

- (2) R. Ugo, *Cat. Rev.-Sci. Eng.*, **11**, 225 (1975).  
 (3) E. L. Muetterties, *Bull. Soc. Chim. Belg.*, **84**, 959 (1975).  
 (4) E. L. Muetterties, *Bull. Soc. Chim. Belg.*, **85**, 451 (1976).  
 (5) E. L. Muetterties, *Science*, **196**, 83 (1977).  
 (6) Until recently, many of these catalytic reactions had not been demonstrated in a homogeneous system.<sup>1,3,4,7,8</sup>  
 (7) K. G. Caulton, M. G. Thomas, B. A. Sosinsky, and E. L. Muetterties, *Proc. Natl. Acad. Sci. U.S.A.*, **73**, 4274 (1976).  
 (8) G. C. Demitras and E. L. Muetterties, *J. Am. Chem. Soc.*, **99**, 2796 (1977).  
 (9) E. L. Muetterties and F. J. Hirsekorn, *J. Am. Chem. Soc.*, **96**, 4063 (1974); F. J. Hirsekorn, M. C. Rakowski, and E. L. Muetterties, *J. Am. Chem. Soc.*, **97**, 237 (1975); E. L. Muetterties, M. C. Rakowski, F. J. Hirsekorn, W. D. Larson, V. J. Basus, and F. A. L. Anet, *J. Am. Chem. Soc.*, **97**, 1266 (1975); M. C. Rakowski, F. J. Hirsekorn, L. S. Stuhl, and E. L. Muetterties, *Inorg. Chem.*, **15**, 2379 (1976).  
 (10) A literature procedure<sup>11</sup> was used for the preparation of this cyclooctadiene complex; the NMR spectrum we obtained for the complex was fully consistent with an  $\eta^3\text{-C}_3\text{H}_5\text{Rh}-\eta^4\text{-C}_8\text{H}_{12}$  structure and was quite different from that reported. Observed  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , TMS reference):  $\delta$  -1.82, -2.03, -2.19 (overlapping doublet and two singlets, 10), -3.36 (doublet, 2,  $J$  = 6.8 Hz), -4.80 (broad singlet, 4), -5.42 (multiplet, 1,  $J_{\text{H-Rh}}$  = 3.2 Hz,  $J$  = 12.8 Hz). This pseudo-four-coordinate complex slowly decomposed (solid state) at 25 °C.  
 (11) A. Kasahara and K. Tanaka, *Bull. Chem. Soc. Jpn.*, **39**, 634 (1966).  
 (12) For example,  $\eta^3\text{-C}_3\text{H}_5\text{Rh}[\text{P}(\text{OCH}_3)_3]_2$  and  $\eta^3\text{-C}_3\text{H}_5\text{Rh}[\text{P}(\text{OC}_2\text{H}_5)_3]_2$  were inactive, whereas  $\eta^3\text{-C}_3\text{H}_5\text{Rh}[\text{P}(\text{O}-i\text{-C}_3\text{H}_7)_3]_2$  was active.  
 (13) Propene elimination was also an observed, competitive reaction in the cobalt-catalyzed reactions. This elimination reaction usually produces a complex(es) catalytically inactive for arene hydrogenations.  
 (14) Single crystals of **1** and **2**, respectively, were obtained by cooling pentane-toluene and pentane solutions of the complex. Satisfactory analyses were obtained for C, H, P, and Rh.  
 (15) At low temperatures, there was some line broadening due to viscosity effects.  
 (16) The three crystallographically independent rhodium atoms were located through direct methods and the remaining nonhydrogen atoms of the totally general position asymmetric unit were located by standard difference Fourier techniques. Further refinement is underway using the more complete ( $2\theta_{\text{Mo K}\alpha} \leq 63.7^\circ$ ) data set; hopefully these results can be combined with those of the anticipated neutron-diffraction study to give a highly definitive characterization of the bonding in these clusters.  
 (17) The first number in parentheses following an averaged value of a bond length or angle is the root mean square estimated standard deviation of an individual datum. The second and third numbers, when given, are the average and maximum deviations from the averaged value, respectively. The fourth number represents the number of individual measurements which are included in the average value.  
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### Deuterium Isotope Effects in the Solvolysis of Benzal Halides. 3. $\beta$ -D<sub>3</sub> Isotope Effects and the Mechanism of Solvolysis of 1,1-Dihaloethylbenzenes in Dioxane-Water Mixtures

