was obtained by distillation through a −96° trap (acetone slush) into a −106° trap. Gas chromatography of this sample (NMR reported in the results section) showed elution of only the methyl acetate impurity. This demonstrated lack of rearrangement of 1 under GC conditions allowed for determination of the methyl acetate to methoxyacetaldehyde product ratio by GC of the crude product mixture.

Other spectra of the purified methoxyoxirane (1) follow: high-resolution MS of parent peak, obsd, 74.0355 (calcd for $C_3H_6O_2$, 74.0367); low-resolution MS (70 eV) *m/e* (rel intensity) 74 (9), 73 (5), 59 (100), 57 (42), 43 (93), 41 (35), 31 (67); ir (vapor phase), 3020, 2960, 2860, 1470, 1382, 1297, 1288, 1280, 1217, 1130, 1160, 910, 828, and 745 cm^{-1}.

Products. For comparison of GC retention times and spectra, samples of products **5, 6, 11, 16, 24, 25,** methyl acetate, ethyl acetate, ethylene, and acrolein were obtained commercially. Tetrahydrofurfural (**23**) was prepared by the oxidation of tetrahydrofurfuryl alcohol with chromium trioxide–pyridine.[20] Spectra of GC-purified products **15** and **22** matched literature spectra of these compounds.[21–23] Spectra of other α-alkoxycarbonyl products, **3, 10, 12,** methoxyacetaldehyde, and ethoxyacetaldehyde, were simple and unambiguous.

An authentic sample of 3,3-dimethyl-2-methoxyoxirane (**9**) was prepared by the reaction of 2-chloro-2-methylpropanal with sodium methoxide.[9] It should be noted that freshly prepared sodium methoxide was needed for this reaction. Three attempts to prepare **9** with commercial sodium methoxide, which had been vacuum dried, were unsuccessful. The NMR spectrum of **9** showed absorptions at δ 1.21 (s, 3 H), 1.31 (s, 3 H), 3.44 (s, 3 H), and 4.22 (s, 1 H).

Epoxides of enol ethers, other than **1**, were not separated from other reaction products, but their yields were calculated by NMR integration vs. other major reaction products and internal integration standards. Ethoxyoxirane (**2**) was determined by its AMX system at δ 4.45–4.60 and 2.45–2.85; 2-methoxy-2-methyloxirane (**4**) by singlets at δ 2.58 and 2.64; 3,3-dimethyl-2-methoxyoxirane (**9**) by its singlet at δ 4.23; and 2,7-dioxabicyclo[4.1.0]heptane (**21**) by its doublet at δ 4.61 and its multiplet at δ 2.98.[10]

Attempted Reaction of 3-Hydroxy-3-methyl-2-butanone (28) with Methanol. Following the procedure of Thorne,[15] a mixture of 14 g of distilled **28**, 50 ml of anhydrous methanol, and 0.012 mol of anhydrous hydrogen chloride was stirred for 4 hr. The NMR spectrum of the mixture showed only starting materials. The reaction mixture was neutralized with Ag_2CO_3, filtered, and vacuum distilled. The fraction boiling at 83–85° (100 mm) contained only **28** by NMR, ir, and mass spectrometry (85% recovery).

This reaction was repeated several times using halved and doubled HCl concentrations, K_2CO_3 neutralization, and reaction times up to 48 hr. In each case, only starting materials were recovered.

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Registry No.—**1,** 57346-02-8; **2,** 53332-61-9; **4,** 57346-03-9; **9,** 26196-04-3; **21,** 286-26-0; **28,** 115-22-0; methyl vinyl ether, 107-25-5; ethyl vinyl ether, 109-92-2; 2-methoxypropene, 116-11-0; 1-methoxy-2-methylpropene, 17574-84-4; 2,3-dihydrofuran, 1191-99-7; dihydropyran, 110-87-2; atomic oxygen, 17778-80-2; methanol, 67-56-1.

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Reactions of Cation Radicals of EE Systems. III. Chlorination of 9,10-Diphenylanthracene[1]

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Stopped-flow kinetic studies of the reaction of 9,10-diphenylanthracene (DPA) cation radical ($DPA\cdot^+$) with chloride ion in acetonitrile gives rise to a rate law which is second order in $DPA\cdot^+$, first order in Cl^-, and independent of DPA. The product of the reaction of electrogenerated $DPA\cdot^+$ with Cl^- was shown to be 9,10-dichloro-9,10-diphenyl-9,10-dihydroanthracene (1), which undergoes both surface catalyzed and thermally induced rearrangement to 2-chloro-DPA (2) via loss of HCl. The mechanism proposed for the addition of Cl^- to $DPA\cdot^+$ to form 1 involves an associative equilibrium and is of a form which accounts for the observed kinetics as well as those previously reported for the hydroxylation and pyridination of $DPA\cdot^+$, which followed a different rate law.

