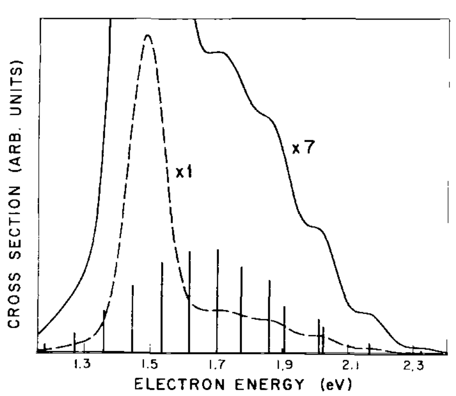


Figure 2. Model photodetachment spectrum of $CH_2^-(^2B_1) \rightarrow CH_2(^3B_1$ and $^1A_1)$. The vertical bars represent Franck-Condon factors for the various vibrational levels of the $^3B_1$ state only. The curves were obtained by folding the Franck-Condon factors obtained from the potentials of Figure 3 with an assumed Gaussian experimental line shape and an experimental ratio of the $^2B_1 \rightarrow {}^3B_1$ and $^2B_1 \rightarrow {}^1A_1$ electronic transition moments.

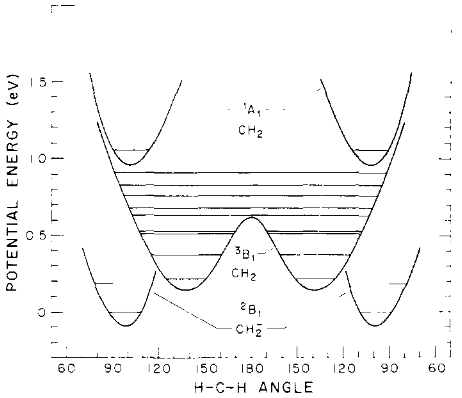


Figure 3. Calculated bending potential curves and pertinent vibrational levels for CH_2 and CH_2^-. This model considers vibrational energy levels only and ignores rotational coupling. The two lowest levels of $^3B_1$ and the lowest indicated levels of $^2B_1$ and $^1A_1$ are nearly degenerate pairs and are unresolved in the figure. The (0-0) splittings are fixed by experiment.

were carried out for a range of HCH angles, with the C-H distances held near their equilibrium positions. Double zeta configuration-interaction calculations were performed for $CH_2^-(^2B_1)$ to supplement similar earlier $CH_2(^1A_1)$ results.[8] Extended basis[9] SCF calculations were carried out for the $CH_2(^3B_1)$ ground state to obtain what is believed to be a reliable[10] barrier height of 3900 cm^{-1}. Bending Franck-Condon factors between $v = 0$ of the $CH_2^-(^2B_1)$ and $CH_2(^1A_1$ and $^3B_1)$ were calculated variationally in a B-spline basis. Combining these with the experimentally determined $^1A_1 \leftarrow {}^3B_1$ splitting, and folding with the experimental line shape, yielded a simulated photoelectron spectrum consisting of a single sharp peak and a long, partially resolved progression in the $^3B_1$ state. Simple parameterized forms of the $^2B_1$ and $^3B_1$ curves were then adjusted to give the simulated spectrum shown in Figure 2, the resulting equilibrium bond angles being $(99 \pm 3°)$ $CH_2^-(^2B_1)$ and $(138 \pm 4°)$ $CH_2(^3B_1)$.

The allowable adjustments of the $^2B_1$ bond angle are severely restricted, since the $^1A_1$ bond angle is accurately known,[5] and the absence of a distinct bending progression in the $^1A_1$ state constrains the change in the HCH angle such that $|\angle{}^2B_1 - \angle{}^1A_1| \lesssim 3°$. The triplet photoelectron spectrum shown in Figure 2 is very sensitive to the *difference* in bond angle between $CH_2^-(^2B_1)$ and $CH_2(^3B_1)$, and the *qualitative* fit indicated deteriorates markedly as this bond angle difference is varied by ±2°. The indicated error bars were determined by this bond angle-difference sensitivity, and absolute angles are relative to the optically determined $^1A_1$ bond angle. The $^3B_1$ geometry is in good agreement with that obtained in matrix ESR studies.[11,12] These optimized potential curves are shown in Figure 3. Using these potentials, a simulated CD_2^- spectrum gives excellent agreement with the experimental CD_2^- spectrum.

