Table I. Asymmetric Hydrosilylation of Olefins with $MeCl_2SiH$ Catalyzed by Chiral Phosphine–Platinum(II) Complexes at 40°

Olefin (30 mmol)	Catalyst (10 mg)	$[\alpha]^{15}D$, deg, of product	Yield, %	$[\alpha]^{15}D$, deg, methylated
$PhMeC{=}CH_2$	*cis*-$(C_2H_4)R_3P^*PtCl_2$[a]	+1.93	43	+1.20
$PhMeC{=}CH_2$	$[R'_3P^*PtCl_2]_2$[b]	+0.37	64	
$EtMeC{=}CH_2$	*cis*-$(C_2H_4)R_3P^*PtCl_2$[a]	−0.12	69	−0.14
$EtMeC{=}CH_2$	$[R'_3P^*PtCl_2]_2$	−0.08	55	

[a] R_3P^*: (+)-(*R*)-$(PhCH_2)MePhP$ (K. Neumann, G. Zon, and K. Mislow, *J. Amer. Chem. Soc.*, **91**, 7102 (1969)) (81% optical purity). [b] R'_3P^*: (−)-(*R*)-MePh-*n*-PrP (see Neumann, *et al.*, footnote *a*) (93% optical purity).

methylbutyl chloride, $[\alpha]^{15}D$ +1.68° (neat) (98% optical purity),[13] (+)-(*S*)-$EtMeCHCH_2SiMeCl_2$, $[\alpha]^{15}D$ +12.8° (neat), and (+)-(*S*)-$EtMeCHCH_2SiMe_3$, $[\alpha]^{15}D$ +15.8° (neat).

cis-Dichloro(ethylene)[(*S*)-1-phenylethylamine]platinum(II), which is known to cause the asymmetric induction of the coordinated olefin by exchanging ethylene with such higher olefins as *tert*-butylethylene and *trans*-2-butene,[14] showed an efficient catalytic activity in hydrosilylation of α-methylstyrene (in essentially quantitative yield under the conditions used), but the adduct was racemic.

These observations are significant for several reasons. First, a system with one asymmetric center as close to the metal as possible is advantageous in order to sustain the asymmetric bias, though this is not always necessary for asymmetric synthesis[15] in general. Second, the stereochemical sequence of coordination of olefins followed by addition of a silicon hydride, which must take place at least within the coordination sphere of the platinum atom, is proved to be identical in all experiments.

Finally, we are aware of the mechanistic similarity between the present hydrosilylation and the asymmetric homogeneous hydrogenation,[15] which at present is restricted to the use of phosphine complexes of rhodium(I) as catalysts, presumably of the type L_3RhCl where L is the chiral ligand.

Further experiments with chiral phosphine complexes of other metals including nickel(II), palladium(II), and rhodium(I) are in progress.

Acknowledgment. We thank Professor S. Suga and Dr. T. Nakajima of Kanazawa University for a generous gift of (+)-(*R*)-2-phenylpropyl alcohol.

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[13] L. Spialter and D. H. O'Brien, *J. Org. Chem.*, **31**, 3048 (1966); $[\alpha]^{18}D$ +1.71° (neat).

[14] A. Panunzi and G. Paiaro, *J. Amer. Chem. Soc.*, **88**, 4843 (1966).

[15] For the recent papers: J. D. Morrison, R. E. Burnett, A. M. Aguiar, C. J. Morrow, and C. Phillips, *ibid.*, **93**, 1301 (1971); T. P. Dang and H. B. Kagan, *Chem. Commun.*, 481 (1971).

Keiji Yamamoto, Tamio Hayashi, Makoto Kumada*
Department of Synthetic Chemistry, Kyoto University
Kyoto 606, Japan

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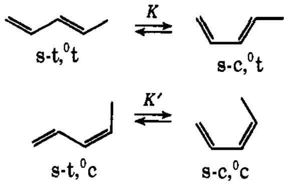
The Role of *s-cis*-1,3-Diene Triplets in Sensitized Cis–Trans Photoisomerization

Sir:

Acyclic 1,3-diene-photosensitized cycloaddition products vary with sensitizer triplet energy.[1,2] High-energy sensitizers, >60 kcal/mol, excite s-cis and s-trans diene conformers indiscriminately producing mainly s-trans triplets which give cyclobutane products. Lower energy sensitizers, $60 > E_T > 50$ kcal/mol, favor excitation of s-cis conformations, yielding s-cis triplets which give chiefly cyclohexene products. The requirement is that s-cis and s-trans triplets do not interconvert. Although photostationary trans–cis ratios for the sensitized isomerization of the 1,3-pentadienes vary over the same triplet energy region, Figure 1, the role of s-cis triplets in cis–trans isomerization has not been evaluated.[3,4]

1,3-Pentadienes. A mechanism for sensitized 1,3-pentadiene cis-trans photoisomerization including the intermediacy of s-cis triplets is given by eq 1–8 (^{3}p denotes relaxed diene triplets).



