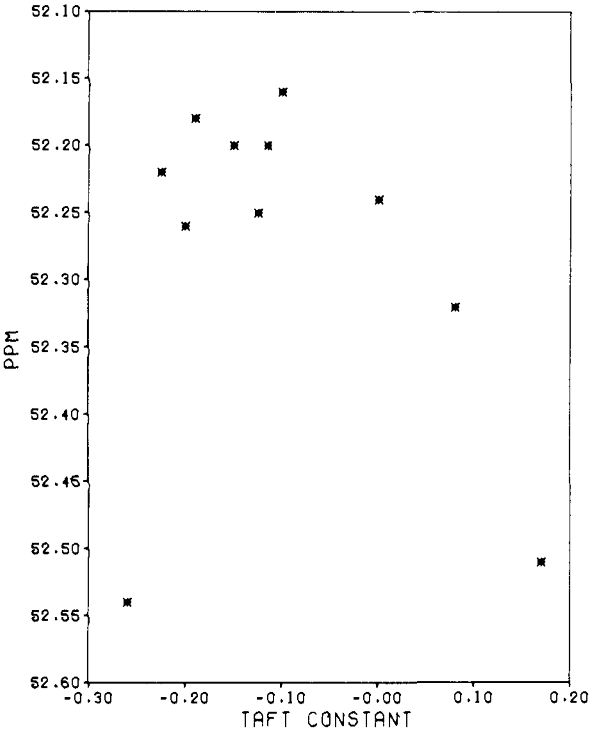

Figure 3. Carbon-13 shift of coordinated trimethyl phosphite in $(CH_3O)_3PCo(DH)_2R$. Points from left to right are $CH_2Si(CH_3)_3$, 3-C_5H_{11}, c-C_5H_9, i-C_3H_7, c-C_6H_{11}, i-C_4H_9, C_2H_5, CH_3, $(CH_2)_2C_6H_5$, and $(CH_2)_3CN$.

synthesize, crystallize, and structurally characterize complexes of the type $LCo(DH)_2(i\text{-}C_3H_7)$, in which L is a very bulky ligand. If such ligands distort the $Co(DH)_2$ moiety, the Co-C bond length in such compounds could be even longer than that found here.

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Supplementary Material Available: A listing of structure factors, atomic parameters, hydrogen atom coordinates, and bond lengths and angles of $Me_2CHCo(DH)_2py$ (12 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Toraya, T.; Krodel, E.; Mildvan, A. S.; Abeles, R. H. *Biochemistry* **1979**, *18*, 417 and references therein.
(2) Abeles, R. H.; Dolphin, D. *Acc. Chem. Res.* **1976**, *9*, 114.
(3) Halpern, J. *Ann. N.Y. Acad. Sci.* **1974**, *239*, 2.
(4) Iijima, T. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 1291.
(5) Iijima, T. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 2311.
(6) Bigotto, A.; Randaccio, L.; Zangrando, E. *J. Chem. Soc., Dalton Trans.* **1976**, 96 and references therein.
(7) Brückner, S.; Randaccio, L. *J. Chem. Soc., Dalton Trans.* **1974**, 1017. Bresciani-Pahor, N.; Calligaris, M.; Randaccio, L.; Marzilli, L. G. *Inorg. Chim. Acta* **1979**, *32*, 181. Bresciani-Pahor, N.; Calligaris, M.; Randaccio, L., unpublished work.
(8) Lenhert, P. G. *Chem. Commun.* **1967**, 980.
(9) Ohashi, Y.; Sasada, Y. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 1710, 2863.
(10) Dodd, D.; Johnson, M. D.; Steeples, I. P.; McKenzie, E. D. *J. Am. Chem. Soc.* **1976**, *98*, 6399.
(11) Stotter, D. A.; Sheldrick, G. M.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1975**, 2124. The short Co-C in this substituted vinyl derivative continues the trend but not the linearity given in Figure 2.
(12) Lenhert, P. G. *Proc. R. Soc. London, Ser. A.* **1968**, *303*, 45. Lenhert, P. G.; Hodgkin, D. C. *Nature (London)* **1961**, *192*, 937.
(13) Weiss, M. C.; Gordan, G. C.; Goedken, V. L. *J. Am. Chem. Soc.* **1979**, *101*, 857.
(14) Wells, P. R. "Linear Free Energy Relationships"; Academic Press: New York: 1968. Chapman, N. B.; Shorter, J., Eds. "Advances in Free Energy Relationships"; Plenum Press: New York, 1972. Hine. J. "Structural Effects on Equilibria in Organic Chemistry"; Wiley: New York, 1975. Newman, M. S., Ed. "Steric Effects in Organic Chemistry"; Wiley: New York, 1963.
(15) Toscano, P. J.; Marzilli, L. G. *Inorg. Chem.* **1979**, *18*, 421.
(16) Note Added in Proof. A recent paper discusses steric factors influencing Co-C bond cleavage in cobalamins (Grate, J. H.; Schrauzer, G. N. *J. Am. Chem. Soc.* **1979**, *101*, 4601). However, it was suggested that the corrin ring system buckles to accommodate bulky alkyl substituents on Co and this distortion leads to cleavage of the Co-C bond.

