cis,trans-1,1′-Bicyclohexenyl: Conformer-Dependent Chemistry in Benzene and in Methanol†

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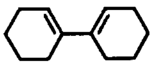
Abstract: *cis,trans*-1,1′-Bicyclohexenyl (*ct*-BCH) generated from BCH triplets is a strained ground-state molecule that reverts to *cis,cis*-1,1′-bicyclohexenyl and gives the *cis*-cyclobutene tricyclo[6.4.0.0^{2,7}]-*cis*-7,8-dodec-1-ene (CB) in benzene or methanol and the ethers 1-(1-cyclohexenyl)-1-methoxycyclohexane (1,2-E) and 2-methoxybicyclohexylidene (1,4-E). Quantum yields for the *ct*-BCH products were determined as a function of triplet energy donor E_T and of temperature. Preferential formation of s-cis triplets by use of donors with progressively lower E_T leads to small but significant and identical increases in $\phi_{CB}/\phi_{1,2\text{-}E}$ and $\phi_{1,4\text{-}E}/\phi_{1,2\text{-}E}$. It is concluded that CB and 1,4-E have a common precursor, *s-cis,ct*-BCH, while 1,2-E forms primarily from *s-trans,ct*-BCH. The effect is small because the *ct*-BCH conformers nearly equilibrate during the transient's lifetime. Temperature effects on these quantum yields (30–47 °C) show that CB formation is slightly more endothermic than overall *ct*-BCH decay while formation of 1,2-E and 1,4-E are nearly barrierless and are controlled by highly unfavorable entropies of activation. Concerted formation of C–H and C–O bonds in the transition states for ether formation is proposed and is supported by large solvent (CH_3OD) deuterium isotope effects; $\phi_{1,2\text{-}E}{}^H/\phi_{1,2\text{-}E}{}^D = 8 \pm 1$, $\phi_{1,4\text{-}E}{}^H/\phi_{1,4\text{-}E}{}^D = 10 \pm 2$.

Direct excitation of *cis,cis*-1,1′-bicyclohexenyl (*cc*-BCH) in hydrocarbon solvents gives the *cis*-cyclobutene, tricyclo[6.4.0.0^{2,7}]-*cis*-7,8-dodec-1-ene (CB),[1-3] and the bond-shifted unconjugated diene, 1,3′-bicyclohexenyl (UD), whereas triplet sensitization gives CB, exclusively.[2,3] In the presence of methanol, two methyl ethers also form under both direct- and triplet-sensitization conditions. The major ether, corresponding to 1,2-addition of methanol to the diene 1,2-E, was first reported by Kropp et al.[4] In an earlier report, we indicated that the ether resulting from addition of methanol to the diene 1,4-E is also observed provided that care is taken to exclude acid from the irradiated solutions.[5] Transient spectroscopic and kinetics observations were shown to be consistent with steady-state quantum yields[5] that taken together established formation of a ground-state transoid intermediate, *cis,trans*-1,1′-bicyclohexenyl (*ct*-BCH). *ct*-BCH was shown to be the sole CB precursor following triplet-sensitized excitation of *cc*-BCH, as initially proposed by Liu.[6] In this paper, we present a fuller account of observations in the presence of triplet energy donors establishing the involvement of *ct*-BCH in ether formation, as proposed by Kropp et al.[4] We further establish a mechanistic relationship between CB and ether formation that is traced to conformational selectivity in product formation.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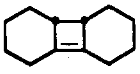
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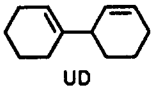
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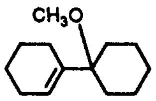
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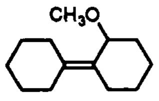
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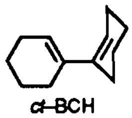
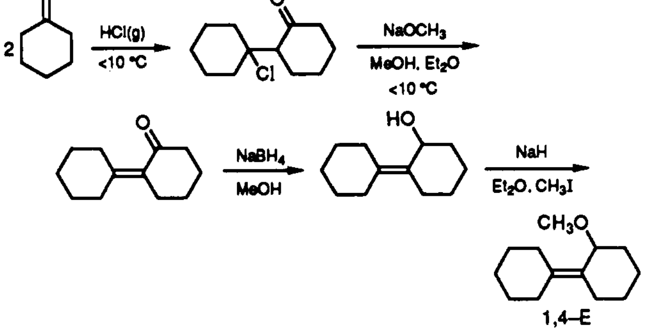

ct–BCH

Results

Products. CB and the ethers 1,2-E and 1,4-E were isolated from preparative-scale triplet-sensitized irradiations of *cc*-BCH in benzene and methanol, respectively, and identified by spectral methods. The new product, 1,4-E, was shown to be identical with material obtained independently from cyclohexanone by use of the following reaction sequence:



1,4–E

Assignment of cis stereochemistry to CB was based on comparison of the ^{1}H NMR (60-MHz) spectrum of the photoproduct with that of the *trans*-cyclobutene isomer[2] synthesized according to the procedure of Moore and Moser.[7] In agreement with the results in ref 7, the ^{1}H NMR (270-MHz) spectrum obtained for CB in this work shows only four allylic protons (δ 2.4, 2 H; δ 2.2, 2 H) separable from the other ring methylene protons (δ 1.7, 8 H; δ 1.2, 6 H) instead of six as reported earlier.[2] Assignment of cis stereochemistry to the photoproduct is secure due to chemical evidence from the thermal[8] and photochemical[9] ring opening of the two isomers[9] and the differences in gas–liquid chromatography (GLC) retention times[9] and ^{1}H NMR (60-MHz) spectra[7] between the two isomers.

Quantum Yields. A merry-go-round apparatus was employed[10] with λ_{exc} = 366 or 313 nm (mercury lines) for sensitized experiments. Irradiated solutions were degassed. BCH conversions to products were determined by GLC relative to unreacted BCH and to added *n*-dodecane (DD) internal standard and were generally small, usually ≤3% but always ≤20%. The benzophenone-sensitized trans → cis photoisomerization of stilbene in benzene, $\phi_{t\to c}$ = 0.55,[11,12] was used for actinometry. Since pho-

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† This paper is dedicated to Professor Paul de Mayo on the occasion of his retirement.

(1) Crowley, K. J. *Tetrahedron* **1964**, *21*, 1001.

(2) Dauben, W. G.; Cargill, R. L.; Coates, R. M.; Saltiel, J. *J. Am. Chem. Soc.* **1966**, *88*, 2742.

(3) Dauben, W. G. In *Solvay Institute 13th Chemistry Conference: Reactivity of the Photoexcited Organic Molecule*; Wiley-Interscience, New York, 1967; p 171.

(4) Kropp, P. J.; Reardon, E. J.; Gaibel, Z. L. F.; Williard, K. F.; Hattaway, J. H., Jr. *J. Am. Chem. Soc.* **1973**, *95*, 7058.

(5) Saltiel, J.; Marchand, G. R.; Bonneau, R. *J. Photochem.* **1985**, *28*, 367.

(6) Liu, R. S. H. *J. Am. Chem. Soc.* **1967**, *89*, 112.

(7) Moore, W. R.; Moser, W. R. *J. Am. Chem. Soc.* **1970**, *92*, 5469.

(8) Criegee, R; Reinhardt, H. G. *Chem. Ber.* **1968**, *101*, 102.

(9) Saltiel, J.; Lim, L.-S. Ng *J. Am. Chem. Soc.* **1969**, *91*, 5404.

(10) Moses, F. G.; Liu, R. S. H.; Monroe, B. M. *Mol. Photochem.* **1969**, *1*, 245.

(11) Hammond, H. A.; DeMeyer, D. E.; Williams, J. L. R. *J. Am. Chem. Soc.* **1969**, *91*, 5180.

