JOURNAL OF PHYSICAL ORGANIC CHEMISTRY, VOL. 9, 751–758 (1996)

DIMETHYLDIOXIRANE REACTIONS: RATE ACCELERATION DUE TO INTRAMOLECULAR H-BONDING*

ROBERT W. MURRAY† AND HONG GU

Department of Chemistry, University of Missouri–St Louis, St Louis, Missouri 63121, USA

Absolute rate studies were carried out on a series of C—H insertion reactions of dimethyldioxirane (1a). The substrates were chosen so that the distance between a single tertiary C—H bond and an OH group could be varied. The measured rate constants indicate that a rate acceleration occurs when the distance between the reacting C—H bond and the OH group permits intramolecular H-bonding stabilization of the transition state. A similar study in related compounds without the OH group showed no effect of chain length on the rate of the C—H insertion reaction. A related study of the epoxidation reaction of 1a also found an increased rate when chain length permitted intramolecular H-bonding by an OH group.

INTRODUCTION

Since the original observation of Baumstark and Vasquez[2] that increasing the mole fraction of water in an acetone–water solvent mixture led to an increased rate in the epoxidation of *p*-methoxystyrene by dimethyldioxirane (**1a**), there has been increasing interest in the influence of H-bonding on dioxirane reactions. We have followed up on their work by carrying out comprehensive studies of the influence of solvent on dioxirane reactions. These studies showed that the rates of dioxirane epoxidation[3] and C—H bond insertion[4] reactions are increased in H-bond donor solvents.

The influence of substrate H-bonding on diastereoselectivity in dioxirane reactions has also been a subject of growing interest. Intramolecular H-bonding leads to pronounced diastereoselectivity in some dioxirane epoxidations.[5] In one case it was concluded[6] that there is insignificant H-bonding with an intramolecular hydroxyl group to influence epoxidation diastereoselectivity. This conclusion was based on results obtained in acetone solvent. Subsequent work[5g,h] demonstrated that changing the solvent reveals the influence of this kind of H-bonding in this example also. A facilitating effect of proximal hydroxyl groups on the C—H bond insertion reaction has also been observed in dioxirane[7a–d] and peracid oxidation.[7e]

In this work, we measured the rates of a number of related epoxidation and C—H insertion reactions of **1a**. The substrates are chosen so that the distance between the reaction site and an internal hydroxyl group may be varied. The resulting rate data are interpreted as indicating that when the substrate structure contains a distance between the hydroxyl group and the reaction center which permits the achievement of a conformation which favors interaction between the hydroxyl group and the activated complex, then a rate acceleration is observed.

RESULTS

In order to determine whether there is any general effect of chain length on the C—H insertion reaction we first treated the hydrocarbon substrates **2** with dimethyldioxirane [equation (1)]. These hydrocarbons were chosen to have a single tertiary C—H bond and a varying number of CH_2 groups. The known[8] greater reactivity of the tertiary versus primary and secondary C—H bonds ensures that a single reaction product is formed under the conditions used. Bach *et al.*[9] have described a theoretical model which explains this observed reactivity based on electronic and steric factors. The rates of these hydrocarbon C—H insertion reactions were measured using pseudo-first-order kinetics to obtain the second-order rate constants. The results, which show that chain length has only a very slight effect on rate constant, are shown in Table 1. In all cases the reactions give a single product.

We next studied the rates of C—H insertion in the series of related compounds **3**. The general reaction is

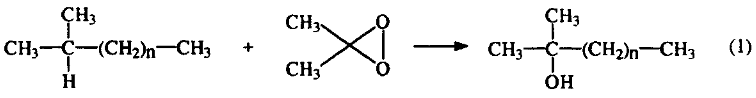
---

* Chemistry of Dioxiranes, Part 32. For Part 31, see Ref. 1.

† Author for correspondence.

CCC 0894–3230/96/100751–08

Received 15 March 1996
Revised 8 July 1996



2 **1a**

2a, n = 1 **2c**, n = 3
2b, n = 2 **2d**, n = 4

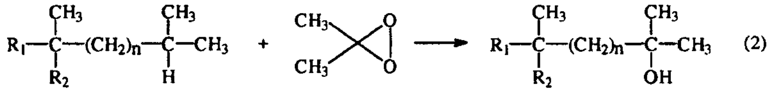
Table 1. Second-order rate constants for C – H insertion reactions of **1** in hydrocarbons and alcohols