These calculations confirm the assignment of the observed peaks (A → F of Figure 1) to a partially resolved bending progression in the $^3B_1$ state, and provide a refined potential surface for ground state methylene. Detailed discussion[13] of these studies in in preparation.

Acknowledgments. The assistance of Dr. A. Kasdan in an early phase of this work is gratefully acknowledged. We would like to dedicate this paper to Professor George J. Schulz, whose untimely death has deprived the scientific community of an invaluable colleague, and an irreplaceable friend.

References and Notes

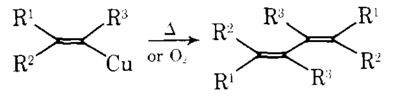
(1) This work was supported by the NSF, ERDA through grants to the University of Colorado and by an NSF grant of computing time through the National Center for Atmospheric Research.
(2) M. W. Siegel, R. J. Celotta, J. L. Hall, J. Levine, and R. A. Bennett, *Phys. Rev. A*, **6**, 607 (1972).
(3) H. Hotop and W. C. Lineberger, *J. Phys. Chem. Ref. Data*, **4**, 539 (1975).
(4) H. Hotop, T. A. Patterson, and W. C. Lineberger, *J. Chem. Phys.*, **60**, 1806 (1974); A. Kasdan, E. Herbst, and W. C. Lineberger, *ibid.*, **62**, 541 (1975); A. Kasdan, E. Herbst, and W. C. Lineberger, *Chem. Phys. Lett.*, **31**, 78 (1975).
(5) G. Herzberg and J. W. C. Johns, *Proc. R. Soc. London, Ser. A*, **295**, 107 (1966); G. Herzberg and J. W. C. Johns, *J. Chem. Phys.*, **54**, 2276 (1971).
(6) R. W. Carr, T. W. Eder, and M. G. Toper, *J. Chem. Phys.*, **53**, 4716 (1970); H. M. Frey and G. J. Kennedy, *J. Chem. Soc., Chem. Commun.*, 233 (1975); J. W. Simons and R. Curry, *Chem. Phys. Lett.*, **38**, 171 (1976).
(7) Ab initio CH_2 calculations have been reviewed by J. F. Harrison, *Acc. Chem. Res.*, **7**, 378 (1974); more recently see A. H. Pakiari and N. C. Handy, *Theor. Chim. Acta*, **40**, 17 (1975).
(8) S. V. ONeil, H. F. Schaefer III, and C. F. Bender, *J. Chem. Phys.*, **55**, 162 (1971).
(9) A 10s, 6p, 2d (carbon), 5s, 1p (hydrogen) Gaussian basis set was contracted to 5s, 3p, 1d (carbon), 3s, 1p (hydrogen). See S. Huzinaga, *J. Chem. Phys.*, **42**, 1293 (1965); T. Dunning, *ibid.*, **55**, 716 (1971); *ibid.*, **55**, 3958 (1971).
(10) See R. M. Stevens, *J. Chem. Phys.*, **55**, 1725 (1971), for SCF results on the ammonia inversion barrier.
(11) R. A. Bernheim, H. W. Bernard, P. S. Wang, L. S. Wood, and P. S. Skell, *J. Chem. Phys.*, **54**, 3223 (1971).
(12) E. Wasserman, V. J. Kuck, R. S. Hutton, E. D. Anderson, and W. A. Yager, *J. Chem. Phys.*, **54**, 4120 (1971).
(13) G. B. Ellison, S. V. ONeil, and W. P. Reinhardt, to be submitted for publication; G. B. Ellison, P. F. Zittel, and W. C. Lineberger, to be submitted for publication.
(14) Camille and Henry Dreyfus Teacher-Scholar.
(15) Address correspondence to this author at the Joint Institute for Laboratory Astrophysics.