Sir:

Secondary deuterium isotope effects are used extensively as probes into mechanisms of solvolytic reactions.<sup>1</sup> The magnitude of the  $\beta$ -D effect reflects changes in the proportion of elimination product(s) with changes of solvent or of leaving group.<sup>2</sup> Two important questions arise where the elimination/substitution ratio changes with solvent or leaving group: (a) is there a change in the rate-limiting step(s) in the solvolytic scheme and (b) what is the identity of the species acting as a base in the elimination process?<sup>2,3</sup> Several examples in the literature clearly point to formation of elimination products from intimate ion-pair or from solvent separated ion-pair intermediates.<sup>4</sup> However, the identity of the species that abstracts the

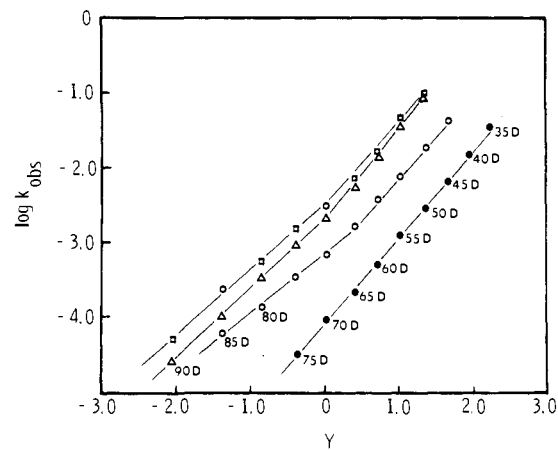
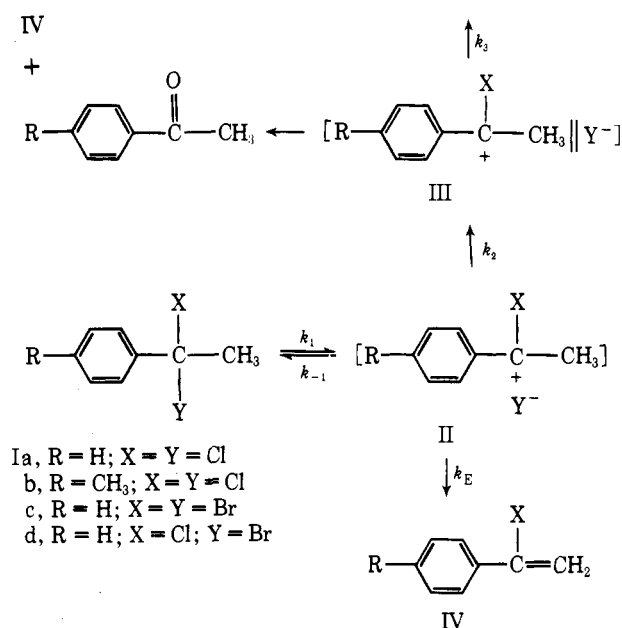


Figure 1. First-order rate constants for solvolysis of 1,1-dihaloethylbenzenes determined spectrophotometrically by monitoring the appearance of acetophenone at 241 nm or *p*-methylacetophenone at 249 nm at 25 °C as a function of solvent polarity,  $Y$ .<sup>6b</sup> Solvent composition is given in volume percent dioxane, e.g., 80D = 80 mL of dioxane + 20 mL of water: filled circles ( $\text{PhC}(\text{Cl})_2\text{CH}_3$ ),  $m = 1.18 (\pm 0.02)$ ; open circles ( $\text{PhC}(\text{Br})_2\text{CH}_3$ ),  $m = 1.12 (\pm 0.01)$  (solvent, 45D-60D) and  $m = 0.58 (\pm 0.08)$  (60D-85D); filled squares ( $\text{PhC}(\text{Cl,Br})\text{CH}_3$ ),  $m = 1.24 (\pm 0.09)$  (50D-65D) and  $m = 0.87 (\pm 0.02)$  (65D-90D); triangles (*p*- $\text{CH}_3\text{C}_6\text{H}_4\text{C}(\text{Cl})_2\text{CH}_3$ ),  $m = 1.26 (\pm 0.07)$  (50D-65D) and  $m = 0.95 (\pm 0.07)$  (65D-90D).

#### Scheme I

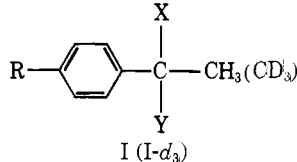


proton from the carbonium ion in an ion-pair intermediate is a more subtle problem.

