Table VI. Calculated Energies of the Systems HR and NR (e.v.)

R	Nuclear energy	Electronic energy	Total energy	Relative energy
N ∞	239.939	−549.836	−309.897	0.000
H 5.909	315.621	−625.502	−309.880	0.017
N 5.909	310.041	−619.938	−309.897	0.000
H 4.909	332.156	−641.921	−309.764	0.133
N 4.909	323.353	−633.247	−309.895	0.002
H 3.909	358.885	−667.297	−308.413	1.484
N 3.909	342.745	−652.633	−309.878	0.019
N 3.000	375.375	−685.046	−309.429	0.469
N 2.000	432.579	−740.633	−304.360	5.537

The adoption of the sp³ hybridization for the nitrogen orbitals may appear at first quite unsuitable, as the bond orbitals have been estimated to contain much more p-character.[22] However, during the course of the calculations it was noticed that repulsion integrals evaluated in different ways, thus having different values, still lead to the same relative energies for different systems. This is not surprising since in this problem the relevent repulsion integrals enter into the molecular integrals J, K, and I in such a manner that they largely cancel out in the expression for total electronic energy. Since a change in the degree of hybridization merely leads to a change in the values of all the repulsion

integrals, we believe that the same relative energy would result from different hybridizations. As a check, when only 5% of s-character was assigned to the N-bond orbitals, the calculated repulsion integrals between He and the nitrogen orbitals did not differ appreciably from the ones calculated using nitrogen sp³ orbitals. This indicates that even the absolute values of the calculated energies are not very sensitive to the degree of hybridization.

The agreement between the quantum mechanical calculation and the van der Waals calculation is extremely good for both systems HR and NR, as can be seen in Figure 1. It is concluded that, to the approximation used here, there is no basis for suspecting any anomalous behavior of the lone pair on nitrogen, and serious doubt is cast upon the conclusions drawn by Aroney and LeFèvre concerning the methyl group on the piperidine ring. Experimental work to be described in the following paper supports the conclusion drawn here, namely, that the methyl group is much "bigger" than the lone pair on nitrogen. The accuracy of the van der Waals calculation, the method, and the parameters used are all fully supported by the quantum mechanical calculation over the repulsive portion of the curve. Since correlation effects were not included in the quantum mechanical calculations, no information was obtained from that calculation concerning the attractive portion of the curve, but there appears to be no reason to question it.

(22) (a) L. Pauling, "The Nature of the Chemical Bond," 3rd Ed., Cornell University Press, Ithaca, N. Y., 1960; (b) A. B. F. Duncan. *J. Chem. Phys.*, **27**, 423 (1957).

Conformational Analysis. XLII. Experimental Approaches to the Problem of the Size of the Lone Pair on Nitrogen[1,2]

Norman L. Allinger, J. G. D. Carpenter, and Frederick M. Karkowski

Contribution from the Department of Chemistry, Wayne State University, Detroit, Michigan 48202. Received September 24, 1964

From the dipole moments of a number of piperidine and piperazine derivatives, the energetic preferences for a methyl group and for a hydrogen atom on nitrogen to assume the equatorial vs. the axial position in N-methylpiperidine and in piperidine have been determined. The methyl group was found to prefer the equatorial position by 1.7 kcal./mole, and the hydrogen atom by 0.4 kcal./mole, in benzene solution.

In 1958 Aroney and LeFèvre published a paper discussing the equatorial *vs.* axial preference for the hydrogen on nitrogen in piperidine (I), and for the methyl in N-methylpiperidine (II).[3] They concluded that the hydrogen atom in I showed a pronounced

preference for the axial position, while the methyl in II was of equal energy in the axial or equatorial position. Our preceding paper[1] discussed a theoretical study of the situation which led us to conclude that the methyl group would strongly prefer to be equatorial in the N-methyl compound, and that the hydrogen on nitrogen in piperidine might preferentially be either axial or equatorial, since the energy difference between the two arrangements should not be very large. The present paper describes our experimental approaches to this problem. Recently other workers have studied the problem experimentally by qualitative methods,[4-6] and to that extent we are in complete agreement with them.

