Photochemistry of Inter- and Intramolecular α-Diketone:Norbornene Systems

Ronald R. Sauers,* Peter C. Valenti, and Charles A. Crichlow

Contribution from the New Brunswick Department of Chemistry, Rutgers, The State University, New Brunswick, New Jersey 08903. *Received March 22, 1982*

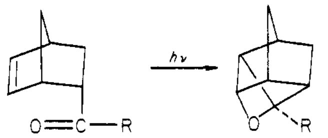
Abstract: Photocycloadditions of biacetyl to norbornene and *syn*-7-methyl- and *syn*-7-*tert*-butylnorbornene have been observed. The stereochemistry and quenching rates are consistent with increasing steric hindrance to the exo face of norbornene as the syn-7-substituent changes from H to CH_3 to t-C_4H_9. The intramolecular analogue of these reactions was studied via 1-(5′-norbornene-2′-yl)-1,2-propanedione, which gave an oxetane on direct irradiation at 300 or 430 nm or on benzophenone-sensitized addition. The direct irradiation reactions are believed to proceed via singlet states as evidenced by estimated lifetimes derived from quenching by *N,N*-dimethylaniline. The effective molarity (EM) for these reactions is estimated to be $>10^4$ (S_1) and $>10^5$ (T_1).

Introduction

Photocycloaddition reactions between excited carbonyl compounds and olefins are an important synthetic method for carbon–carbon bond formation.[1] This process, most commonly known as the Paterno–Büchi reaction, has been extensively studied from both a theoretical and an experimental point of view, and their is general agreement on many of the mechanistic details of these reactions. Thus, the initial stage of the reaction is believed to involve exciplex formation as a consequence of (weak) charge-transfer interactions.[2] This conclusion is based on studies involving quenching of excited carbonyl groups with olefins of varying ionization potential[2] and on a detailed Arrhenius study of phosphorescence quenching.[3]

The intervention of biradical intermediates has been inferred from kinetic studies[4] and from stereochemical results in which olefin geometry is at least partly altered during cycloaddition.[2,5]

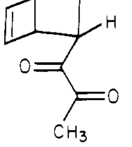
Despite these efforts many facets of these reactions are not well understood. These include prediction of regiochemistry[1] and quantum yields.[1,6] Our own interest in this reaction has been to extend the synthetic utility of the intramolecular oxetane reaction[6] and to further define the factors that govern the efficiency of these reactions. For these and other reasons we have examined the behavior of numerous *endo*-5-acylnorbornenes (**1**), many of which undergo clean cycloaddition to form oxetanes of structure **2** (eq 1). The preparative success of these reactions is a consequence of very rapid intramolecular quenching of the excited carbonyl groups by the double bonds to the exclusion of competing processes. Attempts to measure excited-state lifetimes by standard quenching techniques, i.e., Stern–Volmer analyses, failed because of the short lifetimes involved. By means of internal competition reactions singlet lifetimes of 10^{-11} s were estimated.[6] In at least one case (**1**, R = $C_{10}H_7$) the rate of reaction successfully competed with internal conversion and/or intersystem crossing of a naphthyl ketone. In this system we demonstrated that there were two reactive states, one of which was quenchable with dienes (T_1) and a more reactive upper state that was not (S_1 or T_2). A reactivity difference of ca. 10^6 was estimated for these two states.



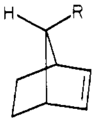
1 **2** (1)

In the present study we hoped to exploit the unique reactivity of acylnorbornenes to probe the behavior of excited states of α-diketones.[7,8] There is evidence from vapor-phase photochemical studies that S_2 states of biacetyl can react competitively with internal conversion.[8] In addition, Lemaire[9a] has proposed that enolization of biacetyl takes place from S_2 in solution phase in contrast to the reactions of monoaryl diketones.[9b] Incorporation of a biacetyl chromophore into the norbornene system affords the opportunity to compare the reactivity of several states of the same molecule that differ in excitation energy[10] (e.g., S_2 vs. S_1) and/or multiplicity and that might lead to differing products depending on these factors.

These objectives were to be met by a study of the photochemical and photophysical behavior of 1-(5′-norbornene-2′-yl)-1,2-propanedione (**3**). This molecule is ideally suited for studies at different wavelengths and sensitized photochemistry. As model systems we examined the photochemistry and reactivity of norbornene and some syn-7-substituted homologues (**4**) with biacetyl S_1 and T_1 states.[11]



3



4a, R = H
b, R = CH_3
c, R = t-C_4H_9

Results and Discussion

Two different synthetic sequences were devised for the preparation of **3**, neither of which was completely satisfactory. The

---

[1] (a) For a recent review that stresses synthetic applications see: Jones, G., II *Org. Photochem.* **1981**, *5*, 1. (b) Cowan, D. O.; Drisko, R. L. "Elements of Organic Photochemistry"; Plenum Press: New York, 1976; pp 181–198. (c) Turro, N. J. "Modern Molecular Photochemistry"; Benjamin/Cummings: 1978; pp 432–452.

[2] (a) Yang, N. C.; Hui, M. H.; Shold, D. M.; Turro, N. J.; Hautala, R. R.; Dawes, K.; Dalton, J. C. *J. Am. Chem. Soc.* **1977**, *99*, 3023. (b) Caldwell, R. A.; Sovocol, G. W.; Gajewski, R. P. *Ibid.* **1973**, *95*, 2549. (c) Kochevar, I. H.; Wagner, P. J. *Ibid.* **1970**, *92*, 3742.

[3] Maharaj, U.; Winnik, M. A. *J. Am. Chem. Soc.* **1981**, *103*, 2328.

[4] Saltiel, J.; Neuberger, K. R.; Wrighton, M. *J. Am. Chem. Soc.* **1969**, *91*, 3658.

