Hz, H13), 3.76 (dd, 1 H, J = 8.8, 7.0 Hz, H10), 3.54 (s, 3 H, OMe mandel), 3.20 (m, 1 H, H16), 3.04 (dd, 1 H, J = 9.3, 7.0 Hz, H4), 2.60 (q, 2 H, J = 7.4 Hz, H22), 2.10 (m, 1 H, H14), 1.97 (s, 6 H), 1.96 (s, 6 H), 1.87 (s, 3 H), 1.78 (s, 3 H), 1.62 (d, 3 H, J = 1.1 Hz, Me28), 1.42 (m, 2 H, H2), 1.28 (d, 3 H, J = 7.0 Hz, Me27), 1.20 (m, 3 H, Me30), 0.84 (m, 3 H, Me29), 0.82 (d, 3 H, J = 6.9 Hz, Me24), 0.80 (t, 3 H, J = 7.3 Hz, Me1). HREIMS: $C_{45}H_{60}O_{11}$ calcd 776.4135. Found: 776.4153. FABMS (+) m/z: 777 (100), 749 (5), 717 (9), 657 (6), 551 (6), 491 (8), 301 (9), 225 (39), 209 (9), 193 (14), 180 (20), 179 (9), 155 (30), 121 (58).

(*R*)-3-*O*-Methylmandelate from Onchitriol I A (16). ^{1}H NMR (Cl_3CD): 7.31 (m, 5 H, arom), 5.62 (bd, 1 H, J = 8, 8 Hz, H11), 5.34 (dd, 1 H, J = 10.2, 2.0 Hz, H15), 5.11 (ddd, 1 H, J = 4.0, 8.3, 9.3 Hz, H3), 4.78 (s, 1 H, H_α mandel), 4.76 (d, 1 H, J = 10.7 Hz, H13), 3.81 (dd, 1 H, J = 8.8, 7.0 Hz, H10), 3.54 (s, 3 H, OMe mandel), 3.20 (m, 2 H, H16, H4), 2.61 (q, 2 H, J = 7.4 Hz, H22), 2.13 (m, 1 H, H14), 1.97 (s, 3 H), 1.96 (s, 3 H), 1.95 (s, 3 H), 1.94 (s, 3 H), 1.91 (s, 3 H), 1.78 (s, 3 H), 1.64 (d, 3 H, J = 1.1 Hz, Me28), 1.28 (m, 2 H, H2), 1.28 (d, 3 H, J = 7.0 Hz, Me27), 1.20 (d, 3 H, J = 6.9 Hz, Me24), 1.18 (m, 3 H, Me30), 0.84 (m, 3 H, Me29), 0.46 (t, 3 H, J = 7.3 Hz, Me1). HREIMS: $C_{45}H_{60}O_{11}$ calcd 776.4135. Found: 776.4118. FABMS (+) m/z: 777 (100), 749 (3), 717 (6), 657 (4), 551 (2), 491 (6), 301 (7), 225 (37), 209 (7), 193 (12), 180 (19), 179 (9), 155 (30), 121 (58).

(*R*)-3,13,15-Tris(*O*-methylmandelate) from Onchitriol I (18). ^{1}H NMR (Cl_3CD): 7.30 (m, arom), 5.55 (bd, 1 H, J = 8.8 Hz, H11), 5.33 (dd, J = 9.9, 1.8 Hz, H15), 5.13 (m, 1 H, H3), 4.80 (s, 1 H, H_α mandel), 4.71 (s, 1 H, H_α mandel), 4.62 (s, 1 H, H_α mandel), 4.56 (d, 1 H, J = 10.8 Hz, H13), 3.48 (s, 3 H, OMe mandel), 3.43 (s, 3 H, OMe mandel), 3.31 (s, 3 H, OMe mandel), 3.18 (m, 1 H, H16), 3.10 (m, 1 H, H4), 2.57 (m, 2 H, H22), 1.97 (s, 6 H), 1.96 (s, 6 H), 1.86 (s, 3 H), 1.79 (s, 3 H), 0.80 (d, J = 7.0, 3 H, Me29), 0.48 (t, 3 H, J = 7.3 Hz, Me1). HREIMS: $C_{59}H_{72}O_{13}$; calcd 988.4973. Found: 988.5031. EIMS m/z: 988 (1), 823 (2), 657 (1), 577 (1), 491 (2), 251 (5), 221 (4), 180 (5), 151 (3), 121 (100).

(*S*)-3,13,15-Tris(*O*-methylmandelate) from Onchitriol I (17). ^{1}H NMR (Cl_3CD): 7.30 (m, arom), 5.57 (bd, 1 H, J = 8.8 Hz, H11), 5.19 (dd, J = 9.9, 1.8 Hz, H15), 5.07 (m, 1 H, H3), 4.79 (s, 1 H, H_α mandel), 4.69 (s, 1 H, H_α mandel), 4.63 (s, 1 H, H_α mandel), 4.49 (d, 1 H, J = 10.8 Hz, H13), 3.48–3.30 (3 s, 3 OMe mandel), 2.55 (m, 2 H, H22), 1.98 (s, 3 H), 1.97 (s, 3 H), 1.96 (s, 3 H), 0.80 (t, 3 H, J = 7.3 Hz, Me1), 0.76 (d, J = 7.0, 3 H, Me29), 0.80 (t, 3 H, J = 7.3 Hz, Me1). HREIMS: $C_{59}H_{72}O_{13}$ calcd 988.4973. Found: 988.5029.

(*S*)-3,13-Bis(*O*-methylmandelate) from Onchitriol II A (20). ^{1}H NMR (Cl_3CD): 7.28 (m, 10 H, arom), 5.38 (bd, 1 H, J = 9.4 Hz, H11), 5.29 (dd, 1 H, J = 10.2, 1.6 Hz, H15), 5.14 (m, 1 H, H3), 4.94 (d, 1 H, J = 10.6 Hz, H13), 4.76 (s, 1 H, H_α mandel), 4.65 (s, 1 H, H_α mandel), 3.54 (m, 1 H, H10), 3.25 (m, 1 H, H16), 3.23 (s, 3 H, OMe mandel), 3.15 (m, 1 H, H4), 2.56 (q, 2 H, J = 7.5 Hz, H22), 2.25 (m, 1 H, H14), 1.96 (s, 3 H), 1.92 (s, 3 H), 1.82 (s, 3 H), 1.80 (s, 3 H), 1.63 (m, 2 H, H2), 1.60 (s, 3 H), 1.52 (d, 3 H, J = 1.2 Hz, Me28), 1.22 (d, 3 H, J = 7.0 Hz, Me30), 1.21 (t, 3 H, J = 7.5 Hz, Me23), 1.13 (d, 3 H, J = 6.9 Hz, Me28), 1.03 (d, 3 H, J = 6.9 Hz, Me24), 0.91 (d, 3 H, J = 6.9 Hz, Me29), 0.88 (t, 3 H, J = 7.3 Hz, Me1). HREIMS: $C_{52}H_{66}O_{12}$ calcd 882.4554. Found: 882.4558. FABMS (+) m/z: 883 (53), 805 (15), 791 (7), 717 (15), 657 (19), 491 (9), 209 (12), 180 (21), 179 (11), 151 (10), 121 (100).