Substrate	10^3k_2(l mol^{-1}s^{-1})	R
2-Methylbutane (**2a**)	0·23 ± 0·01	0·97
2-Methylpentane (**2b**)	0·24 ± 0·01	0·98
2-Methylhexane (**2c**)	0·27 ± 0·01	0·98
2-Methylheptane (**2d**)	0·34 ± 0·01	0·98
2,2,5-Trimethylhexane (**3a**)	0·37 + 0·01	
2,3-Dimethylpentan-3-ol (**3b**)	0·085 ± 0·008	
2,4-Dimethylpentan-2-ol (**3c**)	0·64 + 0·010	
2,5-Dimethylhexan-2-ol (**3d**)	2·33 ± 0·04	
3,7-Dimethyl-octan-3-ol (**3e**)	0·31 ± 0·01	

shown in equation (2). This series contains a hydrocarbon (**3a**) which serves as a comparison standard as well as the alcohols **3b**–**3e**, which differ in the number of methylene groups between the hydroxyl group and the reacting tertiary C—H bond. The alcohol substrates give the derived diol as the only reaction product. The results of the rate measurements are also given in Table 1. In alcohol **3b**, in which the hydroxyl group is immediately adjacent to the reacting C—H bond, the rate is seen to be lower than that for the comparison standard (**3a**). When there is one CH_2 group between the hydroxyl group and the reacting C—H bond as in **3c**, then the rate is higher than in **3a**. In **3d**, with two CH_2 groups between the hydroxyl group and the reacting C—H bond, the rate increases to one which is over six times that of the standard. Finally, the rate of C—H insertion in **3e**, with three CH_2 groups between the hydroxyl group and the reaction site, drops to one which is close to that of the standard. Thus the rate has gone through a maximum as the distance between the hydroxyl group and the reacting C—H bond is increased.

We also completed what apparently is the first determination of the activation energy for the insertion reaction of **1a** in an unactivated C—H bond. The temperature effect on the second-order rate constants for the insertion reaction of **1a** in 2,2,5-trimethylhexane (**3a**) was determined using pseudo-first-order techniques using a minimum ratio of substrate to **1a** of 10 : 1. A summary of the data obtained is given in Table 2. A plot of log k_2 versus $1/T$ gave a straight line from which the values for E_a[= 13·2 ± 0·1 kcal mol^{-1}) (1 kcal = 4·184 KJ)] and log A (=6·314) were obtained. These data were then used with the transition-state theory equation to derive the activation parameters $\Delta H^\ddagger$(= 12·64 kcal mol^{-1}), $\Delta S^\ddagger$(= −32·22 cal k^{-1}) and $\Delta G^\ddagger$ (=22·18 kcal mol^{-1}).

Following procedures similar to those used in our earlier study[4] of the solvent effect on the C—H insertion reaction of **1a**, we measured the rates of the C—H insertion reaction in substrates **3** in a series of binary solvents, acetone–solvent X. The solvents used were CH_2Cl_2, $CHCl_3$ and $(CH_3)_3COH$. Pseudo-first-order

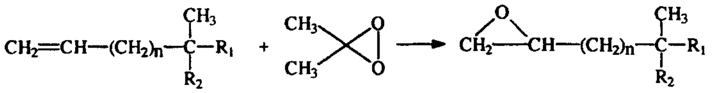


3 **1a**

3a, $R_1 = R_2 = CH_3$, n = 2
3b, $R_1 = CH_3CH_2$, R_2 = OH, n = 0
3c, $R_1 = CH_3$, R_2 = OH, n = 1
3d, $R_1 = CH_3$, R_2 = OH, n = 2
3e, $R_1 = CH_3CH_2$, R_2 = OH, n = 3

kinetics were used with the substrate in excess (10to 20-fold). Plots of k_{obs} versus concentration of **3** gave straight lines from which k_2 values were derived. A summary of the rate data is given in Table 3. Each of the solvents used in the binary mixtures with acetone has a greater H-bond donor capacity than acetone.[4] With one exception each of the substrates **3** has an increased rate of C—H insertion in the greater H-bonding donor solvent pairs. The exception is **3d**, which had a greater rate in acetone than in acetone–CH_2Cl_2. These results are consistent with those observed earlier[4] in hydrocarbon substrates. In Table 4 the same rate data are presented relative to the hydrocarbon standard. This comparison reveals that the order of reactivity is the same in all solvent systems, with **3d** always being the most reactive.

We then turned our attention to a similar study of a possible effect of intramolecular H-bonding on the rate of epoxidation reactions of **1a**. The approach taken is the same as with the non-alkene substrates, that is, we reacted a series of substrates **4** with **1a** and measured the second-order rate constants for epoxidation using pseudo-first-order techniques [equation (3)]. The substrates were chosen so that the distance between a tertiary OH group and the terminal double bond to be epoxidized could be varied. Included in the epoxidation



(3)

4 **1a**

4a, R_1 = CH_3-CH_2, R_2 = H, n = 0
4b, R_1 = CH_3-CH_2, R_2 = OH, n = 0
4c, R_1 = CH_3-CH_2, R_2 = OH, n = 1
4d, R_1 = CH_3, R_2 = OH, n = 2