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Table I. Effects of Triplet Energy and Temperature on Product Quantum Yields[a]

solvent	sensitizer (M)	T (°C)	$\phi_{CB} \times 10^3$	$\phi_{1,2-E} \times 10^3$	$\phi_{1,4-E} \times 10^3$
benzene[b]	XT (0.046)	30.0	*10.7 (3)*		
	BP (0.086)		*11.4*		
	BP (0.034)[c]		*11.4*		
	F (0.028)		*3.83 (10)*		
	F (0.058)		*3.86 (12)*		
	MK (0.0031)		*11.8 (3)*		
	N (0.048)		*5.1 (2)*		
	N (0.100)		*5.1 (2)*		
	α-AN (0.049)[c]		*12.8 (2)*		
	BP (0.034)	35.0	10.3 (1)		
			11.3 (3)		
	β-AN (0.050)		13.0 (3)		
			12.5 (3)		
	α-AN (0.049)		12.4 (4)		
			12.7 (3)		
	β-AN (0.050)	40.5	13.0 (3)		
			12.5 (2)		
	α-AN (0.049)		13.0 (7)		
			12.7 (4)		
	BP (0.034)	47.0	11.7 (3)		
			12.1 (2)		
	β-AN (0.050)		14.1 (3)		
			13.3 (2)		
	α-AN (0.050)		14.1 (3)		
			14.1 (3)		
methanol[d]	XT (0.010)	30.0	6.0 (3)	10.7 (6)	3.4 (2)
			6.3 (3)	*11.2 (4)*	*3.5 (2)*
	BP (0.08)		11.4 (5)	22.0 (15)	6.9 (5)
			11.2 (6)	*21.2 (20)*	*6.6 (5)*
	BP[e] (0.025)		10.5 (5)	21.3 (19)	6.3 (6)
			10.5 (3)	*21.3 (3)*	*6.3 (2)*
	TXT (0.011)		5.1 (4)	8.7 (10)	2.9 (3)
	β-AN (0.072)		10.8 (6)	15.6 (8)	6.3 (7)
			10.9 (8)	*15.9 (5)*	*6.2 (2)*
	α-AN (0.062)		12.6 (5)	15.5 (15)	6.8 (6)
			12.6 (4)	*15.4 (4)*	*6.7 (2)*
	BP (0.058)	40.2	13.2 (6)	15.5 (13)	4.6 (5)
			12.6 (5)	*14.8 (4)*	*4.4 (3)*
	β-AN (0.061)		13.1 (3)	11.9 (0)	4.1 (5)
			12.2 (5)	*11.0 (2)*	*3.8 (2)*
	BP (0.058)	46.4	12.6 (6)	12.0 (12)	3.6 (5)
			13.2 (5)	*12.5 (6)*	*3.8 (4)*
	β-AN (0.061)		13.4 (5)	9.6 (6)	3.5 (3)
			13.2 (3)	*9.4 (3)*	*3.5 (2)*

[a] Quantum yields based on DD internal standard and/or on percent conversion (italics); values in parentheses are deviations from the mean in the last significant figure for duplicate to quadruplicate samples irradiated in parallel. [b] At 30.0 °C, excitation was at 313 nm, unless otherwise shown, and ϕ_{CB} for BP was used for actinometry; at all other *T*'s, excitation was at 365 nm, the BP-sensitized *trans*-stilbene isomerization was used for actinometry; $[BCH]_0$ = 0.040 M for 313-nm experiments and 0.060–0.069 M for 365-nm experiments. [c] 365 nm. [d] Key: $[BCH]_0$ = 0.12–0.14 M; [DD] = (1.1–1.3) × 10^{-3} M; duplicate samples irradiated in all cases, except that triplicate samples were employed for BP at 40.2 °C and β-AN at 46.4 °C. [e] $[BCH]_0$ = 0.052 M.

toproduct formation efficiencies are relatively low, actinometer solutions were irradiated in parallel with BCH samples at selected time intervals and average actinometer conversion (corrected for 0-time cis content and back reaction[13,14]) per unit time was applied to the calculation of BCH product quantum yields (see ref 15 for a detailed tabulation of the data).

Cyclobutene quantum yields, ϕ_{CB}, for the benzophenone-sensitized irradiation of BCH at 30 °C in *n*-pentane, benzene, or methanol were shown to be nearly independent of solvent (within ±10%) and [BCH] provided that [BCH] ≥ 0.02 M. Lower ϕ_{CB}'s were obtained for [BCH] < 0.02 M, suggesting incomplete excitation transfer to BCH, and results from such experiments were discarded. Results from several independent experiments yielded $\phi_{CB} = 0.0105 \pm 0.0005$ in methanol at 30 °C, and this value was employed for actinometry in some experiments. Calculation of quantum yields was based both on percent conversion and on DD internal standard. Values obtained independently from these two methods were in excellent agreement or, at worst, within experimental error of each other, indicating that no significant photoproducts remained undetected. The effects of triplet-sensitizer energy on ϕ_{CB} in benzene at 30.0–47.0 °C and on ϕ_{CB} and ether formation, $\phi_{1,2-E}$, $\phi_{1,4-E}$, in methanol at 30.0–46.4 °C are given in Table I. In addition to benzophenone (BP), the following sensitizers were employed: xanthone (XT), fluorene (F), naphthalene (N), Michler's ketone (MK), β-acetonaphthone (β-AN), α-acetonaphthone (α-AN), thioxanthone (TXT), benzil, and fluorenone. Product quantum yields for the benzophenone-sensitized reactions of BCH in CH_3OH are compared with those in CH_3OD in Table II.

Table II. Solvent Deuterium Isotope Effect on Quantum Yields for Benzophenone-Sensitized Reaction of BCH, 30 °C[a]

solvent	$\phi_{CB} \times 10^3$	$\phi_{1,4-E} \times 10^3$	$\phi_{1,2-E} \times 10^3$
CH_3OH[b]	10.5[c]	7.5 (6)	24.9 (14)
	10.5[c]	*7.4 (8)*	*24.9 (8)*
CH_3OD[d]	11.8 (4)	0.74 (13)	3.0 (3)
	13.1 (3)	*0.77 (15)*	*3.3 (2)*

[a] See footnote *a*, Table I. [b] Key: benzophenone, 0.053 M; $[BCH]_0$ = 0.055 M; [DD] = 1.08 × 10^{-3} M. [c] Assumed and used for actinometry, see text. [d] Key: benzophenone, 0.057 M; $[BCH]_0$ = 0.053 M; [DD] = 9.28 × 10^{-4} M.

Table III. Naphthalene and Fluorene Fluorescence Intensity as a Function of [BCH] in Benzene, 23 °C

compd	[BCH] (M)	$(I_0/I)_{Ar}$	$(I_0/I)_{air}$[a]
N[b]	0	1.00	5.25
	0.025	1.63	5.66
	0.050	2.11	6.66
	0.100	3.14	7.59
	1.51	4.47	8.80
F[c]	0	1.00	1.18
	0.025	1.24	1.32
	0.050	1.43	1.56
	0.100	2.01	2.16
	0.151	2.18	2.43

[a] I_0 for argon-saturated solution. [b] Key: [N] = 0.0103 M, λ_{em} = 336.4 nm, λ_{ex} = 310.0 nm. [c] Key: [F] = 0.0053 M, λ_{em} = 316.3 nm, λ_{ex} = 310 nm.

Fluorescence Quenching. The fluorescence of naphthalene and fluorene, two of the triplet energy donors employed, is quenched by BCH. Relative fluorescence intensities for N and F were measured at 23 °C as a function of [BCH] for argon- and air-saturated benzene solutions (Table III). No quenching of the fluorescence of β-AN or α-AN by BCH was observed at the BCH concentrations employed in the photochemical experiments.

Discussion

As pointed our earlier,[5] the search for *ct*-BCH was inspired by the elegant demonstration of the transient existence of *trans*-1-phenylcyclohexene (*t*-PCH) as a strained ground-state precursor of ether and dimer products.[16,17] Salient features of the *ct*-BCH transient that are shared commonly with other *trans*-cyclohexenes are as follows: (1) a large spectral red shift (14 200 cm^{-1}) relative to λ_{max} of *cc*-BCH, (2) a transient lifetime (0.85 μs, 0.95 μs, and 0.65 μs at 23 °C in methanol, acetonitrile, and cyclohexane, respectively) that is unaffected by molecular oxygen, and (3)

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(12) Valentine, D., Jr.; Hammond, G. S. *J. Am. Chem. Soc.* **1972**, *94*, 3449.

(13) Saltiel, J.; Marinari, A.; Chang, D. W.-L.; Mitchener, J. C.; Megarity, E. D. *J. Am. Chem. Soc.* **1979**, *101*, 2982.

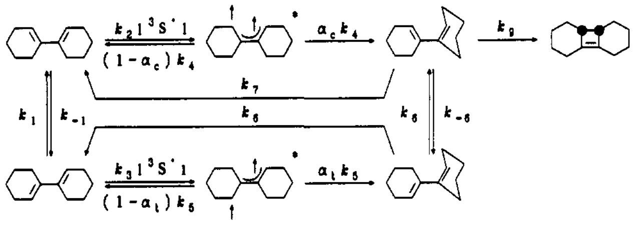
(14) Lamola, A. A.; Hammond, G. S. *J. Am. Chem. Soc.* **1965**, *43*, 2129.

