(21) J. A. Ibers, J. W. Lather, and R. G. Little, *Acta Crystallogr.*, **30**, 268 (1974).
(22) W. R. Scheidt and J. L. Hoard, *J. Am. Chem. Soc.*, **95**, 8281 (1973).
(23) W. R. Scheidt, J. A. Cunningham, and J. L. Hoard, *J. Am. Chem. Soc.*, **95**, 8289 (1973).
(24) R. D. Barnard, *J. Gen. Physiol.*, **16**, 657 (1933).
(25) A. C. Anunsien, J. G. Beetlestone, and D. H. Irvine, *J. Chem. Soc. A*, 357 (1966); 960 (1968).
(26) J. G. Beetlestone, A. A. Epega, and D. H. Irvine, *J. Chem. Soc. A*, 1346 (1968).
(27) J. E. Bailey, J. G. Beetlestone, and D. H. Irvine, *J. Chem. Soc. A*, 2778 (1968).
(28) H. F. Epstein and L. Stryer, *J. Mol. Biol.*, **32**, 113 (1968).
(29) Q. H. Gibson, L. J. Parkhurst, and G. Geraci, *J. Biol. Chem.*, **244**, 4668 (1969).
(30) R. T. M. Fraser and H. Taube, *J. Am. Chem. Soc.*, **81**, 5000, 5514 (1959).
(31) J. P. Candlin and J. Halpern, *J. Am. Chem. Soc.*, **85**, 2518 (1963).

Reversible Reactions of Gaseous Ions. IX. The Stability of C_4–C_7 Tertiary Alkyl Carbonium Ions

J. J. Solomon and F. H. Field*

Contribution from The Rockefeller University, New York, New York 10021.
Received June 25, 1974

Abstract: The hydride transfer equilibria $t\text{-}C_4H_9^+ + RH \rightleftharpoons R^+ + i\text{-}C_4H_{10}$ where R^+ = 2-methylpentyl ion (2-MP$^+$), 3-MP$^+$, 2,3-DMB$^+$, and 2,4-DMP$^+$ have been investigated by pulsed electron beam high pressure mass spectrometry. The equilibrium constants for the reactions and the temperature coefficients of the equilibrium constants over the range 334–610°K have been used to establish a network of thermodynamic quantities for the reactions. The ionic enthalpies determined (relative to $\Delta H_f°$ (*tert*-butyl) = 169.1 kcal/mol as standard) are believed to be accurate to 0.2 kcal/mol with $\Delta H_f°$(2-MP$^+$) = 155.6, $\Delta H_f°$(3-MP$^+$) = 155.3, $\Delta H_f°$(2,3-DMB$^+$) = 153.2, and $\Delta H_f°$(2,4-DMP$^+$) = 134.9 kcal/mol. Trends in stability have been related to structural and ionic factors. The entropies for the reactions of *tert*-butyl ion with the three isomeric tertiary hexanes (2-MP, 3-MP, and 2,3-DMB) vary between 0 and +2 eu. The entropy change of −29.4 eu for the reaction of *tert*-butyl ion with 2,4-DMP suggests that the $C_7H_{15}^+$ ion formed in this reaction is a highly constrained species.

We recently[1] reported an investigation of hydride transfer equilibrium in the $t\text{-}C_4H_9^+$ ($i\text{-}C_5H_{12}$, $i\text{-}C_4H_{10}$) $t\text{-}C_5H_{11}^+$ system using the technique of pulsed electron beam high pressure mass spectrometry. Equilibrium constants, free energies, enthalpies, and entropies were determined for the reaction

$$t\text{-}C_4H_9^+ + i\text{-}C_5H_{12} \rightleftharpoons t\text{-}C_5H_{11}^+ + i\text{-}C_4H_{10} \qquad (1)$$

