Table I lists the starting [(phenylthio)methyl]carbinyl benzoate esters B, the molar ratio of titanium metal to B in tetrahydrofuran, the times for the reductions (5–16.5 h), and the respective yields of alkenes C (67–97%). The advantages of this new reduction technique are (a) ease of preparation of active titanium metal, (b) aprotic reaction conditions, (c) filtration and concentration type of workup, and (d) no observed overreduction even in the case of diene 6.

Experimental Section

Materials and Techniques. All boiling points were measured external to the bulb-to-bulb distillation pot in an Aldrich Kugelrohr apparatus (catalog No. Z10,046-3) and are uncorrected. IR spectra were recorded on a Perkin-Elmer Model 237B spectrometer using 0.10-mm NaCl solution cells or as thin films between NaCl plates. NMR spectra were measured on a Varian Associates Model T-60. Silica gel 60 (F-254, E. Merck No. 5765 and No. 7734, 70–230 mesh) were used for thin-layer and column chromatography and filtration, respectively. All elution solutions were prepared by volume. Ether (Et$_2$O) and tetrahydrofuran (THF) were purified by fresh distillation of anhydrous commercial solvents from LiAlH$_4$ under N$_2$ immediately before use in all reactions. Thioanisole (Aldrich, catalog No. T2,800-2) and benzoic anhydride were distilled just prior to use. *n*-Butyllithium was obtained as a 1.6 M solution in hexane from Aldrich (catalog No. 18, 617-1). Anhydrous titanium(III) chloride (catalog No. 77116) and potassium metal (catalog No. 306692) were purchased from Alfa Inorganics. The term petroleum ether refers to the Baker "Analyzed Reagent" (bp 30–60 °C). For all anhydrous reactions performed under an atmosphere of dry N$_2$ or Ar the equipment was dried in an oven at 120 °C for several hours and then allowed to cool in an atmosphere of dry N$_2$ or Ar. All liquid transfer were made with N$_2$- or Ar-filled syringes. All microanalyses were performed by Spang Microanalytical Laboratory.

General Method for the Preparation of [(Phenylthio)-methyl]carbinyl Benzoate Esters. 1-(Benzoyloxy)-1-[(phenylthio)methyl]cyclopentadecane (3B). To a solution of freshly distilled thioanisole (2.8 mL, 24 mmol) in anhydrous THF (10 mL) was added slowly with stirring *n*-BuLi/hexane (15 mL, 1.6 M, 24 mmol) at 0 °C. The resulting solution was allowed to stir at room temperature for 23 h. Freshly distilled cyclopentadecanone (3A; 1.03 g, 4.6 mmol) was added at 0 °C, and then the resulting reaction mixture was stirred at room temperature for 15 h. The reaction mixture was then poured into H$_2$O (75 mL) and extracted with Et$_2$O (4 × 20 mL). The combined ethereal extracts were washed with 5% HOAc/H$_2$O (2 × 20 mL) followed by 5% KOH/H$_2$O (2 × 20 mL) and then dried over anhydrous K$_2$CO$_3$. Concentration in vacuo and chromatography of the residue on silica gel (200 g) with 10% Et$_2$O/90% petroleum ether affords 1.55 g (96%) of the corresponding (phenylthio)methyl alcohol: IR (CCl$_4$) 3540 (OH), 1585 (aromatic cm^{-1}; NMR (CCl$_4$) δ 1.37 (br, 28 H, CH$_2$), 2.07 (s, 1 H, OH), 3.02 (s, 2 H, CH$_2$SC$_6$H$_5$), 7.05–7.55 (m, 5 H, SC$_6$H$_5$). Anal. Calcd for C$_{22}$H$_{36}$OS: C, 75.80; H, 10.41; S, 9.26. Found: C, 75.61; H, 10.29; S, 9.07.

