INTERNATIONAL JOURNAL OF CHEMICAL KINETICS, VOL. VIII, 563–572 (1976)

The Effect of Alkyl Group Substitution on the Rate of Thermal Isomerization of Small Ring Compounds

RICHARD K. SOLLY
School of Natural Resources, University of the South Pacific, Suva, Fiji
and
EDWARD N. CAIN
Research School of Chemistry, Australian National University, Canberra, A.C.T., 2600 Australia

Abstract

The thermal isomerization of 1-chloro-4-methylbicyclo[2.2.0]hexane and 1-chloro-4-ethylbicyclo[2.2.0]hexane has been studied in the gas phase and in tetrachloroethylene and *o*-dichlorobenzene solvents over the temperature range of 409–512°K. Good first-order kinetics yield the following Arrhenius equations: $\log k_g/(\mathrm{sec}^{-1}) = (13.86 \pm 0.03) - (36.90 \pm 0.07)/\Theta$; $\log k_a/(\mathrm{sec}^{-1}) = (13.55 \pm 0.31) - (35.50 \pm 0.13)/\Theta$; $\log k_b/(\mathrm{sec}^{-1}) = (13.55 \pm 0.15) - (35.87 \pm 0.06)/\Theta$ for the 4-methyl derivative, and $\log k_a/(\mathrm{sec}^{-1}) = (13.68 \pm 0.29) - (36.19 \pm 0.13)/\Theta$; $\log k_b/(\mathrm{sec}^{-1}) = (13.55 \pm 0.15) - (35.87 \pm 0.06)/\Theta$ for the 4-ethyl derivative. The subscripts g, a, and b refer to the gas phase, tetrachloroethylene, and *o*-dichlorobenzene as solvents, respectively, $\Theta = 2.303\ RT$ kcal/mole, and the error limits are least squares deviations. The activation energy is increased by 1.2 ± 0.5 kcal/mole for a methyl group and 1.5 ± 0.5 kcal/mole for an ethyl group with respect to the unsubstituted bridgehead compound. With reference to the reported Arrhenius parameters for all bicyclo[2.2.0]hexane isomerizations, it is shown that this increase in activation energy with alkyl substitution is not due to the steric interaction in the transition complex. It is postulated that the ground-state reactant bicyclo[2.2.0]hexane molecules are stabilized by alkyl substitution. This ground-state alkyl stabilization of small ring compounds may also account for an increase in the activation energy on pyrolysis of alkyl substituted cyclopropanes and cyclobutanes.

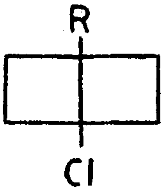
Introduction

The isomerization of small ring compounds has provided the basis of a large amount of experimental and theoretical studies. This has been stimulated by consideration of orbital symmetry requirements during possible concerted rearrangements [1]. All recent evidence would suggest that the thermal isomerization of cyclopropanes [2] and cyclobutanes [3] is predominantly nonconcerted. On the basis of a discrete biradical intermediate, O'Neal and Benson have shown that measured Arrhenius parameters for these isomerizations are in reasonable agreement with thermochemical analyses of these systems [4]. Using the biradical hypothesis, we have studied the effects of various 1,4-substituents in the bicyclo-[2.2.0]hexane system as a means of determining the radical stabilization energies of the substituents [15].

Recently the Arrhenius parameters for the thermal isomerization of 1-chloro-4-methylbicyclo[2.2.0]hexane and 1-chloro-4-ethylbicyclo[2.2.0]hexane were briefly reported [6]. These results were surprising, as the activation energy was increased on substitution of a methyl or ethyl group for a hydrogen atom. By simple analogy with alkanes, an alkyl group might be expected to reduce the activation energy by 3 kcal/mole compared to a hydrogen atom [7]. However, a decrease of this magnitude has not been found previously with alkyl substituted cyclopropanes or cyclobutanes. In their systematic treatment, O'Neal and Benson show how the discrepancy may be explained with a correction for *gauche* type interactions within the transition complex [4]. Cocks and Frey introduce a *trans* ring steric interaction in the transition complex for the ring opening of 1,1,3,3-tetramethylcyclobutane in order to explain the increase in activation energy compared to cyclobutane [8]. To complicate the issue further, Jones and Williamson [3] show how stabilization energies obtained in their bicylco[3.2.0]heptane system are consistent with other cyclobutane systems and question the range of the major method used for determining radical stabilization energies in [7].