(*R*)-3,13-Bis(*O*-methylmandelate) from Onchitriol II A (21). ^{1}H NMR (Cl_3CD): 7.28 (m, 10 H, arom), 5.42 (bd, 1 H, J = 9.4 Hz, H11), 5.22 (dd, 1 H, J = 10.2, 1.6 Hz, H15), 5.07 (m, 1 H, H3), 4.85 (d, 1 H, J = 10.6 Hz, H11), 4.79 (s, 1 H, Hα mandel), 4.60 (s, 1 H, Hα mandel), 3.54 (m, 1 H, H10), 3.52 (s, 3 H, OMe mandel), 3.25 (m, 3 H, H16), 3.24 (m, 3 H, OMe mandel), 3.04 (m, 1 H, H4), 2.60 (q, 2 H, J = 7.4 Hz, H22), 2.25 (m, 1 H, H14), 1.96 (s, 3 H), 1.94 (s, 3 H), 1.93 (s, 3 H), 1.91 (s, 3 H), 1.81 (s, 3 H), 1.76 (s, 3 H), 1.55 (d, 3 H, J = 1.2 Hz Me28), 1.54 (m, 2 H, H2), 1.20 (t, 3 H, J = 7.4 Hz, Me23), 1.15 (d, 6 H, J = 6.9 Hz, Me24, Me30), 1.12 (d, 3 H, J = 7.0 Hz, Me27), 0.85 (d, 3 H, J = 6.9 Hz, Me29), 0.63 (t, 3 H, J = 7.3 Hz, Me1). HREIMS: $C_{52}H_{66}O_{12}$ calcd 882.4554. Found: 882.4561. FABMS (+) m/z: 883 (50), 805 (17), 791 (9), 717 (16), 657 (20), 491 (10), 209 (13), 180 (23), 179 (15), 151 (8), 121 (100).

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Registry No. **4**, 140924-47-6; **5**, 142132-12-5; **6**, 142159-63-5; **7**, 142132-13-6; **8**, 142132-14-7; **9**, 140924-48-7; **10**, 140849-45-2; **11**, 142132-15-8; **12**, 142132-16-9; **13**, 85589-35-1; **14**, 142132-17-0; **15**, 142132-18-1; **16**, 142186-55-8; **17**, 142132-19-2; **18**, 142186-56-9; **19**, 142186-57-0; **20**, 142132-20-5; **21**, 142186-58-1; 2,2-dimethoxypropane, 77-76-9.

Supplementary Material Available: All NMR spectra of **4–14** and **19** (28 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

Intramolecular Photocycloaddition Reactions of 3-(2-Propenoxy)cyclopent-2-en-1-ones and 3-(2-Propenoxy)cyclohex-2-en-1-ones

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The 3-oxa-1,5-hexadienones **4a**, **4b**, **5a**, and **5b** undergo intramolecular [2 + 2] photocycloaddition reactions with quantum yields ranging from 0.2 to 0.002. In general, oxa substitution decreases the quantum yields and favors the formation of crossed closure products in comparison to the alkenyl analogs. Irradiation of stereospecifically deuterated dienones **11a** and **12a** indicate that the intermediate biradical reverts to the starting dienone faster than it proceeds to product. The results are compared with the analogous alkenyl systems. An explanation for changes in regiochemistry, quantum yields, and reversion rates between the two systems is offered.

Enone–alkene [2 + 2] photocycloadditions reactions continue to be the subject of many mechanistic and synthetic studies.[1-4] The utility of this reaction is founded on the predictable manner in which complex ring systems

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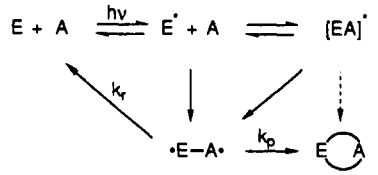
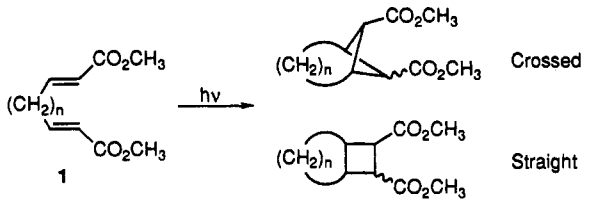
Scheme I

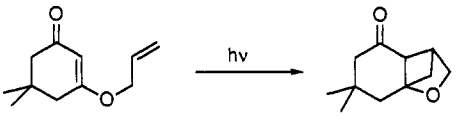


can be constructed.[5] The long-held mechanistic paradigm for the enone–alkene [2 + 2] reaction involves the stepwise formation of the two new σ-bonds (Scheme I).[6] The triplet state of the enone (E*) was proposed to form an exciplex ([EA]*) with the alkene (A), which then collapses to form a biradical intermediate (•E–A•). Typically the reaction pathway bifurcates after formation of the biradical to give products or revert back to starting material. Both steric and electronic factors were believed to govern the orientation in which the exciplex was formed and the selectivity in exciplex formation was used to explain the product composition. Recently, time-resolved studies by Schuster[7] and biradical trapping studies by Hastings and Weedon[8] have challenged the belief that exciplex formation determines the product composition. In place of the exciplex hypothesis they propose that the product composition is a function of the relative rates of reversion and product formation of competing biradical intermediates.

The intramolecular version of the [2 + 2] photocycloaddition has long been noted to favor the formation, where possible, of 5-membered rings in the photoproduct.[9,10] This behavior has been referred to as the "rule of five".[11,12] For example, upon irradiation the 1,5-hexadiene **1** (n = 2) produces the "crossed closure" product (n = 2), whereas irradiation of the 1,6-heptadiene **1** (n = 3) produces the "straight closure" product (n = 3).[13]



Wolff and Agosta have systematically explored the photochemistry of carbonyl-substituted 1,5-hexadienes and have found the 1-acyl- and 3-keto-substituted systems can be induced to undergo nonrule of five straight closure by incorporating the enone double bond into a 5- or 6-membered ring and by placing an alkyl substituent at the 5-position.[14-16] In some cases this reversal of the regiochemistry of the photocycloaddition can be complete. An earlier report by Tamura on the photochemistry of a 1-acyl-3-oxa-1,5-hexadiene, **2**, showed formation of only a crossed closure product **3**.[17] These results suggest that the regiochemical control demonstrated by Wolff and Agosta may not be general. In order to further explore this issue, we sought to systematically study the effect of oxa substitution by preparing a series of dienones which could be directly compared to the alkenyl analogs studied by Wolff and Agosta.[18,19] Our results are reported below.[20]