[5] (a) Turro, N. J., Wriede, P. A. *J. Am. Chem. Soc.* **1970**, *92*, 320. (b) Yang, N. C.; Eisenhardt, W. *Ibid.* **1971**, *93*, 1277.

[6] (a) Sauers, R. R.; Rousseau, A. D.; Byrne, B. *J. Am. Chem. Soc.* **1975**, *97*, 4947. (b) Sauers, R. R.; Lynch, D. C. *J. Org. Chem.* **1980**, *45*, 1286.

[7] For a recent thorough study of biacetyl–olefin cycloadditions see: Jones, G., II; Santhanam, M.; Chiang, S.-H. *J. Am. Chem. Soc.* **1980**, *102*, 6088.

[8] For a summary of earlier work see: Calvert, J. G.; Pitts, J. N., Jr. "Photochemistry"; Wiley: New York, 1966; pp 421–422.

[9] (a) Irradiation of biacetyl below 310 nm is reported to lead to enol via the S_2 state; see: Lemaire, J. *J. Phys. Chem.* **1967**, *71*, 2653. (b) For a contrasting situation, see: Wagner, P. J.; Zepp, R. G.; Liu, K.-C.; Thomas, M.; Lee, T.-J.; Turro, N. J. *J. Am. Chem. Soc.* **1976**, *98*, 8125.

[10] Loutfy, R. O.; Dogra, S. K.; Yip, R. W. *Can. J. Chem.* **1979**, *57*, 342.

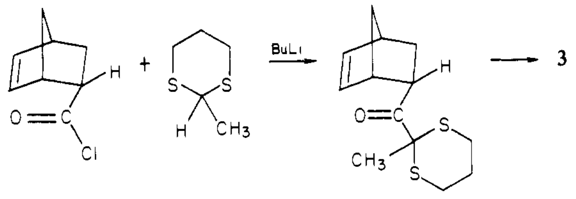
[11] A preliminary account of some of this work has been published: Sauers, R. R.; Valenti, P. C.; Tavss, E. *Tetrahedron Lett.* **1975**, 3129.

0002-7863/82/1504-6378$01.25/0

Table I. UV Absorption Data for α-Diketones

compound	solvent	λ_{max} (ϵ), nm
biacetyl[9a]	C_7H_{16}	273 (17), 422 (22), 448 (21)
6-heptene-2,3-dione[14]	C_5H_{12}	261 (234), 431 (22), 422 (22)
exo-3	*c*-C_6H_{12}	259 (358), 432 (15), 453 (13)
endo-3	*c*-C_6H_{12}	258 (424), 430 (29), 453 (27)

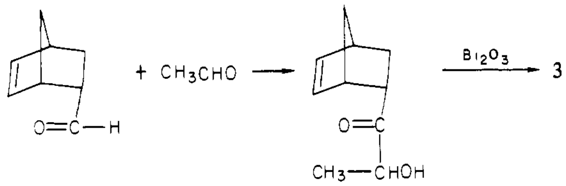
original objective was to use the Corey–Seebach[12a] acylation procedure to form the ketodithiane **5** followed by hydrolysis (eq 2).[12b] Reproducible but poor yields were obtained from this procedure.



5

(2)

The other procedure involved the novel procedure developed by Stetter[12c] in which acetaldehyde was condensed with 5-norbornene-2-carboxaldehyde (eq 3). α-Ketol **6** was oxidized to a diketone by means of bismuth oxide. Although the yields were acceptable, the reactions were accompanied by considerable epimerization as a result of the high basicity of the catalyst.



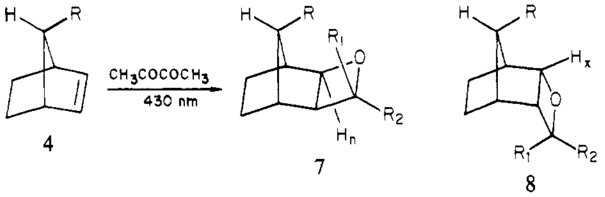
6

(3)

The diketone **3** was an unstable yellow oil whose ultraviolet absorption spectrum showed a striking enhancement of the two principal absorption bands (Table I). In addition, we show data for the corresponding exo isomer and the acyclic γ,δ-unsaturated analogue 6-heptene-2,3-dione.[13] It is interesting to note that the magnitude of the coupling of the chromophores in these systems is a function of both geometry and transition energy. The small enhancement (2-fold) and wavelength shift for the $S_0 \rightarrow S_1$ absorption in *endo*-**3** is typical of molecules in which the n orbital interacts directly with a π system.[14] The enhancement of the $S_0 \rightarrow S_2$ transition (25-fold) is unusually large, and we are unaware of any comparable data. Presumably the better matching of orbital energies gives rise to an increased perturbation interaction. The coupling in *exo*-**3** is attributed to interactions transmitted through the σ framework[15] and is also quite large as reflected by the $S_0 \rightarrow S_2$ transition (20-fold) but not by the $S_0 \rightarrow S_1$ transition.

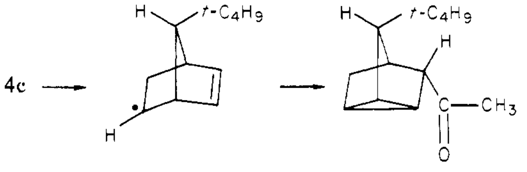
The fluorescence spectra of *exo*-**3** and *endo*-**3** were also quite different. Whereas *exo*-**3** showed emission (λ_{max} 474 nm) of intensity comparable to that of biacetyl[16] (λ_{max} 464 nm, ϕ_f 0.0029), the endo isomer showed virtually no emission (λ_{ex} 254–420 nm). Presumably the internal double bond of *endo*-**3** intercepts the singlet state of the diketone moiety before the latter can fluoresce. It was of interest to carry out the intermolecular analogue of this experiment, namely, the effect of norbornene on the fluorescence of biacetyl. We found that concentrations of up to 1 M norbornene did not affect the fluorescence intensity (±10%) of biacetyl. Thus, the rate of quenching of biacetyl (τ_f = 10.8 ns)[16] by norbornene is less than 10^7 M^{-1} s^{-1}.