The bicyclo[2.2.0]hexane system provides a further series of self-consistent thermochemical results for small ring isomerizations. In all cases, thermal isomerizations of 1,4-substituted compounds yield only one product at relatively low temperatures. As no internal rotations are gained or lost in forming the transition complex, a high degree of confidence may be placed in the interpretation of the Arrhenius parameters. In this paper we present the full kinetic parameters for the thermal isomerization of 1-chloro-4-methylbicyclo[2.2.0]hexane and 1-chloro-4-ethylbicyclo[2.2.0]hexane and show how the results cannot be interpreted in terms of previous postulates for the effect of alkyl group substitution.

Experimental



Synthesis

(a) *Preparation of 1-chloro-4-methylbicyclo[2.2.0]hexane ($R = CH_3$).* The mesylate $R = CH_2OMs$ (melting point 47°C, recrystallized hexane) of 1-chloro-4-hydroxymethylbicyclo[2.2.0]hexane [5] ($R = CH_2OH$) was prepared (90% yield) in the usual way by treatment of the alcohol (3.75 g) with mesyl chloride (8 ml) in dry pyridine (50 ml).

Analysis: Found—C, 42.7; H, 5.9; Cl, 15.8; S, 14.0. $C_8H_{13}O_3SCl$ requires C, 42.8; H, 5.8; Cl, 15.8; S, 14.3%.

The mesylate (3.8 g) was then reduced (60 hr; 20°C) with $LiAlH_4$ (1.1 g) in dry ether (90 ml). Standard workup procedure using aqueous NH_4Cl gave crude 1-chloro-4-methylbicyclo[2.2.0]hexane (R = CH_3) which was purified by distillation (20°C/0.5 mm) onto a cold finger maintained at −80°C to give the pure 4-methyl derivative as a colorless mobile liquid (1.69 g; 77%).

Analysis: Found—C, 64.5; H, 8.2; Cl, 27.9. $C_7H_{11}Cl$ requires C, 64.4; H, 8.5; Cl, 27.2%.

(b) *Preparation of 1-chloro-4-ethylbicyclo[2.2.0]hexane (R = C_2H_5),* The diazoketone (R = $COCHN_2$) of 1-chloro-4-carboxybicyclo[2.2.0]hexane (R = COOH) [5] was prepared in the usual way from the acid by treatment of the acid-chloride (R = COCl; oxalyl chloride) with excess diazomethane in ether (0°C). The diazoketone (2.6 g) was then placed in dry methanol (500 ml) and irradiated with a Hanovia 450-W lamp (Pyrex filter) in a standard immersion well until nitrogen evolution ceased (90 min; 310 ml N_2 evolved). Evaporation of the solvent and distillation of the residue (20°C/0.5 mm) onto a cold finger maintained at −80°C gave the pure methyl ester (R = CH_2CO_2Me) as a colorless sweet smelling mobile liquid (2.0 g; 74% overall yield from the acid, R = CO_2H). The ester (7.7 g) was then reduced to the alcohol (R = CH_2CH_2OH) in the standard way using $LiAlH_4$ (1.6 g) in dry ether (500 ml) at 0°C (4.25 hr). Treatment of the alcohol (6.0 g) with mesyl chloride (10 ml) in dry pyridine (50 ml) for 20 hr at 0°C in the standard way gave the mesylate (R = CH_2CH_2OMs) which was purified by recrystallization from hexane to give colorless white prisms (6.4 g; 64% overall yield from the ester, R = CH_2CO_2Me, melting point 55°C).

