Table VII. Surface Tension, γ {dyn/cm}, of Leucine Solutions at 20 °C as a Function of Concentration and Cosolute

concn, mol/L	aqueous solution	saturated glycine solution (22.8 g/100 mL)
0	72.8	75.7
0.05	72.1	72.1
0.075	71.3	70.0
0.1	70.0	69.2

least 100/batch in the presence of hydrophobic additives, while with hydrophilic ones all the crystals appeared at the bottom of the crystallizer.

Analytical Methods for Quantitative Evaluation of Crystal Orientations. Complete orientation of the glycine crystals was established by the following four independent methods:

a. Crystal Coloring. Crystallization experiments were carried out in the presence of very small amounts (0.01% w/w, which does not have any kinetic effect) of the resolved yellow dye N^{ϵ}-2,4-dinitrophenyl-(*S*)-lysine, which is enantioselectively occluded into the (010) oriented glycine crystals, thus imparting to them a yellow color. These crystals are easily differentiated visually from the non-colored $(0\bar{1}0)$ oriented counterpart.

b. Enantiomeric HPLC Measurements. Samples (20 μL) were injected onto a reverse-phase column (25 cm × 4.6 mm) self-packed with 5 μm Nucleosil C18 (Macherey Nagel), with a mobile phase composition of an aqueous solution of cupric acetate (4×10^{-3} M) and *N*,*N*-di-*n*-propyl-(*S*)-alanine (8×10^{-3} M) at pH 5.3–5.5.[16] The samples were prepared by dissolving the whole batch of floating crystals, after thorough washing in water, into the appropriate amounts of mobile phase.

c. Morphology of the Crystals. The (010) and $(0\bar{1}0)$ oriented glycine crystals assume an enantiomorphous morphology in two-dimensional projection at the interface and are therefore visually differentiable. This enantiomorphism arises from the fact that the β angle is 112° and that within the same batch the ratio of the lengths of the crystals along *a* and *c* is approximately constant.

d. Crystallographic Measurements. The direction of the crystallographic axes and the Miller indexes of the basal {010} faces were assigned by X-ray diffraction measurements on a Siemens diffractometer after the face exposed at the interface was marked.[16]

Methods a–c provide information on the degree of orientation of the entire batch of crystals. Method d which is absolute and unambiguous is only applicable to specimen crystal. Ten percent of each batch containing more than 100 crystals was routinely analized. In addition the few false negatives observed in methods a and c (for example, those crystals which assume a rhombic habit or those which are too thin to occlude sufficient amount of dye) were singularly analyzed by method d.

Growth Experiments. In the experiments of growth from seeds, pairs of seeds of known size (0.5 × 1 mm area, 0.14–0.16 mm thickness) were deposited with opposite ($\pm b$) orientations on the surface of a 2.5% supersaturated glycine solution (300 mL) containing the appropriate additive (Table VI). The solution surface was divided in two compartments by aluminum foil in order to avoid contact between the seeds. Growth of the seeds was performed in closed vessels without stirring in an air thermostat at 26.5 °C, for a period of up to 48 h. The grown crystals were removed and their thickness in the *b* direction remeasured under an optical microscope (×50). The relative growth along *b* is represented by the ratio final:initial thickness.

Amplification Measurements. Crystallizations were performed as described above, both in excess of (*R*) and (*S*) additive. For each enantiomeric excess of the additive used, the appropriate concentration was determined which yields complete orientation of the glycine crystals. In the presence of high concentrations of leucine (>1.5%) of low enantiomeric excess, the floating crystals of glycine are very thin plates. Their orientation was therefore confirmed by all four methods described above.

Surface Tension Measurements. These were performed on a semiautomatic Fisher surface tensiometer by the du Nouy method with use of a platinum iridium ring, for saturated solutions of glycine containing up to 0.1 mol/L of additive.

Acknowledgment. We thank Prof. Z. Berkovitch-Yellin for discussions, E. Gati Shavit for her skillful help, the Israel Academy of Science and Humanities, the U.S.-Israel Binational Foundation, Jerusalem, and the donors of the Petroleum Research Fund, administrated by the American Chemical Society, for financial support. L.A. is a recipient of the Charles S. Revson Career Development Chair.