As part of our continuing study of the solvolysis of benzal halides,<sup>5</sup> we have determined the  $\beta$ -D<sub>3</sub> isotope effects and product distributions in the solvolysis of 1,1-dihaloethylbenzenes in dioxane-water mixtures. This reaction yields two products as shown in Scheme I. In this communication, we propose that in the more polar solvents  $k_2$  is rate-limiting and in the less polar solvents  $k_E$  and  $k_2$  are similar in magnitude ( $k_{-1} \gg k_E$  and  $k_2$ ) and most or all of the elimination product is derived from the intimate ion pair (II). We also propose that elimination from II ( $k_E$ ) involves the counterion as base and that it is the relative stability of the tight ion pair, and hence the relative magnitudes of  $k_2$  and  $k_E$ , rather than the intrinsic basicity of the halide ion,  $Y^-$ , that decides the extent of elimination from II.

The observed  $\beta$ -D<sub>3</sub> kinetic isotope effects are reported in Table I for Ia and Ib in addition to the product distributions

Table I. Solvolysis of I ( $I-d_3$ ) in Aqueous Dioxane at 25 °C.  $\beta$ -D<sub>3</sub> Isotope Effects and Product Analysis Data<sup>a</sup>



I ( $I-d_3$ )

Dioxane, vol %	X = Y = Cl							
	R = H (Ia)			R = CH <sub>3</sub> (Ib)			R = H (% E - 1) <sup>H</sup>	
	(% E - 1) <sup>H</sup>	(% E - 1) <sup>D</sup>	$k_H/k_{\beta-D_3}$	(% E - 1) <sup>H</sup>	(% E - 1) <sup>D</sup>	$k_H/k_{\beta-D_3}$	X = Cl; Y = Br (Id)	X = Y = Br (Ic)
35	5.8	2.4	1.187					
40	6.9	2.9	1.185					
45	7.9	3.2	1.183 ( $\pm 0.009$ )					15.8
50	11.9	4.8	1.215 ( $\pm 0.006$ )	10.0	4.5	1.20	12.1	20.0
55	13.6	4.8	1.242 ( $\pm 0.004$ )	10.4	4.2	1.20	16.5	26.1
60	15.6	5.9	1.261 ( $\pm 0.006$ )	12.8	5.2	1.206 ( $\pm 0.006$ )	19.8	31.2
65 <sup>b</sup>	19.8	7.6	1.285 ( $\pm 0.006$ )	17.7	7.5	1.207 ( $\pm 0.007$ )	25.3	38.0
70	24.6	9.2	1.336 ( $\pm 0.005$ )	21.8	7.7	1.234 ( $\pm 0.008$ )	34.3	45.0
75	33.4	15.2	1.375 ( $\pm 0.007$ )	27.7	11.3	1.292 ( $\pm 0.008$ )	45.0	55.7
80 <sup>c</sup>	38.0	19.8		34.6	16.6	1.364 ( $\pm 0.007$ )	51.4	62.2
85				43.0	22.3	1.458 ( $\pm 0.008$ )	62.4	69.9
95				51.5	34.5	1.640 ( $\pm 0.046$ )	71.5	
97% TFE- 3% H <sub>2</sub> O (by wt)	12.1	7.0	1.234				17.1	39.0

<sup>a</sup>Product analysis was done using a Varian Aerograph Model 2400 with flame ionization detector; (% E - 1)<sup>H</sup> and (% E - 1)<sup>D</sup> refer to mole percent olefin in solvolysis of protio and deuterio compounds, respectively, and the remainder in each case being an acetophenone. The precision in product analysis data is  $\pm 1.0\%$ . <sup>b</sup>The  $\beta$ -D<sub>3</sub> isotope effects for PhC(Cl)<sub>2</sub>CH<sub>3</sub>/CD<sub>3</sub> in 65% aqueous dioxane containing Et<sub>3</sub>N are as follows: 0.05 M, 1.279; 0.10 M, 1.291. <sup>c</sup>Percent eliminations from PhC(Cl)<sub>2</sub>CH<sub>3</sub>/CD<sub>3</sub> in 80% aqueous dioxane with Et<sub>3</sub>N are as follows: 0.02 M, (% E - 1)<sup>H</sup>, 36.7, and (% E - 1)<sup>D</sup>, 17.5; 0.10 M, (% E - 1)<sup>H</sup>, 40.7, and (% E - 1)<sup>D</sup>, 21.2.