Analysis: Found—C, 45.3; H, 6.5. $C_9H_{15}O_3SCl$ requires C, 45.3; H, 6.3%.

Final conversion to 1-chloro-4-ethylbicyclo[2.2.0]hexane (R = C_2H_5) was then effected by treatment of the mesylate (R = CH_2CH_2OMs; 3.0 g) with $LiAlH_4$ (0.62 g) in dry ether (90 ml) at 20°C (65 hr). Standard workup procedure using aqueous NH_4Cl gave crude 1-chloro-4-ethylbicyclo[2.2.0]hexane (R = C_2H_5) which was readily purified by distillation (20°C/0.5 mm) onto a cold finger maintained at −80°C (1.41 g; 77%).

Analysis: Found—C, 66.6; H, 9.2; Cl, 24.7. $C_8H_{13}Cl$ requires C, 66.4; H, 9.1; Cl, 24.5%.

Apparatus

This has been described in detail previously [14]. Additional liquid thermostat baths for the increased temperature range used in this work for solution phase studies were provided by using *m*-xylene (137.4 ± 0.1°C), ethylene glycol (189.0 ± 0.1°C) and benzyl alcohol (202.5 ± 0.1°C) at reflux. Accurate temperatures were measured as previously described [14] using glass thermometers calibrated against a platinum resistance thermometer.

Procedure

This has been described in detail previously [14]. With both compounds under study in this work, analysis of the proportions of reactant and product in the solution phase studies was facilitated by the use of convenient build-in internal standards (methyl and ethyl resonances in the PMR spectra).

Results

In both gas and liquid phases the thermal isomerizations of both 1-chloro-4-methylbicyclo[2.2.0]hexane and 1-chloro-4-ethylbicyclo[2.2.0]hexane were shown to yield only a single product by PMR analysis and by gas chromatography (SE30 and Apiezon). The diene products were isolated in both cases by preparative gas chromatography (SE30) and both infrared and PMR spectra were in accord with the assigned structures. Elemental analysis of 2-chloro-5-methylhexa-1,5-diene gave C, 64.2; H, 8.5; Cl, 26.0. $C_7H_{11}Cl$ requires C, 64.4; H, 8.5; Cl, 27.2%. Elemental analysis of 2-chloro-5-ethylhexa-1,5-diene gave C, 67.0; H, 9.3; Cl, 24.1. $C_8H_{13}Cl$ requires C, 66.4; H, 9.1; Cl, 24.5%. Plots of the logarithm of percent undecomposed reactant against time for at least six different times were linear to more than 90% decomposition. Rate constants obtained graphically from these plots are shown in Table I.

For the majority of runs in the gas phase, an initial reactant pressure of 2 torr was used. However, variation of the initial reactant pressure from 0.8 to 6 torr did not produce any variation in percent decomposition for constant reaction time. Similarly, the addition of up to 300 torr of nitrogen produced no change in the rate of isomerization. Two reaction vessels were used for the gas-phase study, one having a surface-to-volume ratio eightfold that of the other. Rate constants measured in the packed vessel showed no deviation from an Arrhenius plot of those measured in an unpacked vessel. The data in Table I therefore almost certainly refer to a homogeneous first-order isomerization. The Arrhenius equations obtained by the method of least squares are given by $\log k_g/(\mathrm{sec}^{-1}) = (13.86 \pm 0.03) - (36.90 \pm 0.07)/\Theta$; $\log k_a/(\mathrm{sec}^{-1}) = (13.55 \pm 0.31) - (35.50 \pm 0.13)/\Theta$; $\log k_b/(\mathrm{sec}^{-1}) = (13.55 \pm 0.15) - (35.87 \pm 0.06)/\Theta$ for the 4-methyl derivative, and $\log k_a/(\mathrm{sec}^{-1}) = (13.68 \pm 0.29) - (36.19 \pm 0.13)\Theta$; $\log k_b/(\mathrm{sec}^{-1}) = (13.55 \pm 0.15) - (35.87 \pm 0.06)/\Theta$ for the 4-ethyl derivative. The subscripts *g*, *a*, and *b* refer to the gas phase, tetrachloroethylene and *o*-dichlorobenzene as solvents, respectively, $\Theta = 2.303\ RT$ kcal/mole, and the error limits are least squares deviations.