In the present study we report the results of our investigations of the hydride transfer reactions of *tert*-butyl ions with the three isomeric tertiary hexanes, namely

$$t\text{-}C_4H_9^+ + \text{2-MP}^{2} \rightleftharpoons \text{2-MP}^+ + i\text{-}C_4H_{10} \qquad (2)$$

$$t\text{-}C_4H_9^+ + \text{3-MP} \rightleftharpoons \text{3-MP}^+ + i\text{-}C_4H_{10} \qquad (3)$$

$$t\text{-}C_4H_9^+ + \text{2,3-DMB} \rightleftharpoons \text{2,3-DMB}^+ + i\text{-}C_4H_{10} \qquad (4)$$

and our investigation of the hydride transfer equilibrium occurring between *tert*-butyl ions and a tertiary heptane

$$t\text{-}C_4H_9^+ + \text{2,4-DMP} \rightleftharpoons C_7H_{15}^+ + i\text{-}C_4H_{10} \qquad (5)$$

These investigations are being undertaken to establish a network of relative thermodynamic quantities for gaseous carbonium ions. Obtaining accurate thermochemical values will permit the evaluation of the effects of structural variations upon intrinsic carbonium ion stabilities.

Experimental Section

These measurements were made on the Rockefeller Chemical Physics mass spectrometer operated in the pulsed electron beam mode of ionization. The apparatus and experimental technique were identical with those described previously,[1,3,4] except that here the instrument was operated under field-free conditions with the repeller maintained at ion chamber potential. Gas from a mixture of known composition ($i\text{-}C_4H_{10}$/*tert*-alkane) was admitted into the ion source. The ion intensities of the *tert*-butyl ion (*m/e* 57) and the tertiary alkyl ions were monitored at variable reaction times at constant temperatures and pressures. The source pressure was adjusted at each temperature to keep the total number density constant ($N_T \simeq 4.0 \times 10^{16}$ molecules/cm^3). A typical pulsing sequence consisted of the 600 eV electron beam pulsing on for 100 μsec initiating ion production. Ions leaving the source are defocused except for the duration of the ion focus pulse, typically 100 μsec, which occurred at variable delay times (200–800 μsec) after the electron beam "on" pulse.

The reagents used were Matheson Instrument grade (99.5%) isobutane, Matheson Coleman and Bell Chromatoquality grade (99+ mol %) 2-MP, 3-MP, and 2,4-DMP, and K & K 2,3-DMB. Purities were checked by gas chromatography and found to be better than 99%.

Results and Discussion

The equilibrium constant for a general hydride transfer reaction $R_1^+ + R_2H \rightleftharpoons R_2^+ + R_1H$ is given by

$$K = \frac{[R_2^+]}{[R_1^+]}\frac{[R_1H]}{[R_2H]} = \left(\frac{I_{R_2^+}}{I_{R_1^+}}\right)_{eq} \frac{P_{R_1H}}{P_{R_2H}} \qquad (6)$$

We can examine the approach to equilibrium by measuring the ion intensity ratio ($I_{R_2^+}/I_{R_1^+}$) as a function of reaction time. In Figure 1 we show a sample plot of the apparent equilibrium constant, $K_a = (I_{99}/I_{57})(P_{i\text{-}C_4H_{10}}/P_{2,4\text{-DMP}})$ vs. reaction time for reaction 5. K_a initially rises and begins to level off above 300 μsec. Equilibrium has been achieved in the time independent region of K_a. Analogous plots were obtained for reactions 2–4 at several temperatures. van't Hoff plots were constructed from the values of the equilibrium constants in the plateau regions of the plots of K_a vs. reaction time. A typical van't Hoff plot obtained in this manner for one of the (*tert*-butyl, *tert*-hexyl) equilibria is shown in Figure 2 (upper). The temperature and pressure regimes employed for the (C_4, C_6) equilibria studies are 334–610°K and 1.4–2.5 Torr, respectively.

In our previous[1] experiments with the pulsed ionization high pressure technique we found that thermodynamic parameters obtained for reaction 1 by the continuous ioniza-

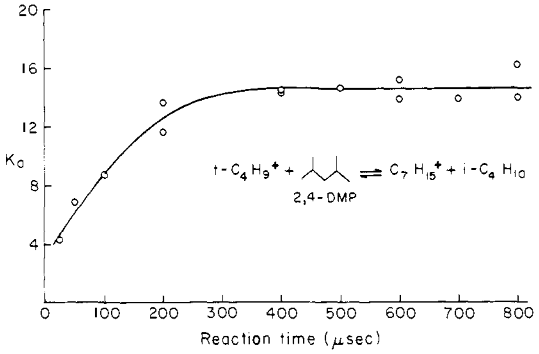


Figure 1. The apparent equilibrium constant vs. reaction time for reaction 5: $T = 521°K$, $P = 2.2$ Torr, $i\text{-}C_4H_{10}/2,4\text{-DMP} = 21.87$.