Results

Dienones **4a**, **4b**, **5a**, and **5b** were readily prepared in 40–80% yield by the acid-catalyzed condensation of cyclopentane-1,3-dione or cyclohexane-1,3-dione with the appropriate allylic alcohol. Hexane or benzene solutions of the dienones were irradiated through Pyrex (λ ≥ 280 nm), and the photoreactions were monitored by GC and GC–MS. The unsubstituted dienones **4a** and **5a** gave rise to solely crossed closure products **6a** and **7**, respectively. Contrary to our initial report,[20] dienone **4b** undergoes a very low yielding intramolecular photocycloaddition. The major product was determined to be the crossed closure product **6b**. However a minor isomeric product was observed (GC–MS) but was not identified due to its low yield and apparent instability to the purification conditions (preparative GC and flash chromatography). This instability suggests that the minor photoproduct from **4b** may be a thermally labile straight closure product (vide infra). Irradiation of dienone **5b** produced the highly strained straight closure product **8**. With the exception of **4a**, the dienones undergo photocycloaddition with low quantum yields (Table I). Although ketone **6a** can be produced in 54% isolated yield, the low quantum yields of dienones **4b**, **5a**, and **5b** give rise to low isolated yields because secondary photochemical processes consume the initial photoproducts. Irradiation of a purified sample of **6a** produced the same aldehydic compound observed in the photolysis mixture of dienone **4a**, suggesting that the primary photoproducts undergo a type I cleavage. Ketones **6b**, **7**, and **8** were isolated at low conversions (<20%) and required several chromatographic (liquid and/or gas) separations. The quantum yields were determined at 313

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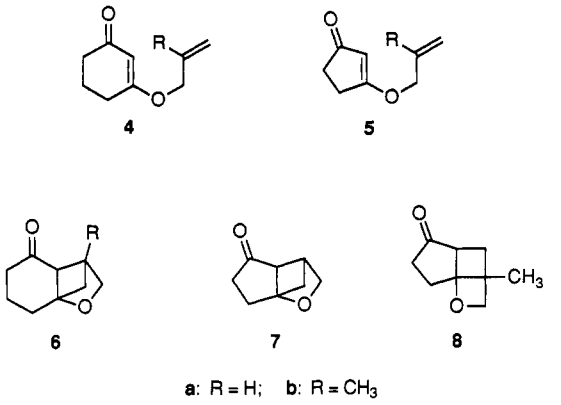
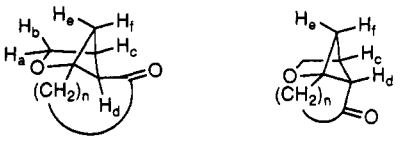
nm using valerophenone as a chemical actinometer.[21]



4 5 6 7 8

a: R = H; b: R = CH_3

Structure of Photoproducts. The crossed photoproducts **6a**, **6b**, and **7** were identified primarily by comparing their ^1H NMR spectra with the related dimedone-derived photoproducts reported by Tamura.[17] The coupling constants and chemical shifts of the bicyclo[2.1.1] portion of the ring system were used to assign the stereochemistry of the ring junctures. The absence of W-coupling between protons on the 1-bridges of the bicyclo[2.1.1] rings in ketones **6a** and **7** is consistent with the formation of the more strained trans annulation, **9**, of the cyclohexanone and cyclopentanone rings to the bicyclo[2.1.1] ring system. Photoproducts **6a** and **7** displayed similar coupling constants for J_{ef}, J_{ec} and J_{cf} values (**6a**: J_{ef} = 7.5, J_{ce} = 1.4, J_{cf} = 3.0 Hz; **7**: J_{ef} = 7.8, J_{ce} = 1.3, J_{cf} = 3.1 Hz). Attempts at epimerization of **6a** with $NaHCO_3$ in methanol were not successful and resulted in addition of water or methanol (GC–MS). The same behavior was reported for **3**.[17] In contrast to ketones **6a** and **7**, ^1H NMR analysis of ketone **6b** indicates that it has the more stable ring juncture **10** (n = 3). The geminal coupling J_{ef} increased slightly to 8 Hz, and W-coupling (J_{de} = 9.2 Hz) was observed. The coupling constants for ring junctures **9** and **10** are very consistent with the amino analog of **3** reported by Tamura and other bicyclo[2.1.1] systems reported by Wolff and Agosta.[14,17]

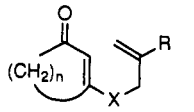


9 10

An estimate of the relative energies of the diastereomeric isomers **9** and **10** was calculated using MM2 (PCMODEL).[22] In the cyclohexanone series **9** (n = 3) was found to be 2.6 kcal/mol lower in energy (ΔH_f) than **10** (n = 3). In both diastereomers the cyclohexanone ring adopts a chair-like conformation. As expected the difference in stability of the two diastereomers in the cyclopentanone series is greater with **9** (n = 2) calculated to be 6.4 kcal/mol below **10** (n = 2).

The bicyclo[2.2.0] ring system in **8** has a distinctive low-field absorption for the protons adjacent to the ether oxygen in the oxetane ring at δ 4.79 (d, J = 6.3 Hz) and 4.52 (dd, J = 2.2, 6.4 Hz).[23] The expected thermal instability of the [2.2.0] system was verified by heating a degassed-benzene solution to 175 °C for 3 h. Ketone **8** decomposed to form dienone **5b** and an unidentified isomer (GC–MS). In contrast, thermolysis of benzene solutions of **6a** and **7** left these samples unchanged after 3 h at 175 °C. Wolff and Agosta have previously used the thermal stability difference as one of the criteria to distinguish [2.1.1] systems from [2.2.0] systems.[14]

Table I. Ring Closure Regioselectivity and Product Quantum Yields of 1-Acyl-1,5-hexadienes

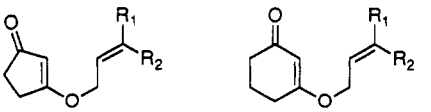


dienone	n	X	R	1,5:1,6 closure	Φ_p
18a[a]	2	CH_2	H	10:90	0.097
5a	2	O	H	100:0	0.011
18b[a]	2	CH_2	CH_3	0:100	0.36
5b	2	O	CH_3	0:100	0.018
17a[a]	3	CH_2	H	74:26	0.26
4a	3	O	H	100:0	0.20
17b[a]	3	CH_2	CH_3	13:87	0.55
4b	3	O	CH_3	100:0[b]	0.002

[a] Data for these compounds taken from ref 13. [b] If the unidentified minor isomeric product is a 1,6 closure product, then the 1,5:1,6 ratio would be 61:49.

The photoreaction of **4a** could be sensitized with either benzophenone or *m*-methoxyacetophenone. The photoreaction was quenched 26% by 5 M 2,3-dimethyl-1,3-butadiene and 14% by 2.3 M biphenyl. These results are consistent with the expectation that the photocycloadditions are coming from the triplet manifold. However no photoproducts were detected in attempts at sensitizing the photoreactions of **4b**, **5a**, or **5b** with *m*-methoxyacetophenone. The results with acetophenone and benzophenone were inconclusive as the photolysis solutions were complicated by the formation of small amounts of several minor products which made it difficult to observe (GC) the appearance of the photoadducts. Analysis by GC–MS showed that the new products were not isomers of the dienones. Attempts at quenching the photolysis of **5a** with 2,3-dimethyl-1,3-butadiene (4.1 M) were unsuccessful.

