0.05 mL of the stock solution was added to 0.95 mL of DEGMEE. The diluted sample was quantitatively transferred to 9.0 mL of the appropriate reagent and mixed. HCl (1 N) was used to obtain the acid form (HL) and 1 M TMAOH for the base form (L<sup>-</sup>). The resulting solutions were scanned in a 1-cm path length cuvette from 700 to 300 nm on a Beckman DU-8B spectrophotometer.

For the  $pK_{a}$  determinations, absorbances were measured at the acid and base wavelength maxima of the chromogenic compounds in a zwitterionic buffer (3-(cyclohexylamino)-1-propanesulfonic acid, CAPS)) at pH values equal to the pK<sub>a</sub> and the pK<sub>a</sub>  $\pm 0.5$ units. These absorbances were used in conjunction with the absorptivities of the acid and base forms to calculate the  $pK_a$ values of 1-3.2b

Responses of Chromoionophores 1 and 3 to Lithium, Sodium, and Potassium in 10% Aqueous DEGMEE. The reagents for obtaining lithium, sodium, and potassium responses consisted of  $5.0 \times 10^{-5}$  M chromoionophore in 10% DEG-MEE/water and an appropriate buffer (Table III). The spectra of the cation complexes (L<sup>-</sup>M<sup>+</sup>) of 1 and 3 in 10% v/v DEGMEE were obtained by adding 0.02 mL of 1.0 M LiCl, NaCl, and KCl to their respective cuvettes containing 2 mL of reagent and scanned from 700 to 300 nm.

The association constant for the lithium complex of 1 in 10%

Responses of Chromoionophore 2 to Lithium, Sodium, and Potassium in CH<sub>2</sub>Cl<sub>2</sub>-Water. Equal volumes (3.0 mL) of a dichloromethane solution of 2 (1.0  $\times$  10<sup>-4</sup> M) and an aqueous solution made of 0.1 M CAPS for pH 11.0, containing 0.05 M LiCl, NaCl, and KCl, respectively, were vortexed in a test tube for 2 min. The organic phase was separated and scanned from 700 to 300 nm (Table II).

For the Li<sup>+</sup> response curve with chromoionophore 2, equal volumes (3.0 mL) of a  $CH_2Cl_2$  solution of 2 (2.0 × 10<sup>-4</sup> M) and an aqueous solution made of 0.1 M CAPS for pH 11.6, containing from 0 to 0.01 M LiCl, were vortexed, and the organic layer was separated and scanned from 700 to 300 nm.

Acknowledgment. The authors wish to thank Drs. Paul F. Corey, Henry Arndt, and James P. Albarella of Miles Inc., Elkhart, IN, for suggesting methylene chloride as a cosolvent for the reduction of diamide 8 and for help with obtaining MS spectra. Thanks are also due to Dr. Carl R. Gebauer for critical remarks and Dr. Anna Czech for the artwork.

# Ionic Photodissociation of Polyenes via a Highly Polarized Singlet **Excited State**

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Received March 3, 1992

Several polyene acetates and polyene methyl ether were prepared. Upon direct excitation these polyenes undergo ionic photodissociation from their singlet excited states. Triplet-sensitization experiments on these polyenes revealed that the ionic photodissociation process is restricted to singlet excited states. The rationale put forward is that the polyene chromophore undergoes charge separation/polarization in the singlet excited state, which leads to ionic photodissociation.

#### Introduction

The spectroscopic and photochemical behavior of polyenes, polyenals, polyenones, and to a certain extent polyene esters and nitriles has been studied.<sup>1</sup> Deactivation of polyene excited states results in cis-trans isomerization, sigmatropic shifts, and electrocyclization reactions.<sup>2</sup> The involvement of a highly polarized excited states in these photochemical reactions has been suggested. Theoretical studies carried out by Salem and others<sup>3</sup> on polyenes revealed the polarized nature of their excited states. A zwitterionic excited state was put forward by Dauben<sup>4</sup> to explain the high stereospecificity observed in the photo-

Table I. Quantum Yield for Direct Excitation Reactions<sup>a</sup>

cis isomers	tetraene	methyl ether
0.243	0.191	0.113
0.197	0.199	0.086
0.195		0.078
0.143	0.092	
	cis isomers 0.243 0.197 0.195 0.143	cis isomers         tetraene           0.243         0.191           0.197         0.199           0.195         0.092

<sup>a</sup>Quantum yields were determined using ferrioxalate actinometry in an Applied Photophysics quantum yield reactor (QYR-20); methanol is the solvent; at 280 nm using solution filters; values are averages of three runs.

