δ 7.10–7.56 (m, integration not determined, 3 aromatics + residual CHCl$_3$), 7.05–7.10 (m, 1.00 H, 1 aromatic), 5.73 (dd, 0.53 H, H-6, $J_{6,5} = 2.5$, $J_{6,7} = 5$), 5.26 (m, 0.95 H, H-7), 4.07 (m, 1.00 H, H-5), 3.80 (m, 0.99 H, H-1), 3.43 (dd, 0.59 H, H-8, $J_{8,1} = 6$, $J_{8,7} = 2.5$).

Sensitized Irradiation of Triene 11a. A solution of 21.0 mg (0.12 mmol) of 11a, 12.7 mg (0.055 mmol) of *p*-(dimethylamino)benzophenone, and 4.0 mg of tetradecane (GC standard) in 20 mL of cyclohexane was divided into two equal portions, and each was separately irradiated for 10 min in Cell B with light filtered through a WG-360 glass (Schott) filter (70% conversion by GC/NMR). The photolysates were worked up as in the case of the sensitized irradiation of unlabeled triene 11 to give 1.1 mg (5%) of COT 10a [^{1}H NMR (400 MHz; CDCl$_3$) δ 7.24–7.36 (m, integration not determined, 3 aromatics + residual CHCl$_3$), 6.99–7.05 (m, 1.00 H, 1 aromatic), 6.89–6.92 (m, 0.99 H, H-6), 6.65 (overlapping s and d, 0.95 H, H-10; $J_{10,9} = 11.5$), 6.03–6.09 (m, 1.51 H, H-8 and residual H-9), and 5.91 (dd, 0.55 H, residual H-7, $J_{7,6} = 4.5$, $J_{7,8} = 11.5$)], 6.1 mg (28%) of recovered triene 11a [^{1}H NMR (400 MHz; CDCl$_3$) δ 7.52 (m, 1.00 H, 1 aromatic), 7.27 (m, integration not determined, 2 aromatics + residual CHCl$_3$), 7.13 (m, 1.00 H, 1 aromatic), 6.76 (m, 0.95 H, H-5), 6.11 (m, 0.96 H, H-7), 6.07 (br d, 0.49 H, H-8; $J_{7,8} = 2.5$), 4.17 (m, 0.99 H, H-1), and 3.79 (t, 0.53 H, H-6, $J_{6,5} = J_{6,1} = 4.5$)], and SB 12a (a residue of 3.2 mg of material was recovered from NMR sample) [^{1}H NMR (250 MHz; CDCl$_3$) δ 7.10–7.56 (m, 3.90 H, 3 aromatics + residual CHCl$_3$), 7.05–7.10 (m, 1.00 H, 1 aromatic), 5.73 (dd, 0.52 H, H-6, $J_{6,5} = 2.5$, $J_{6,7} = 5$), 5.26 (m, 0.96 H, H-7), 4.07 (m, 1.01 H, H-5), 3.80 (t, 0.52 H, H-1, $J_{1,5} = J_{1,8} = 6$), 3.43 (m, 1.01 H, H-8).

Quantum Yield Determinations. Quantum yields were performed on an apparatus previously described,[21] which includes an optical bench arranged for beam splitting into a ferrioxalate actinometer.[22] Cyclohexane solutions (3.5 mL) of reactants (ca. (4.5–6.5) × 10^{-3} M) and sensitizer, if any (*p*-(dimethylamino)benzophenone, ca. 1.0 × 10^{-3} M), were deoxygenated prior to irradiation by flushing with argon. A positive pressure of argon was maintained over the stirred solutions throughout the course of the irradiations. The quantum yields (Φ's) were obtained from several runs extrapolated to zero conversion. Product analyses were determined by a combination of GC (internal tetradecane standard) and HPLC (for the determination of relative amounts of COT 10 and triene 11). The HPLC analyses were performed on a normal-phase 16-μm silica column (Waters, μ Porasil, 3.9 mm × 300 mm). The eluting solvent system was 1% ethyl acetate in hexane. Photometric detection was carried out at 300 nm, chromatograms were integrated using a Waters 740 Data Module, and relative detector responses were calibrated against known mixtures of COT 10 and triene 11. For the direct irradiation of triene 11, light of wavelength 280 nm was used. For sensitized runs with *p*-(dimethylamino)benzophenone, the sensitizer absorbed >95% of the incident light (366 nm) employed.

Acknowledgment. We thank the Spectroscopic Services Laboratory of the University of Alberta (U. of A.) and the Agriculture Canada Research Station at Lethbridge for the 400-MHz NMR. The U. of A. is also thanked for the precision mass spectra. Financial support from the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged.

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Stereochemistry of Photocycloaddition of (*E*)-1,2-Dicyano- and (*Z*)-1,2-Diethoxyethylene to 5-Substituted Adamantanones

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The photocycloaddition of olefins to 5-substituted adamantanones produces two geometrically isomeric oxetanes in which the oxygen atom and the 5-substituent are in anti or syn positions. The substituent was varied from fluoro, chloro, bromo, hydroxyl, and phenyl to *tert*-butyl. Although the mechanisms of the reaction with electron-rich and electron-poor olefins are quite different, the product ratios are similar (~60:40) in all instances. The preference of product formation from the attack on the *zu* face is discussed in terms of transition-state hyperconjugation.