Discussion

The value of thermochemistry is that results obtained in one system may be used to quantitatively predict the rate of reaction of another system. If both the model and the experimental system were corrected to the same absolute standard,

TABLE I. Rate constants for the isomerization of 1-chloro-4-methylbicyclo[2.2.0]hexane.

Temp. (°C)	Gas Phase	Tetrachloroethylene	o-Dichlorobenzene
136.5		4.10×10^{-6}	4.00×10^{-6}
138.6	1.87×10^{-6}		
153.3	8.87×10^{-6}		
153.8		2.50×10^{-5}	2.45×10^{-5}
170.3	4.67×10^{-4}		
175.5		1.72×10^{-4}	1.71×10^{-4}
182.2	1.45×10^{-4}		
189.0		6.07×10^{-4}	6.06×10^{-4}
196.4	5.01×10^{-4}		
216.3	2.35×10^{-3}		
238.6	1.26×10^{-2}		
Rate constants for isomerization of 1-chloro-4-ethylbicyclo-[2.2.0]hexane.			
137.4		2.62×10^{-6}	2.88×10^{-6}
151.5	5.72×10^{-6}		
153.6		1.46×10^{-5}	1.58×10^{-5}
175.8		1.07×10^{-4}	1.20×10^{-4}
177.0	8.23×10^{-5}		
195.7	4.38×10^{-4}		
202.5		1.19×10^{-3}	1.22×10^{-3}

no approximations would be necessary. In the case of free radicals, absolute measurement of enthalpies is rarely possible. Practically all determinations are made in dynamic systems and relative enthalpy values are obtained. Widespread use has been made of iodine and bromine atom abstraction reactions to determine radical enthalpies [7]. The assumption is made that the activation energy for the back reaction of the radical with HI or HBr is small and constant for all radicals.

The thermal isomerization of small ring compounds has been extensively studied. Due to the decrease in stability associated with the ring (ring strain), these compounds generally isomerize cleanly to single (or relatively few) products at low temperature. In the case of saturated small rings, the experimental Arrhenius parameters may be used to derive radical enthalpies, provided the reaction proceeds through a radical centre, and a relevant reference reaction is known. The existence of a biradical as a "stable" intermediate has been questioned in recent papers [2,9]. All evidence suggests that saturated small ring isomerizations are predominantly nonconcerted. For our purposes, the exact nature of the transition complex is immaterial, *provided* a substantial degree of sp^2 character is developed in the transition complex.

The variation of the Arrhenius activation energy with 1,4-substituents and the phase is shown in Table II for a series of bicyclo[2.2.0]hexanes.

TABLE II. Variation of the Arrhenius activation energy[a] with 1,4-substituents and solvent.

1,4-Substituents	Gas Phase	Tetrachloroethylene	o-dichlorobenzene
Cl, H	35.4	34.5	34.6
Cl, Me	36.9	35.5	35.7
Cl, Et		36.2	35.9

[a] Units of kcal/mole.

As found previously [14], the activation energy in the gas phase is 1.0 ± 0.3 kcal/mole greater than in the liquid phase. The effect of substituting a methyl group for a hydrogen atom may also be compared for each of the three experimental conditions, the activation energy being increased by 1.5, 1.0, and 1.6 kcal/mole for the gas phase and tetrachloroethylene and *o*-dichlorobenzene as solvents, respectively. The mean value is 1.2 ± 0.3 kcal/mole. Similarly, substitution of an ethyl group for a hydrogen atom is shown to increase the activation energy by 1.5 ± 0.2 kcal/mole in the two solvents in which comparable measurements were made.