(1) Paper XLI: N. L. Allinger and J. C. Tai, *J. Am. Chem. Soc.*, **87**, 1227 (1965).

(2) This research was supported by Grant GP-1174 from the National Science Foundation. Presented at the 144th National Meeting of the American Chemical Society, Los Angeles, Calif., April 1963. A preliminary communication appeared in *Tetrahedron Letters*, 3345 (1964).

(3) M. Aroney and R. J. W. LeFèvre, *J. Chem. Soc.*, 3002 (1958).

(4) M. Davis and O. Hassel, *Acta Chem. Scand.*, **17**, 1181 (1963).

(5) (a) T. M. Moynehan, K. Schofield, R. A. Y. Jones, and A. R. Katritzky, *J. Chem. Soc.*, 2637 (1962); (b) N. W. J. Pumphrey and M. J. T. Robinson, *Chem. Ind.* (London), 1903 (1963).

(6) A somewhat different aspect of the problem considered here is the conformational enthalpy of the amino group, which was recently studied by J. Sicher, J. Jonáš, and M. Tichý, *Tetrahedron Letters*, 825 (1963), and by E. L. Eliel, E. W. Della, and T. H. Williams, *ibid.*, 831 (1963).

There are various ways in which the problem of the "size" of the lone pair on nitrogen might be attacked.[7] The use of dipole moments in suitable compounds seemed to us to afford a particularly simple and direct method, and was employed in the present work. The methyl group on nitrogen was more easily studied than the hydrogen on nitrogen, and was examined first. It was assumed that the nitrogen in N-methylpiperidine could be regarded as tetrahedral.[8] The piperidine ring was taken to have tetrahedral bond angles and equal bond lengths for purposes of calculation. (While this is not expected to be quite correct, the error introduced by these approximations is negligible.) The resultant dipole moment of N-methylpiperidine contains contributions from the nitrogen lone pair moment and from the C–N bond moments. The direction of this resultant moment must be very nearly along the lone pair axis. We measured the moment of this compound and found that in benzene it had a value of 0.95 D.[9]

The conformational energy of the N-methyl group was determined from the dipole moment of N,N'-dimethylpiperazine. The observed moment of the latter is a function of the conformational composition of the compound. The three chair conformations of dimethylpiperazine are shown. Two of these forms,
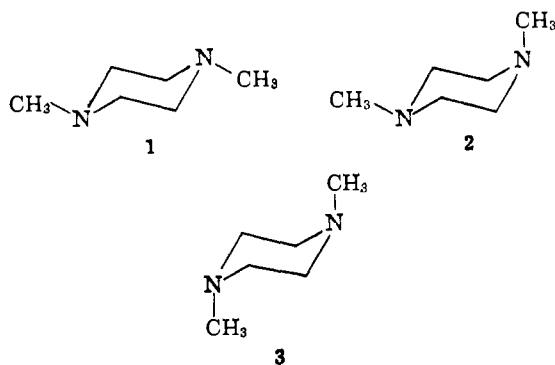
1 and 3, have no net dipole moments. Form 2 has a resultant moment which was calculated from the data on N-methylpiperidine to be 1.55 D. The experimentally determined dipole moment of N,N'-dimethylpiperazine in benzene was 0.50 D.[10]

The equilibrium mixture of conformations may be assumed to contain only these three forms, since the amount of nonchair form present at room temperature is negligible in both cyclohexane[11] and dioxane,[12] and any interpretation of torsional barriers that has been made which correctly predicts these facts also predicts the absence of any significant amount of nonchair form in simple piperidine and piperazine derivatives.[13]

We find claims[14] for the existence of appreciable amounts of boat forms in piperazine unconvincing, as discussed elsewhere.[15] Other data previously interpreted in terms of nonchair forms in these systems[16] can be interpreted in terms of the analysis which follows.