Table 2. Temperature dependence of second-order rate constant for C–H insertion Reaction of **1** in **3a**

T(K)	$1/T$(K^{-1})	10^3k_2 ($l\ mol^{-1}s^{-1}$)	Log k_2	R
298	0.00336	0.26±0·01	−3·59	0·99
301	0·00332	0·36±0·01	−3·45	1·00
306	0·00327	0·48±0·01	−3·32	0·99
310	0·00323	0·64±0·01	−3·20	0·98

Table 3. Second-order rate constants for the C – H insertion reaction of **1** in substrates **3** in binary solvents

Substrate	Acetone–CH_2Cl_2 10^3k_2 ($l\ mol^{-1}s^{-1}$)	Acetone–$CHCl_3$ 10^3k_2 ($l\ mol^{-1}s^{-1}$)	Acetone–$(CH_3)_3COH$ 10^3k_2 ($l\ mol^{-1}s^{-1}$)	Acetone 10^3k_2 ($l\ mol^{-1}s^{-1}$)
2,2,5-Trimethylhexane (**3a**)	0·45±0·01	1·23±0·01	0·98±0·03	0·37±0·01
2,3-Dimethylpentan-3-ol (**3b**)	0·16±0·01	0·79±0·01	0·78±0·02	0·085±0·008
2,4-Dimethylpentan-2-ol (**3c**)	1·04±0·02	1·81±0·01	1·35±0·02	0·64±0·01
2,5-Dimethylhexan-2-ol(**3d**)	1·82±0·01	3·64±0·01	4·87±0·01	2·33±0·04
3,7-Dimethyloctan-3-ol (**3e**)	0·64±0·05	1·03±0·01	1·14±0·01	0·31±0·01

Table 4. Summary of relative reaction rates for the insertion reaction of **1** in substrates **3** in binary solvents

	Relative rate[a]			
Substrate	Acetone–CH_2Cl_2	Acetone–$CHCl_3$	Acetone–$(CH_3)_3CO$ H	Acetone
2,2,5-Trimethylhexane (**3a**)	1·00	1·00	1·00	1·00
2,3-Dimethylpentan-3-ol (**3b**)	0·36	0·64	0·80	0·23
2,4-Dimethylpentan-2-ol (**3c**)	2·33	1·48	1·41	1·74
2,5-Dimethylhexan-2-ol (**3d**)	4·06	2·98	4·99	6·37
3,7-Dimethyloctan-3-ol (**3e**)	1·42	0·84	1·17	0·86

[a] Relative to **3a**

Table 5. Second-order rate constants for the epoxidation of Substrates **4** by **1**

Substrate	10_3k_2(l mol^{-1} s^{-1})
3-Methylpent-1-ene (**4a**)	17·4 + 0·4
3-Methylpent-1-en-3-ol (**4b**)	8·9 ± 0·4
3-Methylhex-5-en-3-ol (**4c**)	13·3 ± 0·6
2-Methylhex-5-en-2-ol (**4d**)	36·8 ± 0·1

substrates is an alkene with no alcohol function (**4a**), which substrate serves as a comparison standard. The rate data obtained are summarized in Table 5. These results follow the same pattern as seen with substrates **3**. In **4b**, with the OH group immediately adjacent to the double bond, the rate falls to a value that is approximately half that of the standard. In **4c**, with one methylene group between the OH group and the double bond, the rate increases over **4b**, but is still slightly less than that of the standard. In **4d**, in contrast, the rate is now over twice that of the standard. This substrate has two methylene groups between the OH group and the reacting double bond. Because these epoxidation reactions are much faster than the insertion reactions, the effect of the intramolecular H-bonding by the OH group is diminished. These reactions gave only epoxide products. For substrates **4a**–**4c** the epoxides were mixtures of diastereomers.

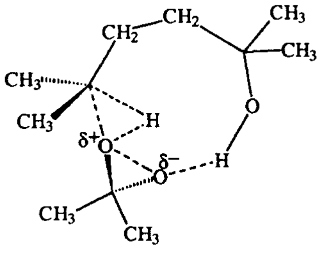
DISCUSSION

Rate studies of C—H insertion reactions in hydrocarbon substrates and in related substrates containing an OH group