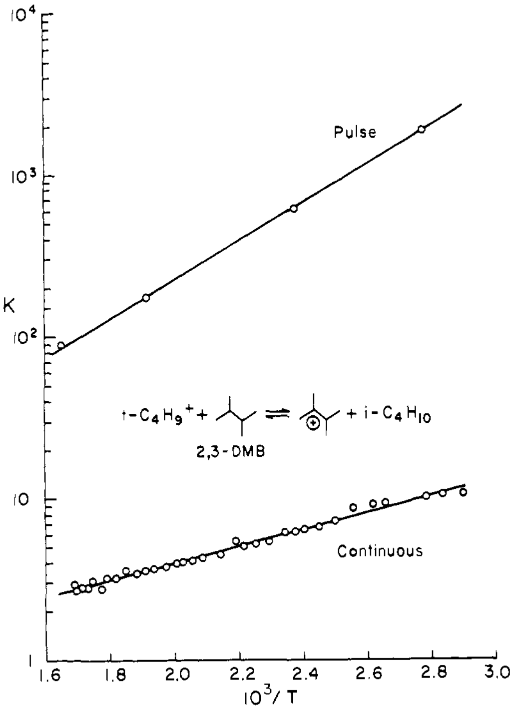


Figure 2. Comparison of van't Hoff plots for reaction 4: pulse technique (upper), continuous technique (lower).

tion method and by the pulse ionization method were in excellent agreement. However, when we compare continuous ionization and pulse ionization van't Hoff plots in the (C_4, C_6) reaction systems, we observe large discrepancies. In Figure 2 we show such a discrepancy for the $t\text{-}C_4H_9^+$ (2,3-DMB, $i\text{-}C_4H_{10}$) 2,3-DMB$^+$ reaction system. The upper portion shows the pulsed ionization van't Hoff plot as was mentioned above. The continuous experiment shown in the bottom portion was done at 2 Torr source pressure at an E/P of 5 V/(cm Torr) for a mixture of 5.05% 2,3-DMB in isobutane over the temperature range 345-592°K. We calculate using the complete Langevin treatment[5] that under the continuous ionization experimental conditions (at $T = 470°K$, $N_T = 4.1 \times 10^{16}$ mol/cm^3) *tert*-butyl ions in isobutane have a residence time of ~30 μsec. Our pulse experiments on this system, which were done at a comparable number density, indicate that an ionic residence time of 400-600 μsec is required for the establishment of equilibrium. Therefore, linear van't Hoff plots obtained in the continuous ionization mode do not necessarily indicate that equilibrium has been established. Accordingly, all thermodynamic parameters reported in this paper have been obtained from the least-squares lines of the van't Hoff plots obtained by the pulsed ionization technique. The experimental thermodynamic values deduced from the van't Hoff plots for the reactions of *tert*-butyl ions with the three isomeric tertiary hexanes are given in Table I.

Table I. Experimental Thermodynamic Values for $t\text{-}C_4H_9^+ + t\text{-}C_6H_{14} \rightleftharpoons t\text{-}C_6H_{13}^+ + i\text{-}C_4H_{10}$

$t\text{-}C_6H_{14}$	$\Delta G°_{300}$, kcal/mol	$\Delta H°$, kcal/mol	$\Delta S°$, eu
2-MP	−4.3	−3.8	+1.6
3-MP	−4.9	−4.8	−0.3
2,3-DMB	−5.4	−5.4	−0.1

