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THE IMPORTANCE OF STERIC EFFECTS ON THE PHOTOCYCLOADDITIONS OF BIACETYL TO NORBORNENES

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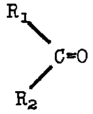
The role of steric effects in photocycloaddition reactions has received relatively little attention, and, at best, the published results are ambiguous. For example, photocycloaddition of benzophenone (1, $R_1 = R_2 = C_6H_5$) to norbornene (2, X = H) is reported to lead to the exo-adduct 3 ($R_1 = R_2 = C_6H_5$ X = H) as the exclusive product.[1] Presumably, the stereochemistry of this addition is controlled by the greater steric accessibility of the exo-face of the norborene skeleton in accord with well-established analogies for ground state reactions.[2] In contradistinction, photocycloadditions of both acetyl cyanide[3a] (1, R_1 = CN, $R_2 = CH_3$) and diethyl oxomalonate[3b] (1, $R_1 = R_2 = CO_2C_2H_5$) to norbornene have been reported to produce significant amounts (48% and 25%, respectively) of endo adducts of general structure 4. A more extensive study of norbornene photocycloadditions was clearly desirable, and we decided to attempt to clarify the role of steric effects in these additions by measuring the response of oxetane stereochemistry to substitution in the norbornene moiety. Biacetyl was chosen as the carbonyl component since the photophysics of this molecule has been extensively documented, and because it affords the possibility of monitoring reactivity by fluorescence and/or phosphorescence quenching.



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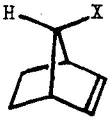

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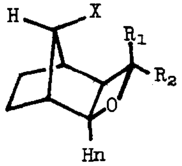

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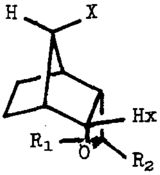

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Preparative experiments were carried out on benzene solutions of biacetyl (0.5 M) and the following syn-X-norbornenes[4] (4 M): 2, X = H, CH_3, t-C_4H_9, and OH. In all cases 430 nm light was used to avoid photodegradation of the products. Configurational assignments are based on the appearance of protons H_x and H_n (above):[3,5] a doublet with J = ~5 Hz signifies an exo-oxetane (3) and a triplet or doubled doublet with Js = 4-8 Hz signifies an endo-oxetane (4). The results are presented in Table I.

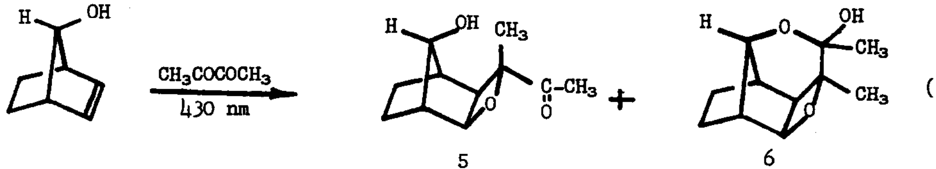
From an examination of the first three entries in Table I, it is clear that steric effects play a major role in the stereochemical outcome of these cycloadditions. The results are not inconsistent with initial formation of an exciplex[6] between the n-orbital of the biacetyl triplet (see below) and the π-system of the norbornene although this complex must be somewhat looser than the transition state for epoxidation. In this reaction the presence of a syn-7-methyl group causes a shift from 99.5% exo-epoxidation in the case of norbornene to 90% endo epoxidation in the case of 7,7-dimethylnorbornene.[2]

TABLE I. Photocycloadditions of Biacetyl to Norbornenes

Olefin 2, X =	Oxetane Distributions [3] : [4]	Oxetane Yields[a,b]	NMR δ	Φ^{c}_{ox}	[Olefin]
H	>24:1	38%[d]	4.43 (d, J=5 Hz)	0.0011	0.856 M
		58%[e]	4.44 (d, J=5 Hz)	0.0017	
CH_3	2.6:1[f]	54%	4.53 (d, J=5 Hz)	0.00050	0.865 M
		21%	4.76 (dd, J=4,8 Hz)	0.00020	
t-C_4H_9	<1:30	40%	4.82 (dd, J=6,7 Hz)	0.00015	0.543 M
HO	>30:1	74%[g]	4.90 (d, J=4 Hz)	0.0015	0.859 M
		15%[h]	4.58 (d, J=5.5 Hz)	0.00030	

