Favorskii-Type Ring Contraction in Bicyclic Chloro Ketones. A Stereochemistry- and Medium-Dependent Photochemical Solvolysis

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Abstract: Irradiation of *exo*-7-chloro-*endo*-7-methylbicyclo[3.2.0]hept-2-en-6-one (**5**) in methanol gives the stereoisomeric 6-carbomethoxy-6-methylbicyclo[3.1.0]hex-2-enes (**11** and **13**) and a long-chain ester **9** (6:2:1). The C-7 epimer **6** gives predominantly an isomeric long-chain ester along with **11** and **13**. 7-Chloro-7-methylbicyclo[3.2.0]heptan-6-ones (**7** and **8**) undergo similar cycloelimination and ring contraction–solvolysis with stereochemical preferences similar to **5** and **6**. For the formation of cyclopropyl esters, a mechanism involving photoionization of chloride, followed by ring contraction to acylium ions which are trapped by solvent, is suggested. Excited-state partitioning between conventional cycloelimination and ring contraction–solvolysis for the cyclobutanones may be understood in terms of preferential loss of axial chlorine in the photoionization step and the availability of conformations with axial chlorine, which is dependent on configuration. A link is established between the propensity for photorearrangement and a red shift in the n,π* transition for the ketones (observed for **5** and **7**, but not for **6** and **8**), which signals the preference for axial chlorine in the ground state. Quantum yields for ketone disappearance are high and undiminished in the presence of a triplet quencher. Product ratios for **5** are markedly a function of medium with an apparent solvent parameter correlation in favor of formation of **11** with increased solvent polarity.

Major reaction pathways for the photochemical decomposition of cyclobutanones have been recently identified in thorough reviews of the literature.[1] According to one view,[1a] the data are consistent with formation via the excited singlet state of a diradical, which partitions to cycloelimination, ring expansion, and decarbonylation products (Scheme I).

Scheme I
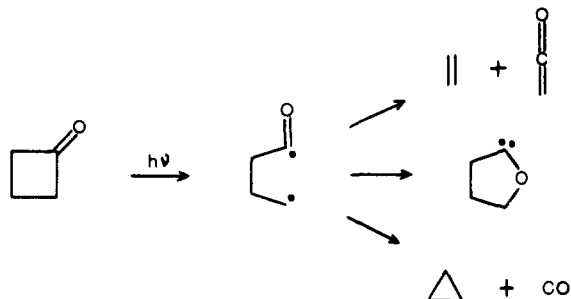
A number of bicyclo[3.2.0]hept-2-en-6-ones, in which the cyclobutanone ring system is fused with an adjacent unsaturated ring, have received attention. The parent ketone **1**[2] and its 7,7-dimethyl[3] and 7,7-dichloro[4] derivatives (**2** and **3**) on
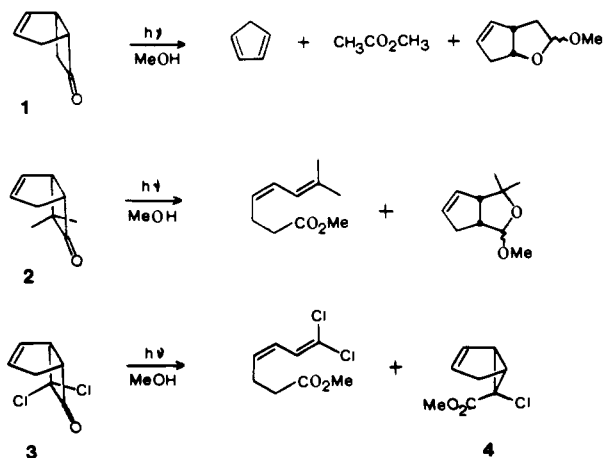
irradiation in methanol give products of cycloelimination and ring expansion as shown (including methanol trapping of ketenes and oxacarbenes). The products are consistent with

the generalized mechanism (Scheme I) to the extent that selection of the more stable diradical for cyclobutanone ring opening in each case leads to the regiochemistry observed.

Given the facility with which bicyclic cyclobutanones can be made via ketene addition,[5] we expected that a useful synthesis of long-chain unsaturated carbonyl compounds could be developed if the principal mode of fragmentation for **2** and **3** could be generalized.[6] For further examination we chose ketones **5–8**, since they offered both regio- and stereochemical possibilities and since electron-withdrawing α substitution has been shown[1] to diminish ring expansion, which competes with photoelimination (e.g., compare **2** and **3**). In addition, the solitary report by Kaplan[4] that an unusual ring contraction–solvolysis product **4** was obtained from **3** was intriguing and suggested examination of similar cyclobutanones. Our study establishes the generality of this latter reaction and highlights its subtle dependence on stereochemistry and medium. In terms of primary photochemistry the ring contraction–solvolysis appears to diverge significantly from the established course of cyclobutanone decomposition.

Results

Ketones **5–8** were obtained in stereochemically pure (>99%) form according to standard procedures. The assignments of stereochemistry followed from NMR spectral data with reference to established analyses.[5a,8] Preparative irradiation of **5** in methanol using a Pyrex filter gave a number of products, three of which (ratio 6:2:1) accounted for >90% of the material balance. Tandem GLC–MS was helpful in initial characterizations and preparative GLC led to the isolation of products in pure form. The least abundant component (a methanol adduct) was identified as **9** on the basis of NMR, ir, and uv data. Fragmentation in the mass spectrometer was consistent with the following scheme. The stereochemistry of **9** was not
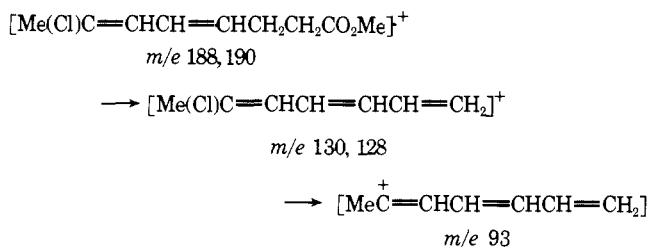
$$[\text{Me(Cl)C}{=}\text{CHCH}{=}\text{CHCH}_2\text{CH}_2\text{CO}_2\text{Me}]^+$$
$$m/e\ 188, 190$$