Thermochemical Study of the Addition of Carbenium Ions to Alkenes

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Abstract: Scales of carbenium ion stabilities have been obtained from ^{1}H NMR equilibrium studies of mixtures of partly ionized para-substituted diarylmethyl chlorides in CD_2Cl_2/BCl_3 at −70 °C and via calorimetric determination of the heats of ionization (ΔH_i) of the alkyl chlorides ($Ar_2CHCl + BCl_3 \rightarrow Ar_2CH^+BCl_4^-$) in CH_2Cl_2/BCl_3 at −70 °C. The heats of the reactions of diarylmethyl tetrachloroborates with 2-methyl-1-pentene ($Ar_2CH^+BCl_4^- + CH_2{=}C(CH_3)C_3H_7 \rightarrow Ar_2CH\text{-}CH_2C(CH_3)ClC_3H_7 + BCl_3$), which were determined by low-temperature calorimetry, increase from −53.1 kJ/mol for $(H_3CC_6H_4)_2CH^+BCl_4^-$ to −33.0 kJ/mol for the better stabilized $(H_3COC_6H_4)(H_3CC_6H_4)CH^+BCl_4^-$. In contrast, the heats (ΔH_a) of the Lewis acid *catalyzed* additions of the corresponding para-substituted diarylmethyl chlorides to 2-methyl-1-pentene are independent of the para substituents ($\Delta H_a = -86.5 \pm 2.7$ kJ/mol). Similar values of ΔH_a were obtained for the addition of *p*-anisylphenylmethyl chloride to trimethylethylene, styrene, β-methylstyrene, and isoprene. ΔH_a is predominantly determined by the conversion of a π(C=C) into a σ(C—C) bond, and the heats of addition of diarylmethyl tetrachloroborates to alkenes in CH_2Cl_2 are given by the equation $\Delta H_b = (9.5 \pm 6.3\ pK_{R^+})$ kJ/mol.

Most synthetic reactions that yield carbon–carbon bonds proceed via polar mechanisms. Charged and neutral species may be used as synthetic equivalents of a- and d-synthons.[2] One conceivable extreme, the reaction of carbenium ions with carbanions, has recently been investigated in detail.[3] In that system, the heats of reaction only depend on the stabilization energies of both ions (pK_a and pK_{R^+}), since the neutral products are characterized by approximately constant σ(C–C) bond increments. The addition

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[1] (a) Medizinische Universität zu Lübeck. (b) Duke University.

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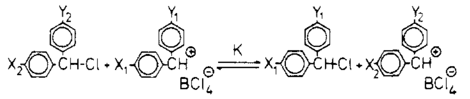
Table I. NMR Spectroscopically Determined Equilibrium Constants and Free Energy Differences (−70 °C; CD_2Cl_2/BCl_3)



$X_1,Y_1/X_2,Y_2$	K_{203}	$\Delta G°_{203}$, kJ/mol
$OCH_3,OCH_3/OCH_3,OPh$	0.014	7.2 ± 0.3
$OCH_3,OPh/OCH_3,CH_3$	0.049	5.1 ± 0.3
$OCH_3,CH_3/OCH_3,H$	0.025	6.2 ± 0.1
$OCH_3,CH_3/OPh,CH_3$	0.0098	7.8 ± 0.3
$OCH_3,H/OPh,CH_3$	0.50	1.2 ± 0.1
$OPh,CH_3/OPh,H$	0.026	6.2 ± 0.1
$OPh,CH_3/OCH_3,Cl$	0.51	1.2 ± 0.4
$OPh,H/CH_3,CH_3$	0.26	2.3 ± 0.3
$OCH_3,Cl/CH_3,CH_3$	0.014	7.2 ± 0.3

Table II. Comparison of Various Stability Scales of Para-Substituted Diarylcarbenium Ions **1**$^+$-X,Y (kJ/mol)

X,Y	$\Delta\Delta G_i°$ [a]	ΔH_i [b]	$\Delta G_i°$ [c]	$\Delta H_r'$ [d]	pK_{R^+} [e]
OCH_3,OCH_3	0.0				−5.71
OCH_3,OPh	7.2				
OCH_3,CH_3	12.3	−49.5 ± 2.1			
OCH_3,H	18.5	−45.4 ± 2.9			−7.9
OPh,CH_3	19.7				
OCH_3,Cl	20.9				
OPh,H	25.9		−8.4		
CH_3,CH_3	28.1	−32.6 ± 2.5	−7.0	−175.4 ± 3.8	−10.4
CH_3,H			3.0		−11.6
H,H				−164.5 ± 2.9	−13.3
H,Cl					−13.7
Cl,Cl				−148.6 ± 3.3	−13.96

[a] From equilibrium measurements in CH_2Cl_2/BCl_3 at −70 °C. Average error is ±0.4 kJ/mol; this work. [b] Heats of ionization of the diarylmethyl chlorides in CH_2Cl_2/BCl_3 at −70 °C; calorimetric investigation, this work. [c] Free energy of ion pair formation in CH_2Cl_2/BCl_3 at −70 °C; from conductivity measurements.[11] [d] Heats of reaction of the diarylmethyl alcohols in SO_2Cl_2, SbF_5/FSO_3H (1:1) at −55 °C, calorimetric investigation.[7a] [e] From equilibrium measurements of the diarylmethyl alcohols in H_2SO_4 at 25 °C.[6]

