and the chloroform was removed to give an oil which had single absorption at 307 mμ (lit.[6] 308 mμ). The carbonyl absorption at 1666 cm^{-1} in mazdasantonin had been shifted to 1670 cm^{-1} in chloroform.

The dinitrophenylhydrazone prepared as above was recrystallized from chloroform–ethanol to give plates, mp 255°. A mixture melting point with a sample provided by Professor Chapman was not depressed and the infrared spectra of the two derivatives were superimposable.[7]

Compound A. Lumisantonin (502 mg) was heated in a sealed degassed ampoule at 200° (Wood's metal bath) for 1 hr. Liquid–liquid partition chromatography of the resulting oil led to recovery of 334 mg (67%) of lumisantonin and yielded 172 mg (33%) of impure A.

Compound A was also obtained directly from photolysis mixtures of santonin or lumisantonin after irradiations for 6–20 hr by liquid–liquid partition chromatography generally in 5–10% yield based on the amount of santonin or lumisantonin which had reacted. The product is a colorless oil which could be induced to crystallize: $\lambda_{max}^{C_2H_5OH}$ 299 mμ; $\nu_{max}^{liq\ film}$ 1783 and 1753 cm^{-1}; $\nu_{max}^{CHCl_3}$ 1781 and 1755 (strong), 1638 cm^{-1} (weak). An analysis of A was not obtained.

When A was passed through alumina (Woelm, neutral grade II), it was converted to pyrolumisantonin which showed absorptions at 1779 and 1716 cm^{-1} in a potassium bromide pellet (lit.[14] 1770 and 1705 cm^{-1} in KBr). Catalytic hydrogenation over platinum of either A or pyrolumisantonin gave the same products with superimposable infrared spectra and major peaks at 1770 and 1735 cm^{-1} in potassium bromide (lit.[14] 1770 and 1730 cm^{-1}).

Compound B was isolated in yields of 1–3% from irradiations of 3–20-hr duration of santonin or lumisantonin as described above for mazdasantonin. After isolation by liquid–liquid partition chromatography, B was recrystallized from acetone–hexane to give colorless prisms: mp 174.4–175.0°; $\lambda_{max}^{C_2H_5OH}$ 244 mμ (log ε 3.67) and 338 (2.01); $\nu_{max}^{KBr\ pellet}$ 1791 and 1697 cm^{-1}. The mass spectrum showed a parent peak at *m/e* 246 ± 1, but the substance did not give an analysis for $C_{15}H_{18}O_3$, but repeated analyses (of the same material which gave a parent peak at *m/e* 246 ± 1) were more in accord with $C_{15}H_{18}O_4$ or $C_{15}H_{20}O_4$.

Anal. Calcd for $C_{15}H_{18}O_3$: C, 73.77; H, 7.32. Calcd for $C_{15}H_{18}O_4$: C, 68.70; H, 6.87. Calcd for $C_{15}H_{20}O_4$: C, 68.18; H, 7.58. Found: C, 68.83; H, 6.95.

Hydrogenation of B over platinum yielded a derivative which had $\nu_{max}^{CHCl_3}$ 1776 and 1715 cm^{-1}.

Compound C. Another substance, C, was also isolated in 1–3% yield by liquid–liquid partition chromatography of the products from irradiation of santonin or lumisantonin as described above. Compound C was a colorless oil which was easily oxidized by air to a yellow-green viscous material; C was also unstable even in the dark under nitrogen. The shape of the ultraviolet spectrum was very like the spectrum of B and lumisantonin and showed a maximum at 237 mμ in ethanol: $\nu_{max}^{CCl_4}$ 1803 and 1700 cm^{-1}; $\nu_{max}^{CHCl_3}$ 1777 and 1715 cm^{-1}. Catalytic hydrogenation over platinum produced a product which had $\nu_{max}^{CHCl_3}$ 1773 and 1714 cm^{-1}. The instability of C and the small amounts available precluded further, more definitive characterization of the substance.