Norbornenes. Photocycloaddition reactions were carried out between biacetyl and the olefins norbornene, *syn*-7-methylnorbornene (**4**, R = CH_3), and *syn*-7-*tert*-butylnorbornene (**4**, R = *t*-C_4H_9). In all cases we isolated 1:1 adducts that were shown to be acyloxetanes. Two major structural isomers, **7** and **8**, were formed as a consequence of exo- and endo-cycloaddition pathways (eq 4). The structural assignments for these products were made on the basis of the expected proton–proton coupling constants for the hydrogens labeled H_n and H_x.[17] The results are summarized in Table II, from which it is seen that the stereochemistry of cycloaddition of norbornenes is controlled by the size of the syn-7-substituent. Two factors could be important in deciding the stereochemical outcome of these reactions, namely, the differential rates of exciplex (and/or biradical) formation and the differential partitioning of exo vs. endo biradical intermediates. We therefore attempted to evaluate the quenching rates of these olefins with biacetyl triplets on the assumption that the singlet state was not the photoactive state (vide supra). The phosphorescence of biacetyl was quenched by norbornene, and a Stern–Volmer analysis of the results gave a linear plot with a slope of 10.8. From this value one can calculate a k_q of 2.4 × 10^4 M^{-1} s^{-1}, assuming τ_p equals 4.6 × 10^{-4} s.[16] Similar experiments with *syn*-7-*tert*-butylnorbornene and *syn*-7-methylnorbornene were more difficult to analyze experimentally because these olefins were very poor quenchers of biacetyl phosphorescence, giving rise to $k_q\tau$ values of 1.1 and 0.6, respectively. The overall quenching rate of **4c** was estimated to be ca. 1.3 × 10^3 M^{-1} s^{-1}. We assume that about half (between 40% and 66%) of this value, i.e., 6.5 × 10^2 M^{-1} s^{-1}, is attributable to exciplex formation and the other half to hydrogen abstraction since we also isolated a 34% yield of a product whose structure is believed to be **9** (eq 5). The quenching rate ratio of norbornene vs. *syn*-7-*tert*-butylnorbornene is thus ca. 37. These results stand in contrast to a related study by Turro and Farrington[18a] in which quenching rates and stereochemical modes of addition were not parallel. In the present context three factors consistently point to a classical steric inhibition of these reactions by the *tert*-butyl group: exo:endo ratios, phosphorescence quenching rates,[18b] and quantum yields of oxetanes.[19]



4 7 8

(4)



9

(5)

---

(12) (a) Seebach, D.; Corey, E. J. *J. Org. Chem.* **1975**, *40*, 231. (b) A modification of a literature procedure was used in which copper(II) chloride was substituted for silver(I) chloride; see: Corey, E. J.; Erickson, B. *Ibid.* **1971**, *36*, 3553. (c) Stetter, H.; Dambkes, G. *Synthesis*, **1980**, *309*.

(13) Bishop, R.; Hamer, N. K. *J. Chem. Soc. C* **1970**, 1197.

(14) (a) For closely related examples, see: Cookson, R. C.; Wariyar, N. S. *J. Chem. Soc.* **1956**, 2302. (b) for other examples, see: Sauers, R. R.; Henderson, T. R. *J. Org. Chem.* **1974**, *39*, 1850. (c) For a discussion of theory see: Houk, K. N. *Chem. Rev.* **1976**, *76*, 1.

(15) Cookson, R. C.; Henstock, J.; Hudec, J. *J. Am. Chem. Soc.* **1966**, *88*, 1060.

(16) (a) Almgren, M. *Photochem. Photobiol.* **1967**, *6*, 829. (b) Turro, N. J.; Engel, R.; *J. Am. Chem. Soc.* **1969**, *91*, 7113.

(17) Shigemitsu, Y.; Odaira, Y.; Tsutsumi, S. *Tetrahedron Lett.* **1967**, 55. Hara, M.; Odaira, Y.; Tsutsumi, S. *Ibid.* **1967**, 2981. Flautt, T. J.; Erman, W. F. *J. Am. Chem. Soc.* **1963**, *85*, 3212. Laszlo, P.; Schleyer, P. von R. *Ibid.* **1964**, *86*, 1171.

(18) (a) Turro, N. J.; Farrington, G. L. *J. Am. Chem. Soc.* **1980**, *102*, 6056. (b) For another example of steric inhibition of an excited carbonyl olefin reaction, see: Maharaj, U.; Winnik, M. A. *Tetrahedron Lett.* **1981**, *22*, 517.

(19) Strictly, the oxetane quantum yields should be normalized to reflect the efficiencies of the product formation from the triplet states that are actually trapped by the double bonds: $\phi_{ox}' = \phi_{ox}^{obsd}[k_q(\mathbf{4})/(k_q(4) + \tau_p^{-1})]^{-1}$. The correction is small for **4a** (ϕ_{ox}' = 0.0036) but significant for **4c** (ϕ_{ox}' = 0.0012).