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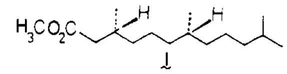
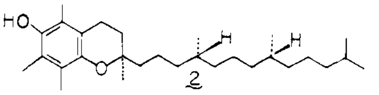
A Stereocontrolled Approach to Acyclic Systems. Stereorelay in Charge-Directed Alkylations via Organopalladium Templates

Sir:

One of the most exciting challenges in synthetic methodology is control of stereochemistry in conformationally nonrigid systems. We report herein a new approach based upon the utilization of a transition metal complex as a temporary template to relay stereochemical information in a normally conformationally nonrigid system.[1] This concept has been examined within the context of the synthesis of an acyclic unit **1** that constitutes the side chain for α-tocopherol (**2**) or vitamin K (**3**).[2a-d] During the course of this investigation, an approach for defining the relative stereochemistry of such remote centers as in **1** emerged.[3]



1



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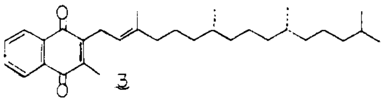
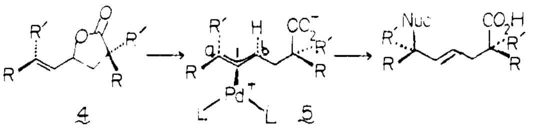


3

In this approach, ring stereochemistry is relayed along a π system by a palladium complex[4] as shown in eq 1. For such an



(1)

approach to be successful, (1) ionization of the vinyl lactone **4** must occur from one conformation, (2) the intermediate π-allylpalladium complex **5** must retain its stereochemistry, and (3) the nucleophile must attack regioselectively at the carbon of the allyl system distal to the carboxylate (i.e., site "a" in **5**).

To check the ability of the charge to direct the approach of the nucleophile, the lactone **6a**[5,6] was reacted with methyl sodiomalonate and 3 mol % tetrakis(triphenylphosphine)palladium in refluxing THF to give after initial workup a >90% yield of product shown to be **7a**[6] (δ 5.52 (ddd, J = 15, 7, 7 Hz), 1 H, 5.43 (dd, J = 15, 8 Hz, 1 H), 1.05 (d, J = 7 Hz, 3 H), decoupling at 2.34 collapses signal at 5.52 (br d, J = 15 Hz)) with >98% regiospecificity. The exclusive formation of the E

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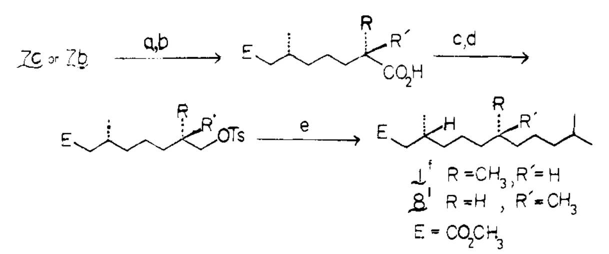
Table I. 67.9-MHz ^{13}C NMR Spectral Data[a,b]

