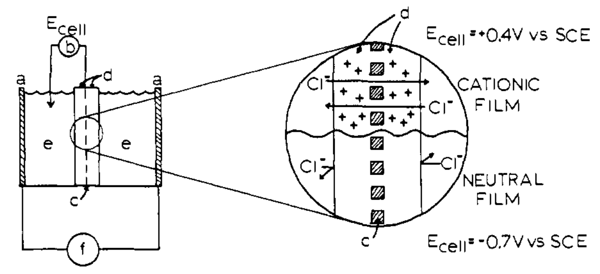

Figure 1. (Left) experimental setup for impedance measurement with electrochemical control of membrane impedance: platinized platinum electrodes (a); constant voltage power supply (b); gold minigrid electrode (c); poly(pyrrole) film (d); 1.0 M KCl(aq) solution (e); constant current ac circuit, which consists of a frequency generator, lock-in amplifier, and a 50 K Ω series resistor to maintain constant ac current to cell (f). (Right) microscopic view of membrane, illustrating effect of membrane potential on ionic resistance.

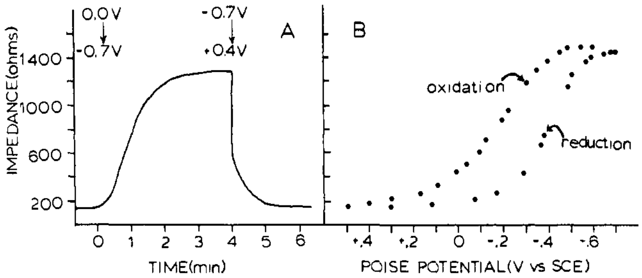

Figure 2. (A) Plot of in-phase impedance (*Z*) in ohms vs. time in minutes after initial −0.7-V step for a freshly prepared polypyrrole electrode. (B) Plot of in-phase impedance (*Z*) vs. poise potential for same electrode as in A.

the membrane from *electronic* conduction with the Pt electrodes, specifically measures the ionic, as opposed to the electronic conductivity, in a membrane at dc or low ac frequencies (<2000 Hz).[7]

Typical results are seen in Figure 2A. Upon stepping the potential applied to the electrode/membrane from 0.0 V vs. SCE to −0.7 V, the in-phase impedence of the virgin electrode at 2 Hz increases from 132 to 1280 Ω in approximately 4 min.[8] The impedance continues to rise very slowly after the initial jump; in an hour it reaches 1500 Ω. Stepping back to 0.0 V lowers the impedance but is not a sufficient potential to oxidize all the reduced polypyrrole. Stepping instead to +0.4 V brings the impedance back to its original value, as seen in Figure 2A. With oxygen excluded from the cell, this pattern can be cyclically repeated many times. Neither a gold minigrid electrode alone nor a membrane/electrode whose holes are incompletely filled produces a change in impedance (constant at 115 Ω) upon stepping from +0.4 to −0.7 V and back.

By choice of other value of potential steps, it can be shown that a polymer redox reaction must occur to produce a change in membrane impedance. Thus, if the potential of a virgin electrode is stepped from 0.0 to +0.5 V, no change in impedance occurs. If after stepping to −0.7 V and allowing the impedance to rise to a fairly constant level the potential is returned to −0.5 V, again no impedance change is seen. These observations suggest that the impedance change is a result of the change in oxidation state of poly(pyrrole), whose electrochemistry is centered at $E_{1/2}$ = ca. −0.26 V in H_2O.

A plot of the poise potential (the potential at which the redox polymer is poised at open circuit) vs. impedance is shown in Figure 2B to more clearly illustrate the influence of the polymer redox state on the impedance of the film. Varying the potential from +0.4 to −0.7V and back in 0.1-V increments, with measurement of poise potential at open circuit[9] after each increment, results in a poise potential vs. impedance curve that remarkably resembles a current-potential curve for a redox species. The potentials corresponding to half the impedance changes occuring during reduction and oxidation, −0.4 and −0.17 V, respectively, are in fact nearly the same as slow potential scan cyclic voltammetric peak potential values, −0.33 and −0.20 V, respectively. The separation between oxidation and reduction potentials in each case must correspond to some degree of electrochemical irreversibility, possibly due to a nonequilibrium distribution of the oxidized and reduced forms in the very thick polymer film.

The facts that the impedance varies nonlinearly with applied potential and that plots of impedance vs. rest potential resemble *i–E* curves for reduction and oxidation of the poly(pyrrole) redox species demonstrates, we believe, that the ionic resistance of the membrane is electrochemically controlled via the oxidation state of the redox sites within the polymer. We term this phenomenon an "ion gate", since the resistance is varied from low to high and vice versa by a step voltage. Further work, elucidating the nature of ion transport as well as development of methods to increase the difference in impedance between the charged and neutral membrane, is currently is progress.