Investigators in several laboratories have examined the reactions of various nucleophiles with the cation radicals derived from aromatic hydrocarbon and heterocyclic fused ring systems such as 9,10-diphenylanthracene (DPA),[1–8] thianthrene,[9–17] dibenzodioxin,[9,18,19] and phenoxathiin.[9,20] Each of these substrates exhibits EE electrochemistry in that one observes two successive monoelectronic oxidation steps, initially to the cation radical and subsequently to the corresponding dication at increasingly anodic potentials. While these aforementioned substrates exhibit strikingly similar electrochemical behavior, the mechanisms postulated for various nucleophilic additions to the cation radicals of these systems have invoked participation by both cation radical and dication.[21] In this report, we show mechanistic findings which are germane to a unifying overview of these apparently divergent reaction pathways.

Results and Discussion

While conducting a series of experiments designed to establish the relative nucleophilicities of various reagents toward the carbon-centered cation radical DPA$\cdot^{+}$,[22] it was noted that the rate of reaction of DPA$\cdot^{+}$ with chloride ion showed unusual dependence on DPA and DPA$\cdot^{+}$ concentrations. These data are shown in Table I. It is evident that a rate law appropriately describing these data assumes the form

$$-\frac{d[\mathrm{DPA}\cdot^{+}]}{dt} = k_{\mathrm{app}}[\mathrm{DPA}\cdot^{+}]^2[\mathrm{Cl}^-] \tag{1}$$

The stoichiometry observed for this reaction was consistent with that reported previously:[2]

$$2\mathrm{DPA}\cdot^{+} + 2\mathrm{Cl}^- \rightarrow \mathrm{DPA(Cl)_2} + \mathrm{DPA} \tag{2}$$

The chlorinated product $\mathrm{DPA(Cl)_2}$ was confirmed to be 9,10-dichloro-9,10-diphenyl-9,10-dihydroanthracene. In combination, these observations are consistent with a mechanism of the form

$$\mathrm{DPA}\cdot^{+} + \mathrm{Cl}^- \overset{K}{\rightleftarrows} \mathrm{DPA(Cl)}\cdot \tag{3}$$

$$\mathrm{DPA(Cl)}\cdot + \mathrm{DPA}\cdot^{+} \xrightarrow{k2} \mathrm{DPA(Cl)}^{+} + \mathrm{DPA} \tag{4}$$

$$\mathrm{DPA(Cl)}^{+} + \mathrm{Cl}^- \xrightarrow{\text{fast}} \mathrm{DPA(Cl)_2} \tag{5}$$

where the electron transfer step (eq 4) is rate determining. In addition, the process described by eq 3 must indeed be an equilibrium condition to ensure an overall second-order dependence of the rate of reaction on the concentration of DPA$\cdot^{+}$.

The intermediate DPA(Cl)$\cdot$ has been proposed as a participant in the electrochemiluminescence observed in the $\mathrm{DPA(Cl)_2}$–DPA$\cdot^{-}$ [23,24] and trihalide–DPA$\cdot^{-}$ [25] systems. The analogous intermediate DPA(F)$\cdot$ has been suggested to participate in the anodic fluorination of DPA.[6] The results presented here lend support to the participation of such free radicals in the halide–DPA redox systems.

It should be noted that the mechanism proposed here is not unlike that demonstrated for the anodic hydroxylation[4] of DPA. The significant fact is that the present system, the second step of the mechanism (eq 4), is rate determining while in the case of the hydroxylation, the initial encounter of DPA$\cdot^{+}$ with nucleophile (eq 6) is rate determining.[4]

$$\mathrm{DPA}\cdot^{+} + \mathrm{H_2O} \xrightarrow{k} \mathrm{DPA(OH_2)}\cdot^{+} \tag{6}$$

$$\mathrm{DPA(OH_2)}\cdot^{+} + \mathrm{H_2O} \overset{K}{\rightleftarrows} \mathrm{DPA(OH)}\cdot + \mathrm{H_3O^+} \tag{7}$$

$$\mathrm{DPA(OH)}\cdot + \mathrm{DPA}\cdot^{+} \xrightarrow{\text{fast}} \mathrm{DPA(OH)^+} + \mathrm{DPA} \tag{8}$$

$$\mathrm{DPA(OH)^+} + 2\mathrm{H_2O} \xrightarrow{\text{fast}} \mathrm{DPA(OH)_2} + \mathrm{H_3O^+} \tag{9}$$

