

myrcene and methyl vinyl ketone (**6**) (two possible isomers).<sup>13</sup> These isomers were first converted to the corresponding conjugated dienone **7** and its isomer. **7** could be purified by simple SiO<sub>2</sub> chromatography. **7** was converted with concentrated sulfuric acid into the locked  $\beta$ -ionone **8** in 91% yield.<sup>14</sup> **8** was converted into retinal **2** via the same four-step sequence as discussed for **1**. Both **1** and **2** were isolated in pure form by HPLC.<sup>15</sup>

In Table I the electronic data of retinals **1** and **2** and their PSB's are given. Retinal **1** reacts very rapidly with bO to form a bR analogue with  $\lambda_{\max}$  564 nm. It shows light-dark adaptation and has a proton pump efficiency of 90%.<sup>16</sup> To study the binding of **1** with bO more carefully, this reaction was carried out at 2 °C (Figure 1). First a 430-460-nm complex with vibrational fine structure is formed just as has been observed for retinal,<sup>17</sup> 5-demethylretinal,<sup>18</sup> and 7,8-dehydroretinal<sup>19</sup> and then the complex was fully converted to bR (**1**). This process is very similar to that of native bR. The rate of bR (**1**) formation is only 50% lower than that of bR.

The reaction of **2** with bO is much more complicated. An equimolar amount of **2** leads slowly to a pigment with  $\lambda_{\max}$  509 nm, close to  $\lambda_{\max}$  of PSB (**2**). The spectrum shows a shoulder at 596 nm. Adding **2** in a very small amount, waiting for the binding to be complete, and adding further small amounts in similar fashion until the equimolar amount is reached lead to a two pigment mixture ( $\lambda_{\max}$  509 and 596 nm) in a 2:3 ratio. Similar complex behavior has been observed for 4-*n*-butyl- and 4-(dimethylamino)retinal.<sup>20</sup> We think that the  $\lambda_{\max}$  596 nm form is the fully regenerated bR (**2**) analogue, which shows a 3800 cm<sup>-1</sup> opsin shift, whereas  $\lambda_{\max}$  509 nm form has a slightly larger  $\lambda_{\max}$  value than the PSB. The pigment mixture does not show light-dark adaptation and has a 20% proton pump efficiency. These bioorganic studies indicate that a native bR structure can only be formed with the 6-*s-trans* conformer of retinal, in strong support of recent solid-state NMR studies.<sup>5</sup> Now that they are available, retinals **1** and **2** should be very important to establish the 6-7 conformation in rhodopsin and halorhodopsin.

Comparing the  $\lambda_{\max}$  values of **1** (400 nm) and its PSB (465 nm) with those of retinal (380 and 440 nm, respectively) shows that twisted 6-*s-cis*  $\rightarrow$  planar 6-*s-trans* isomerization results in a 1200-1300-cm<sup>-1</sup> red-shift in the  $\lambda_{\max}$  value. In the planar **1** and its derivatives, the 5-6 double bond is in full conjugation with the polyene chain; this is reflected in the larger  $\lambda_{\max}$  value compared to retinal and its derivatives which are 40° twisted 6-*s-cis* conformers. In **2** the planar 6-7 bond is locked in the *s-cis* conformation giving rise to the expected 20-nm red-shift from the locked *s-trans* derivative.<sup>21</sup>

These data can now be used to understand the 5100-cm<sup>-1</sup> opsin shift in bR.<sup>22</sup> Part of this shift, 1200 cm<sup>-1</sup>, arises because the chromophore changes upon binding to the protein from a 40° twisted 6-*s-cis* conformation to a planar 6-*s-trans* conformation. For a retinal derivative that has a locked C6-C7 conformation, the observed opsin shift should be  $\sim$ 3800 cm<sup>-1</sup> because no protein-induced change of the C6-C7 conformation is allowed, and that is what is observed for bR (**1**) and bR (**2**). Once the six-membered ring is fixed it does not contribute significantly to the opsin shift. This is consistent with the idea that the opsin shift is mainly due to the perturbation of the Schiff base region and this is in agreement with solid-state <sup>15</sup>N NMR<sup>23</sup> and retinal analogue<sup>6,7</sup> evidence that show that there is a weakened interaction of the Schiff base with the counterion in the protein.

**Acknowledgment.** We thank Dr. R. L. van der Bend and Prof. K. van Dam (University of Amsterdam) for the preparation of the phospholipid vesicles and for using their facilities to measure the proton pump action.