Table II. Photocycloadditions of Biacetyl to Norbornenes

olefin 4, R =	oxetane distributions ([7]:[8])	oxetane yields,[a] %	NMR (100 MHz), δ	ϕ_{ox}[b]	[olefin], M
H	>24:1	38[c]	4.43 (d, $J = 5$[f])	0.001 1	0.856
		58[d]	4.44 (d, $J = 5$)	0.001 7	
CH_2	2.6:1[e]	54	4.53 (d, $J = 5$)	0.000 50	0.865
		21	4.76 (dd, $J = 4,8$)	0.000 20	
t-C_4H_9	<1:30	40	4.82 (dd, $J = 6,7$)	0.000 15	0.543

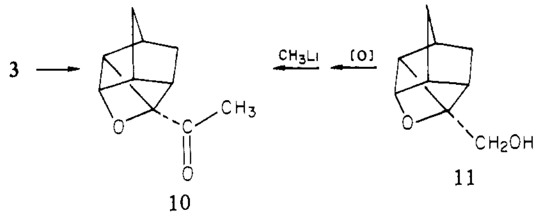
[a] Based on volatile products. [b] Average of duplicate determinations in benzene solution with 2,3-pentanedione as actinometer. [c] Assigned the *syn*-methyl structure 7, $R_1 = CH_3$, $R_2 = COCH_3$, on the basis of steric shielding of the methyl resonance (δ 1.39). [d] Assigned the *anti*-methyl structure 7, $R_1 = COCH_3$, $R_2 = CH_3$ (δ_{CH_3} 1.21). [e] Analyzed as a mixture. [f] J values in Hz.

Table III. Quantum Yield Data for Photocyclization of *endo*-3

concn of *endo*-3, M[a]	additive	concn, M	irradn λ, nm	ϕ_{ox}[b]
0.101			350	0.32[c]
0.041	*N,N*-dimethylaniline	0.22	300	0.32
0.041	*trans*-piperylene	0.15	300	0.32
0.041	oxygen	10^{-3}[d]	300	0.32
0.060	benzophenone[e]	0.24	350	0.41
0.10	*trans*-stilbene[f]	0.002	350	0.41
0.10	*trans*-stilbene[f]	0.003	350	0.38
0.10	*trans*-stilbene[f]	0.004	350	0.38
0.036			430	0.43[c,g]
0.057	*N,N*-dimethylaniline	1	430	0.28

[a] Degassed benzene solutions. [b] Accuracy is estimated to be ±10%. [c] Average of two determinations. [d] Undegassed solution. [e] Additive absorbs ca. 100% of incident light. [f] Also contains 0.5 M benzophenone. [g] $\phi_K = 0.45$.

Photochemistry of 3. Irradiation of **3** in benzene with either 300- or 430-nm light gave rise to a single volatile product to which we assign structure 10. The structural assignment is based on analogy with simpler systems[6] and by an alternate synthesis[20] from oxetane **11**[6] (eq 6). Thus, generation of either the S_1 or S_2 states of the diketone gives rise to the same adduct.[9b,21]



(6)

Quantitative Studies. Quantum yield, sensitization, and quenching studies were carried out in the hope of detecting differences in the reactivity of the various reactive states (Table III). The data reveal a small difference in the efficiency of oxetane formation from S_1 vs. S_2 states, namely, 0.43 ± 0.04 and 0.32 ± 0.03, respectively. Given the large experimental error and the difficulties caused by instability of the diketone **3**, we are reluctant to attach major significance to this result.[22] we were unable to quench oxetane formation from **3** at 300 nm by addition of 0.22 M *N,N*-dimethylaniline or 0.15 M piperylene. Since Turro and Engel[16b] have shown that dimethylaniline quenches biacetyl singlet states at a rate of 1.2×10^{10} M^{-1} s^{-1}, we conclude that the reactive state(s) in these diketone photocyclizations has a lifetime $\leq 4 \times 10^{-11}$ s. This finding is corroborated by the finding that 1 M dimethylaniline gives rise to a ϕ_{ox}^0/ϕ_{ox} of ~1.5 (at 430 nm). The extremely short lifetimes of the singlet states of **3** are consistent with the absence of fluorescence ($k \sim 1.2 \times 10^5$ s^{-1})[16a] and effectively preclude intersystem crossing ($k_{ST} \sim 10^8$ s^{-1}).[16] This conclusion was confirmed by measurement of the intersystem crossing yield using the photosensitized isomerization of *trans*-stilbene as a monitor. A value of ca. 0.02 was obtained by using 0.26–0.59 M olefin. We therefore generated the triplet state of **3** by indirect means, namely, by triplet–triplet energy transfer.

Benzophenone (E_T = 69 kcal/mol) was chosen as a sensitizer since its triplet energy was certain to be higher than that of the lowest triplet of **3** (E_{T_1}(biacetyl) = 55 kcal/mol).[1b,c] Oxetane **10** was produced with a quantum yield of 0.41 on irradiation of solutions of **3** that contained sufficient benzophenone to absorb the incident light at 350 nm. The addition of 0.002–0.004 M *trans*-stilbene (E_T = 50 kcal/mol)[1b,c] did not lead to a significant quenching of the rate of production of **10**.[23,24] This result limits the triplet state lifetime to $<6 \times 10^{-9}$ s.

The emerging picture from these studies shows that the α-diketone **3** (S_1 and/or S_2) is about as reactive as simple monoketone analogues, e.g., **1**, R = CH_3, in the photocycloaddition reaction.[6] Although we did not anticipate this,[9b] there is evidence from the literature that acetone and biacetyl singlet states are quenched by simple olefins at rates that differ by less than a factor of 10^2.[25] If one subjects these systems to the Rehm–Weller[26] analysis as modified by Loutfy et al.,[10] it is clear that relative to acetone the adverse affect brought about by the lower singlet-state energy (E_{S_1}(biacetyl) = 2.91 eV, E_{S_1}(acetone) = 3.48 eV) is counterbalanced by the greater ease of reduction of the diketone moiety ($E_{1/2}{}^R$(biacetyl) = -1.46[27] V, $E_{1/2}{}^R$(acetone)[10] = -2.3 V). The situation is similar for the respective triplet-state reactions. This analysis leads to the prediction that the rates of exciplex formation for α-diketones and monoketones will be similar and that differences in quenching rates will be governed predominantly by the rates of breakdown of the exciplexes.