To a solution of the above (phenylthio)methyl alcohol (1.52 g, 4.4 mmol) in anhydrous THF (15 mL) was added slowly *n*-BuLi/hexane (3.4 mL, 1.6 M, 5.2 mmol) at 0 °C. The resulting reaction mixture was allowed to warm to room temperature (4 h) and then recooled to 0 °C, and freshly distilled benzoic anhydride (1.18 g, 5.2 mmol) was added. The resulting reaction mixture was stirred at room temperature for 12 h and then poured into ice–water (60 mL). The mixture was extracted with ether (4 × 20 mL). The combined ethereal extracts were dried (Na$_2$SO$_4$). Concentration in vacuo and chromatography of the resulting residue over silica gel (350 g) with 3% Et$_2$O/97% petroleum ether produced 1.91 g (97%) [(phenylthio)methyl]carbinyl benzoate ester 3B: bp 90 °C (0.9 mmHg); IR (CCl$_4$) 1720 (CO) cm^{-1}; NMR (CCl$_4$) δ 1.00–2.67 (m, 28 H, CH$_2$), 3.60 (s, 2 H, CH$_2$SC$_6$H$_5$), 6.93–8.00 (2 m, 10 H, aromatic). Anal. Calcd for C$_{29}$H$_{40}$O$_2$S: C, 76.94; H, 8.91; S, 7.08. Found: C, 76.71; H, 8.78; S, 7.05.

General Method for the Reduction of [(Phenylthio)-methyl]carbinyl Benzoate Esters with Titanium Metal. Methylene Cyclopentadecane (3C). To a stirred suspension of anhydrous TiCl$_3$ (0.651 g, 4.2 mmol) in dry THF (20 mL) under

Ar was added potassium metal (0.587 g, 15 mmol, cut in three pieces). The resulting mixture was stirred at reflux for 1 h. To the resulting black suspension of freshly prepared Ti metal was added a solution of [(phenylthio)methyl]carbinyl benzoate ester 3B (0.433 g, 0.96 mmol) in THF (5 mL) and the resulting mixture was stirred at reflux under Ar for 16.5 h. The reaction was cooled to 0–5 °C, quenched with absolute methanol (2 mL), and filtered through a column of silica gel–Celite (4:1, respectively). Concentration in vacuo and filtering through a column of silica gel (100 g) eluted with petroleum ether and again concentration in vacuo gave 0.244 g (84%) of methylenecyclopentadecane (3C): bp 75 °C (0.9 mmHg); IR (CCl$_4$) 3070, 1640, 890 (C=CH$_2$) cm^{-1}; NMR (CCl$_4$) δ 1.20–2.65 (m, 28 H, CH$_2$), 4.70 (s, 2 H, C=CH$_2$).

Ion Pairs of Benzylic Cations, a Theoretical Study

C. Decoret and J. Royer

Equipe de Recherche Associée au CNRS, Université Claude Bernard, 69622 Villeurbanne, France

J. J. Dannenberg*

Department of Chemistry, City University of New York, Hunter College, New York, New York 10021

Our interest in the mechanism of nucleophilic displacement reactions and the structures of the intermediates that occur along these reaction paths has led us to propose that nucleophilic substitution in simple alkyl substrates proceeds via anion-stabilized and anion–cation-stabilized intermediates (ASI and ACSI) rather than true ion pairs. These suggestions were originally based upon molecular orbital studies of model systems,[1] although subsequent experimental studies[2] seem to be in accord with the basic ideas. Nevertheless, there remains a substantial body of evidence in favor of ion pairs as intermediates, particularly in substitutions of benzylic substrates.[3] The charge is much more effectively delocalized away from the α-carbon in a benzyl than in an alkyl cation. We, therefore, reasoned that an anion could interact with the delocalized charge to form an ion-pair intermediate that might be a true minimum on a potential energy surface. Such a species should require an activation energy to return to covalent material.

---

(1) J. J. Dannenberg, *J. Am. Chem. Soc.*, **98**, 6261 (1976).

(2) (a) M. Gillard, F. Metras, S. Tellier, and J. J. Dannenberg, *J. Org. Chem.*, **41**, 3920 (1976); (b) L. S. Miller, D. Zazzaron, J. J. Dannenberg, F. Metras, and M. Gillard, *ibid.*, **45**, 641 (1980); (c) M. Gillard, F. Metras, S. Tellier, and J. J. Dannenberg, submitted for publication.

(3) See for example: (a) V. J. Shiner, Jr., in "Isotope Effects in Chemical Reactions", C. J. Collins and N. S. Bowman Eds., Van Nostrand-Rheinhold, New York, 1979, ACS Monogr. No. 167, Chapter 2; (b) E. Grunwald, A. Heller, and F. S. Klein, *J. Chem. Soc.*, 2604 (1975).

