the solvent evaporated to give a quantitative yield of **25c**: mp 104–105° (methanol); ir (KBr) 1726 cm^{-1}; uv (cyclohexane) 252 nm sh (ϵ 743), 258 (989), 265 (1310), 272 (1360); nmr (CDCl$_3$) δ 2.98 (3 H, s, methoxyl), 3.28 (1 H, d of d, J = 11.8 and 1.8 Hz, C-2 proton), 3.71 (1 H, d of d, J = 11.8 and 2.4 Hz, C-3 proton), 4.25 (1 H, d, J = 2.4 Hz, C-4 proton), 4.64 (1 H, d, J = 1.8 Hz, C-1 proton), 6.18–6.48 (2 H, m, aryl), 6.82–7.42 (10 H, m, aryl), 7.52 (1 H, m, aryl), with Eu(fod)$_3$[32] shift numbers[33] for the first five peaks of 1.9, 2.1, 1.4, 1.0, and 2.1, respectively.

Anal. Calcd for $C_{24}H_{20}O_2$: C, 84.68; H, 5.92. Found: C, 84.84; H, 5.91.

Equilibration of *cis*- and *trans*-2-Carbomethoxy-3-phenyldibenzobicyclo[2.2.2]octa-5,7-dienes. A solution of 34 mg of **25c** and 2 mg of sodium methoxide in 3 ml of methanol was refluxed for 6 hr. Evaporation of the solvent gave 34 mg of residue whose nmr spectrum in CDCl$_3$ was indistinguishable from that of the trans isomer. Similar treatment of the trans isomer gave pure trans product (nmr).

Irradiation of 3-Benzylidenedibenzobicyclo[2.2.2]octadien-2-one (17, R$_1$ = H, R$_2$ = C$_6$H$_5$). A solution of **17** (100 mg) in 150 ml of methanol was irradiated (Pyrex, Hanovia 450 W) for 1 hr. The solution contained a precipitate (24 mg, 42%) whose ir spectrum was identical with that of dianthracene.[38] An nmr spectrum (CDCl$_3$) of the filtrate showed two sharp, nearly equal, singlets at δ 3.68 and 3.80 due to the methoxyl protons of methyl *cis*- and *trans*-cinnamates, respectively.[27] With the exclusion of the cinnamate peaks, all the remaining peaks could be ascribed to *cis*- and *trans*-2-carbomethoxy-3-phenyldibenzobicyclo[2.2.2]octa-5,7-dienes (**25c** and **25t**), present in a ratio of 32:68. No other products were present.

When **17** (100 mg in 190 ml of methanol) was irradiated at 350 nm in a Rayonet apparatus until the uv maximum at 252 nm due to anthracene showed its concentration to be less than 10^{-5} *M*, the yield of dianthracene was 10.6 mg (18%). A similar irradiation at 300 nm monitored by the enone peak at 298 nm until all the starting material was consumed, followed by irradiation at 350 nm to dimerize the anthracene, gave 18.8 mg (32%) of dianthracene.

Irradiation of 3-(*p*-X-Benzylidene)dibenzobicyclo[2.2.2]octadien-2-ones (34, 35, and 36). A solution of each enone (100 mg) in methanol (190 ml) was irradiated (Pyrex, Hanovia 450 W) until the uv maximum at 252 nm due to anthracene showed its concentration to be less than 10^{-5} *M*. The insoluble dianthracene was collected. Two runs with **34** gave 20.3 and 23.0 mg (37 and 42%). Runs with **35** and **36** gave 22.3 mg (38%) and 18.9 mg (37%), respectively. Solvent was evaporated from the filtrate and an nmr spectrum of the crude residue in each case showed the presence only of the cinnamates and the ethanoanthracene esters.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research (PRF #5988-AC 1,4).

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[38] Sadtler standard infrared spectrum No. 20684.

Kinetics and Mechanism of the Thermal Rearrangements of Optically Active α-Hydroxy Ketones. Example of a Cyclic Three-Component Equilibrium[1]

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Contribution from the Department of Chemistry, Wayne State University, Detroit, Michigan 48202. *Received March 8, 1973*

Abstract: Two optically active α-hydroxy ketones, (*R*)- and (*S*)-3-hydroxy-3-phenyl-2-butanones, were synthesized. The rates of rearrangement for these two compounds and their optically inactive isomer, α-hydroxyisobutyrophenone, were studied at 252, 235, and 214°. The reaction kinetics was analyzed using an IBM 360 Model 67 computer. A mathematical model which uses the concentration *vs.* time profile of any one hydroxy ketone and the equilibrium concentrations of all the three isomers was developed to calculate the rate constants. These values were checked by another mathematical model derived from the reaction kinetics of two-component systems. The kinetic data provide evidence that the three isomeric hydroxy ketones exist in a first-order, three-component cyclic equilibrium under the rearrangement conditions. The activation parameters for the reactions were calculated and the mechanism for the rearrangement is discussed.

Although the stereochemistry of the thermal rearrangements of α-hydroxy ketones has been established both in steroids[3] and in bicyclic ring systems,[1] a kinetic analysis of the rearrangement has not been recorded. We are now reporting the stereospecific synthesis of the two optical isomers (**1** and **2**) of 3-hydroxy-3-phenyl-2-butanone and a detailed kinetic study of the rearrangement involving **1**, **2**, and the optically inactive isomer, α-hydroxyisobutyrophenone (**3**). The rate constants calculated from the kinetic data by two mathematical models (Appendix I and Appendix II) support the stereospecific nature of this rearrangement and provide evidence that the reaction kinetics is dictated by a cyclic three-component system[4] (Scheme I).

Results

(*R*)-3-Hydroxy-3-phenyl-2-butanone (**1**) was prepared by the treatment of 3 equiv of methyllithium with (*R*)-(−)-atrolactic acid[5] (**4**) in refluxing ether for 8

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[1] Hydroxy Ketone Rearrangements. II. For part I, see C. L. Stevens, T. A. Treat, and P. M. Pillai, *J. Org. Chem.*, 37, 2091 (1972).

[2] Taken in part from the Ph.D. Dissertation of F. E. Glenn, Wayne State University, 1973.

[3] For a review, see N. L. Wendler in "Molecular Rearrangements," Part II, P. deMayo, Ed., Interscience, New York, N. Y., 1964, p 1114.

