21309-20-6; *erythro*-**28**, 93-53-8; *E*-Ie, 19464-94-9; If, 59069-98-6; Ih, 77-83-8; *E*-Im, 59069-99-7; *Z*-Im, 59070-00-7; Im-d_3, 59070-01-8; ethyl 3,3-dimethyl-2-phenylglycidate, 59070-02-9; ethyl 3,3-diphenylglycidate 5449-40-1; ethyl 3,3-diphenylpyruvate 6362-64-7; ethyl (*E*)-2-methylcinnamate, 7042-33-3; ethyl (*E*)-2 methyl-3-phenylglycidate, 7141-24-4; ethyl 2-phenylacetoacetate, 5413-05-8; ethyl 2-phenylacetoacetate enol, 59070-03-0; ethyl (*E*)-2,3-diphenylglycidate, 7042-27-5; ethyl 3,3-diphenylpyruvate enol, 59070-04-1.

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Valence Photoisomerization of 1-Ethoxycarbonyl-1*H*-azepine and Its Thermal Reversion. Quantitative Aspects Including Energy Surface Relationships

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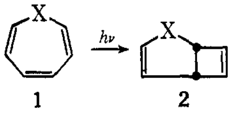
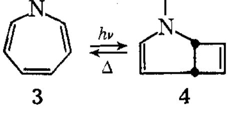
Photolysis of 1-ethoxycarbonyl-1*H*-azepine (**3**) at 325–385 nm gives quantitatively the valence isomer, 2-ethoxycarbonyl-2-azabicyclo[3.2.0]hepta-3,6-diene (**4**). The quantum yield in benzene is 0.013, virtually unchanged in other solvents including *n*-propyl bromide and with the addition of triplet quenchers. Sensitization with fluorenone, benzophenone, or valerophenone does not lead to valence isomerization. Azepine **3** acts as a quencher of the photoelimination of valerophenone ($k_q = 7.0 \times 10^9$ M^{-1} s^{-1}) and the phosphorescence of biacetyl ($k_q = 5.3 \times 10^8$ M^{-1} s^{-1}). Laser photolysis at 457.9 nm affects isomerization **3** → **4** with a quantum efficiency of 0.013. On the basis of absorption, sensitization, and quenching data for **3**, energies of low-lying excited states are estimated ($E_{S_1} = 60 \pm 1$ kcal/mol and $E_{T_1} = 55 \pm 1$ kcal/mol). Pyrolysis of **4** gives **3** in a clean, exothermic, first-order reaction at 113–143 °C in diglyme-d_{14} ($E_a = 28.7$ kcal/mol, $A = 10^{12.3}$ s^{-1}) or in hexadecane ($k = 4.60 \times 10^{-4}$ s^{-1}, 127.5 °C). A mechanism for **3** → **4** and related photochemical isomerizations is suggested, with emphasis on the proximity of ground and excited state potential surfaces at diradical or biradicaloid geometries. For cyclic triene systems, charge separation in diradical species appears to be important in facilitating photochemical ring closure and thermal back reaction.

The photochemistry of 1,3,5-cycloheptatriene (**1a**), its heterocyclic analogues, 1*H*-azepine (**1b**) and oxepin (**1c**), and their derivatives has received considerable attention.[1] A reaction of general importance is valence photoisomerization to bicyclic dienes **2**; in many cases the process is thermally reversible. We became interested in the photoisomerization of 1-ethoxycarbonyl-1*H*-azepine (**3**), since the reported[1d] behavior of this system showed promise for the storage and conversion of radiant energy (in principle, a portion of solar energy). In particular, photolysis of **3**, which absorbs light in the visible, gives **4** cleanly and photochromatically (with bleaching). Photoisomer **4** is kinetically stable but reverts to **3** in a thermal reaction which is uncatalyzed and apparently exothermic.[1d] We wish to provide quantitative details concerning this isomerization of a sort not generally available for the cyclic trienes. The data allow characterization of interconverting states and suggestions for pathways for photochemical and thermal reaction.