$$\longrightarrow [\text{Me(Cl)C}{=}\text{CHCH}{=}\text{CHCH}{=}\text{CH}_2]^+$$
$$m/e\ 130, 128$$

$$\longrightarrow [\text{Me}\overset{+}{\text{C}}{=}\text{CHCH}{=}\text{CHCH}{=}\text{CH}_2]$$
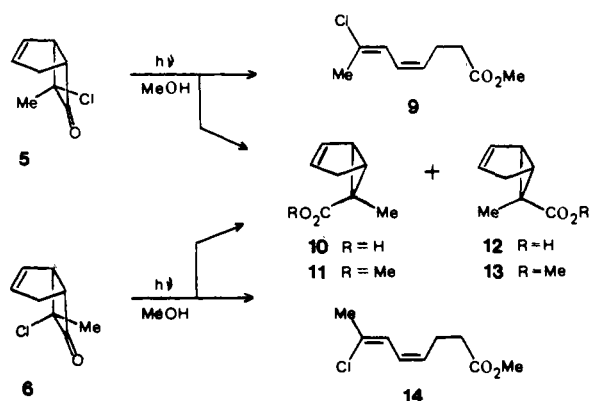$$m/e\ 93$$

Table I. Quantum Yields for Photolysis of Bicyclic Ketones[a]

Starting ketone	Solvent	Additive (M)	(11 or 15)	(13 or 16)	(9 or 14)
5	MeOH		0.59	0.14	0.09
	MeOH[b]		0.55	0.19	
	C_6H_{12}	MeOH (1.2)	0.32	d	0.07
	MeOH	LiCl (0.5)	0.80	0.15	0.12
	MeOH	Diene[e] (0.1)	0.58	0.16	0.07
6	MeOH		0.19	0.04	0.72
7	MeOH		0.48	0.28	
8	MeOH		0.31	0.02	

[a] Rayonet reactor (300 ± 30-nm lamps, Pyrex tubes except where noted). [b] Irradiation at 254 nm. [c] Not analyzed. [d] Analysis difficult due to appearance of two other minor products. [e] 2,5-Dimethyl-2,4-hexadiene.

established, but assumed on the basis of strong precedence for stereospecific cracking already established for cyclobutanones.[1]

The remaining photoproducts from 5 appeared to be esters, arising from formal loss of HCl and addition of MeOH (m/e 152). The minor ester proved to be 13,[9] identical with that obtained from 5 via base-catalyzed (NaOH/MeOH) stereo-

specific ring contraction to 12,[10] followed by diazomethane esterification. Major ester 11 was saponified to give 10; which was identical with the product of base-catalyzed ring contraction of 6.[10] Treatment of an aqueous extract from the photolysis of 5 with $AgNO_3$ indicated that chloride ion had been produced.

Preparative irradiation of 6 gave a methanol adduct 14. NMR, ir, and mass spectra (vide supra) as well as a strikingly long GLC retention time for this major product were quite similar to those recorded for 9. Minor products from the photolysis of 6 were the ring-contracted esters 11 and 13. Saturated ketones 7 and 8 were not photolyzed on a preparative scale, but GLC-MS analysis of samples after irradiation in methanol (Rayonet reactor, 300 ± 30 nm, Pyrex tubes) showed that 15 and 16 were produced. These esters were obtained independently via base-catalyzed ring contraction[10a]-esterification
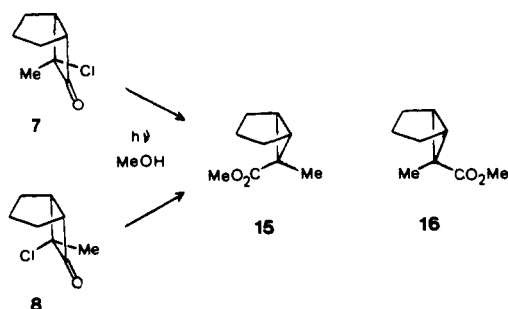
dently via base-catalyzed ring contraction[10a]-esterification of 7 and 8. Cycloelimination products (methanol adducts, m/e 190 and 192, with long retention times; see Experimental Section for GC-MS analysis) were apparently formed as

minor and major products of photolysis of 7 and 8, respectively. If these incompletely characterized products are the expected long-chain unsaturated esters (analogous to 9 and 14), their appearance from 7 and 8 is quantitatively similar to that from 5 and 6, respectively.

A number of control experiments were carried out. (1) Ketones 5-8 were stable for days with respect to epimerization or conversion to cyclopropyl esters when stored in the dark in methanol or methanol saturated with sodium bicarbonate. (2) Ketone 5 after treatment with dilute methanolic HCl was recovered unchanged. (Acid might have been produced during photolysis via 1,2-elimination or some other route involving radicals, perhaps leading to hemiketal or ketal transients which could be responsible for rearrangement.) (3) Ketone 5 was stable in the dark in methanol-water (H_2O mole fraction = 0.6) (vide infra). (4) Ketones 5-8 and cyclopropyl esters 11, 13, 15, and 16 were stable under GLC analysis conditions including retention of isomeric purity (>98%). (5) Cyclopropyl esters were stable under photolysis conditions and product ratios were not significantly altered as a function of time to moderate conversion, showing an independence on concentration of ketone. (6) Ketones 5-8 did not epimerize under photolysis conditions.

