Regioselectivity in Cyclohexadienone Photochemistry. Role of Zwitterions in Type A Photochemical and Dark Rearrangements. Mechanistic and Exploratory Organic Photochemistry^{1,2}

Howard E. Zimmerman* and Robert J. Pasteris

Chemistry Department of the University of Wisconsin, Madison, Wisconsin 53706

Received May 22, 1980

The photochemistry of 3-cyano-4,4-diphenyl-2,5-cyclohexadienone was investigated to elucidate the regioselectivity of the type A rearrangement. Although, a priori, both 4-cyano-6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one and 5-cyano-6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one are possible products, only the 4-cyano regioisomer was formed in direct and sensitized irradiations. To determine if preferential formation of the bicyclic product with cyano substituted on the residual double bond excludes a zwitterionic intermediate in the photochemistry, we investigated the independent generation of the ground-state type A zwitterion. Thus, base treatment of 1-cyano-2-bromo-6,6-diphenylbicyclo[3.1.0]hexan-3-one and its 4-bromo isomer was used to generate the zwitterion. Both reactions led to regioselective formation of the 4-cyano bicyclic photoproduct. Additionally, the reaction of diiron nonacarbonyl with 1-cyano-2,4-dibromo-6,6-diphenylbicyclo[3.1.0]hexan-3-one led to the same bicyclic product. Thus the type A zwitterion leads with complete regioselectivity to that isomer of bicyclic product having the cyano group on the residual double bond, and the photochemistry is consistent with a zwitterionic pathway. The quantum yield observed in benzene was 0.67 and rose to 0.94 in methanol. The regioselectivity, however, did not change with solvent polarity. Sensitization with acetophenone in benzene proved to be a function of acetophenone concentration such that a plot of the reciprocal of quantum yield vs. acetophenone concentration was linear, indicating quenching by the acetophenone ground state. Cyclohexadiene quenching was used to obtain a rate of triplet rearrangement of $k_r = 1.3 \times 10^8$ s⁻¹, corresponding to one of the slowest type A rearrangements known, and a triplet lifetime of 5 ns.

Almost 2 decades ago we advanced mechanistic suggestions to account for the rearrangement of 4,4-disubstituted 2,5-cyclohexadienones to 6,6-disubstituted bicyclo[3.1.0]hex-3-en-2-ones in what we termed a type A rearrangement. We noted that this rearrangement could be understood as involving four basic processes: (1) triplet formation by excitation and intersystem crossing or by sensitization, (2) bond reorganization involving 3,5-bonding, (3) radiationless decay, and (4) rearrangement of the zwitterion resulting from process 3 (note Scheme I).^{3,4} We also considered mechanistic variations in which radiationless decay, then termed "electron demotion", accompanied or followed rearrangement of the bridged excited species (i.e., 2^*).³ In succeeding years the type A zwitterion 2 has proven to rationalize a very large body of 2,5-cyclohexadienone photochemistry.⁶

Closely intertwined with the type A rearrangement mechanism is the matter of regioselectivity of rearrangement expected for unsymmetrically substituted type A zwitterions and their excited states.

Relatively little information is available on the preferred regiochemistry of unsymmetrically α - and β -substituted

(4) We also pointed out that the same basic sequence of steps accounted for a large number of $n-\pi^*$ photochemical reactions. These constituted one of two categories of $n-\pi^*$ reactions. The other category of reactions, including the Norrish type I cleavage, hydrogen abstraction, and the Norrish type II reaction, led to the product geometry directly from the n- π^* excited state. More recently these mechanisms have been formulated in "Salem diagrams".⁵

(5) Salem, L. J. Am. Chem. Soc. 1974, 96, 3486-3501.

 (6) For reviews of cycloheradienone photochemistry see: (a) Kropp,
 P. J. Org. Photochem. 1967, 1, 1–90; (b) Schaffner, K. Adv. Photochem. 1966, 4, 81-112; (c) Schuster, D. I. Acc. Chem. Res. 1978, 11, 65-73.



Scheme II. Literature Argument against Zwitterion Involvement⁸



dienones. In a number of steroid and related examples the regioselectivity is enforced by ring B being fused to the dienone moiety. In several examples a 3-methyl-substituted 2,5-cyclohexadienone has been reported⁷ to rearrange

0022-3263/80/1945-4864\$01.00/0 © 1980 American Chemical Society

⁽¹⁾ This is paper 122 of our photochemical series.

⁽²⁾ For paper 121, see: Zimmerman, H. E.; Factor, R. E. J. Am. Chem. Soc. 1980, 102, 3538-3548.

^{(3) (}a) H. E. Zimmerman, 17th National Organic Symposium of the (b) (a) 11. D. Limithan, Val 14a 14a 161, and Signife Symposium of an example.
 American Chemical Society, June 1961; American Chemical Society:
 Washington, DC, 1961; Abstracts, p 31. (b) Zimmerman, H. E.; Schuster,
 D. I. J. Am. Chem. Soc. 1961, 83, 4486-4487. (c) Zimmerman, H. E.; Schuster,
 D. I. J. Am. Chem. Soc. 1962, 84, 4527-4540.





regioselectively to give the bicyclo[3.1.0]hex-3-en-2-one product having the methyl group on the residual double bond rather than on the three-membered ring, these being the two results of zwitterion rearrangement in opposite directions.

Quite recently it has been reported⁸ that with a 3-cyano group, the preferred bicyclic ketone is the one with the cyano group, again, on the residual double bond of product. This has been interpreted as providing support for our alternative mechanism in which radiationless decay accompanies rearrangement (note Scheme II). Thus it was argued that the type A zwitterion 6, if formed, would not be anticipated to afford the observed 4-cyano product 9 but rather would lead to the unobserved 5-cyano bicyclic ketone 11.

In view of the importance of the type A dienone rearrangement, we wished to study its regioselectivity in greater depth. Also, when this photochemistry was studied, it appeared strategic to investigate the regioselectivity exhibited by the type A zwitterions themselves.

With these goals in mind we proceeded to investigate the photochemistry of 3-cyano-4,4-diphenyl-2,5-cyclohexadienone (12) and also the dark generation (i.e., photochemistry without light)^{9,10} of the 1-cyano-6,6-di-

(9) (a) Zimmerman, H. E.; Döpp, D.; Huyffer, P. S. J. Am. Chem. Soc. (a) Zimmerman, H. E.; Dopp, D.; Huyner, F. S. J. Am. Chem. Soc.
 1966, 88, 5352-5353. (b) Zimmerman, H. E.; Crumrine, D. S. Ibid. 1968, 90, 5612-5614. (c) Zimmerman, H. E.; Crumrine, D. S.; Döpp, D.; Huyffer, P. S. Ibid. 1969, 91, 434-445.
 (10) Brennan, T. M.; Hill, R. K. J. Am. Chem. Soc. 1968, 90, 5614-5614.

5614-5615.





phenylbicyclo[3.1.0] type A zwitterion 13.

Results

Synthesis of the Dienone Reactant, Zwitterion Precursors, and Potential Photoproducts. The synthesis of 3-cyano-4,4-diphenylcyclohexadienone (12; note Scheme III and the Experimental Section) began with the conversion of the very hindered 2,2-diphenylcyclohexanone (14) to the Me₃Si derivative (i.e., 15) of its cyanohydrin by the general method of Evans.¹¹ The yields were good except for the final conversion of enone 18 to dienone 12. Here the use of LDA-phenylselenvl bromide was abortive due to an LDA-induced electron-transfer reduction of the very electron-deficient cyano enone (18), affording the allylic alcohol. However, DDQ was effective.

Two isomeric cyano bicyclic ketones 19 and 20 were a priori type A photoproducts. Scheme III describes their synthesis, and, again, specific details are presented in the Experimental Section. Several aspects are noteworthy. Thus, the required 3-cyanocyclopentenone (23) was not readily obtainable directly from 3-chlorocyclopentenone and cyanide ion. However, the Nesmeyanov approach,¹² in this case utilizing the 3-(trimethylammonium)cyclopentenone 22, afforded an acceptable yield of cyano enone 23. A practical conversion of 23 to the saturated cyano bicyclic ketone 24 was found in a 45-day room-temperature reaction of the cyano enone 23 with diphenyldiazomethane; elevated temperature shortened the required time but diminished the yield. In the case of the 4-cyano bicyclic ketone 20 the Agosta procedure¹³ proved both necessary and convenient. However, each run led to 10% of product and 80% of recovered reactant, and thus recycling was employed.

^{(7) (}a) Chapman, O. L.; Clardy, J. C.; McDowell, T. L.; Wright, H. E. J. Am. Chem. Soc. 1973, 95, 5086-5087. (b) Hart, H.; Rodgers, T. R. *Tetrahedron Lett.* 1969, 4845–4848. (c) Schuster, D. I.; Prahbu, K. U. J. Am. Chem. Soc. 1974, 96, 3511–3523. (d) Kropp, P. J. Tetrahedron 1965, 21, 2183–2189. (e) Dutler, H.; Ganter, C.; Ryf, H.; Utzinger, E. C.; Weinberg, K.; Schaffner, K.; Arigoni, D.; Jeger, O. Helv. Chim. Acta 1962, 45, 2646–2381.

 ⁽⁸⁾ Stille, J. K.; Rettig, T. A.; Kuemmerle, E. W., Jr. J. Org. Chem.
 1976, 41, 2950-2955.

⁽¹¹⁾ Evans, D. A.; Carroll, G. L.; Truesdale, L. K. J. Org. Chem. 1974, 39, 914-917.

^{(12) (}a) Nesmeyanov, A. N.; Rybinskaya, M. I. Dokl. Akad. Nauk SSSR 1957, 115, 315. (b) See also: Benson, W. R.; Pohland, A. E. J. Org. Chem. 1964, 29, 385-391.
(13) Agosta, W. C.; Lowrance, W. W., Jr. J. Org. Chem. 1970, 35, 951. 1951.

³⁸⁵¹⁻³⁸⁵⁶

Scheme IV describes the syntheses of the zwitterion precursors, and the Experimental Section gives complete details. The carbonyl transposition from C-2 in cyano bicyclic ketone 24 to C-3 in cyano bicyclic ketone 32 was realized by using the Trost sequence.¹⁴

One intriguing aspect of the synthesis involves the preferential formation of the less stable endo-phenylsulfenyl isomer of phenylsulfenyl ketone 28a on quenching of its conjugate base with diluted acid. Equilibration to the more stable exo-phenylsulfenyl isomer 28b occurred on KOH treatment or silica gel chromatography. Here one is dealing with the old well-known¹⁵ principle of kinetic control of protonation of delocalized carbanions and enolates, with approach of the proton donor being preferred from the less hindered side of the enolate moiety. This is illustrated in eq 1.



Exploratory Photolyses and Characterization of the Photoproducts. Both direct and m-methoxyacetophenone-sensitized irradiations of 3-cyano-4,4-diphenylcyclohexadienone (12) were carried out in 3% methanol in benzene. In the case of the sensitized runs the known (vide supra) 4-cvano bicvclic enone 20 was isolated as the major product. Additionally two further products (39, mp 90-91.5 °C, and 40, mp 138.5-140 °C) were isolated. Both elemental analysis and high-resolution mass spectra indicated that these photoproducts had incorporated methanol. The infrared spectra of the two compounds revealed the presence of a cyano moiety and a carbonyl group. The NMR spectrum of each showed an ester methoxyl peak and a methylene singlet. Additionally, in the case of the 140 °C product (i.e., 40) an AB quartet suggesting the presence of a -CHCH= moiety was observed. A corresponding absorption for the 91 °C product (i.e., 39) appeared to be obscured by aryl absorption. Finally, the ultraviolet spectrum with a maximum at 320 nm (ϵ 30000) was suggestive of a linearly conjugated system. For comparison the Ph(CH==CH)₂CN moiety is known to absorb at 307 nm (ϵ 31 600).¹⁶

This spectral information, coupled with the knowledge^{3c,17} that the 6,6-diphenylbicyclo[3.1.0]hex-3-en-2one-type compounds undergo secondary photochemistry to afford 6,6-diphenyl-3,5-hexadienoic acid derivatives, allowed assignment of the two photoproducts as the stereoisomeric methyl 3-cyano-6,6-diphenyl-3,5-hexadienoates (39 and 40). The stereochemistry was assigned on

Table I. Summary of Cyano Dienone Quantum Yield Determination

type run	solvent	additive	quantum yield ^f
direct	methanol	none	0.94 ^c
direct	benzene	none	0.67 ^c
sensitized	benzene	acetophenone ^e	0.65 ^{c,d}
quenched	methanol	piperylene ^a	0.20
quenched	benzene	piperylene ^a	0.13
quenched	methanol	cyclohexadiene ^b	0.19
quenched	benzene	cyclohexadiene ^b	0.10

^a 0.20 M. ^b 0.10 M. ^c Extrapolated to 0% conversion. ^d Extrapolated to 0% acetophenone concentration. sorbing >99% of the light. ^f Error limit of $\pm 10\%$. Ab-

the basis of ¹³C compression shifts whereby the more crowded cyano carbon or methylene carbon is shifted up-These ¹³C absorptions are included in eq 2 which field.¹⁸



also describes the photochemistry. Also included in eq 2 are the results of direct irradiation. It is noted, however, that with long irradiation times the primary bicyclic cyano enone photoproduct 20 is consumed almost as rapidly as it is formed in the direct photolyses to form secondary photoproducts 39 and 40.