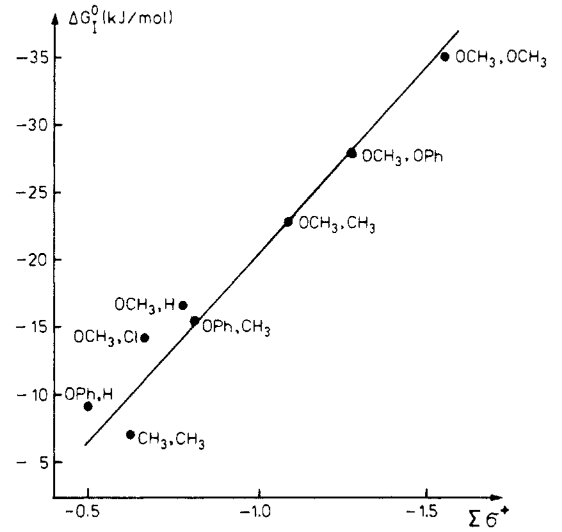


Figure 1. Correlation of the free energies of ionization ($\Delta G_i°$) of para-substituted diarylmethyl chlorides **1**-X,Y in CD_2Cl_2/BCl_3 at −70 °C versus the sum of σ^+ values. The correlation equation (r = 0.980) is $\Delta G_i° = 5 + 26\sum\sigma^+$ (kJ/mol).

Scheme I

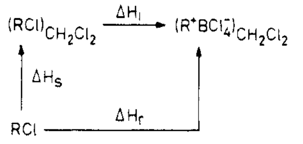
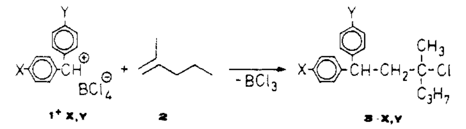


Table III. Heats of Ionization (ΔH_i) of Para-Substituted Diarylmethyl Chlorides **1**-X,Y in CH_2Cl_2/BCl_3 at −70 °C (kJ/mol). Comparison of Relative Carbenium Ion Stabilities from Calorimetric ($\delta\Delta H_i$) and Equilibrium ($\delta\Delta G_i°$) Studies

X,Y	ΔH_r	ΔH_s	ΔH_i	$\delta\Delta H_i$	$\delta\Delta G_i°$
CH_3,CH_3	−18.3 ± 2.3	14.4 ± 1.0	−32.6 ± 2.5	0	0
OCH_3,H	−27.9 ± 2.1	17.4 ± 2.0	−45.4 ± 2.9	−12.8	−9.6
OCH_3,CH_3	−36.2 ± 2.0	13.3 ± 0.5	−49.5 ± 2.1	−16.9	−15.8

of carbenium ions to alkenes is a related reaction type. The Lübeck group has recently developed methods to generate 1:1 addition products via Lewis acid catalyzed reactions of alkyl halides with alkenes,[4] and the kinetics of the model reaction 1 have been studied.[5]



(1)

In this paper we present a thermochemical study of the ionization of diarylmethyl chlorides (**1**-X,Y) and their addition reaction with alkenes.

1. Ionization of Diarylmethyl Chlorides. Equilibrium Studies—Free Energies of Ionization. Since the data on diaryl carbenium ion stabilities that are available refer to different media,[6,7a] we obtained a more comprehensive set of data by ^{1}H NMR spectroscopic studies of equilibria involving diarylmethyl tetrachloroborates in CH_2Cl_2 at −70 °C.

If two cations are of similar stability, the equilibrium constant K (eq 2) may be derived from the ratios of the species observed in the ^{1}H NMR spectrum (Table I). These data can be connected to give a scale of carbenium ion stabilities (column I, Table II).

$$R_1^+ + R_2Cl \overset{K}{\rightleftharpoons} R_1Cl + R_2^+ \qquad (2)$$

In previous work, it has been shown that the heats of ionization of tertiary cumyl alcohols in SbF_5, FSO_3H/SO_2ClF at −55 °C are linearly correlated[7a] with σ^+ parameters.[8] Figure 1 shows that the free energies of ionization of diarylmethyl chlorides also give a fair correlation with $\sum\sigma^+$.[9]

The ^{1}H NMR shifts of the methine protons in the diarylcarbenium ions are correlated by $\delta = 8.79 + 0.027\Delta\Delta G_i°$ to the relative carbenium ion stabilities of Table II.

Investigations of the temperature dependence of equilibrium reaction 2 are complicated by irreversible reactions taking place at elevated temperatures. Furthermore, rapid halide transfers, probably catalyzed by BCl_4^-, lead to coalescences of NMR signals. Analysis of the temperature dependence of eq 2 between −70 and −30 °C gave $\Delta\Delta S_i$ = −3.1 J/K·mol for **1**-OMe,Me/**1**-OMe,H and $\Delta\Delta S_i$ = 0.6 J/K·mol for **1**-OMe,OPh/**1**-OMe,Me. These numbers

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Table IV. Heats of Addition of Para-Substituted Diarylmethyl Chlorides (**1**-X,Y) to 2-Methyl-1-pentene (**2**) in CH_2Cl_2 at −70 °C (kJ/mol)