Finally, the above data can be used to estimate the effective molarity[28] (EM) of the norbornene double bond in these intramolecular cycloadditions. For the singlet-state reactions the EM is ca. 10^4, and for the triplet-state reactions it is ca. 10^5.[29,30]

Summary. These results highlight the propensity of *endo*-5-acylnorbornenes to undergo intramolecular Paterno–Büchi reactions as evidenced by the efficient formation of oxetane **10** from

---

(20) Lynch, D. C., unpublished observations.

(21) (a) For a recent discussion of the electronic states of α-dicarbonyl systems see ref 9b and also: Mueller, W. B.; Harrison, J. F., Wagner, P. J. *J. Am. Chem. Soc.* **1978**, *100*, 33. (b) Verhaart, G. J.; Brongersma, H. H. *Chem. Phys. Lett.* **1980**, *72*, 176.

(22) Wagner et al.[9b] found no evidence for reactions from upper triplets in a study of photocyclization and photoenolization of α-diketones.

(23) The use of a sensitizer and low concentrations of quencher was developed by Cristol et al. (Cristol, S. J.; Daughenbough, R. J.; Opitz, R. J. *J. Am. Chem. Soc.* **1977**, *99*, 6347).

(24) Biacetyl phosphorescence quenching by *trans*-stilbene takes place at a rate of 4.0×10^9 M^{-1} s^{-1} in benzene: Cundall, R. B.; Evans, G. B.; Land, E. J. *J. Phys. Chem.* **1969**, *73*, 3982. See also: Herkstroeter, W. G.; Hammond, G. S. *J. Am. Chem. Soc.* **1966**, *88*, 4769.

(25) Tetramethylethylene quenches the fluorescence of biacetyl with a rate constant 4×10^6 M^{-1} s^{-1} and acetone with a rate constant equal to 1.4×10^8 M^{-1} s^{-1}; Monroe, B. M.; Lee, C. G.; Turro, N. J. *Mol. Photochem.* **1974**, *6*, 271. Yang, N. C.; Hui, M. H.; Shold, D. M.; Turro, N. J.; Hautala, R. R.; Dawes, K.; Dalton, J. C. *J. Am. Chem. Soc.* **1977**, *99*, 3023.

(26) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259.

(27) Guttenplan, J. B.; Cohen, S. G. *Tetrahedron Lett.* **1972**, 2163.

(28) Kirby, A. J. *Adv. Phys. Org. Chem.* **1980**, *17*, 183.

(29) This value was obtained by dividing the reciprocal of the maximum triplet state lifetime of **3** by the rate of attack of biacetyl triplets on the endo face of norbornene. The latter figure is assumed to be comparable to that obtained from the *tert*-butyl derivative **4c**.

(30) A similar value was determined for hydrogen abstraction reactions: Lewis, F. D.; Johnson, R. W.; Kory, D. R. *J. Am. Chem. Soc.* **1974**, *96*, 6100.

both singlet and triplet states. Side reactions, e.g., type II elimination,[9] photoenolization,[9] and α-cleavage,[8] are noncompetitive with oxetane formation. The intermolecular counterpart in contrast involves slow reactions of triplets and is much less efficient, both rates and stereochemistry being strongly affected by the 7-substituent.

Experimental Section

Nuclear magnetic resonance (NMR) spectra were determined on a Varian T-60 spectrometer in deuteriochloroform, and all chemical shifts are relative to internal tetramethylsilane. Integration data were consistent with the assigned structures (±10%). Infrared spectra were determined on Perkin-Elmer 727B or 137 spectrometers. Fluorescence and phosphorescence spectra were determined on either a Farrand Mark I or a Perkin-Elmer Model MPF-3L spectrometer. Gas chromatography was carried out on Varian Aerographs (A90P) with the following columns: A, 6 ft × $^1/_4$ in. 20% Apiezon L; B, 6 ft × $^1/_4$ in. 10% Apiezon L; C, 8.5 ft × $^1/_4$ in. 20% FFAP; D, 5 ft × $^1/_4$ in. 10% Carbowax 20M; E, 10 ft × $^1/_4$ in. 12% SE 30. Ultraviolet spectra (UV) were measured on a Cary Model 17D spectrometer. Mass spectral data were obtained on a Hitachi Perkin-Elmer Model RMU-7 spectrometer.

Chemicals. Benzene for quantum yield measurements was purchased from Baker (Ultrex grade) and was certified to be >99.99% pure. *trans*-Stilbene was purified by gas chromatography on colume E (198 °C) and was shown to be essentially free of the cis isomer after purification. Tetradecane was purified by gas chromatography (D). Pentadecane was purified by either gas chromatography (D) or distillation followed by gas chromatography (C, 138 °C). Camphorquinone was purified by crystallization from ligroin followed by sublimation, mp 201–202.5 °C (lit.[31] mp 198 °C). 2,3-Pentanedione was purified by distillation over molecular sieves (bp 39 °C (36–42 mmHg). Benzil was Baker Sensitizer Grade.

Light Sources and Filters. The 430-nm line from a 450-W medium-pressure immersion lamp was isolated by means of a Nonex glass filter and 1.4-cm path of a copper sulfate solution (19.6 g of $CuSO_4 \cdot 5H_2O$, 33 mL of NH_4OH, dilute to 1 L). Light with wavelength 300 or 350 nm was obtained from a Rayonet Reactor.[32] In both cases Pyrex glass vessels were used.