Thus in the cyano dienone rearrangement, the 4-cyano bicyclic ketone 20 is formed specifically. No trace (<0.5%)of the alternative 5-cyano isomer 19 or its secondary photolysis products was detectable. The absence of the 5-cyano regioisomer 19 was not due to its destruction or due to equilibration to afford the observed 4-cyano isomer 20. This was clear from lack of equilibration of the two regioisomers in independent control runs and from the absence of methyl esters 39 and 40 in the photochemistry of 5-cvano enone 19.

Quantum Yield and Rate Studies. Direct, sensitized, and quenched quantum yields of cyano dienone 12 were determined by using the micro optical bench¹⁹ and electronic integrating actinometer²⁰ described by us earlier. For reliability, frequent checks of the actinometer using ferrioxalate²¹ were made; however, drift proved negligible. Details are given in Table III. A summary is given in Table I.

⁽¹⁴⁾ Trost, B. M.; Hiroi, K.; Hurozumi, S. J. Am. Chem. Soc. 1975, 97, 438-440.

 ^{(15) (}a) Zimmerman, H. E. J. Org. Chem. 1955, 20, 549-557. Zimmerman, H. E. J. Am. Chem. Soc. 1956, 78, 1168-1173. Zimmerman, H. E.; Mais, A. Ibid. 1959, 81, 3644-3651. Zimmerman, H. E.; Mariano, P. S. *Ibid.* **1968**, *90*, 6091–6096. (b) This is so well-known indeed that this work is often quoted without citation.^{15e} (c) Hashimoto, S.; Kogen, H.; work is often quoted without citation.^{15e} (c) Hashimoto, S.; Kogen, H.; Tomioka, D.; Koga, K. Tetrahedron Lett. **1979**, 3009-3012. Posner, G. H.; Chapdelaine, M. J.; Lentz, C. M. J. Org. Chem. **1979**, 44, 3661-3665. Corey, E. J.; Boger, D. L. Tetrahedron Lett. **1978**, 13-16. House, H. O.; Chu, C. Y.; Wilkins, J. M.; Umen, M. J. J. Org. Chem. **1975**, 40, 1460-1469. (d) Footnote 15b has precise precedent. Note: Stork, G.; Buzzolana, A.; Landesman, H.; Szmuszkoviez, J.; Tearell, R. J. Am. Chem. Soc. **1963**, 85, 207-222, footnote 14. (e) In endocyclic enols overlap control fourging evid prechaption dominates as shown by: Corey, F. J. control favoring axial protonation dominates as shown by: Corey, E. J.;

Sneen, R. A. Ibid. 1956, 78, 6296–6278.
 (16) Van Bergen, T. J.; Kellogg, R. M. J. Org. Chem. 1971, 36, 1705-1708.

⁽¹⁷⁾ Zimmerman, H. E.; Keese, R.; Nasielski, J.; Swenton, J. S. J. Am. Chem. Soc. 1966, 88, 4895-4904.

⁽¹⁸⁾ For similar effects on ¹³C chemical shifts in cis-trans isomers, see: (a) Dorman, D. E.; Jautelat, M.; Roberts, J. D. J. Org. Chem. 1971, 36, 2757–2766;
 (b) Johnson, L. F.; Jankowsky, W. C. "Carbon-13 NMR Spectra"; Wiley-Interscience: New York, 1972; Spectra No. 53, 264, and 313; (c) Reference 8.

⁽¹⁹⁾ Zimmerman, H. E. Mol. Photochem. 1971, 3, 281-292. (20) Zimmerman, H. E.; Cutler, T. P.; Fitzgerald, V. R.; Weight, T. J. Mol. Photochem. 1977, 8, 379-385.

⁽²¹⁾ Hatchard, C. G.; Parker, C. A. Proc. R. Soc. London, Ser. A 1956, 235, 518.

Regioselectivity in Cyclohexadienone Photochemistry

Table II.	Summary of	f Rate Data ^a
-----------	------------	--------------------------

solvent	quencher	$k_{q}\tau, M^{-1}$	τ, s	$k_{\rm d(tot)}, {\rm s}^{-1}$	$k_{\rm d}, {\rm s}^{-1}$	$k_{\rm r},{\rm s}^{-1}$
benzene ^b benzene ^b	piperylene cyclohexadiene	19.9 51.6	5.2 × 10 ⁻ °	1.9 × 10 ⁸	0.6×10^8	1.3×10^{8}
methanol ^c methanol ^c	piperylene cyclohexadiene	$\begin{array}{c} 13.9\\ 29.6\end{array}$	$2.7 imes 10^{-9}$	$3.7 imes 10^8$	0.2×10^8	$3.5 imes ext{ 10}^{8}$

^a Obtained from Stern-Volmer analysis of quenching data; see Experimental Section for details of individual runs. ^b $k_{diff} = 1.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$. ^c $k_{diff} = 1.1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$.²⁹



Figure 1. Dependence of the 4-cyanobicyclohexenone quantum yield on acetophenone concentration.

Several aspects of the results require comment. First, the quantum yields are very high. Second, the quantum yields were found to be solvent dependent with the efficiency enhanced in methanol compared with benzene (note Table I). Third, we note that the type A rearrangement is quenchable with modest cyclohexadiene and piperylene concentrations. This is in contrast to the inability to quench 4,4-diphenylcyclohexadienone (41) with 0.1 M naphthalene.^{22,23} Fourth, interestingly, it was found that the sensitized quantum yield was a function of acetophenone concentration. A plot of the reciprocal of quantum yield vs. acetophenone concentration proved linear, and the intercept from this plot (note Figure 1) was used to obtain the quantum yield value listed in Table I. Last, inspection of Table I reveals that the acetophenone-sensitized irradiation of the cyano dienone 12 gave the same quantum efficiency as the direct irradiation. Here dienone concentrations were sufficiently low²² to exclude singlet energy transfer from acetophenone and to ensure complete light capture (>99%) by this sensitizer but high enough to allow efficient triplet transfer. This experiment shows that the triplet, when independently generated, does react in the usual fashion and with the usual efficiency. The identity of direct and sensitized results provides strongly suggestive,^{22,24} but not infallible,²⁵ evidence that the direct irradiation rearrangement proceeds by way of a triplet. Similarly, the observation of diene quenching is characteristic of energy transfer from a triplet species.

As has been noted by us earlier,²⁶ it is excited-state rate constants, rather than quantum yields, which should be



Figure 2. Dependence of the 4-cyanobicyclohexenone quantum yield on piperylene concentration: ● denotes benzene solvent; O denotes methanol solvent.



Figure 3. Dependence of the 4-cyanobicyclohexenone quantum yield on 1,3-cyclohexadiene concentration: • denotes benzene solvent; • denotes methanol solvent.

correlated with excited-state structure and reaction mechanism. Hence, it was of interest to determine the rates of triplet rearrangement of cyano dienone 12. The Stern-Volmer plots of Figures 2 and 3 were utilized to afford the desired rate constants, the slope giving $k_q \tau$. With the assumption of a quenching rate (i.e., k_q) which is diffusion controlled,²⁷ one obtains the results summarized in Table II. Here, as in earlier studies,²⁸ cyclohexadiene proves to be a more efficient triplet quencher

⁽²²⁾ Zimmerman, H. E.; Swenton, J. S. J. Am. Chem. Soc. 1967, 89, 906-912.

^{(23) (}a) Schuster has reported $k_q\tau$ values for 4,4-diphenylcyclohexadienone in benzene at 33 °C of 0.41 for 1,3-cyclohexadiene quenching and 0.097 for piperylene quenching. (b) Schuster, D. I.; Lau, N. K. Mol. Photochem. 1969, 1, 415-432.

⁽²⁴⁾ Zimmerman, H. E.; Bender, C. O. J. Am. Chem. Soc. 1970, 92, 4366-4376.

⁽²⁵⁾ Zimmerman, H. E.; Klun, R. T. Tetrahedron 1978, 34, 1775–1803.
(26) (a) Zimmerman, H. E.; Lewin, N. J. Am. Chem. Soc. 1969, 91,
879–886. (b) Zimmerman, H. E.; Baum, A. A. Ibid. 1971, 93, 3646–3653.
(c) Zimmerman, H. E.; Werthemann, D. P.; Kamm, K. S. Ibid. 1974, 96,
439–449.

⁽²⁷⁾ Justification has been given earlier^{28a} for use of rates of diffusion as approximations to quenching rates despite the knowledge^{28a} that quenching efficiency is known to be less than unity. The argument is based on an asymptotic approach to diffusion control. The rate of quenching may be less than the rate of collision especially for very fast reactions as has also been noted by Schuster.^{28b} The error due to the approximation is generally less than threefold.

<sup>approximation is generally less than threefold.
(28) (a) Zimmerman, H. E.; Hancock, K. G. J. Am. Chem. Soc. 1968, 90, 3749–3760. (b) Schuster, D. I.; Fabian, A. C.; Kong, N. P.; Barringer, W. C.; Curran, W. V.; Sussman, D. H. Ibid. 1968, 90, 5027–5028.
(29) (a) Calvert, J. G.; Pitts, J. N. "Photochemistry"; Wiley: New Vich 1965, a 607. (b) A subset of 50. 109 Millschlar the rate of diffusion</sup>

^{(29) (}a) Calvert, J. G.; Pitts, J. N. "Photochemistry"; Wiley: New York, 1966; p 627. (b) A value of 5.0×10^9 M⁻¹ s⁻¹ for the rate of diffusion in benzene has also been measured. See: (c) Herkstroeter, W. G.; Hammond, G. S. J. Am. Chem. Soc. 1966, 88, 4769–4777; (d) Wagner, P. J.; Hammond, G. S. *Ibid.* 1966, 88, 1245–1251.

than piperylene. Interestingly, again there is a solvent dependence.

Dark Zwitterion Generation. With the photochemistry of the cyano dienone 12 in hand, we proceeded to investigate the behavior of cyano zwitterion 13 expected from the mechanism in Scheme I.

Using the approach utilized in our earlier studies,⁹ we treated the two regioisomeric α -bromo ketones **36** and **37** with potassium *tert*-butoxide (note eq 3). The cyano



zwitterion 13 was also generated from the α, α' -dibromo ketone 33 by using diiron nonacarbonyl.³⁰ In all cases



4-cyano-6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one (20) was the exclusive product; none of the isomeric 5-cyano bicyclic ketone 19 was detectable (<0.5% by high-performance LC and NMR spectroscopy). The mass balances in the monobromo ketone runs were in the range of 95% and 80% in the diiron nonacarbonyl treatment of the dibromo ketone.

In a control experiment, the base treatment of monobromo ketone 36 was run to only partial completion, and it was determined that there was no conversion to the regioisomeric bromo ketone 37. As a second control run, base treatment of enone 19 was required. This showed that the unobserved regioisomeric 5-cyano bicyclic enone 19 was stable to the *tert*-butoxide reaction conditions and would have survived if it had been formed. A third control run was made with the cyano bicyclic ketone 32 where treatment with base under the conditions used with the bromo ketones yielded no observable reaction. The purpose of this control run was to test the possibility of a mechanism not involving a zwitterionic intermediate, and this point is discussed below.

Absorption and Emission Measurements. In nonpolar solvents the $n-\pi^*$ absorption band showed a clearly defined characteristic vibrational structure with a 0–0 peak at 420 nm in cyclohexane and at 415 nm in benzene. In methanol the vibrational structure was not discernible, but a shift to shorter wavelength was noted. The triplet emission spectrum was determined in ethanol-ether at 77 K and, again, revealed a clearly defined vibrational pattern with a 1697-cm⁻¹ spacing corresponding to the ground-state





C=O stretching frequency. The 0–0 band at 440 nm defined the $n-\pi^*$ excited state as 65.0 kcal/mol (2.82 eV) above the ground state.

Discussion

Gross Reaction Mechanism. The first point we note is that the rearrangement of 3-cyano-4,4-diphenylcyclohexadienone (12) is of the usual type A variety leading to a bicyclo[3.1.0]hexenone product (i.e., 20). We also note that only one of the two possible type A products is formed (i.e., 20 but no 19).

In the case of the reaction of the two bromo bicyclic ketones 36 and 37, the same cyano bicyclic regioisomer 20 is formed to the exclusion of the a priori possible alternative 19. This provides evidence that the type A zwitterion 13 is indeed an intermediate in this dark reaction, and, secondly, this shows that the zwitterion does afford the photochemical product.