Introduction

5-Substituted adamantanones 1-X and their derivatives have proved to be useful probes in research aimed at understanding the electronic factors in face selection. The advantages to their use include the presence of two virtually isosteric faces, the absence of conformational uncertainty, the possibility of forming only two geometrically isomeric products, and the ease of handling the (usually) solid products. Almost any reaction involving interconversions between trigonal and tetragonal carbon can be examined by means of them,[1] and a generalization has emerged that the new bond preferentially forms at that face that leaves it antiperiplanar to the most electron-rich vicinal bond(s). This notion, that delocalization of the electrons comprising these bonds into the σ^* component of the incipient one stabilizes the transition state, was first proposed by Cieplak[2] in 1981 to account for the well-known propensity of nucleophiles to attack the axial face of cyclohexanones.

We reported[3] recently in a preliminary paper that the concerted (if not synchronous) photocycloaddition of the electron-poor olefin (*E*)-1,2-dicyanoethylene (2) to 5-sub-

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(1) For a summary of earlier studies and references, see: Bodepudi, V.; le Noble, W. J. *J. Org. Chem.* **1991**, *56*, 2001.

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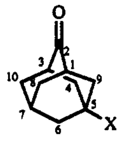
Table I. Key Proton Chemical Shifts and Coupling Constants (*J*) and Melting Points for 5-Substituted *trans*-11,12-Dicyanoadamantanoxetanes[a]

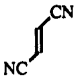
oxetane	H_{12} (δ)	H_{11} (δ)	H_1, H_3[b]	J_{11-12} (Hz)	mp (°C)
(1) 4-H)	5.12 (d)	3.68 (d)	2.40 (s, 2.34 (s)	5.70 ± 0.02	104–106
(2) (*E*)-4-F	5.13 (d)	3.73 (d)	2.62 (s), 2.56 (s)	5.60 ± 0.02	157–158
(3) (*Z*)-4-F	5.15 (d)	3.72 (d)	2.67 (s), 2.61 (s)	5.66 ± 0.02	171–173
(4) (*E*)-4-Cl	5.13 (d)	3.73 (d)	2.55 (s), 2.49 (s)	5.57 ± 0.02	122–124
(5) (*Z*)-4-Cl	5.15 (d)	3.71 (d)	2.58 (s), 2.52 (s)	5.73 ± 0.02	160–162
(6) (*E*)-4-Br	5.13 (d)	3.73 (d)	2.52 (s), 2.45 (s)	5.53 ± 0.02	143–145
(7) (*Z*)-4-Br	5.15 (d)	3.69 (d)	2.67 (s), 2.62 (s)	5.70 ± 0.02	152–154
(8) (*E*)-4-OH	5.13 (d)	3.72 (d)	2.55 (s), 2.48 (s)	5.61 ± 0.02	172–173
(9) (*Z*)-4-OH	5.14 (d)	3.71 (d)	2.59 (s), 2.54 (s)	5.68 ± 0.02	191–192
(10) (*E*)-4-Ph	5.17 (d)	3.73 (d)	2.59 (s), 2.51 (s)	5.71 ± 0.07	147–148
(11) (*Z*)-4-Ph	5.17 (d)	3.77 (d)	2.60 (s), 2.54 (s)	5.64 ± 0.04	199–200
(12) (*E*)-4-*t*-Bu	5.11 (d)	3.67 (d)	2.43 (s), 2.36 (s)	5.73 ± 0.05	151–152
(13) (*Z*)-4-*t*-Bu	5.11 (d)	3.68 (d)	2.44 (m), 2.39 (m)	5.63 ± 0.03	157–158

[a] Partial proton assignment; measured by Bruker AF-250 NMR; chemical shifts refer to $CDCl_3$ (δ 7.25). See Scheme II for the numbering system. [b] Data shown are not necessarily in the correct order.

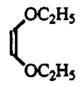
stituted adamantanones occurs with the formation of products in accord with this concept. Presently, we wish to record these observations with experimental detail and add to them the further finding that the use of (*Z*)-diethoxyethylene (**3**) gives the same stereochemical result even though this electron-rich olefin is known to undergo the reaction via a very different pathway. Exciplex formation has been proposed to be the initial step of a quenching interaction between ketone n,π* singlet or triplet states and olefins.[4a] The exciplex appears to have charge-transfer character, with the n,π* state acting as an electron donor to electron-poor olefins such as **2** and as an electron acceptor from electron-rich olefins such as **3**.[4a] Once formed, the exciplex is subject to dissociation or to bond formation leading to oxetanes, either directly (electron-poor olefins) or indirectly via 1,4-biradical intermediates (electron-rich olefins).