	carbon atom														
compd	1,1[c]	2	3	4	5	6	7	8	9	10	11	3a	7a	11a	12	CO_2-CH_3
7a	168.60	57.84	37.2	132.88*	129.23*	27.43	33.89	178.61				18.4				$\begin{Bmatrix}52.29\\52.18\end{Bmatrix}$
7b	168.80	57.85	37.28	134.30	127.94	36.08	39.37	182.04				18.50	16.13			$\begin{Bmatrix}52.34\\52.27\end{Bmatrix}$
7c	$\begin{Bmatrix}168.76\\168.65\end{Bmatrix}$	57.88	37.35	134.23	128.08	36.18	39.43	182.11				18.56	16.20			$\begin{Bmatrix}52.32\\52.24\end{Bmatrix}$
1	173.62	41.68	32.81*	37.25$^{\#}$	24.85^{+}	39.46	30.44*	37.18$^{\#}$	24.40^{+}	37.34$^{\#}$	28.03	19.79‡	19.67‡	22.64†	22.74†	51.19
8	173.63	41.76	32.80*	37.21$^{\#}$	24.85^{+}	39.46	30.42*	37.14$^{\#}$	24.40^{+}	37.41$^{\#}$	28.03	19.77‡	19.66‡	22.63†	22.72†	51.21

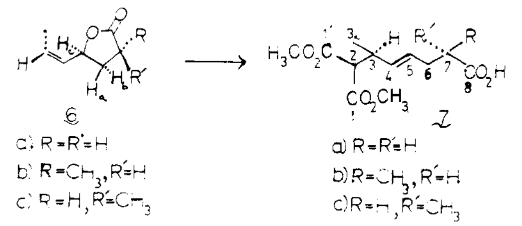
[a] All chemical shifts given in parts per million downfield from internal Me_4Si. [b] The absorptions which bear similar superscript symbols may be interchanged. [c] Reference 1.

Scheme I. Synthesis of Methyl 3(*R**),7(*R**),11- and 3(*R**),7(*S**),11-Trimethyldodecanoate[a]



[a] (a) 5% $Pd/BaCO_3$, 1 atm of H_2, CH_3OH; (b) KOAc, Me_2SO, 135 °C; (c) $BH_3 \cdot THF$, 0 °C; (d) TsCl, C_5H_5N; (e) $(C_5H_{11})_2CuLi$, ether, −20 °C; (f) obtained in 29–33% overall yield from 7b or 7c.

olefin, as well as the regiocontrol, is particularly noteworthy for synthetic applications. We next turned our attention to lactones **6b**[5,6] and **6c**.[5,6] Treatment of **6b** (>95% stereochemically pure) under the above conditions proceeded, within experimental error, stereospecifically to give, upon workup, a single alkylated product (**7b**[6,7] or **7c**[6,7]) in 90% yield. Likewise, alkylation of **6c** proceeded stereospecifically to a single alkylated product (**7b** or **7c**) *different from that formed* from **6b**. Analysis proved particularly difficult until we discovered that 67.9-MHz ^{13}C NMR nicely differentiated the two isomers. The data is summarized in Table I.



While the high degree of stereocontrol is established, the data do not allow the assignment of stereochemistry. For this purpose, we converted the alkylated products into **1** and **8** as outlined in Scheme I. By virtually all criteria, **1** and **8** were indistinguishable from each other. Fortunately 67.9-MHz ^{13}C NMR spectroscopy nicely distinguishes the two isomers (see Table I). Spectra of mixtures confirmed the ability to resolve the closely spaced signals. Particularly useful is the region δ 37.0–37.5 as shown in Figure 1 for differentiating the *R**,*R** from the *R**,*S** series.

Comparison of the spectra of authentic samples[2a-d] of the 3(*R*),7(*R*) and 3(*R*),7(*S*) isomers of methyl 3,7,11-trimethyldocanoate allowed **1**, which arose from **7b**, to be assigned the *R**,*R** configuration and **8**, which arose from **7c**, to be assigned the *R**,*S** configuration. Thus, alkylation of **6b** did produce **7b** (3(*S**),7(*R**)) and **6c** did produce **7c** (3(*S**),7(*S**)).

