. The nmr spectrum of this yellow oil (in $CDCl_3$) consisted of very complex patterns in the aryl (δ 7.26), vinyl (δ 6.80, 5.60–6.60), and allyl (δ 2.00–3.60) regions; decoupling (double and triple irradiation) experiments at 100 MHz failed to simplify significantly the spectrum; ir (neat) 2976, 1497, 1437, 757, 695 cm^{-1}; $\lambda_{max}^{isooctane}$ 234 nm (ϵ 15,000) and 305 (6900); *m/e* 270.140 (calcd, 270.141).

Anal. Calcd for $C_{21}H_{18}$: C, 93.29; H, 6.71. Found: C, 92.89; H, 6.57.

In a separate experiment, this oil was added to a refluxing solution formed by heating 1 g (17 mmol) of ethylenediamine (distilled from sodium) with 90 mg (3.9 mg-atom) of sodium under nitrogen for 4.5 hr. After 3.5 hr the mixture was cooled and quenched with water. Hydrochloric acid was added to bring the pH to 1 and the mixture was extracted with dichloromethane. The dried extract was evaporated under vacuum to leave 116 mg of brown residue, chromatography of which on 15 ml (dry volume) of acidic alumina furnished 87 mg of yellow oil whose nmr spectrum (in $CDCl_3$) clearly was identical with that of authentic **19**. Rechromatography of this material on alumina gave colorless crystals of **19**, mp 111–114°.

Thermal Rearrangement of 16. An evacuated sealed glass tube containing a mixture of 96 mg (0.355 mmol) of **16** and 0.05 ml of pyridine was heated at 108° for 90 min. Since almost no reaction had occurred under these conditions, the temperature was raised to 131° for 60 min. There was obtained a greenish solution which was injected directly into a refluxing solution prepared by heating 200 mg (8.7 mg-atom) of sodium with 2.0 g (33 mmol) of ethylenediamine (distilled from sodium) for 11 hr under nitrogen. After 60 min the reaction mixture was allowed to cool and 3 hr later the opaque mixture was quenched with 3 ml of methanol and partitioned between water and benzene. An insoluble white solid was removed by filtration. The organic phase was washed with water, dried, and evaporated to leave 108 mg of dark residue. The gum was chromatographed on acidic alumina (elution with 10% dichloromethane) in petroleum ether and there was isolated a white solid which had an ir spectrum (KBr) identical with that of **19**.

3,7-Diphenylindene (19). To the Grignard reagent prepared from 0.36 g (15 mg-atom) of magnesium, 2.00 g (12.7 mmol) of bromobenzene, and 0.3 g (1.6 mmol) of 1,2-dibromoethane in 40 ml of anhydrous ether was added 0.57 g (2.75 mmol) of 4-phenyl-1-indanone (**20**)[23] in 5 ml of benzene. After 4 hr at reflux, the mixture was added to a solution of 20 ml of sulfuric acid in 300 ml of water; azeotropic distillation of 200 ml of water from the mixture also removed the benzene, bromobenzene, biphenyl, and ether.

The residue was extracted with chloroform and the combined organic layers were dried and evaporated to leave 0.69 g of crude product. Chromatography of this material on 30 ml (dry volume) of silica gel gave 0.47 g (64%) of crude **19**, crystallization of which from a mixture of dichloromethane and isooctane afforded white flakes: mp 112.5–114.5°; $\delta_{TMS}^{CDCl_3}$ 7.2–7.8 (m, 13, aryl), 6.6 (t, $|J|$ = 3 Hz, 1, vinyl), and 3.55 (d, $|J|$ = 3 Hz, 2, allyl); ir (KBr) 2994, 1597, 1567, 1484, 1462, 1441, 1408, 1346, 1241, 1072, 1021, 984, 914, 846, 810, 788, 723, 697 cm^{-1}.

Anal. Calcd for $C_{21}H_{16}$: C, 93.99; H, 6.01. Found: C, 93.93; H, 6.06.