1 2

a, $X = CH_2$
b, $X = NR$
c, $X = O$



3 4

Results

The ultraviolet spectrum of **3**[2] displays a weak transition at 330 nm. This absorption, which is blue shifted in polar solvent and probably n,π* in character,[3] tails into the visible with onset at about 480 nm and gives **3** its orange color. Luminescence was not observed for **3**, either in benzene at room temperature or in EPA glass at 77 K. Irradiation of **3** at 325–385 nm gave **4** without the appearance of side products (>97% yield by GLC and NMR). Quantum yields for isomerization as a function of solvent and the presence of additives are shown in Table I. Notably, the photolysis was not appreciably altered by (1) moderate concentrations of potential

Table I. Quantum Yields for Photoisomerization 3 → 4

[3]	Solvent	Additives (M)	ϕ^a
0.08	Cyclohexane		0.010
0.09	Diglyme[b]		0.013
0.10	Benzene		0.013
0.03	*n*-Propyl bromide		0.013
0.08	Benzene	COT[c] (0.11)	0.014
0.10	Benzene	Diene[d] (0.02–0.08)	0.012
0.10	Benzene	Fluorenone[e] (0.9)	<0.003[g]
0.09	Benzene	Benzophenone[f] (1.0)	<0.003[g]
0.007	Benzene	Valerophenone[f] (0.4)	<0.003[g]
0.03	Benzene	DMAC[h] (0.08)	0.010[i]

[a] Rayonet reaction (355 ± 30 nm), 30 ± 1 °C, valerophenone actinometer (ref 4), estimated error, ±15%. [b] Bis(2-methoxyethyl) ether. [c] Cyclooctatetraene. [d] 2,4-Dimethyl-2,5-hexadiene. [e] Sensitizer absorbed >88% of light. [f] Sensitizer absorbed >75% of light. [g] Upper limit corrected for azepine absorption. [h] Dimethyl acetylenedicarboxylate. [i] Some light absorption by DMAC.

quenchers of excited triplets, 2,5-dimethyl-2,4-hexadiene and cyclooctatetraene, (2) a heavy atom[5] reagent, *n*-propyl bromide, as solvent, or (3) the addition of dimethyl acetylenedicarboxylate (DMAC), a good dipolarophile.[6]

In experiments where photosensitizers, benzophenone (E_T = 69 kcal/mol), fluorenone (E_T = 53 kcal/mol), and valerophenone, absorbed most of the light, photoisomerization of **3** was negligible. That the excited triplet of **3** could in fact be produced was inferred from experiments in which the photoelimination of valerophenone to acetophenone[7] was quenched. Measurement of ϕ_0/ϕ at concentrations of **3** between 4.5 and 8.2×10^{-3} M gave $k_q\tau = 56 \pm 8\ M^{-1}$, from which the quenching constant, $k_q = 7.0 \times 10^9\ M^{-1}\ s^{-1}$, could be calculated assuming τ (valerophenone) = $8.0 \times 10^{-9}\ M^{-1}$ s.[8] For comparison, the estimated rate constant for diffusion controlled quenching, according to the modified Debye equation,[9] in benzene at 30 °C is $1.8 \times 10^{10}\ M^{-1}\ s^{-1}$, and the "upper limit" quenching constant for dienes in benzene (25 °C) has been determined in several studies to be $5 \times 10^9\ M^{-1}\ s^{-1}$.[9] Quenching of the phosphorescence of biacetyl with $1.0–4.0 \times 10^{-5}$ M azepine was observed at room temperature. From the plot of ϕ_0/ϕ vs. [3], $k_q\tau = 2.3 \pm 0.5 \times 10^5\ M^{-1}$ was obtained, from which $k_q = 5.2 \times 10^8\ M^{-1}\ s^{-1}$ could be calculated assuming τ (biacetyl) = 4.6×10^{-4} s.[10]

Sealed ampule pyrolysis of **4** proceeded nearly quantitatively in solvents at temperatures above 100 °C. Appearance of **3** (NMR analysis) was smoothly first order over 2 half-lives. Kinetics data are shown in Table II along with activation parameters for pyrolysis in diglyme-d_{14}. The results are in good agreement with the approximate rate data for pyrolysis of neat **4** reported by Paquette and Barrett[1d] from which k (**4** → **3**, 126.5 °C) = $6.6 \times 10^{-4}\ s^{-1}$ may be calculated.