Irradiation of Compound B. Fractions D and E. Irradiation of compound B in benzene solution under conditions used previously until the starting material is completely gone yields a mixture which can be separated by vpc into two fractions, D and E, in the ratio 4:1. Both D and E are oils. The infrared spectra of these are analogous to those of compound A and mazdasantonin, respectively. The ketonic carbonyl absorption of E however falls at 1685 cm^{-1} in chloroform.

Fraction F. The last material to be obtained from partition chromatography of mixtures from irradiation of santonin, lumisantonin, or mazdasantonin was F, the amount of which is a function of the concentration of the precursor. For example, at a concentration of about 10^{-2} *M* mazdasantonin, fraction F accounted for almost 25% of the photoproducts, whereas at a concentration of about 10^{-3} *M* mazdasantonin, fraction F was 6% of the products. Further purification was unsuccessful, the material could not be eluted from alumina (even the least active), and sublimation at 10^{-4} mm at 200° led only to decomposition. Fraction F has $\nu_{max}^{CHCl_3}$ 1778 and 1718 cm^{-1}; after hydrogenation in ethyl acetate over platinum (Parr apparatus) the product has $\nu_{max}^{CHCl_3}$ 1781 (broad), 1730, and 1720 cm^{-1}.

A Cyclobutadiene Cation Radical in the Mass Spectrometer. The *p*-Fluoro Substituent as a Label for the Study of Mass Spectral Reactions

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Contribution from the Venable Chemical Laboratory, The University of North Carolina, Chapel Hill, North Carolina 27514. *Received November 14, 1967*

Abstract: The $(M - CO)\cdot^+$ ion in the spectrum of a tetracyclone is shown to have a closed structure, and therefore is a rectangular cyclobutadiene radical cation or possibly its tetrahedrane counterpart. A new general labeling technique is employed to obtain this result.

Several papers have now examined the effects of substituents on mass spectral reactions.[1-4] Some substituents rearrange after electron impact, as, for example, the nitro group,[1c,5] or promote ring expansion, as does the methyl group.[6] Most substituents cause appreciable variation in the intensities of product ions; if the product does not retain the substituent, it is often true that electronic effects similar to those observed in solution regulate intensities.[1a] So, for example, strongly electron-withdrawing substituents greatly decrease product intensities, while electron-releasing substituents enhance them; a product competing with a dimethylamino-substituted ring for the charge will almost never be a major

(1) (a) M. M. Bursey and F. W. McLafferty, *J. Am. Chem. Soc.*, **88**, 529 (1966); (b) *ibid.*, **88**, 4484 (1966); (c) *ibid.*, **88**, 5023 (1966); (d) *ibid.*, **89**, 1 (1967); (e) F. W. McLafferty, M. M. Bursey, and S. M. Kimball, *ibid.*, **88**, 5022 (1966); (f) F. W. McLafferty and M. M. Bursey, *Chem. Commun.*, 533 (1967); (g) *J. Org. Chem.*, **33**, 124 (1968); (h) M. M. Bursey and L. R. Dusold, *Chem. Commun.*, 712 (1967); (i) F. W. McLafferty and T. Wachs, *J. Am. Chem. Soc.*, **89**, 5043 (1967).

(2) J. L. Mateos and C. Perez, *Bol. Inst. Quim. Univ. Natl. Auto. Mex.*, 17, 202 (1965).

(3) P. Brown and C. Djerassi, *J. Am. Chem. Soc.*, **89**, 2711 (1967).

(4) J. H. Bowie, G. E. Lewis, and R. G. Cooks, *J. Chem. Soc., Sect. B*, 621 (1967).

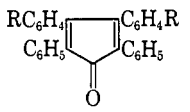
(5) J. H. Beynon, R. A. Saunders, and A. E. Williams, *Ind. Chim. Belge*, **29**, 311 (1964).

(6) H. M. Grubb and S. Meyerson, "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press Inc., New York, N. Y., 1963, p 453.