A parallel series of experiments involved the isomers containing the *E* olefin, **9a**[6-8] and **9b**.[6-8] Whereas the trans lactone-cis olefin isomer **6b** gave **7b** belonging to the 3(*S**),7(*R**) series, the trans lactone-trans olefin **9a** should produce the complementary 3(*S**),7(*S**) series provided that the preferences for ionization and alkylation are independent of olefin geometry. Similarly, the cis lactone-trans olefin **9b** should give an alkylation product of complementary stereochemistry to that from the cis lactone-cis olefin **7c**. Indeed, alkylation of **9a** and **9b** gave **10a**[6] (≡ **7c**) and **10b**[6] (≡ **7b**) respectively with >95% stereospecificity.

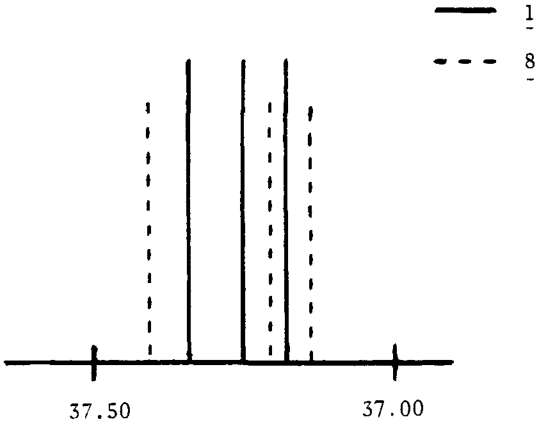
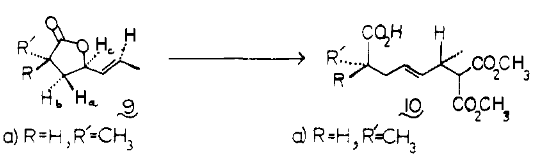


Figure 1. 67.9-MHz ^{13}C NMR spectra of **1** and **8** for δ 37.0–37.5.



The stereospecificity of the reaction indicates a very high preference for ionization via the conformer represented in structure **4**.[9] Presumably, this preference arises, in part, from the bulkiness of palladium and its attendant ligands. Furthermore, the allyl complex once formed retains the stereochemistry imparted by the ring and olefin even though the possibility for loss via rotation does exist. Regiochemical control is attained by charge-charge repulsion since the leaving group is retained in the substrate and bears the same charge as the incoming nucleophile. This approach for control of acyclic stereochemistry is very flexible. Variation of either the ring geometry or the olefin geometry allows entry into opposite stereochemical series. Variation of the position of the substituents on the ring can permit variation of the distance between the chiral centers in the acyclic system. Carbohydrates can serve as precursors of **4** and thus provide access to enantiomerically pure acyclic units. Future work along these latter lines is under active investigation.

Acknowledgment. We thank the National Science Foundation for their generous support of our programs. Drs. N. Cohen and K. K. Chan of Hoffmann-La Roche Co. provided generous comparison samples and Englehardt Industries and Matthey Bishop provided generous gifts of palladium chloride. We are indebted to them.

References and Notes

(1) For some recent results where the stereochemistry of an alcohol group is relayed to an olefin via epoxidation, see: (a) Bartlett, P. A.; Myerson, J. *J. Am. Chem. Soc.* **1978,** *100*, 3950. (b) Bartlett, P. A.; Jernstedt, K. K. *Ibid.* **1977,** *99*, 4829. (c) Chautemas, P.; Pierre, J. L. *Tetrahedron* **1976,** *32*, 549. (d) Tanaka, S.; Yamamoto, H.; Nozaki, H.; Sharpless, K. B.; Michaelson, R. C.; Cutting, J. D. *J. Am. Chem. Soc.* **1974,** *96*, 5254.