Table II. Quantum Yield Data of Pentaene Acetate in Various Solvents<sup>a</sup>

entry no.	solvent	fluores- cence	9-cis	13-cis	anhydro- retinol	methyl ether
1	hexane	0.041	0.012	0.008	0.007	
2	CH <sub>2</sub> Cl <sub>2</sub>	0.011	0.047	0.017	0.028	
3	CH <sub>3</sub> CN	0.003	0.032	0.029	0.106	
4	MeŐH	0.004	0.039	0.026	0.019	0.104

<sup>a</sup>Quantum yield of fluorescence for entry 4 is from ref 11; quantum yield determined is relative to 9,10-diphenylanthracene; values are averages of three runs; product quantum yield was determined using potassium ferrioxalate actinometry, at 320 nm.

cyclization reaction of trans-ethylidenecyclooctene. The same hypothesis was extended to explain vitamin D and triene photochemistry.<sup>5</sup> Similarly, a highly polarized

<sup>(1) (</sup>a) Ottolenghi, M. Adv. Photochem. 1980, 12, 97. (b) Kliger, D. S. Methods Enzymol. 1982, 88, 533. (c) Hudson, B.; Kohler, B. Ann. Rev. Phy. Chem. 1974, 19, 401. (d) Bensasson, R.; Land, E. J.; Truscott, T. G. Flash Photolysis and Pulse Radiolysis; Pergamon Press: Oxford, 1983.
(e) Becker, R. S. Photochem. Photobiol. 1988, 48, 369. (f) Jensen, N. H.;
(wilbrandt, R.; Bensasson, R. J. Am. Chem. Soc. 1989, 111, 7877. (g)
Folken, G. J. In Organic Photochemistry; Chapman, O. L., Eds.; Marcel
Dekker: New York, 1967; Vol. 1, p 155.
(2) (a) Liu, R. S. H.; Asato, A. E. Tetrahedron 1984, 40, 1931. (b)
Mouserron-Canet, M. Adv. Photochem. 1966, 4, 203.
(3) (a) Salem, L. Acc. Chem. Res. 1979, 12, 87. (b) Bonacic-Koutecky,
V.; Persico, Donheet, D.; Sevin, A. J. Am. Chem. Soc. 1982, 104, 6800. (c)
Albert, I. D. L.; Ramasesha, S. J. Phys. Chem. 1990, 94, 6540.
(4) (a) Dauben, W. G.; Ritscher, R. S. J. Am. Chem. Soc. 1970, 92, G. Flash Photolysis and Pulse Radiolysis; Pergamon Press: Oxford, 1983.

<sup>(4) (</sup>a) Dauben, W. G.; Ritscher, R. S. J. Am. Chem. Soc. 1970, 92, 2995. (b) Dauben, W. G.; Kellop, M. S.; Seeman, J. I.; Vietmeyer, N. D.; Lundschuh, P. H. Pure Appl. Chem. 1973, 33, 177.

				isomers <sup>a,e</sup>		
compd	sensitizer	λ <sub>max</sub> (nm)	$E_{\mathrm{T}}^{d}$ (kcal/mol)	% cis	% cis	% trans
1	fluorenone <sup>b</sup>	379, 394	51	10 (9-cis)	42 (7-cis)	48
	benzanthrone <sup>b</sup>	396, 431	46	9 (9-cis)	44 (7-cis)	47
2	fluorenone	379, 394	51	15 (2-cis)	20 (4-cis)	65
	benzanthrone	396, 431	46	18 (2-cis)	19 (4-cis)	63
4	fluorenone	379, 394	51	51 (9-cis and 7-cis)		49
	benzanthrone	396, 431	46	54 (9-cis and 7-cis)		46
5	ervthrocin <sup>c</sup>	515	42	16 (9-cis)	14 (13-cis)	70
	rose bengal	550	39	17 (9-cis)	14 (13-cis)	68
	methylviolet	585	37	no reactio	n	
	methyleneblue <sup>c</sup>	660	32	no reactio	n	

<sup>a</sup> 10<sup>-2</sup> M methanol solutions bubbled with N<sub>2</sub>; Pyrex filter. <sup>b</sup>Reference 9 for triplet energies. <sup>c</sup>Reference 10 for triplet energies. <sup>d</sup>Reaction was monitored by HPLC; there was no detectable reaction when erythrocin and rose bengal were employed for sensitizing 1, 2, and 4. Values are averages of three runs.



singlet excited state has been suggested for polyenes and polyenes in the vitamin A series<sup>6</sup> undergoing isomerizations. Now we have prepared several polyene acetates and a polyene methyl ether (Chart I), whose photochemistry is not well studied, to determine the generality of the above-mentioned hypothesis to these polyenes. The photochemistry of these polyenes clearly supports the hypothesis of "charge separation in the excited state", and this charge separation leads to ionic photodissociation.