The dipole moment of the equilibrium mixture of the three chair conformations of N,N'-dimethylpiperazine is given by

$$\mu_r{}^2 = N_1\mu_1{}^2 + N_2\mu_2{}^2 + N_3\mu_3{}^2$$

but since $\mu_1 = \mu_3 = 0$, $\mu_r{}^2 = N_2\mu_2{}^2$. The mole fraction of N_2 is thus 0.104. From the relationship $-\Delta G^\circ = RT \ln K$, the free energy change from 1 → 2 could be calculated, but what is desired is the enthalpy difference between 1 and 2. To obtain this quantity from the equilibrium data, the entropy differences of the conformers due to the difference in symmetry numbers must be allowed for. The symmetry number of 2 is 1 while that of 1 is 2. This gives 2 an entropy greater than that of 1 by 1.38 e.u. The symmetry number and the entropy of 3 would be the same as for 1. If the enthalpy of the axial methyl on nitrogen minus that of the equatorial methyl is called H_{Me}, then the following relationships exist:

$$\ln K_3{}^2 = (H_{Me} + 0.41)/0.59 \text{ kcal./mole}$$

and

$$\ln K_3{}^1 = (2H_{Me}/0.59) \text{ kcal./mole}$$

where $K_3{}^2$ refers to the equilibrium 3 → 2, etc. Thus the equilibrium mixture contains one part of 3, $K_3{}^2$ parts of 2, and $K_3{}^1$ parts of 1, from which the mole fraction N of each conformer can be calculated. The experimental dipole moment corresponds to a value for H_{Me} of 1.7 ± 0.4 kcal./mole. This value is within experimental error of that found for the axial methyl group in methylcyclohexane.[17] Acually, only the absolute value of the enthalpy of the methyl was found from this experiment. That the enthalpy is more negative when the methyl is equatorial is assumed at this point, and will be established later in this paper.

A similar sort of treatment was possible for piperidine itself, but was more complicated because the N–H bond moment is not the same as the N–C bond moments. The resultant is therefore not directed along the lone-pair axis, but is inclined at some angle (α) to it. The observed moment of piperidine was 1.16 D. (reported values range from 1.07 to 1.52 in earlier work).[18] A portion of the dipole moment is contributed by the lone pair, and a portion by the bonds to nitrogen, but unfortunately the proportions of these various quantities are not known. As will be shown below, it is a good approximation to assume that the moment results only from the lone pair in a trialkylamine, and hence the moment of piperidine results from the sum

(7) It must be recognized at the outset that the lone pair does not have "size" in the usual macroscopic sense. "Size" here means the energy of the system in terms of the location of neighboring atoms or groups, and theory shows that "size" will depend on how it is measured. In a loose sense we will here use "size" to mean preference for the equatorial position.

(8) D. R. Lide, Jr., and D. E. Mann, J. Chem. Phys., 28, 572 (1958).

(9) This compares with literature values of 0.80–0.92 D.: A. L. McClellan, "Tables of Experimental Dipole Moments," W. H. Freeman and Co., San Francisco, Calif., 1963, p. 219.

(10) Lit. values (ref. 9, p. 220) are 0.44–0.59 D.

(11) (a) C. W. Beckett, K. S. Pitzer, and R. Spitzer, J. Am. Chem. Soc., 69, 2488 (1947); (b) W. S. Johnson, V. J. Bauer, J. L. Margrave, M. A. Frisch, L. H. Dreger, and W. N. Hubbard, ibid., 83, 606 (1961); (c) N. L. Allinger and L. A. Freiberg, ibid., 82, 2393 (1960).

(12) F. E. Malherbe and H. J. Bernstein, ibid., 74, 4408 (1952).

(13) E. B. Wilson, Jr., Advan. Chem. Phys. 2, 367 (1959).