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### Application of the Savage-Wood Treatment to the Quantitative Analysis of Kinetic Solvent Effects in Highly Aqueous Binary Solutions

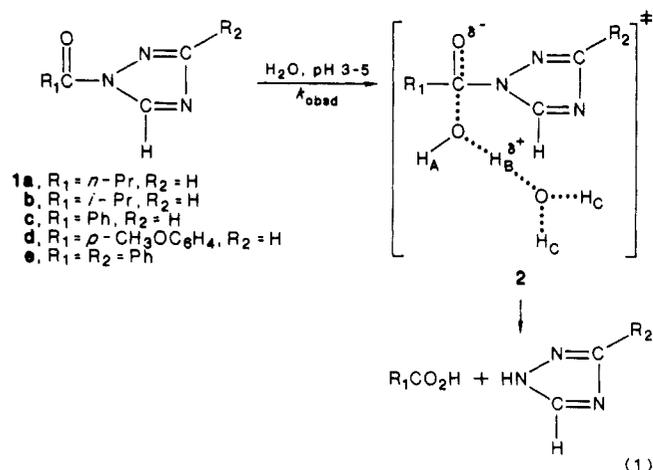
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The interpretation of kinetic solvent effects on organic reactions in water-rich binary mixtures is notoriously difficult.<sup>2</sup> Herein we wish to present an attempt to analyze these medium effects quantitatively, using an extension of the Savage-Wood treatment of solute-solute interactions.<sup>3</sup> To this end, we have measured pseudo-first-order rate constants for the water-catalyzed hydrolysis of 1-acyl-1,2,4-triazoles (**1a-e**) in highly aqueous alcohol-water and 1,4-dioxane-water mixtures (eq 1). The reaction mechanism



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(15) Analytical data: exact mass calcd for **1** (C<sub>21</sub>H<sub>28</sub>O) 296.4516, found 296.4522. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) of *all-trans-1*:  $\delta$  0.95 (1-CH<sub>3</sub>, s), 1.80 (5-CH<sub>3</sub>, s), 2.10 (9-CH<sub>3</sub>, s), 2.34 (13-CH<sub>3</sub>, s), 5.98 (H14, d, *J* = 8 Hz), 6.41 (H12, d, *J* = 15 Hz), 6.42 (H10, d, *J* = 11 Hz), 6.77 (H7, s), 7.20 (H11, dd, *J* = 15, 11 Hz), 10.11 (H15, d, *J* = 8 Hz). <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>) of *all-trans-1*:  $\delta$  13.2 (C19), 14.3 (C20), 18.5 (C3), 18.9 (C18), 23.0 (C16a), 23.3 (C17), 33.3 (C4), 33.8 (C1), 37.3 (C16), 37.7 (C2), 124.2 (C14), 124.4 (C10), 128.7 (C7), 132.2 (C5), 133.3 (C11), 134.3 (C8), 134.4 (C12), 135.1 (C6), 142.6 (C9), 155.0 (C13), 191.1 (C15). Exact mass calcd for **2** (C<sub>21</sub>H<sub>28</sub>O) 296.4516, found 296.4518. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) of *all-trans-2*:  $\delta$  1.04 (1,1'-CH<sub>3</sub>, s), 2.09 (9-CH<sub>3</sub>, s), 2.34 (13-CH<sub>3</sub>, s), 5.97 (H14, d, *J* = 8 Hz), 6.34 (H7, s), 6.38 (H12, d, *J* = 15 Hz), 6.39 (H10, d, *J* = 11 Hz), 7.20 (H11, dd, *J* = 15, 11 Hz), 10.10 (H15, d, *J* = 8 Hz). <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>) of *all-trans-2*:  $\delta$  13.2 (C19), 14.2 (C20), 19.3 (C3), 23.8 (C18a), 28.6 (C16/C17), 29.5 (C18), 31.1 (C4), 32.6 (C1), 39.1 (C2), 123.9 (C14), 124.3 (C10), 128.7 (C7), 132.6 (C5), 133.4 (C11), 134.1 (C12), 135.0 (C8), 135.3 (C6), 141.9 (C9), 155.1 (C13), 191.1 (C15).