P. F. Zittel, G. B. Ellison, S. V. ONeil
E. Herbst, W. C. Lineberger,*[14,15] W. P. Reinhardt[14]
Department of Chemistry, University of Colorado
Boulder, Colorado 80309
and the Joint Institute for Laboratory Astrophysics
National Bureau of Standards and University of Colorado
Boulder, Colorado 80309
Received January 26, 1976

Oxidative Coupling of Optically Active Vinylcopper Reagents. Stereospecific Generation of a Novel Dissymmetric Conjugated Diene

Sir:

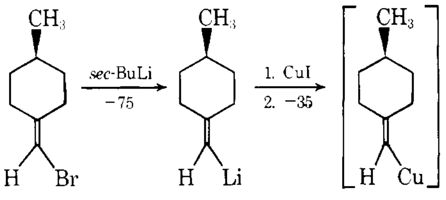
Alkenylcopper(I) reagents couple thermally[1] or oxidatively[2] to give 1,3-dienes with retention of configuration at the double bond (eq 1). As part of a general study of the formation and stereochemical stability of optically active organocopper reagents[3] we have investigated the oxidative coupling and al-



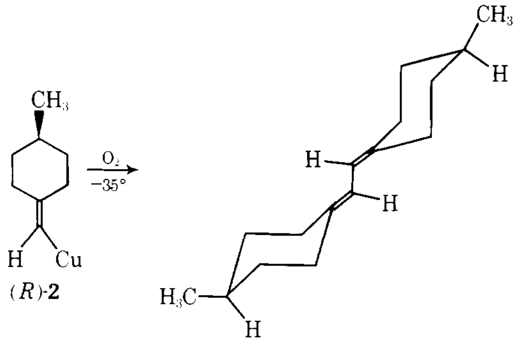
(1)

kylation of a chiral vinylcopper(I) derivative, 4-methylcyclohexylidenemethylcopper (**2**).

Optically active vinylcopper reagent **2** was prepared by the metal-halogen exchange, transmetalation sequence described in eq 2. Reaction of 1 equiv of *sec*-butyllithium with (*R*)-(−)-4-methyl-1-bromomethylenecyclohexane[4] (94% optically pure) in THF-pentane at −75° afforded 4-methylcyclohexylidenemethyllithium (**1**). Addition of 1 equiv of cuprous iodide to **1**, followed by stirring at −35° for 0.5 h, resulted in the formation of a dark suspension of **2**. Passage of a stream of oxygen through the mixture for 20 min, followed by workup and purification of the crude product by chromatography on 25% $AgNO_3$-silicic acid, gave bis(4-methylcyclohexylidene)-ethane (53%), $[\alpha]^{25}{}_{\mathrm{Hg}}$ +37.9° (*c* 0.63, absolute EtOH). Diene **3** was characterized by its uv, ir, NMR, and mass spectra which are similar to those reported for achiral dicyclohexylidene-ethanes,[5] and by its ORD and CD spectra.[6]



(*R*)-(−) **1** (*R*)-**2** (2)

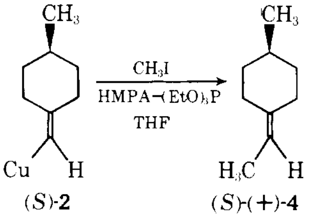


(*R*)-**2**

3

(a*R*, a*R*)-(+)-**3**

In order to determine the stereochemical stability of the optically active vinylcopper reagent, (*S*)-**2** was methylated by the procedure of Normant.[2] To a THF solution of (*S*)-**2**, prepared from 87% optically pure (*S*)-(+)-4-methyl-1-bromomethylenecyclohexane was added 3 equiv of triethyl phosphite and 2 equiv of HMPA, followed by the addition of 1 equiv of methyl iodide. The mixture was stirred at −35° for 15 min and then allowed to slowly reach room temperature and to stir for an additional 12 h. After workup, (*S*)-(+)-4-methyl-1-ethylidenecyclohexane (**4**) was obtained (76%) and further purified by chromatography on 25% $AgNO_3$-silicic acid and bulb-to-bulb distillation, $[\alpha]^{20}{}_{\mathrm{Hg}}$ +14.66 (*c* 0.16, $CHCl_3$), 83% optically pure.[7] Since the overall conversion of (*S*)-(+)-4-methyl-1-bromomethylenecyclohexane to (*S*)-(+)-**4** occurs with greater than 97% retention of configuration, **2** maintains its configuration under conditions similar to those required for oxidative coupling. It is likely that **3** was formed in very high optical purity (~94%) since oxidative coupling is a stereospecific reaction.[1,2]



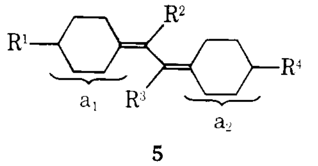
(*S*)-**2** (*S*)-(+)-**4**

Optically active diene **3** arises from stereospecific coupling of two dissymmetric axis of the same chirality and is assigned the absolute configuration (+)-(a*R*,a*R*) according to the Cahn-Ingold-Prelog convention for multiaxial dissymmetry.[8] This assignment relates the configuration of **3** to that of (−)-(*R*)-4-methyl-1-bromomethylenecyclohexane, the absolute configuration of which has been established.[9]