Quantum yields for photolysis of ketones 5-8 are shown in Table I. A Rayonet reactor equipped with a merry-go-round apparatus was employed for parallel irradiations. The values for appearance of products at low conversion were remarkably high, with a sum which approached unity for photolysis of 5 and 6 in methanol (and likewise for 7 and 8 with the inclusion of the major unidentified products). Factors affecting the quantum yields and product distribution for 5 were probed. Irradiation in methanol at 300 or 254 nm gave comparable results. Using cyclohexane as solvent (with enough methanol to intercept expected ketene or other penultimate photoproducts) diminished quantum yields, whereas addition of LiCl increased the production of 11. An efficient quencher of triplet excited species, 2,5-dimethyl-2,4-hexadiene ($E_T < 58$ kcal/mol),[12] had little effect on the course of decomposition of 5. Quantum yields for the appearance of products from 5 and 7 as a function of time were the same within experimental error to at least 15% conversion.

In order to examine further the effect of medium on photochemical ring contraction, 5 and 7 were photolyzed in methanol with increasing amounts of water as cosolvent. Photolysates were titrated with diazomethane to convert water adducts (e.g., 10 and 12) into methanol adducts (e.g., 11 and 13). The results of parallel irradiation experiments are shown in Table II. Quantum yields for the appearance of the minor products 9 and 13 from 5 could not be obtained with precision at low conversion, especially since their importance diminished as the mole fraction of water increased. Estimates for the appearance of 9 and 13 at water mole fraction = 0.49, are $\phi(9)$ < 0.02 and $\phi(13)$ < 0.06.

Table II. Quantum Yields for Photolysis of 5 and 7 in Methanol/Water[a]

| Ketone	Mol fraction H$_2$O	$\phi(11$ or $15)$	$\phi(16)$
5	0.00	0.59	
	0.29	0.78	
	0.36	0.83	
	0.49	0.98	
7	0.00	0.51	0.25
	0.29	0.45	0.27
	0.36	0.35	0.31

[a] Rayonet reactor (300 ± 30-nm lamps, Pyrex tubes).

Discussion

It has been previously noted[1a] that α substitution of electron-withdrawing groups in cyclobutanones leads to a sharp preference for photochemical cycloelimination relative to ring expansion to an oxacarbene (Scheme I). This electronic effect appears to operate for the present system, since ring-expansion products are insignificant and cycloelimination is important (for 5 and 6 and most likely for 7 and 8). The more significant finding, however, is that the competitor for cycloelimination is an unusual photochemical ring contraction leading to cyclopropyl esters, which is analogous to the base-induced Favorskii rearrangement.

The lack of diene quenching of cycloelimination or of ring contraction–solvent capture is consistent with the view that photoproducts from cyclobutanones in solution are singlet derived.[1] A heavy-atom effect by substituent chlorine might have induced rapid intersystem crossing to a very short-lived (unquenchable yet reactive) triplet state. However, Metcalfe and Lee[13] have shown that this factor does not favor triplet-derived products in direct photolysis of 2-chlorocyclobutanone in the gas phase.[14]

The very nature of ring contraction for 5–8 implicates a polar primary photodecomposition which competes with cyclobutanone ring opening. A mechanism involving loss of chlorine atom[17] would require an unfavorable[18] 1,2-shift of carbon to a radical center (17 → 18) and an unattractive combination with solvent (radicals) to give product. Notably, 2-chlorocyclobutanone does not take a free radical course for photodecomposition in the gas phase.[13]
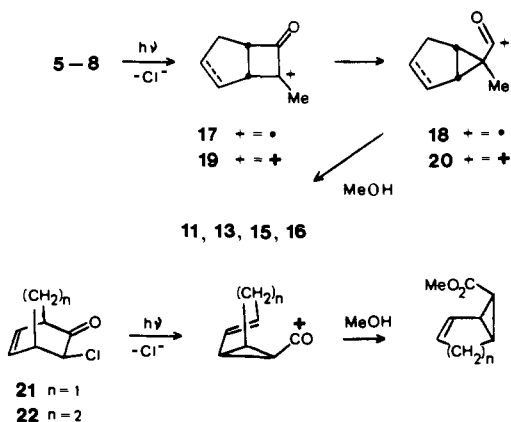
The most likely competitor of ring opening for 5–8 is photoionization followed by, or occurring with, ring contraction and (formally) involving ions 19 and 20. The latter are attractive ground-state intermediates, since cyclopropyl acylium ions (1) are formed readily in solution[19] and have been isolated,[20] (2) resist ring opening and decarbonylation, and (3) are trapped by alcohols to form esters.[20] In addition, cation 20 should be formed irreversibly from 19 in view of the relative stabilities of acylium and tertiary ions.[21] An ionic course has

previously been suggested for photorearrangement–solvent incorporation of 21,[22] 22 and derivatives,[23] α-chloroacetophenones,[24] α-sulfonyl oxy ketones,[25] and N-chloroacetylmescaline and related compounds.[26]

Further mechanistic discussion must include an analysis of the stereochemical details for chloro ketone photolysis, which may be summarized as follows (refer to Table I): cyclopropyl ester formation predominates over cycloelimination where chlorine is substituted exo (for 7 and 5, where the ratio is about 8:1), whereas the situation is reversed with endo-chloro substitution (for 8 and 6, where the ratio is about 0.3). The important influence of ketone stereochemistry on the primary partitioning of the excited state between ring opening and ionization is reminiscent of the stereochemical consequences of base-catalyzed ring contraction. The stereospecific formation of ring-contracted products from 5–8 on treatment with NaOH/MeOH (vide supra) has been rationalized on the basis of a semibenzylic acid type of rearrangement[27] involving intermediates such as 23 (from 5 and 7) and 24 (from 6 and