The photoisomerization **3** → **4** could be carried out in direct sunlight and with use of an argon ion laser. The quantum yield for isomerization at 457.9 nm in benzene was 0.013. The valence isomers could be "cycled". A sealed Pyrex tube containing **3** and **4** in diglyme-d_{14} was alternately irradiated (sunlight or near uv) and pyrolyzed (generally 130 °C). The isomerizations were followed to high conversion by NMR (benzene internal standard). Although the photochemical step was extraordinarily clean, the back reaction built up a small amount of by-product (dimer[11] or polymer), such that after ten passes material balance was about 50%.

Table II. Kinetics of Thermally Induced Isomerization 4 → 3

Solvent	Temp, °C	k, $10^4\ s^{-1}$	
Diglyme-d_{14}	112.5	1.45 ± 0.06	
	122.5	3.44 ± 0.15	
	127.5	5.34 ± 0.05	E_a = 28.7 kcal/mol
	133.0	8.21 ± 0.58	$A = 10^{12.3}\ s^{-1}$
	142.5	19.30 ± 0.11	
Hexadecane	127.5	4.60 ± 0.44	

Discussion

The failure of dienes, 2,4-dimethyl-2,5-hexadiene (E_T < 58 kcal/mol[12]), a well-known efficient quencher of reasonably long-lived excited triplets,[9] and COT, for which a very low triplet energy has been calculated,[13] to alter the photolysis of **3** implicates a reactive singlet state for valence isomerization. The sensitization data, in which common energy transfer agents representing a range of triplet excitation energies (E_T = 53–73 kcal/mol[14]) are ineffective, confirm that a singlet state (probably of n,π* character) is responsible for formation of **4**. The quenching of valerophenone photoelimination at a rate near the diffusion limit further establishes that a triplet state of **3** is accessible but unreactive. It is not certain that this quenching of valerophenone photoelimination by **3** is of the classical energy transfer sort in view of the effective charge transfer mechanism suggested for quenching by tertiary amines.[15] However, **3** quenches valerophenone triplet at a rate more than twice that of the amines ($k_q = 3 \times 10^9\ M^{-1}\ s^{-1}$), yet because of the substitution pattern, **3** should be a less effective electron (charge) donor. Accepting the energy transfer mechanism for photoelimination quenching provides one reference point for the triplet energy of **3** (E_T < 72 kcal/mol).

The phosphorescence of biacetyl is quenched by **3** at a rate short of diffusion control. This quenching might also have energy or charge[10] transfer components, but it is clear that energy transfer from biacetyl to a triplet level of **3** *well below* that of biacetyl (E_T = 55–56 kcal/mol[16]) is not important.[17] The n,π* absorption for **3** (λ_{max} 330 nm, tailing past 450 nm) and the success of laser photolysis at 458 nm (61 kcal/einstein), a wavelength which must be very close to the 0–0 transition, narrow the acceptable range for the energy of S_1. Values of E_{S_1} = 60 ± 1 and E_{T_1} = 55 ± 1 kcal/mol would be consistent with the data and allow for a reasonable n,π* singlet–triplet separation.

Interestingly, the existence of a very low-lying triplet (e.g., E_T < 50 kcal/mol), analogous to "aromatic" species (π,π* triplets) predicted for cyclic polyenes having formally 4*N* cyclic electronic arrays which enjoy resonance stabilization,[13] or analogous to triplet **1a** (E_T = 47 kcal/mol[1c]) appears unlikely for **3**. On the other hand it is probable that the π,π* triplet level lies slightly below 60 kcal/mol if **3** be dienelike.[12] The excited state model then for the heterocyclic triene is one of closely spaced singlet n,π* and triplet n,π* and π,π* states in the region of 55–60 kcal/mol.[18]