Quantum Yields. All quantum yields were determined in benzene solutions containing the appropriate internal standard. Solutions were degassed by four freeze–thaw cycles under a vacuum of ca. 0.05 torr. Actinometers used were as follows: 430 nm, 2,3-pentanedione[33] ($\phi_{\text{type II}}$ = 0.054) or camphorquinone[31] (ϕ_{-K} = 0.07); 300 nm, *endo*-5-acetylnorbornene[6] (ϕ_{ox} 0.14); 350 nm, butyrophenone[34] ($\phi_{\text{type II}}$ = 0.36). The concentrations of both actinometer and test solutions were adjusted to give optical densities ≥2 through the irradiation. Conversions were kept below 15% and were measured by gas chromatography except in the case of camphorquinone consumption, which was monitored by UV.

Norbornenes. Commercial norbornene was purified by sublimation and distillation at 95 °C; *syn*-7-methylnorbornene was prepared by catalytic hydrogenation of 7-methylnorbornadiene[35] in ether in the presence of platinum oxide. The reaction was monitored by GC (A, 80 °C) and stopped when the concentration of **4b** had maximized (ca. 1.2 mol of H_2). The catalyst was removed by filtration, and the solvent was evaporated. Distillation of the residue through a 15-in. spinning band column gave a fraction of boiling point 52–55 °C (110 nmHg) (lit.[36] bp 50–52 °C (35 mmHg) in 50% yield. The ^{13}C NMR spectrum corresponded to that reported in the literature. Final purification was accomplished by preparative gas chromatography (A, 85 °C) and produced a material that was >99.99% **4b**. *syn*-7-*tert*-Butylnorbornene was prepared by the procedure of Baird and Surridge.[37] The product (**4c**) was obtained in 50% yield and had a boiling point of 102 °C (90 mmHg) lit. bp 102 °C (90 mmHg). The ^1H NMR spectrum corresponded with that reported in the literature Final purification was accomplished by preparative gas chromatography (B, 110 °C) and produced material that was >99.99% pure.

Preparative Experiments. Solutions of the appropriate norbornene in benzene were placed in 13 × 100 mm test tubes that were purged with nitrogen and stoppered with serum caps. The tubes were irradiated at 430 nm in a carrousel.

Norbornene. A solution of 4.30 g (0.050 mol) of biacetyl and 37.6 g (0.40 mol) of norbornene in 100 mL of benzene was irradiated for 20 h. The combined solutions were evaporated, and the residue was subjected to preparative gas chromatography (C, 150 °C). Two products in the ratio 38:58 comprised the bulk (~96%) of the volatile constituents. The more volatile (minor) constituent was an oil: IR 3.39, 5.84, 7.40, 9.03, 10.04, 10.38 μm^{-1}; mass spectrum, *m/e* 180 (M^+), 137 (base peak, M^+ – 43). Anal. ($C_{11}H_{16}O_2$) C, H.

The second constituent was an oil: IR 3.36, 5.84, 7.41, 8.99, 10.13, 10.43 μm^{-1}; mass spectrum, *m/e* 180 (M^+), 137 (M^+ – 43, base peak). Anal. ($C_{11}H_{16}O_2$) C, H.

***syn*-7-Methylnorbornene.** Similarly, a solution of 1.52 g (0.0177 mol) of biacetyl and 15.23 g (0.141 mol) of **4b** in 35 mL of benzene was irradiated for 40 h. Removal of the solvent gave a residue that was purified by gas chromatography (C, 170 °C). One major peak (>75%) at long retention time was observed. This material was collected as an oil: IR 3.39, 5.83, 10.67 μm^{-1}; mass spectrum, *m/e* 194 (M^+), 151 (M^+ – 43, 95%), 81 (base peak). Anal. ($C_{12}H_{18}O_2$) C, H.

***syn*-7-*tert*-Butylnorbornene.** A solution containing 18.0 g (0.12 mol) of **4c** and 1.3 g (0.015 mol) of biacetyl in 30 mL of benzene was irradiated for 162 h. The volatile materials were removed by evaporative distillation, and the residue was separated by gas chromatography (B, 148 °C) into two major constituents in the ratio 34:40. The less volatile component proved to be an oxetane: IR 3.32, 5.78 μm^{-1}; mass spectrum, *m/e* 236 (M^+), 193 (M^+ – 43, 54%), 123 (base peak); exact mass calcd. for $C_{15}H_{24}O_2$ 236.1776, found 236.1755.

The more volatile product was assigned structure 3-acetyl-5-*tert*-butyltricyclo[2.2.1.0^{2,6}]heptane (**9**): IR 3.4, 5.84, 7.36 μm^{-1}; NMR δ 2.67 (s, 1 H), 2.07 (s, 3 H); 1.12 (m, 6 H); 0.98 (s, 9 H); mass spectrum, *m/e* 192 (M^+, base peak) 43 ($CH_3C(O)^+$, 76%). Anal. ($C_{13}H_{20}O$) C, H.

1-(5′-Norbornene-2′-yl)-1,2-propanedione (3). (A) From Dithiane. A 500-mL three-necked flask was charged with 100 mL of dry THF and 15.49 g (0.12 mol) of 2-methyl-1,3-dithiane.[12] The stirred solution was purged with nitrogen and cooled to ca. –70 °C. A freshly prepared ethereal solution (93.8 mL) of *n*-butyllithium (1.28 M) was added, and the resulting mixture was kept at –10 °C for 24 h. The chilled solution was transferred to a dropping funnel and added slowly to a cold (ca. –70 °C) solution of 12.22 g (0.078 mol) of 5-norbornen-2-carbonyl chloride (ca. 85% endo) in 100 mL of THF. The resulting mixture was stirred for 24 h at ca. –70 °C. The reaction was quenched with water, diluted with ether, and washed with water until neutral. The organic phase was dried ($MgSO_4$) and evaporatively distilled to give a viscous oil which was distilled to give 10.95 g (41%) of ketone **5**, bp 54 °C (0.025 torr). A sample of the pure endo isomer was obtained by gradient chromatography on alumina (grade III) by using hexane–methylene chloride mixtures as eluent; NMR δ 1.76 (s, CH_3); IR (film) 5.90 (C=O, s) μm^{-1}. Anal. ($C_{13}H_{18}OS_2$) C, H, S.