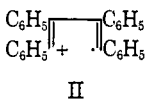
peak, while the ion produced by loss of a cyano-substituted ring will often carry a disproportionate fraction of the ion current. If, on the other hand, the product does carry the substituent, the situation is fundamentally reversed. But there is another effect superimposed upon the fundamental intensity effect; many of the substituents are very easily lost from the ring in a secondary process, so that the population of the substituted ion is depleted.[1d] For this reason, bromo and iodo substituents cause great variation in bromo- and iodo-substituted product intensities from those predicted, and for the related reason that the substituent opens up new fragmentation pathways for the product, product intensities of ions containing the nitro, dimethylamino, methoxy, hydroxy, and amino substituents are greatly reduced.[1d]

With this body of information about substituent effects, it becomes possible to evaluate substituents as inert labels for studying mass spectral decompositions. Inspection of data available indicates that for the reasons stated above, most substituents could be employed only with the application of a correction factor derived from published figures. It is obviously simpler to choose a substituent for which the correction factor is small both for ions containing the substituent and for ions which have lost the substituent. Only a few of all the substituents examined meet these criteria: *m*-CH_3, *p*-F, and perhaps *p*-Cl. The first of these might cause ring expansion in new systems, and the last not only is just at the borderline of meeting the criteria but could complicate interpretation of metastable intensities in decompositions of polyhalogenated systems, because of its isotopic distribution. Then, of all substituents so far studied, the *p*-fluoro substituent is perhaps the best suited as a simple label. In mass spectral reactions where products are formed without alteration of the structure of the substituted ring, the effect of *p*-F on rates of formation is small [$(\log Z/Z_0)/\rho = -0.04$ to $+0.02$],[1a,b] as is its effect on over-all rates of decomposition of substituted ionic products ($\log Z/Z_0 = -0.06$ to $+0.08$).[1d]

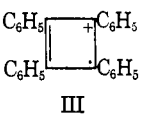
To test the utility of this substituent as a label in a reaction where the entire aryl group acts only as a substituent on another reacting system, we have examined secondary processes in the fragmentation of tetracyclone (Ia). From available evidence, both acyclic (II) and cyclic (III) structures may be written for the $(M - 28)\cdot^+$ ion of tetracyclone.[7,8] If the cyclic structure is



Ia, R = H
b, R = *p*-F
c, R = *p*-D

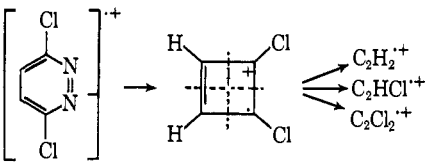


II



III

the correct one, the $(M - 28)\cdot^+$ ion may be described as a cyclobutadiene cation radical. This structure is of inherent interest, and several studies have been directed toward accumulation of evidence in its support. A recent study of the mass spectra of pyrazines and tetrazines[9] finds support for similar structures in the fragmentation of 3,6-dichloropyridazine (IV); the evidence consists of the production of $C_2Cl_2\cdot^+$, $C_2HCl\cdot^+$, and $C_2H_2\cdot^+$ in the spectrum and of the abnormally high current of $C_4H_2Cl_2^{2+}$ ions. Similar data support a diazacyclobutadiene structure in the decomposition of 3,6-dimethyl-*s*-tetrazine. High-resolution data have been used to support the formation of the dication of cyclobutadiene in the fragmentation of pyridazine itself, though the cyclic structure is postulated, not demonstrated.[10] Earlier evidence for the possible formation



IV

of cyclobutadiene cations has been reviewed.[9]

It is not inconceivable that the very high intensity of the $C_2HCl\cdot^+$ fragment in the spectrum of 3,6-dichloropyridazine results from a heavy contribution from an acyclic precursor. It would be of interest to establish what fraction of the precursors are indeed cyclic, but quantitative evaluations based on chlorine substituent effects in four-membered rings cannot be made.[11] In another approach to studying the details of substituted cyclobutadienes, we have prepared a tetracyclone labeled twice with the *p*-fluoro substituent and examined the further decomposition of the M − CO ion with reference to the fate of the labeled rings.