for all four substrates (Ia-Id). The solvolytic reaction is seen to have no bimolecular component as added Et<sub>3</sub>N does not alter the rate,  $\beta$ -D isotope effect, or product ratios (Table I). Solvolysis in 97% TFE-H<sub>2</sub>O gives results that are similar to those in 55% aqueous dioxane indicating that the nucleophilicity of the solvent does not alter the outcome of product-forming steps. In other words, it is the counterion, Y<sup>-</sup>, that abstracts a proton from II to form the elimination product IV.

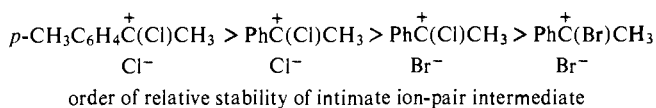
The slight but significant increase in the amount of elimination from Ic in going from 55% D to 97% TFE probably reflects the change in the internal structure of the carbonium ion in Ic compared with Ia and Id. The lower stability of the carbonium ion from Ic would tend to favor elimination ( $k_E$ ) over dissociation ( $k_2$ ) in the less polar solvent TFE.

In more polar solvents, the isotope effect is constant (1.20) for both Ia and Ib, and the amount of elimination levels off at  $\sim 10$ -15% for all four compounds. This observed isotope effect of 1.20 is strikingly similar to that reported by Shiner et al.<sup>1</sup> for the ethanolysis of 1-phenylethyl chloride at 25 °C, where  $k_2$  is rate limiting. That the transition state has significant carbonium ion character (in the more polar solvents) is seen from the large  $m$  values for Ia-Id (Figure 1).<sup>6</sup> The nonpolar nature of the solvents relative to water and the absence of any induced common ion rate depression and the "special salt effect" suggest strong evidence that in the more polar solvents the formation of solvent separated ion pair is rate limiting. If the isotope effect on  $k_2$  is unity, the observed  $\beta$ -D<sub>3</sub> isotope effect becomes the isotope effect on the ionization equilibrium ( $K^H/K^D \approx 1.20$  where  $K = k_1/k_{-1}$ ), a value very similar to the one reported by Humski<sup>4b</sup> (1.22 for the ionization step in the solvolysis of 1,2-dimethyl-2-*exo*-norbornyl *p*-nitrobenzoate).

Increasing the dioxane content of the solvent mixture increases the amount of elimination as well as the  $\beta$ -D effect. The observed isotope effect is the product of primary and secondary  $\beta$ -D<sub>3</sub> effects. The primary isotope effect obtained from the

product ratio ( $(\% E^H/\% S^H) \times (\% S^D/\% E^D)$ ) is  $2.78 \pm 0.28$  and  $2.67 \pm 0.37$  for Ia and Ib, respectively. For compound Ia, addition of LiClO<sub>4</sub> in the range of 0.02-0.16 M in 75% aqueous dioxane results in only a 2.2-fold increase in observed rate and added LiCl in the presence of 0.05 M LiClO<sub>4</sub> in the same solvent does not decrease the rate. For compound Ib, the rate increase in 85% aqueous dioxane upon addition of LiClO<sub>4</sub> in the range of 0.02-0.20 M is  $\sim 4.0$ -fold. These salt effects indicate that return from solvent separated ion pair is negligible in this system; that is the ionization equilibrium is fast compared with the product-forming step(s).<sup>7</sup> We conclude that most or all of the elimination product is derived from II and that the substitution product results from collapse of III with the solvent. Reduced  $m$  values in the range 0.58-0.95 (Figure 1) in this solvent range are also consistent with  $k_E$  and  $k_2$  being competitively rate limiting in the less polar solvents and point to reduced carbonium ion character in the transition state. This is understandable in terms of incipient C=C bond formation in the  $k_E$  step; however, the observed  $\beta$ -D isotope effect increases because of the primary effect on this step.