The dithiane **5** was hydrolyzed[12b] by adding a solution of 9.78 g (0.038 mol) in 190 mL of 80% acetonitrile–water to a stirred solution of 25 g (0.187 mol) of *N*-chlorosuccinimide and 18.27 g (0.11 mol) of $CuCl_2 \cdot 2H_2O$ in 410 mL of 80% acetonitrile–water. The reaction was quenched by addition over 10 min of a solution containing 25.5 g of Na_2CO_3, 62.5 g of Na_2SO_3, and 175.5 g of NaCl in 1.5 L of water. The organic materials were extracted into ether (2×) and hexane (1×). The combined extracts were dried ($MgSO_4$) and evaporated at reduced pressure to give 2.36 g of a yellow oil. Short-path distillation gave 0.82 g (14%) of **3** (ca. 85% endo): bp 50 °C (0.2 torr); NMR δ 2.28 (*endo*-CH_3) 2.37 (*exo*-CH_3), 5.62–6.28 (=CH); IR 5.85 (C=O, s) μm^{-1}. Anal. ($C_{10}H_{12}O_2$) C, H.

The pure exo and endo isomers were separated by flash chromatography using 50:50 CH_2Cl_2–hexane as eluent. The UV spectra for these materials were as follows: *exo*-**3** λ_{max} (C_6H_{12}) 259 nm, 432 (ε 358, 15); *endo*-**3** λ_{max} (C_6H_{12} 258, 430 (ε 424, 29). The exo isomer fluoresced upon irradiation at either 300 or 420 nm, λ_{max} 474 nm. No emission was observed on similar treatment of pure *endo*-**3**.

(B) Stetter's Method.[12(c)] A 100-mL flask was charged with 7.00 g (0.057 mol) of 5-norbornene-2-carboxaldehyde, 1.76 g (0.0174 mol) of triethylamine, 2.0 mL of ethanol, 7.64 g (0.174 mol) of acetaldehyde, and 1.46 g (0.0058 mol) of *N*-benzyl-5-(2-hydroxyethyl)-4-methyl-1,3-thiazolium chloride. After the initial reaction subsided, the mixture was heated at reflux for 24 h. The solution was diluted with chloroform and washed with water and with 0.5% HCl until acidic. Further washing with water was continued until the extracts were colorless. The dried ($MgSO_4$) solution was evaporated to give 2.39 g of oil **6**, bp 82–142 °C (0.05 torr). This material was dissolved in 10 mL of 2-ethoxyethanol and treated with 3 mL of acetic acid and 1.86 g (0.004 mol) of Bi_2O_3. After heating for 36 min at 100 °C, the slurry was cooled and filtered with chloroform rinsing. The organic phase was washed with water until

---

(31) Rubin, M. B.; Labarge, R. G. *J. Org. Chem.* **1964**, *31*, 3286.

(32) Available from the Southern New England Ultraviolet Company, Middletown, CT.

(33) Turro, N. J.; Lee, T. *J. Am. Chem. Soc.* **1969**, *91*, 5651.

(34) Wagner, P. J.; Kelso, P. A.; Kemppainen, A. E.; McGrath, J. M.; Schott, H. N.; Zepp, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 7506.

(35) Story, P. R.; Fahrenholtz, S. R. *J. Org. Chem.* **1963**, *28*, 1716.

(36) Grutzner, J. B.; Jautelat, M.; Deuce, J. B.; Smith, R. A.; Roberts J. D. *J. Am. Chem. Soc.* **1970**, *92*, 7170.

(37) Baird, W. C., Jr.; Surridge, J. H. *J. Org. Chem.* **1972**, *37*, 304.

neutral, dried over Na_2SO_4 and evaporated to give a yellow oil (3), bp 55-63 °C (86-111 torr), yield 1.72 g (67%). The exo-endo ratio was ca. 3:2 as judged from the relative magnitude of the CH_3 peaks in the NMR spectrum.

3-Acetyl-4-oxatetracyclo[4.2.1.$0^{2,5}$.$0^{3,7}$]nonane (10). A solution of 0.37 g of **4** in 1 mL of benzene was irradiated at 300 nm for 65 h. Evaporation of the solvent gave a colorless oil which was purified by gas chromatography (D, 123 °C) to give 80 mg (22%) of **10**: NMR δ 2.24 (s, CH_3), 4.72 (q, HCO). Anal. ($C_{10}H_{12}O_2$) C, H.

The same product was isolated from photolyses at 430 nm and from the benzophenone-sensitized irradiations. Identification was by NMR comparisons.

Acknowledgment. We are grateful to the National Science Foundation (GP 26371, CHE77-16311) and the National Institutes of Health (Special Fellowship 1F03 GM53816) financial support. We also thank Dr. D. Z. Denney for an NMR spectrum. Special thanks goes to Professor Saul Cohen for his hospitality during a sabbatical year at Brandeis University.