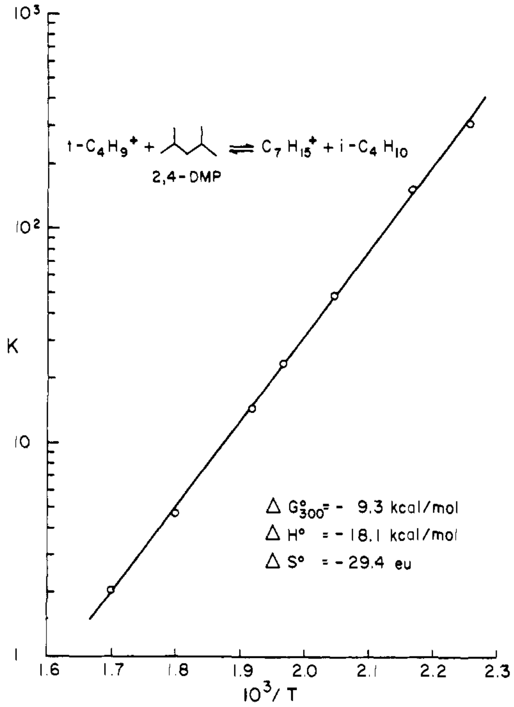
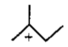
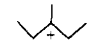
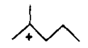
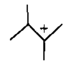


Figure 3. van't Hoff plot for reaction 5.

The thermodynamic quantities $\Delta G°_{300}$ and $\Delta H°$ obtained using this procedure are believed to be accurate to at least 0.2 kcal/mol. There is little difference between the experimental $\Delta G°_{300}$ and $\Delta H°$ values obtained for each of the (C_4, C_6) equilibria, with the largest difference of 0.5 kcal/mol occurring in the $t\text{-}C_4H_9^+$ (2-MP, $i\text{-}C_4H_{10}$) 2-MP$^+$ reaction system. This small difference ($\Delta G° \approx \Delta H°$) implies that $\Delta S°$ is small, as would be expected for hydride transfer between very similar ionic species (tertiary alkyl carbonium ions). The experimental $\Delta S°$ values vary between 0 and 2 eu with an estimated error of ± 1 eu.

In Figure 3 we show the van't Hoff plot obtained for reaction 5. The thermodynamic results obtained for this system, $t\text{-}C_4H_9^+$ (2,4-DMP, $i\text{-}C_4H_{10}$) $C_7H_{15}^+$ are: $\Delta H° = -18.1$ kcal/mol, $\Delta G°_{300} = -9.3$ kcal/mol, and $\Delta S° = -29.4$ eu. These results are very different from the thermodynamic quantities obtained in either the (C_4, C_5) or (C_4, C_6) equilibria. We were initially concerned with the unexpectedly large negative $\Delta S°$ and $\Delta H°$ values, and consequently many experimental points were taken over the temperature range 443-589°K. The thermodynamic parameters we obtained strongly suggest that a very stable, highly constrained $C_7H_{15}^+$ ionic species is formed in this reaction. The appreciable negative entropy change for this reaction leads to the possibility that the $C_7H_{15}^+$ ion is cyclic. Possible cyclic structures for this constrained species include the formation of the 2,4 C-C bond which would produce protonated 1,1,2,2-tetramethylcyclopropane or alternatively 1,5 C-C bond formation resulting in the formation of protonated 1,3-dimethylcyclopentane. Other cyclic structures can result from the formation of intramolecular hydrogen bonds or the existence of a nonclassical carbonium ion. We

Table II. Heats of Formation of Tertiary Alkyl Carbonium Ions and Parent Hydrocarbons

RH	$\Delta H_f°(\mathrm{RH})^a$	R^+	$\Delta H_f°(\mathrm{R}^+)$
i-C_4H_{10}	−32.07		169.1[b]
i-C_5H_{12}	−36.73		161.1
3-MP	−41.11		155.3
2-MP	−41.75		155.6
2,3-DMB	−42.59		153.2
2,4-DMP	−48.20	$C_7H_{15}^+$	134.9

[a] Heats of formation of neutrals are taken from D. W. Scott, *J. Chem. Phys.*, 60, 3144 (1974), and are accurate to 0.14–0.29 kcal/mol. [b] Arbitrary standard. Nonequilibrium value obtained from IP of C_4H_9, radical, ref 7.

have tested for the possibility that the $C_7H_{15}^+$ ion is protonated tetramethylcyclopropane. To do this we have obtained some 1,1,2,2-tetramethylcyclopropane and have conducted proton affinity experiments. We have established that 195 = PA(i-C_4H_8) < PA(tetramethylcyclopropane) < PA(NH_3) = 207 kcal/mol. Based on these measurements, the heat of formation of protonated tetramethylcyclopropane is 145 ± 6 kcal/mol[6] which does not correspond well to the $C_7H_{15}^+$ ion ($\Delta H_f° = 134.9$ kcal/mol, see Table II) formed in reaction 5.