[4] (a) J. A. Benson and R. D. Reynolds, *J. Amer. Chem. Soc.*, **77**, 4434 (1955); (b) R. A. Alberty, W. G. Miller, and H. F. Fisher, *ibid.*, **79**, 3973 (1957); (c) R. A. Alberty and W. G. Miller, *J. Chem. Phys.*, **26**, 1231 (1957); (d) M. Berman, M. F. Weiss, and E. Shahn, *Biophys. J.*, **2**, 303 (1962); (e) D. Kallo and G. Schay, *Acta Chim.* (*Budapest*), **39**, 183 (1963); (f) D. J. Cram and M. R. V. Sahyun, *J. Amer. Chem. Soc.*, **85**, 1257 (1963); (g) R. G. Bergman and W. L. Carter, *ibid.*, **91**, 7411 (1969); (h) R. W. Rozett and E. McLaughlin, *Chem. Tech.*, **1**, 120 (1971); (i) E. McLaughlin and R. W. Rozett, *J. Chem. Educ.*, **49**, 482 (1972); (j) R. S. Schwartz, H. Yokokawa, and E. W. Graham, *J. Amer. Chem. Soc.*, **94**, 1247 (1972).

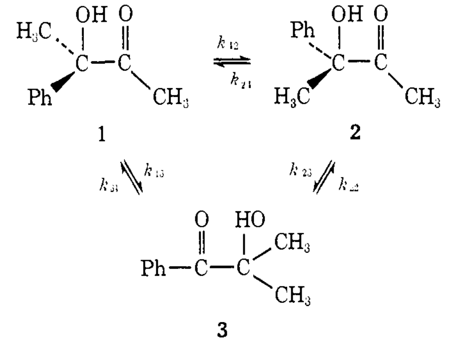
[5] W. Thilacker and H. G. Wenker, *Chem. Ber.*, 87, 690 (1954).

Table I. Summary of Experimental Data on the Hydroxy Ketone Rearrangements

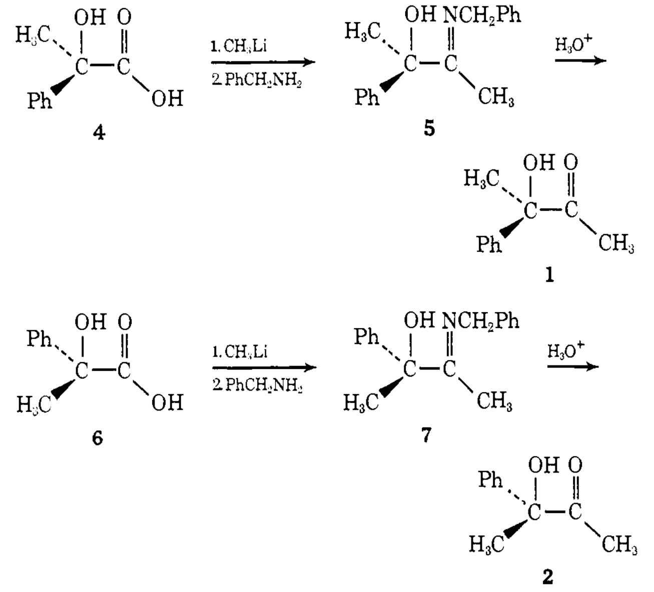
Starting compd	Rearrangement temp, °C	Initial rate of rearrangement, %/min	Equilibrium point, min	Equilibrium concn	Total reaction time, min
12	252	0.16	469	78% of **12**, 22% of **3**	643
12	235	0.08	850	80% of **12**, 20% of **3**	1200
12	214	0.04	3020	83% of **12**, 17% of **3**	4000
3	252	0.30	560	80.5% of **12**, 19.5% of **3**	680
3	235	0.15	900	79.8% of **12**, 20.2% of **3**	1777
3	214	0.06	3350	80% of **12**, 20% of **3**	3730
1	252	0.80	482	40% of **1**, 40% of **2**, 20% of **3**	482
1	235	0.40	950	40.1% of **1**, 40.1% of **2**, 19.8% of **3**	950
1	214	0.17	2900	40.1% of **1**, 40.1% of **2**, 19.8% of **3**	2900
2	214	0.17	2900[a]	40.1% of **1**, 40.1% of **2**, 19.8% of **3**	2600

[a] Extrapolated to equilibrium point from the experimental data.

Scheme I



hr. Similarly, (*S*)-3-hydroxy-3-phenyl-2-butanone (**2**) was obtained from (*S*)-(+)-atrolactic acid[5] (**6**). Purification of the hydroxy ketones was accomplished by the preparation of their crystalline *N*-benzylimines, **5** and **7**, followed by acid hydrolysis. Compounds



1 and **2** were obtained as clear, colorless liquids which had equal but opposite optical rotations. α-Hydroxyisobutyrophenone[6] (**3**) and *dl*-3-hydroxy-3-phenyl-2-butanone[7] (**12**) were prepared by previously described procedures.

Rearrangements. The thermal rearrangements of hydroxy ketones **1**, **3**, and **12** were studied at 252, 235, and 214° using biphenyl as the solvent. The rearrangement of **2** was investigated only at one temperature, 214°. The concentrations of the components at various time intervals were measured by gas chromatography using 4-bromobiphenyl as an internal standard. When optically active hydroxy ketones were rearranged, the progress of the rearrangement was monitored by polarimetry. The experimental percentage concentrations of various hydroxy ketones were calculated as follows: (a) $A_1 + A_2 = A_{12}$ as obtained by gas chromatography; (b) $A_1 - A_2$ = (specific rotation of the rearranged mixture × 100)/specific rotation of **1**.

Solution of the simultaneous equations (a) and (b) gives

$$A_1 = 0.5\left(\frac{\text{specific rotation of the rearranged mixture} \times 100}{\text{specific rotation of } \mathbf{1}} + A_{12}\right)$$

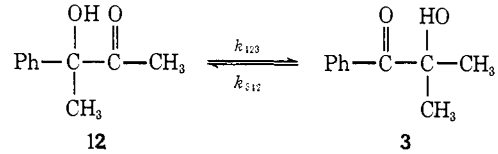
$$A_2 = A_{12} - A_1$$

$$A_3 = 100 - A_{12}$$

where A_1, A_2, A_3, and A_{12} represent the percentage concentrations of hydroxy ketones **1**, **2**, **3**, and **12**, respectively.

Rearrangement of hydroxy ketones **12** and **3** showed that the two compounds exist in a reversible equilibrium (Scheme II) at 252, 235, and 214° (see Table I).