As shown in Table 1, there is a negligible effect of chain length on the rate of C—H insertion by **1a** into a series of related hydrocarbons **2**. This series of compounds serves as a comparison standard for the related series **3** in which an OH group is positioned to be at a varying distance from the reacting C—H bond. As shown in Table 1, compounds **3** vary greatly in the rate of C-H insertion. Within this series **3a** is a hydrocarbon that serves as a comparison standard. In compounds **3b**–**3e** the varying distance between the OH and reacting C—H bond has a profound effect on the reaction rate. In **3b**, with the OH group on the immediately adjacent carbon to the one bearing the reacting C—H bond, the rate actually drops below that of the standard. This is presumably due to the electron-withdrawing inductive effect of the OH group. In **3c**, with one methylene group between the OH group and the reaction site, the rate increases to one that is greater than that of the standard, **3a**. When there are two methylene groups between the OH group and the tertiary C—H bond, as in **3d**, the rate increases to one which is over six times that of the standard. Finally, in **3e** the rate falls off to one that is approximately the same as that of the standard. This substrate has three methylene groups between the OH group and the reacting C—H bond. We interpret these results as being indicative of the ability of **3d** to achieve a conformation permitting maximum stabilization from intramolecular H-bonding in the activated complex. A proposed structure that would accommodate this kind of stabilization is given in **5**. This structure is analagous to a similar one invoked to explain stereochemical outcomes in the epoxidation of OH–[5g–i] and NH_3^+–[5b] substituted cyclohexenes. A similar proximity effect of an OH group has been observed[7e] in a peracid C—H insertion reaction.

Determination of E_a and Log A values for a hydrocarbon insertion reaction

We have completed what apparently is the first determination of an E_a value for the C—H insertion reaction of **1a** in



5

Scheme 5

an unactivated hydrocarbon. The second-order rate constants were determined over a range of temperatures (Table 2) for the insertion reaction into the tertiary C—H bond of 2,2,5-trimethylhexane (**3a**). A plot of log k_2 versus $1/T$ gave a straight line from which E_a was determined to be 13·2 ± 0·1 kcal mol^{-1} with log $A = 6{\cdot}31$. In a related study Kovac and Baumstark[10] measured E_a values of 8·7–10·5 kcal mol^{-1} for the formal C—H insertion reaction of **1a** in a series of *para*-substituted α-methylbenzyl alcohols. In these cases the C—H bond is activated both by the presence of the OH group and by the benzylic location, leading to lower E_a values. The more reactive methyl(trifluoromethyl)dioxirane (**1b**) was used by Mello *et al.*[8b] to insert into the secondary C—H bond of cyclohexane with an activation energy of 14.3 kcal mol^{-1} (log $A = 9{\cdot}9$). Thus, while **1b** is the more reactive dioxirane, the fact that our results were obtained in the case of a tertiary C—H bond insertion leads to a lower E_a value when **1a** is the oxidant.

Solvent effect on rates of insertion in substrates containing an OH substituent

The effect of binary solvents on the insertion reactions of substrates **3** are given in Tables 3 (absolute rates) and 4 (relative rates). As noted above, the absolute rate data reveal that with the exception of **3d** these substrates all experience the rate enhancement in HBD solvents that we described earlier,[4] that is, the rates are all greater in the binary solvents than they are in acetone. The relative rate data show that substrate **3d** maintains its position as most reactive in all the solvents used. However, this enhanced rate, that we have ascribed to intramolecular H-bonding stabilization, is most pronounced in acetone. This suggests that operation of this intramolecular stabilizing influence as shown in structure **5** makes **3d** less able to take advantage of stabilization by HBD solvents.

Rate studies on substituents containing an OH group and a double bond

Based on the results indicating that intramolecular H-bonding can lead to rate acceleration in the C—H insertion reaction of **1a**, we sought to learn whether a similar effect could be observed for the epoxidation reaction. The approach used is the same as for the insertion reaction. Substrates were chosen that would permit a varying distance between a terminal double bond and an OH group. The observed second-order rate constants (Table 5) indicate that there is indeed a dependence of rate on the distance between the OH and the double bond. Substrate **4a**, which has no OH group, is included as a comparison standard. Substrate **4b** with no methylene groups between the double bond and the OH group has a lower rate than the standard. This is similar to the situation seen in the insertion reaction. Again, we believe that the rate decrease is due to the inductive effect of the OH group in its proximal relationship to the double bond. Baumstark and Vasquez[2] had earlier observed that 3-methylbut-1-en-3-ol is epoxidized more slowly by **1a** than is its comparison compound, 3,3-dimethylbut-1-ene. In this case also we believe that the inductive effect of the OH group is primarily responsible for the reactivity order. In **4c**, with one methylene group between the OH group and the double bond, the rate increases over that for **4b**, but is still less than that for the standard **4a**. Here one concludes that the inductive effect of the OH is still strong enough to overcome any positive effect of intramolecular H-bonding. Finally, in substrate **4d**, the epoxidation rate is seen to be more than twice that of the standard. We conclude that the two methylene groups between the OH group and the double bond are sufficient to permit access to the stabilizing intramolecularly H-bonded transition state. It should be noted that the overall higher absolute rates for the epoxidation as compared with the insertion reactions tend to diminish the net effects of H-bonding. For substrates **4a**, **b** and **c**, the epoxide products were obtained as mixtures of diastereomers. Presumably a resolved chiral alcohol with a structure similar to that of **4c**, for example, could show a useful diastereoselectivity in epoxidations similar to those examined here.