In Table II we list the heats of formation of tertiary alkyl carbonium ions and their parent hydrocarbons. The *tert*-butyl ion is our starting reference point, and we have taken for it a heat of formation of 169.1 kcal/mol.[7] Using *tert*-butyl ion as standard and the known heats of formation of the neutrals, we have calculated the heats of formation of the various carbonium ions from the experimentally determined enthalpies of reactions 1–5. The relative ionic heats of formation are believed to be accurate to 0.2 kcal/mol neglecting any uncertainty associated with the neutral heats of formation. The difference of only 0.3 kcal/mol in our experimental heats of formation for 2-MP$^+$ and 3-MP$^+$ is within experimental error, and thus the two hexyl isomers appear to have effectively identical stabilities. However, there is an experimentally significant difference between the heats of formation of the ion formed from 2,3-DMB and those from 2-MP and 3-MP. This constitutes evidence that the ions formed from isomeric hexanes have different structures, i.e., isomerization to a common structure does not occur.

NMR solution experiments of Olah[8] and Brouwer[9] on *tert*-hexyl cations prepared in highly acidic media demonstrate that *tert*-hexyl cations rearrange rapidly to equilibrium mixtures of the isomeric ions. It was deduced from the NMR spectra (−20°) that the equilibrium mixture contained approximately equal amounts of the three ions, and it was concluded that not much difference exists in the stabilities of the isomeric *tert*-hexyl ions. Our experimental finding is that there is a difference of ~2 kcal/mol in the heats of formation of the ion formed from 2,3-DMB and the heats of formation of the ions formed from either 2-MP or 3-MP. Making the reasonable assumption that $\Delta(\Delta H_f°) \approx \Delta(\Delta G_f°)$, this energy difference would correspond to an equilibrium mixture (−20°) wherein the 2,3-DMB would be present at about 50 times the concentration of the ions formed from 2-MP or 3-MP. A possible explanation for the difference between the gas phase and the NMR solution results is that the solvation of ions in condensed phase provides a leveling effect on the ion energies.

In order to compare properly the stabilities of the carbonium ions listed in Table II we must first compare the stabilities of the neutral alkanes. The difference in stability of homologous alkanes which differ by one CH_2 group is ~5 kcal/mol. We shall refer to this stabilization as the skeletal stabilization. The addition of a CH_2 group in alkyl ions has a larger stabilizing effect than in neutrals. For example, introduction of a methylene group into *tert*-butyl ion to form *tert*-pentyl ion involves a greater lowering (8.0 kcal/mol) than the lowering of the heat of formation when a methylene group is added to isobutane to give isopentane (skeletal stabilization = 4.7 kcal/mol). This extra ionic stabilization (3.3 kcal/mol) can be accounted for by a charge stabilization mechanism based on the polarizability of the alkyl substituent. In Figure 4 we show the difference in the heats of formation of the ions we have investigated. Here we have separated the skeletal and ionic (underlined) contributions to the heats of formation of the ions.

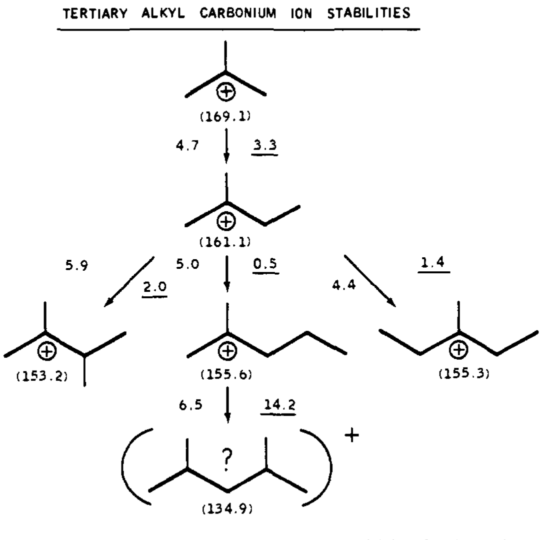


Figure 4. Tertiary alkyl carbonium ion stabilities broken down into skeletal and ionic (underlined) factors.