	ΔH_a					
para-subst X,Y in **1**	procedure A,[a] Scheme II	procedure B, Scheme III	ΔH_r(A)	ΔH_r(B)	ΔH_s(RCl)	ΔH_c
OCH_3,CH_3	−82.5 ± 4.7	−84.9 ± 2.5	−74.0 ± 4.1	−116.4 ± 2.3	13.3 ± 0.5	−44.8 ± 0.9
OCH_3,H	−84.5 ± 3.6	−90.2 ± 2.7	−79.0 ± 1.8	−116.5 ± 1.5	17.4 ± 2.0	−43.7 ± 1.0
CH_3,CH_3	−85.7 ± 4.5	−88.9 ± 2.2	−49.3 ± 3.7	−74.5 ± 2.0	14.4 ± 1.0	0
		−84.2 ± 3.4[b]		−69.8 ± 3.3		
CH_3,H		−90.9 ± 0.9		−91.5 ± 0.7[c]	−0.6 ± 0.5	0
H,H		−86.6 ± 1.9		−76.3 ± 1.7[c]	10.3 ± 0.9	0

[a] $\Delta H_s(\mathbf{2})$ = 3.8 ± 0.3 kJ/mol. [b] Lewis acid: $ZnCl_2\cdot(OEt_2)_{1.5}$.[16] The heat of complexation of the product by the Lewis acid was assumed to be zero. [c] Due to dissolution problems, some of the experiments were carried out with solutions of **1**-X, in CH_2Cl_2. Prior to averaging, ΔH_r was calculated according to $\Delta H_r = \Delta H_r' + \Delta H_s$ in these cases.

show that the $T\Delta\Delta S_i$ term is smaller than the error limits of $\Delta\Delta G_i°$ at −70 °C. The data of Table I, therefore, represent differences in enthalpy, which can independently be determined by calorimetry.

Calorimetric Studies—Enthalpies of Ionization. The diarylmethyl chlorides listed in Table I are completely ionized in the presence of 1 (**1**-OMe,OMe)–200 (**1**-Me,Me) equiv of BCl_3 in CH_2Cl_2 at −70 °C, and we determined the heats of reaction (ΔH_r) by breaking ampules of solid diarylmethyl chlorides **1**-X,Y in the Lewis acid solution. According to Scheme I, heats of ionization (ΔH_i) can be obtained by correcting ΔH_r for the integral heats of solution (ΔH_s) of the pure diarylmethyl chlorides in CH_2Cl_2 (Table III). ΔH_i was not dependent on the total ion concentration within the range of our study (10^{-2}–10^{-3} M), where ion pairing predominates.[10,11]

The comparison of $\Delta\Delta G_i°$ (equilibrium) and ΔH_i (calorimetry) in Table III shows that both scales are parallel within the limits of experimental error ($\Delta\Delta G_i°$, ±0.4 kJ/mol; ΔH_i, ±2.5 kJ/mol; average values). We conclude again that the differential entropies of ionization for two different diarylmethyl chlorides [$\Delta\Delta S_i = \Delta S_i(R_1Cl) - \Delta S_i(R_2Cl)$] are close to zero. This relation has earlier been derived from $pK_{R^+}/\Delta H_i$ correlations[7a] and from correlations of solvolysis rates versus ionization enthalpies.[12]

While $\Delta\Delta S_i \approx 0$, the absolute magnitude of ΔS_i must be quite substantial, since **1**-Me,H ionizes only partially in BCl_3/CH_2Cl_2 at −70 °C though the ionization can be estimated to be exothermic by approximately −25 kJ/mol from pK_{R^+} (Table II). For the ionization of **1**-Me,Me under these conditions $\Delta G_i°$ was derived to be −7.0 kJ/mol;[11] with ΔH_i = −32.6 kJ/mol we obtain ΔS_i = −126 J/K·mol. Reported values for ΔS_i range from −50 to −150 J/K·mol.[13]

Comparison of Different Carbenium Ion Stability Scales. Scales of carbenium ion stabilities have proven to be mutually convertible.[3a,7a] Heats of ionization of carbenium ion precursors in different Lewis acid media differ by a heat of transfer term (ΔH_t). ΔH_t is mainly determined by carbon–leaving group bonding, Lewis acid–leaving group bonding, Lewis acid–solvent bonding, and general dielectric solvation. ΔH_t is constant for different cations, if they are solvated likewise within each medium. This is usually true for large, delocalized cations in nonnucleophilic media.[7a,b,14] Comparison of ΔH_i for **1**-Me,Me in CH_2Cl_2/BCl_3 at −70 °C with the heat of ionization of the corresponding alcohol in SbF_5, HSO_3F, SO_2ClF at −55 °C[7a] yields ΔH_t = −143 kJ/mol for these media. With this number, we can convert the large variety of ΔH_i data obtained in superacidic media into the CH_2Cl_2/BCl_3 system to predict the feasibility of carbenium ion–alkene reactions in this medium.