Labeling Studies. Stereospecifically deuterated dienones **11** and **12** were prepared from the 3-deuterated allylic alcohols. Samples of the (Z)-labeled isomers **11a** and **12a** were irradiated in benzene-d_6, and the reaction was monitored by ^1H NMR (200 MHz). Photolysis of dienone **11a** led to substantial scrambling of the label (28%) without any evidence of photoproduct formation. The progressive scrambling of the label in the dienones gives strong evidence for the reversible formation of an intermediate. The greater rate of reversion of **11a** accounts for most of the difference in the quantum yields between **4a** and **5a**.



11 12

a: R_1 = H, R_2 = D; b: R_1 = D; R_2 = H

Discussion

Oxa substitution has a profound effect on the regiochemistry, quantum yields, and isolated yields of the intramolecular [2 + 2] photocycloaddition reaction. In general, 3-oxa substitution in the 1,5-hexadiene system favors formation of crossed closure products with reduced quantum yields (Table I). At the outset of this investigation we anticipated that oxa substitution would have a similar stabilizing effect on the putative 1,4-biradicals

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formed by 1,5 (13) and 1,6 closure (14). Based on this simple analysis we predicted that the regiochemical selectivity of the photocycloaddition would be similar to that seen with the alkenyl analogs. However, our results point out that the relative energies of the biradical intermediates is not a major controlling factor governing the regioselectivity of the cycloaddition.

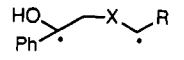
13 14

a: n = 1; b: n = 2

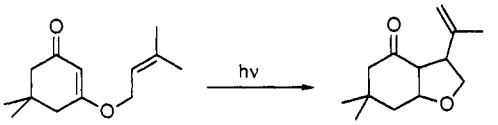
A more in depth analysis shows that introduction of the oxa substituent may affect several facets of the cycloaddition reaction pathway, including the triplet energy of the enone, the lifetimes of the excited enone and biradical intermediates, and the electron distribution (and thus initial site of reaction) of the excited enone. The ability to sensitize the photocycloaddition of dienone **4a** with the common triplet sensitizers benzophenone (E_T = 69 kcal/mol) and *m*-methoxyacetophenone (E_T = 72 kcal/mol) establishes the triplet nature of the reaction and suggests that the oxa substitution does not grossly alter the E_T of the enone system. It is unlikely that the E_T of dienone **4b** differs greatly from **4a**, and the inability to observe sensitization of the photoreaction of **4b** is likely due to the difficulty of observing the photoproduct in the presence of side products in the sensitized reaction mixture.[24] Although the side products are formed in small amounts, they obscure observation of the cycloaddition product (GC) which is formed with a low quantum yield. We believe a similar explanation holds for the inability to observe sensitization in the cyclopentenone series. We cannot discount the alternative explanation that the photocycloaddition reactions of **4b**, **5a**, and **5b** are coming from the singlet manifold. However, since it is well established that upon excitation cyclohexenone and cyclopentenone rapidly and efficiently form reactive triplets,[25,26] and the photocycloaddition of **4a** can be triplet sensitized and quenched, it is reasonable to assume that the photoreactions of **4b**, **5a**, and **5b** are also coming from the triplet manifold.

Studies by Tamura provide strong evidence that the crossed photoproducts are formed by initial 1,5 (as opposed to 2,6 closure).[27] Irradiation of dienone **15** produces the disproportionation product **16**, which demonstrates that the α-enone carbon is the reactive site for the initial bond closure. Similar behavior is seen with 1-acyl-1,5-hexadienes.[28] Thus it appears that the site of reactivity of the excited oxa-substituted enone triplets is similar to the alkenyl analogs.[29]

Table II. Norrish Type II Triplet Biradical Lifetimes (Data Taken from Ref 32)



biradical	X	R	τ, ns (MeOH)	τ, ns (heptane)
19	CH_2	CH_3	93	38
20	CH_2	OCH_3	70 ± 5	30
21	CH_2	Ph	146 ± 18	55 ± 8
22	O	Ph	1.3	1.7



15 16

The lifetimes and fates of the transient intermediates are a more complex matter. Our ability to quench the photocycloaddition of **4a** only with higher quencher concentrations and the inability to quench the photocycloaddition of **5a** suggests that the oxa enone triplet lifetimes are shorter than the alkenyl analogs. For example, Wolff and Agosta reported that **18a** is efficiently quenched by 2,3-dimethyl-1,3-butadiene.[14] It is not clear whether the lifetimes of the excited enones are limited by direct decay to the ground state (radiative and nonradiative) or by formation of the biradical intermediate.

17 18

a: R = H; b: R = CH_3

The deuterium labeling experiments give insight into the formation and fate of the biradical intermediates. The progressive loss of stereochemistry of the deuterium label in **11a** and **12a** is consistent with the reversible formation of biradical intermediates.[6,30] Assuming that the lifetime of the biradical intermediate **13b** is sufficient to allow loss of stereochemical integrity of the deuterium label (rotation faster than cleavage/bond formation), and biradical reversion gives equal amounts of **12a** and **12b**, then the ratio of the rates of reversion to the rate of product formation, k_r/k_p, for dienone **12a** equals twice the slope of the line obtained by plotting percent increase in the *E* isomer versus percent conversion: $k_r/k_p = 1.7$, $y = 4.48 + 0.86x$, $r^2 = 0.994$. For **11a**, the large amount of scrambling observed prior to formation of measurable amounts of photoproduct only permits us to estimate a lower limit for k_r/k_p. Assuming a detection limit of 5% by NMR, $k_r/k_p \geq 11.2$ for **11a**. The larger k_r/k_p ratio seen with the cyclopentenone system may be, in part, a reflection of the increased strain energy of the tricyclic ketone product **7** relative to **6a**. An MM2 calculation places ketone **7** ~11 kcal/mol higher in strain energy than ketone **6a**. Collapse

(24) It should be noted that Dauben has shown that the intramolecular photocycloaddition of 5-methyl-1,5-hexadien-3-one could not be not sensitized by benzophenone or acetone, and it is only weakly sensitized by *m*-methoxyacetophenone. However, the reaction is strongly sensitized by *p*-methoxyacetophenone and xanthone. Here the usual correlation with triplet energy of the sensitizer and acceptor is not followed. It was believed that the ability of *p*-methoxyacetophenone and xanthone to sensitize the reaction was related to the relatively long triplet lifetimes of the $\pi-\pi^*$ triplet states of these sensitizers and not solely a function of the triplet energy. It should also be noted that Dauben and Agosta were unable to quench the photocycloaddition of 5-methyl-1,5-hexadien-3-one with dienes. See: (a) Dauben, W. G.; Cogen, J. M.; Ganzer, G. A.; Behar, V. *J. Am. Chem. Soc.* **1991**, *113*, 5817–5824. (b) Agosta, W. C.; Wolff, S.; Matlin, A. R. *Tetrahedron Lett.* **1983**, *24*, 2961.