1-X



***E*-2**

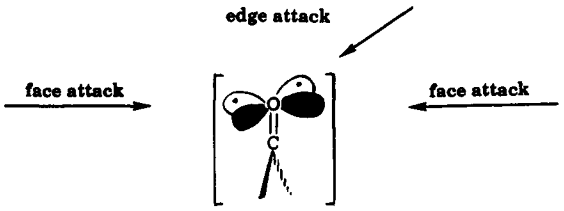


***Z*-3**

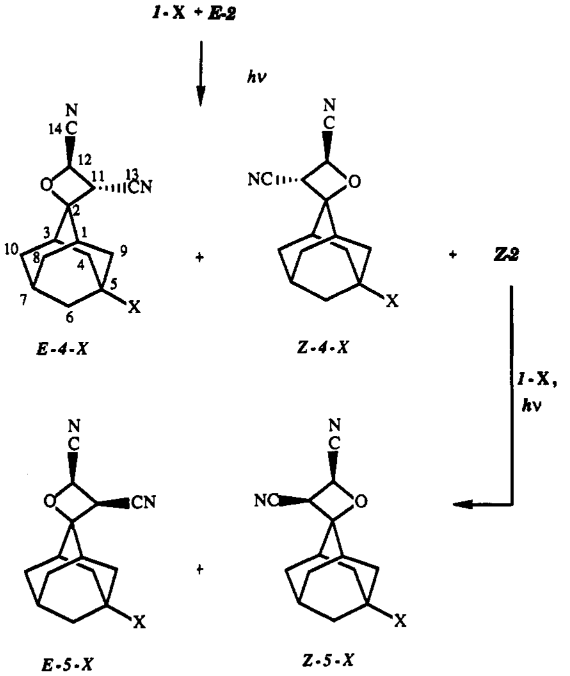
Results and Discussion

The photocycloaddition of ketones to olefins (also known as the Paterno–Büchi reaction) is one of the earliest[5] examples demonstrating the usefulness of photochemistry to the synthetic chemist.[4] Mechanistic studies[6] have been done primarily with acetone. The singlet n,π* state is trapped by electron-poor olefins such as (*E*)-**2** via a concerted or even synchronous [2 + 2] cycloaddition involving the now occupied π* orbital (face attack). The reaction is stereospecific, with retained configuration. The triplet state does not directly lead to an oxetane but results in olefin isomerization; at long reaction times the oxetane with inverted configuration is detectable. With electron-rich olefins such as **3**, both singlet and triplet give rise to a diradical via attack by the electron-deficient oxygen in the plane of the carbonyl group (edge attack; see Scheme I). This intermediate eventually closes to the oxetanes with a selectivity that is governed by the multiplicity and the relative rates of bond rotation and collapse.

Scheme I



Scheme II



Very little is known about the stereochemistry of this reaction when the two faces of the carbonyl group are different. Various 7,7-disubstituted 2-norbornanones have been shown to undergo cycloaddition on the exo side,[7] but there appears to be no guidance for instances in which the face differential results from an electronic perturbation. A study of 1-X in conjunction with 2 and 3 was therefore undertaken. In both cases, all four possible photoproducts

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[4] For reviews, see: (a) Turro, N. J.; Dalton, J. C.; Dawes, K.; Farrington, G.; Hautala, R.; Morton, D.; Niemczyk, M.; Schore, N. *Acc. Chem. Res.* **1972**, *5*, 92. (b) Schreiber, S. W. *Science* **1985**, *227*, 858. (c) Carless, H. A. J. In *Synthetic Organic Photochemistry*; Horspool, W. M., Ed.; Plenum Press: New York, 1984; p 425. (d) Jones, G., II. In *Organic Photochemistry*; Padwa, A., Ed.; Wiley: New York, 1981; Vol. 5, pp 1–122.

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Table II. ^{13}C Chemical Shifts (δ Scale) in Various 5-Substituted *trans*-11,12-Dicyanoadamantanoxetanes (J in Hz)[a]