Table I. Relative Energies and Charge Distributions

species	energy rel to 1a or 1b, kcal	charges X 10^3 [a]									
		C_1	$C_{2,6}$	$C_{3,5}$	C_4	C_7	H or OCH$_3$	B	F_a	$F_{b,c}$	F_d
2a	48.4	−216	+158	−133	+183	+340	+090				
3a	113.9	−232	+136	−127	+188	+302	+112	+377	−349	−353	−322
2b	39.6	−204	+178, +157	−202, −155	+389	+250	+058				
3b	103.2	−230	+154, +128	−209, −157	+379	+238	+104	+377	−352	−349, −352	−325

[a] The value for BF$_4$ is −1000 in all cases.

To test this hypothesis, we performed molecular orbital calculations, using the MNDO semiempirical method,[4] on reaction 1. The geometries of the reactants and products

Y—⟨O⟩—CH$_2$F + BF$_3$ ⟶ ion pair ⟶

2

1a, Y = H
b, Y = OCH$_3$

Y—⟨O⟩—CH$_2$ + BF$_4^-$ (1)

3
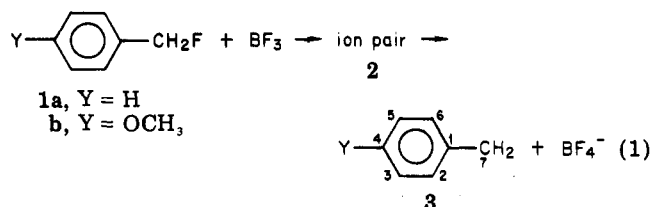
were completely optimized within certain constraints[5] while those of the ion pairs were obtained by optimizing only the distance and orientation between the previously optimized ions. Both benzyl fluoride (**1a**) and *p*-methoxybenzyl fluoride (**1b**) were similarly studied to determine what effect the anticipated greater delocalization of charge in **2a,b** and **3a,b** would have on the energetics of the reaction and the geometry of the ion pair.

The results are summarized in Table I which gives the energetics of the reactions and the charge distributions in the benzylic part of the ion pairs and free cations. The error limits are ±0.2 kcal for the energies and ±0.003 in atomic charges within the constraints of the optimization. Errors in the geometries are difficult to establish as the steepness of the surface can vary considerably along the various coordinates. The results indicate that the *p*-methoxy ion pair (**2b**) is favored by about 8.7 kcal/mol and the *p*-methoxy cation (**3b**) by 10.3 kcal/mol. Thus, the stabilizing power of the methoxy group is apparent primarily in the formation rather than in the dissociation of the ion pairs.

As can be seen from Table I, **2a** has the greatest amount of positive charge on the methylene carbon (+0.34), with more or less equal amounts on the ortho (+0.16) and para (+0.18) carbons. On the other hand, **2b** shows the greatest charge on the methoxy-substituted para position (+0.39), with +0.25 on the methylene carbon and +0.18 on each of the ortho carbons. Upon consideration of these charge distributions, it is not surprising that the BF$_4^-$ anion is farther removed both from the methylene carbon and the ring in **2b** than in **2a** (see Figure 1). The B–C$_7$ distance, B–ring distance, and B–C$_7$–C$_1$ angles are 3.77 Å, 3.54 Å and 78° for **2A** and 4.22 Å, 3.81 Å, 64° for **2B**. The distances of fluorines A-C from the plane of the ring are 3.09, 3.09, and 3.43 Å for **2A** and 3.41, 3.29, and 3.33 Å for **2B**. All B–F distances were 1.398 Å, and BF$_4$ were assumed to be tetrahedral. One should also note that the BF$_4^-$ tends to increase the charge alternation in the ion pairs (**2a,b**) vs.

(4) M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.*, **99**, 4899 4907 (1977); QCPE Program No. 353.