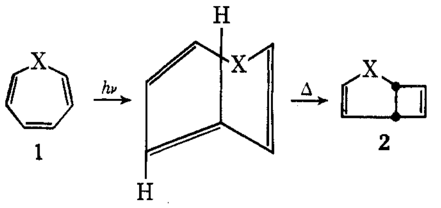
Data for **3** complete an excited state structure–reactivity pattern (Table III) for several cyclic polyene systems which have been the object of comparison in numerous studies.[20] Excited singlets in the series are uniformly reactive whereas triplets do not bring about valence isomerization.[24] The latter is noteworthy in view of the established reactivity under sensitization conditions of diverse seven- and eight-membered conjugated cyclic dienes and trienes such as 1,3-cyclooctadiene,[25] cyclohepta-3,5-dien-1-one,[26] a derivative of 2-aza-1,3-cycloheptadiene,[27] and including cycloocta-2,4,6-trien-1-one[28] (where the reactive state is most likely a triplet for direct irradiation). A mechanism considered for valence isomerization in each case involves cis–trans isomerization via the excited triplet to a strained ring system (with formally one trans double bond), which ring closes to bicyclic product in a symmetry unrestricted thermal reaction. Such a course for

Table III. Photolysis and Pyrolysis Characteristics for Selected Reversible Valence Isomerizations [a]

Cyclic polyene $\underset{\Delta}{\overset{h\nu}{\rightleftarrows}}$	Bicyclic diene	Direct irradiation	Sensitized irradiation	Ref	E_a, kcal/mol[d]	Ref
1a	2a	X	0	1a,c	39.5	21
1c	2c	X	0	1h		
3	4	X	0	This work	28.7	This work
COT[b]	BOT[c]	X	0	22	18.7	23

[a] X = isomerization of polyene observed; 0 = isomerization of polyene unobserved. [b] 1,3,5,7-Cyclooctatetraene. [c] Bicyclo[4.2.0]-octa-2,4,7-triene. [d] Activation parameters for thermal back reaction. Log A values for 2a, 4, and BOT are 14, 12.3, and 12.0, respectively.

trienes 1 is shown below in which 5 is one of several possible geometric photoisomers of 1. In two of the previous studies,[25,28] the intermediate analogous to 5 has been either isolated or trapped. The failure of triplets of 1 to give bicyclic product almost certainly reflects the relatively more severe restrictions due to bond angle strain in 5 compared to the other twisted cyclopolyenes (molecular models show this impressively). Triplet COT may indeed reach a configuration analogous to 5, but the overall result is formation of semibullvalene.[22c]

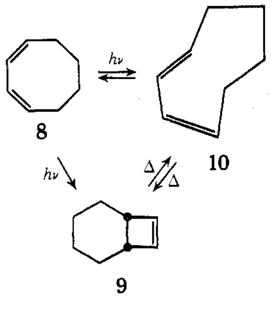


1 5 2

a, X = CH_2
b, X = O
c, X = NR

Excited singlets of 1 may give intermediates 5 prior to valence isomerization. Indeed there is direct evidence that 1,3,5-cyclooctatriene (6),[29] 1,2,4,7-tetraphenylcyclooctatetraene (7),[30] and 1,3-cyclooctadiene (8)[31] give geometric isomers on direct irradiation. The isomers of 6 and 8 may lead to valence isomeric bicyclic polyenes, while the isomer of 7 may be responsible for formation of diphenylacetylene and *p*-terphenyl (via a bicyclic triene).[30b] However, Nebe and Fonken have shown that 8 gives 9 under conditions where geometric isomer 10 is stable. In addition, thermal reversion to 7 from its geometric photoisomer is "quantitative",[30a] meaning that valence photoisomerization of 7 by way of the geometric isomer is extremely inefficient if not absent.

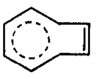
The point here is that in the singlet manifold for the cyclic dienes and trienes, there exists a path for ring closure to a bicyclic valence isomer which does not require formation of a *geometric* isomer. For the cyclic polyene triplets, valence isomerization proceeds through prior cis–trans isomerization and thermal ring closure, but only where the geometric isomer is accessible (not the case for trienes 1 on geometric grounds) and reactive enough to give bicyclic product under photolysis conditions (marginally the case for 8[31]).[32] After examination of the thermal surface for 4 → 3, we will return to the mechanism of singlet valence isomerization of 3.