#### **Results and Discussion**

Direct excitation of the polyenes was carried out in hexane and methanol, and the reaction was monitored by HPLC. Direct excitation of triene acetates 1 and 2 and methyl ether 4 in hexane in a Rayonet photochemical reactor equipped with RPR-2537 (254-nm) lamps gave an isomeric mixture along with tetraene. Irradiation of the same trienes gave the corresponding methyl ether along with an isomeric mixture and tetraene in methanol. Irradiation of phenyl-substituted diene acetate 3 in hexane under the same conditions gave an isomeric mixture. When 3 was irradiated in methanol gave an isomeric mixture and the methyl ether of 3 were the products. The quantum yields of these reactions were determined and are presented in Table I. Similarly, pentaene acetate 5

was irradiated in hexane, CH<sub>2</sub>Cl<sub>2</sub>, CH<sub>3</sub>CN, and methanol with a 450-W Hg arc lamp to afford hexaene 12 and an isomeric mixture. In methanol, methyl ether 11 was obtained in addition to 12 and an isomeric mixture. Quantum yield data for the products are presented in Table II. All these polyenes show similar behavior upon direct excitation from their singlet excited states. We have determined the quantum yield of fluorescence for pentaene acetate 5 at room temperature to understand the behavior of the singlet excited state. The relative quantum yield of fluorescence was determined in various solvents by using 9,10-diphenylanthracene<sup>7</sup> ( $\phi = 1.0$ ) as the standard, and the quantum yield of product formation was also determined (Table II). Interestingly, quantum yield data for 5 show a marked difference when the solvent polarity is changed from hexane to methanol. The trend is clear that a polar solvent quenches the fluorescence of the singlet excited state more effectively than a nonpolar solvent does. A similar trend is reported in the studies on the benzofluorenol system.<sup>8</sup>

Triplet-sensitization experiments were carried out on all polyenes to differentiate singlet-triplet reactivities. Triplet-sensitization experiments were designed such that under the irradiation conditions only the sensitizer absorbed light. Sensitizers of varying triplet energies (fluorenone<sup>9</sup> ( $E_{\rm T} = 51$  kcal/mol), benzanthrone<sup>9</sup> ( $E_{\rm T} = 46$ kcal/mol), erythrocin<sup>10</sup> ( $E_{\rm T}$  = 42 kcal/mol) and rose ben $gal^{10}$  ( $E_T = 39$  kcal/mol)) were used to obtain information about the triene triplet energy levels. Fluorenone- and benzanthrone-sensitized reactions of triene acetates gave only isomeric mixtures (Table III), not the tetraene and methyl ether products isolated from the direct irradiation. Sensitization experiments with erythrocin and rose bengal did not effect any reaction. Products originating from the triplet-sensitization experiments are comparable with those from the triene ester and nitrile<sup>12</sup> systems reported earlier and also indicate that for these polyenes triplet-state reactivity is restricted to isomerization. Systematic variation of the energy of the sensitizers used in the sensitization experiments revealed that the triplet energy levels are above 42 kcal/mol for 1, 2, and 4 and above 39 kcal/mol for 5.

Polyene singlet excited states appear to have high dipolar character. It has been shown experimentally that

<sup>(5)</sup> Jacobs, H. J. C.; Havinga, E. Adv. Photochem. 1979, 11, 305. (6) (a) Jayathirtha Rao, V.; Fenstemacher, R. J.; Liu, R. S. H. Tetrahedron Lett. 1984, 25, 1115.
 (b) Muthuramu, K.; Liu, R. S. H. J. Am. Chem. Soc. 1987, 109, 6510.
 (c) Arjunan, P.; Liu, R. S. H. Tetrahedron Lett. 1988, 29, 853.
 (d) Jayathirtha Rao, V.; Bhalerao, U. T. Tetrahedron Lett. 1990, 31, 3444.

<sup>(7)</sup> Photochemistry; Calverts, J. G., Pitts, Jr., J. N., Eds.; John Wiley: New York, 1966; p 799. (8) Krogh, E.; Wan, P. Can. J. Chem. 1990, 68, 1725.

<sup>(9)</sup> Hand Book of Photochemistry; Murov, S., Ed.; Marcel Dekker: New York, 1973.

<sup>(10)</sup> Denny, R. W.; Nickon, A. Org. React. 1973, 20, 133.