Isobaric and Isochoric Activation Parameters for the Water-Catalyzed Hydrolysis of *p*-Methoxyphenyl 2,2-Dichloropropionate in Typically Aqueous Solutions

Herman A. J. Holterman and Jan B. F. N. Engberts*

Contribution from the Department of Organic Chemistry, University of Groningen, Nijenborgh 16, 9747 AG Groningen, The Netherlands. Received October 22, 1981

Abstract: Isobaric thermodynamic activation parameters ($\Delta G_p^{\ddagger}$, $\Delta H_p^{\ddagger}$, $\Delta S_p^{\ddagger}$) and volumes of activation ($\Delta V^{\ddagger}$) have been measured for the water-catalyzed hydrolysis of *p*-methoxyphenyl 2,2-dichloropropionate (**1**) in water and in *t*-BuOH-H_2O (n_{H_2O} = 0.950 and 0.925) and 2-*n*-butoxyethanol-H_2O (n_{H_2O} = 0.980) at 25 °C. These data, in combination with the isobaric thermal expansivities (α) and the isothermal compressibilities (β) of the solvent, were used to calculate the isochoric activation parameters $\Delta U_v^{\ddagger}$ and $\Delta S_v^{\ddagger}$. It is found that the solvent dependence of the sets ($\Delta H_p^{\ddagger}$, $\Delta S_p^{\ddagger}$) and ($\Delta U_v^{\ddagger}$, $\Delta S_v^{\ddagger}$) is widely different as a result of the large changes in α/β and in $\Delta V^{\ddagger}$. The results are interpreted mainly in terms of hydrophobic interactions between **1** and the organic cosolvent and the large electrostriction, as expressed in the strongly negative $\Delta V^{\ddagger}$ values. The analysis is facilitated by consideration of thermodynamic parameters for transfer of a model substrate (*p*-nitrophenyl propionate) from water to the *t*-BuOH-H_2O system. It is concluded that both isobaric and isochoric activation parameters contain fundamental information about the solvation changes during the activation process. There is no compelling evidence to prefer either of these sets for an analysis of kinetic solvent effects on the hydrolysis of **1** in the solvent systems used.

The interpretation of rate constants (k) and thermodynamic activation parameters for organic reactions in typically aqueous (TA) solutions[1] of high water content constitutes a long-standing problem of utmost difficulty.[2] A fundamental approach in recent studies involves a rationalization of changes in thermodynamic activation parameters like Gibbs free energies ($\Delta G_p^{\ddagger}$), enthalpies ($\Delta H_p^{\ddagger}$), entropies ($\Delta S_p^{\ddagger}$), volumes ($\Delta V^{\ddagger}$), and heat capacities of activation ($\Delta C_p^{\ddagger}$) with solvent composition in terms of interactions of the substrate(s) and the transition state with the TA solvent systems.[2-6] But the results are often a matter of considerable controversy which has its seat in the peculiar features of TA solutions.[1]

Previously, the question has also been asked whether isobaric (constant pressure) or isochoric (constant volume) activation parameters best reflect the actual solvation changes during the activation process.[7,8] We define

$$\Delta U_v^{\ddagger} = RT^2\left(\frac{\delta \ln (k/T)}{\delta T}\right)_v$$

$$\Delta H_p^{\ddagger} = RT^2\left(\frac{\delta \ln (k/T)}{\delta T}\right)_p$$

$$\Delta V^{\ddagger} = -RT\left(\frac{\delta \ln k}{\delta P}\right)_T$$

then it follows from the mathematical relations between derivatives[8] that

$$\Delta U_v^{\ddagger} = \Delta H_p^{\ddagger} - (T\alpha\Delta V^{\ddagger})/\beta$$

$$\Delta S_v^{\ddagger} = \Delta S_p^{\ddagger} - (\alpha\Delta V^{\ddagger})/\beta$$

in which α is the isobaric thermal expansivity and β the isothermal compressibility of the solvent system. In the high water concentration region of TA solutions, α/β varies strongly with changes

---

(1) For a definition of TA solutions and a summary of their properties, see: Franks, F. In "Water. A Comprehensive Treatise"; Franks, F., Ed.; Plenum Press: New York, 1973; Vol. 2, Chapter 1.

(2) (a) Blandamer, M. J.; Burgess, J. *Chem. Soc. Rev.* **1975**, *4*, 55. (b) Engberts, J. B. F. N. In "Water. A Comprehensive Treatise"; Franks, F., Ed.; Plenum Press: New York, 1979, Vol. 6, Chapter 4.

(3) (a) Arnett, E. M.; McC. Duggleby, P.; Burke, J. J. *J. Am. Chem. Soc.* **1963**, *85*, 1350. (b) Arnett, E. M.; McKelvey, D. R. *Rec. Chem. Prog.* **1965**, *26*, 184.

(4) (a) Schaleger, L. L.; Richards, C. N. *J. Am. Chem. Soc.* **1970**, *92*, 5565. (b) Abraham, M. H. *Prog. Phys. Org. Chem.* **1974**, *11*, 1. (c) Menninga, L.; Engberts, J. B. F. N. *J. Org. Chem.* **1976**, *41*, 3101. (d) Jones, J. R.; Fuchs, R. *Can. J. Chem.* **1977**, *55*, 99. (e) Holterman, H. A. J.; Engberts, J. B. F. N. *J. Phys. Chem.* **1979**, *83*, 443.

(5) (a) Engbersen, J. F. J.; Engberts, J. B. F. N. *J. Am. Chem. Soc.* **1975**, *97*, 1563. (b) Holterman, H. A. J.; Engberts, J. B. F. N. *Ibid.* **1980**, *102*, 4256.

(6) During the last decades, many attempts have been made to correlate rate constants with solvent parameters: (a) Reichardt, C. "Solvent Effects in Organic Chemistry"; Verlag Chemie: Weinheim, 1979. (b) Symons, M. C. R. *Acc. Chem. Res.* **1981**, *14*, 179. Although sometimes useful trends have been found, the physical significance of these correlations is usually far from clear since no distinction is made between solvation effects on the reactant molecule(s) and the transition state.

(7) (a) Evans, M. G.; Polanyi, M. *Trans. Faraday Soc.* **1935**, *31*, 875. (b) Whalley, E. *Adv. Phys. Org. Chem.* **1964**, *2*, 93.

(8) Moelwyn-Hughes, E. A. "Physikalische Chemie"; George Thieme Verlag: Stuttgart, 1970; p 683.