(15) Marchand, G. R. Ph.D. Dissertation, Florida State University, 1984.

(16) Bonneau, R.; Joussot-Dubien, J.; Salem, L.; Yarwood, A. J. *J. Am. Chem. Soc.* **1976**, *98*, 4329.

(17) Dauben, W. G.; van Riel, H. C. H. A.; Hauw, C.; Leroy, F.; Joussot-Dubien, J.; Bonneau, R. *J. Am. Chem. Soc.* **1979**, *101*, 1901. Dauben, W. G.; Van Riel, H. C. H. A.; Robbins, J. D.; Wagner, G. J. *J. Am. Chem. Soc.* **1979**, *101*, 6363.

Scheme I



extremely efficient protonation of the transient by acid, $k_p = 1.1 \times 10^8$ M^{-1} s^{-1} in methanol at 23 °C.[5] The use of proton trapping of the transient to establish that *ct*-BCH is the sole intermediate leading to CB following triplet excitation transfer to BCH was a main subject of our earlier report.[5] In this paper, we explore the mechanism of ether formation and its relationship to the mechanism of CB formation following excitation of *cc*-BCH by triplet excitation transfer.

At the relatively high temperatures employed in this work, triplet excitation transfer to *cc*-BCH leads only to CB in the aprotic solvents *n*-pentane, benzene, and acetonitrile. In the absence of acid, inclusion of methanol leads also to ethers 1,2-E and 1,4-E. Since the quantum yields for formation of these products are independent of [BCH] and these products have been shown to account quantitatively for BCH depletion on the basis of DD as an internal standard, we can exclude significant formation of undetected products such as dimers. The absence of dimers appears at first glance surprising since *cc*-BCH should be a much more reactive diene in Diels–Alder reactions with *trans*-cyclohexenes than 1-phenylcyclohexene. However, dimerization via *t*-PCH has been reported only at low temperature (−75 °C)[17] under conditions for which *t*-PCH disappearance should have a strong second-order component.[18] If, as appears likely, dimerization results from interaction between two transoid species, the shorter lifetime of *ct*-BCH (approximately a factor of 10 at ambient *T*) may account for the absence of dimer under our conditions.

Effect of Triplet Excitation Energy. The strong dependencies of 1,3-diene dimer[19] crossadduct[20] and cis/trans photoequilibrium ratios and of photoisomerization quantum yields[21] on sensitizer triplet excitation energy provided elegant early demonstrations of Havinga's NEER (nonequilibration of excited rotamers) principle[22] in triplet-state chemistry. S_0–T_1 energy gaps of ~60 kcal/mol and close to 52 kcal/mol for s-trans and s-cis diene triplets, respectively, lead to indiscriminate excitation of the two conformers by high-energy sensitizers, $E_T \gtrsim 60$ kcal/mol, producing mainly s-trans triplets, and increased preference for excitation of s-cis conformers as the triplet excitation energy of the donors is decreased below 60 kcal/mol.[19-21] Since s-cis and s-trans triplets exhibit different chemical reactivities and do not interconvert, the dependence of product ratios on donor E_T is readily explained.

Having established that *ct*-BCH is the sole CB and ether precursor following triplet excitation transfer to *cc*-BCH,[5] we now address the question of whether CB and ether quantum yields are sensitive to the s-cis to s-trans conformer ratio of nascent *ct*-BCH. We note first that within the time resolution of our transient spectroscopic study (~20-ns excitation pulse width) no differences could be discerned using xanthone (E_T = 74 kcal/mol) or β-propionaphthone ($E_T \simeq 59$ kcal/mol) to excite *cc*-BCH.[5] The same *ct*-BCH transient was observed, λ_{max} = 365 nm, to grow in with a lifetime of ~45 ns assigned to ^{3}BCH* and to decay following a first-order rate law with a lifetime slightly smaller than 1 μs.[5] The effects of changing the donor's triplet excitation energy on BCH product quantum yields in benzene and in methanol are shown in Table I. A mechanism for CB formation that includes differences in behavior between the s-cis and s-trans conformers of *cc*- and *ct*-BCH is shown in Scheme I.

Table IV. Effect of Sensitizer E_T on ϕ_{CB}/ϕ_{is} in Benzene, 30 °C

sensitizer	E_T[a] (kcal/mol)	ϕ_{is}[b]	$(\phi_{CB}/\phi_{is}) \times 10^3$
XT	74.2	0.94[c]	(11.4)
BP	68.5	1.00	11.4
F	67.6	~(0.31)	~12
MK	61.0	1.00	11.8
N	60.9	0.82 (0.43)	11.9
β-AN	59.3	0.84	
α-AN	56.4	0.89	14.4

[a] For hydrocarbon solvents at 77 K from ref 26. [b] For carbonyl compounds from ref 14, except for α-AN, which is from ref 27; for N from refs 14 and 28, and for F from ref 14, and see text; values in parentheses corrected for fluorescence quenching by BCH. [c] Based on (ϕ_{CB}/ϕ_{is}) = 11.4 for benzophenone.

Application of the steady-state approximation on all transient intermediates gives

$$\phi_{CB} = \frac{\phi_{is}k_9[\alpha_c f_c + \alpha_t f_t k_6/(k_6 + k_8)]}{(k_7 + k_9) + k_{-6}k_8/(k_6 + k_8)} \tag{1}$$

for ϕ_{CB}, where ϕ_{is} is the effective intersystem crossing yield of the sensitizer and f_c and f_t, the triplet excitation fractions of *s-cis,cc*- and *s-trans,cc*-BCH conformers, are given by eqs 2 and 3, respectively. For the special case of full equilibration of s-cis/s-trans

$$f_c = \frac{k_2K_1}{k_3 + k_2K_1} = 1 - f_t \tag{2}$$

$$f_t = \frac{k_3}{k_3 + k_2K_1} = 1 - f_c \tag{3}$$

conformers of *ct*-BCH during its lifetime, i.e., $k_6 \gg k_8$ and $k_{-6} \gg k_7 + k_9$, eq 1 reduces to

$$\phi_{CB} = \frac{\phi_{is}k_9[\alpha_c f_c + \alpha_t f_t]}{k_7 + k_9 + K_{-6}k_8} \tag{4}$$

For this case, ϕ_{CB}/ϕ_{is} is predicted to be independent of the triplet energy of the sensitizer, provided that $\alpha_c \simeq \alpha_t$. Conversely, if no conformer interconversion occurred, i.e., $k_8 \gg k_6$ and $k_7 + k_9 \gg k_{-6}$, eq 1 simplifies to

$$\phi_{CB} = \frac{\phi_{is}k_9\alpha_c f_c}{k_7 + k_9} \tag{5}$$

which predicts a steep dependence of ϕ_{CB}/ϕ_{is} on triplet excitation energy, provided that f_c follows the pattern of other flexible 1,3-dienes and increases as E_T is decreased.[19,20]

We consider first the effect of sensitizer E_T on ϕ_{CB} in benzene at 30 °C. Literature values of E_T and ϕ_{is} of the sensitizers are collected in Table IV, which also gives ϕ_{CB}/ϕ_{is} ratios. Quenching of excited singlet states by BCH was neglected for the ketone sensitizers. This is in accord with the absence of a diene concentration dependence on ϕ_{CB} in different experiments and the absence of α- or β-AN fluorescence quenching by BCH. In the case of the longer lived lowest excited singlet states of the hydrocarbon sensitizers F and N, it is necessary to consider both self-quenching and BCH quenching interactions. Since doubling the concentration of either F or N has no effect on ϕ_{CB}, self-quenching appears to have no effect on ϕ_{is} in the concentration ranges employed in our experiments. Studies on naphthalene monomer and excimer fluorescence are consistent with this conclusion.[23-25] Excimer fluorescence is observed only at very high

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(18) Caldwell, R. A.; Misawa, H.; Healy, E. F.; Dewar, M. J. S. *J. Am. Chem. Soc.* **1987**, *109*, 6869.

(19) Liu, R. S. H.; Turro, N. J.; Hammond, G. S. *J. Am. Chem. Soc.* **1965**, *87*, 3406.

(20) Dilling, W. L.; Kroening, R. D.; Little, J. C. *J. Am. Chem. Soc.* **1970**, *92*, 928.

(21) Saltiel, J.; Metts, L.; Sykes, A.; Wrighton, M. *J. Am. Chem. Soc.* **1971**, *93*, 5302.

(22) Jacobs, H. J. C.; Havinga, E. *Adv. Photochem.* **1979**, *11*, 305.