Table I
Stopped-Flow Kinetic Data for Reaction of DPA$\cdot^{+}$ with Cl^{-a}

$[\mathrm{DPA}]_0 \times 10^4$	$[\mathrm{DPA}\cdot^{+}]_0 \times 10^5$	$[\mathrm{Cl}^-]_0 \times 10^4$	Replicates	k_2K,[b] M^{-2} sec^{-1} × 10^{-9}
4.64	2.73	47.3	5	4.75 (± 0.13)[c]
4.69	2.46	4.73	9	4.56 (± 0.13)
4.61	1.03	0.473	5	4.18 (± 0.07)
0.233	2.59	4.73	6	5.00 (± 0.11)

[a] Chloride as tetra-*n*-butylammonium salt; all concentrations in moles/liter; $T = 25.0\ (\pm\ 0.1)°$. [b] $k_2K = k_{\mathrm{app}}/2$ (eq 1). Data fitted for 75% reaction (minimum) via method of least squares, giving rise to a coefficient of correlation of at least 0.995 for all cases. [c] Standard deviation.

In the hydroxylation mechanism (eq 6–9), this difference in kinetic control is tenable in view of the equilibrium deprotonation of the product of the rate-determining step, $\mathrm{DPA(OH_2)}\cdot^{+}$. It is quite reasonable to expect the acid–base equilibrium embodied in eq 7 to lie far to the right and preclude any significant back reaction to $\mathrm{DPA(OH_2)}\cdot^{+}$. Consequently, application of steady-state kinetics to $\mathrm{DPA(OH_2)}\cdot^{+}$ and DPA(OH)$\cdot$ results in a rate expression identical with that reported previously,[4] namely[26]

$$-\frac{d[\mathrm{DPA}\cdot^{+}]}{dt} = 2k[\mathrm{DPA}\cdot^{+}][\mathrm{H_2O}] \tag{10}$$

The anodic pyridination of DPA as studied by single potential step spectroelectrochemical techniques in these laboratories[1a] gave rise to data which were shown to fit a mechanism similar to that proposed for the corresponding hydroxylation reaction. The proposed mechanism yielded a rate law reflecting first-order dependence on the concentration of DPA$\cdot^{+}$ and first-order dependence on the concentration of pyridine (Py). This mechanism is restated here for the sake of the ensuing argument.

$$\mathrm{DPA}\cdot^{+} + \mathrm{Py} \xrightarrow{k} \mathrm{DPA(Py)}\cdot^{+} \tag{11}$$

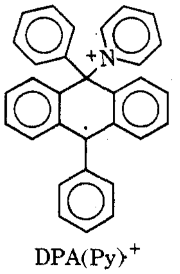
$$\mathrm{DPA(Py)}\cdot^{+} + \mathrm{DPA}\cdot^{+} \xrightarrow{\text{fast}} \mathrm{DPA(Py)^{2+}} + \mathrm{DPA} \tag{12}$$

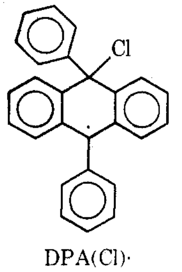
$$\mathrm{DPA(Py)^{2+}} + \mathrm{Py} \xrightarrow{\text{fast}} \mathrm{DPA(Py)_2^{2+}} \tag{13}$$

In this case, the initial encounter of nucleophile with cation radical was also proposed to be the rate-determining step (eq 11) followed by fast electron transfer with DPA$\cdot^{+}$ (eq 12). The intermediate DPA(Py)$\cdot^{+}$ which is involved in this *fast electron transfer step* is analogous to the DPA(Cl)$\cdot$ intermediate proposed to participate in the *rate-determining electron transfer step* (eq 4) of the mechanism for the reaction of DPA$\cdot^{+}$ with Cl$^-$ advanced in this present work.