(1)

(2)

$$^3D + \text{s-t},^0\text{t} \xrightarrow{k_3} {}^0D + \text{s-t},^3\text{p} \tag{3}$$

$$^3D + \text{s-c},^0\text{t} \xrightarrow{k_4} {}^0D + \text{s-c},^3\text{p} \tag{4}$$

$$^3D + \text{s-t},^0\text{c} \xrightarrow{k_5} {}^0D + \text{s-t},^3\text{p} \tag{5}$$

$$^3D + \text{s-c},^0\text{c} \xrightarrow{k_6} {}^0D + \text{s-c},^3\text{p} \tag{6}$$

$$\text{s-t},^3\text{p} \xrightarrow{k_7} \alpha^0\text{t} + (1 - \alpha)^0\text{c} \tag{7}$$

$$\text{s-c},^3\text{p} \xrightarrow{k_8} \alpha'^0\text{t} + (1 - \alpha')^0\text{c} \tag{8}$$

Using the steady-state approximation for all excited species, eq 9–11 are

$$\left(\frac{[\text{t}]}{[\text{c}]}\right)_\text{s} = \frac{1 + K}{1 + K'}\left(\frac{\alpha k_5 + \alpha' k_6 K'}{(1 - \alpha)k_3 + (1 - \alpha')k_4 K}\right) \tag{9}$$

$$\phi_{\text{t}\to\text{c}} = \frac{a}{k_3 + k_4 K}((1 - \alpha)k_3 + (1 - \alpha')k_4 K) \tag{10}$$

$$\phi_{\text{c}\to\text{t}} = \frac{a}{k_5 + k_6 K'}(\alpha k_5 + \alpha' k_6 K') \tag{11}$$

derived (*a* represents the sensitizer's intersystem crossing efficiency). Benzophenone, fluorenone, and pyrene photoisomerization data are compared in Table I. For high-energy sensitizers, $k_3 = k_4 = k_5 = k_6 = k_\text{dif}$ and since K and K' are small, terms containing α' are negligible. For fluorenone, $\phi_{\text{c}\to\text{t}}/a = 0.55 = \alpha$, indicating that s-cis triplets are not produced from *cis*-1,3-pentadiene, *i.e.*, $K' \ll 1$.[5] Since steric interactions in *s-cis*-1,3-butadiene and *s-cis,trans*-1,3-pentadiene are similar, the same distribution of s-cis and

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[1] R. S. H. Liu, N. J. Turro, and G. S. Hammond, *J. Amer. Chem. Soc.*, **87**, 3406 (1965), and references cited therein.

[2] W. L. Dilling, R. D. Kroening, and J. C. Little, *ibid.*, **92**, 928 (1970).

[3] G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, N. C. Counsell, V. Vogt, and C. Dalton, *ibid.*, **86**, 3197 (1964).

[4] N. J. Turro, *Photochem. Photobiol.*, **9**, 555 (1969).

[5] Identical photodimer compositions are obtained from *cis*-1,3-pentadiene using benzophenone and fluorenone as sensitizers: J. Saltiel and D. Townsend, preliminary observations.

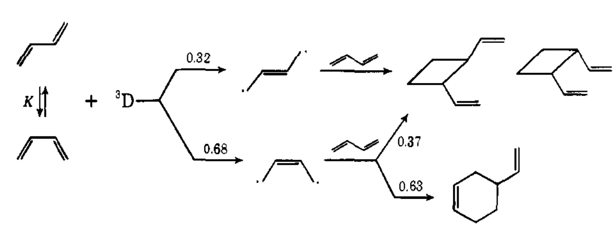
Table I. Sensitized Photoisomerization of the 1,3-Pentadienes[a]

Sensitizer (E_T)	a	$\phi_{c\to t}$	$\phi_{t\to c}$	% $[t]_s$
Benzophenone (68)[b]	1.00[c]	0.55_5	0.44_5	$55._5$
Fluorenone (53)	0.94[c]	0.52	0.31	$67._2$
Pyrene (48)	0.11 ± 0.04[d]	0.04_4	0.03_8	$64._6$

[a] Quantum yields in Tables I and II are independent of diene concentration in the range employed. [b] A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965). [c] From footnote *b* assuming a = 1.00 for benzophenone. [d] W. Heinzelmann and H. Labhart, *Chem. Phys. Lett.*, **4**, 20 (1969); pyrene 2×10^{-3} *M*. For 2×10^{-3} *M* pyrene $a = 0.08$ was obtained from the $\phi_{c\to t}$ value in Table I assuming only s-trans conformer excitation. The $\phi_{t\to c}$ value obtained for the pyrene–1,3-pentadiene system is higher than expected. Pyrene fluorescence quenching by the dienes was negligible.

s-trans conformers is likely for both dienes. Values of $k_3/(k_3 + k_4K)$ and $k_4K/(k_3 + k_4K)$ can be estimated by assuming that the minimum in the dimer plot reflects exactly the reactivity of s-cis triplets, Scheme I.[6] Using eq 10 and the fluorenone $\phi_{t\to c}/a$ value, $\alpha' = 0.72$ is obtained. This suggests that the decreased trans content in 1,3-pentadiene photostationary states, $E_T <$ 56 kcal/mol, is due to selective formation of s-cis triplets from *trans*-1,3-pentadiene.