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**Table I.** Pseudo-First-Order Rate Constants<sup>a</sup> for the Neutral Hydrolysis of **1a–e** in Water and in *t*-BuOH–H<sub>2</sub>O ( $m_A = 1.72$  mol·kg<sup>-1</sup>) at 25 °C

compd	$k_{\text{obsd}} \times 10^4, \text{s}^{-1}$		rate retardation, %
	H <sub>2</sub> O	<i>t</i> -BuOH–H <sub>2</sub> O	
<b>1a</b>	17.4	10.4	59.8
<b>1b</b>	33.4	20.0	59.9
<b>1c</b>	20.9	13.7	65.6
<b>1d</b>	38.9	22.3	57.3
<b>1e</b>	12.4	7.22	58.2

<sup>a</sup> Estimated error  $\pm 2\%$ .

involves rate-determining water-catalyzed nucleophilic attack of water at the carbonyl group.<sup>4,5</sup> If  $k_{\text{obsd}}$  is the rate constant for hydrolysis in water-rich alcohol–water (molality of alcohol,  $m_A$ ) and  $k_{\text{obsd}}^0$  the rate constant for hydrolysis in water ( $m_A = 0$ ), then

$$\ln(k_{\text{obsd}}/k_{\text{obsd}}^0) = \ln \gamma_S - \ln \gamma_{\ddagger} - n\phi m_A M_1 \quad (2)$$

where  $\gamma_S$  and  $\gamma_{\ddagger}$  are the activity coefficients of the 1-acyl-1,2,4-triazole (S) and transition state ( $\ddagger$ ), respectively,  $n$  is the molecularity of the hydrolysis reaction with respect to water ( $n = 2$  for **2**),  $\phi$  is the practical osmotic coefficient for the solution, and  $M_1$  is the molar mass of water.<sup>6</sup> In the binary mixture  $\gamma_S$  is related<sup>7,8</sup> to the Gibbs function substrate–alcohol pairwise interaction parameters  $g_{AS}$  and  $g_{SS}$  via

$$RT \ln \gamma_S = 2g_{AS}m_A/(m^0)^2 + 2g_{SS}m_S/(m^0)^2 \quad (3)$$

where  $m_S$  is the molality of the substrate and  $m^0 = 1$  mol·kg<sup>-1</sup>. A similar equation holds for  $\gamma_{\ddagger}$ . For solutions with  $m_A \gg m_S$  and  $m_A \gg m_{\ddagger}$ ,

$$\ln(k_{\text{obsd}}/k_{\text{obsd}}^0) = (2/RT)(1/m^0)^2(g_{AS} - g_{A\ddagger})m_A - n\phi m_A M_1 \quad (4)$$

Following the Savage–Wood treatment and accepting the “additivity principle”,<sup>3</sup> the pairwise interaction parameter  $g_{AS}$  is determined by the number of functional groups  $i$  ( $n_{i(A)}$ ) and  $j$  ( $n_{j(S)}$ ) in the alcohol (A) and 1-acyl-1,2,4-triazole (S), respectively, and by the pairwise group interaction parameters  $G_{i \rightarrow j}$  for the groups  $i$  and  $j$ . Hence

$$g_{AS} = \sum_{ij} n_{i(A)} n_{j(S)} G_{i \rightarrow j} - M_1 RT/2 \quad (5)$$

By analogy, a similar equation can be derived for  $g_{A\ddagger}$ . We assume that during the activation process (eq 1) the solvation of the groups  $R_1$  and  $\text{Tr}-R_2$  ( $\text{Tr} = 1,2,4\text{-triazolyl}$ ) does not change substantially. Thus, group interaction parameters involving these groups and alcohol cancel in the term  $(g_{AS} - g_{A\ddagger})$ , cf. eq 4. The data in Table I<sup>9</sup> support this assumption. Despite considerable variation in the structure of  $R_1$  and  $\text{Tr}-R_2$  the relative retardations in *t*-BuOH–H<sub>2</sub>O ( $m_A = 1.72$  mol·kg<sup>-1</sup>) are almost identical. Proton inventories<sup>4a,10</sup> have shown that in the transition state (**2**) three protons are in flight, which is consistent with  $n = 2$ . We submit that the solvation changes during the activation process are predominantly determined by interactions involving three polarized OH groups ( $\text{OH}_A$ ,  $2 \text{OH}_C$ ), and in a first approximation, the polarization of the carbonyl group in **2** is neglected. Thus,

$$g_{AS} - g_{A\ddagger} = -3G_{\text{OH} \leftrightarrow \text{OH}} - 3G_{\text{R} \leftrightarrow \text{OH}} \quad (6)$$