The reactivity of these radicals is essentially the same[27] owing to the inability of the pyridinium and chloro substituents to participate in resonance stabilization of the respective radicals.[28] One might then conclude the reactivity of the DPA(Py)$\cdot^{+}$ and DPA(Cl)$\cdot$ radicals toward DPA$\cdot^{+}$ to be very similar.[29] Consequently, the rate constants for the two processes (eq 4 and 12) would be comparable.

The foregoing, then, presents an incongruity between the results of the previous kinetic study of the anodic pyridination[1a] of DPA and the results presented here. Pyridine, the stronger[30] nucleophile, follows a mechanism wherein formation of the radical species, DPA(Py)$\cdot^{+}$ (eq 11), is rate de-


DPA(Py)$\cdot^{+}$


DPA(Cl)$\cdot$

termining whereas chloride, the weaker[30] nucleophile, follows a mechanism in which the electron-transfer step (eq 4) is rate determining. Why should this be the case if the rate constants for the corresponding electron transfer reactions of the two systems (eq 4 and 12) are expected to be of comparable magnitudes?

In the previous study[1a] employing electrogeneration of DPA$\cdot^+$, a pertinent consideration is that the concentrations of cation radical, nucleophile, intermediates, and products are inhomogeneously distributed in solution as a function of distance from the electrode surface.[31] Thus, for the Py/DPA concentration ratios employed, there existed excesses of cation radical in that portion of the reaction zone close to the electrode surface, and this effect was augmented by the regenerative nature of the reaction (eq 12). In view of this it is tenable that although the rate constants for the electron-transfer reactions of DPA(Py)$\cdot^+$ and DPA(Cl)$\cdot$ with DPA$\cdot^+$ are most likely of similar magnitudes, the relative rates of these two reactions (eq 4 and 12) compared to the respective preceding steps (eq 3 and 11) may be quite different. This is attributable to the different relative concentrations of DPA$\cdot^+$ and nucleophile arising as a consequence of the different experimental conditions *and* techniques employed in the previous[1a] and present study. A reexamination of the *homogeneous* reaction of DPA$\cdot^+$ with Py under conditions similar to those reported here for the chloride reaction is presently in progress.[22]

The pathway for the reaction of DPA$\cdot^+$ with water, pyridine, and chloride is seen to be essentially the same with definition of the rate-determining step depending upon (1) the type of nucleophile (containing active hydrogen or not), (2) the intrinsic nucleophilicity of the nucleophile in question, and (3) the experimental conditions under which the kinetic parameters are measured. Moreover, the mechanism proposed here is compatible with that recently advanced for the anisylation of the cation radical of thianthrene.[17]

It is clear that the reversible nature of all steps in such mechanisms must be considered en route to a comprehensive understanding of nucleophilic additions to EE systems.[32]

Experimental Section

Materials. DPA (Aldrich Gold Label) was doubly recrystallized from ethanol, mp 251–252°. Authentic 9,10-dichloro-9,10-diphenyl-9,10-dihydroanthracene [DPA(Cl)$_2$] was prepared after the manner of Chandross and Sonntag,[23] mp 187–189° dec. All tetraalkylammonium salts were obtained from Eastman Organic Chemicals. Tetra-*n*-butylammonium perchlorate (TBAP) was twice recrystallized from acetone–water (15:85) and vacuum dried at 60° for 6 hr prior to use, mp 211.5–212.5°. Tetraethylammonium perchlorate (TEAP) was doubly recrystallized from water and vacuum dried at 70° for 12 hr. After preliminary drying in a vacuum desiccator, tetra-*n*-butylammonium chloride (TBAC) was three times precipitated from acetone with anhydrous ether and vacuum dried at 56° for 18 hr, mp 76–77.5°. Acetonitrile (Burdick and Jackson Laboratories, uv grade) was purified in the manner previously described.[33] Water content of this purified material was determined by vapor phase chromatography to be ca. 1 m*M*. All other chemicals were reagent grade or equivalent. All solutions were prepared in an inert, anhydrous atmosphere.

Apparatus. The electrochemical cell used for large-scale reactions has been previously described.[1b] The potentiostat used was similar to that reported by Pilla.[34] Electrode potentials are quoted relative to the aqueous saturated calomel electrode. Kinetic runs were made using a Durrum Model D-110B stopped-flow spectrophotometer interfaced to a dedicated minicomputer for acquisition and reduction of data. The cation radical of DPA was generated by partial electrolysis of acetonitrile solutions containing 0.10 *M* TBAP and the appropriate concentration of DPA. This oxidation was carried out at a platinum gauze working electrode potentiostatted at +1.40 V. The solution so generated was then delivered via a closed system to one drive syringe of the stopped-flow spectrophotometer, the other drive syringe containing the desired concentration of TBAC in a solution of 0.10 *M* TBAP in acetonitrile.[35] The analytical wavelength used was the λ_{max} of DPA$\cdot^+$, 653.0 nm, and the molar absorptivity of this species[3] was taken as 8.70×10^3 l./(mol cm).