Thus one might have concerned oneself with the possibility of a "push-pull" mechanistic alternative⁹ for the dark, base-catalyzed reaction of the bromo ketones. This alternative is depicted in Scheme V. It can be seen that such a mechanism would regiospecifically³¹ afford one cyano enone isomer (e.g., 19) from one α -bromo ketone (36) and the other cyano enone isomer (e.g., 20) from the second α -bromo ketone (37). Also, treatment of the nonbrominated cyano bicyclic ketone 32 with *tert*-butoxide under the same conditions was observed not to ring open (note eq 4). This, too, indicates the role and need for a

$$O \xrightarrow{Ph} \xrightarrow{Ph} \frac{t - BuOK}{t - BuOH} NO REACTION (4)$$

32

departable bromine for fission of the 1,6-bond in the rearrangement of the bromo ketones 36 and 37. Hence the push-pull alternative seems unlikely.

Finally, the lack of interconversion of the two α -bromo ketones 36 and 37 on base treatment (vide supra) rules out

⁽³⁰⁾ Noyori, R.; Hayakawa, Y.; Takaya, H.; Murai, S.; Kobayashi, R.; Sonoda, N. J. Am. Chem. Soc. 1978, 100, 1759-1765.

^{(31) (}a) Here we use "regiospecific" and "regioselective" in the same sense as we defined stereospecific and stereoselective years ago.^{31b.c} Thus, a regiospecific reaction is one where each of two regioisomers is formed from the corresponding reactant regioisomer while a regioselective reaction is one where there is a preference for formation of one regioisomer (generally through a common intermediate) independent of which regioisomeric reactant is used. This definition differs from the original one of Hassner^{31d} but seems useful.^{31e} (b) Zimmerman, H. E.; Singer, L.; Thyagarajan, B. S. J. Am. Chem. Soc. 1959, 81, 108–116, footnote 16. (c) Eliel, E. "Stereochemistry of Carbon Compounds"; McGraw-Hill: New York, 1962; p 436. (d) Hassner, A. J. Org. Chem. 1968, 33, 2684–2691. (e) Thus, it is operationally impossible to define a reaction as giving precisely zero percent of one of two stereoisomers or regioisomers. Any definition (e.g., a less common one in the case of stereoselectivity and -specificity) of a specific reaction as one giving only one of two possible products becomes a function of both the year of the investigation, the instrument employed for analysis, and the skill of the investigator.



an equilibration of these, accounting for the regioselectivity.

The type A zwitterionic mechanism for rearrangement of the bromo ketones 36 and 37 is outlined in Scheme VI.

With the preceding evidence in mind, we conclude that the rearrangement regioselectivity of a cyano zwitterion such as 13 is the reverse of that suggested earlier.⁸

Also, we note that the formation of the same cyano bicyclic ketone 20 from the zwitterion and from the photochemistry of 3-cyano dienone 12 provides necessary and consistent, although not mandatory, evidence that the type A zwitterion is an intermediate in the photochemistry of cyano dienone 12. Some intervention of excited zwitterion is permissible.

Source of the Regioselectivity of the Type A **Zwitterion Rearrangement.** The preferential formation of that regioisomer having the cyano moiety on the product double bond in the zwitterion rearrangement needs discussion. Clearly the argument against formation of a conjugated cyano enone such as 9 (note Scheme II) or 20 in the present study must have a weakness, since it is the doubly bonded cyano regioisomer which is preferentially formed. The paradox is resolved with the realization that a species such as 10 is not involved in the reaction. This species (i.e., 10) is just a very high energy resonance structure of product 9, and drawing this does not impose a barrier to formation of 9. We note that one could argue against nature giving any of the known organic reaction products by invoking a high-energy resonance structure for each product. Thus, in the case of conversion of type A zwitterion 6 to product 9, the enolate electron density is fed toward the positive centers as the rearrangement proceeds with direct formation of product without buildup of positive charge adjacent to the cyano group.

The source of the regioselectivity is seen most readily from Hückel molecular orbital calculations, in which 46 and 47, shown in Figure 4, represent the two alternative transition states for zwitterion rearrangement. Several aspects are of interest. The simple calculations show a large difference in the energies of the two alternatives, with transition state 46 being favored. Although the calculations are of the simple Hückel variety^{32a} and include only



Figure 4. Two alternative transition states for zwitterion rearrangement.

a truncated system consisting of those orbitals whose bonding changes during the reaction, the large effects encountered reflect fundamental consequences of placement of the cyano moiety in or out of conjugation.

A second difference observed in the calculations is a higher bond order for the three-ring bond being formed in the case of the preferred transition-state 46 relative to the unfavorable transition state 47. Also, a lower bond order for the three-ring bond breaking is encountered for the favored transition state 46 compared to the less favorable alternative 47.

The calculations also reveal the source of the preference of transition state 46 over 47. We note that in zwitterion 46 negative charge is distributed between the oxygen and the cyano group in the favored transition-state 46 with the positive charge centered in the Möbius^{32b-d} five ring. Thus the cyano group assists in delocalizing the negative charge, and the interposition of the positive five ring between the two negative moieties is irrelevant. In transition-state 47 the cyano group is separated, to a first order, from the zwitterionic system and cannot assist in delocalization.

A final effect favoring transition-state 46 is relief of van der Waals repulsions between the diphenylmethyl and cyano moieties.

Quantitative Studies and Mechanistic Conclusions. The first noteworthy point is the high quantum yields encountered for the dienone rearrangement (note Table I). This high efficiency seems characteristic of the type A dienone rearrangements in general. Thus, 4,4-diphenylcyclohexadienone (41) was found to have a 0.86 efficiency,²² α -santonin has been reported as having a 0.86 quantum yield,³³ and several other dienones have quantum yields reported^{7c,34} in the range of 0.61–0.75.

Another characteristic of the type A dienone rearrangement is an exceptionally rapid triplet reaction rate. This is evidenced by the lack of quenching of the rearrangement of diphenyl dienone 41 in 0.1 M naphthalene²² and in 0.8 M piperylene. Schuster^{23b} has reported a triplet rate of 2.5×10^{10} s⁻¹ for this dienone (i.e., 41) from Stern-Volmer quenching studies using still higher concentrations of 1,3-cyclohexadiene.

In the case of the presently studied 3-cyano dienone 12 the triplet proved to be a much slower reacting species. Here k_r and k_d are both slower than those for the parent 4,4-diphenyl dienone 41. We note that the excited triplet rate of type A rearrangement for the cyano dienone is k_r = 1.3 × 10⁸ s⁻¹ compared with the 2.5 × 10¹⁰ s⁻¹ diphenyldienone rate (note Table II).

Interestingly, the rate of type A rearrangement of triplet 4-methyl-4-(trichloromethyl)cyclohexadienone (48) has

^{(32) (}a) The trends described were relatively parameter independent as long as the migrating carbon did not overlap too weakly. The results in Figure 4 are obtained with $\alpha_{\rm ory} = \beta$, $\alpha_{\rm N} = 0.5\beta$, and β (transannular) = $\pm\beta$. (b) Zimmerman, H. E. J. Am. Chem. Soc. 1966, 88, 1564–1565. (c) Zimmerman, H. E. Joid. 1966, 88, 1566–1567; (d) Zimmerman, H. E. Acc. Chem. Res. 1971, 4, 272–280.

⁽³³⁾ Schuster, D. I.; Fabian, A. C. Tetrahedron Lett. 1968, 1301-1306.
(34) (a) Patel, D. J.; Schuster, D. I. J. Am. Chem. Soc. 1968, 90, 5145-5152.
(b) Schuster, D. I.; Curran, W. V. J. Org. Chem. 1970, 35, 4192-4201.

been measured^{23b,28b,34a} as 8.9×10^8 s⁻¹. Thus it seems that dienone triplets with electron-withdrawing moieties near the β -carbon rearrange more slowly.

The rates are controlled by two energies. First, such dienones have a lower triplet energy than those without electronegative substitution. The trichloromethyl dienone 48 has^{34a,35} a 67.0-kcal/mol triplet energy which is lower by 1.9 kcal/mol than the 68.9-kcal/mol energy of the 4,4-diphenyl dienone 41. This stabilization of the excited-state reactant is a rate-inhibiting factor as encountered in some of our earlier studies.³⁶ A 1.9-kcal/mol excitedstate stabilization would inhibit the rate 25-fold, if we assume that the reaction-transition-state energy is unaffected by the change in substitution. The observed rate difference is 28-fold.

However, in the case of the cyano dienone (i.e., 12) the experimental rate inhibition on introduction of the cyano moiety is 192-fold despite a 3.9-kcal/mol starting triplet stabilization, corresponding to a 720-fold rate inhibition calculated on the assumption of no transition-state effects. Thus, here there must be a slight (3.75-fold, corresponding to 0.8 kcal/mol) stabilization of the cyano transition state compared to the parent dienone transition state due to cyano conjugation with the delocalized system. The activation energy for the cyano compound is still less favorable than that for the parent dienone.

SCF-CI calculations³⁷ reveal that the β . β -bond order for the n- π^* triplet of cyano dienone 12 is only +0.051 compared with +0.120 for the unsubstituted diphenyl dienone 41. With a more positive bond order, the rate should be enhanced. Hence we can understand a rate inhibition by the electron-withdrawing cyano moiety which diminishes the β , β -bond order. We note that the bond order is related to the energy difference discussed above rather than either individual energy.

One result requiring discussion is the decreased quantum yield and the rate diminution (note Tables I and II, respectively) on substitution of benzene for methanol as a reaction solvent. Concurrently, the rate of triplet decay (k_d) is increased by about a factor of 3 in benzene compared with that in methanol. Our calculations³⁷ show that β , β -bond order is not appreciably affected by hydrogen bonding at oxygen; this was determined by changing the electron affinity at oxygen in the calculations as would be expected if the oxygen were hydrogen bonded. However, the destabilization of the $n-\pi^*$ excited state by the polar solvent without comparable effect on the transition state is a reasonable source of the rate acceleration in methanol.

The decrease in k_d in methanol could arise from several sources. First, there could be a more efficient formation of the $n-\pi^*$ triplet coupled with a less efficient formation of π - π * triplet. This is without experimental support. A second possibility is that reversion of the zwitterion to the starting dienone is inhibited. Any such reversion contributes to a diminution of the quantum yield and leads to an operational increase in $k_{\rm d}$.

Finally, we need to discuss the unusual quantum yield dependence on acetophenone concentrations. The selfquenching of some ketone triplets at very high concentration of ketone has been observed.³⁸ Cogently, the rate of acetophenone triplet quenching by ground-state acetophenone has been reported^{38d} as 8.0×10^5 L mol⁻¹ s⁻¹, a rate too slow to account for the presently observed $3.8 \times$ 10⁸ L mol⁻¹ s⁻¹ rate for triplet quenching by the acetophenone ground state. Additionally, acetophenone has been used as a sensitizer at very high concentrations without observation of self-quenching.^{38a} Thus it appears that the cyano dienone 12 is involved presently. The most reasonable possibility is quenching of the cyano dienone triplet (12*) by ground-state acetophenone. And this ketone then is both a sensitizer and a quencher.^{38f}

Conclusion

It is seen that the type A zwitterions exhibit a marked regioselectivity which is understandable on the basis of maximization of electron delocalization. The photochemistry of the cyano dienone is remarkable in exhibiting one of the slowest type A rates of rearrangement known, a result deriving from starting excited-state stabilization and from the effect of cyano substitution in lowering the common tendency for the n- π^* excited state to undergo β,β bonding.

Throughout one is left with the conclusion that excited-state photochemistry is inherently no more complex than ground-state behavior. All that is needed is extension of our knowledge of the behavior of a broader range of electronically excited species.

Experimental Section³⁹

1-Cyano-1-(trimethylsiloxy)-2,2-diphenylcyclohexane, A mixture of 34.0 g (136 mmol) of 2,2-diphenylcyclohexanone,⁴⁰ 15.0 g (151 mmol) of trimethylsilyl cyanide,¹¹ and 1 mg of zinc iodide was heated at 100 °C for 18 h. The resulting dark oil was taken up in hot hexane, treated with Norite, filtered, and allowed to cool to give 38.7 g (110 mmol, 81%) of colorless prisms, mp 98-104 °C dec. The mother liquor was concentrated in vacuo and chromatographed on a 2.5 cm \times 50 cm silica gel column slurry packed in hexane. Elution with 1500 mL of hexane, in one fraction, gave an additional 4.5 g of Me₃SiCN adduct as a clear, colorless oil which crystallized on standing: total yield 43.2 g (124 mmol, 91%); 100-MHz NMR (CDCl₃) & 7.6-7.0 (m, 10 H, arom), 3.0-1.0 (m, 8 H, aliph), 0.0 (s, 9 H, trimethylsilyl); IR (thin film) 1505, 1460, 1270, 1150, 880 cm⁻¹ (no CN); high-resolution mass spectrum calcd for $C_{22}H_{27}NOSi m/e 349.1845$, found m/e 349.1844. Anal. Calcd for C₂₂H₂₇NOSi: C, 75.59; H, 7.79. Found: C, 75.78; H, 7.90.