(23) Döller, E.; Förster, Th. *Z. Phys. Chem.* **1962**, *31*, 274; **1962**, *34*, 132.

(24) Mataga, N.; Tomura, M.; Nishimura, N. *Mol. Phys.* **1965**, *9*, 367.

(25) Selinger, B. K. *Aust. J. Chem.* **1966**, *19*, 825.

(26) Herkstroeter, W. G.; Lamola, A. A.; Hammond, G. S. *J. Am. Chem. Soc.* **1964**, *86*, 4537.

(27) Saltiel, J.; Jones, B. Unpublished results based on the method in ref 14 using 1,3-pentadiene photoisomerization.

[N] $\gtrsim$ 0.5 M[23,24] with the same lifetime as that of the monomer,[24] and N's fluorescence lifetime is independent of [N] for [N] $\gtrsim$ 0.5 M in hydrocarbon solvents. Thus, at room temperature, at least for naphthalene, monomer and excimer exist in equilibrium and direct deactivation of the excimer by spontaneous processes is negligible.[25] The data in Table III and the relationship

$$\phi_{is} = \phi_{is}^0/(1 + k_q\tau_f[\mathrm{BCH}]) \qquad (6)$$

were used to correct ϕ_{is} for F and N for the quenching of their singlet states by BCH. Stern–Volmer plots of the fluorescence quenching data in Table III are linear and give $k_q\tau_f$ values of 8.2 ± 0.9 M^{-1} (Ar purged) and 8.9 ± 0.7 M^{-1} (air) for fluorene and 22.5 ± 0.7 M^{-1} (Ar purged) and 23.7 ± 1.4 M^{-1} (air) for naphthalene. Use of eq 6 with average $k_q\tau_f$ values gives $\phi_{is} = 0.75\phi_{is}^0$ and $\phi_{is} = 0.52\phi_{is}^0$ for fluorene and naphthalene, respectively.

Evaluation of the ϕ_{CB}/ϕ_{is} values in Table IV is somewhat clouded by uncertainties in some of the ϕ_{is} values. No values of ϕ_{is} for XT could be found, but on the basis of its ϕ_{CB} value, it must be close to unity. Of greater concern are uncertainties in the ϕ_{is}^0 values of N and F. The $\phi_{is}^0 = 0.82$ for N reported by Horrocks and Wilkinson[28] was corrected for BCH fluorescence quenching to give $\phi_{is} = 0.43$, in very good agreement with $\phi_{is} = 0.39$ obtained by Lamola and Hammond[14] in the presence of 0.05 M 1,3-pentadiene. It should be noted here that correction for 1,3-pentadiene quenching of N fluorescence had yielded $\phi_{is}^0 = 0.67$,[29] which is somewhat lower than the Horrocks and Wilkinson value adopted here. More serious is the uncertainty in ϕ_{is}^0 for F for which ϕ_{is} values in the range 0.10–0.32 have been reported at different [F] and in different solvents.[14,28,30,31] There is also significant variation in ϕ_f values for F depending on solvent and investigator.[28,30-32] A $\phi_{is} = 0.31$ value for benzene as solvent, based on the cis → trans photoisomerization of 1,3-pentadiene, provides the lower limit for ϕ_{is}^0 under our conditions since it is not corrected for 1,3-pentadiene fluorescence quenching.[14] If the fluorescence of F were quenched by 1,3-pentadiene and BCH with similar efficiencies, as is the case for N, this value of ϕ_{is} should be close to the effective value under our conditions and it has accordingly been used in Table IV. We note that $\phi_{is}^0 = 0.45$ for F in benzene together with our fluorescence quenching measurements would give $\phi_{is} = 0.34$ in the presence of 0.040 M BCH and would result in $\phi_{CB}/\phi_{is} = 11.4 \times 10^{-3}$, the value obtained with benzophenone as sensitizer. Some support for this ϕ_{is}^0 value is provided by the reported $\phi_f = 0.52 \pm 0.10$ in *n*-hexane,[31] which is consistent with $\phi_{is} + \phi_f = 1$ for F, as is commonly the case for aromatic hydrocarbons.[28] The much larger ϕ_f reported for F in cyclohexane[32] seems suspect.

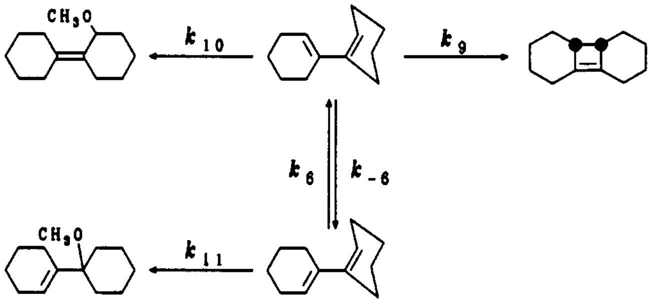
In light of the previous results, we conclude that ϕ_{CB}/ϕ_{is} in benzene is independent of donor E_T for $E_T \gtrsim 60.9$ kcal/mol but increases slightly at $E_T = 56.4$ kcal/mol. Our confidence in this conclusion is enhanced by the observation that ϕ_{CB} values for β- and α-AN are systematically higher than those of BP at all temperatures examined (Table I). The change is sufficiently small to be readily accommodated by the limiting case of full equilibration of *ct*-BCH conformers, eq 4, with α_c slightly larger than α_t. However, the change would also be accommodated if *ct*-BCH conformer equilibration were not fully attained so that favoring of s-cis triplets by the lower energy donor favors initial formation of *s-cis,ct*-BCH accounting for the increase in ϕ_{CB}/ϕ_{is}. This latter mechanism is supported by the observations in methanol, as discussed in the following text.

Table V. Effect of Sensitizer E_T on Product Ratios in Methanol, 30 °C

sensitizer	E_T[a] (kcal/mol)	relative ϕ ratios[b] $(\phi_{CB}/\phi_{1,2\text{-}E})_S/(\phi_{CB}/\phi_{1,2\text{-}E})_{XT}$	$(\phi_{1,4\text{-}E}/\phi_{1,2\text{-}E})_S/(\phi_{1,4\text{-}E}/\phi_{1,2\text{-}E})_{XT}$	$(\phi_{1,4\text{-}E}/\phi_{CB})_S/(\phi_{1,4\text{-}E}/\phi_{CB})_{XT}$
XT	74.2	1.00	1.00	1.00
BP	69.2	0.92 (9)	1.00 (4)	1.05 (6)
TXT	65.5	1.06 (6)	1.08 (3)	1.01 (9)
β-A	59.5	1.22 (7)	1.23 (2)	1.00 (9)
α-A	56.4	1.44 (6)	1.39 (2)	0.97 (10)

[a] BP and β-A in EPA glass, 77 K; others in hydrocarbon glass, 77 K. [b] Based on $\phi_{CB}/\phi_{1,2\text{-}E} = 0.564$ (30), $\phi_{1,4\text{-}E}/\phi_{1,2\text{-}E} = 0.313$ (5), and $\phi_{1,4\text{-}E}/\phi_{CB} = 0.565$ (30) for XT, Table I.

Scheme II



Analysis of ϕ_{CB}/ϕ_{is} values in methanol is hampered by the absence of ϕ_{is} values for most of the sensitizers in that solvent. The benzene to methanol solvent change can seriously attenuate ϕ_{is} as is evident in the relatively low product quantum yields obtained for XT and TXT in methanol. It is also noteworthy that benzil and fluorenone, ϕ_{is} = 0.92 and 0.93 in benzene,[14,21,33] respectively, failed to sensitize BCH product formation in methanol. That the result with fluorenone reflects inefficient formation of triplets[33,34] rather than the lower E_T value is suggested by the observation of very low efficiency of singlet oxygen sensitization by fluorenone in methanol.[35] Strong evidence based on fluorenone sensitization of stilbene photoisomerization and of fluorenone photoreduction by triethylamine indicates that ϕ_{is} of fluorenone drops to ~0.11 in isopropyl alcohol.[36]

Evaluation of conformational control of products in methanol is achieved by considering the effect of E_T on the product ratios (Table V). Product ratios are more accurate than quantum yields and are independent of ϕ_{is} and, for the full equilibration case, of the efficiency of formation of *ct*-BCH (i.e., any differences between $\alpha_c f_c$ and $\alpha_t f_t$). The ratios in Table V reveal identical, small but significant increases in $\phi_{CB}/\phi_{1,2\text{-}E}$ and $\phi_{1,4\text{-}E}/\phi_{1,2\text{-}E}$ as E_T is decreased to 65.5 kcal/mol and below. This behavior suggests strongly that CB and 1,4-E have a common precursor whose formation is favored as E_T is lowered. Obviously, an attractive mechanism that explains the observed trends involves exclusive formation of CB and 1,4-E from *s-cis,ct*-BCH. Scheme II shows the minimum expansion of Scheme I that would account for the observations in methanol. As expected, the limiting case of full conformer equilibration requires that product ratios be independent of E_T. It follows that, though nearly complete, equilibration of

$$\frac{\phi_{CB}}{\phi_{1,2\text{-}E}} = \frac{k_9K_6}{k_{11}} \qquad (7)$$

$$\frac{\phi_{1,4\text{-}E}}{\phi_{1,2\text{-}E}} = \frac{k_{10}K_6}{k_{11}} \qquad (8)$$

ct-BCH conformers is not fully achieved during their short lifetime. Furthermore, since changes in the product ratios with E_T in methanol (Table V) are very similar to corresponding changes in ϕ_{CB}/ϕ_{is} (Table IV), it seems reasonable to conclude that incomplete equilibration of conformers accounts for ϕ_{CB}/ϕ_{is} changes in benzene as well.