(14) M. Aroney and R. J. W. LeFèvre, J. Chem. Soc., 2161 (1960).

(15) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. B. Morrison, "Conformational Analysis," John Wiley and Sons, Inc., New York, N. Y., 1965, p. 250. See also P. J. Hendra and D. B. Powell, Spectrochim. Acta, 18, 299 (1962), and M. Davis and O. Hassel, Acta. Chem. Scand., 17, 1181 (1963).

(16) M. V. George and G. F. Wright, Can. J. Chem., 36, 189 (1958).

(17) The best value for the methyl group on a cyclohexane ring appears to be 1.7 kcal./mole (ref. 15, p. 439).
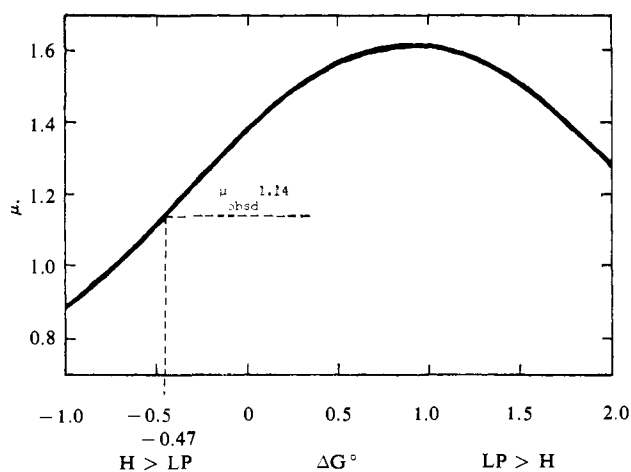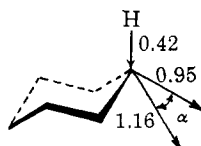
(18) Ref. 9, p. 151.

Figure 1. Dipole moment of N-methylpiperazine as a function of the conformational energy of the lone pair relative to hydrogen.

of the lone-pair moment, which is the same as for the trialkylamine, and the N–H moment acting at the tetrahedral angle.[19] There are two alternative values for the N–H bond moment a priori, which would correspond to different directions for the resultant moment observed. The N–H bond moment must be either 0.42 D., acting with the hydrogen as the positive end to give a resultant with an α of 20.0°, or else the N–H bond moment must be 1.06 D. in the other direction, and α is 60.0°. A consideration of the piperazine molecule shows that the first of these alternatives must be cor-

rect. If the second alternative were correct the dipole moments calculated for the three conformations of piperazine would be 0, 0.17, and 0 D., respectively. Since the observed moment of the molecule in benzene is 1.47 D., the second alternative can be dismissed. The first alternative, on the other hand, by a similar calculation gives moments of 0, 2.24, and 0 D. for the three conformers, respectively. Calculations exactly analogous to those made for the dimethylpiperazine lead to an energy difference between the lone pair and the hydrogen atom on nitrogen of 0.46 kcal./mole, but it cannot be determined from these data alone which of the two groups is the larger, the hydrogen or the lone pair.

It is possible to check the assumption about the additivity of the lone pair and bond moments. Tri-methylamine has an axis of symmetry. Its dipole moment must therefore point along that axis and it has a value of 0.61 D.[8,20] Methylamine has a (gas phase)

(19) It has been shown that the dipole moment of H–F results mainly from the lone pair on fluorine, rather than from a bond moment: R. K. Nesbet, J. Chem. Phys., 36, 1518 (1962).