(5) The bond lengths and valence angles were coupled to enforce the plane of symmetry that bisects the methylene and para carbons in the benzyl cation. As the ion was considered to be planar, no dihedral angles were optimized. For the methoxy ion, two of the three methyl hydrogens were coupled with respect to their bond lengths and angles. Optimization was complete for all remaining variables (19 or 29).
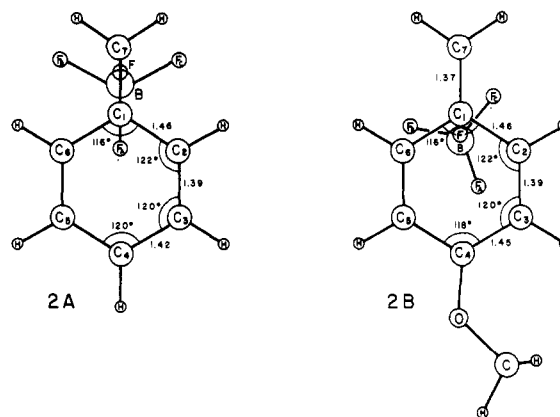
Figure 1. Calculated geometries of the ion pairs.

the cations (**3a,b**). Furthermore, it polarizes the positive charge toward the methylene carbon in **2a** while the ortho carbons (C$_{2,6}$) are most positively charged in **2b**.

The implications of these results are reasonably clear. An ion pair can be anticipated as a minimum of a potential surface (i.e., an intermediate in a reaction path) when the charge on one of the ions is sufficiently delocalized from the point of bond rupture (in this case the methylene carbon) to permit a stabilizing attractive coulombic interaction that gives rise to a geometry sufficiently different from that of the reagent to cause an activation barrier between the ion pair and the neutral reagents. It is likely (but not specifically demonstrated by this work) that an ion pair with a geometry more removed from that of reagents will experience a greater activation barrier to reforming the reagents. Thus **2a** should return to **1a** more readily than **2b** to **1b**. Examination of Figure 1 indicates that the methylene carbon is much freer of BF$_4^-$ in **2b** than in **2a**. Therefore, **2b** is more likely to interact with external nucleophiles than is **2a**. Both of these effects should make return to reagent less favorable in **2b** than in **2a**.

The BF$_4^-$ side of the benzylic cation is much less blocked from nucleophilic attack in these ion pairs than in the ACSIs proposed for simple alkyl systems.[1] Some frontside attack (with retention of configuration for an optically active molecule) should be observable, particularly in the *p*-methoxy case where Figure 1 indicates the methylene carbon of **2b** to be less blocked to frontside attack than **2a**. Although we know of no reports of retention of configuration for uncomplicated (i.e., no neighboring group participation, double inversions, etc.) nucleophilic substitutions on simple alkyl substrates, such reports do exist for benzyl substrates.[3]

As the substitution reactions to which we wish to apply the model under study are solution reactions, it is worthwhile to consider the likely effects of solvent upon the systems. A good solvent for such a reaction will clearly stabilize the ionic products relative to the neutral starting reagents. One would, therefore, expect the activation energies for the overall ionization process to be lowered by virtue of the Hammond postulate. It seems likely that the

major part of the solvent stabilization should be manifest during the dissociation rather than the formation of the ion pairs. This should be true as (a) it is the step where most of the charge separation is being effected (as the distance between the ions increases), (b) a partial desolvation of at least one side of each reagent must occur during the formation of the ion pair, while no such impediment to the dissociation of the solvated ion pair exists, and (c) the significant stabilization that each counterion affords the other in the ion pair lowers the chemical activity of the ions thereby making additional stabilization less necessary.

The results of this study lead us to suggest, within limits, that variation of substituents are likely to have a greater effect upon formation than dissociation of ion pairs, while variation of solvent is likely to have the reverse order of importance. The overall rate of the substitution reaction, although limited by one or the other of the two processes under consideration, will often depend upon the relative rates of reaction of the ion pairs vs. the return to starting reagent. The results of this study cannot, therefore, be easily compared with overall rates.

Reaction of Pyrrolidone with Phosphorus Pentachloride

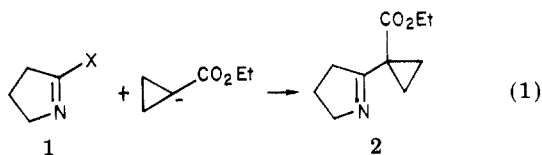Stanford L. Smith and W. John Layton

Department of Chemistry, University of Kentucky, Lexington, Kentucky 40506

Meledath Govindan and Harold W. Pinnick*

Department of Chemistry, University of Georgia, Athens, Georgia 30602

In the course of attempts to prepare the cyclopropylimine 2[1] according to eq 1, a pyrroline more reactive than

the imino ether 1 (X = OCH$_3$) was desired. An obvious possibility was the chloropyrroline 1 (X = Cl).[2] Indeed, when pyrrolidone and phosphorus pentachloride were allowed to react, the same compound reported earlier[2] was obtained; however, the proton NMR spectrum did not match the expected structure. In addition, sodium methoxide in refluxing methanol had no effect on the compound and alcoholic silver nitrate gave no silver chloride. The sample turned brown when exposed to the air for a week but was stable under nitrogen either in a desiccator or a freezer. Combustion analysis and the mass spectrum established the molecular formula as C$_8$H$_{10}$N$_2$Cl$_2$.