1-Cyano-2.2-diphenylcyclohexanol. A solution of 38.7 g (110 mmol) of 1-cyano-1-(trimethylsiloxy)-2,2-diphenylcyclohexane in

(39) All melting points were determined by using a calibrated hot-stage apparatus. Mass spectra were obtained by using an AEI MS-902 mass spectrometer at 70 eV. Proton nuclear magnetic resonance spectra were obtained by using a JEOL MH-100 or Bruker WH-270 spectrometer. Carbon nuclear magnetic resonance spectra were obtained by using a JEOL FX-60 spectrometer. All reactions were run under an atmosphere of dry nitrogen, with magnesium sulfate being used as the drying agent. High-pressure liquid chromatography employed an LDC 254-nm UV detector which was calibrated for the relative responses of detected compounds and standards. Column chromatography was performed on silica gel (Matheson Coleman and Bell, grade 62, 60–200 mesh) packing mixed with Sylvania 2282 phosphor and slurry packed into Vycor columns such that band elution could be monitored by hand-held UV lamp.
 (40) Zaugg, H. E.; Freifelder, N.; Horrom, B. W. J. Org. Chem. 1950, 15, 1191–1196.

⁽³⁵⁾ Zimmerman, H. E.; Binkley, R. W.; McCullough, J. J.; Zimmerman, G. A. J. Am. Chem. Soc. 1967, 89, 6589-6595.

⁽³⁶⁾ Zimmerman, H. E.; Welter, T. R. J. Am. Chem. Soc. 1978, 100, 4131-4145.

⁽³⁷⁾ Zimmerman, H. E.; Pasteris, R. J. J. Org. Chem., following paper in this issue.

^{(38) (}a) Chapman, O. L.; Wampfler, G. J. Am. Chem. Soc. 1969, 91, 5390–5392. (b) Koch, T. H.; Jones, A. H. *Ibid*. **1970**, *92*, 7503–7505. (c) DeBoer, C. D.; Schlessinger, R. H. *Ibid*. **1972**, *94*, 655–656. (d) Giering, L. P. Diss. Abstr. Int. B 1975, 36, 255–256. (e) Note also the comparable, 1.6×10^5 L M⁻¹ s⁻¹, quenching rate of benzophenone reported by: Schuster, D. I.; Weil, T. M. J. Am. Chem. Soc. 1973, 95, 4091–4092. (f) The ca. tenfold lower than diffusion controlled quenching by acetophenone permits this interpretation since this means that ca. nine out of ten acetophenone triplets can collide with cyano dienone and successfully escape without quenching the cyanodienone triplet formed. Hence, sensitization can be efficient. One notes further that this mech-anism involves cyano dienone quenching without energy transfer. (g) The UV showed no ground-state complexation.

Anal. Calcd for $C_{19}H_{19}NO$: C, 82.27; H, 6.90. Found: C, 82.38; H, 6.91.

1-Cyano-6,6-diphenylcyclohexene. To an ice-cooled solution of 26.2 g (95 mmol) of 1-cyano-2,2-diphenylcyclohexanol in 100 mL of dry benzene and 100 mL of dry pyridine was slowly added a solution of 13.5 mL (190 mmol) of thionyl chloride in 30 mL of benzene. The ice bath was removed, and the mixture was stirred at room temperature for 1 h, refluxed for 1.5 h, cooled, poured onto ice, and ether extracted. The extract was washed with 10% hydrochloric acid solution and brine, dried, and concentrated in vacuo to give a cream-colored solid. Recrystallization from chloroform-hexane gave 18.8 g (72.7 mmol, 77%) of colorless prisms: mp 135–136 °C; 100-MHz NMR (CDCl₃) δ 7.4-7.1 (m, 10 H, arom), 6.87 (t, 1 H, J = 3 Hz, vinyl), 2.5–2.1 (m, 4 H, 2 CH₂), 1.7–1.3 (m, 2 H, CH₂); IR (KBr) 2200, 1615, 1490, 1445, 1420 cm⁻¹; high-resolution mass spectrum, calcd for C₁₉H₁₇N m/e 259.1355, found m/e 259.1350.

Anal. Calcd for C₁₉H₁₇N: C, 87.99; H, 6.61. Found: C, 88.11; H, 6.72.

3-Cyano-4,4-diphenylcyclohexenone. The allylic oxidation procedure of Dauben and co-workers⁴¹ was used. To an ice-cooled solution of 79.1 g (1.0 mol) of dry pyridine in 1200 mL of dry dichloromethane was added 50.0 g (0.50 mol) of chromium trioxide, the ice bath removed, and the mixture stirred for 1 h. A solution of 6.48 g (25 mmol) of 1-cyano-6,6-diphenylcyclohexene in 30 mL of dichloromethane was added in one portion, and the mixture was stirred at room temperature for 45 h. The dichloromethane solution was decanted, the residues were washed with anhydrous ether, and the combined dichloromethane and ether solutions were washed with 10% sodium hydroxide, 10% hydrochloric acid, saturated aqueous sodium bicarbonate, and brine, dried, and concentrated in vacuo to give an orange oil which was chromatographed on a 2.5 cm \times 90 cm silica gel column slurry packed in 2% ether in hexane. Collection of 1-L fractions gave the following: fractions 1-3, nil; 4-5, 380 mg (6%) of starting olefin; 6-10, 5.88 g (86%) of the cyano enone, pure by NMR. The enone was recrystallized from chloroform-hexane to give 5.21 g (76%) faintly yellow plates: mp 97-98 °C; 100-MHz NMR (CDCl₃) δ 7.6–7.1 (m, 10 H, arom), 6.73 (s, 1 H, vinyl), 2.82 (t, 2 H, J = 7Hz, CH₂), 2.40 (t, 2 H, J = 7 Hz, CH₂); IR (KBr) 2215, 1680 cm⁻¹; high-resolution mass spectrum calcd for $C_{19}H_{15}NO m/e$ 273.1154, found m/e 273.1151

Anal. Calcd for $C_{19}H_{15}NO$: C, 83.49; H, 5.53. Found: C, 83.56; H, 5.69.

3-Cyano-4,4-diphenylcyclohexadienone. A solution of 2.73 g (10 mmol) of 3-cyano-4,4-diphenylcyclohexenone, 2.72 g (12 mmol) of dichlorodicyanobenzoquinone, and 5 mg of *p*-toluene-sulfonic acid in 50 mL of benzene was refluxed for 5 days, cooled, filtered, diluted with ether, washed with 10% sodium hydroxide, 10% hydrochloric acid, saturated aqueous sodium bicarbonate, and brine, dried, and concentrated in vacuo to give a yellow solid. Recrystallization from chloroform-hexane gave 1.2 g (4.42 mmol, 44%) of the cyano dienone as faint yellow prisms: mp 192–193 °C; 100-MHz NMR (CDCl₃) δ 7.6–7.2 (m, 10 H, arom), 7.18 (d, 1 H, J = 10 Hz, vinyl), 6.90 (d, 1 H, J = 1.5 Hz, vinyl), 6.41 (dd, 1 H, J = 10, 1.5 Hz, vinyl); IR (KBr) 2212, 1680 cm⁻¹; UV (EtOH) λ_{max} 233 nm (ϵ 20500), shoulder at 286 nm (ϵ 2400); high-resolution mass spectrum calcd for C₁₉H₁₃NO m/e 271.0997, found m/e 271.0999.

Anal. Calcd for $C_{19}H_{13}NO: C, 84.11; H, 4.83$. Found: C, 84.09; H, 4.85.

Exploratory Direct Photolysis of 3-Cyano-4,4-diphenylcyclohexadienone. A solution of 200 mg (0.74 mmol) of 3-

cyano-4,4-diphenylcyclohexadienone in 250 mL of 5% methanol in photolysis grade benzene⁴² was purged with purified nitrogen⁴³ for 1.5 h prior to and during photolysis. Irradiation was performed for 30 min with a Hanovia 450-W, medium-pressure, mercury lamp through a 2-mm Pyrex filter and 4 mm of a 0.05 M sodium hydroxide solution of 0.025 M sodium vanadate (0% transmission at <330 nm) which was circulated as lamp coolant. The photolysate was concentrated in vacuo to give 227 mg of a slightly yellow solid which was chromatographed on a $2.5 \text{ cm} \times 90 \text{ cm}$ silica gel column slurry packed in hexane. Elution with hexane, monitored by a UV scanner with collection of 40-mL fractions, gave the following: fractions 1-250, nil; 251-305, 60 mg (0.22 mmol, 30%) of starting cyano dienone; 306-355, 84 mg (0.28 mmol, 37%) of methyl trans-3-cyano-6,6-diphenyl-3,5-hexadienoate; 356-450, 81 mg (0.27 mmol, 36%) of methyl cis-3-cyano-6,6-diphenyl-3,5hexadienoate.

Fractions 306–355 were recrystallized from methanol to give 62 mg of the trans ester as colorless prisms: mp 90–91.5 °C; 100-MHz NMR (CDCl₃) δ 7.6–7.0 (m, 11 H, arom and vinyl), 6.68 (d, 1 H, J = 12 Hz, vinyl), 3.70 (s, 3 H, OCH₃), 3.20 (br s, 2 H, methylene); ¹³C NMR (CDCl₃) 39.1, 52.3, 105.4, 117.4, 122.8, 128.2, 128.4, 129.1, 130.2, 138.4, 140.5, 145.1, 151.5, 169.2 ppm; IR (KBr) 2220, 1730, 1335, 1210, 1180 cm⁻¹; UV (EtOH) λ_{mar} 235 nm (ϵ 14 700), λ_{sh} 251 (10 000), λ_{max} 320 (27 800); high-resolution mass spectrum calcd for C₂₀H₁₇NO₂ m/e 303.1259, found m/e 303.1259. Anal. Calcd for C₂₀H₁₇NO₂: C, 79.18; H, 5.65. Found: C, 79.31;

H, 5.85.

Fractions 356–450 were recrystallized from methanol to give 61 mg of the cis ester as colorless prisms: mp 138.5–140 °C; 100-MHz NMR (CDCl₃) δ 7.6–7.0 (m, 10 H, arom), 6.90 (d, 1 H, J = 12 Hz, vinyl), 6.72 (d, 1 H, J = 12 Hz, vinyl), 3.78 (s, 3 H, OCH₃), 3.44 (br s, 2 H, CH₂); ¹³C NMR (CDCl₃) 34.6, 52.6, 104.7, 120.0, 120.3, 128.4, 128.8, 129.2, 130.3, 137.9, 140.8, 144.0, 152.7, 168.9 ppm; IR (KBr) 2220, 1740, 1200, 1175 cm⁻¹; UV (EtOH) λ_{max} 236 nm (ϵ 14 200), λ_{sh} 252 (10 000), λ_{max} 323 (31 800); high-resolution mass spectrum calcd for C₂₀H₁₇NO₂ m/e 303.1259, found m/e 303.1256.

Anal. Calcd for $C_{20}H_{17}NO_2$: C, 79.18; H, 5.65. Found: C, 79.04; H, 5.76.

Exploratory Sensitized Photolysis of 3-Cyano-4,4-diphenylcyclohexadienone. A solution of 500 mg (1.84 mmol) of 3-cyano-4,4-diphenylcyclohexadienone and 58 g (0.39 mol) of *m*-methoxyacetophenone in 700 mL of 3% methanol in photolysis grade benzene⁴² was purged with purified nitrogen⁴³ for 1 h and irradiated with continued purging for 2.4 h on the "Wisconsin Black Box"¹⁹ apparatus utilizing the following filter combination: cell 1, 2.0 M nickel sulfate hexahydrate in 5% sulfuric acid; cell 2, 1.0 M cobalt sulfate heptahydrate in 5% sulfuric acid; cell 3, 0.1 M cupric sulfate pentahydrate in 5% sulfuric acid. The transmission was 0% below 280 nm, 33% at 317 nm, and 0% above 350 nm. The light output was measured by a digital electronic actinometer²⁰ calibrated by ferrioxalate actinometry²¹ and indicated that the sample absorbed 4.5 mEinsteins of light.

The photolysate was concentrated in vacuo, and the *m*-methoxyacetophenone was removed via bulb to bulb distillation at 55 °C (0.005 mm) and chromatographed on a 2.5 cm × 150 cm silica gel column slurry packed in hexane. Elution with 2 L of hexane and 8.5 L of 1%, 8.5 L of 2%, and 20 L of 3% ether in hexane, monitoring with a UV scanner, and collection of 40-mL fractions gave the following: fractions 1–290, nil; 291–360, 30 mg of *m*methoxyacetophenone; 361–460, nil; 461–600, 370 mg (74%) of a (2:1 by NMR) mixture of starting cyano dienone and 4cyano-6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one; 601–710, 68 mg (12%) of methyl *trans*-3-cyano-6,6-diphenyl-3,5-hexadienoate; 711–900, 82 mg (15%) of methyl *cis*-3-cyano-6,6-diphenyl-3,5hexadienoate.

