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DIVERGENT STEREOSELECTIVITY IN THE PHOTOADDITION OF ALKANALS AND MEDIUM RING CYCLOALKENES

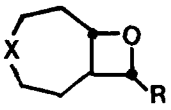
Guilford Jones, II*, Zarif H. Khalil, Xuan T. Phan,
Tai-Jun Chen, and Sudha Welankiwar
Department of Chemistry, Boston University, Boston, MA 02215 USA

Summary: Photocycloaddition of alkanals and cycloheptene, cyclooctene, and 1,5-cyclooctadiene results in stereoisomeric oxetanes, the composition of which depends on the concentration of starting alkene.

The stereochemistry of photocycloaddition of aliphatic carbonyl compounds and simple alkenes has been studied by several groups.[1] Acetaldehyde and 2-butene add with high stereoselectivity,[2] whereas reaction of acetone with the butenes[3] or cyclooctene[4] follows a stereorandom path. The results have been interpreted in terms of stereospecific reaction of the aldehyde excited singlet state as opposed to a less stereoselective route via biradical for reaction with ketone triplets. The stereoselective singlet reaction is dominant for addition of aliphatic carbonyls to conjugated dienes[5] and styrenes.[6]

We have investigated the photoaddition of alkanals and medium ring cycloalkenes as part of a study of sequential photolysis-pyrolysis steps[7] directed to the synthesis of long chain enals and derivatives.[8] Important variations in product distribution have been found, including a critical dependence of stereoselectivity on the concentration of the alkene photoaddend.

Preparative irradiation of butanal or pentanal in the presence of cycloalkenes gave photoadducts in moderate yield (Table 1) (typically 15-30 g of adduct fraction for 24 hr irradiation; yields uncorrected for recovered addends). The major products were assigned oxetane structures (1-3) on the basis of elemental analysis, ir and nmr spectral data, and their pyrolytic behavior (cleavage to the addends among other products[8]). The assignment of stereochemistry was based in part on pmr coupling constants and criteria previously applied[8,9] (wider splitting patterns for cis-oriented oxetane alpha ring protons). Cmr chemical shift data provided an even more revealing pattern. Pairs of downfield resonances assigned to oxetane alpha carbons were observed for distillation fractions and for photoadducts purified by repetitive preparative glc (FFAP). Structures A, B, and C are consistent with the appearance of 2, 1, and 0 relatively deshielded ring carbons, respectively (note pairs of chemical shifts in Table 2), and an expected "steric shift"[10] (i.e., higher field for carbons bearing a cis substituent) which has been noted for epoxide stereoisomers.[11] Only two isomers were obtained for 3 and the ^{13}C data appear to exclude the trans,trans configuration (A). A photoadduct component from pentanal and cycloheptene, which could not be completely separated from the oxetanes, was important at low but not high concentration of cycloheptene (note percentages, Table 1). This compound was not fully characterized, but the spectral data were consistent with a saturated ketone structure, arising from Kharasch radical chain addition of aldehyde and alkene.[2] Other minor photoproducts obtained in higher boiling fractions were unsaturated alcohols, which were also more abundant at low concentrations of alkene.[12,13]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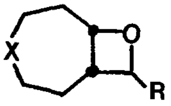
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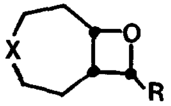
C

1, X = CH_2CH_2, R = C_3H_7
2, X = CH = CH, R = C_4H_9
3, X = CH_2, R = C_4H_9

The most notable feature of our results is the divergent stereochemistry observed at moderate vs. high concentration of alkene (Table 1). The effect is primarily a concentration dependence as shown in the Figure. Fluorescence quenching data parallel the concentration dependence of photoadduct yield. Butanal emission was quenched by cycloctene ($k_q\tau$ = 0.22, acetonitrile and 0.23 M^{-1}, cyclohexane) and cyclooctadiene ($k_q\tau$ = 0.52 M^{-1}, acetonitrile). The Stern-Volmer quenching constants indicate that singlet quenching is minimal at 0.5 M alkene (<20%) but substantial at 5.0 M addend (>60%).[14]

Our results show that combination of aldehydes and medium ring non-conjugated cycloalkenes is successful in providing synthetically useful yields of bicyclic oxetanes. Allylic hydrogen abstraction[13,15] is not a serious competitor, especially at high alkene concentrations, and aldehyde self quenching (photodimerization) and Type II photoelimination[16] do not dominate. Variation in photoadduct distribution is due to stereospecific addition of aldehyde singlets (via exciplexes)[2,5,6] accompanied with the more stereorandom triplet path at lower concentrations of cycloalkene. The less stereoselective triplet reaction has been previously associated with ketone photoaddition,[3,4] where oxetane formation completes poorly with hydrogen abstraction - radical coupling.[13] It follows that triplet biradical intermediates for this series favor closure to trans-fused adducts.