23

24
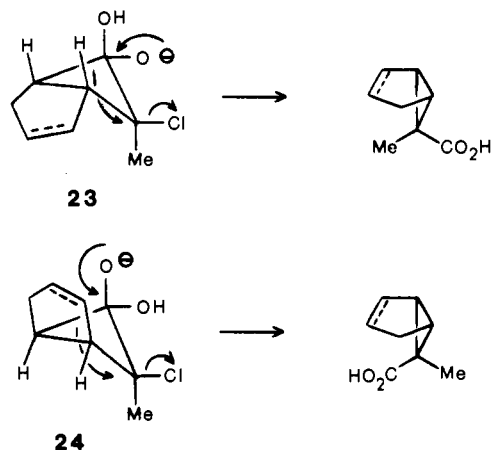
8).[10a] These conformations are preferentially reactive owing to their favorable arrangement for equatorial[28] loss of chloride, which includes a controlling bond alignment factor[29] which influences concerted 1,2-migration to electron-deficient carbon. A similar conformational dependence might have been expected for puckered[1a] excited singlet cyclobutanones. This influence would explain the preference in cyclopropyl ester stereochemistry for 6 and 8, but would fail to rationalize the results for 5 and 7. It is unsatisfying that the stereoselectivity, reflecting favorable stereoelectronic factors for *concerted* ring contraction, would be primarily manifest where rearrangement–solvolysis competes poorly with cycloelimination.

A simple steric factor might influence photoheterolysis of chlorine in 5–8. That the endo face of the bicycloheptene system is the more sterically congested is suggested by stereoselectivities of the hydride reduction in the 6-keto series[5a,30] and the hydroboration of the 2,6-diene[31] and by the propensities for pyrolytic elimination of xanthates of the isomeric 2-en-6-ols.[32] This factor leading to inhibition in the loss of endo chlorine would be expected also in the saturated series (7 vs. 8) in view of the steric hindrance to ionization noted for related bicyclic systems.[33,34]

A clue that the influence may be more subtle than a simple steric factor is found in the ultraviolet spectral data for 5–8 and related bicyclic cyclobutanones,[37] as shown in Table III. A bathochromic shift in the n,π* maximum for 3, 5, and 7 is noticeable. This effect on transition energy is well known for α-halo ketones and appears to be most pronounced in cyclic systems where halogen is axially oriented.[38] There are indications[8b,39] that the four-membered ring in substituted cyclobutanones (even for fused systems[10a,40]) is not planar.[41] In particular, Conia and co-workers[42] have noted an axial pref-
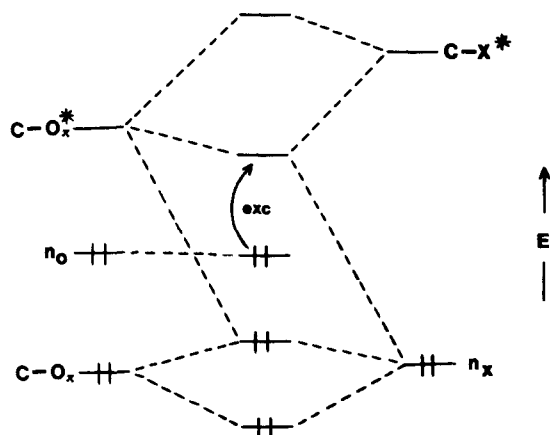
Figure 1. Molecular orbital diagram for mixing of carbonyl and halogen orbitals in α-halo ketones.

**Table III.** Ultraviolet Spectral Data for Bicycle Cyclobutanones in Methanol

Cyclobutanone	n,π^* transition, λ_{max}, nm (ϵ)
1	292 (30)[a]
3	314 (50)[b]
5	318 (152)
6	304 (161)
7	318 (182)
8	294 (177)

[a] Reference 36. [b] Reference 37, ethanol solvent.

erence for halogen in a series of 2-halocyclobutanones, revealed in part by the bathochromic shift in the carbonyl n,π^* band.

The stabilization of axial halogen and the concomitant bathochromic shift may be understood in terms of the molecular orbital diagram in Figure 1 and structure **25**. The principal interactions noted previously[38,43] include: (1) perturbation of the carbonyl bonding orbital (C–O) by a nonbonding halogen orbital (n_x); (2) perturbation of n_x by the antibonding carbonyl MO (C–O*); and (3) perturbation of C–O* by the antibonding carbon–halogen orbital (C–X*). Allinger and co-workers[38] have pointed to the stabilization of C–O* by C–X* as the principal influence in producing the n,π^* bathochromic shift, whereas Salem et al.[43] have noted the stabilization of nonbonding electrons (in the "peri" orbital) on halogen by "superjacent" C–O*, which leads to the preference for axial conformer in the ground state.[44,45] Both of these influences are potentially important, but greatly diminished for equatorially oriented halogen, where overlap of the appropriate orbitals is reduced. If halogen–carbonyl perturbation leads to a conformer preference in the ground state and a bathochromic spectral shift, it follows that the same conformer preference (axial) will hold for the equilibrium geometry in the first excited state (overall three-electron stabilization, see Figure 1).

The mixing of C–O* and C–X* orbitals in α-halo ketones is almost surely a determinant of photoreactivity. Where mixing is strong (axial halogen) the wave function for the lowest n,π^* excited state has considerable antibonding C–X character, and cleavage of the C–X bond should be generally important. Charge separation will accompany deexcitation to the extent that medium, substituent, and other effects are favorable. A polar route for decomposition is attractive, considering the relatively high electron density on carbonyl carbon for n,π^* excited ketone. In terms of resonance reasoning, canonical form **26** is important[47] (i.e., the excited carbonyl is a good electron-donating group). Axial departure of chloride
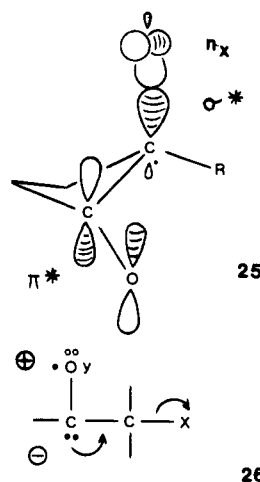
affords favorable overlap of an emptying α-p orbital with electron-rich π orbitals on carbon. An early transition state resembling excited ketone would be significantly stabilized. This heterolysis is a manifestation of π^*-assisted cleavage, of which there are a growing number of examples.[48]