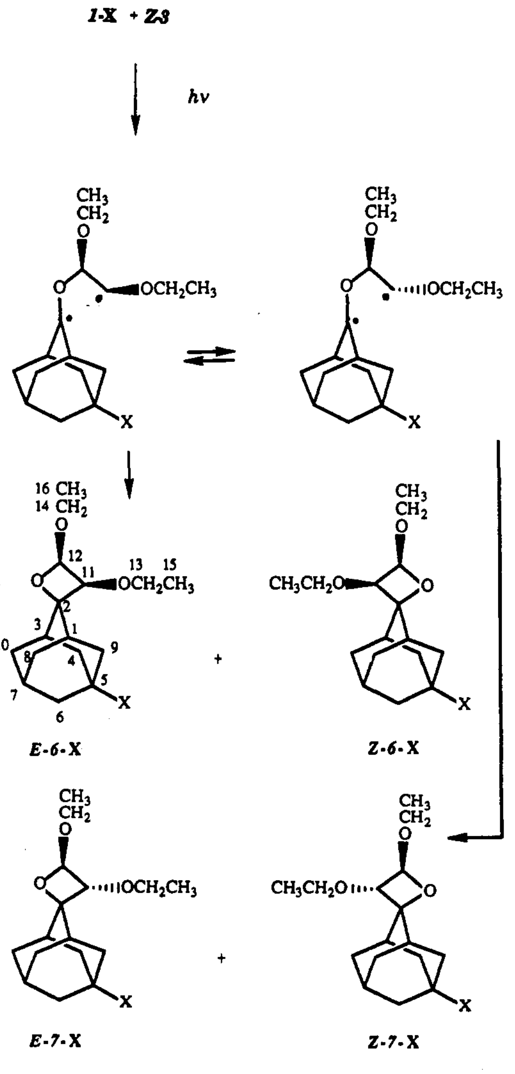
carbon	1 4-H	2 (*E*)-4-F	3 (*Z*)-4-F	4 (*E*)-4-Cl	5 (*Z*)-4-Cl	6 (*E*)-4-Br	7 (*Z*)-4-Br	8[b] (*E*)-4-OH	9 (*Z*)-4-OH	10 (*E*)-4-Ph	11 (*Z*)-4-Ph	12 (*E*)-4-*t*-Bu	13 (*Z*)-4-*t*-Bu
C1, C3	38.98	41.23 $J = 10.1$	41.86 $J = 10.3$	41.36	41.75	42.09	42.27	40.78	41.31	39.58	39.69	39.51	39.69
	35.66	38.06 $J = 10.0$	38.69 $J = 10.4$	38.26	38.66	39.01	39.32	37.85	38.08	36.23	36.43	36.04	36.34
C2	91.41	89.45	89.05	89.20	88.88	89.10	88.80	90.09	89.63	90.91	90.58	91.56	91.23
C4, C9	32.79	37.39 $J = 19.8$	36.23 $J = 20.1$	42.27	40.85	43.76	42.37[c]	39.86	38.79	38.30	36.80	31.82	32.45
	33.27	37.88 $J = 20.1$	36.35 $J = 20.3$	42.71	40.93	44.19	42.37[c]	40.47	38.90	38.52	36.94	32.43	32.91
C5	25.82	89.69 $J = 186.0$	89.72 $J = 185.7$	63.72	63.99	59.07	59.66	66.41	66.35	34.61	34.61	34.91	34.89
C7	25.61	28.97 $J = 10.0$	28.76 $J = 9.9$	29.03	28.73	29.78	29.45	28.29	28.04	26.64	26.38	26.44	26.29
C6	35.88	41.35 $J = 17.7$	41.25 $J = 18.0$	46.02	45.90	47.45	47.33	43.97	43.61	42.10	41.46	34.66	34.76
C8, C10	31.42	30.07	31.87	29.70	31.52	29.70	31.48	30.17	32.01	30.70	32.53	31.02	30.79
	31.30	29.90	31.35	29.53	31.02	29.52	30.98	30.03	31.50	30.55	32.04	30.92	30.54
C11	37.96	37.78	37.04	37.73	37.09	37.78	37.24	37.57	37.19	38.08	37.66	38.08	37.70
C12	61.94	61.99	61.98	61.98	61.94	62.00	61.96	61.97	61.97	62.06	62.03	61.92	61.98
C13	115.12	114.52	114.70	114.56	114.65	114.55	114.61	114.76	114.87	114.99	115.05	115.10	115.21
C14	116.72	116.33	116.36	116.35	116.34	116.34	116.33	116.47	116.49	116.66	116.64	116.73	116.76
Ci										148.10	148.55	C15	
Co										124.67	124.66	(35.02)	(35.09)
Cm										128.42	128.30	C16	
Cp										126.30	126.11	(24.67)	(24.60)

[a] Measured by Bruker AF-250 NMR. See Scheme II for the numbering system. In the parent compound 4-H, the oxygen is understood to be syn to C_8 and C_{10}. [b] Measured by VXR-300. [c] Two peaks at δ 42.37 overlap.

were observed, as expected from the pathways portrayed in Schemes II and III.[8]

Thus, when a Xe/Hg lamp was used in conjunction with a potassium chromate filter to irradiate an acetonitrile solution of 1-F and excess (*E*)-2, the product of brief exposure was shown by means of VPC to be a mixture of two components in the ratio of 57:43. Integration of the oxetane-ring proton (OC*H*CN) NMR signals confirmed the ratio. The trans configuration of the cyano groups is easily recognized by inspection of these same signals; characteristically, the H_{11}–H_{12} coupling constants equal 5.6–5.7 Hz (see Table I). The assignment of configuration of the spiro skeleton was found to be consistent with a ^{13}C NMR study of a type we have described elsewhere.[9] In essence, this is an additivity scheme in which the chemical shifts are calculated from those of the corresponding carbons in adamantane, 1-fluoroadamantane, and the parent spirooxetane. The $C_{4,9}$ and $C_{8,10}$ pairs, by far the most informative beacons in this regard, are readily distinguished from one another by virtue of the ^{13}C–^{19}F splittings, which are roughly 20 and 0 Hz, respectively (see Table II). In the parent compound, they can be recognized by means of their chemical shifts: when one of the two substituents at C_2 is an electronegative atom such as oxygen, the carbon pair "below" it is always shielded compared to the anti pair.[9] Another indication is that the C_8 and C_{10} signals differ by only 0.1 ppm, whereas C_4 and C_9, which are close to one of the cyanomethylene groups, differ by 0.5 ppm.