Hydrolysis of 2,2-dihalopropanes in H<sub>2</sub>O at 25 °C yields almost exclusively elimination product (2-halopropene).<sup>8</sup> Absence of any significant quantity of acetone in the products reflects the tendency of the intimate ion-pair intermediate to undergo elimination in preference to substitution, presumably with the halide ion acting as base. Substitution of a methyl group by phenyl is expected to enhance the stability of the carbonium ion intermediate(s) and to allow the formation of solvent separated ion pair ( $k_2$ ) to be more competitive with elimination from II ( $k_E$ ). We infer that the observed extent of elimination depends on the relative stability of the carbonium ion in the intimate ion-pair intermediate rather than the basicity of the counterion, thus



It is interesting to note that in the solvolysis of *t*-BuX (where X = Cl, Br, and I) the percent elimination follows the order  $\text{Cl}^- > \text{Br}^- > \text{I}^-$ , the reverse of what we observe (compound Ia gives less elimination product than compound Id in the same solvent, Table I).<sup>4d</sup> For our system, if the extent of elimination depends on the relative magnitude of  $k_2$  and  $k_E$  rather than the intrinsic basicity of the halide ion as we assume, it is easy to see that the ion pair with bromide counterion will give more olefin than the one with chloride counterion since the more concentrated charge on  $\text{Cl}^-$  will stabilize the ion pair more effectively.

Addition of HCl to styrene in glacial acetic acid has been shown to proceed through the rate-limiting protonation of the C=C bond followed by fast combination of  $\text{Cl}^-$  ion with the carbonium ion in the tight ion-pair intermediate.<sup>9</sup> Although similar examples of addition of HX to C=C in nonpolar solvents are scarce in the literature,<sup>10</sup> the mechanism proposed for the styrene-HCl system strongly suggests that our proposal that  $k_E$  is partly rate limiting in the less polar aqueous dioxane solvents is essentially correct.

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## References and Notes

- (1) V. J. Shiner, Jr., in "Isotope Effects in Chemical Reactions", C. J. Collins and N. S. Bowman, Ed., Van Nostrand-Reinhold, Princeton, N.J., 1970, pp 90-159 and references cited therein.
- (2) A. Fry, *Chem. Soc. Rev.*, **1**, 167-180 (1972).
- (3) W. H. Saunders, Jr., and A. F. Cockerill, "Mechanisms of Elimination Reactions", Wiley, New York, N.Y., 1973.
- (4) (a) V. J. Shiner, Jr., W. Dowd, R. D. Fisher, S. R. Hartshorn, M. A. Kessick, L. Milakofsky, and M. W. Rapp, *J. Am. Chem. Soc.*, **91**, 4838 (1969); (b) K. Humski, *Croatica Chem. Acta*, **42**, 501 (1970); (c) S. G. Smith and J. W. Goon, *J. Org. Chem.*, **34**, 3127 (1969); (d) V. J. Shiner, Jr., V. Sendjarevic, and K. Humski, *J. Am. Chem. Soc.*, **95**, 7722 (1973); (e) S. Winstein and M. Covicvera, *ibid.*, **85**, 1702 (1963).
- (5) (a) V. P. Vitullo and N. R. Grossman, *J. Org. Chem.*, **38**, 179 (1973); (b) V. P. Vitullo and F. P. Wilgis, *J. Am. Chem. Soc.*, **97**, 458, 5616 (1975).
- (6) (a) S. R. Hartshorn, "Aliphatic Nucleophilic Substitution", Cambridge University Press, New York, N.Y., 1973, pp 93, 94; (b) J. E. Leffler and E. Grunwald in "Rates and Equilibria of Organic Reactions", Wiley, New York, N.Y., 1963, pp 288-293.
- (7) The possibility that the absence of a special salt effect in this system is due to inefficient trapping of an intermediate has not been ruled out.
- (8) A. Queen and R. E. Robertson, *J. Am. Chem. Soc.*, **88**, 1363 (1966).
- (9) R. C. Fahey and C. A. McPherson, *J. Am. Chem. Soc.*, **91**, 3865 (1969).
- (10) R. C. Fahey, *Top. Stereochem.*, **3**, 237 (1968).

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## New Geometric Isomers of Vitamin A and Carotenoids.