(25) Schuster, D. I.; Dunn, D. A.; Heibel, G. E.; Brown, P. B.; Rao, J. M.; Woning, J.; Bonneau, R. *J. Am. Chem. Soc.* **1991**, *113*, 6245–6255.

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(27) Tamura, Y.; Ishibashi, H.; Ikeda, M. *J. Org. Chem.* **1976**, *41*, 1277.

(28) Wolff, S.; Barany, F.; Agosta, W. C. *J. Am. Chem. Soc.* **1980**, *102*, 2378.

(29) It should be noted that in the [2 + 2] photocycloadditions of 1-acyl-1,6-heptadienes, the initial bond formation may involve either the α- or β-enone carbon. See ref 16 and Becker, D.; Denekamp, C.; Haddad, N. *Tetrahedron Lett.* **1992**, *33*, 827–830.

(30) In principle the excited enone functionality could energy-transfer to the alkene which would then be able to isomerize the label without formation of biradical intermediates **13** or **14**. However the high E_T of simple alkenes (~80 kcal/mol) makes energy transfer from the enones ($E_T \leq 70$ kcal/mol) unlikely.

of the biradical **13a** to the tricyclic product may be retarded relative to **13b** due to the higher strain, and as a result reversion becomes more competitive.

The deuterium labeling studies make it possible to access the efficiency of biradical formation. The quantum yield for the formation of the biradical intermediates, Φ_{bi}, is equal to $[(k_r/k_p)(\Phi_p)] + \Phi_p$: **13b**, $\Phi_{bi} = 0.54$; **13a**, $\Phi_{bi} \geq 0.13$. The Φ_{bi} for the alkenyl system **17a** has been reported to be 0.46.[31] The comparable values for the two cyclohexenone systems indicates that oxa substitution does not affect the efficiency in which the photoexcited enones form a biradical intermediate by bond formation at the α-carbon.

Placement of an oxygen adjacent to a radical center in a 1,4 biradical affects both the stability of the radical and the intersystem crossing rate between the triplet and singlet energies surfaces. Caldwell has shown that oxa substitution has a profound effect on the triplet lifetimes of 1,4 biradical intermediates in the Norrish type II reaction.[32] Surprisingly Caldwell found that the connectivity of the oxa-substitution is an important factor governing the magnitude of the effect (Table II). Methoxy substitution at one of the radical centers (external substitution) in **20** decreased the triplet lifetime by ~25%, whereas incorporation of the oxygen in the biradical backbone (internal substitution) in **22** decreased the triplet lifetime by 30–100-fold. The large effect of internal oxygen substitution was attributed to the decrease in the average distance between the unpaired electrons due to the resonance interaction of the intervening oxygen. This results in an increase in the spin–orbit coupling which increases the intersystem crossing rate from the triplet to the singlet surface, and decreases the triplet lifetime.[33]

Oxa substitution should also decrease the triplet lifetimes of the 1,4 biradicals formed in the [2 + 2] photocycloadditions. However, the two biradical intermediates **13** and **14** differ with respect to the connectivity of the oxa substitution corresponding to the two cases mentioned in the Caldwell studies. Following Caldwell's results, we expect that the internally oxa-substituted triplet biradical **14** will have a substantially shorter lifetime than the externally substituted biradical **13**. In fact, the lifetime of biradical **14** may be less than a nanosecond due to the absence of the conjugating phenyl groups present in the Caldwell systems.[34] The k_r/k_p is 2.3 times larger for **4a** compared to the alkenyl analog **17a**. This difference may be a manifestation of the external oxa substitution effect which decreases the triplet lifetime of the biradicals formed by 1,5 closure.

The overall regioselectivity of the photocycloaddition is determined by the selectivity in the initial bond closure (1,5 vs 1,6) and the relative k_r/k_p ratios for the competing biradical intermediates. The extremely short triplet lifetimes expected for the oxa-substituted biradicals formed by 1,6 closure may give rise to such large k_r/k_p ratios that little or no straight closure photoproducts are formed. Examination of the Φ_p's for dienones **4a**, **4b**, **5a**, and **5b** show that the values markedly decrease as the proportion of 1,6-closure increases in the related alkenyl analogs (Table I). When the ring size and 5-alkyl substitution effects promote 1,6 closure,[14] the oxa dienones form a larger percentage of relatively nonproductive biradical intermediates. Straight closure is only seen with dienone **5b** where the alkenyl analog, **18b**, only closes 1,6. In this case there must be no competing 1,5 pathway and therefore the 1,6 closure mode eventually collapses to form the straight closure product. Thus it seems that oxa substitution does not severely change the selectivity in the initial bond closure, but alters the final product composition by differentially effecting the fates of the biradical intermediates. Although oxa substitution strongly effects the overall regiochemistry of the cycloaddition, the ring size and 5-alkyl substitution effects noted by Wolff and Agosta still play an important role in determining the reaction path.

Experimental Section

General Procedures. All reactions and photolyses were carried out under a N_2 atmosphere. All chemicals were reagent grade or better. Benzene was distilled from sodium benzophenone, and hexanes were distilled from CaH_2 prior to use. Flash chromatography was carried out with Merck grade 60 (230–400-mesh) silica gel. Preparative GC was conducted on a 5-ft × 0.25-in. 5% OV101 column. Analytical GC was conducted on a 2-mm × 15-m OV101 fused silica capillary column. High-resolution mass spectral analyses were performed by the Mass Spectrometry Center at the Department of Chemistry, University of Pennsylvania.

3-(2-Propenoxy)cyclohex-2-en-1-one (4a). Cyclohexane-1,3-dione (3.0 g, 24.6 mmol) was dissolved in 25 mL of benzene along with allyl alcohol (4.3 mL, 63 mmol) and a catalytic amount of toluenesulfonic acid (~5 mg). The reaction mixture was heated at reflux for 16 h using a Dean–Stark trap to remove the water. The crude reaction mixture was transferred to a separatory funnel and washed with $NaHCO_3$, water, and brine. The organic layer was dried over $MgSO_4$ and the solvent stripped with a rotorary evaporator. The resultant oil was purified by Kugelrohr distillation (75–85 °C, 0.15 mmHg) to give 3.15 g (84%) of dienone **4a** as a clear oil: ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.92 (1 H, ddt, J = 17.3, 10.5, 5.5 Hz), 5.30 (1 H, s), 5.30 (2 H, mult), 4.24 (1 H, dt, J = 1.2, 5.5), 2.39 (2 H, t, J = 6.2 Hz), 1.94 (2 H, t, J = 6.4 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 199.5, 177.3, 131.2, 118.7, 103.0, 68.9, 36.5, 28.8, 21.0; IR 1630, 1530; UV (cyclohexane) ϵ_{236} = 18650, ϵ_{306} = 42.1 cm^{-1} M^{-1}; HRMS (CI-NH_3) calcd for $C_9H_{13}O_2$ (M + H) 153.0915, obsd 153.0908.