 <sup>(11)</sup> Thompson, A. J. J. Chem. Phys. 1969, 51, 4106.
 (12) Ramamurthy, V.; Butt, Y.; Yang, C.; Yang, P.; Liu, R. S. H. J. Org. Chem. 1973, 38, 1247.



retinol, retinal,<sup>13</sup> retinol acetate<sup>14</sup> and even diphenylpolyenes<sup>15</sup> experience a large change in polarizability and dipole moment upon excitation to their singlet excited states. In addition, theoretical studies have predicted that the polyene excited state is associated with charge redistribution.<sup>3,16</sup> A change in dipole moment and polarizability upon excitation leads to charge redistribution over the polyene chain, and this charge redistribution results in the change in bond order, thus facilitating the isomerization process. The change in dipole moment and polarizability of the polyene leads to charge redistribution or the typical highly polarized structure (Scheme I) depicted for triene acetate 1, which undergoes an ionization process, resulting in a highly resonance-stabilized carbonium ion 6, or it can lead to isomerization process (Scheme I). Formation of the carbonium ion intermediate was suggested by the fact that tetraene 7 and methyl ether 4 were isolated (Scheme I). Similar behavior was expected and observed experimentally from the other polyenes prepared (2-5), further supporting the intermediacy of a highly polarized singlet excited state. Triplet-sensitization studies indicate that this ionic dissociation process is restricted to the singlet excited state. That triplet sensitization leads exclusively to isomerization processes is probably due to a combination of the low energy and the biradical nature of the triplet state. Another piece of information was obtained from the fluorescence studies carried out on pentaene acetate 5. The drastic reduction in the fluorescence quantum yield (Table II) of 5 in a polar

(15) Ponder, M.; Mathies, R. J. Phys. Chem. 1983, 87, 5090.



solvent suggests that the possible intermediacy of the highly polarized singlet excited state and its efficient interaction with polar solvent leads to the ionic dissociation process (Scheme II).

In conclusion, we believe that the photochemical properties displayed by the polyenes are consistent with the intermediacy of a highly polarized singlet excited state and with those in the earlier reports.<sup>17</sup> The role of the polarized excited state in controlling the selective isomeri-

<sup>(13)</sup> Mathies, R.; Stryer, L. Proc. Natl. Acad. Sci. U.S.A. 1976, 78, 2169.

<sup>(14)</sup> Bondarev, S. L.; Belkov, M. V.; Pavlenko, V. B. Chem. Abstr. 1985, 102, 204125d.

<sup>(16)</sup> Birgre, R. R.; Bennett, J. A.; Hubbard, L. M.; Fang, H. L.; Pierce, B. M.; Kliger, D. S.; Leroi, G. E. J. Am. Chem. Soc. 1982, 104, 2519.

 <sup>(17) (</sup>a) Rossenfeld, T.; Alchalal, A.; Ottolenghi, M. Chem. Phys. Lett.
 1973, 20, 291. (b) Wan, P.; Krogh, E. J. Am. Chem. Soc. 1989, 111, 4887.

Table IV. <sup>1</sup>H NMR Spectroscopic Data (Chemical Shifts and Coupling Constants) of Polyenes<sup>a</sup>