A conjugated diene is chiral if the diene unit is structurally or sterically distorted from planarity (skewed) or if there are other elements of dissymmetry in the molecule (nonskewed). Previous research has focused primarily on skewed dienes.[10] The chiroptical properties of such nonplanar dienes are characteristic of inherently dissymmetric chromophores—large molecular rotations and intense CD maxima paralleling intense uv absorption.[11] The signs of the Cotton effects observed for a large number of homo- and heteroannular cisoid and heteroannular transoid dienes have been related to the sense of skew of the diene moieties.[12] Recently, the enantiomerization barriers of skewed conformers of several cyclic and acyclic conjugated dienes have been determined by dynamic NMR measurement.[13]

Relatively few investigations have been made of planar diene chromophores in dissymmetric environments. The CD spectra of *cis*-and *trans*-(*S*)-(+)-5-methyl-1,3-heptadiene show weak maxima associated with asymmetric perturbation of the symmetrical butadiene chromophore.[14]

The chromophore of **3** fits between the extremes of the inherently dissymmetric (skewed) and symmetric (asymmetrically substituted) butadiene. The molecular dissymmetry of **3** arises from the combination of two chiral olefinic axes, rather than from skewed or asymmetrically substituted double bonds. Diene **3** is the first member of this new class of dissymmetric conjugated dienes—the dicyclohexylidene-ethane derivatives, **5**. This family includes **3** or a special case in which the dissymmetric axes, a_1 and a_2, are structurally identical ($R^1 = R^4$, $R^2 = R^3$). Similar optically active dicycloalkylidene-alkanes may be envisioned.



5

Suitable substituents, R^1 and R^3, of the diene **4** should stabilize skewed rotamers with respect to the planar form and, therefore, introduce an additional element of chirality for this type of molecule. However, there is no evidence that **3** is sufficiently hindered to prevent rapid interconversion of the two skewed diastereomers.[15]

Since **3** is unique the interpretation of its ORD and CD spectra is difficult. The structure of the CD maxima of **3** is analogous to that of the corresponding uv absorption, and the Cotton effects associated with both the CD and ORD are very intense. These intense Cotton effects probably reflect the distortion of each double bond with respect to its attached cyclohexane ring, rather than the twistedness of the diene chromophore itself.[16] In fact, the positive Cotton effects associated with the long-wavelength absorption maxima of (a*R*,a*R*)-**3** correlate with the positive Cotton effects observed for similar cyclohexylidenealkane derivatives containing extended conjugation and having the same absolute configuration about the chiral olefinic axes.[17]

Acknowledgment. The support of this work by a Public Health Service Research Grant CA-04065, from the National Cancer Institute, is gratefully acknowledged.