An 80-mg portion of the mixture of starting dienone and the bicyclic enone (fractions 461-600) was subjected to preparative high-pressure LC using a $60 \text{ cm} \times 0.8 \text{ cm}$ column packed with

⁽⁴¹⁾ Dauben, W. G.; Lorber, M.; Fullerton, P. S. J. Org. Chem. 1969, 34, 3587-3592.

⁽⁴²⁾ Benzene for photolysis was purified by repeated washing with acidic saturated potassium permanganate solution followed by repeated washing with concentrated sulfuric acid, water, and brine, drying over magnesium sulfate, and distillation through a 30-cm column of metal helices from CaH.

⁽⁴³⁾ Meites, L.; Meites, T. Anal. Chem. 1948, 20, 984-985.

Table III.	Photolysis of 3-Cyano-4,4-diphenylcyclohexadienone to Afford
4-Cya	no-6.6-diphenylbicyclo[3.1.0]hex-3-en-2-one Photoproduct

run	cond ^a	[additive], M	$\frac{\text{mmol of rctnt}}{(\times \ 10^2)}$	mmol of prdt (× 10 ³)	mEinsteins absd (× 10 ³)	% conv	Φ^{g}
1	A	с	10.3	10.1	19.5	9.82	0.530
2	Α	с	10.8	6.84	10.0	6.31	0.684
3	А	с	11.2	4.11	5.26	3.66	0.782
4	А	с	10.3	1.70	1.95	1.65	0.867
5	В	с	12.5	6.15	10.1	4.94	0.609
6	В	с	11.9	4.95	7.94	4.16	0.624
7	В	с	11.2	4.61	7.46	4.11	0.618
8	В	с	11.8	3.30	5.17	2.79	0.639
9	В	С	11.7	1.67	2.55	1.43	0.655
10	С	0.10^{d}	3.72	2.15	4.20	5.79	0.513
11	С	0.10^{d}	3.35	1.54	3.02	4.59	0.510
12	Ċ	0.10^{d}	3.69	1.43	2.74	3.88	0.522
13	C	0.10^{d}	3.69	1.33	2.59	3.60	0.513
14	С	0.10^{d}	3.47	0.805	1.52	2.32	0.530
15	С	0.20^{d}	3.69	1.18	2.59	3.20	0.454
16	С	0.30 ^d	3.69	1.02	2.59	2.76	0.392
17	$\mathbf{A}^{\boldsymbol{b}}$	С	11.4	5.44	7.34	4.77	0.741
18	\mathbf{A}^{b}	0.10^{e}	11.4	2.19	7.34	1.93	0.299
19	A^b	0.20 ^e	11.4	1.48	7.34	1.30	0.202
20	\mathbf{A}^{b}	0.30 ^e	11.4	1.04	7.34	0.91	0.142
21	\mathbb{B}^{b}	с	11.8	4.35	6.92	3.68	0.628
22	\mathbb{B}^{b}	0.10^{e}	11.8	1.38	6.92	1.17	0.200
23	\mathbb{B}^{b}	0.20 ^e	11.8	0.886	6.92	0.75	0.128
24	\mathbf{B}^{b}	0.40 ^e	11.8	0.484	6.92	0.41	0.070
25	A^b	с	11.1	5.33	7.20	4.80	0.740
26	A^b_{\cdot}	0.05^{f}	11.1	2.12	7.20	1.91	0.294
27	A^b	0.10^{t}	11.1	1.33	7.20	1.20	0.185
28	\mathbf{A}^{b}	0.15^{t}	11.1	0.979	7.20	0.88	0.136
29	\mathbf{B}^{b}	с	11.1	4.45	7.10	4.01	0.626
30	\mathbf{B}_{\cdot}^{b}	0.057	11.1	1.21	7.10	1.09	0.170
31	\mathbf{B}_{i}^{b}	0.10^{f}	11.1	0.706	7.10	0.64	0.099
32	\mathbf{B}^{b}	0.15^{7}	11.1	0.510	7.10	0.46	0.072

^a A, 40 mL of methanol, 313 nm; B, 40 mL of benzene, 313 nm; C, 40 mL of benzene, 334 nm. ^b No nitrogen purge prior to run. ^c None. ^d Acetophenone. ^e Piperylene. ^f 1,3-Cyclohexadiene. ^g Error limit of ±10%.

porous $10-20-\mu m$ Carbowax 400 coated silica beads.⁴⁴ Elution with 30% ether in hexane at a flow rate of 4.8 mL/min gave two peaks: band 1, retention time 15 min, 23 mg (0.085 mmol, 29%) of the bicyclic enone, pure by NMR; band 2, retention time 20 min, 54 mg (0.199 mmol, 67%) of starting dienone, pure by NMR.

The bicyclic enone was recrystallized from methanol to give colorless prisms (mp 178.5–179.5 °C) whose spectral properties were identical with those of independently prepared material (vide infra).

Summary of Quantum Yield Results for 3-Cyano-4,4-diphenylcyclohexadienone. All direct, sensitized, and quenched quantum yield determinations were performed by using a micro optical bench¹⁹ employing a Bausch and Lomb Model 33-86-79 monochromator having a 5.4-mm entrance slit and a 3.0-mm exit slit (22-nm half-width band-pass) and an Osram HBO 200-W high-pressure mercury lamp. Light output was monitored by a digital electronic actinometer²⁰ calibrated with ferrioxalate actinometry.²¹

All runs were analyzed by high-pressure LC using a 25 cm \times 0.4 cm column packed with 5–10- μ m porous silica beads⁴⁴ and eluted with 20% ether in hexane at a flow rate of 1.1 mL/min. The internal standard used was 4,4'-dimethoxybenzophenone.

All direct and sensitized runs were purged with purified nitrogen⁴³ for 1 h prior to and during each run. All runs are summarized in Table III.

3-(Trimethylammonio)cyclopent-2-en-1-one Chloride. To a solution of 19.24 mL (165 mmol) of 3-chlorocyclopent-2-en-1one⁴⁵ in 500 mL of anhydrous ether was added 100 mL of a 1.7 M solution of trimethylarnine in toluene. The mixture was stirred at room temperature for 4 days and filtered, and the solids were washed thoroughly with anhydrous ether and dried under a stream of dry nitrogen to give 25.9 g (148 mmol, 90%) of a gray powder. The powder was recrystallized from absolute ethanol to give 20.7 g (72%) of slightly colored crystals, pure by NMR. An analytical sample was prepared by recrystallization from absolute ethanol, giving colorless prisms: mp 158–160 °C dec; 100-MHz NMR (D₂O) δ 6.48 (m, 1 H, vinyl), 3.40 (s, 9 H, trimethylammonium), 2.95 (m, 2 H, CH₂), 2.60 (m, 2 H, CH₂); IR (KBr) 1705, 1685, 1630, 1200 cm⁻¹.

Anal. Calcd for C_8H_{14} NOCl: C, 54.70; H, 8.02. Found: C, 54.48; H, 7.88.

3-Cyanocyclopent-2-en-1-one. The procedure of Benson and Pohland^{12b} for the preparation of 4-cyano-3-buten-2-one was modified. Thus, 20.7 g (118 mmol) of 3-(trimethylammonio)-cyclopentenone chloride was dissolved in 100 mL of saturated aqueous ammonium chloride, the mixture was placed in a separatory funnel with 500 mL of benzene, and 7.67 g (118 mmol) of solid potassium cyanide was added. The mixture was shaken vigorously for 5 min, the phases were separated, the aqueous layer was washed with benzene, and the combined organic layer was washed with brine, dried, and concentrated in vacuo to give 12.04 g of a brown oil. Vacuum distillation gave 9.98 g (79%) of the cyanocyclopentenone as a slightly yellow oil: bp 91–92 °C (2.0 mmHg); 100-MHz NMR (CDCl₃) δ 6.78 (m, 1 H, vinyl), 2.95 (m, 2 H, CH₂); IR (thin film) 2222, 1710 cm⁻¹; high-resolution mass spectrum calcd for C₆H₅NO *m/e* 107.0371, found *m/e* 107.0372.

Anal. Calcd for C_6H_5NO : C, 67.28; H, 4.71. Found: C, 67.14; H, 4.87.

5-Cyano-6,6-diphenylbicyclo[3.1.0]hexan-2-one. A solution of 2.14 g (20 mmol) of 3-cyanocyclopentenone and 5.0 g (25 mmol) of diphenyldiazomethane in 100 mL of anhydrous ether was stirred in an acid-washed flask for 45 days at room temperature. The still-purple solution was filtered to give 4.77 g (87%) of a white crystalline solid, pure by NMR. The solid was recrystallized from methanol to give the cyano bicyclic ketone as colorless prisms: mp 170–171 °C; 100-MHz NMR (CDCl₃) δ 7.5–7.0 (m, 10 H, arom), 3.22 (s, 1 H, bridgehead), 2.6–1.8 (m, 3 H, aliph), 1.2–0.7 (m, 1 H, aliph); IR (KBr) 2235, 1730 cm⁻¹; high-resolution mass spectrum calcd for C₁₉H₁₅NO *m/e* 273.1154, found *m/e* 273.1152.

⁽⁴⁴⁾ Zimmerman, H. E.; Welter, T. R.; Tartler, D.: Bunce, R. A.; Ramsden, W. D., unpublished results.

⁽⁴⁵⁾ Clark, R. D.; Heathcock, C. H. J. Org. Chem. 1976, 41, 636-643.

Anal. Calcd for $C_{19}H_{15}NO$: C, 83.49; H, 5.53. Found: C, 83.34; H, 5.70.

exo-3-(Phenylseleno)-5-cyano-6,6-diphenylbicyclo[3.1.0]hexan-2-one. The general method of Reich et al.⁴⁶ was used. To a -78 °C solution of 6.0 mmol of lithium diisopropylamide (prepared by the addition of 4.0 mL of 1.5 M n-butyllithium in hexane to 0.92 mL of diisopropylamine in 15 mL of tetrahydrofuran) was added a solution of 1.36 g (5.0 mmol) of 5-cyano-6,6-diphenylbicyclo[3.1.0]hexan-2-one in 15 mL of tetrahydrofuran. The solution was stirred at -78 °C for 15 min, a solution of 0.96 g (6.0 mmol) of phenylselenyl chloride in 2 mL of tetrahydrofuran was added in one portion, and the mixture was allowed to warm to room temperature. Dilution with ether, washing with 2 N hydrochloric acid, water, saturated aqueous sodium bicarbonate, and brine, drying, and concentrating in vacuo gave 2.27 g of an orange foam which was crystallized twice from chloroform-hexane to give 550 mg (26%) of the phenyl selenide as colorless crystals: mp 174-175 °C; 100-MHz NMR (CDCl₃) δ 7.6-7.0 (m, 15 H, arom), 3.24 (s, 1 H, bridgehead), 3.1-2.4 (m, 3 H, CH₂ and CH); IR (KBr) 2235, 1720 cm⁻¹; high-resolution mass spectrum calcd for $C_{25}H_{19}NOSe m/e$ 429.0632, found m/e429.0622.

Anal. Calcd for $C_{25}H_{19}NOSe: C, 70.09; H, 4.47$. Found: C, 69.95; H, 4.49.

5-Cyano-6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one. The general method of Reich et al.⁴⁶ was used. To a solution of 533 mg (1.25 mmol) of exo-3-(phenylseleno)-5-cyano-6,6-diphenylbicyclo[3.1.0]hexan-2-one in 10 mL of dichloromethane and 0.20 mL (2.5 mmol) of pyridine was added a solution of 340 mg (3.0 mmol) of 30% H_2O_2 in 0.30 mL of water. The solution was stirred at room temperature for 2 h, diluted with ether, washed with saturated aqueous sodium bicarbonate, water, 2 N hydrochloric acid, and brine, dried, and concentrated in vacuo to give 310 mg of an orange solid. Recrystallization from ether gave 210 mg (62%) of the cyano enone as colorless needles: mp 120-122 °C; 100-MHz NMR (CDCl₃) & 7.6-7.0 (m, 11 H, arom and vinyl), 5.64 (d, 1 H, J = 6 Hz, vinyl), 3.56 (s, 1 H, bridgehead); IR (KBr) 2240, 1705 cm⁻¹; UV (cyclohexane) λ_{sh} 218 nm (ϵ 15 340), λ_{max} 262 (3900), 335 (239), 342 (210), 370 (165), 388 (68); high-resolution mass spectrum calcd for $C_{19}H_{13}NO m/e$ 271.0997, found m/e 271.0990.

Anal. Calcd for $C_{19}H_{13}NO$: C, 84.11; H, 4.83. Found: C, 83.91; H, 5.02.