The conclusion that 1,4-E formation occurs by addition of the elements of methanol to the s-cis conformer of *ct*-BCH seems to

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(28) Horrocks, A. R.; Wilkinson, F. *Proc. R. Soc. London, A* **1968**, *306*, 257.

(29) Stephenson, L. M.; Hammond, G. S. *Pure Appl. Chem.* **1968**, *16*, 125.

(30) Sandros, K. *Acta Chem. Scand.* **1969**, *22*, 2815.

(31) Heinzelmann, W.; Labhart, H. *Chem. Phys. Lett.* **1969**, *4*, 20.

(32) Berlman, I. B. *Handbook of Fluorescence Spectra of Aromatic Molecules*, 2nd ed.; Academic Press: New York, 1971.

(33) Andrews, L. J.; Deroulede, A.; Linschitz, H. *J. Phys. Chem.* **1978**, *82*, 2304.

(34) Caldwell, R. A. *Tetrahedron Lett.* **1969**, 2121.

(35) Oliveros, E.; Suardi-Murasecco, P.; Braun, A. M. Private communication.

(36) Guttenplan, J. B.; Cohen, S. G. *Tetrahedron Lett.* **1969**, 2125.

rule out a stepwise mechanism of protonation of the trans double bond followed by reaction of the resulting allylic cation with methoxide or methanol. We favor, therefore, a mechanism involving concerted C–H and C–O bond formation in the rate-limiting step.

Solvent Deuterium Isotope Effect. Intimate involvement of proton transfer in the transition state for ether formation is established by the pronounced solvent isotope effects measured for the BP-sensitized excitation of BCH at 30 °C (Table II). Deuterium substitution of the hydroxylic hydrogen of methanol gives $\phi_{1,2\text{-E}}{}^{H}/\phi_{1,2\text{-E}}{}^{D} = 8 \pm 1$ and $\phi_{1,4\text{-E}}{}^{H}/\phi_{1,4\text{-E}}{}^{D} = 10 \pm 2$. These large values probably include contributions from secondary and transfer isotope effects.[37,38] The decrease in ether yields is accompanied by an increase of 12–25% in ϕ_{CB}, again implicating *ct*-BCH as the common intermediate in cyclobutene and ether formation. Though the uncertainties in the deuterium isotope effects for the two ethers are large, there is no doubt that the 1,2-E/1,4-E ratio is significantly larger in CH_3OD. The difference in isotope effects is consistent with separate transition states involving the *s-cis*,-*ct*-BCH conformation for the 1,4-E and the *s-trans*,*ct*-BCH conformation for 1,2-E. Observations concerning the methanol concentration dependence of ether formation will be presented in a separate paper. They suggest that more than one methanol molecule is involved in the transition states of ether formation.[39]

Temperature Effect on Product Quantum Yields. Examination of the quantum yields in Table I shows that as the temperature is increased from 30.0 to ~47 °C, ϕ_{CB}'s *increase* slightly in both benzene (~4–10%) and methanol (~6–14%) whereas $\phi_{1,2\text{-E}}$'s and $\phi_{1,4\text{-E}}$'s in methanol undergo a much more pronounced *decrease* (~60–90%). Interestingly, the relative increase of the $\phi_{1,4\text{-E}}/\phi_{1,2\text{-E}}$ ratio as E_T is lowered at 30 °C is maintained at all temperatures.

(a) Cyclobutene. Treatment of the small ϕ_{CB} changes cannot reasonably be based on as complex an expression as eq 1 in the absence, at least, of independent observations concerning the energetics of conformer equilibration in *cc*- and *ct*-BCH. In the cases of *β*- and *α*-AN, ϕ_{is} may also be temperature dependent. Consideration of the energetics for s-trans ⇄ s-cis conformer equilibration in 1,3-butadiene is, however, instructive. Numerous determinations place the potential energy difference between the two conformers at ~3.0 kcal/mol[40,41] and the barrier height for interconversion of the conformers at ~7 kcal/mol relative to the more stable s-trans conformer (e.g., see refs 42–44). Assuming a conservative *A* factor of 10^{12} s^{-1}, these energies predict $k_6 \simeq 9 \times 10^6$ and $k_{-6} \simeq 1.3 \times 10^9$ s^{-1} at 30 °C. Clearly, k_{-6} is much larger than the observed decay rate constant of *ct*-BCH, ~10^6 s^{-1}, whereas k_6 is ~1 order of magnitude larger than the decay rate constant. These approximate rate constants taken together with the identity of the *ct*-BCH transient absorption spectra and decay rate constants obtained with BP and *β*-propionaphthone as sensitizers[5] suggest strongly that conformer equilibration is nearly complete within the lifetime of *ct*-BCH and that eq 4 gives ϕ_{CB} to a very good approximation. Furthermore, as full equilibration conditions are approached, the effective lifetime of *ct*-BCH in benzene should be given by

$$\tau_{obsd} = \frac{1}{k_8 + K_6(k_7 + k_9)} \qquad (9)$$

and eq 4 can be rewritten as

$$\phi_{CB} = \phi_{is}k_9K_6[\alpha_c f_c + \alpha_t f_t]\tau_{obsd} \qquad (10)$$

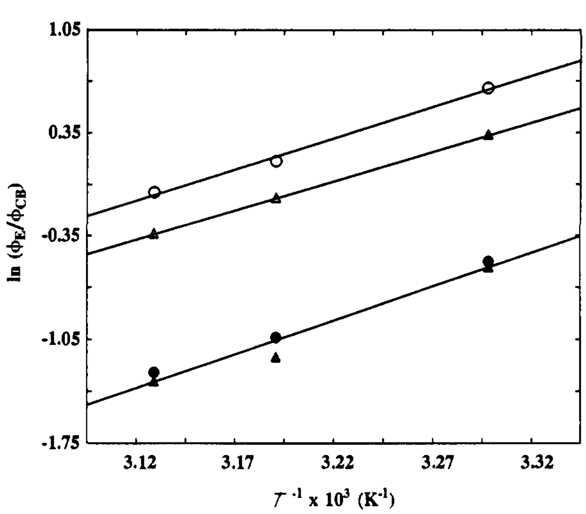

Figure 1. Plots of ln ($\phi_{1,2\text{-E}}/\phi_{CB}$) (open symbols) and ln ($\phi_{1,4\text{-E}}/\phi_{CB}$) (closed symbols) vs T^{-1} for BP- (circles) and *β*-AN- (squares) sensitized reaction of BCH in methanol.

Since, as is evident from its UV absorption spectrum, *cc*-BCH exists mainly in the s-trans conformation in our temperature range, $f_t \simeq 1$ for BP and eq 10 can be simplified to

$$(\phi_{CB}/\phi_{is}) = k_9K_6\alpha_t\tau_{obsd} \qquad (11)$$

Equations 10 and 11 can be applied to account for the small sensitivity of ϕ_{CB} to temperature changes in the 30–47 °C range by assuming that for benzophenone and the acetonaphthones ϕ_{is}'s are independent of temperature, a safe assumption at least in the case of benzophenone.[45] The temperature independence of the decay fractions of twisted olefin triplets has been established for the 2,4-hexadienes[46] and for stilbene.[47] It seems likely, therefore, that α_t and α_c are similarly insensitive to temperature changes. Accordingly, plots of ln (ϕ_{CB}/ϕ_{is}) vs T^{-1} should be linear with slopes, $s = -(\Delta H_6 + E_9 - E_{obsd})/R$ where E_{obsd} is the Arrhenius activation energy of the *ct*-BCH decay rate constants. In view of the small changes in ϕ_{CB} and the small *T* range, such plots are rather erratic; however, the overall trends with all three sensitizers are accounted for by $\Delta H_6 + E_9 - E_{obsd} = 1.7 \pm 0.7$ kcal/mol. If these quantities are nearly solvent independent, we may use E_{obsd} for acetonitrile[5] to obtain $\Delta H_6 + E_9 \simeq 9.9 \pm 0.9$ kcal/mol.