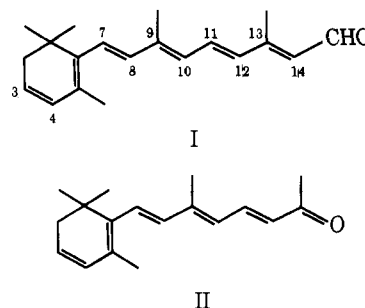
### 5. 7-*cis*-3-Dehydroretinal and 7-*cis*-3-Dehydro C<sub>18</sub> Ketone from Direct Irradiation of the Trans Isomers in Polar Solvents<sup>1</sup>

Sir:

In an earlier paper we reported results of photoisomerization of retinal in the aprotic polar solvent acetonitrile giving directly all the mono-*cis* isomers including the hindered 11-*cis* and 7-*cis*.<sup>1</sup> The latter isomers are not formed in nonpolar solvents.<sup>2</sup> The results in polar solvents appear to be consistent with the zwitterionic character of the excited singlet state of polyenes as suggested by recent calculations.<sup>3</sup>

Although all four mono-*cis* isomers are formed from irradiation of the all-*trans* isomer of retinal, there appears to be some selectivity preferring formation of the isomer (11-*cis*) from isomerization near the central most double bond.<sup>4</sup> It

occurred to us that this preference may be more profitably used in the 3-dehydrovitamin A series (vitamin A<sub>2</sub>) for preparation of the unknown 7-*cis* isomers,<sup>5</sup> where the 7,8 bond is closer to the central most position in the polyene chain. In this paper we describe results on dehydroretinal (I) and the corresponding C<sub>18</sub> ketone (II).<sup>6</sup>



Electronically II is similar to retinal in that it is a pentaene conjugated with a carbonyl group. However, it has the obvious advantage of having one fewer exocyclic double bond, thus reducing the number of possible geometric isomers to eight. Also, the 7,8 and the 9,10 bonds are now the central most double bonds. Therefore we first studied this system.

When a sample of the all-*trans* isomer of II<sup>7</sup> in acetonitrile was irradiated with light of 360 nm,<sup>8</sup> the appearance of two closely spaced new major peaks in the HPLC chromatogram<sup>9</sup> was immediately detected.<sup>10</sup> The retention time of the first peak was identical with that of 9-*cis*-II. Initially the two peaks (detecting beam 380 nm, not corrected for different molar absorptivities at this wavelength) were of approximately equal magnitude. The two isomers were isolated by preparative HPLC. The <sup>1</sup>H NMR of the minor product was clearly that of 9-*cis*-II and that of the major only consistent with 7-*cis*-II. (Data listed in Table I; see below for a discussion of the <sup>1</sup>H NMR signals characteristic of the geometry). Consistent with the expected blue shift of the UV absorption maximum of the hindered 7-*cis* that we found when irradiating with light >410 nm (Corning 3-74 filter plates) the amount of the 7-*cis* isomer reached 60% of the total isomer composition. Although the ratio of isomers did not seem to vary to a great extent when other polar solvents were used (acetone and methanol), formation of the 7-*cis* isomer was not favored in nonpolar solvents (in hexane 4:1 in favor of the 9-*cis* isomer).

The 7-*cis* C<sub>18</sub> ketone II is an obvious precursor to the 7-*cis* isomers of vitamin A<sub>2</sub>. Unfortunately we found this compound surprisingly unreactive toward the C<sub>2</sub> phosphonate III in the Horner reaction. No reaction was detected when an irradiated mixture of II and the C<sub>2</sub> phosphonate was stirred in THF with lithium diisopropyl amide at room temperature for 5 h. At 55 °C the Horner reaction proceeded at a moderate rate. However, although 7-*cis*-II appeared stable at this temperature, the resultant condensation products apparently were not. Thus, we found the eventual retinal mixture obtained after treating the retinoate mixture consecutively with LiAlH<sub>4</sub> and MnO<sub>2</sub> containing little of the 7-*cis* isomer<sup>11</sup> (by the absence of a strong high field CH<sub>3</sub>-5 peak in the <sup>1</sup>H NMR spectrum<sup>12</sup> and by comparison of 1c retention time with authentic 7-*cis*-I; see below). Preparative 1c yielded only the all-*trans*, 9-*cis*, and 13-*cis* isomers of dehydroretinal (assignment based on their <sup>1</sup>H NMR spectra, data in Table I)<sup>13</sup> and another minor deconjugated aldehyde with its <sup>1</sup>H NMR spectrum consistent with the cyclized structure IV. Therefore 7-*cis*-retinoate obtained from the Horner reaction must have undergone 6e electrocyclicization<sup>14</sup> and/or geometric isomerization at 55 °C.

We next turned to direct irradiation of dehydroretinal I. When a mixture of 13-*cis* and all-*trans* isomers of the aldehyde was irradiated in acetonitrile first with light >380 nm (Corning