The pK_{R^+} values[6d] of four diaryl carbenium ions are linearly related to ΔH_i (Figure 2). The slope of the correlation line, $\Delta H_i = mpK_{R^+} + b$, corresponds to that obtained in superacidic medium[7a] [$m(CH_2Cl_2/BCl_3)$ = −6.3 kJ/mol; m'(superacid) = −6.9 kJ/mol], while the intercepts [$b(CH_2Cl_2/BCl_3)$ = −96 kJ/mol; b'(superacid) = −250 kJ/mol) differ by a value close to ΔH_t.

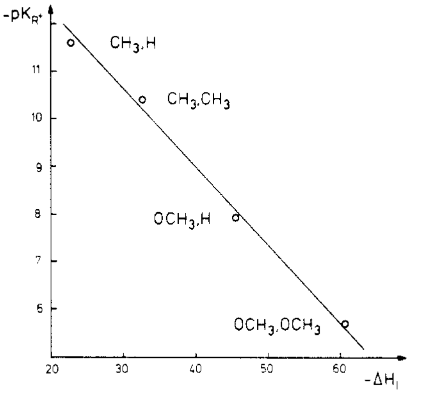
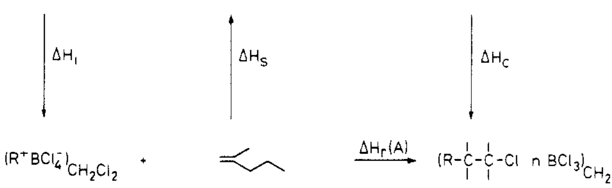


Figure 2. Correlation of heats of ionization (ΔH_i) of **1**-X,Y in BCl_3/CH_2Cl_2 at −70 °C versus pK_{R^+} for equilibria of the same cations with their carbinols in aqueous H_2SO_4. ΔH_i(**1**-OMe,OMe) was derived from equilibrium studies and ΔH_i(**1**-Me,H) from conductivity experiments. The correlation equation (r = 0.997) is $\Delta H_i = -96 - 6.3pK_{R^+}$ (kJ/mol).

Scheme II



2. Calorimetric Study of the Addition of Diarylmethyl Chlorides to Alkenes. Addition of Diarylmethyl Chlorides to 2-Methyl-1-pentene. The addition of diarylmethyl chlorides to 2-methyl-1-pentene in CH_2Cl_2 at −70 °C is selectively terminated after the formation of the 1:1 products.[4,5] We have evaluated the heats of addition (ΔH_a) in two different ways.

In approach A (Scheme II), a definite amount of neat alkene was added to an excess of completely ionized **1**-X,Y. In order to obtain ΔH_a for the CH_2Cl_2-solvated components, we have to correct the observed heats of reaction [ΔH_r(A)] for the heats of ionization of **1**-X,Y (ΔH_i, see above), the heats of solution of the alkene in CH_2Cl_2 (ΔH_s), and the complexation enthalpy (ΔH_c) of the addition products with the Lewis acid (eq 3). The latter was determined by introducing CH_2Cl_2 solutions of the adducts **3**-X,Y into mixtures of CH_2Cl_2/BCl_3.

$$\Delta H_a = \Delta H_r(A) + \Delta H_i - \Delta H_s(\text{alkene}) - \Delta H_c \quad (3)$$

In approach B, ΔH_a was obtained by introducing samples of pure RCl into a solution of excess alkene in CH_2Cl_2/Lewis acid (Scheme III). For the evaluation of ΔH_a, the heat of reaction ΔH_r(B) has to be corrected for the heats of solution of **1**-X,Y in CH_2Cl_2 (ΔH_s) and ΔH_c (eq 4). ΔH_a ought to be further corrected

$$\Delta H_a = \Delta H_r(B) - \Delta H_s(RCl) - \Delta H_c \quad (4)$$

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Scheme III

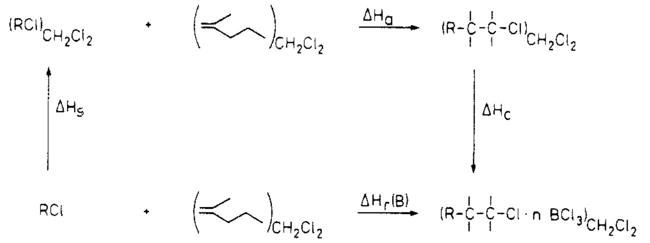
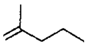
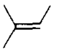
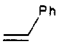
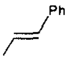
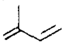


Table V. Heats of Addition of Anisylphenylmethyl Chloride (**1**-OMe,H) to Various Alkenes in CH_2Cl_2/BCl_3 at −70 °C (kJ/mol)

alkene	ΔH_a[a]	$\Delta H_r(A)$[b]	ΔH_c[c]
	−84.5 ± 3.6		−43.7 ± 1.0
	−78.9 ± 3.8	−80.6 ± 2.2	−47.1 ± 1.0
	−83.4 ± 3.2	−82.5 ± 1.2	−44.5 ± 0.4
	−78.1 ± 4.4	−77.8 ± 3.2	−45.1 ± 0.7
	−74.2 ± 2.9	−77.2 ± 0.4	−48.4 ± 0.1