(b) Ethers. Since *s-cis*,*ct*-BCH has been established as the common precursor for CB and 1,4-E, use of the complex expression, analogous to eq 1, for $\phi_{1,4\text{-E}}$ in accounting for its *T* dependence can be circumvented by considering the *T* dependence of $\phi_{1,4\text{-E}}/\phi_{CB}$

$$\frac{\phi_{1,4\text{-E}}}{\phi_{CB}} = \frac{k_{10}}{k_9} \qquad (12)$$

Indeed, plots of ln ($\phi_{1,4\text{-E}}/\phi_{CB}$) vs T^{-1} for the sets of BP and *β*-AN data in Table I are linear with slopes corresponding to $E_9 - E_{10} = 8.85$ and 9.27 kcal/mol, respectively, and intercepts giving ln (A_{10}/A_9) = −15.2 and −16.0, respectively. Furthermore, as expected from the common precursor mechanism, the points for the two sets of data do not deviate significantly from a common line (Figure 1). The interesting conclusion is that $E_{10} \simeq -\Delta H_6$, indicating that the rate constant for 1,4-E formation from *s-cis*,*ct*-BCH is either activationless or has a slightly negative activation energy, and that the process is controlled primarily by an unfavorable entropy of activation, $\Delta S_{10}{}^{\ddagger} - \Delta S_9{}^{\ddagger} \simeq -31$ cal/(deg·mol).

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(37) Bell, R. P. *The Proton in Chemistry*, 2nd ed.; Cornell University Press: New York, 1973; Chapters 11 and 12.

(38) Buncel, E., Lee, C. C., Eds.; *Isotopes in Organic Chemistry II*; Elsevier: New York, 1976; Chapter 2.

(39) Saltiel, J.; Marchand, G. R.; Sears, D. F., Jr. Manuscript in preparation.

(40) Sun, Y.-P.; Sears, D. F., Jr.; Saltiel, J. *J. Am. Chem. Soc.* **1988**, *110*, 6277 and references cited therein.

(41) Mui, P. W.; Grunwald, E. *J. Am. Chem. Soc.* **1982**, *104*, 6562.

(42) Bock, C. W.; George, P.; Trachtman, M.; Zanger, M. *J. Chem. Soc., Perkin Trans. 2*, **1979**, 26.

(43) Carreira, L. A. *J. Chem. Phys.* **1975**, *62*, 3851.

(44) Durig, J. R.; Bucy, W. E.; Cole, A. R. H. *Can. J. Phys.* **1975**, *53*, 1832.

(45) Sun, Y.-P.; Sears, D. F., Jr.; Saltiel, J. *J. Am. Chem. Soc.* **1989**, *111*, 706.

(46) Saltiel, J.; Rouseau, A. D.; Sykes, A. *J. Am. Chem. Soc.* **1972**, *94*, 5903; **1973**, *95*, 988.

(47) Saltiel, J.; Rousseau, A. D.; Thomas, B. *J. Am. Chem. Soc.* **1983**, *105*, 7631.

On the basis of Schemes I and II, the full expression for $\phi_{1,2\text{-E}}$ is given by

$$\phi_{1,2\text{-E}} = \frac{\phi_{is}k_{11}[\alpha_t f_1(k_{-6} + k_7 + k_9 + k_{10}) + \alpha_c f_c k_{-6}]}{(k_7 + k_9 + k_{10})(k_6 + k_8 + k_{11}) + k_{-6}(k_8 + k_{11})} \tag{13}$$

and the $\phi_{1,2\text{-E}}/\phi_{CB}$ ratio is given by

$$\frac{\phi_{1,2\text{-E}}}{\phi_{CB}} = \frac{k_{11}[\alpha_t f_t(k_{-6} + k_7 + k_9 + k_{10}) + \alpha_c f_c k_{-6}]}{k_9[\alpha_t f_t k_6 + \alpha_c f_c(k_6 + k_8 + k_{11})]} \tag{14}$$

As pointed out previously, eq 14 reduces to eq 7 if *ct*-BCH conformer equilibration is fully established. Interestingly, this same limiting equation should also be approached for high E_T donors even in the absence of full conformer equilibration. This can be seen by setting $f_t = 1$ in eq 14 to obtain

$$\frac{\phi_{1,2\text{-E}}}{\phi_{CB}} = \frac{k_{-6} + k_7 + k_9 + k_{10}}{k_9 k_6} \tag{15}$$

which is nearly equivalent to eq 7 since $k_{-6} \gg (k_7 + k_9 + k_{10})$. Plots of ln ($\phi_{1,2\text{-E}}/\phi_{CB}$) vs T^{-1} for the BP and β-AN data are linear (Figure 1) and have nearly identical slopes, *s*: $sR = 8.39$ kcal/mol, $iR = -26.4$ cal/(deg·mol) for BP; $sR = 7.89$ kcal/mol, $iR = -25.4$ cal/(deg·mol) for β-AN. The slope for the benzophenone line gives, to a good approximation, $E_{11} - E_9 - \Delta H_6 = -8.39$ kcal/mol. Together with our estimate of $E_9 + \Delta H_6$, this leads to $E_{11} \simeq 1.5 \pm 1.0$ kcal/mol, indicating that formation of 1,2-E from the s-trans conformer of *ct*-BCH is also nearly barrierless. The intercept of the BP plot gives $\Delta S_{11}^{\ddagger} - \Delta S_9^{\ddagger} - \Delta S_6 = -25$ cal/(deg·mol), reflecting a very unfavorable activation entropy for 1,2-E formation. The activation entropies for both ethers are consistent with highly ordered transition states involving simultaneous formation of C–H and C–O bonds as suggested previously. The small negative activation enthalpies associated with these reactions may suggest that an exothermic preequilibration between *ct*-BCH and methanol molecules gives complexes that are in the paths to the rate-determining steps for ether formation. Examples of excellent precedents for this inference are provided by photocycloaddition reactions for which a negative temperature dependence of apparent rate constants has led to the postulation of reversible exciplex formation in the pathway to cycloadducts.[48]

Summary

Identical but weak dependencies of quantum yield ratios $\phi_{1,4\text{-E}}/\phi_{1,2\text{-E}}$ and $\phi_{CB}/\phi_{1,2\text{-E}}$ for the triplet-sensitized reactions of BCH in methanol on donor E_T suggest that *s-cis,ct*-BCH is a common precursor for 1,4-*E* and CB, while 1,2-E forms predominately from the more abundant s-trans conformer. The temperature dependence of these ratios (30–47 °C) shows that CB formation from *ct*-BCH has a slightly higher activation energy than isomerization back to *cc*-BCH. Ether formation is nearly barrierless and is controlled by unfavorable entropies of activation. An exothermic preequilibrium of BCH with methanol molecules followed by concerted C–H and C–O bond formation in this reactive complex could account for these observations. The intimate involvement of proton transfer in the rate-determining steps for ether formation is indicated by large solvent deuterium isotope effects. In view of the likely involvement of more than one methanol molecule in these ether formations, alternative, entropy-controlled, one-step mechanisms that proceed with negative activation enthalpies, without the intervention of complexes, seem less probable. We note, however, that one-step processes have been postulated for additions of certain singlet carbenes to olefins.[49,50]