The partitioning to products on photolysis of **5–8** may be understood finally as a linked dependence on configuration and conformation and the stereoelectronics of photoionization. As shown in Scheme II, the electronic preference for axial chlorine in the ground and excited state can be accommodated in **5** and **7** but is mitigated in **6** and **8** due to nonbonded interaction with the fused five-membered ring. This reversal in the preference for axial halogen has been previously explained for simple halocyclohexanones in terms of steric requirements of interacting substituent groups.[49] A case can be made for preferential photoionization, where conformations with axial chlorine are more important (**5, 7a**), and for preferential photochemical ring opening (cycloelimination), where conformations with axial chlorine are not favored (**6, 8a**). It should be noted that the suggested differences in conformer geometry cannot be great (the bicyclic structures are relatively rigid and idealized in Scheme II). It follows that the electronic and steric energetic

Scheme II
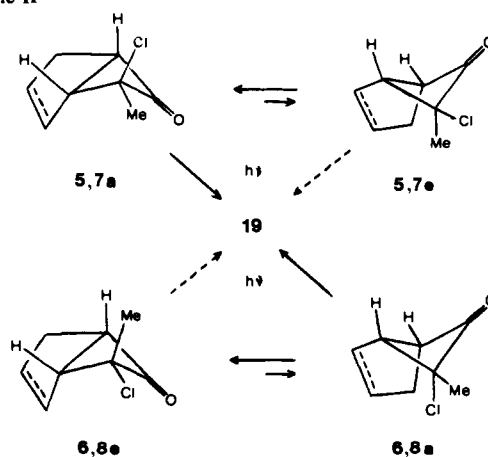
factors which favor "axial" and "equatorial" orientations are relatively weak, the conformations are separated by a low barrier at which the eclipsing of groups is at a maximum, and the differential spectral behavior and photoreactivity have pronounced angular dependences. The situation where two conformational types give rise to different photoproducts takes one limiting form in which the activation energy for product formation is lower than that for conformational interchange.[50] If this scheme is applicable to the present system and barriers for conformational change are of the order found for other four-membered ring systems (1–3 kcal/mol), depletion of

reactive conformations of **5–8** would have to be exceedingly fast ($k > 10^{10}$ s^{-1}).[51] In any event the leaving-group orientation factor as a stereochemical phenomenon in ketone photoionization may be general in view of the configurational-conformation control of partitioning to products found for the isomeric 2-tosyloxy-3,3,5-trimethylcyclohexanones and related systems.[25]

Product ratios for **5** and **7** are a function of photoreaction medium. The effects are subtle, but in general support a mechanistic scheme of competitive polar and nonpolar decomposition paths. Photolysis **5 → 11** is relatively diminished in cyclohexane and enhanced with added salt (Table I) and the addition of water as cosolvent (Table II). The data for photolysis in MeOH/M$_2$O are striking, since the increased preference for **11** is at the expense of formation of both **9** and **13**.[52] That the effect is one of response to solvent polarity is apparent in the correlation of relative quantum yields for formation of **11** and the solvent parameter Y[53] (Figure 2).

A large number of factors could account for solvent perturbation, including the adjustment of energies of ground- and excited-state conformations and excited-state barriers. We tentatively suggest that the effects point again to the importance of ground-state conformation. The data for **5** are consistent with the increased preference for axial chlorine in more polar media (n,π^* λ_{max} 310 nm, cyclohexane). The concomitant favor for photochemical ring contraction–solvolysis giving **11**, but not **13**, is understandable if the latter solvolysis product is formed concertedly with equatorial loss of chloride (from **5e***) analogous to the decomposition of **23** and the stereochemistry of two-step ionization–ring contraction is controlled by incipient homoaromatic stabilization, which is possible for endo acylium ion.[54] The effect of added water on the photolysis product ratio for **5**, while qualitatively striking, is quantitatively small. Generously interpreted, it would point to a shift in conformer equilibrium constant in favor of axial halogen (K = 0.6 → >0.9) ($\Delta\Delta G$ = 0.3 kcal/mol).[55]

The preference for axial chlorine with increased solvent polarity is puzzling in view of the data for halocyclohexanones, where conformations with equatorial chlorine are favored in the ground state due to dipole stabilization. That the effects on the photochemistry of **5** may be attributed to some specific solvation phenomenon is suggested by the contrasting solvent perturbation for **7** (Table III). The sum of ring contraction quantum yields as a function of H$_2$O mole fraction is hardly outside experimental error, but the slight shift in the ratio of cyclopropyl esters with increased polarity would be consistent with a trend favoring **7e** (and concerted ring contraction leading to exo ester).[59]

We are now examining simple halo ketones with fixed or well-characterized stereochemistries in order to determine the generality of the photochemical Favorskii rearrangement and more precisely define the unusual stereochemical and medium effects observed in the present study.

Experimental Section

General. Mass spectra were obtained using an Hitachi Perkin-Elmer RMU-6L instrument equipped with a GLC interface and a Perkin-Elmer 990 flame-ionization gas chromatograph. Spectra were recorded at 70 eV using the direct evaporation sampling procedure with a cooled ion source (30–80 °C) or the GLC inlet. Preparative GLC was performed on a Varian Aerograph Model 90P instrument with helium carrier gas. All quantitative analyses were carried out using the interfaced flame-ionization instrument. GLC columns and retention times for all compounds studied are listed in Tables IV and V.