Scheme III



The chemical shifts thus computed for $C_{4,9}$ and $C_{8,10}$ agree with the observed values to within a few tenths of 1 ppm; differences of 2 ppm or more result if the opposite configurations are assumed. Column chromatography was

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(8) Perhaps it goes without saying that all chiral compounds encountered in our study were racemic. It may also be noted that for the sake of convenience and continuity we refer to all of our adamantanes as 2,5-substituted even though this is technically sometimes incorrect (e.g. 2,5-dimethyladamantane is really 1,4-, etc.). Finally, we wish to point out that the *E*,*Z* descriptors now in general use for olefins (Blackwood, J. E.; Gladys, C. L.; Loening, K. L.; Petrarca, A. E.; Rush, J. E. *J. Am. Chem. Soc.* **1968**, *90*, 509; see ref 2) are generally not adequate for disubstituted rings since these will often be chiral; however, even-membered carbocyclic rings with two to four substituents at two opposite corners have C_s symmetry, and the *E*/*Z* symbols can then be used without ambiguity (olefins may be regarded as a special case, with two-membered rings). 2,5-Disubstituted adamantanes fit this criterion, and hence we have used these descriptors for them hitherto. In the present case, the oxetanes 4–7 do not have this symmetry because of the cyano and ethoxy groups; nevertheless, we continue to use the *E*/*Z* symbols for the sake of simplicity.

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Table III. Key Proton Chemical Shifts and Coupling Constants for 5-Substituted *cis*-11,12-Dicyanoadamantanoxetanes[a]

oxetane	H_{12} (δ)	H_{11} (δ)	H_1, H_3[b]	J_{11-12} (Hz)
14 5-H	5.28 (d)	3.78 (d)	2.58 (s), 207 (s)	8.52 ± 0.02
15 (*E*)-5-F	5.29 (d)	3.85 (d)	2.80 (m), 2.31 (m)	8.56 ± 0.07
16 (*Z*)-5-F	5.30 (d)	3.83 (d)	2.87 (m), 2.36 (m)	8.48 ± 0.03
17 (*E*)-5-Cl	5.29 (d)	3.84 (d)	2.74 (d), 2.38 (dd)	8.45 ± 0.02
18 (*Z*)-5-Cl	5.30 (d)	3.82 (d)	2.77 (m), 2.43 (m)	8.50 ± 0.02
19 (*E*)-5-Br	5.29 (d)	3.84 (d)	2.70 (d), 2.57 (dd)	8.48 ± 0.02
20 (*Z*)-5-Br	5.30 (d)	3.80 (d)	2.74 (d), 2.61 (m)	8.52 ± 0.04
21 (*E*)-5-Ph	5.32 (d)	3.84 (d)	2.78 (m), 2.26 (m)	8.50 ± 0.05
22 (*Z*)-5-Ph	5.33 (d)	3.88 (d)	2.79 (m), 2.29 (m)	8.49 ± 0.02

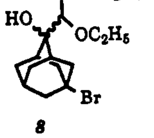
[a] Partial proton assignment; measured by VXR-300 NMR; chemical shifts refer to $CDCl_3$ (δ 7.25). See Scheme II for the numbering system. [b] Data shown are not necessarily in the correct order.

used to obtain samples of these compounds in pure form; the major product was shown to be (*E*)-4 by way of an X-ray diffraction study.[3]

Upon longer irradiation times, small amounts of two other components also begin to be observable. These new products are readily recognized to be the *E* and *Z* isomers 5; on the basis of the ^1H NMR spectra, the C*H*CN protons have a coupling constant of 8.5 Hz in compounds 5-F (see Table III). This difference is quite characteristic of cyano substituted oxetanes,[7,10] and it agrees well with that calculated on the basis of the Karplus equation.[11] The amounts of the *cis*-oxetanes 5-F were sufficient to determine the *E*/*Z* ratio; it turned out to be identical with that of 4.

The experiments with 1-Cl, -Br, -OH, -Ph, and -*t*-Bu followed a similar course; the *E* and *Z* assignments in these instances rested entirely on the ^{13}C additivity method. As with the fluoro products, the chemical shifts calculated for $C_{4,9}$ and $C_{8,10}$ agree with the observed values (Table IV) to within a few tenths of 1 ppm.

The photocycloadditions with (*Z*)-3 were also carried out in the same way; *E* and *Z* assignments were made on the basis of ^{13}C NMR additivities, and distinctions between 6 and 7 were based on the coupling constants of the C_2H_5OCHCH protons, those for 6 being larger than those of 7 in all cases, as with the dicyanooxetanes. In addition, the empirical observation that one of the four diastereotopic ethoxy methylene protons in 7 was consistently deshielded somewhat compared to the other three and to the four methylene protons in 6 was also helpful. The NMR data for these compounds are given in the supplementary material. On the other hand, the diethoxy compounds were more labile than the dicyanooxetanes; in particular, the isolated cis compounds 6 were stable only for a few days even at temperatures below 0 °C. The 5-bromooxetanes 6 proved to be the most sensitive, vanishing within hours after irradiation even if some sodium bicarbonate was added. Ethanolysis of these acetals was shown to be the culprit; the (*E*)- and (*Z*)-triethoxyadamantanols 8 could be isolated.



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The mass spectra of the oxetanes are also given in the supplementary material. They generally showed weak parent peaks (0–30% by the EI method); the main fragments arise from fission across the oxetane ring. Such ring fission is a known process;[12] thus, the parent oxetane predominantly gives ethylenes via ring cleavage.[12,13] The use of chemical ionization techniques[14] greatly improved the detection of molecular ions of all dicyanooxetanes 4 and 5 but not of diethoxyoxetanes 6 and 7.