Registry No. Au, 7440-57-5; KCl, 7447-40-7; poly(pyrrole), 30604-81-0.

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[7] Poly(pyrrole) is known[5,6] to be an electronic as well as an ionic conductor, so this type of cell is necessary to distinguish the two. The frequency dependence of the in-phase and out-of-phase components of the ac signal in the cell of Figure 1 has been measured down to dc, and the impedance behavior is consistent with an ionic conduction pathway through the cell.

[8] This relatively slow time is a consequence of the relatively thick poly(pyrrole) film that is being reduced and oxidized. Possibly, all of the polypyrrole is not reduced.

[9] These potentials are stable at least for 2 min, the time taken to make these measurements.

Orchestrated Silylene to Silene to Silylene Rearrangement. The Unusual Behavior of C_3H_5 Silylsilylenes

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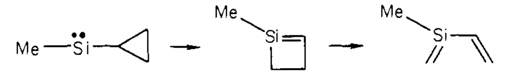
Received June 28, 1982

In 1980 we first proposed a thermally induced isomerization of a silene to a silylene when we suggested that the origin of 1,3-disilacyclobutane **3** (Scheme I) from the pyrolysis of allylpentamethyldisilane was the cyclization of β-silylsilylene **2** formed from 1,2-silyl migration in silene **1**.[1] Later we were able to present confirming evidence for this sequence[2] and in unpublished work have again demonstrated the rearrangement of a silene to a silylene when **1** was generated through pyrolysis of **4**.

Most recently we have presented evidence for the first thermally induced silylene to silene rearrangement when we demonstrated that cyclopropylsilylene **5** (eq 1) underwent ring expansion to silene **6**, which in turn opened to 2-sila-1,3-butadiene **7**.[3]



5 6 7 (1)

We now report that these rearrangements can be combined to produce a predictable sequence of silylene to silene to silylene rearrangements. The desired starting material for this sequence,

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[1] Barton, T. J.; Jacobi, S. A. *J. Am. Chem. Soc.* **1980**, *102*, 7979.

[2] Barton, T. J.; Burns, S. A.; Burns, G. T. *Organometallics* **1982**, *1*, 210.

[3] Barton, T. J.; Burns, G. T.; Goure, W. F.; Wulff, W. D. *J. Am. Chem. Soc.* **1982**, *104*, 1149.

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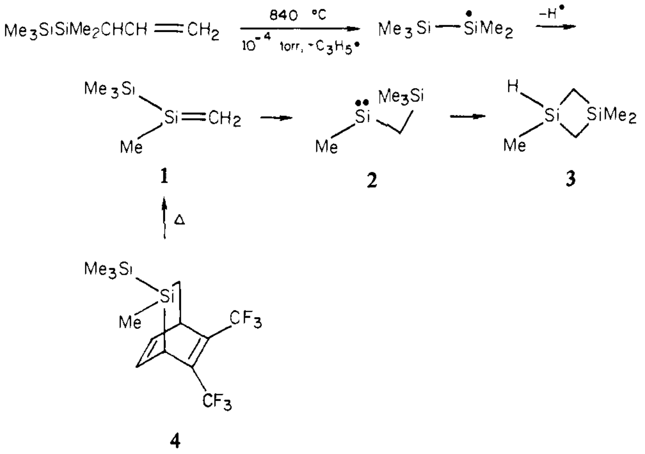
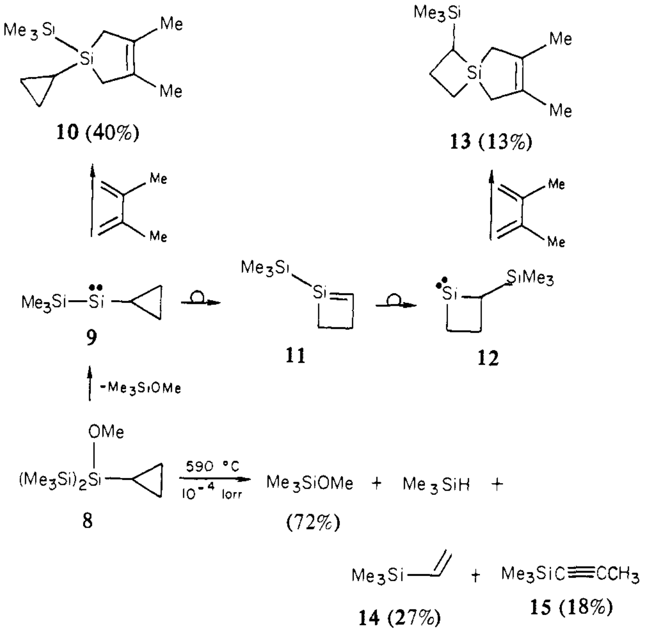
Scheme I