The Arrhenius parameters for all 1,4-substituted bicyclo[2.2.0]hexanes may now be considered. This comparison is simplified if only gas phase parameters are included. Where experimental gas phase values are not available, 1.0 kcal/mole has been added to the solution activation energy. The Arrhenius *A* factor has been shown to undergo no change from the gas phase to solution for the bicyclo[2.2.0]hexane system [6], and the values shown in Table III are the solution values in the few cases where experimental gas phase *A* factors are not available.

The mechanism that can be considered for the isomerization may be written as follows:

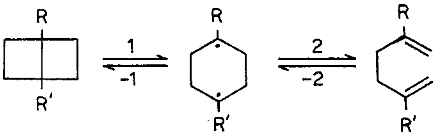
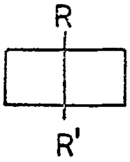


TABLE III. Gas phase Arrhenius parameters for the thermal isomerization of 1,4-substituted bicyclo[2.2.0]hexanes.



No.	R	R'	log A	E_a (kcal/mol)	Ref.
I	H	H	13.5	36.0	10
	H	H	13.5	36.2	11
	H	H	13.7	36.8	12
II	H	Cl	13.5	35.4	13
III	Cl	Cl	13.3	33.9	14
IV	Cl	Me	13.9	36.9	this work
V	Cl	Et	13.7	37.2	this work
VI	Me	Me	11.3	31.0	11
	Me	Me	14.0	37.0	see text
VII	Cl	CO_2Me	13.6	31.2	6
VIII	CO_2Me	CO_2Me	13.5	28.3	6,16
IX	Cl	CH_2OMe	14.1	37.2	17

Arguments for placing the transition complex either between bicyclo[2.2.0]hexane and the biradical or between the biradical and the hexa-1,5-diene have been considered previously [15]. Alternately, if the postulates of Doering and Sachdev [2] are extrapolated to the bicyclo[2.2.0]hexane system, the biradical itself is the transition complex. However, for our thermochemical discussion the actual position of the transition complex is immaterial, provided differences in experimental activation energies reflect differences in enthalpy between the reactant and a biradical-like transition complex. The calculations of O'Neal and Benson [4] support this postulate in the case of a biradical intermediate.

It is preferable to consider thermochemical parameters under standard conditions. For this it is necessary to convert experimental E_a values to 298°K. As the bicyclo[2.2.0]hexanes have $\Delta S^{\ddagger} \sim 0$, $\Delta C^{\ddagger}_p$ values are also ~ 0 and temperature corrections are insignificant [15]. To a good approximation, the experimental E_a values may be considered to be those at 298°K.

From Table III we may compare the activation energy for methyl group substitution at the bridgehead carbon relative to a hydrogen atom. A mean activation energy of 36.3 kcal/mole is calculated for the unsubstituted reference compound I. The activation energy for IV is increased by 1.5 kcal/mole relative to II. However, substitution of methyl groups for the two bridgehead positions reduces the activation energy by 5.3 kcal/mole, as seen from E_a (VI–I). The extraordinary low Arrhenius A factor reported for VI would suggest that the Arrhenius parameters are suspect. The only thermal isomerizations which have A factors of this magnitude are those in which a six-membered cyclic transition complex is formed from a linear ground-state molecule [18]. Using reasonable ground-state and transition complex frequency assignments as for RRKM type calculations [19], it is not possible to obtain an A factor less than $10^{13.0}$ for *any* type of mechanism for the thermal isomerization of VI. The experimental Arrhenius parameters are most likely in error. On the basis of the results in Table III, an A factor of $10^{14.0}$ would be more appropriate. The reported rate of reaction in the middle of the temperature range is much less likely to be in error. From this rate and the estimated A factor of $10^{14.0}$, an activation energy of 37.0 kcal/mole may be calculated for VI. This is 0.7 kcal/mole greater than the mean value of I. As *cis* type 1,4-methyl interaction in the ground state would be expected to decrease the activation energy by 1.0 kcal/mole [4], the intrinsic activation energy due to substitution of two methyl groups is increased by 1.7 kcal/mole. The value of 0.85 kcal/mole is in good agreement with that derived from II and IV.