1,6-Diphenyl-10,11-diazatetracyclo[4.3.2.0^{2,5}.0^{7,9}]undec-10-ene (21). A suspension of 124 mg (0.416 mmol) of **14** and 5.4 g (27.8 mmol) of potassium azodicarboxylate in 25 ml of anhydrous ethanol was vigorously stirred while 4–5 ml (*ca.* 60 mmol) of acetic acid was added during 3 hr. The mixture was filtered, concentrated under vacuum to a slurry, and partitioned between water and chloroform. The organic layer was dried and filtered through a short column of alumina. The eluate was concentrated *in vacuo* and diluted with benzene and isooctane; two crops of white crystals were collected totaling 91 mg (73%): mp 171–172°; $\delta_{TMS}^{CDCl_3}$ 7.3–8.0 (m, 10, aryl), 3.2–3.6 (m, 2, tertiary cyclobutyl), 1.2–2.3 (m, 6, $-CH_2CH_2-$ and tertiary cyclopropyl), 0.1–0.5 (m, 2, cyclopropyl); ir (KBr) 2907, 1603, 1488, 1439, 1318, 1256, 1072, 1050, 1028, 818, 754, 746, 696 cm^{-1}; *m/e* 300.

Anal. Calcd for $C_{21}H_{20}N_2$: C, 83.96; H, 6.71. Found: C, 83.87; H, 6.59.

Photolysis of 21. A. Room Temperature. A solution of 126 mg (0.420 mmol) of **21** in 6 ml of chloroform contained in a quartz tube was irradiated in a Rayonet reactor fitted with 3500 Å lamps. After 30 min, thin-layer chromatography (silica gel, dichloromethane) indicated total conversion of **21** (R_f 0.5) to **22** (R_f 0.9). The solvent was removed under vacuum and the residue was chromatographed on 20 ml (dry volume) of alumina. Elution with 40% benzene–60% petroleum ether gave 95 mg of oil, crystallization of which from isooctane–methanol gave 36 mg (32%) of **22** as white prisms: mp 53–55°; $\lambda_{max}^{isooctane}$ 243 nm (ϵ 15,000); $\delta_{TMS}^{CDCl_3}$ 7.2 (s, 10, aryl), 6.0 (t, $|J|$ = 6 Hz, 2, vinyl), 3.6–4.0 (m, 2, bridgehead), 3.1 (t of d, J_t = 6 Hz, J_d = 1 Hz, 2, *gem*-allyl), 1.1–2.3 (m, 4, $-CH_2CH_2-$); ir (neat) 2985, 2899, 2825, 1942, 1678, 1639, 1597, 1572, 1488, 1439, 1227, 1074, 1030, 911, 840, 758, 697 cm^{-1}.

Anal. Calcd for $C_{21}H_{20}$: C, 92.60; H, 7.40. Found: C, 92.41; H, 7.58

B. At Low Temperature. A solution of 25 mg of **21** in $CDCl_3$ contained in an nmr tube was photolyzed (200-W Hanovia lamp through Pyrex) for 30 min and examined by nmr, all below −55°; the spectrum was that of **22**.

Pyrolysis of 21. A solution of 25 mg of **21** and 100 mg of tetrachloroethylene was sealed under vacuum in a thick-walled nmr tube. During 90 min in an nmr probe at 135°, the spectrum of the solution changed cleanly from that of **21** to that of **22**. The half-life of the reaction was estimated to be approximately 20 min.

Acknowledgment. Financial support for this research was provided by the donors of the Petroleum Research Fund, administered by the American Chemical Society. We also express appreciation to Dr. Paul Demarco for assistance with the NOE and LIS studies, to Dr. Louis Leichter for his help with the low-temperature nmr experiments, and to Dr. Stanley Wilson for his part in the kinetic determinations.