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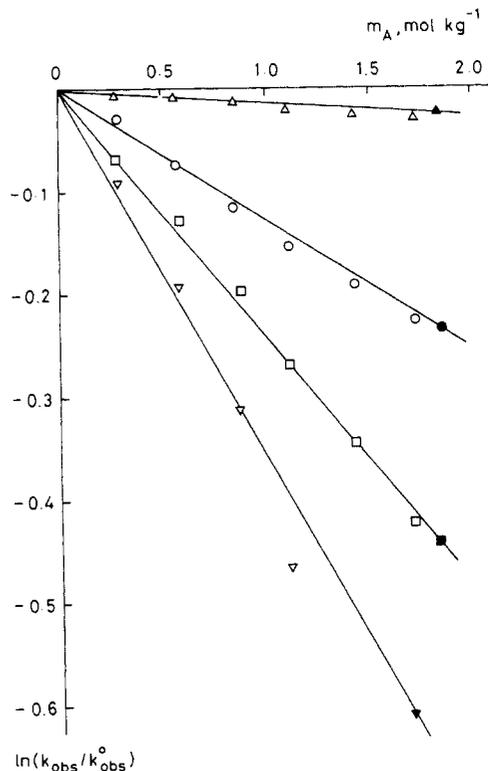
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**Table II.** Experimental and Calculated Slopes of Plots of  $\ln(k_{\text{obsd}}/k_{\text{obsd}}^0)$  vs. Molality of Cosolvent for the Neutral Hydrolysis of **1e** at 25 °C

medium	SL <sub>exp</sub>	SL <sub>calcd</sub>	SL* <sub>calcd</sub> <sup>a</sup>
MeOH–H <sub>2</sub> O	-0.0139	-0.0856	-0.0122
EtOH–H <sub>2</sub> O	-0.133	-0.156	-0.127
<i>n</i> -PrOH–H <sub>2</sub> O	-0.244	-0.226	-0.242
<i>n</i> -BuOH–H <sub>2</sub> O	-0.378 <sup>b</sup>	-0.296	-0.357
1,4-dioxane–H <sub>2</sub> O	-0.348		-0.348

<sup>a</sup> Calculated using adjusted pairwise group interaction parameters, see text. <sup>b</sup> Slope based on data points in the region  $m_A = 0\text{--}0.84$  mol·kg<sup>-1</sup>.



**Figure 1.** Plots of  $\ln(k_{\text{obsd}}/k_{\text{obsd}}^0)$  vs. molality of alcohol for the neutral hydrolysis of **1e** at 25 °C. Experimental data: ( $\Delta$ ) MeOH; ( $\circ$ ) EtOH; ( $\square$ ) *n*-PrOH; ( $\nabla$ ) *n*-BuOH. Closed points: calculated values using adjusted pairwise group interaction parameters (see text).

where the alcoholic cosolvent is designated by ROH. Substitution of eq 6 in eq 4 yields

$$\ln(k_{\text{obsd}}/k_{\text{obsd}}^0) = (2/RT)(1/m^0)^2(-3G_{\text{OH} \leftrightarrow \text{OH}} - 3G_{\text{R} \leftrightarrow \text{OH}})m_A - 2\phi m_A M_1 \quad (7)$$

Using  $\phi = 1$  for water-rich<sup>11,12</sup> ROH–H<sub>2</sub>O and assuming that one methyl can be represented by 1.5 methylene groups,<sup>13</sup> it is now possible to calculate the slopes (SL) of linear plots of  $\ln(k_{\text{obsd}}/k_{\text{obsd}}^0)$  vs.  $m_A$  by using pairwise group interaction parameters (e.g.,  $G_{\text{OH} \leftrightarrow \text{OH}} = -23$  J·kg·mol<sup>-2</sup> and  $G_{\text{CH}_2 \leftrightarrow \text{OH}} = +29$  J·kg·mol<sup>-2</sup>) taken from a recent compilation reported by Wood et al.<sup>14</sup> Table II compares experimental<sup>15</sup> and calculated values of the slopes for neutral hydrolysis of **1e** in a series of ROH–H<sub>2</sub>O mixtures at 25 °C. The trends are encouraging, but better agreement is obtained

(11) We restrict our analysis to those water-rich binary aqueous solutions in which aggregation of the cosolvent is not a serious complicating factor. Compare: Haak, J. R.; Engberts, J. B. F. N. *J. Am. Chem. Soc.* **1986**, 108, 1705.