3-(2-Methyl-2-propenoxy)cyclohex-2-en-1-one (4b). Following the general procedure as described for the synthesis of **4a**, 1,3-cyclohexadione (3.0 g, 24.6 mmol) was condensed with 2-methyl-2-propenol (5.1 mL, 61 mmol) to give 3.45 g (84%) of dienone **4b** after Kugelrohr distillation (84–95 °C, 0.25 mmHg): ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.13 (1 H, s), 4.80 (2 H, d), 4.08 (2 H, br s), 2.25 (2 H, t), 2.13 (2 H, t), 1.80 (2 H, quint), 1.60 (3 H, s); ^{13}C NMR (50 MHz, $CDCl_3$) δ 199.3, 177.2, 138.8, 113.5, 102.8, 71.7, 36.4, 28.7, 21.0, 19.1; IR 1640, 1590; UV (cyclohexane) ϵ_{308} = 45 cm^{-1} M^{-1}; HRMS (CI-NH_3) calcd for $C_{10}H_{15}O_2$ (M + H) 167.1072, obsd 167.1077.

3-(2-Propenoxy)cyclopent-2-en-1-one (5a). The general procedure as outlined above for the synthesis of **4a** was followed using cyclopentane-1,3-dione (1.0 g, 10.4 mmol), allyl alcohol (3.4 mL, 50 mmol), and TsOH (~5 mg) to give 0.58 g (40%) of dienone **5a** after Kugelrohr distillation (65–80 °C, 0.20 mmHg): ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.55 (1 H, m), 4.96 (3 H, m), 4.12 (2 H, dt, J = 5.7, 1.3 Hz), 2.20 (2 H, m), 1.96 (2 H, m); ^{13}C NMR (50 MHz, $CDCl_3$) δ 205.1, 189.3, 130.8, 118.6, 104.6, 71.9, 33.5, 27.9; IR 1700, 1600; UV (cyclohexane) ϵ_{290} = 37.4 cm^{-1} M^{-1}; HRMS (CI-NH_3) calcd for $C_8H_{11}O_2$ (M + H) 139.0759, obsd 139.0758.

3-(2-Methyl-2-propenoxy)cyclopent-2-en-1-one (5b). The general procedure as described for the synthesis of **4a** was followed using cyclopentane-1,3-dione (1.56 g, 16 mmol), allyl alcohol (6.8 mL, 81 mmol), and TsOH (~5 mg) to give 1.3 g (51%) of dienone **5b** after Kugelrohr distillation (75–85 °C, 0.20 mmHg): ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.20 (1 H, s), 4.93 (2 H, d J = 6.0), 4.30 (2 H, s), 2.53 (2 H, m), 2.32 (2 H, m), 1.69 (3 H, s); ^{13}C NMR (50 MHz, $CDCl_3$) δ 206.0, 189.9, 138.5, 114.3, 105.0, 75.2, 33.8, 28.3, 19.1; IR 1700, 1600; UV (cyclohexane) ϵ_{294} = 43 cm^{-1} M^{-1}; HRMS (CI-NH_3) calcd for $C_9H_{12}O_2$ (M^+) 152.0837, obsd 152.057.

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(34) From the Caldwell studies (ref 32) it appears that the increase in lifetime caused by phenyl substitution (1.5–3.5 times) out weighs the decrease in lifetime engendered by external oxygen substitution (~0.75).

Synthesis of (*Z*)-3-Deuterioallyl Alcohol. The deuterated alcohol was prepared following the procedure described by Korth,[35] except that THF was used as the solvent in place of diethyl ether.[36] Propargyl alcohol (47.2 g, 840 mmol) was dissolved in 150 mL of dry THF (distilled from sodium benzophenone) and slowly added to $LiAlH_4$ (33.5 g, 840 mmol) in 500 mL of THF at −8 °C. The reaction mixture was stirred at −8 °C for 2 h and then allowed to warm to rt and stirred overnight (~15 h). The reaction mixture was cooled to −8 °C and quenched by the slow addition of D_2O (60.5 g, 3.0 mol). The mixture was stirred for 4 h, filtered, dried over $MgSO_4$, and fractionally distilled. The desired allyl alcohol distilled at 98 °C (15 g, 29%); ^1H NMR ($CDCl_3$) 5.95 (m, 1 H), 5.25 (m, 0.05 H), 5.08 (dt, 0.95 H), 4.10 (2 H, d).

Synthesis of (*E*)-3-Deuterioallyl Alcohol.[35] Propargyl alcohol-d_2 (≥95% d_2) was prepared by three rounds of treatment of propargyl alcohol with 1.5 M NaOD following the procedure of Grant and Djerassi.[37] The dideuterated alcohol (2 g, 34 mmol) was dissolved in 15 mL of dry THF and then slowly added (−5 °C) to a suspension of $LiAlH_4$ (1.29 g, 34 mmol) in 50 mL of THF. The reaction mixture was stirred for 1 h at 0 °C and then quenched with 4 mL of a saturated Na_2SO_4 solution. The solution was filtered and the bulk solvent removed by distillation through a 15-cm column packed with glass helices and then with a microspinning band column. Some THF and starting material remained in the product mixture: ^1H NMR ($CDCl_3$) 5.96 (1 H, dt), 5.26 (0.9 H, dt), 5.17 (0.1 H, br d), 4.14 (2 H, dd).

(*Z*)-3-(2-Propenoxy)cyclopent-2-en-1-one-d_1 (11a). Via the general procedure as described for the synthesis of **4a**, cyclopentane-1,3-dione (2.25 g, 23 mmol) was condensed with (*Z*)-3-deuterioallyl alcohol-*d* (2.7 g, 46 mmol) to give after Kugelrohr distillation 38% (1.23 g, 8.8 mmol) of dienone **11a**. Some deuterium from the hydroxyl of the dideuterated allyl alcohol exchanged into the 2-position (δ 5.20) of the dienone. The exchange presumably occurred with the dione starting material prior to the condensation with the alcohol: ^1H NMR (200 MHz, C_6D_6) δ 5.65 (1 H, m), 5.20 (0.77 H, s), 5.10 (0.05 H, dt), 5.01 (0.95 H, dt), 4.0 (2 H, d), 2.05 (4 H, br s).

(*E*)-3-(2-Propenoxy)cyclopent-2-en-1-one-d_1 (11b). Via the general procedure as described for the synthesis of **4a**, cyclopentane-1,3-dione (980 mg, 10 mM) was condensed with (*E*)-3-deuterioallyl alcohol (0.85 g, 14.6 mmol) to give dienone **11b**. A spectroscopic sample was obtained by prep GC (120 °C): ^1H NMR (200 MHz, $CDCl_3$) δ 5.55 (1 H, m), 5.15 (0.1 H, m) 5.1 (1 H, br s), 4.97 (0.9 H, dt) 4.12 (2 H, dt, J = 5.7, 1.3 Hz), 2.20 (2 H, m), 1.96 (2 H, m).