[a] Based on volatile products. [b] All oxetanes gave satisfactory elemental analyses except that from the t-butyl system. This was characterized by an exact mass determination. [c] Average of duplicate determinations in benzene solution using 2,3-pentanedione as actinometer.[6] [d] Assigned the syn-methyl structure 3, $R_1 = CH_3$, $R_2 = COCH_3$ on the basis of steric shielding[7] of the methyl resonance ($\delta = 1.39$). [e] Assigned the anti-methyl structure 3, $R_1 = COCH_3$, $R_2 = CH_3$ ($\delta_{CH_3} = 1.21$). [f] Analyzed as a mixture. [g] Assigned the anti-acetyl structure 5, does not ketalize in acid ($\delta_{CH_3} = 1.60$ and 2.40). [h] Assigned syn-acetyl structure 6, exists as a hemiketal (no carbonyl in infrared, $\delta_{CH_3} = 1.32$ and 1.42).

The results with syn-7-hydroxynorbornene are especially interesting (eq. 1). From steric arguments one would expect to find ca. 10% endo addition, yet less than 3% could have been formed. Conceivably, hydrogen bonding forces between the hydroxyl function and the electron-rich π^* system orient the reactive species on the exo-face of the molecule.[9]



5 6 (1)

The finding that all of the quantum yields for biacetyl cycloadditions were unusually low compared to simpler analogs, prompted a more extensive study of the photodynamics of these reactions. The triplet state of biacetyl was implicated as the photoactive one since norbornene (1 M) quenched biacetyl phosphorescence, but not the fluorescence (± 10%). From the slope of

Stern-Volmer plots of norbornene quenching of phosphorescence and the known lifetime of biacetyl triplets in benzene[10] (4.6×10^{-4} sec), a value of 2.4×10^4 M^{-1} sec^{-1} could be calculated for k_r.[11] Since the principle products are oxetanes (>96%) this rate constant represents almost exclusively the rate of reaction of biacetyl triplets with the double bond. The low efficiency of oxetane formation in this system must be due to rapid decay of the exciplex[8] and/or inefficient closure of 1,4-biradical intermediates.

Similarly, t-butylnorbornene was shown to be a very poor quencher of biacetyl phosphorescence, and k_r was estimated to be *ca.* 1.3×10^3 M^{-1} sec^{-1}. Assuming that 40% of this value represents the rate of *endo*-attack of triplet biacetyl on norbornene double bonds in general, one can calculate an approximate k_r^{exo} / k_r^{endo} ratio equal to 42.

In conclusion, this work has demonstrated that the stereochemistry of photocycloaddition of biacetyl and substituted norbornenes responds in a rational manner to changes in steric environment. The stereochemical preferences of the reactions of norbornene with acetyl cyanide and diethyl ketomalonate remain unexplained. These anomalies can only be resolved by detailed kinetic and stereochemical studies. Unfortunately, we have been unable to repeat the acetyl cyanide-norbornene photocycloaddition reaction.

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11. This rate constant represents the sum of all bimolecular rate constants for reactions of triplet biacetyl with norbornenes. In addition to the oxetane, a product with molecular formula $C_{13}H_{20}O$ (molecular ion m/e 192) was isolated in 34% yield. This compound contained a t-butyl group (δ = 0.97) and an acetyl group [δ = 2.07, ir 5.84 μ (s), mass spectrum m/e 43 (relative intensity 76% of base peak)]. A reasonable structure for this compound is shown below; cf. P. W. Jolly and P. deMayo, Can. Journ. Chem., 42, 170 (1964) and W. G. Bentrude and K. R. Darnall, Chem. Commun., 810 (1968).