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(15) Nearly equal solvent effects are found in *n*-BuOH–H<sub>2</sub>O and *t*-BuOH–H<sub>2</sub>O. The clear tendency toward nonlinearity at high molalities of the C-4 alcohols is most likely the result of either the onset of aggregation<sup>11</sup> or the enhanced importance of triplet interactions<sup>14</sup> for the more hydrophobic alcohols.

when the pairwise group interaction parameters are adjusted to allow for the considerable polarization and increased hydrogen bonding of the water molecules in the transition state. Satisfactory slopes ( $SL_{\text{calcd}}^*$ )<sup>16</sup> are obtained by using  $G_{\text{CH}_2 \rightarrow \text{OH}} = +47.5 \text{ J}\cdot\text{kg}\cdot\text{mol}^{-2}$  and  $G_{\text{OH} \rightarrow \text{OH}} = -81.1 \text{ J}\cdot\text{kg}\cdot\text{mol}^{-2}$  (Table II). The plots are shown in Figure 1.

As a check for the reasonableness of the present approach, rate constants for neutral hydrolysis of **1e** were determined in 1,4-dioxane (D)-water ( $m_D = 0-1.72 \text{ mol}\cdot\text{kg}^{-1}$ ) at 25 °C. Rate constants decrease with increasing molality of 1,4-dioxane and a straight line is obtained by plotting  $\ln(k_{\text{obsd}}/k_{\text{obsd}}^0)$  vs.  $m_D$ . Correlation of the data in terms of eq 4 with  $n = 2$  and employing the adjusted  $G_{\text{CH}_2 \rightarrow \text{OH}}$  leads to  $G_{\text{O} \rightarrow \text{OH}} = -30.6 \text{ J}\cdot\text{kg}\cdot\text{mol}^{-2}$ . Comparison of this value with that taken from the literature ( $G_{\text{O} \rightarrow \text{OH}} = -23 \text{ J}\cdot\text{kg}\cdot\text{mol}^{-2}$ )<sup>14</sup> shows satisfactory agreement, the augmentation will again reflect the polarization of the waters in the transition state.

In summary, the treatment based on practical pairwise group interaction parameters accounts for the general pattern of rate constants as a function of the nature and molality of the cosolvent. Further applications to other aqueous binaries as well as other reactions are under active investigation and will be given in the full paper. At this stage we conclude that the present results signal a novel and important quantitative procedure for drawing together kinetic and thermodynamic data for organic reactions in highly aqueous reaction media.

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**Supplementary Material Available:** Table III showing pseudo-first-order rate constants for the neutral hydrolysis of **1e** as a function of the molality of cosolvent in the ROH-H<sub>2</sub>O and 1,4-dioxane-H<sub>2</sub>O mixtures (2 pages). Ordering information is given on any current masthead page.

(16) The increments in the experimental slopes ( $SL_{\text{exp}}$ ) going from the C-1 alcohol to the C-4 alcohol are of the same magnitude. This is consistent with the stepwise addition of one  $G_{\text{CH}_2 \rightarrow \text{OH}}$  parameter in eq 4 and allows the calculation of the adjusted value of this parameter.

## Reactions of H Atoms Produced by Microwave Discharge with Olefins in Acetone and Toluene

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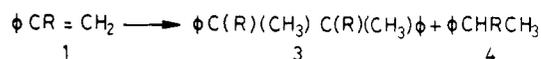
Previous results from this laboratory have shown that microwave discharge is a convenient and effective source of oxygen atoms for organic synthesis, in condensed phases.<sup>1</sup> Now we report that this source also provides an excellent means of generating hydrogen atoms for the same purpose.

The reaction of H atoms with organic substrates in both liquid<sup>2</sup> and gas phase,<sup>3</sup> have been extensively studied. H atoms were

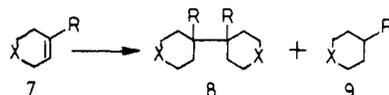
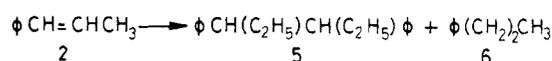
generated for this purpose mainly by electric discharge of H<sub>2</sub>, radiolysis of water and organic liquids,<sup>2d,3</sup> and photolysis of thiols<sup>2b,3</sup> and *tert*-butyl peroxyformate.<sup>2c</sup> In the gas phase, reactions of H atoms generally result in the vibrationally excited radicals which lead to extensive fragmentations.<sup>3</sup> However, in the liquid phase, the atoms were found to be less reactive.<sup>2</sup>

The reactions of H atoms with olefins were performed in a flow system at 2 torr, the H atoms being generated by microwave discharge (2540-MHz, 60-W output) of a mixture of H<sub>2</sub> and He (1:50). The discharged gases were passed over a neat liquid or a solution of the substrate.<sup>4</sup> Since acetone was found to be inert toward H atoms, we have used it as a solvent in these reactions.<sup>5</sup>

