Tetrahedron Letters No. 13, pp 1229 - 1232, 1972. Pergamon Press. Printed in Great Britain.

STEREOSELECTIVITY AND REGIOSELECTIVITY OF THE PHOTOCYCLOADDITION OF 2-METHYL-2,4-HEXADIENE AND ACETONE.[1]

Richard R. Hautala, Keith Dawes and Nicholas J. Turro
Department of Chemistry
Columbia University
New York, New York 10027

(Received in USA 19 January 1972; received in UK for publication 17 February 1972)

Until recently (2), 1,3-dienes were considered to be photochemically inert toward cycloaddition with alkanones. It is now clear that triplet ketones can cycloadd to 1,3-dienes, albeit inefficiently, if energy transfer to the diene (inducing diene isomerization and/or dimerization) is exothermic (3). More importantly, from both the standpoint of synthetic and mechanistic studies, singlet alkanones are quenched by 1,3-dienes, and cycloaddition products, not cis-trans-isomerization, are observed (4). We report here results of a study of the photocycloaddition of acetone to 2-methyl-2,4-hexadiene (1).

Barltrop and Carless (5) have reported that irradiation of solutions of acetone and 1,3-dienes (butadiene, isoprene, 2,3-dimethylbutadiene and 2,5-dimethyl-2,4-hexadiene) leads to the formation of oxetanes. No data on the stereoselectivity of oxetane formation were given in this report, but (a) butadiene was reported to yield a 2-vinyl oxetane and a 3-vinyl oxetane in 2% and 8% yield, respectively and (b) isoprene was reported to yield a mixture of 2- and 3-vinyl oxetanes in about 20% yield (in an unspecified ratio). Dowd, *et al.* (6) reported that 3-methylenecyclobutanone adds to cis- and trans-1,3-pentadiene stereospecifically, but with only modest regioselectivity. Since the photoreactions of cyclobutanone are somewhat atypical relative to other alkanones (7), we felt study of the stereoselectivity and regioselectivity of a more representative alkanone-diene system (Scheme I) was warranted. In particular, this system offers the possibility of eight isomeric oxetanes as products.

Irradiation of solutions of trans-1 in acetone leads to formation of four of the oxetanes, 2, 3, 4, and 6. In addition, isomerization of the diene is observed. Table I summarizes a study of the yields of 2-6 and cis-1 as a function of concentration of trans-1. It is apparent that at high (~2M) concentrations of trans-1, the reaction is stereospecific, since only trans-oxetanes are formed. The regioselectivity with respect to formation of 2- or 3- alkenyl oxetanes strongly favors the formation of the 3-alkenyl oxetane. However, within the experimental error, no regioselectivity is found with regard to which double bond of trans-1 undergoes 2+2 addition to acetone. Finally, the occurrence of trans-cis isomerization decreases markedly as the concentration of trans-**1** is increased. This result suggests that most (and possibly all) of the significant isomerization is due to incomplete trapping of singlet acetone, thereby allowing formation of triplet acetone which sensitizes trans-cis isomerization. Barltrop and Carless (5) and Yang _et al_. (4b) have presented evidence that the major, if not the exclusive, path for oxetane formation is _via_ the addition of alkanone _singlets_ to 1,3-diene. Stern-Volmer quenching of the fluorescence of acetone with trans-1 leads to a $k_q^F \tau_F$ value of 0.58 M^{-1} (k_q^F = rate of fluorescence quenching, τ_F = fluorescence lifetime). A plot of $1/\phi_{ox}$ _versus_ 1/[1,3-diene] is linear with a slope of 14M and intercept of 6.6. Interpretation of the slope and intercept in terms of a Stern-Volmer analysis, yields a limiting ϕ_{ox} of 0.15 (ϕ_{ox} if the _total_ oxetane formation), and a value of k_q^{ox} of 0.47M^{-1}, in excellent agreement with the value from fluorescence quenching. Independent measurement of τ_F by the single photon counting method (8) allows us to evaluate $k_q^F = 2.7 \times 10^8\ M^{-1}\ sec^{-1}$.