(*Z*)-3-(2-Propenoxy)cyclohex-2-en-1-one-d_1 (12a). Via the general procedure as described for the synthesis of **4a**, cyclohexane-1,3-dione (2.8 g, 25 mmol) was condensed with (*Z*)-3-deuterioallyl alcohol (3.0 g, 50 mmol) to give 73% (2.8 g, 18 mmol) of dienone **12a** after Kugelrohr distillation. Some deuterium from the hydroxyl of the dideuterated allyl alcohol exchanged into the 2-position (δ 5.35) of the dienone. The exchange presumably occurred with the dione starting material prior to the condensation with the alcohol: ^1H NMR (200 MHz, C_6D_6) δ 5.62 (1 H, m), 5.35 (0.75 H, s), 5.08 (0.05 H, m), 4.96 (0.95 H, dt J = 1.1, 8.6 Hz), 3.82 (2 H, d), 2.15 (2 H, t), 1.85 (2 H, t), 1.4 (2 H, quint).

(*E*)-3-(2-Propenoxy)cyclohex-2-en-1-one-d_1 (12b). Via the general procedure as described for the synthesis of **4a**, cyclohexane-1,3-dione (1.1 g, 10 mmol) was condensed with (*E*)-3-deuterioallyl alcohol (0.85 g, 14.6 mmol) to give 60% (0.9 g, 6 mmol) of dienone **12b**. A spectroscopic sample was prepared by prep GC (120 °C): ^1H NMR (200 MHz, C_6D_6) δ 5.60 (1 H, dt), 5.34 (1 H, s), 5.03 (0.9 H, dt), 4.96 (0.1 H, m), 2.15 (2 H, t), 1.85 (2 H, t), 1.4 (2 H, quint).

General Procedure for Irradiation of Dienones. Dienones were dissolved in hexanes or benzene and irradiated through a Pyrex filter using a 450-W medium-pressure Hanovia lamp under a nitrogen atmosphere. The solutions were purged with nitrogen for at least 10 min prior to irradiation. The reaction progress was monitored by capillary GC. After irradiation the solvent was removed (rotovap), and the residue was purified by flash chromatography and/or preparative GC.

Irradiation of 4a. Dienone **4a** (1.35 g, 8.9 mmol) was dissolved in 300 mL of hexanes and irradiated for 24 h. Flash chromatography (2:1 hexane–ether, R_f 0.35) gave 730 mg (54%) of ketone **6a** as a clear oil: ^1H NMR (200 MHz, $CDCl_3$) δ 3.77 (1 H, d, J = 5.9 Hz), 3.55 (1 H, d, J = 5.8 Hz), 3.07 (1 H, t, J = 2.8 Hz), 2.43 (1 H, br s), 2.0–1.6 (6 H, m), 1.76 (1 H, d,d J = 7.5, 3.0 Hz), 1.53 (1 H, dd, J = 7.5, 3.0 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 207.4, 92.0, 65.0, 56.8, 42.1, 42.0, 39.6, 26.6, 24.9; IR 1720 cm^{-1}; MS m/e 152; HRMS (CI-NH_3) calcd for $C_9H_{13}O_2$ (M + H) 153.0915, obsd 153.0908.

A secondary photolysis product comprised 19% (GC) of the product mixture (R_f = 0.21). Preliminary structural analysis by ^1H NMR showed aldehydeic protons. Irradiation of purified **6a** produced the same aldehydic compound.

Irradiation of 4b. Dienone **4b** (5.26 g, 27.1 mmol) was dissolved in 75 mL of hexanes and irradiated for 61 h. Analysis by GC showed ~1.7% conversion to ketone **6b** and 1.1% conversion to an unidentified isomer. The starting material was present in >90%. Ketone **6b** was isolated following a series of three chromatographic procedures: initial prep GC (125 °C), flash chromatography (1:1 hexane–ether) and final prep GC (125 °C): ^1H NMR (200 MHz, $CDCl_3$) δ 3.58 (2 H, dd, J = 6.0, 10.2 Hz), 2.35–1.35 (7 H, m), 1.75 (1 H, d, J = 8.0 Hz), 1.46 (3 H, s), 1.37 (1 H, dd, J = 8.0, 9.2 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 210.40, 89.76, 75.06, 61.15, 49.52, 42.32, 41.35, 26.43, 22.56, 13.10; IR 1710 cm^{-1}; MS m/e 166; HRMS (CI-NH_3) calcd for $C_{10}H_{15}O_2$ (M + H) 167.1072, obsd 167.1075.

Irradiation of 5a. Dienone **5a** (740 mg, 5.4 mmol) was dissolved in 50 mL of hexanes and irradiated for 100 h. Analysis by GC showed that ketone **7** was formed in ~95% at 30% conversion of the starting dienone. Ketone **7** was isolated by flash chromatography (2:1 hexanes–ether) followed by prep GC (110 °C): ^1H NMR (200 MHz, $CDCl_3$) δ 3.60 (2 H, br s), 3.30 (1 H, t, J = 3.1 Hz), 2.70–2.45 (2 H, m), 2.45–2.25 (2 H, m), 2.20 (1 H, m), 1.90 (1 H, dd, J = 3.1, 7.7 Hz), 1.70 (1 H, dd, J = 1.3, 7.8 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 208.67, 89.76, 64.70, 56.98, 43.39, 40.19, 38.85, 26.45; IR 1747 cm^{-1}; MS m/e 138; HRMS (CI-NH_3) calcd for $C_8H_{11}O_2$ (M + H) 139.0759, obsd 139.0784.

Irradiation of 5b. Dienone **5b** (550 mg, 3.6 mmol) was dissolved in 50 mL of benzene and irradiated for 43 h. Analysis by GC showed that ketone **8** was present in 20% at 53% conversion. Ketone **8** was isolated by prep GC (120 °C): ^1H NMR (200 MHz, $CDCl_3$) δ 4.79 (1 H, d, J = 6.3 Hz), 4.52 (1 H, dd, J = 2.2, 6.4 Hz), 3.04 (1 H, ddd, J = 1.4, 4.7, 6.4 Hz), 2.77 (1 H, dd, J = 9.6, 12.9 Hz), 2.53–2.28 (3 H, m), 1.95–1.74 (2 H, m), 1.23 (3 H, s); ^{13}C NMR (50 MHz, $CDCl_3$) δ 217.43, 95.35, 82.16, 48.93, 43.20, 38.57, 34.20, 27.14, 16.06; IR 1740 cm^{-1}; MS m/e 152 (M^+).

Thermal Stability of Photoproducts. Benzene solutions (~2 mg/mL) of photoadducts **6a**, **7**, and **8** were placed in separate Pyrex tubes, degassed (3 freeze–pump–thaw cycles) and sealed in vacuo (~0.75 mmHg). The tubes were immersed in a silicon oil bath at 175 °C for 3 h and then analyzed by GC and GC–MS. Under these conditions photoproducts **6a** and **7** remained unchanged. Ketone **8** gave rise to dienone **5b** (GC–MS) and an unidentified isomeric compound (GC–MS).