8 10 9

Circumstantial arguments may be brought against two mechanisms for the thermal isomerization 4 → 3. The first mechanism involves formation of 5 via conrotatory ring opening of 4, following the suggestion of Baldwin and Kaplan[33] in their study of ring openings of bicyclic dienes. Such a mechanism is apparent in the thermal degenerate rearrangement which accompanies valence isomerization of deuterium labeled bicyclo[4.2.0]octa-2,7-diene[34] and in the pyrolytic ring opening of 9.[35] The evidence for cis–trans isomers appears again for the more flexible ring systems, in fact those cases where the strained geometric isomers are available photochemically from the all-cis cyclic polyenes.[25,29,31] The relatively low barriers observed for ring opening of the seven-membered bicyclic dienes (see activation parameters, Table III, especially 4 → 3) do not support a general mechanism involving a cis,trans,cis intermediate. That 5 would be prohibitively strained is revealed in the sizable (24.1 kcal/mol) strain energy estimated for marginally accessible 10.[36]

Thermal disrotatory ring opening of 4 may give 3 directly in a concerted process. It is apparent from the magnitude of the activation energy for valence isomerization (Table III) that BOT enjoys significant six-electron transition state stabilization (11) (for disrotatory opening, a 6e Huckel[37] aromatic[38] system) and suffers little from four-electron destabilization such as in 12 (a 4e Huckel, antiaromatic transition state).[39] Ring opening of 4 could likewise benefit from delocalization as in 13, to the extent that the lone pair on nitrogen could contribute to a pyrrolelike aromatic sextet.[40] However, the heteroatom substituent effect appears to be more general and manifest in accelerations of thermal disrotatory ring openings of fused cyclobutenes in which a stabilizing six-electron transition state cyclic array is not available. For example, 14 is thermally stable, while 15 ring opens readily.[41] Likewise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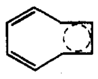
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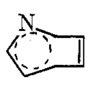

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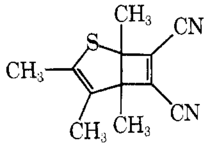

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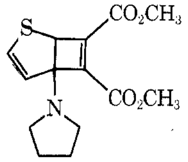

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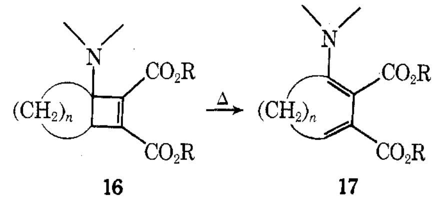
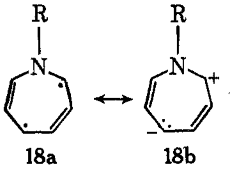


16 17

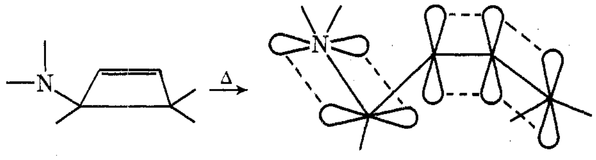
cycloadducts **16** of dimethyl acetylenedicarboxylate and cyclic enamines are generally unstable even near room temperature with respect to ring opening to **17**.[42]

We prefer a mechanism for the thermal isomerization **4** → **3** involving a nonsynchronous ring opening in which all-cis **3** emerges following motions which are overall disrotatory but where π bond development in **3** lags bond breaking in **4** early along the reaction coordinate. In the extreme, diradical **18** (geometry unspecified) would be important. Orbital overlap for such a species (from **4**, **15**, or **16**) as in **19** would be involved. Structures **18** and **19** could correspond to transition states or to intermediates[36] (secondary minima on the ground state potential surface, vide infra), the important point being that the central cyclobutene bond is essentially broken.