Another unusual stereochemical feature is the abundance of the all cis isomers, which is apparent also in an earlier study.[2] This selectivity may be the result of a non-parallel (ideally perpendicular) arrangement of alkene and carbonyl moieties in the singlet exciplex, obtained by "edge-on" attack of electrophilic carbonyl oxygen (n,π* state)[17] and reminiscent of the stereochemistry of addition of unsymmetrical ketenes and cycloalkenes.[18]

Table 1. Photoadduct Properties, Yields and Isomer Ratios

Addends		Solvent	Bp(mm)	Yield(%)	Isomer Ratio A	B	C
butanal	cycloctene	acetonitrile	70-90°(0.5)	34	65.0	17.0	18.0
		alkene		43	2.8	47.5	49.7
pentanal	cyclooctadiene	acetonitrile	75-83°(0.3)	59	63.4	11.2	25.4
		alkene		52	15.6	28.7	55.7
pentanal	cycloheptene	acetonitrile	65-69°(0.1)	30		26.0	27.0
		alkene		41		42.5	52.9

[a] Photolysis conditions: 450 W Hanovia immersion apparatus, nitrogen purging, 0.5 M aldehyde, acetonitrile solutions 0.5 M in alkene.

Table 2. Cmr Chemical Shifts for Oxetane Alpha Carbons (δ, ppm vs TMS, $CDCl_3$)

Photoadduct	Isomer A	B	C
1	85.17, 84.54	84.73, 82.74	83.22, 80.90
2	84.48, 83.63	85.31, 82.31	82.69, 81.28
3		84.45, 81.96	81.84, 80.01

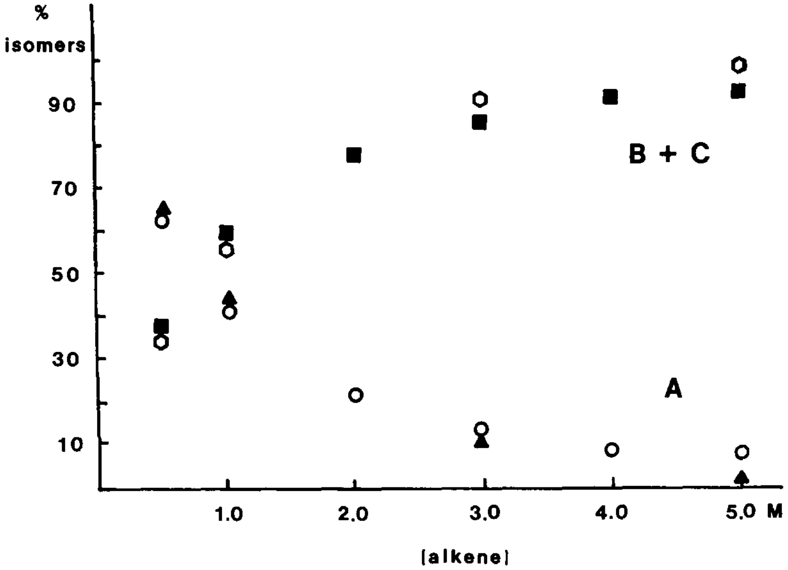

Figure. Stereoisomer distributions for photoadduct oxetanes 1 (▲, ⬡) and 2 (○, ■).

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(12) Alcohol adducts appeared to be mixtures of isomers. The physical data were for byproducts of 1: bp 105-112°(0.5 mm); ir (film) 3390 cm^{-1}; nmr (CDCl$_3$) 5.10-5.96 (m, 2H), 3.18-4.10 (m, 2H), 0.50-2.85 (m, 18H); 2, bp 98-105°(0.3 mm); 3, bp 78-80°(0.1 mm).

(13) Unsaturated alcohols, resulting from allylic hydrogen abstraction and radical coupling, are principal products of addition of ketones and olefins. H. A. J. Carless, J. C. S. Perkin Trans. II, 834 (1974); P. Borrell and J. Sedlar, Trans. Far. Soc., 66, 1670 (1970).

(14) Linear Stern-Volmer plots were obtained for 0.1 - 1.5 M alkene. Upward curvature (static quenching) was observed for quencher concentrations above 2.0 M. Aldehyde fluorescence was negligible when alkene was the solvent.

(15) The results for medium ring addition contrast with data concerning alkanals and cyclopentene or cyclohexene. Alcohol products persist at high concentrations of alkene, consistent with a reduced rate of singlet quenching for the smaller rings: G. Jones, II, D. A. Schwartz, and X. T. Phan, unpublished results.

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