Scheme II



$$\underset{\mathbf{12}}{\mathrm{Ph{-}C(OH)(CH_3){-}C(=O){-}CH_3}} \xrightleftharpoons[k_{312}]{k_{123}} \underset{\mathbf{3}}{\mathrm{Ph{-}C(=O){-}C(OH)(CH_3){-}CH_3}}$$

Rate constants for this rearrangement were calculated by using mathematical model 1 (Appendix I). The experimental points were compared with concentration *vs.* time profiles generated from the rate constants using a computer program.[8] The close agree-

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(6) C. L. Stevens, P. Blumbergs, and M. E. Munk, *J. Org. Chem.*, **28**, 331 (1963).

(7) J. Wegman and H. Dahn, *Helv. Chim. Acta*, **29**, 101 (1946).

(8) The computer programs can be made available on request.

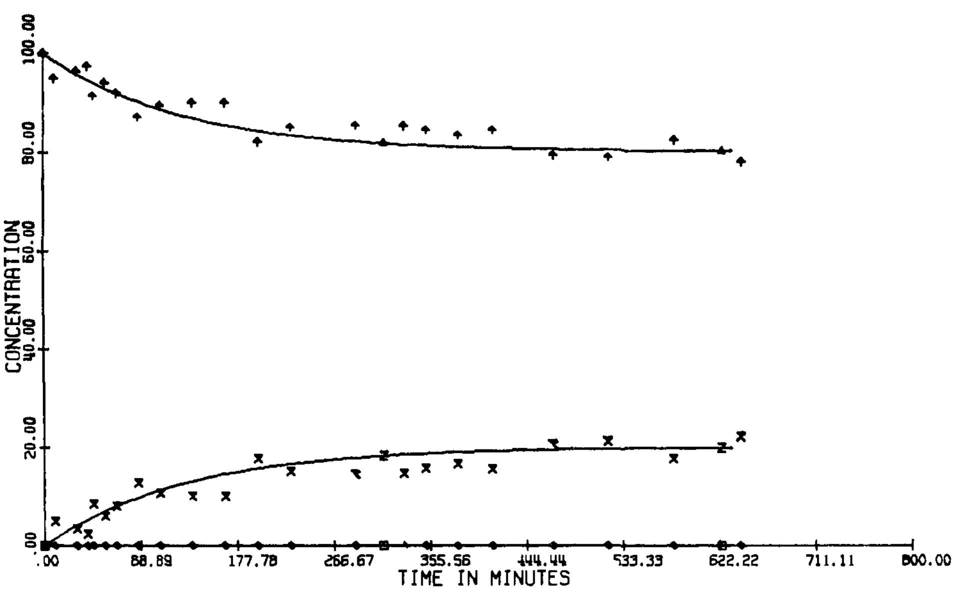

Figure 1. Concentration *vs.* time plot of the rearrangement of **12** at 252°. Solid lines are concentrations generated by the computer from rate constants in Table III: (vertical arrow) experimental concentration of **12**; (×) experimental concentration of **3**.

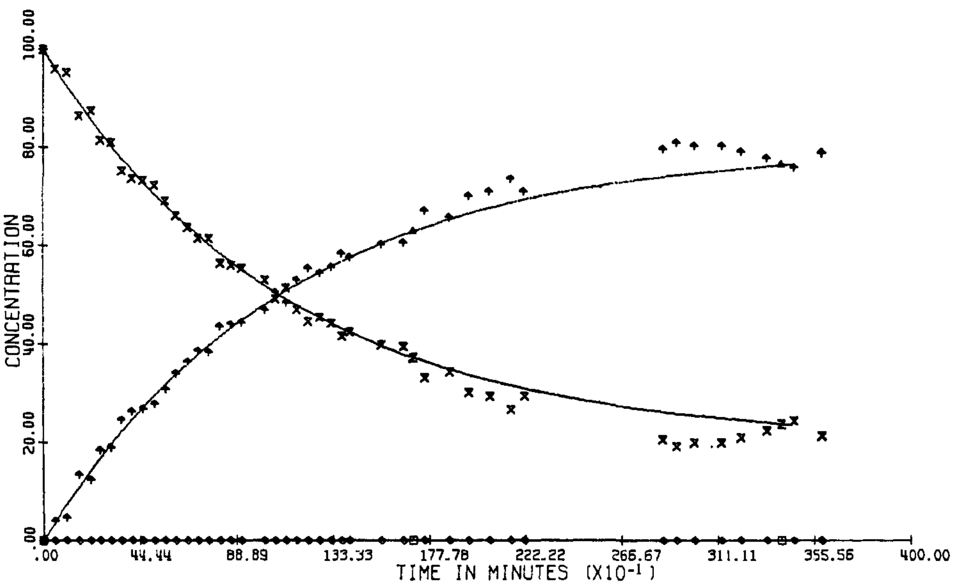

Figure 2. Concentration *vs.* time plot for the rearrangement of **3** at 214°: (×) experimental concentration of **3**; (vertical arrow) experimental concentration of **12**.

ment between the experimental points and the calculated results as represented in Figure 1 and Figure 2 indicates that this rearrangement is a first-order reaction. The rate constants, k_{123} and k_{312}, are listed in Table II.

Table II. Rate Constants for α-Hydroxy Ketone Rearrangements in Scheme II Calculated by Mathematical Model 1

Temp, °C	k_{123}, min^{-1} × 10^3	k_{312}, min^{-1} × 10^3
252	1.60	6.30
235	0.61	3.1
214	0.18	0.72

As phenyl migration from hydroxy ketone **12** does not produce any structural change in the molecule, the rate of decay of **12** and consequently the rate constant, k_{123}, reflect only the rate of methyl migration from **12** to form hydroxy ketone, **3**. In order to determine the rate of phenyl migration, the rearrangements of optically active hydroxy ketones **1** and **2** were investigated. Compound **1** was rearranged at 252, 235, and 214° and the rearrangement was followed by a change in optical rotation. Figure 3 depicts the rearrangement profile of **1** at 235° as an example. Hydroxy ketone **2** was rearranged at 214° to establish that the two optical isomers **1** and **2** rearranged at the same rate under identical conditions (see Table I). All six rate constants, k_{12}, k_{21}, k_{13}, k_{31}, k_{23}, and k_{32} were calculated as described in mathematical model 1 and are given in Table III.

The concentrations *vs.* time profiles for the rearrangements were constructed using the rate constants in Table III. Representatives of these plots are shown in Figures 4 and 5.