Stoichiometry experiments were carried out in the stopped-flow spectrophotometer by monitoring the DPA regenerated[36] upon reaction of solutions of partially electrolyzed DPA with solution of TBAC in anhydrous acetonitrile.[37] The DPA regenerated was found to be 53.1 (±2.8)% of DPA$\cdot^+$ initially present for 17 experiments conducted at 25.0 (± 0.1)°.

Macroscale Reaction of DPA$\cdot^+$ with TBAC. DPA (75.6 mg, 0.229 mmol) was added to 150 ml of 0.10 *M* TEAP in acetonitrile in the anode chamber of a two-compartment electrolysis cell.[1b] This vessel was fitted with a buret containing 0.050 *M* TBAC in acetonitrile. The platinum gauze working electrode was potentiostatted at +1.40 V and as the characteristic blue color of DPA$\cdot^+$ appeared, it was discharged nearly to completion by the addition of the TBAC solution. At no time was excess TBAC added. The use of numerous such "titration" steps ensured against the buildup of cation radical concentration and thus minimized the likelihood of appreciable side reactions of DPA$\cdot^+$ with residual water in the solvent. After 5 hr the blue fluorescence of DPA was absent in the anolyte and the oxidative current had diminished to essentially zero. The acetonitrile was removed by rotary evaporation and the resulting yellow residue was vacuum dried at room temperature. A 25-ml volume of nitromethane was then added with stirring, giving rise to a yellow solution and a suspension of fine white crystals. The latter were filtered, crushed, and washed with several portions of cold nitromethane. After drying, the material was recrystallized from methylene chloride–hexane to give colorless crystals of 9,10-dichloro-9,10-diphenyl-9,10-dihydroanthracene (**1**, 78.2 mg, 0.195 mmol), mp 189–190° dec (lit. 187–189° dec), mmp (with authentic[23]) 187–189° dec.

Alternatively, removal of the acetonitrile from the reaction mixture and introduction of the benzene-soluble portion of the resulting yellow solids onto a silica gel chromatographic column and subsequent elution with benzene and methanol resulted in degradation of **1** (nonfluorescent) to a material exhibiting blue fluorescence. This fluorescence was manifest both on the column and in the eluent. Removal of solvent from the major fraction of this material gave rise to yellow needles, **2**, from methylene chloride, mp 185–187°. Anal. Calcd for $C_{26}H_{17}Cl$: C, 85.59; H, 4.70; Cl, 9.72. Found: C 85.77; H, 4.29; Cl, 9.94. It is concluded that **2** is 2-chloro-9,10-diphenylanthracene, mp 185°.[38] Authentic **1** was prepared as described earlier.[23] Chromatography of this material in the manner described above also gave rise to the surface-catalyzed loss of HCl and yielded a mixture of **2** (80%) and DPA (20%).

Mass spectral analysis of the electrolysis product[39] and authentic **1** showed a parent ion of *m/e* 364 (DPA + Cl − H) rather than the expected *m/e* 400 [DPA(Cl)$_2$] under electron impact ionization. Most probably, the heated glass sample probe induced degradative rearrangement[38] of **1** to **2** prior to volatilization from the probe, since a high relative abundance of HCl was noted in the mass spectra of both compounds as the probe temperature was increased.

The decomposition of **1** to **2** was examined by thermogravimetric analysis (TGA) of both the electrolysis product[39] and authentic **1**. In both cases, a well-defined weight loss was observed between 160 and 205°, followed by a plateau in the thermogram up to 230°. For **1**, calcd weight loss to give **2** (**1** − HCl): 9.08%. Observed weight loss: authentic **1**, 9.36%; electrolysis product, 9.20%.

Registry No.—**1**, 6486-01-7; **2**, 43217-28-3; DPA, 1499-10-1; TBAP, 1923-70-2; TBAC, 1112-67-0; TEAP, 2567-83-1.