In summary, we conclude that (1) singlet acetone adds stereospecifically to trans-1; (2) regiospecificity is achieved with respect to formation of 3-alkenyl oxetane (no 2-alkenyl oxetane is observed); (3) no regioselectivity is achieved with respect to formation of 2,2-dimethyl or 2-methyl oxetane; (4) acetone _singlet_ sensitized trans to cis-**1** isomerization does not occur efficiently; (5) the rate constant for fluorescence quenching is the same, within the experimental error, as the rate constant for the interaction leading to oxetane formation.

Table I. Quantum Yields of Formation of Oxetanes and cis-1.[a]

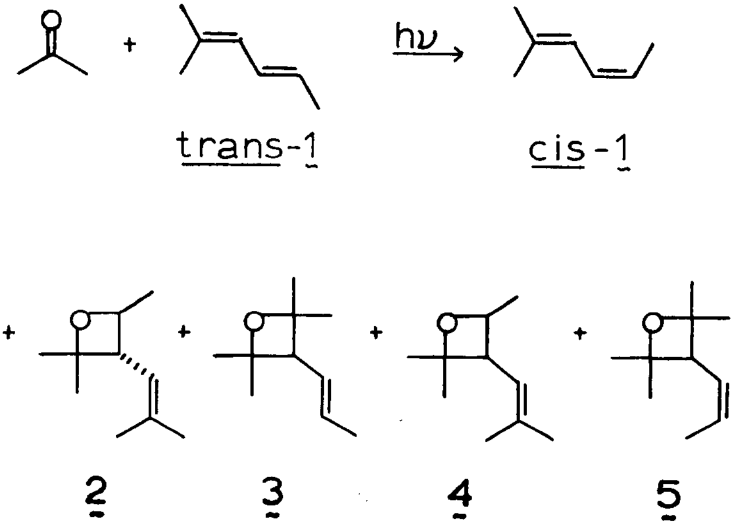
[trans-1]	% ^{1}A[b]	2	3	4	5	cis-1
3.9M	70	0.049	0.049	c	c	0.2
2.2M	55	0.037	0.036	c	c	0.5
1.2M	40	0.028	0.029	c	c	-----
0.61M	30	0.018	0.020	c	c	-----
0.24M	10	0.006	0.006	c	c	>.5

(a) 6.8M acetone. Excitation 313 nm. Actinometer valerophenone in benzene (ϕ acetophenone assumed to be 0.33). Values extrapolated to zero conversion.

(b) Approximate % of the acetone singlets trapped. Calculated from the measured τ_F and k_q^F values (see text).

(c) Trace amounts (<5% of 2 or 3) in all cases.

Scheme I.



REFERENCES

1. Molecular Photochemistry. LII. Paper LI. Nicholas J. Turro and Peter Lechtken, *J. Am. Chem. Soc.*, 94, 0000 (1972). The authors thank the Air Force Office of Science Research (Grant AFOSR-70-1848) for their generous support of this work. K.D. thanks the SRC for a NATO Fellowship.

2. D.R. Arnold, *Adv. Photochem.*, 6, 301 (1968).

3. J.A. Barltrop and H.A.J. Carless, *J. Am. Chem. Soc.*, **93**, 4794 (1971).

4. (a) R.R. Hautala and N.J. Turro, *ibid.*, **93**, 5595 (1971).
   (b) N.C. Yang, M.H. Hui and S. Bellard, *ibid.*, 4056 (1971).

5. J.A. Barltrop and H.A.J. Carless, *Chem. Commun.*, 1637 (1970).

6. P. Dowd, A. Gold and K. Sachdev, *J. Am. Chem. Soc.*, **92**, 5725 (1970).

7. N.J. Turro, J.C. Dalton, K. Dawes, G. Farrington, R. Hautala, D. Morton, M. Niemczyk and N. Schore, *Accounts Chem. Res.*, in press.

8. See W. Ware in "Creation and Detection of the Excited State", ed. A.A. Lamola, Marcel Dekker, New York, 1971.