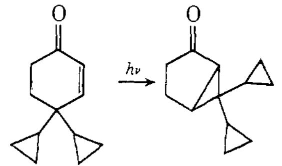
Cyclopropane in Photochemistry. II. Photochemistry of 4-Cyclopropyl-4-phenylcyclohexenone[1]

Roger C. Hahn* and David W. Kurtz[2]

Contribution from the Department of Chemistry, Syracuse University, Syracuse, New York 13210. *Received May 2, 1973*

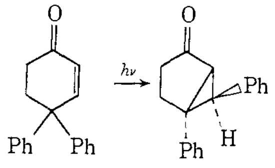
Abstract: Irradiation of 4-cyclopropyl-4-phenylcyclohexenone (**5**) in heptane and benzene gave 5-cyclopropyl-*trans*-6-phenylbicyclo[3.1.0]hexan-2-one (**7**), 5-cyclopropyl-*cis*-6-phenylbicyclo[3.1.0]hexan-2-one (**8**), and 3-phenyl-4-cyclopropylcyclohex-2-enone (**9**). Irradiation of **5** in methanol yielded, in addition to **7–9**, ~20% of *endo*-6-phenyl-*exo*-6-cyclopropylbicyclo[3.1.0]hexan-2-one (**10**). The results are consistent with a narrowing of the gap between n,π* and π,π* triplet energy levels on going from nonpolar to polar solvents. Comparisons of the behavior of several analogous 4,4-disubstituted cyclohexenones indicate that C-4 substituent stabilization of π,π* triplets relative to n,π* triplets increases in the order phenyl < cyclopropyl < methyl.

Recently[1] we reported the photorearrangement of 4,4-dicyclopropylcyclohexenone (**1**) to give exclusively products derived from the enone "type A" reaction[3] (*e.g.*, **2**). In contrast, 4,4-diarylcyclohexenones rearrange exclusively *via* 1,2-aryl migration.[4] These divergent photoreactions of 4,4-dialkyl- and 4,4-diarylcyclohexenones have been attributed to π,π* and n,π* triplet excited states, respectively.[4,5]

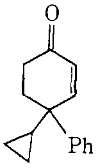


1 **2**

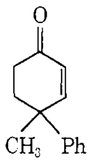
However, spectroscopic studies[5] have shown that the energy levels of π,π* and n,π* triplets lie close together in cyclohexenones; it therefore seemed possible, through the effects of selected substituents, that 4,4-disubstituted cyclohexenones could be constructed which would undergo both types of photochemical reaction. Such behavior would afford an opportunity to explore the influence of medium polarity on the choice of reaction pathways, since solvent changes are known to alter energy differences between n,π* and π,π* triplet states.[6] Given the divergence in photochemical behavior of **1** and 4,4-diphenylcyclohexenone (**3**),[4] we chose to look for borderline behavior in 4-cyclopropyl-4-phenylcyclohexenone (**5**). This compound also would test the suggestion[7] that stabilization by a nonmigrating C-4 aryl substituent is necessary for aryl migration to take precedence over type A rearrangement. Recently Dauben, Spitzer, and Kellogg,[8] for reasons similar to those enumerated above, reported a study of the photochemistry of 4-methyl-4-phenylcyclohexenone (**6**); comparison of their results with those



3 **4**



5



6

---

[1] Part I: R. C. Hahn and G. W. Jones, *J. Amer. Chem. Soc.*, **93**, 4232 (1971).

[2] N.D.E.A. Predoctoral Fellow, 1966–1969.

[3] H. E. Zimmerman, R. G. Lewis, J. J. McCullough, A. Padwa, S. Staley, and M. Semmelhack, *J. Amer. Chem. Soc.*, **88**, 1965 (1966).

[4] H. E. Zimmerman and W. R. Elser, *J. Amer. Chem. Soc.*, **91**, 887 (1969), and references therein.

[5] G. Marsh, D. R. Kearns, and K. Schaffner, *J. Amer. Chem. Soc.*, **93**, 3129 (1971), and references therein.

[6] A. A. Lamola, *J. Chem. Phys.*, 47, 4810 (1967).

[7] (a) H. E. Zimmerman and R. L. Morse, *J. Amer. Chem. Soc.*, **90**, 954 (1968); (b) H. E. Zimmerman, *Angew. Chem.*, **81**, 45 (1969); *Angew. Chem., Int. Ed. Engl.*, **8**, 1 (1969).

[8] W. G. Dauben, W. A. Spitzer, and M. S. Kellogg, *J. Amer. Chem. Soc.*, **93**, 3674 (1971).