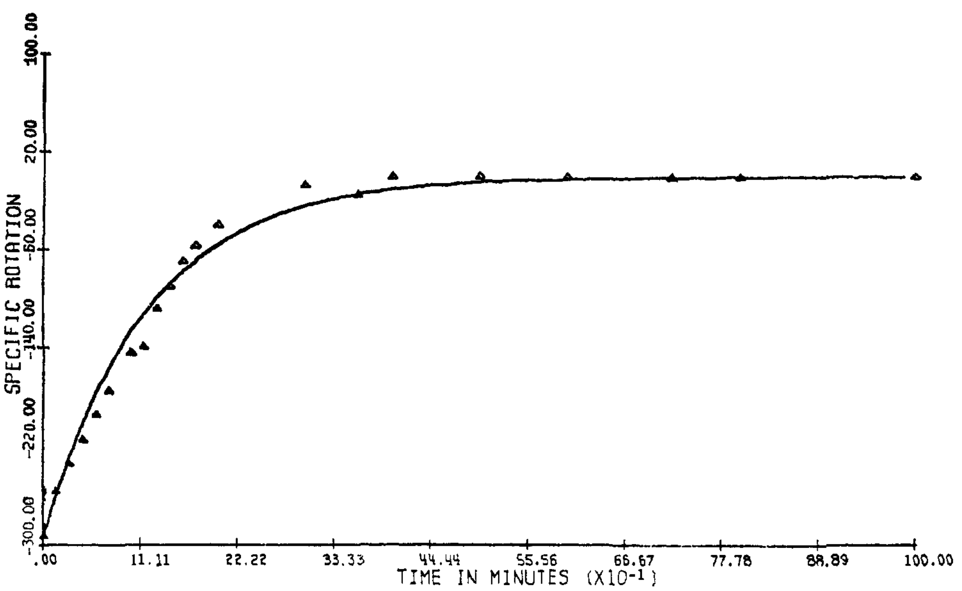

Figure 3. Specific rotation *vs.* time profile for the rearrangement of **1** at 235°: (▲) experimental specific rotation of the mixture.

Table III. Rate Constants for α-Hydroxy Ketone Rearrangements in Scheme I Calculated According to Mathematical Model 1

Temp, °C	Rate constants, $min^{-1} \times 10^3$					
	k_{12}	k_{21}	k_{13}	k_{31}	k_{23}	k_{32}
252	8.7	8.7	1.6	3.1	1.6	3.1
235	3.9	3.9	0.6	1.5	0.6	1.5
214	1.0	1.0	0.18	0.36	0.18	0.36

The experimental data for the decay of hydroxy ketone **1** were used in conjunction with mathematical model 2 (Appendix II) to determine the six rate constants for the rearrangements. These values are given in Table IV. The rate profiles for all the reactions were regenerated using the rate constants in Table IV and were found in agreement with experimental results within acceptable maximum deviations (see Table V).

Table IV. Rate Constants for α-Hydroxy Ketone Rearrangements in Scheme I According to Mathematical Model 2

Temp, °C	Rate constants, $min^{-1} \times 10^3$					
	k_{12}	k_{21}	k_{13}	k_{31}	k_{23}	k_{32}
252	8.8	8.8	1.60	3.2	1.6	3.2
235	4.0	4.0	0.7	1.6	0.7	1.6
214	1.1	1.1	0.19	0.39	0.19	0.39

Table V. Maximum Deviations between Experimental and Computer Generated Rate Profiles[a]

Starting compd	Temp, °C	Maximum deviation for		
		A_1	A_2	A_3[b]
1	252	2.3	2.3	1.0
1	235	3.1	3.1	1.5
1	214	2.3	1.0	0.7
3	252	1.0	1.0	3.1
3	235	2.3	2.3	4.6
3	214	2.3	2.3	4.6
2	214	2.3	2.3	1.0

[a] Rate constants in Table IV were used to generate the rate profiles by computer. [b] A_1, A_2, and A_3 represent percentage concentrations of hydroxy ketones **1**, **2**, and **3**, respectively.

The high maximum deviations when **3** was used as the starting material can be explained as follows. At longer reaction times, hydroxy ketone **3** was found to decompose, probably by elimination of water, producing a small amount of an impurity, as shown by gas chromatography. Because the experimental concentrations were estimated based on the internal standard and the total of the percentages of **3**, **1**, and **2** were always taken as 100, the formation of the impurities gives rise to lower values for **3** and corresponding higher values for the other hydroxy ketones as seen in Figures 2 and 4 at long reaction times. As compounds **1** and **2** were relatively more stable (see Figures 1, 3, and 5), the equilibrium concentrations were obtained principally from the rearrangement data of these hydroxy ketones.

The thermodynamic constants for the rearrangement were calculated at three temperatures. The values were averaged and are presented in Table VI.

Table VI. Activation Parameters for the α-Hydroxy Ketone Rearrangements[a]

Rate constant	E_a, kcal/mol	$\Delta S^{\ddagger}$, eu	$\Delta G^{\ddagger}$, kcal/mol
k_{12}	27.1	−8.5	31.6
k_{21}	27.1	−8.5	31.6
k_{13}	27.7	−10.9	33.4
k_{31}	28.0	−9.0	32.7
k_{23}	27.7	−10.9	33.4
k_{32}	28.0	−9.0	32.7

[a] Calculated using the Arrhenius and Eyring equations by a least-squares program.[8]

Discussion

An examination of Table I shows that the initial rate of rearrangement of optically active hydroxy ketone, **1**, is four to five times faster than the rate of rearrangement of its *dl* isomer, **12**. As the rate of rearrangement of **12** is a measure of methyl migration (phenyl migration does not produce any structural change in the molecule), the higher rate of decay of **1** suggests that compound **2** is mostly formed from **1** by