(20) The fact that the value for trimethylamine is so much lower than for N-methylpiperidine is not to be taken as a result of a larger C–N bond moment from the ethyl group. The values in the present work are apparent moments in benzene solution, while the microwave value is the actual (gas phase) moment. Triethylamine has a moment of 0.61 D by the microwave method, while benzene solution values reported range from 0.79 to 0.91 D. (ref. 9, p. 223). Unfortunately, no microwave study of dimethylamine has yet been reported.

moment of 1.33 D.[21] Taking the former moment as being solely from the lone pair, from the latter one can calculate as before the angle the resultant makes with the C–N bond, and it is found to be 76.7°. This angle is also known from the microwave spectrum, and has the value 73.2°. The value calculated by the vector additivity method is therefore accurate to about 4° in this case, and should be similarly accurate in the piperidine case. This uncertainty in α would lead to the axial–equatorial conformation of piperidine having a calculated moment uncertain by ±0.04 D., which leads to an uncertainty in $\Delta G°$ of only about 0.1 kcal./mole. Considering the other sources of error, it would seem that $\Delta G°$ is probably accurate to about ±0.3 kcal./mole.

So far only the magnitude of the conformational energy difference for the hydrogen on nitrogen has been established. The sign of this energy difference, and that in fact the hydrogen prefers the equatorial position in piperidine, was determined by a study of N-methyl-piperazine. N-methylpiperazine is a mixture of the four conformations 4–7. The resultant moments were
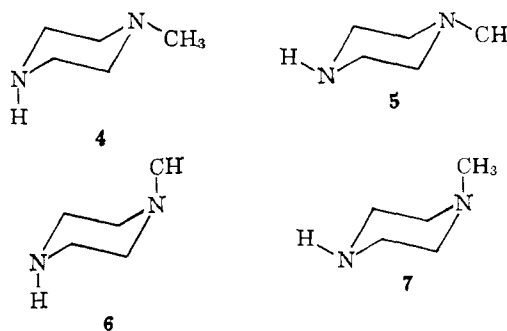
calculated for each of these forms (using $\alpha = 20.0°$), and the values obtained were $\mu_4 = \mu_7 = 1.91$ D. and $\mu_5 = \mu_6 = 0.43$ D. The proportions of the con-formers 4–7 in the equilibrium were determined by the conformational energies of the methyl group, which was taken as 1.7 kcal./mole (the results are insensitive to the exact value used here), and of the hydrogen. The latter is called H_H, and the free energies of the conformations are then seen to be as follows (kcal./mole): $G_4 = H_H$, $G_5 = 0$, $G_6 = H_H + 1.7$, $G_7 = 1.7$. Various values of H_H from −1.7 to +1.0 were assumed, and the composition of the corresponding equilibrium mixture was calculated. For each such mixture, the total resultant dipole moment (μ_r) was then calculated, and a plot of μ_r against H_H is shown in Figure 1. The experimental dipole moment was 1.14 D., which would correspond to a conformational energy for the hydrogen of either 0.43 or −2.16 kcal./mole. The work on piperazine eliminates the latter value, and the hydrogen therefore prefers the equatorial position by 0.43 kcal./mole in this molecule, essentially the same number as obtained from piperazine (0.46 kcal./mole).

The work described above is in good agreement with the theoretical calculations,[1] and indicates that the axial methyl on nitrogen in N-methylpiperidine has a conformational enthalpy similar to that of the axial methyl of methylcyclohexane, while a similarly located hydrogen in the former compound is only slightly less favorable than the corresponding equatorial hydrogen.

(21) D. R. Lide, Jr., J. Chem. Phys., 27, 343 (1957).

Table I. Dipole Moment Data at 25°

Compd.	M_R	α	ϵ_1	d_1	β	$P_{2\infty}$	μ
N-Methylpiperidine	31.58	0.901	2.2760	0.87355	0.101	50.2	0.95 ± 0.02
Piperidine	26.74	1.667	2.2728	0.87310	0.030	54.5	1.16 ± 0.01
N,N'-Dimethylpiperazine	35.42	0.027	2.2728	0.87308	0.040	40.6	0.50 ± 0.02
Piperazine	25.75	2.981	2.2725	0.87308	0.100	70.2	1.47 ± 0.02
N-Methylpiperazine	30.59	1.641	2.2698	0.87252	0.038	57.2	1.14 ± 0.01
p-Chlorophenylcyclohexane	56.706	4.786	2.2729	0.87255	0.381	125.2	1.83 ± 0.03
N-Methyl-(p-chlorophenyl)piperidine	60.552	7.196	2.2741	0.87309	0.422	164.4	2.25 ± 0.01