[a] ΔH_a evaluated according to Scheme II, procedure A. [b] Heat of reaction between the carbenium ion and the CH_2Cl_2-solvated alkenes. [c] Heat of complexation of the CH_2Cl_2-solvated products by BCl_3 in CH_2Cl_2 at −70 °C.

for the enthalpy of interaction between alkene and Lewis acid. Since we found it not to exceed 4 kJ/mol, in line with studies on other Lewis acids,[15] it has been disregarded.

Table IV shows that both pathways gave heats of addition of diarylmethyl chlorides to 2-methyl-1-pentene (average value, $\Delta H_a = -86.5 \pm 2.7$ kJ/mol) that are independent of the para substituents.

The slightly larger ΔH_a values obtained by pathway B are probably due to a small degree of polymerization, because the heats of reaction moderately increased with increasing alkene concentrations when BCl_3 was used for procedure B. Since polymerization does not take place in the $ZnCl_2{\cdot}(OEt_2)_{1.5}$ catalyzed[16] reactions, the ΔH_a value obtained with $ZnCl_2$ from procedure B is in fair agreement with ΔH_a of pathway A.

Para-substituted diarylmethyl chlorides are related to systems with important anomeric interactions.[17] Instead of the direct interaction between the geminally bonded groups X and Y with Cl as in $H_2C(X)Cl$ and $H_2C(Y)Cl$, a benzene ring separates both ligands from the anomeric center. The invariance of ΔH_a with varying X,Y indicates that such ground-state effects are small (<3 kJ/mol), in line with recent X-ray crystallographic evidence.[18]

The invariance of ΔH_a for a set of related alkyl halides had been assumed earlier in the derivation of rules for the scope of aliphatic Friedel–Crafts alkylations.[4a–d]

Addition of the Anisylphenyl Carbenium Ion to Different Alkenes. For the reaction of anisylphenyl carbenium ion $\mathbf{1}^+$-OMe,H with different alkenes, ΔH_a values between −74 and −85 kJ/mol were evaluated by procedure A (Scheme II; Table V).

Reaction 1 involves the conversion of a CC double bond into two CC single bonds. In accordance, ΔH_a predominantly reflects the difference between the bond energy increments of two CC single (2 × 350 kJ/mol) and one CC double bond (610 kJ/mol).[19] Preliminary force field studies showed that steric effects, the extent of alkyl halide substitution, and loss of alkene π-resonance usually make only a minor contribution to ΔH_a. Since steric effects and π-resonance contributions are small for the compounds investigated, the corresponding values of ΔH_a fall within the same range.

3. Conclusion. A Correlation Equation of Carbon–Carbon Bond Formation. The heats of coordination ($\Delta H_{\mathrm{coord}}$) of different carbocations with various carbanions in benzonitrile, acetonitrile,[3a,b] and sulfolane/3-methylsulfolane[3c] have previously been derived to follow eq 5. The heat of the reaction of carbenium tetrachloroborates with alkenes in CH_2Cl_2 yielding unionized adducts **3** (ΔH_b) is given by eq 6. Since the ΔH_a values are almost

$$\Delta H_{\mathrm{coord}} = \mathrm{const} + a\mathrm{p}K_{\mathrm{R}^+} + b\mathrm{p}K_a = -50.2 + 4.93\ \mathrm{p}K_{\mathrm{R}^+} - 4.92\mathrm{p}K_a\ \mathrm{(kJ/mol)} \quad (5)$$

$$\Delta H_b = \Delta H_a - \Delta H_i(\mathrm{RX}) = \Delta H_r(\mathrm{A}) - \Delta H_s(\mathrm{alkene}) - \Delta H_c \quad (6)$$

constant when strong steric effects are absent and ΔH_i is linearily correlated with $\mathrm{p}K_{\mathrm{R}^+}$, eq 6 is equivalent to eq 7.

$$\Delta H_b = \mathrm{const}' + a'\mathrm{p}K_{\mathrm{R}^+} = 9.5 + 6.3\mathrm{p}K_{\mathrm{R}^+}\ \mathrm{(kJ/mol)} \quad (7)$$

While the carbanion is replaced by a neutral nucleophile, the anion stability term ($\mathrm{p}K_a$) of eq 5 is omitted in eq 7. The constants in eq 5 and 7 include a C–C bond increment and an ion solvation term. In addition, the constant in eq 7 incorporates a C–Cl bond increment, the enthalpy for the separation of Cl^- from the complex anion and the interaction of BCl_3 with the solvent. Whereas a', which is of similar magnitude as a (eq 5), is expected to be almost invariant toward a change of solvent and counterion, const′ will increase with increasing solvent polarity and increasing acceptor strength of the Lewis acid.