References and Notes

(1) "EE" systems are those species capable of undergoing two monoelectronic oxidation (or reduction) processes E_1 and E_2, where $E_2 > E_1$. For

$$A \rightarrow A\cdot^+ + e^- \qquad (E_1)$$

$$A\cdot^+ \rightarrow A^{2+} + e^- \qquad (E_2)$$

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(26) Previous experiments[4] were conducted at relatively high water concentrations (2.5–4.0 *M*). Recent stopped-flow experiments conducted in these laboratories over the range of water concentrations 5.0×10^{-3}–1.50 *M* yielded data exhibiting first-order kinetic dependence on [DPA·$^+$] and [H_2O]; $k = 5.78\ (\pm\ 0.31) \times 10^{-2}\ M^{-1}\ \text{sec}^{-1}$ for fit to eq 10. The concentration of DPA·· in these experiments was on the order of 3.0×10^{-5} *M*. The rate of decay of DPA·$^+$ was found to be independent of DPA concentration, thereby ruling out cation radical disproportionation.
(27) On the basis of HMO calculations.
(28) Through-space interactions of these substituents with the ring system would be unlikely, although such cannot be dismissed a priori.
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(35) Inclusion of TBAP in this solution is essential to prevent thermal effects and changes in refractive index upon mixing.
(36) The DPA absorbance at 392.5 nm is free from interference by DPA·$^+$ and all reaction products.
(37) See ref 2 for details.
(38) E. Bergmann and O. Blum-Bergmann, *J. Am. Chem. Soc.*, **59**, 1439 (1937).
(39) "Electrolysis product" refers to the material isolated and purified from the macroscale electrolysis.

Racemization and Bromide-Exchange Studies on 1-Phenylbromoethane and the Question of the Ion-Pair Mechanism for Bimolecular Nucleophilic Substitutions at Saturated Carbon

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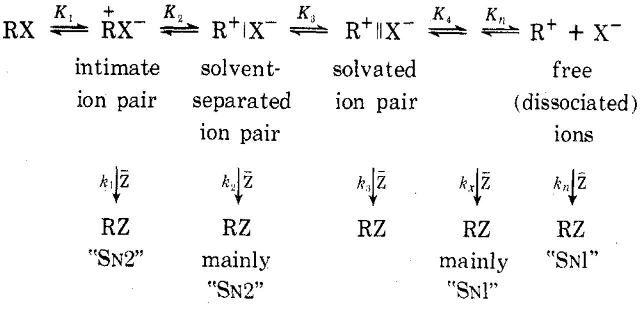
In an effort to determine whether the ion-pair mechanism for nucleophilic substitution at saturated carbon operates in bimolecular reactions, the racemization and bromide–radiobromide exchange of 1-phenylbromoethane were examined in anhydrous acetone containing lithium bromide. Within experimental error, the rate constants and Arrhenius and thermodynamic activation parameters are identical for the racemizations and exchanges. There is no evidence for inversion without exchange or exchange without inversion. Consequently, for the ion-pair mechanism to be operating, all of the ion pairs formed by the substrate and leaving group must be intercepted (or collapse to starting material) before the ions separate sufficiently to allow the alkyl group to turn over and give, on the collapse of the ion pair, inversion without halide exchange. On the other hand, the results are completely consistent with the classical Hughes–Ingold SN2 mechanism.

The observation that the rates of halide–radiohalide exchange and racemization of optically active 1-phenylbromoethane[1] and those of 2-iodooctane[2] were the same within experimental error was the basis for the postulation of the SN2 mechanism for the bimolecular nucleophilic displacement at saturated carbon by Gleave, Hughes, and Ingold.[3] It was the carbonium ion route, the SN1 or unimolecular mechanism of the mechanistic pair, which was the more difficult to establish;[4,5] chemists, on the other hand, readily accepted the concerted nucleophilic attack–leaving group departure of the SN2 mechanism. As Sneen and Larsen point out, however, it is the traditional SN2 reaction pathway which is the less likely.[6] They have proposed an elaboration of the ion-pair scheme of Winstein and his colleagues[7] as a single unified mechanism to replace the SN1–SN2 dichotomy. In their ion-pair mechanism, which is summarized in Scheme I, it is proposed that the initial step is the formation of a contact or intimate ion pair by the substrate with its leaving group. The reaction could show the characteristics of SN2, mixed, or SN1 mechanisms depending upon where in the series of solvation equilibria from intimate ion pair to the free, independently solvated ions nucleophilic attack occurs.

Scheme I



Should such a mechanistic scheme be proven correct, it has wide ramifications not only for all nucleophilic substi-

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