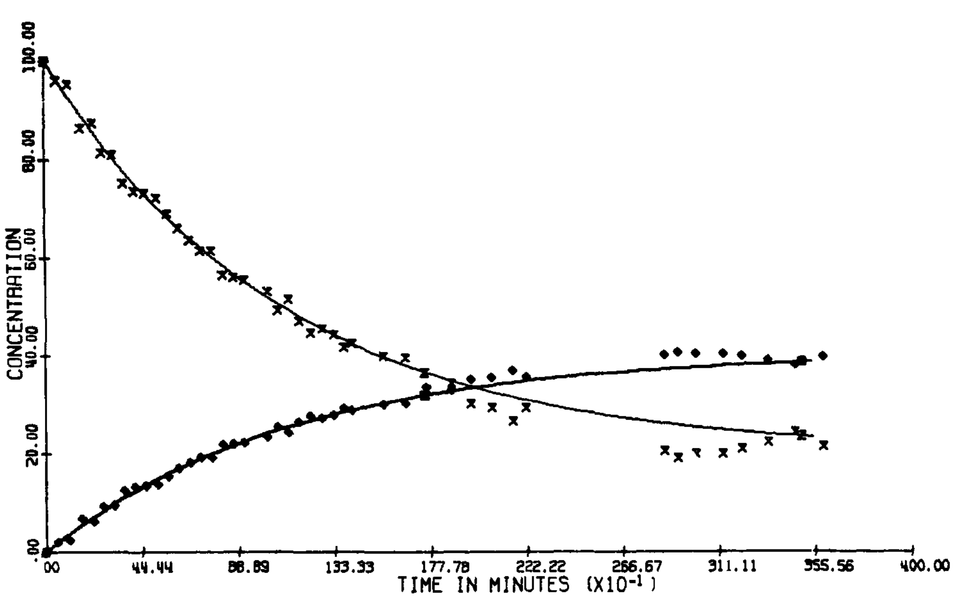

Figure 4. Concentration *vs.* time plot for the rearrangement of **3** at 214°: (×) experimental concentration of **3**; (◆) concentrations for **1** and **2**. The curves for the buildup of **1** and **2** coincide.

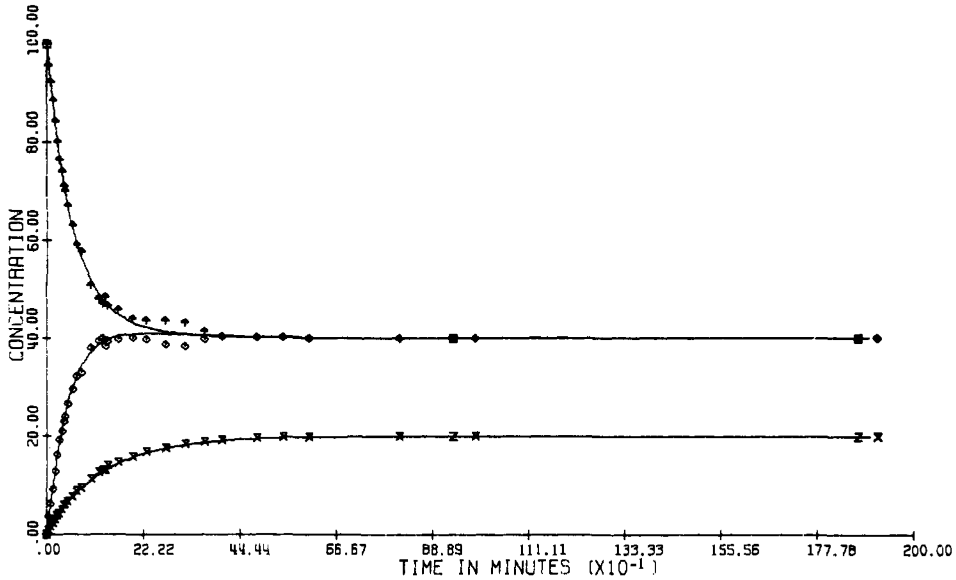

Figure 5. Concentration *vs.* time plot for the rearrangement of **1** at 252°: (vertical arrow) concentration of **1**; (◇) concentration of **2**; and (×) concentration of **3** as calculated by computer using the specific rotation data and rate constants in Table III.

means of phenyl migration. The principle of microscopic reversibility dictates that the reverse process, phenyl migration from **2** to form **1**, must be occurring simultaneously. The rearrangements of **12** and **3** provide evidence that these interconversions produce a reversible equilibrium. In short, compound **1** rearranges to **2** and **3** by means of phenyl and methyl migrations, respectively, and compound **3** reversibly forms **12** which in fact is a 1:1 mixture of **1** and **2**. It has also been established that compound **2** rearranges to **1** and **3**. Since all rearrangements are reversible and reach the same equilibrium point under the same rearrangement conditions, the three components exist in a cyclic equilibrium. Further evidence to this effect was obtained from reaction kinetics. Experimental results are in close agreement with the calculated values obtained by using mathematical model 2 which was derived on the basis of a cyclic three-component system. It may also be noted that the rate constants calculated according to mathematical model 1 (derived from a simple two-component system and extended to include the rearrangement of an optically active hydroxy ketone using its specific rotation *vs.* time data) and mathematical model 2 which did not presuppose $k_{13} = k_{23}$, $k_{31} = k_{32}$, and $k_{12} = k_{21}$ are the same within experimental error (compare Tables III and IV), providing an independent check on the validity of this concept.

The entropies of activation ($\Delta S^{\ddagger}$) found for these reactions, -8.54 eu to -10.93 eu (Table VI), are within the range expected for unimolecular isomerizations.[9] The negative sign of $\Delta S^{\ddagger}$ is also indicative of highly ordered transition states for the migration of phenyl and methyl groups as shown below. Sim-

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(9) S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill, New York, N. Y., 1960, pp 254–255.

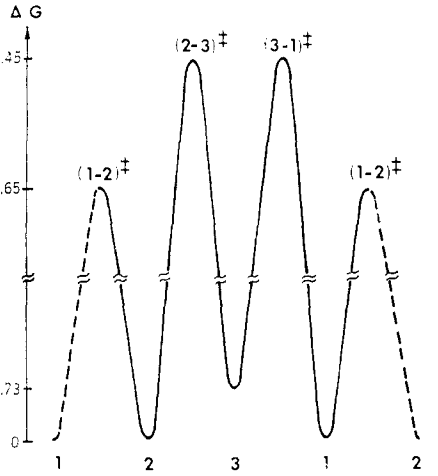
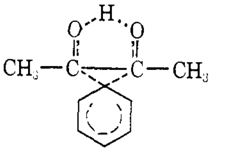
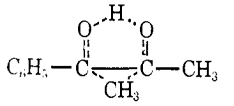


Figure 6. Relative free energies of species involved in the hydroxy ketone rearrangements. Dotted lines are to indicate that it is a cyclic equilibrium.