This mean activation energy increase of 1.2 ± 0.3 kcal/mole per methyl group may be ascribed to increased steric interaction in the transition complex as the biradical is formed. This proposal has been put forward by Cocks and Frey to explain an increase in the activation energy for the thermal isomerization of 1,1,3,3-tetramethylcyclobutane [8]. Increased transannular interaction in the transition complex should be apparent in the Arrhenius parameters for the thermal isomerization of VIII, which has 1,4-CO_2Me groups as substituents.

As a reference point, the relative effect of a single CO_2Me group with respect to a hydrogen atom may be obtained by comparison of II and VII. The CO_2Me group is found to decrease the activation energy by 4.2 kcal/mole. Comparison of the activation energy for I and VIII yields a decrease of 8.0 kcal/mole for substitution of two CO_2Me groups. The agreement with the value derived from the substitution of a single CO_2Me group is excellent. It follows that the difference in 1,4-bridgehead interactions between the ground-state and transition complex molecules must be the same for both sets of comparisons (bridgehead H,Cl, and CO_2Me,Cl; H,H and, CO_2Me,CO_2Me). There is no evidence for any increased transition complex interaction in the comparison containing the two 1,4-CO_2Me substituents.

If the increase in activation energy for the thermal isomerization on substitution of an Me or Et group for a hydrogen atom is not a factor of relative transition state stabilities, the difference must be in relative ground-state (reactant) stabilities. It is postulated that alkyl bridgehead substitution in bicyclo[2.2.0]hexanes provides relative ground-state stabilization compared to a hydrogen atom. This may be considered as a reduction in ground-state ring strain energy due to an inductive decrease in ring bonding electron density. A variation of alkyl group stabilization with bonding electron density is seen in the comparison of the ΔH°_{f298} for the pairs [21] C_2H_6/C_3H_8, C_2H_4/C_3H_6, and C_2H_2/C_3H_4. The effect of methyl group substitution is seen as an increase in stability of 4.6, 7.6, and 10.1 kcal/mole, respectively, as the electron density increases from that for a single bond to a triple bond. It is likely that this alkyl stabilization is a factor in all small ring isomerizations to a degree which will depend upon the relative decrease in the ring strain.

We may consider the stabilization energy of the CO_2Me group compared to a Et group. A value of 6.0 kcal/mole is obtained from the difference in activation energies for compounds V and VII. This may be considered an "absolute" value, if relative reactant stabilities are the same and the energy difference between biradical and transition complex is the same for both the test and reference compounds. Neither of these premises may be proved or disproved at the current time. However, the stabilization energy derived in the bicyclo[2.2.0]hexane system may be compared with similar stabilization energies from other systems. Previously we compared the stabilization energy of the carbomethoxy group with that for the methylacetonyl group [15]. With an experimental value for the ethyl group now available, the stabilization energy of the carbomethoxy group is 6.0 ± 1.0 kcal/mole. This is now greater than the 2.7-kcal/mole resonance energy of the methylacetonyl group [22] and would appear to invalidate the discussion in the previous paper [15]. However, Jones and Williamson [3] have questioned the postulate upon which the value of 2.7 kcal/mole for the methylacetonyl radical is based. This requires that the back activation energy for the reaction of the radical with HI is the same for both the reference and the test radical. They find that a stabilization energy of 7.0 kcal/mole for the methylacetonyl group is consistent with their results obtained in the bicyclo[3.2.0]heptane system and previous values obtained from acyl substituted cyclobutane systems. The value of 6.0 kcal/mole for the carbomethoxy group is in agreement with this higher value for the methylacetonyl stabilization energy and also previous values for carboxyl substituted cyclobutanes [4]. The work of Jones and Williamson [3] has also shown that it is unlikely that acyl and carboxyl substituted cyclobutanes isomerize via a concerted mechanism as previously postulated to explain the discrepancy in resonance energies [15].