In comparing the stabilities of C_5 and C_6 ionic species we note that the addition of a methylene group α to the charged carbon is more effective in stabilizing the charge (2.0 and 1.4 kcal/mol ionic stabilization in 2,3-DMB$^+$ and 3-MP$^+$, respectively) than the addition of a methylene group β to the charged carbon (only 0.5 kcal/mol ionic stabilization in 2-MP$^+$). We also find that for α-(CH_2) ionic stabilization, the first CH_2 group added is the most effective, with the next one more effective when added to the same carbon atom as the first. (For example, compare the ionic contributions to the heats of formation of t-$C_4H_9^+$, t-$C_5H_{11}^+$, 2,3-DMB$^+$, and 3-MP$^+$.)

The above considerations apply to the C_4–C_6 ionic species. Our thermodynamic data on the t-$C_4H_9^+$ (2,4-DMP, i-C_4H_{10}) $C_7H_{15}^+$ system show that there is a sharp discontinuity in energy and entropy between this system and the (C_4, C_5) and (C_4, C_6) reaction systems. As a result we find that in comparing the stability of 2-MP$^+$ and 2,4-DMP$^+$ the addition of the CH_2 group β to the charge in 2-MP$^+$ results in a 14.2 kcal/mol ionic stabilization. This may be looked upon as another manifestation of the fact that the $C_7H_{15}^+$ species formed in reaction 5 does not have the properties associated with conventional branched tertiary alkyl carbonium ions.

Acknowledgement. This research was supported in part by a grant from the National Science Foundation.

References and Notes

(1) J. J. Solomon, M. Meot-Ner, and F. H. Field, *J. Am. Chem. Soc.*, 96, 3727 (1974).
(2) Throughout the paper we use the abbreviations 2-MP = 2-methylpen-

tane, 3-MP = 3-methylpentane, 2,3-DMB = 2,3-dimethylbutane, 2,4-DMP = 2,4-dimethylpentane.
(3) S. L. Bennett and F. H. Field, *J. Am. Chem. Soc.*, **94,** 5188 (1972).
(4) D. P. Beggs and F. H. Field, *J. Am. Chem. Soc.*, **93,** 1567 (1971).
(5) E. W. McDaniel, "Collision Phenomena in Ionized Gases", Wiley-Interscience, New York, N.Y., 1964, Chapter 9.
(6) Calculated using $\Delta H_f°$ (tetramethylcyclopropane) = −19.6 kcal/mol obtained by the method of group equivalents: J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.*, **No. 26,** 45 (1969).
(7) The heat of formation of *tert*-butyl ion was obtained by an electron impact measurement of the ionization potential of *tert*-butyl radical: F. P. Lossing and G. P. Semeluk, *Can. J. Chem.*, **48,** 955 (1970).
(8) G. A. Olah and C. U. Pittman, *Adv. Phys. Org. Chem.*, **4,** 305 (1966).
(9) D. M. Brouwer, *Recl. Trav. Chim. Pays-Bas*, **87,** 210 (1968); D. M. Brouwer and H. Hogeveen, *Prog. Phys. Org. Chem.*, **9,** 179 (1972).

Calculation of Dihedral Angles from Vicinal Proton Coupling Constants and Substituent Electronegativities

T. P. Forrest

Contribution from the Chemistry Department, Dalhousie University, Halifax, Nova Scotia, Canada.
Received June 1, 1974

Abstract: A method is presented for the calculation of proton dihedral angles from vicinal coupling constants and electronegativities of substituents. Results for several examples of conformationally mobile systems are compared to results obtained by the *R*-value method of calculating dihedral angles. Other examples of compounds to which the *R*-value method cannot be applied are given and the values of dihedral angles obtained from this method are compared to those obtained by empirical valence-force minimization calculations.