The free enthalpy of the carbenium tetrachloroborate additions is given by eq 8.

$$\Delta G_b^\circ = \Delta G_i^\circ - \Delta G_i^\circ(\mathrm{RX}) = \Delta H_a - \Delta H_i(\mathrm{RX}) - T(\Delta S_a - \Delta S_i) = \Delta H_b - T(\Delta S_a - \Delta S_i) \quad (8)$$

With the incremental system reported by Benson,[20] the entropy of addition (ΔS_a) for the reaction of diarylmethyl chlorides with 2-methyl-1-pentene is estimated to be $\Delta S_a = -164$ J/K·mol, and ΔS_i was calculated to be approximately −130 kJ/mol (see above). Substitution of these numbers in eq 8 yields eq 9.

$$\Delta G_b^\circ = 16 + 6.3\mathrm{p}K_{\mathrm{R}^+}\ (\mathrm{kJ/mol\ at\ -70\ ^\circ C}) \quad (9)$$

Since ΔH_a and ΔS_a[20] and probably ΔS_i fall into the same range for a variety of alkyl halides and alkenes, the addition of carbenium tetrachloroborates to alkenes is thermodynamically unfavorable in CH_2Cl_2 at −70 °C, if $\mathrm{p}K_{\mathrm{R}^+} > -2.6$. Different values are obtained when steric interactions cannot be neglected and when the products are stabilized by complexation with the Lewis acid.

We are currently investigating the influence of alkene and alkyl halide variation on ΔH_a and ΔG_a° by force field methods.

Experimental Part

General Procedures. Diarylmethyl chlorides **1**-X,Y and their alkene addition products were prepared according to literature procedures.[4b,11] Alkenes were distilled over $LiAlH_4$ prior to use or employed as purchased (isoprene, styrene; Aldrich Gold Label). For the equilibrium studies, gaseous BCl_3 (99.9%, Messer Griesheim) was transferred via gas-tight syringes. For calorimetric studies, a 1 M solution of BCl_3 in CH_2Cl_2 (Aldrich) was used. The $ZnCl_2{\cdot}(OEt_2)_x$ catalyst was prepared according to ref 16. CH_2Cl_2 was subsequently stirred over $CaCl_2$, concentrated sulfuric acid, and K_2CO_3 and then distilled over P_4O_{10} and finally Na–Pb alloy (Fluka). CD_2Cl_2 was stored over Na–Pb alloy prior to use. NMR spectra were obtained on a Varian XL-200 spectrometer. Chemical shifts are reported relative to $Si(CH_3)_4$. Errors given are mean standard deviations of measured quantities. Errors of derived data have been evaluated according to laws of propagation of errors.

Equilibrium Studies. Partial ionization of the mixtures of the alkyl halides is usually obtained by adding 0.5–1 equiv of BCl_3 in CD_2Cl_2 at −70 °C. ^{1}H NMR spectral data are given in the supplementary material.

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Typical example: *p*-Anisyl(*p*-phenoxyphenyl)methyl chloride (**1-OMe,OPh**; 40.2 mg, 0.124 mmol) and *p*-anisyl-*p*-tolylmethyl chloride (**1-OMe,Me**; 72.4 mg, 0.293 mmol) were dissolved in 0.6 mL of CD_2Cl_2 in an NMR tube. 1,1,2,2-Tetrachloroethane (20.0 μL, 31.5 mg, 0.188 mmol) was added as standard. Partial ionization of the mixture is accomplished by addition of 2.3 mL (0.094 mmol) of BCl_3 gas at −70 °C. The signals of para methyl (δ = 2.33, **1-OMe,Me**; δ = 2.58, **1^+-OMe,Me**), para methoxy (δ = 3.75, **1-OMe,Me**, **1-OMe,OPh**; δ = 4.14, **1^+-OMe,OPh**; δ = 4.22, **1^+-OMe,Me**), and methine protons (δ = 6.14, **1-OMe,OPh**; δ = 6.17, **1-OMe,Me**; δ = 8.94, **1^+-OMe,OPh**; δ = 9.13, **1^+-OMe,Me**) in both carbenium ion and precursors were recorded with those of tetrachloroethane (δ = 6.01). The signal integrals gave nine equations for the determination of the concentrations of **1-OMe,OPh**, **1^+-OMe,OPh**, **1-OMe,Me**, and **1^+-OMe,Me**. Regression analysis[21] led to $K_{203} = 0.0480$ and $\Delta G_{203}{}^\circ = 5.13$ kJ/mol. Further determinations of $\Delta G_{203}{}^\circ$ for six different samples ($\Delta G_{203}{}^\circ$ = 4.84, 5.15, 5.36, 4.71, 5.02, 5.60 kJ/mol) gave an average value of $\Delta G_{203}{}^\circ = 5.1 \pm 0.3$ kJ/mol.