Conclusion

Methyl and ethyl group substitution at the bridgehead positions in bicyclo[2.2.0]hexane have been found to increase the activation energy by 1.2 ± 0.3

and 1.5 ± 0.2 kcal/mole, respectively, as compared to the isomerization of the unsubstituted compound. It has been shown that this is due to stabilization of the ground-state bicyclo[2.2.0]hexane reactant and not steric interaction in the transition complex.

The stabilization energy for the carbomethoxy group with reference to the ethyl group is 6.0 ± 1.0 kcal/mole. This is consistent with values derived from the Arrhenius parameters for the isomerization of analogous cyclobutane and bicyclo[3.2.0]heptane systems but not with values derived from iodine or bromine atom abstraction reactions. While the uncertainties are greater in the cyclic systems, in view of the self-consistency which is obtained across a number of compounds studied by several laboratories, the results obtained from the halogen atom abstraction reactions should be interpreted with caution.

Acknowledgment

Financial assistance to R. K. S. is gratefully acknowledged while a Visiting Fellow in the Research School of Chemistry, Australian National University.

Bibliography

[1] R. B. Woodward and R. Hoffman, *J. Amer. Chem. Soc.*, **87**, 395, 2511 (1965).
[2] W. von E. Doering and K. Sachdev, *J. Amer. Chem., Soc.*, **96**, 1168 (1974).
[3] G. Jones and M. H. Williamson, *J. Amer. Chem. Soc.*, **96**, 5617 (1974).
[4] H. E. O'Neal and S. W. Benson, *J. Phys. Chem.*, **72**, 1866 (1968).
[5] W. G. Dauben, J. L. Chitwood, and K. V. Scherer, *J. Amer. Chem. Soc.*, **90**, 1014 (1968).
[6] E. N. Cain and R. K. Solly, *J. Amer. Chem. Soc.*, **95**, 7884 (1973).
[7] H. E. O'Neal and S. W. Benson, in "Free Radicals," vol. II, J. K. Kochi, Ed., Wiley, New York, 1973, p. 275.
[8] A. T. Cocks and H. M. Frey, *J. Chem. Soc. (A)*, 1671 (1969).
[9] M. J. S. Dewar, S. Kirschner, H. W. Kollmar, and L. E. Wade, *J. Amer. Chem. Soc.*, **96**, 5242 (1974).
[10] C. Steel, R. Zand, P. Hurwitz, and S. G. Cohen, *J. Amer. Chem. Soc.*, **86**, 679 (1964).
[11] R. Srinivasan, *Int. J. Chem. Kinet.*, **1**, 133 (1969).
[12] M. J. Goldstein and M. S. Benzon, *J. Amer. Chem. Soc.*, **94**, 5119 (1972).
[13] E. N. Cain and R. K. Solly, to be published.
[14] E. N. Cain and R. K. Solly, *J. Amer. Chem. Soc.*, **94**, 3830 (1972).
[15] E. N. Cain and R. K. Solly, *J. Amer. Chem. Soc.*, **95**, 4791 (1973).
[16] D. C. Owsley and J. J. Bloomfield, *J. Org. Chem.*, **36**, 3768 (1971).
[17] E. N. Cain and R. K. Solly, *Aust. J. Chem.*, **25**, 1443 (1972).
[18] H. M. Frey and R. Walsh, *Chem. Rev.*, **69**, 103 (1969).
[19] D. M. Golden, R. K. Solly, and S. W. Benson, *J. Phys. Chem.*, **75**, 1333 (1971).
[20] N. C. Craig, L. G. Piper, and V. L. Wheeler, *J. Phys. Chem.*, **75**, 1453 (1971).
[21] American Petroleum Institute, "Selected Values of Hydrocarbons and Related Compounds."
[22] R. K. Solly, D. M. Golden, and S. W. Benson, *Int. J. Chem. Kinet.*, **2**, 381 (1970).

Received March 3, 1975
Revised December 3, 1975