References and Notes

(1) G. M. Whitesides and C. P. Casey, *J. Am. Chem. Soc.*, **88,** 4541 (1966).
(2) J. F. Normant, G. Cahiez, C. Chuit, and J. Villieras, *J. Organomet. Chem.*, **77,** 269 (1974).
(3) M. P. Periasamy and H. M. Walborsky, *J. Am. Chem. Soc.*, **97,** 5930 (1975).
(4) W. H. Perkin and W. J. Pope, *J. Chem. Soc.*, **99,** 1510 (1911).
(5) I. T. Harrison, B. Lythgoe, and S. Trippett, *J. Chem. Soc.*, 4016 (1956), and references therein; K. K. Kukawa, K. Sakai, K. Asoda, and T. Matusuda, *J. Organomet. Chem.*, **77,** 131 (1974).
(6) MS (*m/e*), relative intensity: 218(100), 161(40.5), 122(45.3), 108(47.6), 107(57.3), 93(82.9), 91(64.6); exact mass of $M\cdot^+$ 218.2023 ($C_{16}H_{26}$) measured, 218.2034 ($C_{16}H_{26}$) calculated; NMR (CCl_4) (ppm) 5.81 (singlet, 1 H), 0.85–2.9 (complex, 12 H's); ir (CCl_4) (cm^{-1}) 3040, 2920, 1620, 1455, 1390, 960; uv (c 95 × 10^{-5}, 95% EtOH) λ 259 (ε 27 500), 250 (ε 38 820), 242 (ε 31 860), sh 233 (ε 23 000); CD (c 9.53 × 10^{-5}, 95% EtOH) $[\theta]_{270}$ 0, $[\theta]_{258.5}$ +14 560, $[\theta]_{249}$ +22 360, $[\theta]_{241.5}$ +20 176, $[\theta]_{234}$ +7280 (shoulder), $[\theta]_{217.5}$ −12 376, $[\theta]_{206}$ −6136 (shoulder). RD (c 9.53 × 10^{-5}, 95% EtOH): $[\phi]_{310}$ +1049, $[\phi]_{262}$ +1539, $[\phi]_{255}$ +3147, $[\phi]_{251}$ + 6294, $[\phi]_{229}$ −23 078, $[\phi]_{210}$ −2098.
(7) (a) Specific rotation of authentic samples of **4:** 1. $[\alpha]^{24}{}_{\mathrm{Hg}}$ +17.7° (c, 2.03, $CHCl_3$; 96% optically pure), unpublished work of H. M. Walborsky and M. L. Banks; 2. $[\alpha]_{\mathrm{D}}$ +14° (isooctane), Ph.D. Dissertation of A. T. Worm with J. H. Brewster, Purdue University, 1970. (b) Triethyl phosphite could be completely removed from the product mixture by several extractions with dilute silver nitrate solution.
(8) R. S. Cahn, C. Ingold, and V. Prelog, *Angew. Chem., Int. Ed. Engl.*, **5,** 385 (1966).
(9) (a) Carbonation of **1** gives (*R*)-(−)-4-methylcyclohexylideneacetic acid, the absolute configuration of which has been established by chemical means;[9b] (b) H. Gerlach, *Helv. Chim. Acta*, **49,** 1291 (1966).
(10) (a) U. Weiss, H. Ziffer, and E. Charney, *Tetrahedron*, **21,** 3105 (1965); E. Charney, H. Ziffer, and U. Weiss, *ibid.*, 3121 (1965); E. Charney *ibid.*, 3127 (1965); (b) L. W. Jelinski and E. F. Kiefer, *J. Am. Chem. Soc.*, **98,** 281 (1976); L. W. Jelinski and E. F. Kiefer *ibid.*, **98,** 282 (1976); and references therein.
(11) A. Moscowitz, Chapter 12 in "Optical Rotatory Dispersion: Applications to Organic Chemistry", C. Djerassi, Ed., McGraw-Hill, New York, N.Y., 1960; A. Moscowitz, *Tetrahedron*, **13,** 48 (1961).
(12) Reference 10a.
(13) (a) H. Bodecker, V. Jones, B. Kolb, A. Mannschrech, and G. Kobrich, *Chem. Ber*, **108** 3497 (1975), and references therein; (b) ref 10b.
(14) A. Di Corato, *Gazz. Chim. Ital.*, **98,** 810 (1968).
(15) (a) The first resolution of optically stable nonplanar open-chain butadienes has recently been reported;[15b] the enantiomeric stability of the latter compounds is due to the presence of sufficiently bulky substituents; (b) M. Rosner and G. Kobrich, *Angew. Chem., Int. Ed. Engl.*, **14,** 708 (1975).
(16) (a) J. H. Brewster and J. F. Privett, *J. Am. Chem. Soc.*, **88,** 1419 (1966); (b) D. N. Kirk and R. J. Mullins, *J. Chem. Soc., Perkin Trans. 1*, 14 (1974), and references therein.
(17) Reference 16a; J. F. Arnett and H. M. Walborsky, *J. Org. Chem.*, **37,** 3678 (1972), and references therein; H. J. Bestmann and J. Lienert, *Angew. Chem., Int. Ed. Engl.*, **8,** 763 (1969).

R. Bruce Banks, H. M. Walborsky*
Department of Chemistry, Florida State University
Tallahassee, Florida 32306

Received February 23, 1976

Quantitative Preparation and Enthalpy of Rearrangement of the *sec*-Butyl Cation

Sir:

We wish to communicate here: (1) the development of a dynamic calorimeter for measuring enthalpies of rearrangement at low temperatures, (2) its application to the study of a clean solution of *sec*-butyl cation in SO_2ClF which we have used to determine the energy difference between the *sec*-butyl and *tert*-butyl cations in solution, and (3) the implications of this measurement for comparing solvation energies of carbonium ions and hence for solvent effects on reactions proceeding through such intermediates.