(1–2)‡

(2–1)‡



(1–3)‡

(3–2)‡

ilar cyclic five-membered ring transition states were proposed earlier for the thermal rearrangements of α-hydroxy ketones[1] and α-amino ketones.[10]

The free energy of activation ($\Delta G^{\ddagger}$) for the rearrangement 1 ⇆ 2 is lower than that for the conversion 1 ⇄ 3 by 1.8 kcal (Table VI). This is expected as the phenyl group is known to delocalize more effectively the charge deficiency created at the carbonyl center, thereby making it a better migrating species than the methyl group. This phenyl migration from **1** to form **2** is a faster process than methyl migration to form **3** as the transition state energy for $(1 - 2)^{\ddagger}$ is lower than that for $(1 - 3)^{\ddagger}$. This means that when **1** is rearranged, the major mode of racemization is the formation of its enantiomer **2** by direct phenyl migration from **1**. A relatively small amount of **2** is also formed by two methyl migrations through the intermediacy of the optically inactive isomer, **3**.

Although the transition states for the formation of hydroxy ketone **3** from **1** and **2** and for the formation of **1** and **2** from **3** are either identical or enantiomeric (see the potential energy diagram, Figure 6), the rate of methyl migration from **3** (k_{31} and k_{32}) is faster than that from **1** and **2** (k_{13} and k_{23}). This may be explained on the basis of the relative ground-state energies of **3** and **1** (compounds **1** and **2** will have the same ground-state energy as they are enantiomers). The ground-state energy of **3** is higher than that of **1** and **2** because of the nonbonded interactions between the two methyl groups on the same carbon atom in **3**.[11] The planar nature of the phenyl group will minimize the steric interaction between the phenyl and methyl groups in **1** and **2**, thus lowering their ground-state energies. Therefore, the energy of activation for methyl migration from **1** and **2** to form **3** is greater than that for methyl migration from **3** to form **1** and **2** by 0.73 kcal (Table VI). Consequently, the rate of methyl migration from **3** (k_{31} and k_{32}) is faster than the rate of methyl migration from **1** and **2** (k_{13} and k_{23}).

Experimental Section[12]

(*R*)-3-Hydroxy-3-phenyl-2-*N*-benzyliminobutane (5). A solution of 40 ml of 2 *M* methyllithium in ether was added dropwise to a stirred solution of 4.7 g (0.0283 mol) of (*R*)-(−)-atrolactic acid[5] in dry ether under a nitrogen atmosphere. The solution was refluxed for 2 hr and cooled and 40 ml of water was carefully added. The mixture was neutralized by adding solid NH_4Cl and the ether layer was separated. The aqueous layer was extracted twice with ether; the ether solutions were combined, dried (K_2CO_3), and evaporated to give 4.8 g of crude (*R*)-3-hydroxy-3-phenyl-2-butanone (**1**) as a colorless oil. This material mixed with 5 g of benzylamine and a trace of *p*-toluenesulfonic acid was dissolved in 20 ml of benzene and the solution was refluxed with water separation for 18 hr. The volatile materials were removed by evaporation under reduced pressure and the residue was crystallized from hexane to give 6.40 g (88%) of **5**: mp 63–64°, $[\alpha]^{27}\mathrm{D}$ −167.65° (*c* 1.04, EtOH), ir 1675 cm^{-1} (C═N).

Anal. Calcd for $C_{17}H_{19}NO$: C, 80.63; H, 7.51; N, 5.53. Found: C, 80.35; H, 7.60; N, 5.53.

(*R*)-3-Hydroxy-3-phenyl-2-butanone (1). A mixture of 4.5 g (0.018 mol) of hydroxyimine, **5**, and 3.1 g (0.018 mol) of anhydrous *p*-toluenesulfonic acid was dissolved in 200 ml of water and the solution was stirred at room temperature for 6 hr. The mixture was extracted with ether (5 × 50 ml) and the combined ether extracts were washed with $NaHCO_3$ solution, dried (Na_2SO_4), and evaporated to dryness. The yellow oil was distilled under reduced pressure to give 2.46 g (83%) of **1** as a clear, colorless liquid: bp 99–102° (3.5 mm); $[\alpha]^{27}\mathrm{D}$ +67.3° (neat); $n^{27}\mathrm{D}$ 1.521; ir 1715 cm^{-1} (C═O); nmr ($CDCl_3$) δ 1.8 (s, 3, CH_3), 2.2 (s, 3, CH_3), 4.7 (s, 1, OH), 7.3–7.6 (m, 5, phenyl). The ORD curve showed a positive Cotton effect with a peak at 280 nm and a trough at 320 nm.

Anal. Calcd for $C_{10}H_{12}O_2$: C, 73.17; H, 7.32. Found: C, 72.89; H, 7.51.

(*S*)-3-Hydroxy-3-phenyl-2-*N*-benzyliminobutane (7). (*S*)-(+)-Atrolactic acid[5] (6.0 g, 0.036 mol) was converted to 6.1 g of crude (*S*)-3-hydroxy-3-phenyl-2-butanone (**2**) by the same procedure used for the preparation of **5**. A mixture of this material with 8 g of benzylamine and a trace of *p*-toluenesulfonic acid was dissolved in 150 ml of benzene and the solution was refluxed for 18 hr at which point a gc analysis showed that the reaction was complete. The solvent and excess benzylamine were removed *in vacuo* and the residue was crystallized from hexane to give 5.8 g (63% for two steps) of **7**:[13] mp 62–63°; $[\alpha]^{29}\mathrm{D}$ +163.8° (*c* 1.10, EtOH); ir 1675 cm^{-1} (C═N).

Anal. Calcd for $C_{17}H_{19}NO$: C, 80.59; H, 7.56; N, 5.53. Found: C, 80.66; H, 7.69; N, 5.59.

(*S*)-3-Hydroxy-3-phenyl-2-butanone[13] (2). Hydroxyimine, **7** (4.5 g, 0.018 mol), was hydrolyzed with 3.1 g (0.018 mol) of anhydrous *p*-toluenesulfonic acid in 200 ml of water as described earlier for the preparation of **1**. The product was distilled under reduced pressure to give 2.35 g (80%) of **2** as a clear colorless liquid: bp 106–109° (5 mm); $[\alpha]^{27}\mathrm{D}$ −66.4° (neat); $n^{27}\mathrm{D}$ 1.521; ir and nmr

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(10) (a) C. L. Stevens, H. T. Hanson, and K. G. Taylor, *J. Amer. Chem. Soc.*, 88, 2769 (1966); (b) for a review, see C. L. Stevens, P. M. Pillai, M. E. Munk, and K. G. Taylor in "Mechanisms of Molecular Migrations," B. S. Thyagarajan, Ed., Wiley-Interscience, New York, N. Y., 1971, p 271.