4-(Diphenylmethoxy)-6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one. A solution of 4.80 g (50 mmol) of cyclopentene-1,4-dione⁴⁷ and 20.0 g (103 mmol) of diphenyldiazomethane in 250 mL of benzene was stirred in an acid-washed flask for 12 h at room temperature followed by refluxing for 2 h. The cooled solution was concentrated and chromatographed on a 5 cm × 70 cm silica gel column slurry packed in 10% ether in hexane. Elution with 20 L of 10% ether in hexane gave the crude bicyclic enone as a yellow solid. Recrystallization from methanol gave 13.4 g (63%) of pure enone as colorless prisms: mp 150–152 °C; 100-MHz NMR (CDCl₃) δ 7.5–7.0 (m, 20 H, arom), 5.66 (s, 1 H, CH), 4.48 (s, 1 H, vinyl), 3.10 (d, 1 H, J = 5 Hz, bridgehead), 2.74 (d, 1 H, J =5 Hz, bridgehead); IR (KBr) 1680, 1575, 1225 cm⁻¹; high-resolution mass spectrum calcd for C₃₁H₂₄O₂ m/e 428.1776, found m/e 428.1772.

Anal. Calcd for $C_{31}H_{24}O_2$: C, 86.89; H, 5.65. Found: C, 87.01; H, 5.76.

4-Methoxy-6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one. A solution of 5.0 g (11.6 mmol) of 4-(diphenylmethoxy)-6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one in 100 mL of methanol containing 5 mg of p-toluenesulfonic acid was refluxed for 24 h, cooled, and concentrated in vacuo to give a yellow oil. The oil was chromatographed on a 4.0 cm \times 100 cm silica gel column slurry packed in 5% ether in hexane. Elution with 22 L of 10% ether in hexane with collection of 1-L fractions gave the following: fractions 1 and 2, nil; 3 and 4, 2.29 g (11.6 mmol, 100%) of diphenylmethyl methyl ether (pure by NMR analysis); 5-13, nil; 14-22, 2.82 g (88%) of the title compound. Recrystallization of the enone from methanol gave 2.54 g (79%) of colorless prisms:

mp 126–127 °C; 100-MHz NMR (CDCl₃) δ 7.4–7.0 (m, 10 H, arom), 4.48 (s, 1 H, vinyl), 3.54 (s, 3 H, OCH₃), 2.95 (d, 1 H, *J* = 5.5 Hz, bridgehead), 2.76 (d, 1 H, *J* = 5.5 Hz, bridgehead); IR (KBr) 1675, 1580, 1370, 1230 cm⁻¹; UV (cyclohexane) $\lambda_{\rm max}$ 314 nm (ϵ 400), $\lambda_{\rm sh}$ 245 (8000); high-resolution mass spectrum calcd for C₁₉H₁₆O₂ *m/e* 276.1150, found *m/e* 276.1151.

Anal. Calcd for $C_{19}H_{16}O_2$: C, 82.58; H, 5.84. Found: C, 82.72; H, 5.96.

4-Cyano-6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one. The general method of Agosta¹³ was used. To a solution of 1.38 g (5.0 mmol) of 4-methoxy-6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one in 20 mL of benzene was added 16 mL (25 mmol) of 1.56 M diethylaluminum cyanide in toluene. The mixture was stirred for 48 h at room temperature, stirred with ice and 10% hydrochloric acid for 0.5 h, and ether extracted. The extract was washed with 2 N sodium hydroxide, water, and brine, dried, and concentrated in vacuo to give a dark oil which was chromatographed on a 2.5 cm \times 50 cm silica gel column slurry packed in 10% ether in hexane. Elution with 10% ether in hexane with collection of 200-mL fractions gave the following: fractions 1 and 2, nil; 3 and 4, 135 mg (10%) of the 4-cyano bicyclic enone, pure by NMR; 5-10, nil; 11-15, 1.10 g (80%) of recovered 4-methoxy bicyclic enone, pure by NMR.

Fractions 3 and 4 were recrystallized from methanol to give 82 mg of the 4-cyano bicyclic enone as yellow crystals: mp 178–179 °C; 100-MHz NMR (CDCl₃) δ 7.4–7.0 (m, 10 H, arom), 6.10 (s, 1 H, vinyl), 3.50 (d, 1 H, J = 5.5 Hz, bridgehead), 3.02 (d, 1 H, J = 5.5 Hz, bridgehead); IR (KBr) 2220, 1705 cm⁻¹; UV (cyclohexane) λ_{max} 248 nm (ϵ 5700), λ_{sh} 254 (5500), λ_{max} 292 (4400), 364 (286), 382 (313), 401 (220), 420 (60); high-resolution mass spectrum calcd for C₁₉H₁₃NO m/e 271.0997, found m/e 271.0999.

Anal. Calcd for C₁₉H₁₃NO: C, 84.11; H, 4.83. Found: C, 84.23; H, 4.82.

endo- and exo-3-(Phenylsulfenyl)-5-cyano-6,6-diphenylbicyclo[3.1.0]hexan-2-ones. The general method of Trost and Salzmann⁴⁸ was used. To a -78 °C solution of 10 mmol of lithium diisopropylamide (prepared by addition of 6.7 mL of 1.5 M nbutyllithium in hexane to 1.40 mL of diisopropylamine in 20 mL of tetrahydrofuran) was added 1.36 g (5.0 mmol) of 5-cyano-6,6-diphenylbicyclo[3.1.0]hexan-2-one in 15 mL of tetrahydrofuran. The solution was stirred at -78 °C for 30 min and added via cannula to a 0 °C solution of 2.18 g (10 mmol) of diphenyl disulfide in 15 mL of hexamethylphosphoramide, stirred at room temperature for 1 h, and partitioned between 50 mL of 2 N hydrochloric acid and 100 mL of ether. The organic layer was washed with water, saturated aqueous sodium bicarbonate, and brine, dried, and concentrated in vacuo to give 3.52 g of an orange solid. The solid was washed with anhydrous ether $(4 \times 5 \text{ mL})$ to leave 1.44 g (3.78 mmol, 75%) of a white powder which was used in subsequent reactions without further purification. NMR analysis indicated this was 95% endo-3-(phenylsulfenyl)-5cyano-6,6-diphenylbicyclo[3.1.0]hexan-2-one.

The solid underwent severe decomposition upon attempted further purification. Small amounts of pure *endo*-phenylsulfenyl ketone could be obtained, however, by repeated recrystallization from chloroform-hexane at low temperatures: mp 180–185 °C dec; 270-MHz NMR (CDCl₃) δ 7.6–7.0 (m, 15 H, arom), 3.89 (ddd, 1 H, J = 1.3, 6.1, 12.5 Hz, C-3 H), 3.45 (d, 1 H, J = 1.3 Hz, bridgehead), 3.25 (dd, 1 H, J = 12.5, 14.9 Hz, C-4 H), 2.60 (dd, 1 H, J = 6.1, 14.9 Hz, C-4 H); IR (KBr) 2215, 1735 cm⁻¹; high-resolution mass spectrum calcd for C₂₅H₁₉NOS m/e 381.1187, found m/e 381.1192.

Anal. Calcd for $C_{25}H_{19}NOS$: C, 78.71; H, 5.02. Found: C, 78.56; H, 5.05.

The exo-3-(phenylsulfenyl)-5-cyano-6,6-diphenylbicyclo-[3.1.0]hexan-2-one could be readily obtained by either washing the crude reaction mixture with cold 5% potassium hydroxide or chromatographing the initially obtained *endo*-phenylsulfenyl ketone on silica gel. The *exo*-phenylsulfenyl ketone thus obtained was crystallized from chloroform-hexane to give colorless prisms: mp 187-189 °C; 270-MHz NMR (CDCl₃) δ 7.5–7.0 (m, 15 H, arom), 3.35 (d, 1 H, J = 0.7 Hz, bridgehead), 2.99 (dd, 1 H, J = 8.8, 14.4

⁽⁴⁶⁾ Reich, H. J.; Renga, J. M.; Reich, I. L. J. Am. Chem. Soc. 1975, 97, 5434-5447.

⁽⁴⁷⁾ Rasmussen, G. H.: House, H. O.; Zaweski, E. F.; De Puy, C. H. "Organic Syntheses"; Wiley: New York, 1973; Collect. Vol. V, p 324-326.

^{(48) (}a) Trost, B. M.; Salzmann, T. N. J. Am. Chem. Soc. 1973, 95, 6840–6842. (b) Trost, B. M.; Salzmann, T. N.; Hiroi, K. Ibid. 1976, 98, 4887–4902.

Hz, C-4 H), 2.62 (dd, 1 H, J = 8.1, 14.4 Hz, C-4 H), 2.35 (ddd, 1 H, J = 0.7, 8.1, 8.8 Hz, C-3 H); IR (KBr) 2215, 1730 cm⁻¹; high-resolution mass spectrum calcd for C₂₆H₁₉NOS m/e 381.1187, found m/e 381.1188.

Anal. Calcd for C₂₅H₁₉NOS: C, 78.71; H, 5.02. Found: C, 78.78; H, 4.90.

endo-2-Hydroxy-endo-3-(phenylsulfenyl)-5-cyano-6.6-diphenylbicyclo[3.1.0] hexane. To an ice-cooled suspension of 1.44 g (3.7 mmol) of the crude endo-phenylsulfenyl ketone in 40 mL of methanol was added 140 mg (3.7 mmol) of sodium borohydride. The mixture was stirred for 45 min at 0 °C, poured into saturated aqueous ammonium chloride, and water and chloroform extracted. The extract was washed with water and brine, dried, and concentrated in vacuo to give 1.51 g of a white solid, pure by NMR. Recrystallization from chloroform-hexane gave 1.15 g (80%) of the hydroxy bicyclic compound as colorless crystals: mp 209–210 °C; 270-MHz (CDCl₃) δ 7.5–7.0 (m, 15 H, arom), 5.05 (ddd, 1 H, J = 6.1, 9.0, 9.4 Hz, C-2 H), 4.02 (ddd, 1 H, J = 5.1, 100)9.4, 11.0 Hz, C-3 H), 3.24 (d, 1 H, J = 6.1 Hz, bridgehead), 3.17 (dd, 1 H, J = 11.0, 15.4 Hz, C-4 H), 3.03 (d, 1 H, J = 9.0 Hz, C-4H); IR (KBr) 3500-3300, 2210, 1090 cm⁻¹; high-resolution mass spectrum calcd for $C_{25}H_{21}NOS m/e$ 383.1355, found m/e 383.1354.

Anal. Calcd for $C_{26}H_{21}NOS$: C, 78.29; H, 5.52. Found: C, 78.37; H, 5.74.

endo-2-Hydroxy-exo-3-(phenylsulfenyl)-5-cyano-6,6-diphenylbicyclo[3.1.0]hexane. To an ice-cooled suspension of 381 mg (1 mmol) of the exo-phenylsulfenyl ketone in 10 mL of methanol was added 38 mg (1 mmol) of sodium borohydride. The ice bath was removed, and the mixture was stirred for 2 h at room temperature, poured into saturated aqueous sodium chloride, and water and ether extracted. The extract was washed with water and brine, dried, and concentrated in vacuo to give 370 mg (0.97 mmol, 97%) of a white solid, pure by NMR. Recrystallization from methanol gave 319 mg (83%) of colorless prisms: mp 198–200 °C; 100-MHz NMR (CDCl₃) δ 7.6–7.0 (m, 1 H, arom), 4.58 (m, 1 H, C-2 H), 3.0 (d, 1 H, J = 6 Hz, bridgehead), 3.0–2.0 (m, 3 H, alkyl), 2.0 (s, 1 H, OH); IR (KBr) 3600–3300, 2215, 1070 cm⁻¹; high-resolution mass spectrum calcd for C₂₅H₂₁NOS m/e 383.1355, found m/e 383.1351.

Anal. Calcd for $\rm C_{25}H_{21}NOS:$ C, 78.29; H, 5.52. Found: C, 78.52; H, 5.82.

exo-2-Chloro-exo-3-(phenylsulfenyl)-5-cyano-6,6-diphenylbicyclo[3.1.0]hexane. To an ice-cooled solution of 95 mg (0.25 mmol) of the exo-phenylsulfenyl alcohol in 1.0 mL of benzene and 1.0 mL of pyridine was added 40 μ L (0.5 mmol) of thionyl chloride. After the mixture was stirred for 15 min, the ice bath was removed, and the solution was refluxed for 16 h, cooled, poured onto ice, and ether extracted. The extract was washed with 10% hydrochloric acid, saturated aqueous sodium bicarbonate, and brine, dried, and concentrated in vacuo to give 84 mg of an orange solid. Recrystallization from ether gave 54 mg (54%) of the chloro bicyclic compound as colorless prisms: mp 199-201 °C; 100-MHz NMR (CDCl₂) δ 7.6-6.7 (m, 10 H, arom), 4.66 (m, 1 H, C-2 H), 3.30 (s, 1 H, bridgehead), 2.8-2.4 (m, 3 H, aliph); IR (KBr) 2222 cm⁻¹; high-resolution mass spectrum calcd for C₂₅H₂₀NClS m/e 401.1005, found m/e 401.1012.