Experimental Section

Materials. Melting points were measured with a Buchi oil-bath apparatus and are uncorrected. α-Acetonaphthone (J. T. Baker, practical grade) was distilled twice under reduced pressure on a 19-in. Nester-Faust spinning band column to 95% purity according to GLC. β-Acetonaphthone (Matheson, Coleman and Bell) was recrystallized twice from 95% ethanol and sublimed under reduced pressure, mp 53–54 °C. Benzene (Mallinkrodt, SpectrAR) was used as received. Benzil (J. T. Baker) was recrystallized from 95% ethanol and chromatographed on alumina, mp 95°C. Benzophenone (Fisher, Certified reagent) was recrystallized twice from *n*-hexane and sublimed under vacuum, mp 48 °C. Chloroform (Mallinkrodt, SpectrAR) was used as received. Chrysene (J. T. Baker) was chromatographed on alumina with benzene as eluent, mp 254.0–255.0 °C. Deuteriochloroform (Aldrich, Gold Label, 99.8 atom % D) was used as received. *n*-Dodecane (Chemical Samples Co., 99%) was distilled prior to use. Fluorene (Aldrich, 98%) was recrystallized from ethanol and sublimed under reduced pressure, mp 113–114 °C. Fluorenone (Matheson, Coleman and Bell) was recrystallized twice from toluene and sublimed under reduced pressure, mp 83.5–84.0 °C. *n*-Hexane (Mallinkrodt, reagent grade) was distilled prior to use. Methanol (J. T. Baker, Photrex; Eastman, Spectro ACS; or Mallinkrodt, SpectrAR, anhydrous) was distilled from anhydrous sodium or potassium carbonate immediately prior to use. Methanol-O-*d* (Aldrich, Gold Label, 99.5 atom % D) was used as received. Michler's ketone (4,4′-bis(dimethylamino)benzophenone, Matheson, Coleman and Bell) was recrystallized from ethanol and sublimed under reduced pressure, mp 175–176 °C. Naphthalene (Matheson, Coleman and Bell) was recrystallized from ethanol and sublimed under reduced pressure, mp 78–79 °C. Potassium bromide (Mallinkrodt, IR gade) was used as received. Sodium borohydride (J. T. Baker, 98%) was used as received. *trans*-Stilbene (Aldrich, reagent grade, 96%) was recrystallized twice from ethanol, chromatographed on alumina with *n*-hexane as eluent, and sublimed under reduced pressure to 99.8% purity according to GLC, mp 123.5–124.5 °C. Tetramethylsilane (J. T. Baker, analyzed reagent grade) was used as received. Thioxanthone (Aldrich, research grade) was chromatographed on alumina with benzene as eluent and recrystallized from chloroform, mp 210.5–211.0 °C. Xanthone (Aldrich, research grade) was chromatographed on alumina with benzene as eluent and zone refined, mp 175.0 °C. 1,1′-Bicyclohexenyl was synthesized by procedures a and b.

Procedure a. 2′-Ketobicyclohex-1-ene. The compound was prepared from cyclohexanone (J. T. Baker) as described by Gault et al.[51] It was contaminated by 10% of the conjugated ketone.[52,53]

2′-Hydroxybicyclohex-1-ene. To 2′-Ketobicyclohex-1-ene (348 g, 1.9 mol) dissolved in 1.2 L of methanol in a 2-L round-bottomed (RB) flask was added $NaBH_4$ (42 g, 1.1 mol) over a period of 3 h while the flask was cooled in an ice bath to keep the reaction temperature at ~30 °C. After being left to stand overnight, the reaction mixture was diluted with H_2O (1.5 L) and extracted with ether (4 × 250 mL), the ether layers were dried with Na_2SO_4 (anhydrous), and the ether was removed under reduced pressure (rotoevaporator). 2′-Hydroxybicyclohex-1-ene was obtained as a colorless oil (307 g, 90% yield) contaminated by 10% 2-hydroxybicyclohexylidene: ^{1}H NMR (60 MHz, $CDCl_3$), $\delta = 1.0$–2.7 (m, 19.6 H), 3.9 (broad s, 1 H), 5.5 (m, 1 H) ppm.

1,1′-Bicyclohexenyl. 2′-Hydroxybicyclohex-1-ene (300 g, 1.7 mol) dissolved in 1.5 L of pyridine (distilled from KOH) was placed in a 3-L, three-neck RB flask equipped with an efficient reflux condenser and an addition funnel. $POCl_3$ (340 mL, 3.7 mol, Mallinkrodt) was added over the course of 0.5 h and the solution gently refluxed for 1 h. After being cooled for 1 h, ice (800 g) was added to the reaction through the top of the reflux condenser (exothermic) while the flask was cooled in an ice–water bath. After being left to stand for 45 min, the top organic layer was removed, ether (400 mL) was added to the aqueous layer, the mixture was agitated, and the ether layer was removed. The combined organic layers were washed with 3 × 200 mL portions of water and dried with $MgSO_4$ (anhydrous), and the ether was removed (rotoevaporator). The resulting colorless oil (228 g, 85% theoretical, 90% BCH, GLC) was twice recrystallized from methanol (500 mL) and cooled to dry-ice temperature in 50-g batches. The recrystallized BCH (94.3 g, 99%, GLC) was distilled at reduced pressure (101–102 °C (0.25 Torr)), yielding 76.3 g, 99.5% pure according to GLC: ^{1}H NMR (270 MHz, $CDCl_3$) $\delta = 1.59$ (m, 8 H), 2.13 (m, 8 H), 5.75 (s, 2 H), ppm; IR (cm^{-1}, neat) 2870, 1530, 1440, 1325, 1260, 1240, 1130, 1070, 1050, 1000, 920, 860, 820, 790, 740, 725, 690.

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(48) (a) Chapman, O. L.; Lura, R. D. *J. Am. Chem. Soc.* **1970**, *92*, 6352. (b) Saltiel, J.; D'Agostino, J. T.; Chapman, O. L.; Lura, R. D. *J. Am. Chem. Soc.* **1971**, *93*, 2804.

(49) Houk, K. N.; Rondan, N. G.; Mareda, J. *J. Am. Chem. Soc.* **1984**, *106*, 4291. Houk, K. N.; Rondan, N. G. *J. Am. Chem. Soc.* **1984**, *106*, 4293 and references therein. Houk, K. N.; Rondan, N. G.; Mareda, J. *Tetrahedron* **1985**, *41*, 1555.

(50) Moss, R. A.; Kawrynowicz, W.; Turro, N. J.; Gould, I. R.; Cha, Y. *J. Am. Chem. Soc.* **1986**, *108*, 7028 and references therein.

(51) Gault, M. H.; Daltroff, L.; Eck-Tridon, J. *Bull. Soc. Chim. Fr.* **1945**, *12*, 952.

(52) Creese, M. W.; Smisswam, E. E. *J. Org. Chem.* **1976**, *41*, 169.

(53) Wenkert, E.; Bhattacharya, S. K.; Wilson, E. M. *J. Chem. Soc.* **1964**, 5617.

Procedure b for 1,1′-bicyclohexenyl formation was essentially as described by Gruber and Adams.[54] Distillation of the final product through a 19-in. Nester–Faust spinning band column (60 °C (~0.05 Torr)) removed a lower boiling impurity and gave 99.9% pure BCH according to GLC, with physical properties identical with those of the material from procedure a.

2-(1′-Chlorocyclohexyl)cyclohexanone. The compound was synthesized using the procedure of Wenkert et al.:[53] 97 g; 98% yield; light pink crystals; mp 35–37 °C; IR (cm^{-1}, KBr pellet) 2900, 1710, 1440, 1310, 1200, 1060, 920, 825, 800.

2-Ketobicyclohexylidene. The compound was sensitized as described by Reese:[55] 17 g; 22% yield; white needle-like crystals; 99% pure by GLC; mp 50–52 °C; IR (cm^{-1}, KBr pellet) 2900, 1670, 1440, 1270, 1205, 1120, 1055, 1000, 930, 890, 850, 820.

2-Hydroxybicyclohexylidene. To 2-ketobicyclohexylidene (16 g, 0.09 mol) dissolved in 60 mL methanol was added NaBH$_4$ (2 g, 0.053 mol, J. T. Baker) over 0.5 h. To the reaction mixture, left to stand overnight, were added 200 mL of ether and 200 mL of water; the ether layer was separated, washed with 3 × 100 mL portions of water, and dried with MgSO$_4$ (anhydrous), and the ether was removed (rotoevaporator). The yield was 17 g (0.094 mol, 104% theoretical) of a white solid. A portion of the solid (1 g) was recrystallized from CH$_3$OH/H$_2$O (70:30): mp 102.0 °C (sharp); ^{1}H NMR 60 MHz, CDCl$_3$), δ = 1.2–2.0 (m, 13 H), 2.2 (m, 6 H), 4.9 (m, 1 H) ppm; IR (cm^{-1}, KBR pellet) 3300, 3000, 2940, 1860, 1500, 1300, 1265, 1200, 1150, 1020, 990, 970, 920, 890, 880, 860, 820.