CONCLUSIONS

The second-order rate constants measured in this work indicate that for both C—H insertion and epoxidation reactions of dimethyldioxirane a rate acceleration is realized when the structure of the substrate permits intramolecular H-bonding stabilization of the activated complex. Achievement of the stabilization is maximized when the distance between the reaction site and an OH group is of a length which allows for formation of a conformation accommodating the reaction site and the stabilizing H-bonding group.

EXPERIMENTAL

Instrumental and general methods. ^{1}H and ^{13}C NMR spectra were recorded on a 300 MHz spectrometer. Solvents used (all deuterated) were chloroform, acetone, methanol and water. Analytical gas chromatography was performed using either a fused silica capillary column (30 m × 0·32 mm i.d.) with DB-210 as liquid stationary phase (film thickness 0·25 μm) or a fused-silica capillary column (30 m × 0·32 mm i.d.) with DB-5 as liquid stationary phase (film thickness 0·25 μm). The gas chromatograph was interfaced with an integrator. Electron input (EI) mass spectra were recorded at 70 eV ionizing voltage on a twin EI and chemical ionization (CI) quadrupole mass spectrometer connected to a gas chromatograph fitted with an Ultra 1 cross-linked methyl silicone gum column (12 m × 0·2 mi.d., film thickness 0·33 μm). Preparative GLC was performed on a preparative gas chromatograph using either a 20 ft × 3/8 in i.d. column [liquid stationary phase 15% SE–30 on Chrom W, 30–60 mesh (PG)] or a 12 ft × 3/8 in i.d. column [liquid stationary phase 8% SF-96 on Chrom 9, acid-washed, 60–80 mesh (DMCS)]. UV–visible spectra were obtained on a spectrophotometer equipped with a six-cell positioner. The temperature could be controlled at 25, 30, and 37 °C. IR spectra were obtained using an FT-IR spectrometer using an NaCl cell and $CHCl_3$ as solvent. Kinetic data were obtained in a constant-temperature bath using an immersion circulator. Melting points were measured using a capillary melting point apparatus and are uncorrected.

Materials and reagents. Acetone and hexane (Aldrich, reagent grade) were distilled over anhydrous potassium carbonate prior to use. Methylene chloride and chloroform (Fisher certified grade) were distilled from P_2O_5 prior to use. *tert*-Butanol (Fisher, certified grade) was refluxed with sodium for 24 h and distilled prior to use. Anhydrous diethylether (Fisher, certified grade) was used as received. Oxone (DuPont) ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$) was purchased from Aldrich. and used as received. Decane (99+%) and dodecane (99+%) (purchased from Aldrich) were used as received. 3-Methylpent-1-en-3-ol (99%) was purchased from Aldrich and used as received. 3-Methylhex-5-en-3-ol (99·5%), 3-methylpent-1-ene (99%) and 2-methylhex-5-en-2-ol (97·5%), all purchased from Wiley Organics, were used as such. 2,2,5-Trimethylhexane (99%) (Chemical Service) was used as received. 2,5-Dimethylhexan-2-ol (99·5%) and dimethyloctan-3-ol (99 %) (Wiley Organics) were used as received. 2,4-Dimethylpentan-2-ol (99·5%) (Lancaster Synthesis) was used as such. 2,3-Dimethylpentan-3-ol and 2,4-dimethylpentane-2,4-diol (both 99%, Aldrich) were used as such. 2,5-Dimethylhexane-2,5-diol (97%, Aldrich) was recrystallized from acetone prior to use. Silica gel (80–200 mesh) was obtained from Fisher Scientific. Dimethyldioxirane was prepared following the literature procedure.[11]

General procedure for kinetic experiments. (a) C—H insertion in hydrocarbons. A freshly prepared solution of **1a** was dried over Na_2SO_4 for at least 24 h. The concentration of **1a** was determined by UV absorption and a previously constructed calibration graph. Suitable equivalents of the various substrates were weighed into a UV cell. UV cells containing solutions of **1a** and the substrate in acetone were kept in the compartment of the UV spectrophotometer in order to attain temperature equilibrium. A portion (2 ml) of the solution of **1a** was transferred to the cell containing the substrate using a volumetric pipette. The cell was shaken and recording of kinetic data was begun immediately. The absorption at 335 nm was monitored for 5 min. The reaction solution was then kept at room temperature for 1–2 days in order to record the final absorption [Abs(∞)]. This series of steps was repeated four times at different concentrations of the substrate. Pseudo-first-order conditions were used with the hydrocarbon substrate in excess (7–15-fold). Plots of ln [Abs(t)–Abs(∞)] gave straight lines with slopes equal to k_{obs}. Plots of k_{obs} versus hydrocarbon concentration gave straight lines with slopes equal to k_2. Analysis of the reaction mixtures by GLC indicated that a single product was formed in each case.