The mass spectrum of 3,4-bis(*p*-fluorophenyl)-2,5-diphenylcyclopentadienone (Ib), obtained by direct insertion of the sample into a Hitachi RMU 6E instrument at 270°,[13] includes peaks shown in Table I. Metastable

Table I

m/e	Rel intensity
420, $M\cdot^+$	100
392, $(M - 28)\cdot^+$	32
214, $(C_{14}H_8F_2)\cdot^+$	15
196, $(C_{14}H_9F)\cdot^+$	89
178, $(C_{14}H_{10})\cdot^+$	29

ions occur at *m/e* 81.0 (392 → 178), 98.0 (392 → 196), and 117.0 (392 → 214), of relative intensities[14] 1:3.1:0.89, which are a measure of the relative rates of formation of the three products because the effect of variable decomposition rates[1d] should be absent. These latter

(7) J. H. Beynon, R. C. Cookson, R. R. Hill, D. W. Jones, R. A. Saunders, and A. E. Williams, *J. Chem. Soc.*, 7052 (1965).

(8) J. H. Beynon, R. F. Curtis, and A. E. Williams, *Chem. Commun.*, 237 (1966).

(9) S. J. Weininger and E. R. Thornton, *J. Am. Chem. Soc.*, **89**, 2050 (1967).

(10) M. H. Benn, T. S. Sorensen, and A. M. Hogg, *Chem. Commun.*, 574 (1967).

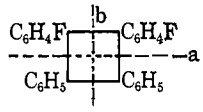
(11) There is a chance that the $C_2H_2\cdot^+$ and $C_2Cl_2\cdot^+$ fragments arise from a linear precursor as well if the monovalent atoms can scramble, as they do in deuterated benzenes,[12] but this hypothesis is considered weakened by the observation that in substituted benzenes, *m*-chloro and *p*-chloro isomers retain positional identity in most cases.[1] We thank Dr. Earl W. Baker of the Mellon Institute for interesting discussions.

(12) C. G. Macdonald and J. S. Shannon, *Australian J. Chem.*, **15**, 771 (1962).

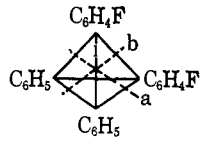
(13) Similar relative intensities were obtained in spectra recorded at high sensitivity at temperatures as low as that of the unheated probe; this observation precludes contribution to the spectrum by pyrolysis products.

(14) Integrated intensities on a linear *m/e* scale. Since the precursor is the same ion, the intensities may be compared to each other. *Cf.* ref 1a,e.

data suggest cyclic structures of the approximate symmetry of V or VI, which yield the disubstituted fragment and the unsubstituted fragment in approximately



V



VI

equal amounts (log $Z/Z_0 = -0.02$, within the limits previously found) by cleavage at a; cleavage b gives the monosubstituted fragment in greater abundance than that predicted from an intermediate of square symmetry. Either a rectangular or distorted tetrahedral structure for the "cyclobutadiene monocation,"[15] or contribution from an additional amount of acyclic ions, predominantly producing the monosubstituted compound, would explain this observation.[16] On the basis of intensities of normal ions, one fluorine is calculated to decrease the logarithm of the intensity of the fragment ion by 0.12, a not unreasonable effect for typical reaction-constant values for mass spectral reactions.[1d] It should be borne in mind that the normal ions reflect both relative rates of formation and of decomposition; on the other hand, the metastable ions reflect the single process of formation unless sequential decomposition is extraordinarily rapid for a metastable process.[17] Consequently, relative rates of formation may be measured from accurate metastable intensities, and any differences between these values and those of the normal peaks corresponding to the ions in question are measures of the relative rates of decomposition. If the ions are not identical in every respect, the metastable intensities need not correspond to the normal ion intensities.[18,19]

It is next necessary to demonstrate that the *p*-fluoro substituent is indeed inert, and that the values arrived at with the difluoro compound are not the result of coincidence. To establish this point, the tetracyclone derivative containing two deuterium atoms in the same positions as the fluorine atoms in first compound was examined. The *p*-deuterio substituent should not affect rates of mass spectral reactions of interest in this case within the limits of reproducibility.