There are, however, quite a number of hidden assumptions involved in the interpretation given to the work just described. It is, for example, assumed that dipole moment at one end of the piperazine molecule does not induce in the other end a moment which is significantly different from that induced by the corresponding nitrogen in the piperidine system,[22] and it assumes that atomic polarization can be neglected in the dipole moment calculation.[24] Because there are several of these reasonable, but not really provable, assumptions involved in the work just described, it was deemed desirable to establish the same facts again by a series of independent measurements on quite different systems. The variation that could be made relatively easily was to study a series of N-methylpiperidines in which another group was located in the 4-position which possessed a dipole moment of known direction and magnitude. The p-chlorophenyl group has previously been exploited for this purpose, and its advantages have been discussed.[25] This group was utilized in the present work.
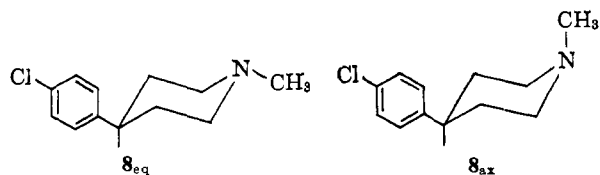
The energy of the axial phenyl group has been measured in different systems and found to be greater than 2.0 kcal./mole.[26] This means that in each case **8** will exist to the extent of at least 97% in conformations having the phenyl equatorial, so for present purposes these compounds can be considered as composed of the two conformations indicated. In **8**, the p-chlorophenyl vector points along the C–Cl bond, and the lone pair on nitrogen has its vector directed at an angle of 180° if the methyl is axial. The dipole moment of p-chlorophenylcyclohexane was measured and found to be 1.83 D. From this value and with the other information available, the dipole moments for the two conformations **8eq** and **8ax** were calculated to be 2.33 and 0.88 D., respectively. The compound was prepared and its dipole moment was measured in benzene solution at 25° and had the value 2.25 D., which indicates that under these conditions the compound exists as an

equilibrium mixture containing 92% of **8eq** and 8% of **8ax**. The $\Delta G°$ for the equilibrium indicated, which is assumed to be equal to the conformational enthalpy of the methyl group on nitrogen, is 1.5 kcal./mole. Because of the experimental errors involved when an equilibrium point is measured by the dipole moment method, an equilibrium this one-sided is difficult to determine accurately. Taking the various errors into account, these measurements would indicate a value for the conformational energy of the methyl group of 1.5 (−0.3 to +0.8) kcal./mole, in satisfactory agreement with the value from the dimethylpiperazine study.

In summary, the experimental data presented here do not support the conclusions of Aroney and LeFèvre concerning the "size" of the lone pair on nitrogen. While it is emphasized that this "size" is a function of its environment, it appears that, with regard to the equilibrium between an axial and an equatorial N-methyl, the "size" of the lone pair is best thought of as being negligible. Thus the methyl group shows a strong preference for the equatorial position.

Experimental

Piperidine, N-methylpiperidine, piperazine, N-methylpiperazine, and N,N'-dimethylpiperazine were commercial materials purified by fractional distillation or by crystallization of the free base or hydrochloride salt as appropriate. The physical constants of the compounds were in good agreement with the reported values.