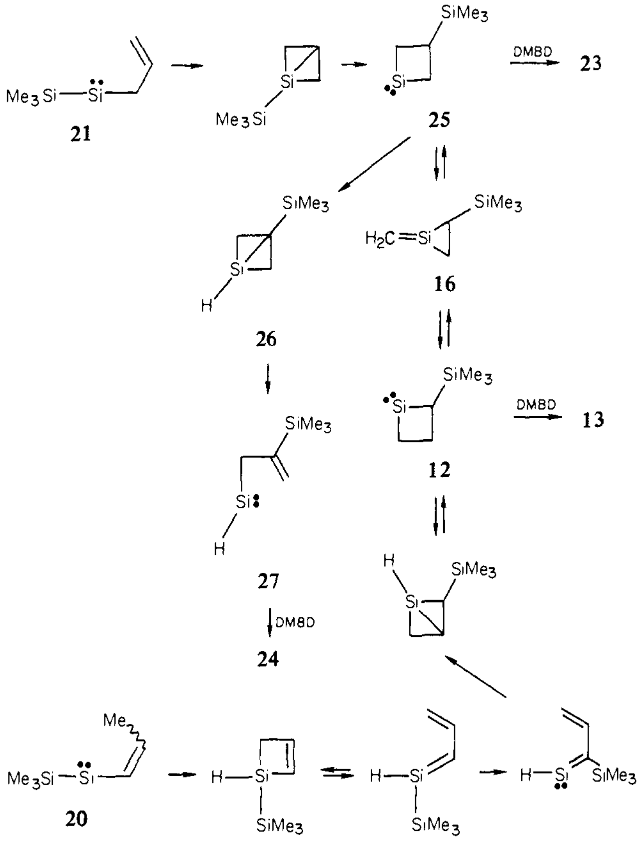


Scheme II

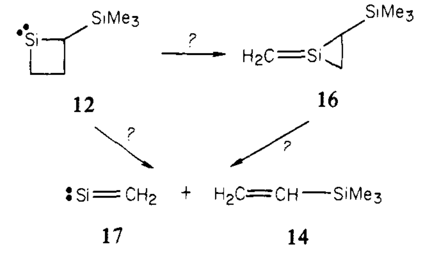


2-cyclopropyl-2-methoxyhexamethyltrisilane (**8**, Scheme II), was synthesized in 50% yield by the slow addition of cyclopropyllithium to bis(trimethylsilyl)dichlorosilane followed by addition of sodium methoxide.[4] Distillation of **8** (25 °C (10^{-4} torr)) through a horizontal, quartz-packed tube heated at 590 °C afforded a light yellow oil in 76% mass recovery. GC analysis showed the presence of four products. These were isolated by preparative GC and identified by spectral comparison with authentic samples: Me_3SiH, Me_3SiOMe (72%), trimethylvinylsilane (**14**, 27%), and 1-(trimethylsilyl)propyne (**15**, 18%). In order to demonstrate the formation of the initial silylene **9** (from α elimination of Me_3SiOMe) we conducted a copyrolysis of **8** and a 6-fold excess of 2,3-dimethyl-1,3-butadiene (DMBD); (450 °C, N_2 flow ca. 30 mL/min, vertical quartz-packed tube). GC–MS analysis of the product mixture revealed two isomeric trapping products, and these were separated by preparative GC. The major product **10** was formed in a notable 40% yield.[5] The ^{13}C NMR of **10** consists of six peaks (δ -7.09, -1.56, 1.91, 19.18, 21.73, 130.89) as required, and the three upfield absorptions are indicative of a (trimethylsilyl)cyclopropylsilane unit (e.g., the analogous carbons in **8** absorb at δ -5.07, -0.68, 1.76). The isomeric minor product (13%) was assigned structure **13** on the basis of its NMR spectra,[6] which clearly revealed a loss of the integrity of the basic structure of **8**. These results are explained by the initial formation of silylene **9**, rearrangement via ring expansion to silene **11**, followed by rearrangement to silylene **12**.