(2) For transfer of stereochemistry via Claisen and [2,3] sigmatropic rearrangements, see: (a) Chan, K. K.; Specian, A. C., Jr.; Saucy, G. *J. Org. Chem.* **1978,** *42*, 3435. (b) Chan, K. K.; Saucy, G. *Ibid.* **1977,** *42*, 3828. (c) Cohen, N.; Eichel, W. F.; Lopresti, R. J.; Neukom, C.; Saucy, G. *Ibid.* **1976,** *41*, 3505, 3512. (d) Chan, K. K.; Cohen, N.; DeNoble, J. P.; Specian, A. C., Jr.; Saucy, G. *Ibid.* **1976,** *41*, 3497. (e) Evans, D. A.; Baillargeon, D. J.; Nelson, J. V. *J. Am. Chem. Soc.* **1978,** *100*, 2242. (f) Ireland, R. E.; Mueller, R. H.; Willard, A. K. *Ibid.* **1976,** *98*, 2868. (g) Wilson, S. R.; Myers, R. S. *J. Org. Chem.* **1975,** *40*, 3309. (h) Sucrow, W.; Richter, W. *Chem. Ber.* **1971,** *104*, 3679. For an alternative approach to this side chain, see Schmid, M.; Barner, R. *Helv. Chim. Acta* **1979,** *62*, 464.

(3) For an indirect alternative based upon derivatization, see Valentine, Jr., D.; Chan, K. K.; Scott, G.; Johnson, K. K.; Toth, K.; Saucy, G. *J. Org. Chem.* **1976,** *41*, 62.

(4) While ionization of allylic carboxylates to π-allylpalladium complexes is known, vinyl lactones have been reported only once: Trost, B. M.; Verhoeven, T. R.; Fortunak, J. M. *Tetrahedron Lett.* **1979,** 2301. For a review see Trost, B. M. *Tetrahedron* **1977,** *33*, 2615.

(5) The vinyl lactones possessing a *Z* olefin were prepared by addition of 1-propynylmagnesium bromide to methyl β-formylpropionate followed by acetylene reduction and methylation. ^{1}H NMR allows assignment of stereochemistry. **6b** vinyl protons: δ 5.74 and 5.49 (J = 10.5; H_a, 2.17; H_b, 2.13; H_R, 2.73; H_c, 5.31 (J_{ab} = 12; $J_{aR'}$ = 8.5; J_{ac} = 5.2, $J_{bR'}$ = ~7.5; J_{bc} = ~7 Hz). **6c** vinyl protons: δ 5.75 and 5.44 (J = 10.5 Hz); H_a, 1.73; H_b, 2.53; H_R, 3.69; H_c, 5.14 (J_{ab} = 12.2; J_{aR} = 10.5; J_{ac} = 10.5; J_{bR} = 5.5; J_{bc} = 8 Hz). Full details will be published in a full account of this work.

(6) All new compounds have been fully characterized including combustion analysis and/or high resolution mass spectra. Known compounds have been fully characterized by spectral means.

(7) In the 270-MHz proton spectrum of **7**a there appeared at δ 1.66 a doublet which may correspond to the methyl group of the allylically transposed product. The signal was <2% of the intensity of the doublet at δ 1.05. Similar doublets in the 270-MHz proton spectra of **7b, 7c, 10a,** and **10b** were <1% of the intensity of the major methyl doublet.

(8) The vinyl lactones possessing an *E* olefin were prepared by addition of 3,3-ethylenedioxypropylmagnesium bromide to crotonaldehyde, hydrolysis, oxidation, and methylation. ^{1}H NMR allows assignment of stereochemistry. **9**a vinyl protons: δ 5.82 and 5.56 (J = 16.5 Hz); H_a, 2.22; H_b, 2.07; H_R, 2.69; H_c, 4.92 (J_{ab} = 13; J_{aR} = 8.5; J_{ac} = 4.5; J_{bR} = 8.0, J_{bc} = 8.0 Hz). **9b** vinyl protons: δ 5.49 and 5.84 (J = 16.5 Hz); H_a, 1.62; H_b, 2.53; $H_{R'}$, 2.70; H_c, 4.74 (J_{ab} = 12.2; $J_{aR'}$ = 12; J_{ac} = 10.5; $J_{bR'}$ = 5.5; J_{bc} = 8.2 Hz). Full details will be published in a full account of this work.

(9) Support for this conformation being favored in the ground state arises by the deshielding of H_c in the *Z* olefin isomers **6b** and **6c** relative to the *E* olefin isomers **9a** and **9b** which has been attributed to steric compression. See Cardenas, C. G. *J. Org. Chem.* **1971,** *36*, 1631.