1	1 9-cis	10 H 5.55 5.40	8 H 6.05 6.35	7 H 6.18 6.22	J <sub>7H-8H</sub> 15.6 15.4	5-CH <sub>3</sub> 1.65 1.75	9-CH <sub>3</sub> 1.9 1.98	(CH <sub>3</sub> ) <sub>2</sub> 1.11 1.1	CH <sub>3</sub> -Acetyl 2.22 2.18	O-CH <sub>2</sub> 4.75 4.70	J <sub>10H-CH2</sub> 7.24	
2	<b>2</b> 2-cis	2 H 5.55 5.4	4 H 6.15 6.1	5 H 6.50 6.35	6 H 5.85 5.80	3-CH <sub>3</sub> 1.80 1.85	(CH <sub>3</sub> ) <sub>2</sub> 1.70 1.7	CH <sub>3</sub> 2.20 2.15	J <sub>4H-5H</sub> 15.80 15.6	<b>J<sub>5Н-6Н</sub></b> 10.4 10.3	OCH <sub>2</sub> 4.75 4.78	J <sub>2H-CH2</sub> 6.84
	3	2 H 5.85	3 H 6.75	4 H 6.4	5 H 6.52	OCH <sub>2</sub> 4.65	CH <sub>3</sub> 2.05	<b>arom</b> 7.1–7.5	J <sub>2H-3H</sub> 15.8–15.46	Ј <sub>3Н−4Н</sub> 11.0	J <sub>4Н-5Н</sub> 15.63	J <sub>2H-CH2</sub> 6.80
4	<b>4</b> 9-cis	10 H 5.56 5.46	8 H 6.02 6.38	7 H 6.13 6.17	OCH <sub>2</sub> 4.1 4.1	OCH <sub>3</sub> 3.35 3.30	9-CH <sub>3</sub> 1.84 1.92	5-CH <sub>3</sub> 1.68 1.70	(CH <sub>3</sub> ) <sub>2</sub> 1.002 1.015	J <sub>7Н-8Н</sub> 16.0 15.8	J <sub>10H-OCH2</sub> 6.84	
9	9 2-cis	2 H 5.5 5.38	4 H 6.1 6.1	5 H 6.4 6.36	6 H 5.8 5.85	OCH <sub>2</sub> 4.0 4.0	OCH <sub>3</sub> 3.25 3.33	CH <sub>3</sub> 1.75 1.83	(CH <sub>3</sub> ) <sub>2</sub> 1.72 1.72	J <sub>5Н-6Н</sub> 10.2 10.0	J <sub>4H-5H</sub> 15.4 15.6	J <sub>2H-OCH2</sub> 7.01
	10	2 H 5.9	3 H 6.8	4 H 6.4	5 H 6.55	OCH <sub>2</sub> 4.0	OCH <sub>3</sub> 3.4	<b>arom</b> 7.2–7.7	J <sub>2H-3Н</sub> 15.4	J <sub>3H-4H</sub> 10.2	$J_{ m 4H-5H}$ 15.42	$J_{2\mathrm{H-OCH}_2}$ 6.92
	7	11 Ha 5.25	11 Hb 5.05	4 H 5.75	10 H 6.5	7 H 6.75	8 H 6.35	9-CH <sub>3</sub> 1.95	5-CH <sub>3</sub> 1.9	(CH <sub>3</sub> ) <sub>2</sub> 1.25	J <sub>10H-11Ha</sub> 15.8	<i>J</i> <sub>10Н-11НЪ</sub> 12.1
		$J_{8\mathrm{h-7H}}$ 11.5	$J_{ m 4H-3H}$ 5.0									
	11	7 H 6.12	8 H 6.0	10 H 6.16	11 <b>H</b> 6.55	12 H 6.25	14 H 5.57	OCH <sub>2</sub> 4.05	OCH <sub>3</sub> 3.3	13-CH <sub>3</sub> 1.9	9-CH <sub>3</sub> 1.8	5-CH <sub>3</sub> 1.65
		(C <b>H</b> <sub>3</sub> ) <sub>2</sub> 1.1	J <sub>14H-ОСН2</sub> 6.8		$J_{10\mathrm{H}-11\mathrm{H}}\ 10.8$	J <sub>11H-12H</sub> 15.2	J <sub>7Н-8Н</sub> 15.3					
	12	4 H 5.78	7 H 6.38	8 H 6.78	10 H 6.44	11 H 6.61	12 H 6.19	14 H 6.45	15 Ha 5.17	15 Hb 5.05	13-CH <sub>3</sub> 1.94	9-CH <sub>3</sub> and 5-CH <sub>3</sub> 1.91
		(CH <sub>3</sub> ) <sub>2</sub> 1.22	J <sub>4Н-3Н</sub> 6.2	<b>J<sub>7H-8Н</sub></b> 12.0	$J_{ m 10H-11H}\ 15.2$	$J_{11\mathrm{H} ext{-}12\mathrm{H}}\ 11.2$	J <sub>14H-15Ha</sub> 16.1	$J_{14\mathrm{H}-15\mathrm{Hb}}\ 12.4$				

<sup>a</sup> CDCl<sub>3</sub> as solvent; 200-MHz NMR spectrometer; J = coupling constant in Hz.

compd	$\lambda_{max}$ (nm)	$\epsilon \times 10^{-4}$
1	276	3.6
2	276	4.2
3	284	3.8
4	272	3.7
9	274	4.3
10	282	3.9
11	320	4.1
7	326, 312, 298	4.0
8	310, 296, 284	4.1
12	390, 364, 340	4.4

<sup>a</sup>Solvent = hexane;  $\epsilon$  = molar absorption coefficient.

zation process in polyenes is under investigation.

### **Experimental Section**

<sup>1</sup>H-NMR spectra ( $\delta$ ) were measured at 200 or 80 MHz in CDCl<sub>3</sub>. Mass spectra were recorded on a GV Micromass 7070 H instrument. UV-visible absorption spectra were recorded on a Shimadzu instrument. A SPEX Fluorolog fluorimeter was used to obtain fluorescence data. Solvents were distilled prior to use. Other chemicals were purchased and are commercially available. Wittig reagents ethyl diethylphosphonoacetate (C2-unit) and triethyl 3-methyl-4-phosphonocrotonate (C5-unit) were prepared according to published procedures.<sup>18</sup> <sup>1</sup>H-NMR data and UV-visible absorption data for selected polyenes are provided in Tables IV and V, respectively.