All commercial chemicals were of reagent or spectrophotometric quality and, unless specified, were used without further purification. Valerophenone and *tert*-butylbenzene were fractionally distilled. Benzene and cyclohexane were prepared for use as photolysis solvents by conventional treatment with sulfuric acid, extractive workup, and
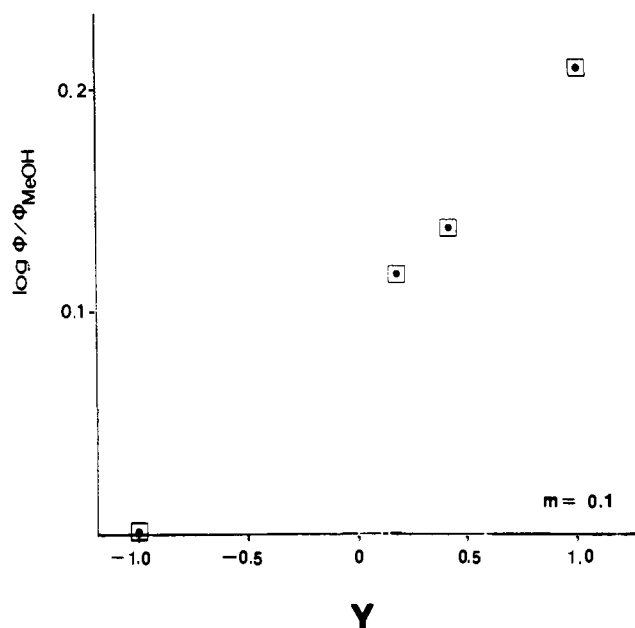

Figure 2. Relative quantum yields for formation of **11** vs. the solvent parameter Y (ref 53) for MeOH–H$_2$O solvent mixtures.

Table IV. GLC Columns Employed for Analyses

Column	Dimensions	Liquid phase[a]
A	10 ft, ⅜ in.	20% Carbowax 20 M
B	12 ft, ⅜ in.	20% GE-SF 96
C	6 ft, ⅛ in.	20% GE-SF 96
D	6 ft, ⅛ in.	20% Carbowax 20 M
E	12 ft, ⅛ in.	20% Carbowax 20 M
F	12 ft, ⅛ in.	20% FFAP
G	12 ft, ⅛ in.	20% GE-SF 96

[a] Stationary phase, Chromosorb W (generally 60–80 mesh).

Table V. Retention Times (min) for Cyclobutanones and Photoproducts

	Column			
	C (130 °C)	E (150 °C)	F (140 °C)	G (160 °C)
5	10.5	21.5	12.5	
6	16.0	23.0		
7	7.8			15.5
8	12.0			17.0
9	34.0	46.0		
11	7.5	11.0	7.5	
13	13.5	17.0	10.5	
114	26.0	38.0		
15	5.5			11.8
16	10.2			18.5
27a	21.0			41.0
27b				38.0

distillation over sodium. Lithium chloride was dried for 10 h at 120 °C.

Preparation of Cyclobutanones. 7-Chloro-7-methylbicyclo-[3.2.0]hept-2-en-6-one (**5, 6**) was prepared following standard procedures[61] and the isomers were obtained by distillation (40–80 °C (3 mm)) and replicate preparative GLC (column A, 180 °C, followed by column B, 145 °C). The major isomer was assigned the *endo*-methyl configuration according to previous analysis[5a,8] with special reference to the chemical shift of methyl protons in NMR spectra (δ 1.5 and 1.8 for **5** and **6**, respectively, CDCl$_3$).

7-Chloro-7-methylbicyclo[3.2.0]heptan-6-one (**7, 8**) was similarly prepared and the isomers, obtained in pure form after preparative

Table VI. Spectral Data for Photoproducts

Structure	NMR (δ vs. Me$_4$Si)		Ir, cm^{-1}	MS, m/e, 20 eV[a]
9[b]	[c]2.2–2.8	7 H, m (–CH$_2$CH$_2$–, CH$_3$)	1735[c]	190 (M$^+$ + 2, 41),
	3.7	3 H, s (CH$_3$O–)		188 (M$^+$, 100), 130 (33),
	5.3–6.8	3 H, m (vinylic)		128 (54), 93 (82)
11	[d]1.3	3 H, s (CH$_3$–)	1735[d]	152 (M$^+$, 47), 93 (100,
	1.7	1 H, m (C(5)–H)		–CO$_2$Me), 91 (55), 77 (49)
	2.1	1 H, m (C(1)–H)		
	2.6	2 H, m (–CH$_2$–)		
	3.6	3 H, s (CH$_3$O–)		
	5.6	2 H, m (vinylic)		
13	[c]1.0	3 H, s (CH$_3$–)	1705[c]	152 (M$^+$, 7), 125 (32),
	2.4	4 H, m (bridgehead, –CH$_2$–)		93 (100, –CO$_2$Me), 91 (67),
	3.7	3 H, s (CH$_3$O–)		77 (47), 66 (15), 65 (17)
	5.8	2 H, m (vinylic)		
14	[c] 1.7–2.9	7 H, m (–CH$_2$CH$_2$–, CH$_3$–)	1740[c]	190 (M$^+$ + 2, 31), 188
	3.7	3 H, s (CH$_3$O–)		(M$^+$, 87), 130 (30), 128 (84),
	5.7–7.2	3 H, m (vinylic)		93 (100, –HCO$_2$Me, –Cl)
15	[d]1.2	3 H, s (CH$_3$–)	1730[c]	154 (M$^+$, 100), 125 (50),
	1.4	8 H, m (ring hydrogens)		122 (54), 95 (18), 94 (36),
	3.2	3 H, s (CH$_3$O–)		79 (45), 67 (82)
16	[d] 1.8	3 H, s (CH$_3$–)	1725[d]	154 (M$^+$, 100), 125 (26),
	1.2	8 H, m (ring hydrogens)		122 (52), 95 (75), 94 (30),
	3.6	3 H, s (CH$_3$O–)		79 (33), 67 (48)

[a] Relative intensities in parentheses; base peak = 100. [b] Uv λ_{max} 244 nm (ϵ 18 400). [c] CCl$_4$ solvent. [d] CDCl$_3$ solvent.