N-Methyl-4-(p-chlorophenyl)piperidine (III). Into a 500-ml. flask fitted with a Dry Ice condenser was placed 250 ml. of 95% ethanol. Methylamine was bubbled through the alcohol until the weight gain was equal to 4.65 g. To this solution was added with vigorous stirring 8.5 g. of 3-(4-chlorophenyl)-1,5-dibromopentane.[27] The reaction mixture was heated on a steam bath for 48 hr. The ethanol was then removed under reduced pressure and 200 ml. of concentrated potassium hydroxide solution was added to the residue. The basic aqueous solution was extracted with ether and the ether layers were combined, dried over magnesium sulfate, filtered, and the ether was evaporated. The oily residue was distilled through a 20-cm. Podbielniak column to yield 2.6 g. (50%) of product, b.p. 122° (2.5 mm.), which immediately solidified. Recrystallization from ether was carried out under nitrogen, m.p. 31–33°.

Anal. Calcd. for $C_{12}H_{16}ClN$: C, 68.72; H, 7.69; Cl, 16.91; N, 6.68. Found: C, 68.84; H, 7.74; Cl, 16.93; N, 6.48.

(22) The polarizability[23] of the N–H group (4.90 cc.) is similar to that of the –CH₂– group (5.89 cc.), and it is rather distant from the other dipole.

(23) A. I. Vogel, W. T. Cresswell, G. J. Jeffery, and J. Leicester, *Chem. Ind.* (London), 358 (1950).

(24) The atomic polarization of compounds similar to dimethylpiperazine has been shown to be negligible.[16]

(25) (a) N. L. Allinger and S. Greenberg, *J. Am. Chem. Soc.*, **81**, 5733 (1959); (b) N. L. Allinger, J. Allinger, M. A. DaRooge, and S. Greenberg, *J. Org. Chem.*, **27**, 4603 (1962).

(26) Ref. 15, p. 441.

(27) N. L. Allinger and S. Greenberg, *J. Am. Chem. Soc.*, **81**, 5733 (1959).

Dipole Moments. The dipole moments of the various compounds were determined at 25° in benzene solution using the dipole moment apparatus described previously.[28] The moments were calculated essentially by the method of Halverstadt and Kumler,[29] utilizing an IBM 7070 computer as described earlier.[30] The

(28) N. L. Allinger, H. M. Blatter, M. A. DaRooge, and L. A. Frieberg, *J. Org. Chem.*, 26, 2550 (1961).

(29) I. F. Halverstadt and W. D. Kumler, *J. Am. Chem. Soc.*, 64, 2988 (1942).

(30) N. L. Allinger and J. Allinger, *J. Org. Chem.*, 24, 1613 (1959).

molar refractivities were obtained from tables,[21] and atomic polarization was neglected. The data are summarized in Table I.

(31) A. R. Katritzky, *Proc. Chem. Soc.*, in press.

A Kinetic and Mechanistic Study on the Cleavage of the Carbon–Boron Bond. The Importance of Coordination

Louis H. Toporcer, Raymond E. Dessy,[1] and Stuart I. E. Green

Contribution from the Department of Chemistry, University of Cincinnati, Cincinnati, Ohio 45221. Received September 3, 1964

The mechanism of the reaction of triethylboron with carboxylic acids has been examined kinetically in aprotic solvents. The reaction is first order in each reagent, and log k_2 is an inverse function of the pK_a of the acid. A Taft correlation ($\rho^* = -0.94$) is observed. The effect of added nucleophiles and a primary isotope effect ($k_{RCOOH}/k_{RCOOD} = 3.3$) indicate that pre-rate-determining nucleophilic coordination of the organoborane by the oxy functions of the acid occurs, a step which activates both the incipient carbanion and the electrophilic hydrogen of the acid.
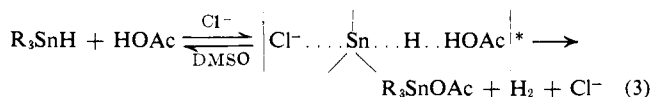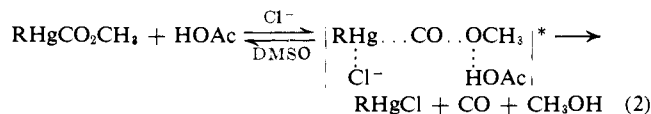
During the last decade considerable attention has been paid to the detailed mechanistic processes involved in the cleavage of carbon–metal bonds, particularly by protic acids, a process fundamental to an understanding of organometallic chemistry in general.