Analysis of all mixtures of the four halodiethoxyoxetanes was possible by GC; in every case, base-line separation prevailed between all four peaks (Carbowax column). The *E*/*Z* product ratios are shown in Table V. The preference for attack of the olefin at the *zu* face (syn to the 5-substituent) is, again, without exception. The product-controlling step is the collapse of the diradical, as shown in Scheme III; it may be noted that 5-substituted 2-adamantyl radicals in their abstraction of a bromine atom also prefer the *zu* face.[1] The present results add to the already extensive evidence for the proposition that addition to trigonal carbon occurs at the face antiperiplanar to the more electron-rich vicinal bond(s). It would seem difficult to find a reason for this preference in so many reactions as described here and elsewhere without involving transition-state hyperconjugation. The fact that essentially the same data emerge in reactions of quite different mechanism lends especially strong support.

We must take note of the fact that, while all of the 5-substituents used in this study are electron-withdrawing[15] and all induce predominant *zu*-face attack, there is no obvious correlation between the magnitude of the *E*/*Z* ratios and the strength of the induction. Such a correlation is clearly present in reactions producing 2-adamantyl cations[16,17] and a more modest one has been observed in reductions and methylations of 1-X.[18,19] It must be realized, however, that our knowledge of inductive power is based almost exclusively on ground-state chemistry and also that with the *E*/*Z* ratios generally rather close to unity such correlations will remain difficult to prove or disprove satisfactorily. What is really needed is more powerful induction in our probe. We hope to bring this about by building heteroatoms in the adamantane skeleton in future projects.

Experimental Section

Proton nuclear magnetic resonance spectra were taken on 250-, 300-, and 400-MHz spectrometers. The data reported were recorded at 300 MHz unless otherwise specified. Natural abundance ^{13}C NMR spectra were taken by use of the pulsed Fourier-transform method on a 300-MHz high-resolution NMR spectrometer operating at 75.4 MHz. Broad-band decoupling was used to simplify spectra and aid peak identification. For both nuclei, chemical shifts are reported in parts per million and coupling constants in Hz, with the solvent (usually $CDCl_3$) peak as an internal standard. The reference peak for ^{13}C is δ = 77.00 ppm,

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Table IV. ^{13}**Chemical Shifts (δ scale) in Various 5-Substituted *cis*-11,12-Dicyanoadamantanoxetanes**[a]

	oxetanes								
carbon	14 5-H	15 (*E*)-5-F	16 (*Z*)-5-F	17 (*E*)-5-Cl	18 (*Z*)-5-Cl	19 (*E*)-5-Br	20 (*Z*)-5-Br	21 (*E*)-5-Ph	22 (*Z*)-5-Ph
C_1,C_3	38.91	41.12 J = 10.1	41.82 J = 10.4	41.34	41.72	42.04	42.37[b]	39.56	39.70
	35.92[b]	38.27 J = 10.1	38.86 J = 10.2	38.52	38.90	39.25	39.58	36.42	36.65
C_2	91.59	89.55	89.24	89.30	89.07	89.18	89.02	91.06	90.79
C_4,C_9	33.02	37.55 J = 20.1	36.27 J = 19.9	42.51	40.92	43.98	42.54	38.60	36.84
	33.30	37.88 J = 20.1	36.46 J = 20.1	42.77	41.08	44.23	42.37[b]	38.49	37.13
C_5	25.65	89.77 J = 186.2	89.77 J = 185.6	63.78	64.06	59.16	59.65	34.64	34.68
C_7	25.87	28.99 J = 9.8	28.78 J = 9.9	29.10	28.89	29.58	29.53	26.65	26.44
C_6	35.92[b]	41.37 J = 17.1	41.28 J = 18.1	46.10	45.98	47.52	47.44	42.05	41.51
C_8,C_{10}	31.56	30.15	31.88	29.84	31.55	29.83[b]	31.55	30.82	32.56
	31.33	29.91	31.54	29.61	31.23	29.83[b]	31.21	30.57	32.30
C_{11}	37.57	37.36	36.52	37.38	36.68	37.41	36.87	37.62	37.25
C_{12}	61.98	62.05	62.02	62.05	62.05	62.04	62.06	62.04	62.06
C_{13}	114.41	113.88	113.88	113.83	113.91	113.81	113.81	114.19	114.22
C_{14}	115.52	115.19	115.09	115.12	115.13	115.10	115.08	115.37	115.34
C_i								148.14	148.62
C_o								124.71	124.70
C_m								128.42	128.33
C_p								126.30	126.14

[a] Measured by VXR-300 NMR, $CDCl_3$ (δ 77.00); J is in Hz. See Scheme II for the numbering system. [b] Peaks overlap for these carbons.

Table V. *E*:*Z* Epimer Distributions in the Photocycloadditions of (*E*)- and (*Z*)-2 and -3 to 5-Substituted Adamantanones (1-X)[a]

X	(*E*)-2	(*Z*)-2	(*E*)-3	(*Z*)-3
F	57:43	57:43	55:45	57:43
Cl	58:42	60:40	54:46	57:43
Br	59:41	60:40	55:45	60:40
OH	53:47			
C_6H_5	65:35	60:40		
t-C_4H_9	64:36			

[a] Analysis by VPC and ^{1}H NMR; error limit ±2%.

which is set at the center peak of $CDCl_3$, and for ^{1}H it is δ = 7.25 ppm of $CHCl_3$.