The conclusions above are supported by comparison with the analogous fragmentations of 3,4-di-*p*-deuteriophenylcyclopentadienone (d_2 83%, d_1 16%, d_0 1%), for which relative intensities of the fragment ions (uncorrected for doubly charged ions and ^{13}C isotopes: 178, 1; 179, 2.5; 180, 0.77; corrected: 178, 1; 179, 2.8; 180, 0.64) suggest once again a structure[20] of rectangular or distorted tetrahedral structure (calculated ratio for square symmetry: 178, 1; 179, 1.7; 180, 0.69; for tetrahedral symmetry:[16] 178, 1; 179, 2.7; 180, 0.60). These calculations are based on the assumption that further rates of decomposition of the deuterated species are similar to those of the unlabeled species; the metastables for the three cleavages are calculated to be at *m/e* 88.5, 89.5, and 90.5, but they overlap, and are not easily resolved on our instrument, so that rates of formation cannot be calculated as for the difluoro compound. The assumption that rates are very similar is not irregular, as we have stated above.

Our data indicate that the $(M - CO)\cdot^+$ ion in the mass spectra of the tetracyclone studied, and presumably the parent tetracyclone, is indeed a cyclic ion, and is not of square symmetry. It would be of interest to find if similar $(C_6H_5)_4C_4\cdot^+$ ions generated from other sources, particularly $(C_6H_6)_4C_4$ obtained by pyrolysis reactions, have the same symmetry.[21]

More generally, our data also indicate that the *p*-fluoro substituent is indeed employable as a "dead" label for the study of mass spectral reactions, either in conjunction with deuterium labeling or, more usefully, alone. For successful application in the latter category, restrictions are necessary. By word of caution, the *p*-fluoro substituent may exert an appreciable electronic effect when the structure of the substituted ring is greatly altered during the reaction (*e.g.*, formation of intermediates with quinone structures[1c,1g,3] [log Z/Z_0 = 0.73], of expanded rings[1e] [log Z/Z_0 = 0.04], and of structures with loss of resonance energy[1g] [log Z/Z_0 = −0.70]). To repeat, the fluorine-label technique is applicable only when the entire aromatic group acts solely as a substituent on another reacting system. Its use resolves overlapping metastable peaks found in the spectra of deuterated analogs because of the large mass of fluorine,[22] and because many aromatic fluorides are commerically available, preparation of specifically labeled compounds is much less tedius than the preparation of the corresponding deuterated compounds. These two advantages recommend the technique for study of the structures of gaseous ions.

Experimental Section

Mass spectra were obtained on a Hitachi RMU 6E mass spectrometer with ionizing current of 80 μA and energy of 70 V for high-voltage spectra. Low-voltage spectra were recorded with reduced repeller voltage (0.5 V) and reduced trap current (*ca.* 2 μA). All samples were introduced through the heated inlet (190°) except for the tetracyclones, which were introduced on the direct-insertion probe. The source was maintained at 175°.

3,4-Bis(*p*-fluorophenyl)-2,5-diphenylcyclopentadienone was prepared by Fieser's method[23] from 4,4′-difluorobenzil (mp 119–120°; lit.[24] mp 121.5–2.5°) and 1,3-diphenylpropanone-2 (Matheson Coleman and Bell), mp 211–213°.

Anal. Calcd for $C_{29}H_{18}OF_2$: C 82.83; H, 4.31. Found:[25] C, 82.78; H 4.48.