(11) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience, New York, N. Y., 1965, p 191.

(12) Melting points were taken on a Thomas-Hoover melting point apparatus and are uncorrected. Gas chromatographic analyses were performed on an F & M Model 810 instrument fitted with a flame ionization detector. A 0.25 in. × 10 ft 1% cyanoethylsucrose on Chromosorb W (nonacid washed) column was used at 135°. Infrared spectra were determined on a Perkin-Elmer 237B grating spectrophotometer. Nuclear magnetic resonance spectra were obtained with a Varian Associates T-60 spectrometer using tetramethylsilane as an internal standard. Optical rotations were measured using a Perkin-Elmer Model 141 polarimeter, and optical rotatory dispersion curves were obtained on a Cary 60 instrument. Refractive indices were determined with a B and L refractometer. Microanalyses were performed by Midwest Microlab, Inc., Indianapolis, Ind.

(13) S. Yamada, H. Mizuno, and S. Terashima [*Chem. Commun.*, 1058 (1967)] have reported this compound as a liquid. No analytical data were given.

spectra were superimposable with those of hydroxy ketone, **1**; the ORD curve showed a negative Cotton effect with a peak at 320 nm and a trough at 283 nm.

Anal. Calcd for $C_{10}H_{12}O_2$: C, 73.17; H, 7.32. Found: C, 72.97; H, 7.31.

Rearrangements. An oil bath was prepared from a 5-l. Pyrex dish filled with silicone oil and insulated with glass wool and asbestos tape. The oil bath was heated and the temperature held constant by using a relay system from Brinkman's oil bath assembly. No change in temperature was observed during the course of a rearrangement.

In the rearrangement of hydroxy ketones **3** and **12**, a 10-ml round-bottomed flask with a ground-glass stopper and a side arm fitted with a Teflon stopcock was used as the reaction vessel. In a typical experiment, 161 mg of **3**, 169 mg of *p*-bromobiphenyl (internal standard), and 2.7 g of biphenyl[14] (solvent) were weighed into the flask and the flask was flushed with nitrogen. The flask was stoppered and submerged into the oil bath which had been preheated to the required temperature. Samples (*ca.* 0.01 ml each) were withdrawn through the side arm at various time intervals using a heated syringe. The samples were dissolved in $CHCl_3$ and analyzed by gc. As there was no complete base line separation for the hydroxy ketones in the chromatograms, the peaks heights were measured and compared with that of the internal standard. The original concentration of the starting hydroxy ketone was taken as 100% and the concentrations in subsequent samples were derived accordingly. Analysis of standard mixtures had shown that this type of estimation was accurate within ±3%.

Rearrangements of optically active hydroxy ketones, **1** and **2**, were conducted as follows. In a typical experiment, 299.6 mg of **1**, 300.3 mg of *p*-bromobiphenyl, and 14.8 g of biphenyl[14] were weighed into a 50-ml flask and the components were thoroughly mixed by heating the mixture at 80° for 15 min under a nitrogen atmosphere. Samples of *ca.* 500 mg were withdrawn using a Pasteur pipet and placed in 0.5-g ampoules. The ampoules were sealed under nitrogen and immersed in an oil bath preheated to the desired temperature. The reaction was quenched by removing ampoules from the oil bath at various time intervals. From each ampoule, 200 mg of the rearranged mixture was dissolved in 1 ml of $CHCl_3$ and its optical rotation was measured. A few samples were also analyzed by gc to check the concentrations of the hydroxy ketones. Table VII represents an example of optical rotations *vs.* time data.

As all the rearrangements were conducted in closed systems, no separate mass balance determination was carried out as it was deemed unnecessary.

Table VII. Rotation *vs.* Time Data for the Rearrangement of Hydroxy Ketone, **1**, at 214°

Time, min	Optical rotation[a]	Specific rotation[b]
0.0	−1.168	−272.550
25.0	−1.1063	−250.550
50.0	−0.967	−230.250
75.0	−0.900	−216.510
100.0	−0.848	−205.050
125.0	−0.828	−202.310
150.0	−0.799	−196.260
200.0	−0.760	−188.660
250.0	−0.620	−155.230
360.0	−0.574	−145.430
460.0	−0.406	−103.200
580.0	−0.305	−78.209
750.0	−0.233	−60.077
926.0	−0.136	−35.261
1026.0	−0.087	−22.759
1130.0	−0.189	−49.553
1341.0	−0.028	−7.424
1610.5	−0.045	−12.070
1967.0	−0.011	−2.9916
2830.5	−0.000	−0.000

[a] As obtained from the polarimeter. [b] Based on the weight of hydroxy ketones present in the sample. The specific rotation of pure **1** under these conditions is −272.55.

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Appendix I. Mathematical Model 1

Because of the enantiomeric relationships between hydroxy ketones **1** and **2**, the analysis for the rate constants can be determined by considering simple two-component systems. The rearrangements of **1** and **2** *via* enantiomeric transition states dictate the following relationships

$$k_{12} = k_{21}$$

$$k_{13} = k_{23}$$

In a similar manner, the conversion of ketone **3** to **1** and **2** proceeds through enantiomeric transition states indicating that $k_{31} = k_{32}$. When the two-component equilibrium between **12** and **3** was compared with the differential rate expression for the three-component system, the following relationships became apparent.

$$k_{123} = k_{13} = k_{23}$$

$$k_{312} = 0.5k_{31} = 0.5k_{32}$$

The relationship among the rate constants coupled with the rate equation for the decay of **1** allows the determination of k_{12} and k_{21} *via* a least-squares analysis of the following equation

$$\mathrm{f}(t) = k_{21}\mathrm{g}(t)$$

where $\mathrm{f}(t) = \mathrm{d}A_1/\mathrm{d}t + k_{123}A_1 - 2k_{312}A_3$ and $\mathrm{g}(t) = A_2 - A_1$. The rate constants k_{123} and k_{312} for the two-component system were determined from the experimental rate of decays of **12** and **3**, respectively. An optimum fit for the two constants was ascertained by a least-squares analysis using the IBM 360 Model Computer under the command of the Michigan Terminal System (MTS).[8] The rate constant k_{12} was determined from the values of k_{123} and k_{312} and the experimental data for the decay of **1** using another computer program.[8] The rates of reaction $\mathrm{d}A_1/\mathrm{d}t$ were obtained at different time intervals by drawing the tangents to the concentration *vs.* time curves for the decay of **1** at different points.