Calorimetric Studies. General Procedures. A calorimeter of the type previously described[22] was used with minor modifications. Experimental details and procedures closely followed the description given there[22] if not otherwise reported. Each measurement was repeated at least twice. A determination of the heat capacity of the calorimeter was undertaken before and after every calorimeter run. The reliability of the data was checked independently by the determination of the heat of interaction of tetrahydrofuran with $SbCl_5$ in CH_2Cl_2 at −55 °C.[23] All further determinations were run in CH_2Cl_2 at −70 °C.

Heats of Addition of Diarylmethyl Chlorides to 2-Methyl-1-pentene. A 1 M solution of BCl_3 in CH_2Cl_2 (10 mL) or of $ZnCl_2{\cdot}(OEt_2)_{1.5}$ in CH_2Cl_2 (5 mL) was added to a solution of the alkene (≈1 mmol) in CH_2Cl_2 (≈10^{-2} M). The heat of reaction upon introduction of 0.50–0.75 mmol of the neat diarylmethyl chloride was recorded. Heats of solution of the diarylmethyl chlorides in CH_2Cl_2 were determined separately.

Heats of Addition of Diarylcarbenium Ions to Alkenes. Ampules of less than stoichiometric amounts (0.2–2 mmol) of the alkene were introduced into a 10^{-3}–10^{-2} M solution (≈200 mL) of the carbenium tetrachloroborates. For 2-methyl-1-pentene the integral heat of solution in CH_2Cl_2 was determined subsequently. All other alkenes have been introduced as 5–20% solutions in ≈1 mL of CH_2Cl_2 and heats of dilution were neglected.

Heats of Interaction with BCl_3. Solutions of the addition products in ≈1.5 mL of CH_2Cl_2 were sealed in an ampule. The heat of reaction upon its introduction into excess BCl_3/CH_2Cl_2 was recorded.

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Supplementary Material Available: ^1H NMR spectral data for diarylmethyl chlorides **1-X,Y** and diarylcarbenium tetrachloroborates in CD_2Cl_2 at −70 °C and compilations of NMR spectroscopic determinations of K and ΔG° (5 pages). Ordering information is given on any current masthead page.

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Host–Guest Complexation. 45. A Highly Preorganized Chromogenic Spherand Indicator System Specific for Sodium and Lithium Ions[1]

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Abstract: The synthesis and chromogenic properties of **1** as a sodium and lithium ion selective indicator system are described. The pK_a values of **1** in the absence and presence of various metal ions were measured in 80% dioxane–20% water (v/v). Observed values were as follows: Li^+, 5.9; Na^+, 6.9; K^+, 12.7; Ca^{2+}, 12.8; Mg^{2+}, 13.2; 1,5-diazabicyclo[4.3.0]non-5-ene (DBN), 13.0. The noncomplexing model system **21** gave a pK_a of 10.8 in the same medium. Spherand **1** is yellow (λ_{max} 396 nm; ϵ_{max} 17 500 L/(mol·cm)), whereas spheraplexes $1^-{\cdot}Li^+$ (λ_{max} 586 nm, ϵ_{max} 35 500 L/(mol·cm)), and $1^-{\cdot}Na^+$ (λ_{max} 596 nm, ϵ_{max} 35 500 L/(mol·cm)) as well as uncomplexed 1^- (λ_{max} 610 nm, ϵ_{max} 53 000 L/(mol·cm)) are deep blue or violet in 80% dioxane–20% water (v/v) and other solvents. Thus **1** is a chromogenic ion-selective indicating system capable of detecting Li^+ and Na^+ at concentrations as low as 10^{-8} M in the presence of other common ions. The binding free energies of spherands **4**–**6** binding lithium picrate and sodium picrate at 25 °C in $CDCl_3$ saturated with D_2O were measured and found to range between 8.4 and 12.5 kcal mol^{-1}, somewhat higher than those for **7**, but much lower than those for **2**.

This paper describes the synthesis and properties of **1** as an ion-selective chromogenic indicator system for Na^+ and Li^+. The binding properties and ion selectivities of analogues **2**–**8** are compared.

Spherand **2** binds lithium, sodium, and potassium picrates at 25 °C in $CDCl_3$ saturated with D_2O with $-\Delta G^\circ$ values of >23, 19.3, and <6 kcal mol^{-1}. The very strong binding of Li^+ and Na^+ and nondetectable binding to K^+ have been attributed to the high complementarity and preorganization of the cavity in **2**.[2] The crystal structure of **2** shows it contains a hole lined with 24 electrons having a diameter between that of Li^+ and Na^+. The six octahedrally arranged oxygens defining the cavity are shielded from solvation by six aryl and six methyl groups to provide a microdielectric environment for complexation between that of a vacuum and that of a hydrocarbon. The potassium ion is too large to enter this structurally defined cavity. Divalent ions of small enough diameters (e.g., Mg^{2+} or Ca^{2+}) do not enter this cavity because of their very high heats of hydration.[3,4]

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