GLC (column B, 145 °C), were identified according to spectral data, as described previously[8] (methyl protons at 1.48 and 1.70 ppm for 7 and 8, respectively, CCl$_4$).

Preparative Photolysis of 7-Chloro-7-methylbicyclo[3.2.0]hept-2-en-6-one (5, 6). GLC purified (>99%) stereoisomers 5 and 6 (about 1 g in 200 ml of MeOH) were photolyzed with nitrogen purging and a trace of solid sodium bicarbonate present,[62] using a 450-W Hanovia immersion apparatus and a Pyrex filter. After photolysis for 90 min, a 60–80% conversion of the ketones was apparent (column D, 120 °C). The photolysates were concentrated in vacuo and products analyzed by GLC–MS (column D, temperature programmed, 70–100 °C). The products were then isolated by preparative GLC (column A, 110 °C) and characterized according to spectral data (Table VI) and comparison with authentic samples (vide infra). From 5, products 9, 11, and 13 (1:6:2) were obtained, while 6 gave 11, 13, and 14 (20:0.5:7). Long-chain esters 9 and 14 obtained as pure oils by GLC decomposed slowly on standing and were not submitted for combustion analysis.

Cyclopropyl ester 11 (30 mg, 0.2 mmol) from the photolysis of 5 was stirred at reflux with 3.6 N KOH (25 ml) and methanol (10 ml) for 2 h. Extraction with ether and acidification of the aqueous layer gave quantitatively an acid, mp 87–89 °C, which was identical with the product of base-catalyzed ring contraction of 6, mp 95–96 °C.[10a]

Photolysis of 7-Chloro-7-methylbicyclo[3.2.0]heptan-6-one (7, 8). Samples of ketones, 6 × 10^{-2} M in methanol, were irradiated in Pyrex tubes using a Rayonet reactor (RUL 3000 lamps). Photolysis was followed by GLC–MS (column C, 130 °C) and products were characterized on the basis of retention times (Table V) and mass spectral data (Table VI). Cyclopropyl esters 15 and 16, derived from both 7 and 8, were identified by comparison with authentic samples (vide infra). Other products from 7 and 8 were tentatively identified as isomers of methyl 7-chlorooct-6-enoate (27a and b) on the basis of chemical analogy, the similarity to 9 and 14 in GLC retention times, and mass spectral data.

For 27a, a minor product from 7, the GLC–MS data (20 eV) were: m/e 192 (M$^+$ + 2, 15), 190 (M$^+$, 33), 161 (15), 160 (30), 159 (37), 158 (67), 123 (67), 95 (100, –HCO$_2$Me, –Cl), 89 (81), 87 (50), 81 (56), 74 (78), 59 (89), 55 (67), 53 (85).

For 27b, a major product from 8, the GLC–MS data (20 eV) were: m/e 192 (M$^+$ + 2, 10), 190 (M$^+$, 40), 161 (15), 160 (30), 159 (45), 158 (45), 157 (72), 123 (70), 95 (95), 89 (90), 87 (45), 81 (58), 74 (85), 59 (100, CO$_2$Me), 55 (55), 53 (90).

The mass spectral decompositions of 27 are consistent with the following fragmentation pattern:

190 (192) → 159 (161) → 158 (160) → 123 → 95 → 81 → 53

$$m/e\ 59 = [CO_2Me]^+$$
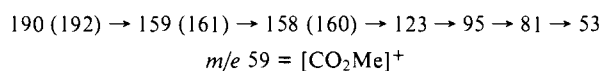
Esterification of Carboxylic Acids from Base-Catalyzed Ring Contraction of 5, 7, and 8. Ether solutions of 12 or the isomers of 6-methylbicyclo[3.1.0]hexane-6-carboxylic acid[10a] were titrated with diazomethane solution[63] until evolution of nitrogen ceased. The excess diazomethane was back-titrated with dilute hydrochloric acid. A small amount of water was added and the resulting mixture was extracted with ether. The organic layer was dried (MgSO$_4$) and concentrated and the esterification products were obtained in pure form by preparative GLC (column A, 110 °C). The spectral data are listed in Table VI.

The product of base-catalyzed ring contraction–esterification of 5 was 13,[9] which was identical with the major and minor photoproducts of 6 and 5, respectively. Similarly, 7 and 8 gave after base-catalyzed ring contraction–esterification 15 and 16, respectively, which were identical with the photoproducts of 7 and 8. Anal. (C$_9$H$_{14}$O$_2$): C, H.

Quantum Yields.[64] General Method. Samples of the cyclobutanones were delivered by syringe to 5-ml volumetric flasks, containing an additive where appropriate, and diluted to volume with solvent (ketone concentration generally 6 × 10^{-2} M). Solutions were transferred to cylindrical (15 × 1.5 cm) Pyrex tubes (quartz where indicated). Tubes were sealed with rubber septa and degassed by passing a slow stream of nitrogen through the solution for 15 min. A Rayonet reactor equipped with a merry-go-round attachment was employed for irradiation of cyclobutanone samples in parallel with actinometer solutions. RUL 3000 lamps (300 ± 30 nm) were generally used; some runs utilized RUL 2537 lamps and quartz tubes. The actinometer was valerophenone (0.4 M in benzene with 0.005 M dodecane internal standard) and the quantum yield for its photolysis to acetophenone was assumed to be 0.33.[11] The temperature in the irradiation chamber was maintained at 30 ± 1 °C by a fan which circulated air from beneath the chamber.

For GLC analysis (column C) aliquots of cyclobutanone photolysate were diluted with benzene containing tert-butylbenzene as internal standard. Photoproduct compositions in actinometer and cyclobutanone samples were computed from GLC peak areas, which were analyzed by triangulation with reference to the internal standards and corrected with detector response factors. Conversions were kept to <10% for cyclobutanone samples and <5% for the actinometer; however, it was shown in experiments with extended irradiation time that product composition for the cyclobutanones was not significantly

a function of degree of conversion. For irradiations in methanol–water, 300-μl aliquots of photolysate were titrated with diazomethane solution before analysis. Standard deviations in replicate quantum yield measurements indicated an error of $\pm10\%$ for ϕ (**11, 14, 15,** and **16**) and $\pm20\%$ for ϕ (**9** and **13**).