3,4-Bis(*p*-deuteriophenyl)-2,5-diphenylcyclopentadienone was prepared by the following unexceptional series of reactions, with isotopic analysis by low-voltage mass spectrometry. A reported

(15) Evaluation of the ^{13}C isotope peak at *m/e* 196.5 suggests that 10% of the peak at *m/e* 196 is $C_{28}H_{10}F_2^{2+}$, which would correspond to the cyclobutadiene dication.

(16) Recent SCF MO calculations indicate that for the neutral molecule the tetrahedral structure is much less stable than a cyclobutadiene structure. Substituents should increase the relative instability: N. C. Baird and M. J. S. Dewar, *J. Am. Chem. Soc.*, **89**, 3966 (1967).

(17) K. R. Jennings, *Chem. Commun.*, 283 (1966).

(18) See R. G. Cooks, R. S. Ward, and D. H. Williams, *ibid.*, 850 (1967).

(19) D. T. Roberts, Jr., W. F. Little, and M. M. Bursey, *J. Am. Chem. Soc.*, 90, 973 (1968).

(20) The same ratio of intensities of the fragment ions is observed near the appearance potentials; this speaks for one structure, not a mixture of structures.

(21) Professor McLafferty has informed us of such experiments in progress in his laboratory.

(22) Laboratories equipped with double-focusing instruments also have the defocusing technique available for resolving metastable ions: M. Barber and R. M. Elliott, ASTM E-14 Conference on Mass Spectrometry, Montreal, June 1964; T. W. Shannon, T. E. Mead, C. G. Warner, and F. W. McLafferty, *Anal. Chem.*, **39**, 1748 (1967). We thank Professor McLafferty for informing us of the latter paper.

(23) L. F. Fieser, "Organic Experiments," D. C. Heath and Company, Boston, Mass., 1964, p 303.

(24) A. Kaluszyner, *J. Org. Chem.*, 24, 995 (1959).

(25) Galbraith Laboratories, Inc., Knoxville, Tenn.

procedure was used for the conversion of *p*-bromotoluene into *p*-deuteriotoluene (n^{28}D 1.4936, bp 105–108°, d_1 92% and d_0 8%), *via* the Grignard reagent.[26] The deuteriotoluene was then converted by procedures routinely available for toluene to benzyl bromide,[27] benzaldehyde,[28] benzoin,[29] benzil,[30] and tetracyclone[23] sequentially into the desired dideuteriotetracyclone, d_2 83%, d_1 16%, d_0 1%, mp 217–218° (lit.[23] 219°).

Acknowledgments. We are grateful for the assistance of Dr. Manning P. Cooke and Mr. Ned A. Moore. This work was supported through Contract SD-100 of the University of North Carolina Materials Research Center with the Advanced Research Projects Agency.

(26) S. Meyerson, P. N. Rylander, E. L. Eliel, and J. D. McCollum, *J. Am. Chem. Soc.*, **81**, 2606 (1959).
(27) H. Schmid and P. Karrer, *Helv. Chim. Acta*, **29**, 573 (1946); C. Djerassi, *Chem. Rev.*, **43**, 271 (1948).
(28) H. B. Hass and M. L. Bender, *J. Am. Chem. Soc.*, **71**, 1767 (1949).
(29) Reference 23, p 213.
(30) A. I. Vogel, "Practical Organic Chemistry," Longmans Green and Co., Ltd., London, 1956, p 715.

Conformational Analysis. XV. The Conformational Enthalpy, Entropy, and Free Energy of the Carboxyl, Carboxylate, Carbomethoxy, Carbonyl Chloride, and Methyl Ketone Groups[1,2]

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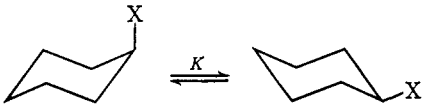
Contribution from the Department of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556. *Received September 18, 1967*