Diradical **18** may well have more complicated electronics than that associated with canonical form **18a**. The latter would be substituent stabilized relative to the analogous species for **2a** by an amount associated with the degree to which the carboxamido group (RCONR′–) stabilizes a radical center. This value is unknown but may be approximated by the effect of the acyloxy (RCO_2–) substituent on C–H bond dissociation energies ($\Delta BDE < 1$ kcal/mol).[43] The reduction in activation energy for **4** vs. **2a** (11 kcal/mol) is inconsistent with this kind of transition state stabilization. An alternative view recognizes the extent to which the odd electron centers in **18** interact with adjacent polarizing fragments (e.g., **19**). Respecting the electron releasing ability of nitrogen, contributing structures of the type **18b** gain importance; i.e., the singlet diradical wave function has some ionic character.[44] In the extreme, **18** would be a discrete zwitterion as suggested by Criegee and coworkers[45] for ring opening of highly polarized cyclobutenes.



18a **18b**



19

Our analysis respects the basic similarity between isomerizations **2** → **1** and the disrotatory cyclobutene → 1,3-butadiene ring opening, a reaction restricted by orbital topology in the ground state.[37,38] The important relationships between ground and excited state potential surfaces for systems which involve formal surface crossings have been known for some time.[46] We wish to emphasize the linked dependence between photochemical and thermal reactivities for these systems and the effect of substituents thereon. A proposed energy surface scheme for the **3**,**4** couple is shown in Figure 1. (The heat of reaction **4** → **3** has been measured by differential scanning calorimetry.[47])

The scheme submits to the following considerations. (1) Isomerization **3** → **4** is a G-type photochemical reaction[48] in which adiabatic formation of the excited state of product is energetically prohibited[49] and dissociation into fragments is not important. (2) The similarity with cyclobutene ring opening requires that the ground state isomerization **4** → **3** be "forbidden" involving at some point along the reaction coordinate a formal HOMO–LUMO orbital crossing.[50] (3) The orbital crossing or avoided crossing[51] provides an orbitally degenerate (diradical) ground state in proximity with a minimum in the excited singlet manifold, radiationless transition between which is facilitated.[52] (4) The minimum in the triplet surface (not shown) will occur at a loose geometry (flexible somewhat flattened ring) resembling more the boatlike ground state of **3**, whereas the minimum or funnel in the excited singlet surface will assume a tight geometry (more folded or "pinched", less flexible ring) resembling the ground state of **4** to a degree related to the extent of charge separation (zwitterionic character[44]) (vide infra) at the diradical geometry.[52] (5) Decay from S_1 proceeds with little or no activation (no accompanying fluorescence) by way of mixing with the upper, "double excited" singlet (S_n), the state of intended crossing with the ground configuration.[53]

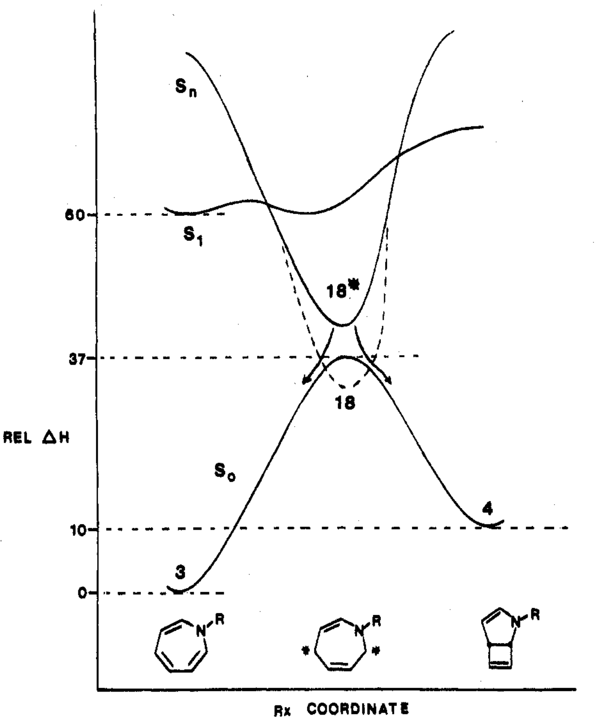
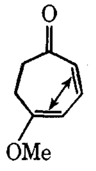
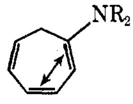


Figure 1. Potential energy surfaces for photochemical and thermal interconversions of **3** and **4**, $\Delta H^{\ddagger}$ (**4** → **3**, 128 °C) = 27 kcal/mol.