Methyl  $\beta$ -Ionylideneacetate and  $\beta$ -Ionylideneethanol. These compounds were prepared according to the reported procedure.<sup>19</sup> Methyl  $\beta$ -ionylideneacetate (90% yield): <sup>1</sup>H-NMR (all-trans isomer) 6.05 (d, 7 H, J = 15.5 Hz), 6.5 (d, 8 H), 5.7 (s, 10 H), 3.65 (s, COOCH<sub>3</sub>), 2.3 (9-CH<sub>3</sub>), 1.65 (5-CH<sub>3</sub>), 1.0 (gemmethyls); mass fragments 262 (M<sup>+</sup>), 247, 233, 217, 189. Anal. Calcd for  $C_{17}H_{26}O_2$ : C, 77.82; H, 9.99. Found: C, 77.52; H, 9.89.  $\beta$ -Ionylideneethanol (60% yield): <sup>1</sup>H-NMR (all-trans isomer) 6.2 (d, 7 H;  $J_{7H-8H} = 15.6$  Hz), 6.05 (d, 8 H), 5.6 (t, 10 H,  $J_{10H-CH_2OH} = 8$  Hz), 4.3 (d, CH<sub>2</sub>OH), 1.9 (9-CH<sub>3</sub>), 1.8 (5-CH<sub>3</sub>), 1.1 (gemmethyls); mass fragments 220 (M<sup>+</sup>), 202, 189. Anal. Calcd for  $C_{15}H_{24}O$ : C, 81.76; H, 10.98. Found: C, 81.65; H, 11.06.

β-Ionylideneethanol Acetate (1). This compound was synthesized by treating β-ionylideneethanol with acetic anhydride and pyridine and was purified by flash chromatography (90% yield): mass fragments 262 (M<sup>+</sup>), 218, 189. Anal. Calcd for  $C_{17}H_{28}O_2$ : C, 72.82; H, 9.99. Found: C, 77.68; H, 9.99.

3,7-Dimethylocta-2,4,6-trienoic Acid Methyl Ester. Sodium hydride (4.6 g, 95 mmol, 50% in mineral oil) was slurried in dry DMF (100 mL), and triethyl 3-methylphosphonocrotonate (C5unit, 25 g, 95 mmol, in 50 mL of DMF) was added very slowly at room temperature while stirring. Stirring was continued for another 15 min until the NaH was completely consumed. Then 3-methyl-2-butenal (7.2 g, 85 mmol, in 20 mL of DMF) was added very slowly while stirring. The reaction mixture was poured over ice and extracted with ether. The ether extract was washed with water and evaporated, and the residue was chromatographed over silica gel with hexane to afford the pure all-trans triene ester and 2-cis isomer mixture (8.2 g, 50% yield): <sup>1</sup>H-NMR (all-trans) 5.7 (s, 2 H), 6.1 (d, 4 H,  $J_{4H-6H} = 15.8$  Hz), 6.8 (dxd, 5 H), 5.9 (d, 6 H,  $J_{6H-6H} = 10$  Hz), 2.3 (s, 3-CH<sub>3</sub>), 1.8 (s, gem-methyls), 3.65 (s, COOCH<sub>3</sub>); mass fragments 194 (M<sup>+</sup>), 179, 165, 149, 121. Anal. Calcd for C<sub>11</sub>H<sub>15</sub>O<sub>2</sub>: C, 73.3, H, 8.95. Found: C, 73.4; H, 9.05.

3,7-Dimethylocta-2,4,6-trien-1-ol and 3,7-Dimethylocta-2,4,6-trienyl 1-acetate (2). These compounds were synthesized as per the procedure given above. 3,7-Dimethylocta-2,4,6-trien-1-ol (80% yield): <sup>1</sup>H-NMR (all-trans) 5.6 (t, 2 H, J = 7 Hz), 6.15 (d, 4 H,  $J_{4H-5H} = 16$  Hz), 6.45 (dxd, 5 H), 5.9 (d, 6 H,  $J_{6H-5H} = 11$ Hz), 4.3 (d, CH<sub>2</sub>OH), 1.8 (3-CH<sub>3</sub> and gem-methyls); mass fragments 152 (M<sup>+</sup>), 134, 121, 109. Anal. Calcd for C<sub>10</sub>H<sub>18</sub>O: C, 78.89; H, 10.59. Found: C, 78.69; H, 10.80. 3,7-Dimethylocta-2,4,6-trienyl 1-acetate (2) (90% yield): mass fragments 194 (M<sup>+</sup>), 151, 135,

<sup>(18)</sup> Wadsworth, W. S. Org. React. 1977, 25, 73.

<sup>(19)</sup> Andrews, A. G.; Jensen, L. Acta Chem. Scand. 1973, 27, 1401.