Estimates of the relative stabilities of alkyl carbonium ions show a considerable variation.[1] The order: tertiary > secondary > primary > methyl is well established both in solution and gas phase; however, there is disagreement regarding the quantitative differences between specific isomeric pairs of ions (e.g., sec → tert).[2]

Previous attempts at quantitative preparation of *sec*-butyl cation have not been entirely successful.[3-7] The best of these was via the molecular beam technique of Saunders, Cox, and Olmstead who prepared a solution of *sec*-butyl ion of approximately 95% purity containing 5% tertiary ion formed during the preparation.[7]

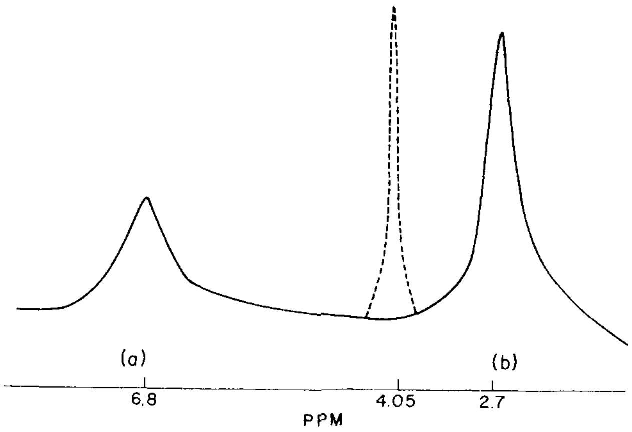


Figure 1. (—) NMR spectrum of *sec*-butyl cation/SbF_5SO_2ClF at −106 °C; (---) ^1H spectrum of solution after warming to 25 °C.

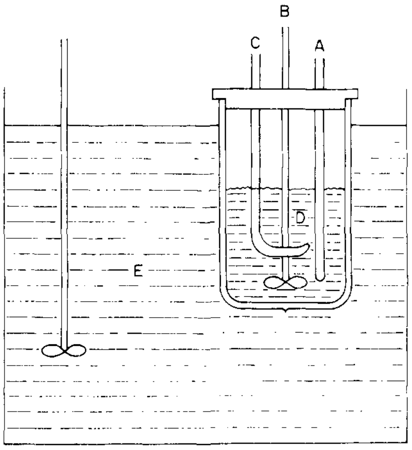


Figure 2. Block diagram of dynamic calorimeter. (A) quartz thermometer; (B) stirrer; (C) heating coil; (D) 50.0 ml of 0.5 M *sec*-butyl ion in SbF_5/SO_2ClF; (E) constant temperature bath (H_2O).

We have prepared the *sec*-butyl ion quantitatively in SbF_5/SO_2ClF solution at −120 °C by the slow addition of a solution of SbF_5/SO_2ClF (8 ml/10 ml) to a cooled (−120 °C) solution of 0.5 M *sec*-butyl chloride in 40 ml of SO_2ClF. At no time did the temperature exceed −100 °C. The ^1H NMR spectrum at −106 °C (Figure 1) of the resulting solution exhibited only two broad signals at 2.7 and 6.8 ppm with relative areas 2:1, respectively. This would be expected if the hydride shift is rapid between the C-2 and C-3 carbon atoms at this temperature.[8] The *tert*-butyl cation, if present, would come at 4.05 ppm[6] where we see no observable signal at −106 °C. The spectrum is temperature dependent exhibiting the same characteristics as that previously described by Saunders, Hagen, and Rosenfield.[6]

The enthalpy of rearrangement of the *sec*-butyl cation to the *tert*-butyl ion was measured directly by dynamic calorimetry.[9] The dynamic calorimeter used in this study consisted of a Dewar flask equipped with a stirrer, a quartz thermometer with printout (Model 2801A, DYMEC, Hewlett Packard), an electrical calibration heater and an external constant temperature bath (Figure 2). In a typical experiment the Dewar flask was immersed in the constant temperature bath[10] containing water at 25° and the calorimeter temperature was monitored as a function of time (Figure 3, curve a). The solution was cooled again to −80 °C and the apparent heat capacity of the calorimeter and contents was now ascertained by passing a known current through the resistance heater ($\Delta H = I^2Rt$) during the programmed heating. The resulting curve