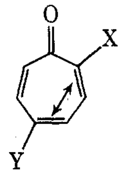
The substituent effect on reactivity in the cyclic diene and triene series, which we wish to relate to the energy surface scheme, is modest for **3**,**4** (i.e., moderately efficient formation of an energy-rich product coupled with a fairly rapid thermal back reaction). The effect is more pronounced in the facile photochemical–thermal interconversions of **20**[1b]–**22** and their valence isomers (modes of ring closure as shown). For example, the relative quantum efficiency for isomerization of **21** is 50 000 times that of the parent cycloheptatriene.[54] Likewise, efficient photoisomerization of **22** (directed as shown) is coupled with an extremely rapid thermal back reaction of the valence isomer (at or below room temperature) in cases where X = electron-donating and Y = electron-withdrawing substituents.[55] Other similar directive substituent effects have been noted for tropones[56] and cycloheptatrienes.[57]



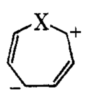
20



21



22



23

Although the importance of a substituent stabilized polar state (e.g., **23**) in these valence photoisomerizations has been recognized,[1b,57] the linked dependence of the thermal reversion has not been noted and the driving force has been incompletely understood. (For example, Herndon[58] has pointed out that electron distribution in the *lowest vertical* excited state[59] does not uniformly correlate with modes of ring closure for substituted tropones.) We suggest that it is substituent control of the relative positioning of the ground and *upper* excited state surfaces which is responsible for the variance in photothermal reactivity in these isomerizations. "Push–pull" substitution serves to greatly stabilize the upper doubly excited configuration (S_x) at the diradical[44] or biradicaloid[60] geometry. Correspondingly, the ground surface is stabilized through configuration interaction[61] (mixing with the upper surface) which is quite large at the transition state (at the point of lowest total bond order, the diradical geometry). This admixing of ground and doubly excited configurations assures efficient radiationless decay to a point on the ground surface which is near product geometry.[62] For isomerization systems involving avoided crossings, substituent control of dipolar character and the positioning of minima for excited surfaces should be quite general.[63]

The extent of polarization in the transition state (ground surface) diradical **18** is uncertain. However, development of *substantial* charge in this species (predominance of canonical form **18b**) is unlikely since a solvent effect on the rate of the thermal back reaction is absent. In addition, it appears improbable that the doubly excited or zwitterionic state (**18***) has become the ground state of the system at the diradical geometry.[64,65] With a good dipolarophile (DMAC) in photochemical experiments with **3**, trapping of such an intermediate would be possible but is unobserved.[66] Whereas the substituent polarizing influence on the rate of ring opening of **4** is predictably[39a] intermediate, the influence on **15** and **16** is quite large,[67] implicating a high degree of charge separation (configuration interaction) for the ground surface. In cases where a more polarizing substitution pattern is present, formation and partitioning of a ground state diradical–zwitterion could be important (note dashed line in Figure 1).

Experimental Section

General. 1-Ethoxycarbonyl-1*H*-azepine (**3**)[2] was photolyzed in acetonitrile on a preparative scale (Hanovia immersion apparatus) to give **4**, following generally the procedure of Paquette and Barrett.[1d]

Benzene, cyclohexane, and *n*-propyl bromide were purified for use in photolysis by washing with (1) sulfuric acid, (2) aqueous $NaHCO_3$, and (3) distilled water followed by distillation from P_2O_5 or sodium. Valerophenone (Aldrich) was distilled under reduced pressure. Biacetyl was purified by spinning band distillation (bp 87–88 °C). Diglyme was distilled over sodium. Cyclooctatetraene, 2,4-dimethyl-2,5-hexadiene, fluorenone, and dimethyl acetylenedicarboxylate were commercial reagent grade materials used as received.

Varian 920 (thermal conductivity detector) and 1400 (flame ionization detector) instruments were used for analytical GLC. Columns employed were (A) 5 ft × 0.25 in., 3% SE-30 on 100/120 Varaport 30 and (B) 8 ft × 0.125 in., 3% FFAP on Chromosorb W.