111. Anal. Calcd for  $C_{12}H_{18}O_2$ : C, 74.19; H, 9.34. Found: C, 74.03; H, 9.40.

5-Phenylpenta-2,4-dienoic Acid Methyl Ester, 5-Phenylpenta-2,4-dien-1-ol, and 5-Phenylpenta-2,4-dienyl 1-Acetate (3). These are synthesized as per the above sequence. 5-Phenylpenta-2,4-dienoic acid methyl ester (95% yield): mp 78 °C; <sup>1</sup>H-NMR 6.0 (d, 2 H, J = 15.8 Hz), 7.2–7.5 (3 H and aromatic), 6.9 (m, 4 H and 5 H), 3.8 (s, COOCH<sub>3</sub>); <sup>13</sup>C-NMR 14.19, 60.15, 121.19, 126.09, 127.04, 127.81, 128.64, 128.96, 135.88, 140.19, 144.38, 166.85; mass fragments 202 (M<sup>+</sup>), 173, 157, 129. Anal. Calcd for C<sub>13</sub>H<sub>14</sub>O<sub>2</sub>: C, 77.2; H, 6.98. Found: C, 77.15; H, 6.95. 5-Phenylpenta-2,4-dien-1-ol (60% yield): mp 67 °C; <sup>1</sup>H-NMR 5.92 (m, 2 H,  $J_{2H-3H}$  = 15.8 Hz), 6.78 (dxd, 3 H), 6.4 (q, 4 H,  $J_{4H-3H}$ = 16.0 Hz), 6.55 (d, 5 H, J = 16 Hz), 7.2-7.5 (m, aromatic), 4.25(d, CH<sub>2</sub>OH); <sup>13</sup>C-NMR 63.33, 126.34, 127.58, 128.11, 128.57, 129.03, 131.55, 132.46, 132.71, 137.06; mass fragments 160 (M<sup>+</sup>), 142, 129. Anal. Calcd for C<sub>11</sub>H<sub>12</sub>O: C, 82.46; H, 7.55. Found: C, 82.56; H, 7.57. 5-Phenylpenta-2,4-dienyl 1-acetate (3): <sup>13</sup>C-NMR 20.87, 64.66, 126.4, 126.79, 127.61, 128.54, 133.68, 134.44, 136.82, 170.67; mass fragments 202 (M<sup>+</sup>), 159, 129. Anal. Calcd for  $C_{13}H_{14}O_2$ : C, 77.20; H, 6.98. Found: C, 77.05; H, 7.04.

Methyl ethers were prepared by extending the published procedure to the present systems.<sup>20</sup>

β-Ionylideneethanol methyl ether (4): 80% yield; mass fragments 234 (M<sup>+</sup>), 219, 212, 189. Anal. Calcd for  $C_{16}H_{26}O$ : C, 81.99; H, 11.18. Found: C, 81.89; H, 11.39.

**3,7-Dimethylocta-2,4,6-trienyl methyl ether (9)**: 75% yield; mass fragments 166 (M<sup>+</sup>), 151, 134, 121. Anal. Calcd for  $C_{11}H_{18}O$ : C, 79.46; H, 10.92. Found: C, 79.36; H, 11.03.

**5-Phenylpenta-2,4-dienyl methyl ether (10):** 80% yield; <sup>13</sup>C-NMR 57.93, 72.78, 126.38, 126.80, 127.59, 128.22, 128.59, 129.94, 132.73, 132.93; mass fragments 174 (M<sup>+</sup>), 159, 142, 128, 115. Anal. Calcd for  $C_{12}H_{14}O$ : C, 82.62; H, 8.10. Found: C, 82.62; H, 8.20.

**Retinyl methyl ether** (11): 70% yield; mass fragments 300 (M<sup>+</sup>), 285, 268, 255. Anal. Calcd for  $C_{21}H_{32}O$ : C, 83.94; H, 10.73. Found: C, 83.12, H, 10.80.

Anhydroretinol (12) was prepared as per the reported procedure:<sup>21</sup> mass fragments 268 (M<sup>+</sup>), 253, 205, 107. Anal. Calcd

(20) Ando, T.; Yamawaki, J.; Kawate, T.; Sumi, S.; Hanafusa, T. Bull. Chem. Soc. Jpn. 1982, 55, 2504.

(21) Sahntz, E. M.; Cawley, J. D.; Embree, N. D. J. Am. Chem. Soc. 1943, 65, 901.

for C<sub>20</sub>H<sub>28</sub>: C, 89.49; H, 10.51. Found: C, 89.13; H, 10.68.