Anal. Calcd for C₂₅H₂₀NClS: C, 74.70; H, 5.06. Found: C, 74.65; H, 5.12.

endo-2-Hydroxy-exo-3-(phenylsulfenyl)-5-cyano-6,6-diphenylbicyclo[3.1.0]hexyl Methanesulfonate. An ice-cooled solution of 204 mg (0.54 mmol) of endo-2-hydroxy-exo-3-(phenylsulfenyl)-5-cyano-6,6-diphenylbicyclo[3.1.0]hexane, 113 μ L (0.81 mmol) of triethylamine, and 46 μ L (0.60 mmol) of mesyl chloride was stirred for 1 H, poured into 10 mL of 2 N hydrochloric acid, and ether extracted. The extract was washed with water, saturated aqueous sodium bicarbonate, and brine, dried, and concentrated in vacuo to give 250 mg of a white foam. Recrystallization from chloroform-hexane gave 224 mg (90%) of the mesylate as colorless prisms: mp 171-174 °C dec; 100-MHz NMR (CDCl₃) δ 7.7-6.9 (m, 15 H, arom), 5.30 (m, 1 H, C-2 H), 3.28 (d, 1 H, J = 5 Hz, bridgehead), 2.98 (s, 3 H, methylsulfonyl), 3.0-2.2 (m, 3 H, aliph); IR (KBr) 2215, 1360, 1335, 1180 cm⁻¹.

Anal. Calcd for $C_{26}H_{23}NO_3S_2$: C, 67.65; H, 5.02. Found: C, 67.62; H, 5.13.

endo-2-Hydroxy-endo-3-(phenylsulfenyl)-5-cyano-6,6-diphenylbicyclo[3.1.0]hexyl Methanesulfonate. A solution of 1.70 g (4.45 mmol) of *endo*-2-hydroxy-*endo*-3-(phenylsulfenyl)-5-cyano-6,6-diphenylbicyclo[3.1.0]hexane and 0.42 mL (5.34 mmol) of mesyl chloride in 25 mL of dry pyridine was stirred at room temperature for 12 h, poured into water, and chloroform extracted. The extract was washed with 2 N hydrochloric acid, water, and brine, dried, and concentrated to give 2.21 g of a cream-colored solid. Recrystallization from chloroform-hexane gave 1.65 g (80%) of the desired mesylate as colorless needles: mp 115–118 °C; 270-MHz NMR (CDCl₃) δ 7.6–7.0 (m, 15 H, arom), 5.83 (dd, 1 H, J = 6.3, 8.8 Hz, C-2 H), 4.20 (ddd, 1 H, J = 7.2, 8.8, 9.9 Hz, C-3 H), 3.36 (d, 1 H, J = 6.3 Hz, bridgehead), 3.01 (dd, 1 H, J = 9.9, 15.1 Hz, C-4 H); IR (KBr) 2212, 1335, 1170 cm⁻¹; high-resolution mass spectrum calcd for C₂₈H₂₃NO₃S₂ m/e 461.1107, found m/e 461.1108.

Anal. Calcd for $C_{26}H_{23}NO_3S_2$: C, 67.65; H, 5.02. Found: C, 67.71; H, 5.09.

3-(Phenylsulfenyl)-5-cyano-6,6-diphenylbicyclo[3.1.0]hex-2-ene. A solution of 3.45 g (7.5 mmol) of the endophenylsulfenyl mesylate and 1.05 mL (8.3 mmol) of diazabicyclononene in 100 mL of dry benzene was refluxed 15 h, cooled, diluted with ether, and washed with 2 N hydrochloric acid, water, saturated aqueous sodium bicarbonate, and brine, dried, and concentrated in vacuo to give 2.78 g (100%) of the vinyl sulfide as white powder, pure by NMR. Recrystallization from chloroform-hexane gave 2.48 mg (90%) of colorless needles: mp 173-174 °C; 270 MHz NMR (CDCl₃) δ 7.6-6.7 (m, 15 H, arom), 5.74 (m, 1 H, vinyl), 3.38 (dd, 1 H, J = 2.4, 2.6 Hz, bridgehead), 3.03 (dd, 1 H, J = 1.3, 17.8 Hz, C-4 H), 2.63 (ddd, 1 H, J = 2.0, 2.6, 17.8 Hz, C-4 H); IR (KBr) 2202 cm⁻¹; high-resolution mass spectrum calcd for C₂₅H₁₉NS m/e 365.1230, found m/e 365.1229.

Anal. Calcd for C₂₅H₁₉NS: C, 82.15; H, 5.24. Found: C, 82.06; H, 5.36.

1-Cyano-6,6-diphenylbicyclo[3.1.0]hexan-3-one. A suspension of 2.78 g (7.5 mmol) of 3-(phenylsulfenyl)-5-cyano-6,6diphenylbicyclo[3.1.0]hex-2-ene and 2.45 g (9.0 mmol) of mercuric chloride in 60 mL of 95% ethanol and 1 mL of concentrated hydrochloric acid was refluxed 24 h, cooled, and filtered, and the filtrate was diluted with ether and washed with saturate aqueous sodium bicarbonate. Drying and concentrating in vacuo gave 1.95 g of a slightly yellow solid which was recrystallized from methanol to give 1.82 g (89%) of the ketone as colorless prisms: mp 129–130.5 °C; 270-MHz NMR (CDCl₃) δ 7.6–7.0 (m, 10 H, arom), 3.08 (d, 1 H, J = 6.5 Hz, bridgehead), 2.95 (dt, 1 H, J = 1.1, 19.4 Hz, C-2 H), 2.86 (ddt, 1 H, J = 1.1, 6.5, 19.1 Hz, C-4 H), 2.80 (dd, 1 H, J = 0.9, 19.4 Hz, C-2 H), 2.53 (dd, 1 H, J = 1.1, 19.4 H; (KBr) 2205, 1755 cm⁻¹; high-resolution mass spectrum calcd for C₁₉H₁₅NO m/e 273.1154, found m/e 273.1144.

Anal. Calcd for $C_{19}H_{15}NO$: C, 83.49; H, 5.53. Found: C, 83.63; H, 5.64.

1-Cyano-3-acetoxy-6,6-diphenylbicyclo[3.1.0]hex-2-ene and 1-Cyano-3-acetoxy-6,6-diphenyl[3.1.0]hex-3-ene. A mixture of 546 mg (2.0 mmol) of 1-cyano-6,6-diphenylbicyclo[3.1.0]hexan-3-one, 190 mg of p-toluenesulfonic acid, and 15 mL of isopropenyl acetate was refluxed for 12 h during which time 10 mL of distillate was collected. The solution was cooled, diluted with ether, washed with saturated aqueous sodium bicarbonate, dried, and concentrated in vacuo to give a dark oil which was filtered through a short silica gel column by using 20% ether in hexane as eluent to give 451 mg (72%) of a slightly yellow solid. Recrystallization from cyclohexane gave colorless crystals which were shown by NMR analysis to be a 1:1 mixture of the isomeric enol acetates.

The enol acetate mixture was separated by preparative highpressure liquid chromatography in the recycle mode utilizing a 60 cm \times 0.8 cm column packed with 15–25-µm porous Carbowax 400 coated silica beads⁴⁴ eluted with 30% ether in hexane. The mixture exhibited a retention volume of 180–270 mL, and this portion was automatically recycled through the column. Continued elution, collecting the front and back "wings" of the band and recycling the center portion gave, after four such operations, the separated components. Results for a 50-mg portion of the mixture were 19.0 mg (pure bicyclic 3-ene by NMR) of the faster eluting component, 23 mg (pure bicyclic 2-ene by NMR) of the slower eluting component, and 5 mg of unresolved mixture. Runs of up to 200 mg were made with similar results. The faster eluting component was recrystallized from cyclohexane to give colorless prisms (mp 158–160 °C) and identified as 1-cyano-3-acetoxy-6,6-diphenylbicyclo[3.1.0]hex-3-ene on the basis of the mode of formation and upon the following data: 270-MHz NMR (CDCl₃) δ 7.6–7.0 (m, 10 H, arom), 5.72 (m, 1 H, vinyl), 3.33 (d, 1 H, J = 2.7 Hz, bridgehead), 3.25 (dd, 1 H, J = 1.6, 17.8 Hz, HCH), 2.68 (ddd, 1 H, J = 2.0, 3.1, 17.8 Hz, HCH), 1.92 (s, 3 H, CH₃); IR (KBr) 2220, 1760, 1200 cm⁻¹; high-resolution mass spectrum calcd for C₂₁H₁₇NO₂ m/e 315.1262, found m/e 315.1260.

Anal. Calcd for $C_{21}H_{17}NO_2$: C, 79.98; H, 5.44. Found: C, 79.81; H, 5.54.

The slower eluting component was recrystallized from cyclohexane to give colorless prisms (mp 158–160 °C) and was identified as 1-cyano-3-acetoxy-6,6-diphenylbicyclo[3.1.0]hex-2-ene on the basis of the following data: 270-MHz NMR (CDCl₃) δ 7.6–7.0 (m, 10 H, arom), 5.78 (t, 1 H, J = 1.8 Hz, vinyl), 3.12 (ddd, 1 H, J = 1.8, 7.9, 17.3 Hz, HCH), 3.02 (br d, 1 H, J = 7.9 Hz, bridgehead), 2.31 (ddd, 1 H, J = 0.8, 1.8, 17.3 Hz, HCH), 1.94 (s, 3 H, CH₃); IR (KBr) 2210, 1775, 1195 cm⁻¹; high-resolution mass spectrum calcd for C₂₁H₁₇NO₂ m/e 315.1262, found m/e 315.1260.

Anal. Calcd for $C_{21}H_{17}NO_2$: C, 79.98; H, 5.44. Found: C, 79.94; H, 5.53.

1-Cyano-2-bromo-6,6-diphenylbicyclo[3.1.0]hexan-3-one. The general method of Conia et al.⁴⁹ was used. To a -10 °C cooled solution of 110 mg (0.35 mmol) of 1-cyano-3-acetoxy-6,6-diphenylbicyclo[3.1.0]hex-2-ene in 5.0 mL of tetrahydrofuran was added 62 mg (0.35 mmol) of N-bromosuccinimide. The solution was stirred at -10 to 0 °C for 1.5 h, diluted with ether, washed with saturated aqueous sodium bicarbonate and water, dried, and concentrated in vacuo to give 150 mg of a yellow oil. The oil was subjected to preparative high-pressure LC using a 0.8 cm \times 50 cm column packed with 10-20-µm porous silica beads.⁴⁴ Elution with 35% ether in hexane at a flow rate of 4.8 mL/min gave two major bands: band 1, retention time 8 min, 52 mg (0.165 mmol, 47%) of recovered starting enol acetate, pure by NMR; band 2, retention time 15 min, 50 mg (0.14 mmol, 41%) of the monobromo ketone, 90% pure by NMR. Recrystallization of the monobromo ketone from chloroform-hexane gave 39 mg (32%) of colorless prisms: mp 165-167 °C dec; 270-MHz NMR (CDCl₃) δ 7.6-7.0 (m, 1 H, arom), 4.46 (d, 1 H, J = 0.7 Hz, methine), 3.30 (ddd, 1)H, J = 0.7, 6.3, 20.4 Hz, HCH), 3.29 (dd, 1 H, J = 6.3, 2.4 Hz, bridgehead), 2.57 (dd, 1 H, J = 2.4, 20.4 Hz, HCH); IR (KBr) 2222, 1760 cm⁻¹; high-resolution mass spectrum calcd for C₁₉H₁₄NOBr m/e 351.0258, found m/e 351.0260.

Anal. Calcd for $C_{19}H_{14}NOBr$: C, 64.78; H, 4.01. Found: C, 65.00; H, 4.07.

1-Cyano-4-bromo-6,6-diphenylbicyclo[3.1.0]hexan-3-one. The general method of Conia et al.⁴⁹ was used. To an ice-cooled solution of 121 mg (0.38 mmol) of 1-cvano-3-acetoxy-6,6-diphenylbicyclo[3.1.0]hex-3-ene in 5.0 mL of tetrahydrofuran was added 0.80 mg (0.45 mmol) N-bromosuccinide. The solution was stirred for 15 min, diluted with ether, washed with saturated aqueous sodium bicarbonate and water, dried, and concentrated to give 148 mg of a white foam. The material was subjected to preparative high-pressure LC using a 60 cm \times 0.8 cm column packed with 15-25-µm porous Carbowax 400 coated silica beads.⁴⁴ Elution with 30% ether in hexane at a flow rate of 4.8 mL/min gave two bands: band 1, retention time 23 min, 500 mg (0.159 mmol, 42%) of recovered starting enol acetate, pure by NMR; band 2, retention time 29 min, 70 mg (0.199 mmol, 52%) of the monobromo ketone, pure by NMR. Recrystallization of the monobromo ketone from ether-hexane gave 50 mg (37%) of prisms: mp 161-162.5 °C; 270-MHz NMR (CDCl₃) δ 7.6-7.0 (m, 10 H, arom), 4.35 (d, 1 H, J = 0.7 Hz, methine), 3.41 (br d, 1 H, J = 18.1 Hz, HCH), 3.35 (s, 1 H, bridgehead), 2.85 (d, 1 H, J =18.6 Hz, HCH); IR (KBr) 2222, 1755 cm⁻¹; high-resolution mass spectrum calcd for $C_{19}H_{14}NOBr$ m/e 351.0258, found m/e351.0256.