Gas chromatographic analyses were carried out on an instrument equipped with a flame ionization detector and a reporting integrator. The capillary column employed included HP-1 cross-linked methylsilicone (SE-30, 25 m) and carbowax column (25 m). GC/Mass spectral analyses were carried out with the CH_4 chemical-ionization method.[14]

Materials. All commercially obtained chemicals were reagent or spectrophotometric grade and were not purified prior to use unless otherwise specified. The synthesis of 5-*tert*-butyladamantan-2-one (1-*t*-Bu),[20] 5-phenyladamantan-2-one (1-Ph),[21] 5-hydroxy-(1-OH),[21,22] 5-chloro-(1-Cl),[21] 5-bromo-(1-Br),[23] and 5-fluoroadamantan-2-ones (1-F)[16,24] have all been described. The 1-F was obtained by refluxing a mixture of 20 mL of the 1-Br in 150 mL of cyclohexane with 50 mM anhydrous silver fluoride,[14] which is an adaptation of a procedure given by Schleyer for 1-fluoroadamantane.[25]

***trans*-1,2-Dicyanoethylene ((*E*)-2).** Commercial material (Aldrich) is a black crystalline material containing an impurity with λ_{max} (CH_3CN) ~270 nm. It was decolorized with activated carbon (Fisher Scientific) and recrystallized from methylene chloride/hexane (50:50 v/v) until no residual absorption above 240 nm was observed.

***cis*-1,2-Diethoxyethylene ((*Z*)-3)** was prepared by pyrolysis of 1,1,2-triethoxyethane according to the procedure of McElvain and Stammer.[26] About 40 g Al_2O_3 was packed into a column and heated to 230 ± 5 °C; 32 g of triethoxyethane (I, Aldrich) was then passed through this column with nitrogen as a carrier gas to a dry ice–acetone trap. The recovered light yellow liquid (25 g) was heated on a steam bath to strip off ethanol and acetaldehyde, and the yellow residue was fractionally distilled under nitrogen. Material collected below 110 °C was discarded. The fraction that distilled between 110–135 °C was used; it was found to contain 92% (*Z*)-3 and 4% (*E*)-3 (~70% yield based on unrecovered I). (*Z*)-3: bp 130.5–137 °C[26] NMR ($CDCl_3$) δ 5.12 (s, 2 H), 3.73 (q, 4 H, J = 7.1 Hz), 1.25 (t, 6 H, J = 7.1 Hz).[27]

X-ray Structure Analysis of (*E*)-4-F.[3] (*E*)-4-F, mp 157 °C, was crystallized from 20% ethyl acetate in hexanes. Its structure was determined by means of single-crystal X-ray analysis in a Nicolet R3m diffractometer with Mo (⟨λ⟩ = 0.71073 Å) radiation at 298 K, with an ω-type scane at 4.88–19.53 deg/min. The crystals are orthorhombic, with space group *Pbca* and unit cell dimensions a = 10.854 (5) Å, b = 7.706 (4) Å, c = 28.681 (9) Å, α = 90°, β = 90°, γ = 90°, V = 2399 (2) Å^3, Z = 8, ρ_{calcd} = 1.36 g/cm^3, crystal size (mm) 0.44 × 0.49 × 0.77, μ_{calcd} 1.1 cm^{-1}, $F(000)$ = 1040, 3174 reflections, 2751 unique reflections, 1775 with $I > 3\sigma(I)$ and with 223 variable parameters. Three-dimensional diffractometer data were refined with unit weight (F, O, N, C anisotropic, H isotropic) by least-squares methods with $\omega = 1/[\sigma^2(F_0) + 0.00042\,(F_0)^2]$ to final R values of 0.0399, R_w = 0.0490, and goodness of fit indicator (GOF) = 1.539 (for details, see supplementary material in ref 3).

Irradiation of 1-X with (*E*)-2. A relatively high concentration of (*E*)-2 (0.3 M) was employed to favor the formation of *trans*-oxetanes. Thus, a solution of 0.5 g of 1-X and 1 g of (*E*)-2 in 50 mL of spectrograde acetonitrile was placed in a Pyrex tube stoppered with a rubber septum. The solution was irradiated (Xe/Hg 1 KW lamp) for 48 h (~60–80% conversion) through a 313-nm filter solution (0.002 M K_2CrO_4 in 1% aqueous K_2CO_3). The solvent was removed from the dark red solution on a rotary evaporator and the residue distilled under vacuum. The fraction collected at 150–220 °C (50 mm) was allowed to solidify. The residues of all 5-substituted oxetanes (except 5-hydroxyl) were chromatographed over silica gel with ethyl acetate in hexanes as eluant (10–20% by volume). The use of 40–63-μm silica gel 60

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(E. Merck No. 9385) and a pressure-driven rate of 2.0 in./min leads to a successful separation.[28] In every instance, (*E*)-**4**-X eluted first, followed by (*Z*)-**4**-X, (*E*)-**5**-X, and finally (*Z*)-**5**-X. (*E*)- and (*Z*)-**4**-OH were chromatographed with aluminum oxide (80–200 mesh neutral) and 40% ethyl acetate in hexanes; (*Z*)-**4**-OH has a larger R_f value than (*E*)-**4**-OH.