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(52) We consider unlikely effects on the product ratios which involve less than quantitative capture by methanol–water solvent mixtures of penultimate intermediates (which might have reversibly formed) or fractionation during diazomethane esterification of water adducts. Material balances (note quantum yields!) in the solvent effect studies were high. Also, a systematic problem in this experiment probably would have given unusual results for **7** also, which was not the case.

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$$19 \longrightarrow \quad \longrightarrow \quad \longrightarrow \quad 11, 15$$

i   ii
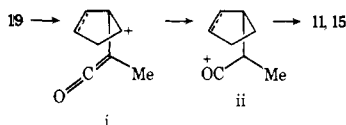
(b) Concerted rearrangement of excited ketones might give acid chlorides (which are trapped by methanol) via four-center ring contraction–chlorine migration. However, conformations with equatorial chlorine are best arranged for this process, and the products predicted for decomposition of **5, 7e*** (analogous to **23**) would be inconsistent with our pattern of results. (c) We thank Professor R. G. Bergman for helpful discussions concerning these points.

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Excited-State Multiplicity for the Direct Photochemical Isomerization of Azomethine Dyes
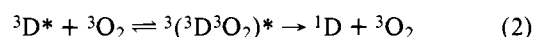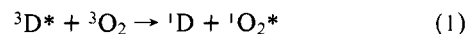
William G. Herkstroeter

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Abstract: Azomethine dyes are known to isomerize readily about the C=N bond following photochemical excitation in fluid solution at ambient temperatures. This excitation of the dyes can be brought about either directly by absorption of light or indirectly by energy transfer from an appropriate triplet sensitizer. To determine whether the isomerization following direct excitation occurs in the singlet or triplet manifolds, the effects of oxygen as well as external and internal heavy atoms on the isomerization of selected benzoylacetanilide and pyrazolone azomethine dyes were examined. In the absence of any heavy atoms, deaerated and air-saturated solutions produce the same quantities of transient species following flash excitation. The presence of either solvent heavy atoms or appropriately substituted intramolecular heavy atoms increases the quantity of transient species produced and, furthermore, part of the transient species formation can be quenched when oxygen is dissolved in the experimental solutions. The conclusion is that in the absence of any heavy atoms, isomerization proceeds via the lowest excited-singlet state of the dyes, but with internal or external heavy atoms present, triplet isomerization, partially quenchable by dissolved oxygen, makes a contribution. By assuming diffusion-controlled quenching of dye triplets by molecular oxygen, one can estimate the triplet-state lifetime of a pyrazolone azomethine dye with an intramolecular heavy atom to be 10 ns.

Azomethine dyes are known to undergo geometric isomerization about the carbon–nitrogen double bond following excitation with light.[1,2] If flash photolysis techniques are employed, dye isomerization can be readily observed through changes in the dye absorption spectra following flash excitation. In fluid solution at ambient temperatures, the photochemical isomerization to the less-stable dye isomers is only temporary and followed by thermal relaxation to regenerate the more stable isomers. Both direct excitation with light and indirect excitation by energy transfer from appropriate triplet-state photosensitizers are effective in bringing about dye isomerization. The results show that the photosensitizers lead to excitation of the lowest excited triplet states in the dyes and demonstrate that the dyes can isomerize in this state. Until now, however, there has been no evidence to distinguish between singlet- and triplet-state isomerization when the dyes are excited directly.

The two possible excited electronic states for isomerization about essential double bonds are the lowest excited singlet and triplet states. For each case there are known examples. Stilbene, one of the most extensively investigated systems insofar as isomerization is concerned, isomerizes in the singlet manifold following absorption of light.[3,4] Singlet isomerization also obtains with the O-methyloxime ethers of acetophenone[5] and the 4-nitrophenylhydrazones of benzaldehyde.[6] Compounds shown to isomerize in their lowest excited triplet states include 3,3'-diethyl-9-methylthiacarbocyanine,[7] thioindigo,[8] 6,6'-diethoxythioindigo,[8] and *trans*-1-phenyl-2-(2-naphthyl)ethylene.[9]

On the basis of past results, we knew of no way to predict reliably a singlet- or triplet-state isomerization path in azomethine dyes and found it necessary to devise experiments to make this distinction. These experiments are based upon two well-known phenomena in photochemistry. The first of these is quenching of excited electronic states. Ideally, one tries to employ a quencher that, by virtue of the position of its energy levels, quenches exclusively the triplet state by energy transfer. Even if one must settle for a quencher that has the potential for quenching both singlets and triplets, quenching experiments will usually accomplish their purpose because lowest excited triplet states are, in most cases, substantially longer-lived and thus more easily quenched than their singlet-state counterparts. Because of the very low triplet-state energies in azomethine dyes,[10,11] we were severely limited in our choice of quenchers. The one quencher that met our requirements was molecular oxygen. Although the lowest triplet states of many of the azomethine dyes actually are lower in energy than the lowest singlet state of oxygen,[10,11] the lowest excited electronic state in this molecule, oxygen still has the potential for quenching such dye triplet states by catalyzing intersystem crossing from the dye triplet to the dye ground state. We consider two possible quenching reactions involving dye triplet states and molecular oxygen as shown in the equations

$$^3D^* + {}^3O_2 \rightarrow {}^1D + {}^1O_2^* \qquad (1)$$

$$^3D^* + {}^3O_2 \rightleftharpoons {}^3(^3D{}^3O_2)^* \rightarrow {}^1D + {}^3O_2 \qquad (2)$$

where D represents an azomethine dye, the superscripts denote