Dihedral angles have frequently been estimated from vicinal proton coupling constants by means of a Karplus[1] relationship, in spite of the problems inherent in this type of calculation.[2] In a Karplus equation, (1) for example, the

$$J = A \cos^2 \phi - B \cos \phi + C \qquad (1)$$

constants *A*, *B*, and *C* may vary considerably from compound to compound and difficulties arise in the selection of appropriate values of these constants.

One of the major factors which can alter the values of these constants is the electronegativity of the substituents on the atoms to which the coupled protons are bonded. Alteration of the constants in order to take into account the effect of the electronegativity of substituents does not appear to be completely satisfactory since the effect of an electronegative substituent is also angle dependent, being greatest when the substituent is antiperiplanar to a coupled proton.[3]

Buys[4] has developed a method of calculating dihedral angles, which attempts to compensate for other factors influencing the coupling constant, by quantification of Lambert's[5] *R*-value method of detecting distortion in cyclic systems. In this method the ratio, *R*, of $J_{\rm trans}$ to $J_{\rm cis}$ is determined and the dihedral angle, $\phi_{\rm ae}$, is calculated from eq 2.

$$\cos \phi_{\rm ae} = [3/(4R + 2)]^{1/2} \qquad (2)$$

The *R* value may be obtained only for compounds having one of the specific structural types listed by Lambert:[6] (i) a CH_2CH_2 or CH_2CHR group in a molecule with two rapidly equilibrating equivalent conformers, (ii) a CH_2CH_2 group in a completely rigid molecule, or (iii) a $CHRCH_2CHR'$ group in a completely rigid molecule with R and R′ trans to each other.

In this paper we wish to report a method of calculating dihedral angles which may be applied to these systems as well as other ring systems which cannot be analyzed by the *R*-value method. In the present study we have used a method[7] for estimating gauche coupling constants in ethane fragments, based on a correlation between coupling constants and electronegativity of substituents as well as their orientation relative to the coupled protons. The expected value of a gauche coupling constant of two protons with a dihedral angle of 60° is calculated from eq 3, where ΔX is

$$J = (4.1 + 0.63\Sigma\Delta X)(1 - 0.462\Delta X_1)(1 - 0.462\Delta X_2) \qquad (3)$$

the electronegativity[8] difference between the substituent and hydrogen, $\Sigma\Delta X$ is the sum of ΔX's of all substituents on the ethane framework, and ΔX_1 and ΔX_2 are the ΔX's of the two substituents antiperiplanar to the coupled protons.

The calculated coupling constant is then compared to the observed coupling constant and the difference taken to indicate a divergence of the dihedral angle from normal. The method of calculation of the dihedral angle is illustrated below for the example 1,4-dioxane. The expected value of $J_{\rm ae}$ is calculated from eq 3 to be 2.06 Hz, whereas the observed[5] value, $J_{\rm cis}$, is 2.78 Hz. From the calculated value of $J_{\rm ae}$ and eq 4, a value for *A* is determined.

$$J_{\rm calcd} = A \cos^2 60 - 0.3 \qquad (4)$$

This calculated value of the constant *A* (10.4 in this case) is then used with the observed coupling constant (eq 5) to cal-

$$\cos \phi_{\rm ae} = [(J_{\rm obsd} + 0.3)/A]^{1/2} \qquad (5)$$

culate a value for the dihedral angle $\phi_{\rm ae}$.

The calculated values of $\phi_{\rm ae}$ for a series of conformationally mobile compounds are given in Table I and are compared with the values of $\phi_{\rm ae}$ calculated by the ratio method of Buys.[4] It can readily be seen that the two methods are compatible, the results obtained in each case being remarkably close.

For those compounds in Table I where X and Y (Figure 1) are different, the observed $J_{\rm cis}$ will be the average of two different gauche coupling constants, $J_{\rm 2a3e}$ and $J_{\rm 3a2e}$. In order to calculate $\phi_{\rm ae}$ in these cases the two dihedral angles, $\phi_{\rm 2a3e}$ and $\phi_{\rm 3a2e}$, are assumed to be the same (as was assumed in the calculations by the ratio method[4]) and the average of $J_{\rm 2a3e}$ and $J_{\rm 3a2e}$ is used to calculate a value for *A*.

Having obtained good agreement of the results from this method with those of the ratio method, dihedral angles which could not be determined by the ratio method were