The peak patterns in the ^{1}H and ^{13}C NMR spectra for all the oxetanes are very similar. For **6** and **7**, complete assignments of the ^{13}C peaks and full descriptions of the ^{1}H NMR spectra are given in the supplementary material.

Irradiation of 1-X and (*Z*)-3. A relatively high concentration of (*Z*)-**3** (0.3 M) was employed to favor the formation of *cis*-oxetanes **6**. A solution of 0.2 g of **1**-X and 1 g of (*Z*)-**3** in 50 mL of spectrograde acetonitrile was placed in a Pyrex tube stoppered with a rubber septum. The solution was irradiated (Xe/Hg 1-kW lamp) for 48 h (60–90% conversion) through a 313-nm filter solution (0.002 M K_2CrO_4 in 1% aqueous K_2CO_3). The solvent was removed from the light yellow solution on a rotary evaporator, and the residue was chromatographed over silica gel with ethyl acetate (4% in hexanes) as eluant. In every case, (*Z*)-**6**-X eluted first, followed by (*E*)-**6**-X, (*Z*)-**7**-X, and finally (*E*)-**7**-X. Fluorooxetanes were analyzed by means of GC with a carbowax column and separated by repeated column chromatography (silica gel). Since the diethoxyoxetanes are acid sensitive and decompose within hours after drying, they were stored in a sealed tube in a freezer.

The peak patterns in the ^{1}H and ^{13}C NMR spectra for these oxetanes are also similar (see supplementary material).

The unstable products (*E*)- and (*Z*)-**6**-Br were converted into (*E*)- and (*Z*)-**8**-Br by acid-catalyzed alcoholysis. (*E*)-**8**: ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 104.15, 79.62, 75.20, 68.70, 65.44, 65.27, 64.49, 50.06, 46.09, 45.34, 38.36, 37.87, 31.60, 31.12, 30.84, 15.73, 15.47, 15.25; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.55 (d, *J* = 5.4 Hz, 1 H), 3.97 (dq, *J* = 7.1, 9.1 Hz, 1 H), 3.81 (dq, *J* = 7.1, 9.1 Hz, 1 H), 3.61–3.73 (m, 3 H), 3.54 (dq, *J* = 7.1, 10.0 Hz, 1 H), 3.45 (dq, *J* = 7.1, 9.2 Hz, 1 H), 2.93 (s, 1 H, –OH), 2.61–2.64 (m, 1 H), 2.48–2.53 (m, 1 H), 1.95–2.32 (m, 9 H), 1.43–1.51 (m, 2 H), 1.16–1.24 (3t, 9 H). (*Z*)-**8**: ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 104.07, 79.78, 74.83, 68.61, 65.87, 65.50, 64.35, 49.85, 44.36, 44.18, 39.06, 38.24, 32.74, 31.99, 31.32, 15.71, 15.46, 15.20; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.54 (d, *J* = 5.5 Hz, 1 H), 3.41–3.97 (m, 8 H), 2.87–2.94 (m, 3 H), 1.31–2.45 (m, 10 H), 1.15–1.25 (3t, 9 H).

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Supplementary Material Available: ^{1}H and ^{13}C NMR data for **6**- and **7**-H, (*E*)- and (*Z*)-**6**-F and -Cl, (*E*)- and (*Z*)-**7**-Cl and -Br; mass spectral data for **4**- and **5**-H, (*E*)- and (*Z*)-**4**- and -**5**-F, -Cl, -Br, and -OH, and (*E*)- and (*Z*)-**6**- and -**7**-F and -Cl (7 pages). Ordering information is given on any current masthead page.

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Photochemistry of Stilbene–Amine. Spin-Trapping Study

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2-Methyl-2-nitrosopropane (MNP) was used as a spin-trap reagent to study the radicals formed in the photochemical reaction of substituted *trans*-stilbenes (TS) with tertiary amines. Seven 1,2-(*p*,*p*′-disubstituted phenyl)ethyl radicals were trapped by MNP and isolated and identified by HPLC-EPR. The nitrogen hyperfine splitting constants (hfsc) of these radicals are linearly correlated with the Hammett substituent constants σ_P. There is also a linear correlation of the nitrogen hfsc with both the single σ_P parameter and the dual $\sigma_{R'}$, σ_I parameters. The inductive and resonance effects are of equal importance. The correlation between proton hfsc and a single σ_P parameter is not linear. There is fair correlation between the β-proton hfsc and the dual parameters $\sigma_{R'}$, σ_I. The only fair correlation may be due to the large dihedral angle between the nitrogen π orbital and the N–C–H plane.

Introduction

The spin-trapping technique[1-3] has been useful for the study of radical species formed in various chemical reactions.[4-9] Thus, unstable free radicals can be trapped by such reagents as 2-methyl-2-nitrosopropane (MNP) and α-phenyl-*N*-*tert*-butylnitrone (PBN) to form stable nitroxide radicals that can be studied by electron paramagnetic resonance (EPR). We have used the spin-trapping technique to study the unstable free radical species formed from the *trans*-stilbene (TS)–amine exciplex system, since it has been reported that the mechanism for the photochemical reaction between TS and tertiary amines involves consecutive electron and proton transfer.[10-13] The experimental evidence for the reactive intermediates formed

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