Appendix II. Mathematical Model 2

Integration of the rate expressions for the three components in a cyclic equilibrium using the LaPlace transformation gave the following rate equations.[4h,i,15]

$$A_1(t) = \sum_{i=1}^{3} D_i \exp(-m_i t)$$

$$A_2(t) = \sum_{i=1}^{3} F_i \exp(-m_i t)$$

$$A_3(t) = \sum_{i=1}^{3} E_i \exp(-m_i t)$$

$$m_3 = 0$$

Least-squares analysis of the experimental data based on the linear combination of exponential functions[16]

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[14] Practical grade biphenyl was recrystallized several times from absolute ethanol until it showed only one peak on gc.

[15] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, Wiley, New York, N. Y., p 160.

[16] P. E. Rakita and G. A. Taylor, *Inorg. Chem.*, **11**, 2136 (1972).

provided the numerical values of the coefficients and exponential terms.[17] The initial guesses for this computer program were determined according to Prony's method.[18] Having obtained the optimum fit for the experimental data, the six linearly independent equations obtained from the LaPlace transform solution of the cyclic equations were used to determine the six rate constants.

This method using the equilibrium concentrations, exponential terms, and the coefficient, D_1, allowed the determination of the six rate constants from the experimental concentration *vs.* time profile of the rearrangement of only one hydroxy ketone.

(17) R. H. Moore and R. K. Ziegler, "Solution of the General Least Squares Problem with Special References to High Speed Computers," Report LA-2367 (Los Alamos Scientific Laboratory) Office of Technical Services, U. S. Department of Commerce, Washington, D. C., 1963.

(18) F. B. Hilderbrand, "Numerical Analysis," McGraw-Hill, New York, N. Y., 1956, p 378.

Mechanism and Kinetics of Cyclohexyl Radical Addition to Chloroethylenes and of the Subsequent Reactions of the Adduct Radicals

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Abstract: The mechanism and kinetics of the free-radical chain addition reaction between cyclohexane (RH) and chloroethylenes (ECl) have been reinvestigated. The intermediacy of unimolecular β-chlorine scission from the RECl type radicals in the chain propagation sequence has been confirmed. Relative Arrhenius parameters for the addition of R radicals to C_2Cl_4, C_2Cl_3H, and the cis and trans isomers of $C_2Cl_2H_2$ were determined. Arrhenius parameters for Cl atom elimination from $RC_2Cl_2H_2$ and RC_2Cl_3H radicals were evaluated from studies of the temperature dependence of the yields of the saturated and unsaturated addition products.

We have shown[1] that γ irradiation of dilute solutions of chloroethylenes (ECl) in alkanes (RH) leads to a free-radical chain substitution of a chlorine of the chloroethylene by an alkyl radical R. The occurrence of similar substitution reactions has also been observed in other RH–chloroethylene systems where free radicals were generated by decomposition of peroxides,[2-4] photolysis,[5] and pyrolysis.[6] Our kinetic analysis of the substitution reaction was based on a mechanism originally suggested by Schmerling[2] and recently confirmed by Tanner, *et al.*[4] According to this mechanism the following reactions constitute the propagation step of the chain sequence. In recent

$$R\cdot + ECl \longrightarrow RECl\cdot$$

$$RECl\cdot \longrightarrow RE + Cl$$

$$Cl + RH \longrightarrow HCl + R\cdot$$

works we studied the reactions of various chloroethyl radicals in cyclohexane solution.[7,8] It was found that the chloroethyl radicals disappear from the system both by β-chlorine scission and by hydrogen abstraction from the solvent. It would thus appear that in the chloroethylene–alkane system the hydrogen abstraction reaction by the RECl· radicals might have been overlooked by us as a result of its marginal effect in the temperature range at which these experiments were carried out. Furthermore, Tanner, *et al.*,[9] have found that alkyl radicals react with hydrogen chloride in a relatively fast reaction. The importance of this reaction was clearly demonstrated by the above authors in their studies of the chlorovinylation of alkanes.[4] The possibility of a secondary reaction of R and RECl radicals with HCl was not considered by us previously. Because of these facts it seemed to us that further studies of the mechanics and kinetics of the free-radical reactions in the alkane–chloroethylene system are in order. The elucidation of this mechanism appears to be important in view of the potential value of radiolytic techniques for the synthesis of substituted chloroolefins.[10]

Unlike in our previous studies,[1] a competitive kinetic method was used in the present work to obtain the Arrhenius parameters for the addition of cyclohexyl radicals to $C_2Cl_2H_2$, C_2Cl_3H, and C_2Cl_4. This method is free from the somewhat arbitrary assumptions made by us previously[1] in evaluating k_2 at 150°. In the competitive studies the rate of the reaction between cyclohexyl radicals and C_2Cl_4 was used as a standard and therefore it was carefully redetermined.

Experimental Section

Materials and Procedure. Tetrachloroethylene (Matheson Spec-

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(1) (a) A. Horowitz and L. A. Rajbenbach, *J. Amer. Chem. Soc.*, **91**, 4626 (1969); (b) *ibid.*, **91**, 4631 (1969); (c) *ibid.*, **92**, 1634 (1970).

(2) L. Schmerling and J. P. West, *ibid.*, 71, 2015 (1949).

(3) F. F. Rust and C. S. Bell, *ibid.*, **92**, 5530 (1970).

(4) D. D. Tanner, S. C. Lewis, and N. Wada, *ibid.*, **94**, 7034 (1972).

(5) A. Horowitz and L. A. Rajbenbach, *ibid.*, 90, 4105 (1968).

(6) T. J. Hardwick, *Int. J. Chem. Kinet.*, 1, 325 (1969).

(7) A. Horowitz and L. A. Rajbenbach, *J. Phys. Chem.*, 74, 678 (1970).

(8) M. G. Katz, A. Horowitz, and L. A. Rajbenbach, *Trans. Faraday Soc.*, 67, 2354 (1971).

(9) D. D. Tanner and T. N. Bunce, *J. Amer. Chem. Soc.*, **91**, 3028 (1969).

(10) A. Horowitz and L. A. Rajbenbach, Proceedings of Symposium on Large Radiation Sources for Industrial Processes, I.A.E.A., Vienna, 1969, p 21.