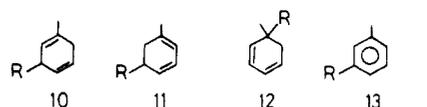
Phenyl and alkylethylenes **2** and **7** were converted almost quantitatively into the respective dimers **3**, **5**, and **8**<sup>6,7</sup> and hydrogenated products **4**, **6**, and **9**. No products of radical inter-



- a R = H  
b R = CH<sub>3</sub>  
c R = φ



- R X  
a φ CH<sub>2</sub>  
b H CH<sub>2</sub>  
c H (CH<sub>2</sub>)<sub>3</sub>  
d H CH<sub>2</sub>CH = CH  
e Me CH<sub>2</sub>



- a R = C(CH<sub>3</sub>)<sub>2</sub> φ  c R =
- b R = C<sub>6</sub>H<sub>11</sub>  d R =

(3) References for these investigations are summarized in ref 2a and also by: Cvetanovic, R. J. *Adv. Photochem.* **1963**, *1*, 115. Wagner, H. G.; Wolfrum, J. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 604. Jones, W. E.; MacKnight, S. D.; Teng, L. *Chem. Rev.* **1975**, *73*, 407. See also references cited therein. Yang, K. *J. Am. Chem. Soc.* **1962**, *84*, 3795. Benson, S. W.; Shaw, R. *J. Chem. Phys.* **1967**, *47*, 4052; *J. Am. Chem. Soc.* **1967**, *89*, 5351. Lambert, R. M.; Christie, M. I.; Linett, J. W. *J. Chem. Soc. D* **1967**, 388. McKnight, S. D.; Niki, H.; Weinstock, B. *J. Chem. Phys.* **1967**, *47*, 1962. Daby, E. E.; Niki, H.; Weinstock, B. *J. Phys. Chem.* **1971**, *75*, 1601. Cowfer, J. A.; Keil, D. G.; Michael, J. V.; Yeh, C. *J. Phys. Chem.* **1971**, *75*, 1584. Suhr, H., unpublished results. Künzel, K. M.Sc. Thesis, Ebhardt Karl University, Tübingen, 1973.

(4) The experimental techniques were similar to those used previously in the reactions with O(<sup>3</sup>P), ref 1.

(5) The relative inertness of H atoms toward acetone is in accord with the rate constants found previously for the reactions of H atoms generated by radiolysis of water with organic substrates, cf. ref 2d.

(6) The reaction products were analyzed by GC-MS and separated by column chromatography on silica gel. The known compounds were identified by comparison with authentic samples, while the structures of the new compounds were established by MS and NMR.

(7) **3a**, found, *meso/dl* = 1.16. **5**, found, *meso/dl* = 1.20; lit.: Gibian, M. J.; Covely, R. C. *J. Am. Chem. Soc.* **1972**, *94*, 4178. Gouverneur, P. J. L.; Mukinayi Mulangala, J. *Bull. Soc. Chim. Belg.* **1977**, *86*, 699. Green, F. D.; Berwick, M. A.; Stowell, J. C. *J. Am. Chem. Soc.* **1970**, *92*, 867. **8a**, lit.: Beckmans, H. D.; Schloch, J.; Rückhardt, C. *Chem. Ber.* **1967**, *100*, 1369. **8d**, found, *meso/dl* = 1.0; MS, *m/e* (relative intensity) 67 (100%), 55 (46), 79 (46), 94 (25), 135 (16), 162 (12), 190 (8), 218 (M<sup>+</sup> 1); <sup>1</sup>H NMR (90 MHz, CDCl<sub>3</sub>, 7.24 ppm), δ 5.61 (m, 4H), 2.11 (m, 4H), 1.32 (m, 8H); <sup>13</sup>C NMR (67.9 MHz, CDCl<sub>3</sub>, 77 ppm) δ 130.5, 130.44, 44.76, 44.74, 32.87, 31.64, 30.70, 29.93, 28.74, 25.91, 25.75, 25.33, 25.22. **8e**, lit.: Liebman, S. A.; Donovan, P. F.; Koch, S. D. *J. Org. Chem.* **1962**, *27*, 4636.

(1) Zadok, E.; Rubinraut, S.; Frolow, F.; Mazur, Y. *J. Am. Chem. Soc.* **1985**, *107*, 2489 and references cited therein.

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