Quantum Yield Determinations. The quantum yields for product formation, Φ_p, were determined at 313 nm by filtering the light from the mercury vapor lamp through a 2 mM K_2CrO_4–5% K_2CO_3 solution. The sample cuvettes were irradiated using a rotating merry-go-round sample holder and the reactions were monitored by capillary GC. All samples contained nonane as an internal standard, and response factors were calculated for the FID detector. All samples (0.1–0.004 M) were prepared from freshly distilled benzene and out-gassed with N_2 for 10 min prior to irradiation. Valerophenone (0.1–0.004 M) was irradiated concurrently and the formation of acetophenone was used as a chemical actinometer.[21] Samples were run in at least duplicate. The reaction was monitored by capillary GC and conversions were kept below 10%.

Quenching Studies of Dienones 4a and 5a. Pyrex cuvettes containing cyclohexane solutions of dienone, quencher, and nonane (internal standard) where irradiated simultaneously with samples which lacked the quencher using the merry-go-round set up. The concentrations of the dienone and standard were identical for both

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samples. Each run was performed in at least duplicate, and each sample was analyzed at least twice by capillary GC. In the presence of 5.0 M 2,3-dimethyl-1,3-butadiene (quencher) the photocycloaddition of dienone **4a** (4.7 mM) was quenched by 27% after 2 h of irradiation. In the presence of 2.3 M biphenyl (quencher) the photocycloaddition of dienone **4a** (1.4 mM) was quenched by 14% after 2 h of irradiation. Irradiation of dienone **5a** (3.9 mM) in the presence of 4.1 M 2,3-dimethyl-1,3-butadiene for 70 h showed no quenching of the photocycloaddition reaction.

Sensitization Studies of Dienones 4a, 4b, 5a, and 5b. Benzene solutions (~3 mL) containing dienone (1.9–7.1 mM), sensitizer (10–20 mM), and an internal standard (nonane) were prepared so that the sensitizer absorbed all the light in the portion of the spectrum where the dienone absorbed. The samples were irradiated ($\lambda \geq 280$ nm) using the merry-go-round set up concurrently with control samples which contained identical concentrations of dienone but no sensitizer. All samples were run in at least duplicate and analyzed by capillary GC.

Stereochemical Scrambling Studies. ^{1}H NMR samples of dienones **11a** and **12a** (~0.1 M in benzene-d_6) were irradiated at $\lambda \geq 280$ nm. The degree of scrambling was measured by integration of the appropriate C6 hydrogens NMR signals: **12a**, δ 5.08 vs 4.96; **11a**, δ 5.10 vs 5.01. The use of benzene-d_6 as solvent gave rise to large changes in chemical shift that permitted the separation of signals in the vinyl region. The key vinyl protons that needed to be integrated were doublets of triplets. In mixtures of the (*Z*)- and the (*E*)-deuterio isomers of the dienones one of the triplet pairs was partially obscured by overlapping resonances. Because the intensity of the two halves of the signal were not equal, a weighting factor was used to determine the correct integral value by measurement of one of the triplets of the dt multiplet. The weighting factors were determined from the highly enriched isomers. The ratio of the integrals of the two triplets was 56:44 in dienones **11a** and **12a** and in the *E* and *Z* deuterated allylic alcohols. The extent of conversion of dienone **12a** to photoproduct was monitored by the appearance of signals at δ 4.02 (1 H, d) and δ 3.42 (1 H, d). Dienone **11a** showed large amounts of scrambling of the label before any product could be observed by NMR. An estimated 5% of the product would have been accurately detected.

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Supplementary Material Available: ^{1}H NMR spectra of **4a**, **4b**, **5a**, **5b**, **6a**, **6b**, **7**, **8**, **11a**, **11b**, **12a**, and **12b** and ^{13}C NMR spectra of **4a**, **6a**, **7**, and **8** (16 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

Stereoelectronic Effect of the Trimethylsilyl Substituent upon C–O Bond Lengths at the β Position: Some Structural Studies

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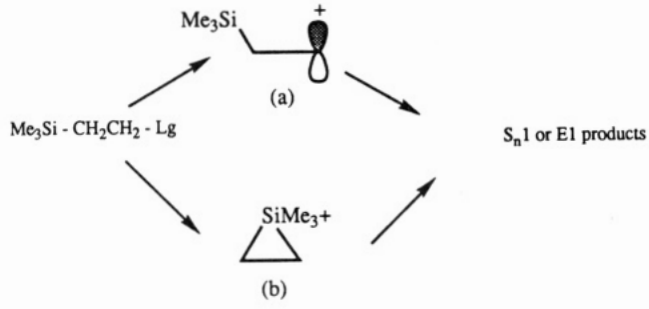
Results of low-temperature (130 K) crystal structure analyses for seven β-trimethylsilyl-substituted cyclohexylnitrobenzoate esters are reported. For those molecules (three) with the Si–C and C–O bonds antiperiplanar the C–O bond lengths are increased by 0.014 Å av (Δ/σ min = 2.9) compared with that in the silicon-free analogue. For those molecules (four) with the Si–C and C–O bonds gauche no such systematic lengthening of the C–O bonds is observed. The result is in qualitative agreement with that [$\Delta l \propto \cos^2$ (Si–C–C–O)] predicted from semiempirical MO calculations on a simple model complex and is attributed to the effects of interactions between the Si–C σ and C–O σ^* orbitals. It is suggested that existence of the observed ground-state effect constitutes persuasive, if circumstantial, evidence that the major kinetic effects known to result from the presence of a β silicon substituent also have their genesis in the same σ–σ^* interactions.

Introduction

The ability of silicon to accelerate reactions which lead to the development of positive charge on a β carbon atom, the so called β effect, is pivotal to the chemistry of organosilicon compounds.[1,2] For example, the presence of β $SiMe_3$ has been shown, in stereochemically constrained systems, to enhance solvolysis rates (relative to β H) by a factor of 10^{12}.[3] In addition to its inductive effect, the $SiMe_3$ substituent is believed to stabilize the developing carbocation by one or other of two mechanisms (Scheme I). The first involves internal displacement of the leaving group to form the silacyclopropylium cation b and the second involves hyperconjugation of the C–Si σ bond with the unfilled β carbon p-orbital a. The relative importance of these two intermediates in systems containing primary β carbon atoms remains substantially unresolved.[2]

Recently, however, Lambert and co-workers, in a series of elegant experiments employing conformationally constrained systems based on 5- and 6-membered rings,[3,4] have demonstrated a marked dependence of reaction rate upon

Scheme I. Stabilization of Positive Charge by β Silicon



the Si–C–C–Lg dihedral angle (Lg = leaving group) and conclude that, at least in such secondary (carbon atom) systems, there is necessarily substantial involvement of the "open" cation a in the reaction pathway. The increasing

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