Quantum Yields. Solution samples in 15-mm stoppered cylindrical Pyrex tubes were irradiated in a Rayonet chamber reactor (Model RPR 204) equipped with RUL 3500A lamps and a merry-go-round accessory (Model MGR 100) (Southern New England Ultraviolet Co.). Samples were purged with nitrogen prior to irradiation. Solutions of **3** in the appropriate solvents (with additives) were irradiated in parallel with valerophenone (0.4 M in benzene) which served as actinometer and for which a quantum yield of production of acetophenone of 0.33[4] was assumed. Concentrations for all parallel irradiation samples were employed which ensured complete absorption (measured absorbance >1 at 0.1 path maximum) over the range of lamp emission (325–385 nm). Samples were analyzed by GLC for the appearance of **4** (column A, 100 °C, vs. **3**) and acetophenone (column B, 150 °C, vs. dodecane internal standard). Quantum yields are averages of at least two runs at low conversions of valerophenone (~15%) and **3** (5–10%). Statistical analysis of area ratios for **4** (area from cut out and weigh procedure) and acetophenone (area from disk integration) in replicate runs indicated a precision of ±15%.

Quenching of Valerophenone Photoelimination. The appearance of acetophenone from valerophenone was monitored as previously indicated for samples of valerophenone in benzene with increasing concentrations of **3** ($4.5–8.2 \times 10^{-3}$ M). Relative amounts of acetophenone formed, obtained with good precision (±5%), were used for ϕ_0/ϕ. Values were corrected for competitive absorption by **3** by computing relative absorbances at several wavelengths in the region of lamp emission. This correction became significant at higher concentrations of **3**, and at lower concentrations, values of ϕ_0/ϕ were within experimental error of 1.0; therefore, quenching behavior was assessed only over a limited range.

Luminescence Experiments and Biacetyl Phosphorescence Quenching. Using an Hitachi Model MFP fluorescence spectrophotometer, emission from **3** was undetectable for samples at room temperature (0.02 M in benzene) and at 77 K (EPA glass, 0.001 M). The phosphorescence emission of biacetyl in benzene (λ_{max} 522 nm) at room temperature was monitored as a function of [**3**]. Samples were degassed through several freeze-thaw cycles on a vacuum line. Relative intensities at the emission maximum gave ϕ_0/ϕ. The fluorescence of biacetyl was not quenched with the addition of **3**.

Pyrolysis Experiments. Samples of **4** in diglyme-d_{14} or hexadecane (with benzene internal standard) were degassed in cleaned medium wall Pyrex NMR tubes (Wilmad Co.). Sealed ampules were pyrolyzed in an insulated oil bath, thermostated using a Therm-o-watch (Instruments for Research and Industry) and a calibrated ASTM thermometer. Temperature fluctuation was <0.5 °C. Ampules were quenched and analyzed by NMR. Formation of **3** was followed by the appearance of a multiplet at δ 5.58 (vinyl C–H), and disappearance of **4** was monitored with reference to signals at δ 4.9 and 5.2 (multiplets, C_1 and C_4[1d]). In experiments where benzene signal integration was used as an internal standard, a material balance for isomerization of >95% was obtained. Rate constants were calculated from the integrated first-order rate equation and errors are average deviations for at least four points at each temperature.

Laser Photolysis of 3. Samples of **3**, 0.1 M in benzene, were irradiated with an argon ion laser (Spectra-Physics, Model 164). The emission at 457.9 nm (rated at 250 mW) was focused on the optically flat circular window of a standard 5-cm Pyrex cell containing sample. Beam intensity was checked by irradiation of a 10-cm cell containing potassium ferrioxalate[68] actinometer solution. The quantum yield for appearance of Fe(II) was assumed to be 0.95. Concentrations of sample and actinometer solutions were employed which ensured complete absorption of incident light. With a beam intensity of 1.05 ± 0.05 mE/h, a measurable conversion of **3** → **4** was observed (GLC analysis) in 4 h. The calculated quantum yield for isomerization was 0.013 ± 0.004.

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Registry No.—**3,** 2955-79-5; **4,** 7556-62-9.

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