Abstract: The following thermodynamic parameters for conformational equilibria in cyclohexyl compounds (axial $C_6H_{11}X \rightleftharpoons$ equatorial $C_6H_{11}X$) have been determined: X = COOH, *n*-dodecane solvent, $\Delta H°$ −1.64 ± 0.03 kcal/mol, $\Delta S°$ −0.85 ± 0.05 cal/deg mol, $\Delta G°_{25}$ −1.38 ± 0.04 kcal/mol; aqueous diethylene glycol dimethyl ether solvent (mole fraction H_2O 0.1), $\Delta H°$ −1.56 ± 0.05 kcal/mol, $\Delta S°$ −0.68 ± 0.10 cal/deg mol, $\Delta G°_{25}$ −1.36 ± 0.08 kcal/mol; (mole fraction H_2O 0.5), $\Delta H°$ −1.71 ± 0.03 kcal/mol, $\Delta S°$ −0.87 ± 0.06 cal/deg mol, $\Delta G°_{25}$ −1.46 ± 0.05 kcal/mol; X = COO^-, $\Delta H°$ −2.13 ± 0.06 kcal/mol, $\Delta S°$ −0.56 ± 0.13 cal/deg mol, $\Delta G°_{25}$ −1.96 ± 0.10 kcal/mol; X = $COOCH_3$, $\Delta H°$ −1.12 ± 0.04 kcal/mol, $\Delta S°$ +0.50 ± 0.11 cal/deg mol, $\Delta G°_{25}$ −1.27 ± 0.08 kcal/mol; X = COCl, $\Delta H°$ −1.39 ± 0.05 kcal/mol, $\Delta S°$ −0.32 ± 0.11 cal/deg mol, $\Delta G°_{25}$ −1.29 ± 0.09 kcal/mol; X = $COCH_3$, $\Delta H°$ −1.17 ± 0.01 kcal/mol, $\Delta S°$ +1.16 ± 0.03 cal/deg mol, $\Delta G°_{25}$ −1.52 ± 0.02 kcal/mol. The rationale of the data is discussed.

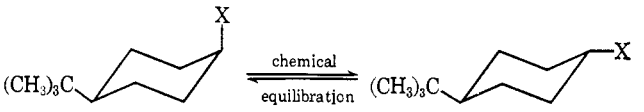
By now, a large number of conformational equilibria[3] of the type shown in eq 1 have been studied by a variety of methods[3,4] and the conformational free



(1)

energies, $-\Delta G°$, derived from the equilibrium constants K have been summarized quite recently for all the known cases.[5] In contrast, very little is known about the derived parameters of conformational enthalpy ($-\Delta H°$) and conformational entropy ($\Delta S°$). We have undertaken a program of study to obtain such parameters for a select number of nonconically symmetrical substituents.

Of the various methods of determining conformational equilibria,[4] the ones most often used have been the kinetic method, the nuclear magnetic resonance method, and the method of equilibrating model compounds, such as 4-*t*-butyl-substituted homologs of the cyclohexyl compounds to be studied (eq 2). It has been found, over



(2)

the years, that, because of systematic difficulties, the kinetic method often does not give reliable results,[6,7] and the nmr method is also subject to limitations which have been discussed in detail elsewhere.[1] It is therefore fortunate that the equilibration method (eq 2) proved applicable to the groups investigated in the present study: the carboxyl group (COOH), its derivatives, the carboxylate (COO^-), carbomethoxy ($COOCH_3$), and carbonyl chloride (COCl) groups, and the methyl ketone ($COCH_3$) group. The method gives equilibrium constants of sufficient accuracy and precision to obtain quite precise values of $\Delta H°$ and $\Delta S°$. Values for $\Delta G°_{25}$ were obtained directly in the case of the CH_3CO group and were calculated from the $\Delta H°$ and $\Delta S°$ values obtained at higher temperatures in the case of the other groups.

(1) Paper XIV: E. L. Eliel and R. J. L. Martin, *J. Am. Chem. Soc.*, **90**, 689 (1968).
(2) From the Ph.D. dissertation of M. C. Reese, University of Notre Dame, 1966. Presented at the 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 30, 1966.
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