(b) C—H insertion reactions in alcohols. The general procedure was followed except that the UV absorption at 335 nm was monitored for 15 min and in the pseudo-first-order kinetic studies the alcohol substrates were present in 8·5–20 fold excess. These reaction solutions also contained a single reaction product.

(c) Activation energy study for Insertion into 2,2,5-Trimethylhexane. The general procedure was followed except that measurements were made at 23, 28, 35, and 43 °C. The temperature was controlled to within 0·1 °C. Two determinations of k_2 were made at each temperature.

(d) Rate studies on alcohols in binary solvents. The general procedure for the hydrocarbons was used with the following modifications. Suitable equivalents of the alcohols were weighed into 1 ml UV cells. A portion (0·5 ml) of the co-solvent was added using a volumetric pipette. A similar portion of the solution of **1a** in acetone was added to the UV cell. The concentrations of **1a** and alcohol substrate were corrected for the volume change. The UV absorption at 335 nm was monitored for 5 min. Solvents used were CH_2Cl_2, $CHCl_3$ and $(CH_3)_3COH$.

(e) Rate studies on hydroxyalkenes. The general procedure was used with the decay of the absorption at 335 nm being followed for 15 min. In the pseudo-first-order experiments the hydroxyalkene was present in excess (8.5–28-fold).

Identification of products. General procedure. Reaction products were prepared by adding freshly prepared **1a** (usually in portions) to the pure substrates. The ratio of substrate to **1a** was usually 1 : 1. Reactions were carried out at room temperature with stirring for 24 h. The reaction flask was covered with aluminum foil to protect it from light. The reaction progress was monitored by GLC. Solvent was removed by rotary evaporation and the products were separated and purified by column chromatography or preparative GLC.

2,5,5-Trimethylhexan-2-ol. The general procedure was followed using 50 ml of an acetone solution of **1a** (0·05 M) and 0·3 g (2·3 mmol) of 2,2,5-trimethylhexane. The only product was 2,5,5-trimethylhexan-2-ol, which was isolated by silica gel chromatography using hexane–diethylether (80 : 20) as eluent. ^{1}H NMR (CDCl$_3$):δ 0·859 (s, 9H), 1·12 (s, 6H), 1·20–1·48 (m, 4H); lit.[12] ^{1}H NMR (acetone-d_6), δ 0·89 (s, 9H), 1·18 (s, 6H), 1·20–1·50 (m, 4H). ^{13}C NMR (acetone-d_6):δ 15·75, 29·65, 29·81, 38·61, 39·01, and 71·52. MS (EI):*m/z* 128·1 (M$^+$–15, 1·65), 109·0 (10), 95·1 (3·65), 85·1 (100), 57·1 (45·7).

2,3-Dimethylpentane-2-,3-diol. The general procedure was followed. A solution of **1a** (100 ml, 0·06 *M*) was added to 2,3-dimethylpentan-3-ol (0·7 g, 6 mmol). Two more aliquots of a dried solution of **1a** (50 ml, 0·06 M) were added to the reaction mixture, at 24 avd 48 h. Only one product, 2.3-dimethylpentane-2,3-diol, was detected by analytical GLC. The pure product was isolated by preparative GLC (column, SE-30; column temperature, 90 °C; detector temperature, 90 °C; injector temperature, 85 °C). ^{1}NMR (CDCl$_3$):δ 0·91 (t, 3H, *J* = 7·5 Hz), 1·07 (s, 3H), 1·07 (s, 3H), 1·15 (s, 3H), 1.43 (q, 2H, *J* = 7·5 Hz), 1·66 (2H, OH); lit.[13] ^{1}H NMR (CDCl$_3$) δ 0·92 (t, 3H), 1·07 (s, 3H), 1·15 (s, 6H), 1·43 (q, 2H), 1·65 (2H, OH).

2,6-Dimethyloctane-2,6-diol. The general procedure was followed. Pure 2,6-dimethyloctane-2,6-diol was isolated by preparative GLC (column, SE-30; column temperature, 90 °C; detector temperature, 90 °C; injector temperature, 85 °C). ^{1}H NMR (CDCl$_3$):δ 0·847 (t, 3H), 1·108 (s, 3H), 1·174 (s, 6H), 1·39 (m, 6H), 1·45 (q, 2H). ^{13}C (CDCl$_3$):δ 8·30, 18·61, 26·38, 29·32, 34·36, 41·70, 44·36, 70·93, 72·68. Analyses calculated for C$_{10}$H$_{22}$O$_2$, C 68·91, H, 12·72; found, C 68·66, H 12·73%.