Scheme I. Fluorenone-Sensitized 1,3-Butadiene Dimerization



2,4-Hexadienes. Corrected quantum yields for the benzophenone-, the fluorenone-, and the pyrene-sensitized photoisomerizations of the 2,4-hexadienes are compared in Table II. Fluorenone and benzophenone data starting with either *cis,cis-* or *trans,cis*-2,4-hexadiene are similar, suggesting that interaction of fluorenone triplets with these isomers produces mainly *s-trans*-2,4-hexadiene triplets. By contrast, isomerization quantum yields obtained with fluorenone or pyrene as sensitizer for the trans,trans isomer are lower than with benzophenone. It follows that excitation of s-cis diene conformers is important when *trans,trans*-2,4-hexadiene is the acceptor. If s-cis triplets decay only to tt and tc, the ratios of $\phi_{tt\to cc}/a$ and the decay fractions of the s-trans triplets[7] indicate that 31 and 10% of the fluorenone and pyrene excitation transfer events, respectively, produce s-trans triplets. The resulting values for α'', the decay fraction of s-cis triplets to tt, are 0.70 and 0.69 from the fluorenone and pyrene $\phi_{tt\to ct}/a$, respectively, in agreement with $\alpha' = 0.72$ for the 1,3-pentadiene triplets. Scheme II summarizes the interpretation of the fluorenone results.

Table II. Sensitized Photoisomerization of the 2,4-Hexadienes

Sensitizer	$\phi_{tt\to ct}/a$	$\phi_{cc\to ct}/a$	$\phi_{ct\to tt}/a$	$\phi_{cc\to tt}/a$	$\phi_{tt\to cc}/a$	$\phi_{ct\to cc}/a$
Benzophenone[a]	0.48	0.50	0.33	0.29	0.18	0.16
Fluorenone	0.36	0.52	0.29	0.27	0.05_8	0.12_3
Pyrene[b]	0.33				0.02_0	

[a] J. Saltiel, L. Metts, and M. Wrighton, *J. Amer. Chem. Soc.*, **91**, 5684 (1969). [b] Assuming a = 0.08 for 2×10^{-3} *M* pyrene (see footnote *d*, Table I).

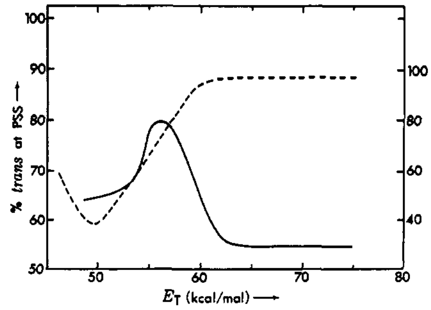
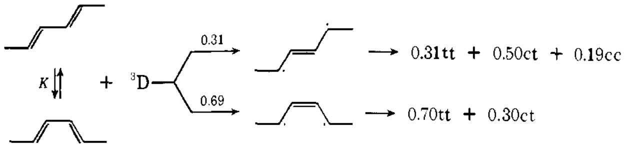


Figure 1. 1,3-Butadiene dimer compositions from ref 1 (dashed line); 1,3-pentadiene photostationary states from ref 4, except for benzil (−69.7%), fluorenone (−67.2%), and pyrene (−64.6%) values which are from this work (solid line).

Scheme II. Fluorenone-Sensitized Isomerization of *trans,trans*-2,4-Hexadiene



In conclusion, it is encouraging that two independent methods predict almost identical distributions of s-trans and s-cis triplets by excitation transfer from fluorenone, and pyrene, as well as identical decay fractions for the s-cis triplets of two related 1,3-dienes.

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(6) The sensitivities of adduct compositions to sensitizer energy changes differ for dimerization and cross-adduct formation reactions suggesting different contributions of s-cis triplets to cyclobutane formation.[2]

(7) J. Saltiel, L. Metts, and M. Wrighton, *J. Amer. Chem. Soc.*, **91**, 5684 (1969).

(8) (a) Alfred P. Sloan Foundation Fellow, 1971–1973; (b) Petroleum Research Fund Fellow; (c) Petroleum Research Fund Scholar.

Jack Saltiel,*[8a] Lewis Metts,[8b] Alan Sykes, Mark Wrighton[8c]
Department of Chemistry, The Florida State University
Tallahassee, Florida 32306

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Mechanism of Sulfonium Ylide Reactions. Synthesis of Cyclopropanes and Oxiranes of High Optical Purity[1]

Sir:

Sulfur ylides are popular and practical reagents for the synthesis of oxiranes and cyclopropanes. The

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(1) Part XXXIV in the series "Chemistry of Sulfoxides and Related Compounds." We gratefully acknowledge support by the National Science Foundation (GP 19623).