*Address correspondence to this author at the Department of Chemistry, Bucknell University, Lewisburg, PA 17837.

Table I. ¹H and ¹³C NMR Parameters for Compound 3[a]

position	¹H chemical shift	apparent H–H coupling, Hz	¹³C chemical shift
1	3.43	7.2	54.9 (t)
2	1.79	7.2, 8.2	23.8 (t)
3	2.68	8.2	32.6 (t)
4			162.9
5	3.88	9.3	48.2 (t of t)
6	2.57	9.3	31.1 (t of t)
7			109.1
8			126.6

[a] Chemical shifts are in parts per million relative to Me$_4$Si.

The structure of this novel compound was unambiguously established as 3 (eq 2) by examination of its proton
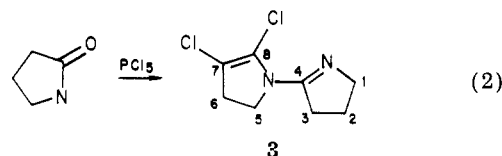
and carbon NMR spectra (Table I) and by selective homo- and heteronuclear decoupling experiments. The 200-MHz proton spectrum displayed five signals of equal intensity (two protons each)—four triplets at 3.88 (H-5, J = 9.3 Hz), 3.43 (H-1, J = 7.2 Hz), 2.68 (H-3, J = 8.2 Hz), and 2.57 ppm (H-6, J = 9.3 Hz) and a "pentuplet" at 1.79 ppm (H-2, J = 7.2 and 8.2 Hz). Irradiation of the signal assigned to H-5 collapsed the signal assigned to H-6 to a singlet and vice versa. Irradiation of either the signal assigned to H-1 or the signal assigned to H-3 reduced the pentuplet to a triplet, whereas irradiation of the pentuplet at 1.79 reduced the signals assigned to H-1 and H-3 to singlets. This clearly established the presence of the two- and three-methylene fragments in structure 3. The chemical shifts of the various protons are fully consistent with the positions to which they are assigned. Also, the proton NMR spectrum did not show any signal attributable to N-H. The proton-decoupled 50-MHz ¹³C spectrum of 3 showed eight lines: five NOE enhanced signals in the aliphatic region [54.9 (C-1), 48.2 (C-5), 32.6 (C-3), 31.1 (C-6), and 23.8 ppm (C-2)], each of which is a triplet in a coupled spectrum, and three weak signals from nonprotonated carbons in the sp^2 region [162.9 (C-4), 126.6 (C-8), and 109.1 ppm (C-7)], which remain singlets in the coupled spectrum. The aliphatic carbons were unambiguously assigned by a series of selective decoupling experiments in which irradiation of each individual proton signal collapsed the corresponding carbon multiplet to a singlet. Examination of a high-resolution coupled carbon spectrum revealed numerous long-range C-H couplings. For example, C-5 and C-6 are actually triplets of triplets. Selective decoupling of individual hydrogens with low decoupler power removed only these long-range couplings and was particularly useful in confirming the assignments of the three nonprotonated sp^2 hybridized carbons. Again, the carbon chemical shifts are completely consistent with the structural assignments presented.

Structure 3 is the only structure consistent with the molecular formula obtained from elemental analysis and

(1) This compound has been used as an intermediate in a convergent synthesis of pyrrolizidine alkaloids: Pinnick, H. W.; Chang, Y.-H. *Tetrahedron Lett.* **1979**, 837.

(2) Reportedly prepared from pyrrolidone and phosphorus pentachloride: (a) Tafel, J.; Wassmuth, O. *Chem. Ber.* **1907**, *40*, 2831. (b) Etienne, A.; Correia, Y. *Bull. Soc. Chim. Fr.* **1969**, 3704.