2,4-Dimethylpentane-2,4-diol. The general procedure was used. Analytical GLC indicated that the only product formed was 2,4-dimethylpentane-2-,4-diol. The reaction product had the same retention time as an authentic sample (Aldrich, 99%) using two different temperature programs: (1); $T_1 = 60$ °C, time$_1$ = 2 min, rate = 20 °C/min^{-1}, $T_2 = 200$ °C, time$_2$ = 3 min, retention time = 5·74 min; (2) $T_1 = 70$ °C, time$_1$ = 5 min, rate = 20 °C min^{-1}, $T_2 = 200$ °C, time$_2$ = 5 min, retention time = 7·54 min.

2,5-Dimethylhexane-2,5-diol. The general procedure was followed. Analytical GLC indicated that a single product was formed and that this product had the same retention time as authentic material (Aldrich, 99%) under several column conditions.

3-Methyl-1,2-epoxypentane. The general procedure was followed. The substrate 3-methylpent-1-ene (0·504 g, 6 mmol) was mixed with **1a** (100 ml, 0·06 M) and stirred at room temperature for 12 h. GLC analysis indicated the presence of diastereomeric epoxides (46 : 54 ratio). The products were collected together using preparative GLC [20 ft × 3/8 in i.d. column containing 15% SE-30 liquid stationary phase on Chrom W, 30–60 mesh (PIGV), column temperature 65 °C, detector temperature 80 °C, injector temperature 85 °C, collector temperature 25 °C. ^{1}H NMR (CDCl$_3$):δ 2·68–2·76 (m, 2H), 2·44–2·53 (m, 1H), 1·56 (m, 2H), 1·45–1·15 (m, 1H), 0·89–1·01 (m, 6H). ^{13}C NMR (CDCl$_3$):δ (diasteromers observed) 56·97 and 56·89, 46·99 and 46·64, 37·91 and 37·64, 27·30 and 26·47, 16·80 and 15·20, 11·73 and 11·36. MS (EI):*m/z* 99·95 (M$^+$, 0·34), 85·05 (8·38), 70·00 (52·68), 55·10 (100·0). Analysis calculated for C$_6$H$_{12}$O, C 71·95, H 12·07; found, C 71·89, H 12·01%.

2-Methyl-5,6-epoxyhexan-2-ol. The general procedure was followed using 0·69 g (6 mmol) of 2-methylhex-5-en-2-ol and 100 ml of **1a** in acetone solution (0·06 M). The reaction mixture was stirred at room temperature for 12 h. A second portion of **1a** was added to the reaction mixture and stirring continued until all of the substrate was consumed. The product was isolated by preparative GLC. ^{1}H NMR (CDCl$_3$):δ 4·07 (m, 1H), 3·65 (dd, 1H), 3·45 (dd, 1H), 1·95–1·69 (m, 4H), 1·23 (d, 6H). ^{13}C NMR (CDCl$_3$):δ 81·43, 79·77, 65·25, 38·58, 28·95, 27·79. Analysis calculated for C$_7$H$_{14}$O$_2$, C 64·58, H, 10·84; found, C 64·14, H 10·78%.

3-Methyl–5,6-epoxyhexan-3-ol. The general reaction procedure was followed using 0·68 g (6 mmol) of the substrate and 100 ml of a solution of **1a** (0·06 M) in acetone. The reaction mixture was stirred at room temperature for 12 h. Analytical GLC indicated the presence of two products. The diastereomeric epoxides were isolated together using preparative GLC [20 ft × 3/8 in i.d. column, liquid stationary phase 15% SE-30 on Chrom W, 30–60 mesh (PIGV), column temperature 70 °C detector temperature 85 °C, injector temperature 85 °C, collector temperature 25 °C. ^{1}H NMR (CDCl$_3$):δ 3·05 (m, 1H), 2·73 (q, 1H), 2·40 (q, 1H), 1·64–1·78 (m, 4H), 1·18 (d, 3H), 0·84 (t, 3H). ^{13}C NMR (CDCl$_3$) (diastereomers observed; 47 : 53):δ 72·61, 49·24 and 49·15, 46·84 and 46·60, 43·62 and 43·44, 34·93 and 34·86, 26·43 and 26·41, 8·20 and 8·13. Analysis calculated for C$_7$H$_{14}$O$_2$, C 64·59, H 10·84; found, C 63·76, H 10·70%. Exact mass (HRFAB): calculated 130·1074, found, 131·1073.