There is considerable *qualitative* evidence for nucleophilic participation[2] at metal in addition to the electrophilic attack at adjacent carbon.

$$\left|\begin{array}{cc} m\text{--}R \\ | \quad | \\ N \quad E \end{array}\right|^* \quad \left|\begin{array}{cc} m\text{--}R \\ \uparrow \quad | \\ S \quad E \end{array}\right|^* \quad \left|\begin{array}{cc} m\text{--}R \\ | \quad | \\ N\text{--}E \end{array}\right|^* \quad (1)$$

The nucleophile may be an independent species, solvent, or incorporated in an electrophile–nucleophile pair.

In order to elaborate further on the details of this type of process, and to demonstrate the validity of the concept across the periodic table, two previous studies[3] have explored kinetically the cases where the central metal ion was d[10] (mercury) and d[0] (tin) as in eq. 2 and 3. It was concluded that the function of the

(1) Alfred P. Sloan Foundation Fellowship.

(2) See Discussion.

(3) (a) R. E. Dessy and T. Hieber, *J. Am. Chem. Soc.*, 86, 28 (1964); (b) R. E. Dessy and F. E. Paulik, *ibid.*, 85, 1812 (1963).

$$RHgCO_2CH_3 + HOAc \underset{DMSO}{\overset{Cl^-}{\rightleftharpoons}} \left|RHg\cdots CO\cdots OCH_3\right|^* \longrightarrow$$
$$\left| \begin{array}{cc} Cl^- & HOAc \end{array} \right.$$
$$RHgCl + CO + CH_3OH \quad (2)$$

$$R_3SnH + HOAc \underset{DMSO}{\overset{Cl^-}{\rightleftharpoons}} \left|Cl^-\cdots Sn\cdots H\cdots HOAc\right|^* \longrightarrow$$
$$R_3SnOAc + H_2 + Cl^- \quad (3)$$

added halide ion was to coordinate with the metal, thus weakening the metal–carbon (or hydrogen) linkage, and serve as an assistor for the subsequent, and rate-determining, proton attack. It was pointed out that this type of nucleophilic catalysis was solvent dependent, and was not observed in the tin system if a protic environment was used,[4] one in which nucleophilic activity of added anions was diminished by hydrogen bonding.

The present paper reports on the last of this series, one in which the cleavage of carbon–boron bonds is studied. This involves what might be termed as a "no d" case, since no low-lying d-orbitals are available to boron, although an open p is. In particular, the reaction

$$Et_3B + RCOOH \xrightarrow{glyme} Et_2BO_2CR + RH \quad (4)$$
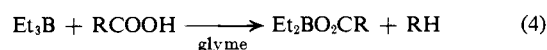
has been examined. The published evidence records the fact that although carboxylic acids cleave the C–B bond readily, hydrohalic acids are relatively inefficient.[5] Recognizing the incompatible hard–soft properties of boron and chloride ion,[6] the hypothesis that nucleophilic attack at boron, as well as electrophilic attack at carbon, were important in determining the height of the tran-

(4) H. Kuivila, personal communication.

(5) (a) J. Goubeau, R. Epple, D. D. Ulmschneider, and H. Lehmann, *Angew. Chem.*, 67, 710 (1955); (b) H. Meerwein, G. Hinz, H. Majert, and H. Sönke, *J. prakt. Chem.*, 147, 226 (1936); (c) H. C. Brown and K. J. Murray, *J. Am. Chem. Soc.*, 81, 4108 (1959); (d) H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962, p. 65.

(6) R. G. Pearson, *J. Am. Chem. Soc.*, 85, 3533 (1963).