2-Methoxybicyclohexylidene (1,4-E). 2-Hydroxybicyclohexylidene (17 g, 0.094 mol) was dissolved in 100 mL of dry ether and the solution placed in a 500-mL, two-neck, RB flask equipped with an addition funnel, reflux condenser, and a CaCl$_2$ drying tube. NaH (9 g, 0.19 mol, 50% in oil, J. T. Baker) was added and the reaction mixture refluxed for 0.5 h. Methyl iodide (18 g, 0.13 mol, Fisher) was added slowly and the mixture refluxed gently for 2 h: ^{1}H NMR (270 MHz, CDCl$_3$) was identical to that of the isolated photoproduct, see the following text; ^{13}C NMR (CDCl$_3$), δ = 135.1 (s), 128.0 (s), 74.4 (d), 54.7 (quartet), 33.2, 30.6, 28.75, 28.68, 27.9, 27.2, 24.6, 21.0 (all triplets) ppm.

Photoproduct Isolation. Tricyclo[6.4.0.0^{2,7}]-*cis*-7,8-dodec-1-ene (CB). The compound was prepared from BCH by chrysene-sensitized excitation in benzene. It was purified by chromatography first on 20% AgNO$_3$/aluminum with *n*-pentane as eluent and then on alumina with *n*-hexane as eluent. An analytical sample (99.4% pure, GLC) was obtained by recrystallization 2× from methanol at dry-ice temperature: ^{1}H NMR (200 MHz, CDCl$_3$) δ = 1.17 (m, 6 H), 1.72 (m, 8 H), 2.2 (m, 2 H), 2.4 (m, 2 H) ppm; ^{13}C NMR (67.9 MHz, CDCl$_3$) δ = 137.8 (s), 42.4 (d), 27.6 (t), 27.1 (t), 24.8 (t) ppm.

1-(1-Cyclohexenyl)-1-methoxycyclohexane (1,2-E). A solution of BCH (5 g, 0.031 mol) and BP (1.3 g, 0.0071 mol) in 250 mL of absolute methanol (Mallinckrodt, SpectrAR) was irradiated for 103.5 h in a cylindrical Pyrex Hanovia reactor fitted with a Pyrex lamp probe, a 550-W Hanovia medium-pressure mercury lamp, and a fritted-glass bubbler for N$_2$ bubbling. The reaction was monitored by GLC, and several 0.5-g BP additions were necessary to replenish consumed sensitizer. The final composition was 2.8% CB, 6% BCH, 20% 1,4-E, and 58% 1,2-E by GLC. The methanol was removed (rotoevaporator), and 30 mL of *n*-hexane was added to the residue. The solution was decanted from the insolubles and a portion of it containing ~250 mg of the photoproducts chromatographed on silica gel (3%) ether/hexane as eluent, MPLC). Chromatography fractions were monitored by GLC. 1,2-E was isolated (~40 mg) 95% pure (^{1}H NMR (270 MHz, CDCl$_3$): δ = 1.1–1.6 (m, 12 H), 1.76 (m, 2 H), 1.93 (m, 2 H), 2.04 (m, 2 H), 2.95 (s, 3 H), 5.58 (m, 1 H) ppm). GLC–MS (EI, 70 eV) on a fresh photoproduct mixture gave the following for the peak corresponding to 1,2-E: *m/e* (% base peak) 194.2 (M$^+$, 45), 163.2 (12), 162.1 (15), 151.1 (100), 119.1 (24), 113.1 (20), 95.1 (14), 91.1 (30), 81.1 (28), 79.1 (21), 67 (21); similarly, GLC–MS (CI, isobutane, 70 eV) *m/e* (% base peak) 195.2 ((M + 1)$^+$, 5), 194.2 (M$^+$, 11), 193.2 (6), 164.2 (14), 163.2 (100).

2-Methoxybicyclohexylidene (1,4-E). The minor ether product, 20%, of the preparative reaction mixture described immediately above was isolated by chromatography on alumina. A sample of the *n*-hexane-soluble portion of the reaction mixture (~250 mg) was placed on a 5 × 30 cm column of alumina (Alcoa F-20) and eluted with 180 mL of *n*-hexane followed by 3% ether/hexane. Fractions were monitored by GLC. 1,4-E isolated (~20 mg) was contaminated by 7% 1,2-E and 10% *n*-hexane. The cleanly resolved region of the ^{1}H NMR spectrum was identical with that of the synthetic sample (see the previous text; ^{1}H NMR (270 MHz, CDCl$_3$) δ = 2.21 (m, 4 H), 2.45 (m, 1 H), 3.16 (s, 3 H), 4.34 (m, 1 H) ppm). An attempt to purify this material further by distillation at reduced pressure led to decomposition of 1,4-E. GLC–MS (EI, 70 eV) on a fresh photoproduct mixture gave, for the peak corresponding to 1,4-E, the following: *m/e* (% base peak) 194.2 (M$^+$, 6), 162.1 (100), 151.1 (24), 147.1 (9), 133.1 (19), 119.1 (19), 111.1 (12), 106.7 (13), 105.1 (11), 95.2 (20), 94.1 (37), 93.1 (16), 91.0 (31), 81.1 (32), 80.1 (20), 79.1 (35), 77.0 (16), 67.1 (24); similarly, GLC–MS (CI, isobutane, 70 eV) *m/e* (% base peak) 195.2 ((M + 1)$^+$, 2), 194.2 (M$^+$, 2), 193.2 (4), 164.2 (22), 163.2 (100), 162.2 (16), 161.2 (8).

Spectroscopic Measurements. Fluorescence measurements were made with a Hitachi/Perkin-Elmer MPF-2A spectrometer.[56] Square 1 × 1 cm quartz cells with Teflon stoppers (Wilmad Inc.) were employed. Sample solutions were outgassed by purging solutions with argon for 3 min. Spectra were recorded at ambient temperature (~23 °C). UV absorption spectra were obtained with Cary Model 14, 15, or 219 spectrophotometers. NMR spectra were recorded at room temperature with Varian HA-60-, Bruker HX-270-, or Bruker-IBM WPY-200-MHz instruments with tetramethylsilane or CHCl$_3$ as internal standard. IR spectra were obtained with a Perkin-Elmer Model 137 NaCl-prism IR spectrophotometer. Spectra of solids were in pressed KBr pellets. GLC–MS spectra were obtained with a Finnegan 4510 GC/MS System spectrometer.

Gas–Liquid Chromatography. Measurements were made with a Varian–Aerograph Model 2700 instrument equipped with dual flame ionization detectors and a Hewlett-Packard 3390A electronic integrator. CB, 1,2-E, and 1,4-E determinations were made using a 50-m fused silica capillary column with an OV-1 (poly(dimethylsiloxane)) liquid phase (Alltech) and operated over a programmed temperature range of 80 or 100–220 °C (10–20 °C/min). Samples requiring concentration prior to analysis were reduced in volume on a warm hot plate under a gentle stream of N$_2$ while gradually replacing the solvent with CHCl$_3$ or CS$_2$. Injection ports and flame detectors were maintained at 200–210 and ~250 °C, respectively. Molar response factors of BCH and the photoproducts relative to DD internal standard were obtained using standard solutions: BCH/DD = 0.965 ± 0.026; (1,2-E or 1,4-E)/DD = 1.06 ± 0.04; CB/DD = 0.96 ± 0.03. *trans*-Stilbene actinometers were analyzed using the same capillary GLC column[56] or a pair of matched $^1/_8$ in. × 5 ft columns packed with 5% Apiezon N or Supelcoport (80–100 mesh) and operated over a programmed temperature range of 170–210 °C (4–10 °C/min).

Quantum Yield Measurements. Solutions were loaded (3.0 mL, calibrated syringe) into ampules made from 13-mm o.d. Pyrex culture tubes fitted with 10/30 $\overline{\mathrm{T}}$ joints and grease traps. Solutions were degassed with ≥4 freeze–pump–thaw cycles to 10^{-6} Torr and the ampules flame sealed at a constriction. The Moses merry-go-round apparatus was immersed in a thermostated water bath. Hanovia medium-pressure Hg lamps (450- or 550-W, Ace Glass, Inc.) were used. Corning CS 7-37 and 0-52 filters transmitting a band of light between 355 and 380 nm were used to isolate the group of Hg lines around 366 nm. A 0.2–0.3-cm path length of a 500-mL aqueous filter solution of K$_2$Cr$_2$O$_7$ (1.0 g) and K$_2$CO$_3$ (15.0 g) was used for excitation at 313 nm.

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(54) Gruber, R. E.; Adams, R. *J. Am. Chem. Soc.* **1935**, *57*, 2555.

(55) Reese, J. *Chem. Ber.* **1942**, *75*, 384.

(56) Saltiel, J.; Dabestani, R.; Schanze, K. S.; Trojan, D.; Townsend, D. E.; Goedken, V. L. *J. Am. Chem. Soc.* **1986**, *108*, 2674.