3-Methyl-1,2-epoxypentan-3-ol. The general procedure was followed using 0·60 g (6 mmol) of 3-methylpent-1-en-3-ol and 100 ml of an acetone solution of **1a** (0·06 M). The reaction mixture was stirred at room temperature for 12 h. The diastereomeric epoxides

(53 : 47 ratio) were collected together by preparative GLC [20 ft × 3/8 in i.d. column containing, 15% SE-30 on Chrom W, 30–60 mesh (PIGV), column temperature 65 °C, detector temperature 80 °C, injector temperature 85 °C, collector temperature 25 °C]. ^{1}H NMR ($CDCl_3$):δ 0·83 (t, 3H), 1·05 (s, 3H), 1·45 (m, 2H), 2·66–2·54 (m, 2H), 2·83–2·80 (m, 1H). ^{13}C NMR ($CDCl_3$) (diastereomers observed):δ 70·47 and 70·11, 58·23, 44·13 and 44·07, 32·88 and 32·25, 23·27 and 23·05, 7·86 and 7·59. Analysis calculated for $C_6H_{12}O_2$, C 62·04; H 10·41; found, C 61·74, H 10·23%.

ACKNOWLEDGEMENT

We gratefully acknowledge support of this work by the National Institutes of Health through Grant No. ES1984. The XL-300 NMR spectrometer was purchased with support from the National Science Foundation.

REFERENCES

1. R. W. Murray and M. Singh, *Polycyclic Aromat. Hydrocarb.*, in press.
2. A. L. Baumstark and P. C. Vasquez, *J. Org. Chem.*, **53**, 3437–3438 (1988).
3. R. W. Murray and D. Gu, *J. Chem. Soc., Perkin Trans.* 2 2203–2208 (1993).
4. R. W. Murray and D. Gu, *J. Chem. Soc., Perkin Trans.* 2 451–453 (1994).
5. (a) G. Cicala, R. Curci, M. Fiorentino, and O. Laricchiuta, *J. Org. Chem.*, **47**, 2679–2681 (1982); (b) G. Asensio, R. Mello, C. Boix-Bernadini, M. E. Gonzalez-Nunez and G. Castellano, *J. Org. Chem.*, **60**, 3692–369 (1995); (c) R. Curci, A. Dinoi and M. F. Rubino, *Pure Appl. Chem.* **67**, 811–822 (1995); (d) M. Abou-Elzahab, W. Adam and C. R. Saha-Moller, *Liebigs Ann. Chem.* 445–450 (1991); (e) M Kurihara, S. Ito, N. Tsutsumi, and N. Miyata, *Tetrahedron Lett.* **35**, 1577–1580 (1994); (f) K. Chow and S. J. Danishefsky, *J. Org. Chem.* **55**, 4211–4214 (1990); (g) R.W. Murray, M. Singh, B. L. Williams and H. M. Moncrieff, *Tetrahedron Lett.* **36**, 2437–2440 (1995); (h) W. Adam and A. K. Smerz, *Tetrahedron* **47**, 13039–13044 (1995); (i) R.W. Murray, M. Singh, B.L. Williams and H.M. Moncrieff, *J. Org. Chem.* **61**, 1830–1841 (1996).
6. W. Adam, F. Prechtl, M.J. Richter and A.K. Smerz, *Tetrahedron Lett.* **52**, 8427–8430 (1993).
7. (a) B. A. Marples, J. P. Muxworthy and K. H. Baggaley, *Tetrahedron Lett.* **32**, 533–536 (1991); (b) D. Kuck, A. Schuster, C. Fusco, M. Fiorentino and R. Curci, R. *J. Am. Chem. Soc.* **116**, 2375–2381 (1994); (c) R. Curci, L. D'Accolti, A. Detomaso, C. Fusco, K. Takeuchi, Y. Ohga, P. E. Eaton and Y. C. Yip, *Tetrahedron Lett.* **28**, 4559–4562 (1993); (d) R. W. Murray, and H. Gu, *J. Org. Chem.* **60**, 5673–5677 (1995); (e) H. J. Schneider and W. J. Muller, *J. Org. Chem.* **50**, 4609–4615 (1985).
8. (a) R. W. Murray, R. Jeyaraman and L. Mohan,. *J. Am. Chem. Soc.* **108**, 2470–2472 (1986); (b) R. Mello, M. Fiorentino, C. Fusco and R. Curci, *J. Am. Chem. Soc.* **111**, 6749–6757 (1989).
9. R. D. Bach, J. L. Andres, M. D. Su and J. W. McDouall, *J. Am. Chem. Soc.* **115**, 5768–5775 (1993)
10. F. Kovac and A. L. Baumstark, *Tetrahedron Lett.* **47**, 8751–8754 (1994).
11. (a) R. W. Murray and R. Jeyaraman, *J. Org. Chem.* **50**, 2847–2853 (1985); (b) M. Singh, and R. W. Murray, *J. Org. Chem.* **57**, 4263–4270 (1992).
12. C. A. Grob and A. Waldner, *Helv Chim. Acta* **62**, 1854–1865 (1979).
13. N. Shimizu, T. Miyahara, M. Mishima and Y. Tsuno, *Bull. Chem. Soc. Jpn.* **62**, 2032–2039 (1989).