Photolysis. A rayonet photochemical reactor equipped with RPR-2537 (254 nm) lamps was used for the irradiation of compounds 1-4; a 450-W medium-pressure Hg arc lamp was used for the irradiation of 5. All reactions were monitored by Shimadzu LC-6A with a UV-visible detector and coupled with a CR-3A integrator. An amino silica column, 4.6/250 mm, was used with hexane as eluent for all the systems. In sensitization experiments, the sensitizers were well-separated on LC conditions and did not interfere with polyenes, except in the case of 3. Variation in light intensity was achieved by reducing the number of lamps used in the Rayonet photochemical reactor. A typical experiment involved 10 mL of a  $10^{-3}$  M solution of 1-4. The polyene solution was purged with nitrogen gas in a quartz tube and irradiated with 254-nm lamps in a Rayonet reactor. After the irradiation, products were characterized based on the spectral information and comparison with the authentic samples. Prolonged irradiation leads to other products.

Fluorescence spectra were obtained on a SPEX-Fluorolog fluorimeter. Analytical-grade solvents were used. Identical conditions were maintained for all the fluorescence measurements. A xenon arc lamp equipped with the fluorescence instrument was used for the excitation. The excitation wavelength was 320 nm, the slit width was 4 mm, and the emission spectral range was 330–600 nm; all operations were at room temperature. 9,10-Diphenylanthracene was the standard ( $\phi_f = 1.0$ ). Relative quantum yield of fluorescence was calculated as per Calverts and Pitts.<sup>7</sup> A 2 × 10<sup>-4</sup> M concentration of 5 was used for fluorescence measurements in all solvents.

Quantum yields were determined in an Applied Photophysics Model QYR-20 quantum yield reactor equipped with a 200-W Hg arc lamp. Solution filters were used to isolate the required wavelength band. Quantum yield of product formation for 5 was determined in various solvents. The quantum yields of product formation for 1-4 were determined in methanol. Potassium ferrioxalate was used as an actinometer.

Acknowledgment. We thank Prof. R. S. H. Liu, University of Hawaii, Honolulu, for the kind suggestions. We thank Dr. A. V. Rama Rao, Director, IICT, and Dr. U. T. Bhalerao, Deputy Director, IICT, Hyderabad, India, for their encouraging support in these investigations. IICT Communication No.: 2877.

## Double Group-Transfer Reactions: A Theoretical (AM1) Approach

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Received April 7, 1992

The mechanisms of several concerted and stepwise dyotropic transfer reactions have been studied using the AM1 semiempirical SCF-MO procedure. Dihydrogen transfer on cyclobutene is best described by means of a stepwise diradical pathway. Moreover, the symmetric stationary point corresponding to the concerted reaction is no longer a true transition state. In contrast, the thermal intramolecular isomerization of diaxial 2,3-dibromo-*tert*-butylcyclohexane to the diequatorial isomer is a concerted process with an energy barrier of 62.2 kcal mol<sup>-1</sup>. The activation energy of the concerted dyotropic transfer in syn-sesquinorbornene systems (i.e., pentacyclo[7.6.0.0<sup>213</sup>.0<sup>38</sup>.0<sup>10,14</sup>]pentadeca-4,6,11-triene) is linearly dependent of the size of the intracavity gap (C-H--C<sub>sp2</sub>), thus in agreement with Menger's spatiotemporal hypothesis.

The concerted transfer of two hydrogen atoms from an eclipsed ethane to an ethylene group is a thermally allowed pericyclic  $[\sigma^2 s + \sigma^2 s + \pi^2 s]$  reaction.<sup>1</sup> Other well-known examples involving the transfer of two hydrogen atoms on different substrates such as the reduction of alkenes with diimide species,<sup>2</sup> and related reactions with hydrocarbons,<sup>3</sup>

have also been mechanistically interpreted as involving such types of processes.

<sup>(1)</sup> Woodward, R. B.; Hoffman, R. The Conservation of Orbital Symmetry; Verlag Chemie: Weinheim, 1971; pp 141-144.

<sup>(2)</sup> See, for example: Van Tamelen, E. E.; Dewey, R. S.; Lease, M. F.; Pirkle, W. H. J. Am. Chem. Soc. 1961, 83, 4302. Hünig, S.; Müller, H. R.; Thier, W. Angew. Chem., Int. Ed. Engl. 1965, 4, 271. Garbisch, E. W., Jr.; Schildcrout, S. M.; Patterson, D. B.; Sprecher, C. M. J. Am. Chem. Soc. 1965, 87, 2932. Willis, C.; Back, R. A.; Parsons, J. M.; Purdon, J. G. J. Am. Chem. Soc. 1977, 99, 4451. Franck-Neumann, M.; Dietrich-Buchecker, C. Tetrahedron Lett. 1980, 671.