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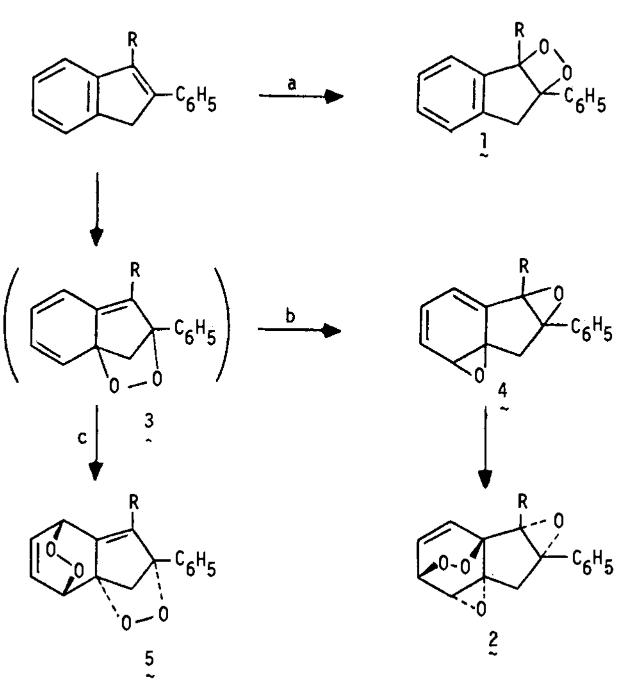
Chemistry of Singlet Oxygen. 32. Unusual Products from Low-Temperature Photooxygenation of Indenes and *trans*-Stilbene[1]

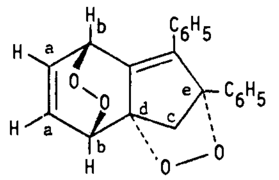
Sir:

Indenes are interesting substrates for photooxidation, producing a wide variety of products. Photooxidation in methanol at −78 °C provides dioxetanes **1** (path a).[2] In acetone at −78 °C (Rose Bengal sensitizer), the observed products are diepoxyendoperoxides **2**.[3] Product **2** is probably derived from a [2 + 4] addition of singlet oxygen to give **3**, followed by rearrangement to a diepoxydiene **4** which is capable of adding a second mole of oxygen (path b). In an effort to learn the origin of this solvent effect, 2,3-diphenylindene was photooxidized at −78 °C in acetone with TPP (*meso*-tetraphenylporphine) as the sensitizer; a novel product was formed (path c).[4,5] The product was stable for extended periods in the solid state, but rapidly decomposed in solution. Explosive decomposition occurred at 110 °C. High resolution mass spectrum was consistent with the molecular formula $C_{21}H_{16}O_4$. The product was assigned structure **5** based on the following data.



R = a: C_6H_5
b: CH_3
c: p-ClC_6H_4

Reaction with triphenylphosphine produced 1.9 equiv of triphenylphosphine oxide, suggesting two peroxide functionalities,[3] and the IR showed no -OH absorption. The ^{1}H NMR (200 MHz) had, in addition to aromatic signals, H_a proton resonances at δ 6.97 (unsymmetrical t)[6a] and 6.81 (unsymmetrical t), H_b protons at δ 5.49 (br d) and 5.28 (br d), and H_c protons as an AB system at δ 3.16 (d, J = 8.5 Hz) and 2.60 (d, J = 8.5 Hz). The ^{13}C NMR (50 MHz) had C_e and C_d resonances at δ 101.2 (s) and 88.9 (s), C_b resonances at δ 72.9 (d) and 71.1 (d), C_c at δ 56.8 (t), and C_a's at δ 133.7 (d) and 130.5 (d), consistent with the assigned structure.[6b] An X-ray crystal structure determination confirmed the structural assignments and showed the stereochemistry of the two oxygen bridges to be anti.[7]



The ratio of the photooxidation products had a strong and unprecedented dependence on the photosensitizer and conditions used. Some conditions produced all three products (**1, 2,** and **5**); however, by careful choice of conditions, any of the three products could be formed preferentially. Table I lists the results with 2,3-diphenylindene using various sensitizers.

The dyes used in runs 5-8 gave ratios of products which changed greatly with only slight changes in the reaction con-

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