Anal. Calcd for $C_{19}H_{14}NOBr$: C, 64.78; H, 4.01. Found: C, 65.02; H, 4.17.

1-Cyano-2,4-dibromo-6,6-diphenylbicyclo[3.1.0]hexan-3one. To a solution of 60 mg (0.22 mmol) of 1-cyano-6,6-diphenylbicyclo[3.1.0]hexan-3-one in 2 mL of glacial acetic acid was added 0.1 mL of 48% hydrobromic acid followed by 1.0 mL of a solution of 0.25 mL of bromine in 10 mL of acetic acid. The mixture was stirred at room temperature for 3 h, diluted with benzene, washed with water and saturated aqueous sodium bicarbonate, dried, and concentrated in vacuo to give 97 mg of a red oil. Recrystallization from chloroform-hexane gave 51 mg (54%) of the dibromide as colorless prisms: mp 175–177 °C; 100-MHz NMR (CDCl₃) δ 7.6–7.0 (m, 10 H, arom), 4.60 (s, 1 H, methine), 4.46 (s, 1 H, methine), 3.65 (s, 1 H, bridgehead); IR (KBr) 2230, 1760 cm⁻¹; high-resolution mass spectrum calcd for C₁₉H₁₃NOBr₂ m/e 428.9361, found m/e 428.9365.

Anal. Calcd for C₁₉H₁₃NOBr₂: C, 52.93; H, 3.04. Found: C, 52.75; H, 3.08.

Reaction of 1-Cyano-4-bromo-6.6-diphenylbicyclo[3.1.0]hexan-3-one with Potassium tert-Butoxide. To a solution of 35 mg (0.1 mmol) of the monobromo ketone in 4.0 mL of tert-butyl alcohol and 1.0 mL of benzene was added 1.0 mL of a 0.1 M solution of potassium tert-butoxide in tert-butyl alcohol. The mixture was stirred at room temperature for 5 min, diluted with ether, washed with saturated aqueous ammonium chloride, water, and brine, dried, and concentrated in vacuo to give 28 mg of a slightly yellow solid. NMR analysis indicated that only the 4-cyano-6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one isomer was formed. The material was subjected to preparative high-pressure LC using a 50 cm \times 0.8 cm column packed with 10–20- μm porous silica beads.⁴⁴ Elution with 35% ether in hexane at a flow rate of 4.8 mL/min gave one band: retention time 11 min; 26 mg (96%) of the pure 4-cyano enone as faint yellow microcrystals; mp 178-179 °C; the mixture melting point was undepressed at 178-179 °C.

No 5-cyano-6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one (retention time 21 min) was observed by high-pressure LC. Under the conditions used, 0.1 mg of this isomer could easily be detected.

Reaction of 1-Cyano-2-bromo-6,6-diphenylbicyclo[3.1.0]hexan-3-one with Potassium tert-Butoxide. To a solution of 24 mg (0.068 mmol) of the monobromo ketone in 4.0 mL of tert-butyl alcohol and 1.0 mL of benzene was added 0.68 mL of a 0.1 M solution of potassium tert-butoxide in tert-butyl alcohol. The mixture was stirred for 5 min at room temperature, diluted with ether, washed with saturated aqueous ammonium chloride, water, and brine, dried, and concentrated in vacuo to give 20 mg of a slightly yellow solid. NMR analysis indicated that only the 4-cyano-6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one isomer was formed. The material was subjected to preparative high-pressure LC using a 50 cm \times 0.8 cm column packed with 10-20- μ m porous silica beads.⁴⁴ Elution with 35% ether in hexane at a flow rate of 4.8 mL/min gave one band: retention time 11 min; 17 mg (92%) of the pure 4-cyano enone as faint yellow microcrystals; mp 178-179 °C; the mixture melting point was undepressed at 178-179 °C.

No 5-cyano-6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one (retention time 21 min) was observed by high-pressure LC. Under the conditions used, 0.1 mg of this isomer could easily be detected.

Reaction of 1-Cyano-2,4-dibromo-6,6-diphenylbicyclo-[3.1.0]hexan-3-one with Diiron Nonacarbonyl. A solution of 43 mg (0.1 mmol) of the dibromo ketone and 43 mg (0.12 mmol) of diiron nonacarbonyl³⁰ in 2.0 mL of dry benzene was stirred for 20 h at room temperature, diluted with ether, washed with saturated aqueous sodium bicarbonate and water, dried, and concentrated in vacuo to give 30 mg of a yellow oil. NMR analysis indicated that only 4-cyano-6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one was formed. The material was subjected to preparative high-pressure LC using a 50 cm \times 0.8 cm column packed with 10-20- μ m porous silica beads.⁴⁴ Elution with 35% ether in hexane at a flow rate of 4.8 mL/min gave one band: retention time 11 min; 22 mg (80%) of the pure 4-cyano enone as faint yellow microcrystals; mp 178-179 °C; the mixture melting point was undepressed at 178-179 °C.

No 5-cyano-6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one (retention time 21 min) was observed by high-pressure LC. Under the conditions used, 0.1 mg of this isomer could easily be detected.

Control Experiment. Reaction of 1-Cyano-2-bromo-6,6diphenylbicyclo[3.1.0]hexan-3-one with a Deficiency of Potassium tert-Buroxide. To a solution of 28 mg (0.08 mmol) of the monobromo ketone in 4.0 mL of tert-butyl alcohol and 1.0

⁽⁴⁹⁾ Blanco, L.; Amice, P.; Conia, J. M. Synthesis 1976, 194-196.

mL of benzene was added 0.40 mL of a 0.1 M solution of potassium tert-butoxide in tert-butyl alcohol. The mixture was stirred for 5 min at room temperature, diluted with ether, washed with saturated aqueous ammonium chloride, water, and brine, dried, and concentrated in vacuo to give 26 mg of a yellow solid. The material was subjected to preparative high-pressure LC using a 50 cm \times 0.8 cm column packed with 10–20-µm porous silica beads.⁴⁴ Elution with 35% ether in hexane at a flow rate of 4.8 mL/min gave two bands: band 1, retention time 11 min, 13 mg (48%) of 4-cyano-6,6-diphenylbicyclo[3.1.0]hex-3-ene-2-one as faint yellow microcrystals, mp 178–179 °C; band 2, retention time 15 min, 11 mg (45%) of starting monobromo ketone. No 1-cyano-4-bromo-6,6-diphenylbicyclo[3.1.0]hexan-3-one (retention time 21 min) was observed.

Control Experiment. Treatment of 1-Cyano-6,6-diphenylbicyclo[3.1.0]hexan-3-one with Potassium tert-Butoxide. To a solution of 18 mg (0.066 mmol) of the 3-oxobicyclic compound in 4 mL of tert-butyl alcohol and 1 mL of benzene was added 0.66 mL of a 0.1 M solution of potassium tert-butoxide in tert-butyl alcohol. The mixture was stirred for 5 min at room temperature, diluted with ether, washed with saturated aqueous ammonium chloride, water, and brine, dried, and concentrated in vacuo to give 18 mg of a colorless oil. NMR analysis indicated pure starting ketone.

Control Experiment. Treatment of 5-Cyano-6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one with Potassium tert-Butoxide. To a solution of 27 mg (0.1 mmol) of the 5-cyano enone in 4.0 mL of tert-butyl alcohol and 1.0 mL of benzene was added 1.0 mL of a 0.1 M solution of potassium tert-butoxide in tert-butyl alcohol. The mixture was stirred for 5 min at room temperature, diluted with ether, washed with saturated aqueous ammonium chloride, water, and brine, dried, and concentrated in vacuo to give 27 mg of a white solid. NMR analysis indicated pure starting enone.

Emission Measurements. Phosphorescence measurements were made on an Aminco-Kiers spectrophosphorimeter equipped with a Hanovia 901C-1, 150-W, xenon arc lamp and modified with internal baffles to eliminate scatter. The spectra were obtained at 77 K in ethanol-ether (2:1) with the samples being thoroughly degassed immediately before measurements were made. The emission spectra were calibrated by use of a low-pressure mercury lamp in each run.

Acknowledgment. Support of this research by National Institutes of Health Grant GM07487, the National Science Foundation, and the U.S. Army Research Office is gratefully acknowledged. Also we acknowledge the technical assistance of Mr. Bruce Berris, an undergraduate research student, in synthetic efforts.

Registry No. 12, 75010-94-5; 14, 22612-62-0; 15, 75011-32-4; 16, 75011-33-5; 17, 75011-34-6; 18, 75011-35-7; 19, 75011-36-8; 20, 75011-37-9; 21, 53102-14-0; 22, 75011-38-0; 23, 34250-16-3; 24, 75011-39-1; 25, 930-60-9; 26, 75011-40-4; 27, 75011-41-5; 28a, 75011-42-6; 28b, 75045-13-5; endo,endo-29, 75011-43-7; endo,exo-29, 75011-44-8; endo,endo-30, 75011-45-9; endo,exo-30, 75011-46-0; 31, 75011-47-1; 32, 75011-48-2; 33, 75011-49-3; 34, 75011-50-6; 35, 75011-51-7; 36, 75011-52-8; 37, 75011-53-9; 39, 75011-54-0; 40, 75011-55-1; trimethylsilyl cyanide, 7677-24-9; diphenyldiazomethane, 833-40-9; exo-3-(phenylseleno)-5-cyano-6,6-diphenylbicyclo[3.1.0]hexan-2-one, 75011-56-2; exo-2-chloro-exo-3-(phenylsulfenyl)-5-cyano-6,6-diphenylbicyclo[3.1.0]hexane, 75011-57-3; isopropenyl acetate, 108-22-5; N-bromosuccinimide, 128-08-5.

Type A Zwitterions and Cyclohexadienone Photochemical Rearrangements. Mechanistic and Exploratory Organic Photochemistry^{1,2}

Howard E. Zimmerman* and Robert J. Pasteris

Chemistry Department of the University of Wisconsin, Madison, Wisconsin 53706

Received May 22, 1980

The photochemistry of 3-methoxy-4,4-diphenyl-2,5-cyclohexadienone was studied. The type A rearrangement proved to be regioselective with a preference for formation of 4-methoxy-6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one relative to 5-methoxy-6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one (1.4:1 in benzene). An unexpected product was 3-methoxy-4,5-diphenylphenol, a product deriving from phenyl migration; normally phenyl migration in dienones is considerably slower than the type A rearrangement. The quantum yields in benzene were $\phi = 0.27$ for the 4-methoxy bicyclic enone, $\phi = 0.19$ for the 5-methoxy bicyclic enone, and $\phi = 0.12$ for the methoxyphenol formation. Acetophenone sensitization gave the same product distribution with the same quantum efficiencies. Interestingly, in methanol the type A efficiencies increased without appreciable change in the regioselectivity, and the phenyl migration efficiency decreased. In this solvent the quantum yields were $\phi = 0.49$, $\phi = 0.30$, and $\phi = 0.069$, respectively. Rearrangement rates for the triplet excited state were obtained by a Stern-Volmer treatment using cyclohexadiene quenching. The rate for the methoxy dienone triplet undergoing the type A rearrangement was comparable to that of the parent diphenylcyclohexadienone but faster than the 3-cyano-4,4-diphenylcyclohexadienone triplet. SCF-CI calculations were performed with a truncated basis orbital set consisting of the n orbital and the π system AO's. The calculations were carried out on the parent dienone, the presently studied methoxy dienone, and the corresponding 3-cyano dienone. Triplet and singlet energies for the lowest $n-\pi^*$ and π - π * states were derived as well as the corresponding wave functions, bond orders, and electron densities. As in previous studies of the triplets, only the n- π^* state is $\beta_i\beta$ bonding while the π - π^* state tends to be $\beta_i\beta$ antibonding. For comparison purposes the type A zwitterion was generated from a series of α -bromo-, α -chloro-, and α, α' dibromo-1-methoxy-6,6-diphenylbicyclo[3.1.0]hexan-3-ones. 4-Methoxy-6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one was formed completely regioselectively, thus defining the behavior of the zwitterion. The difference between the zwitterior behavior and the photochemical regioselectivity is construed to mean that part of the β , β -bridged $n-\pi^*$ excited state undergoes bicycling to a product geometry concomitant with radiationless decay without formation of a zwitterion.

Previously we have studied the regioselectivity of both the type A cyclohexadienone photochemistry and the dark type A zwitterion rearrangement. In these studies^{1,2} we investigated the photochemistry of 3-cyano-4,4-di-