Scheme III



Thus, while the original goal of producing a sequential silylene–silene–silylene isomerization is achieved, the origin of the ultimate products **14** and **15** is unknown. It is intriguing to consider the possibility that vinylsilane **14** (eq 2) arises from



(2)

decomposition of silylene **12** or, after rearrangement, from silamethylenecyclopropane **16**. In either case the decomposition would also produce silylidene **17**, which has been calculated to be the most stable structure on the CH_2Si energy surface (rather than HSi≡CH!).[7]

To add to the difficulty in establishing the origin of silapropyne **15**, we find that the pyrolyses of **18** and **19** (eq 3 and 4, 650 °C, 10^{-4} torr; conditions where (trimethylsilyl)cyclopropane does *not* isomerize)[8] to produce silylenes **20** and **21** (isomeric with **9**) affords

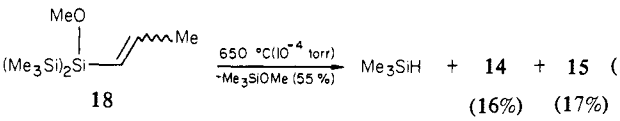
---

[4] **8**: ^1H NMR (CCl_4) δ 0.14 (s, 18 H), -0.30 to 0.72 (m, 5 H), 3.35 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ -5.07, -0.68, 1.76, 53.22; calcd for $C_{10}H_{26}OSi_3$ (M^+) *m/e* 246.129 16, measured 246.129 17.

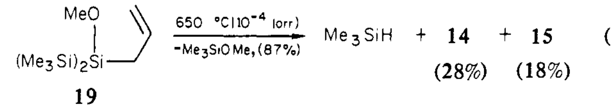
[5] **10**: ^{13}C NMR (CCl_4) η 0.10 (s, 9 H, $SiMe_3$), -0.40 to 0.72 (m, 5 H), cyclopropyl), 1.30 (br s, 4 H, CH_2), 1.65 (br s, 6H, Me): ^{13}C NMR (C_6D_6) -7.09, -1.56, 1.91, 19.18, 21.73, 130.89; calcd for $C_{12}H_{24}Si_2$ (M^+, 13%) *m/e* 224.141 66, measured 224.141 81.

[6] **13**: ^1H NMR (C_6H_6) δ 0.05 (s, 9 H), 0.86 (d of d, 1 H, J = 10, 7 Hz, collapses to br s with $h\nu$ at δ 2.12), 1.25 (apparent t, 2 H, J = 8 Hz, collapses to br s with $h\nu$ at δ 2.12), 1.58 (br s, 4 H), 1.68 (br s, 6 H), 2.12 (m, 2 H): ^{13}C NMR (C_6D_6) δ -1.07, 15.33, 16.74, 17.50, 19.07, 19.72, 26.12 26.87, 130.13, 130.29; calcd for $C_{12}H_{24}Si_2$ (M^+, 38%) *m/e* 224.1417, measured 224.1420.

[7] Gordon, M. S.; Pople, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 2945.

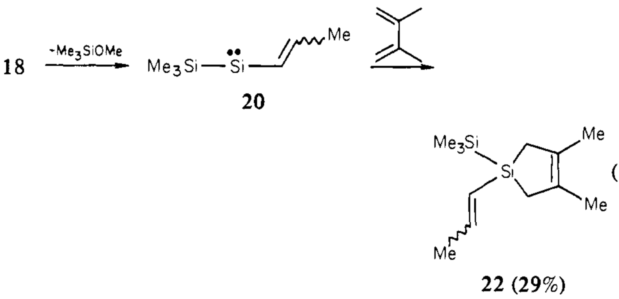


(3)

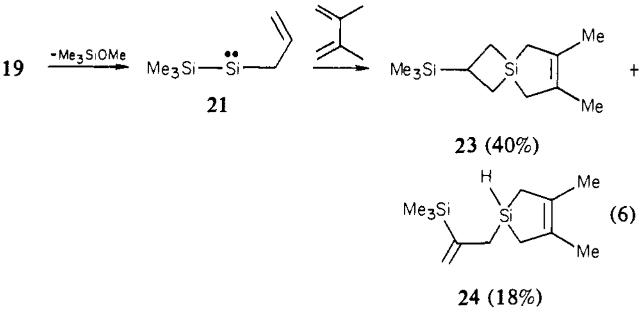


(4)

the same products (Me_3SiH, **14** and **15**) in very similar yields. Copyrolysis of **18** (eq 5) and DMBD afforded only trapping of



(5)



the initially formed silylene **20** to give silacyclopentene **22**.[9] However, copyrolysis of **19** (eq 6) and DMBD afforded in 40% yield silacyclopentene **23**,[9] clearly derived from rearrangement of silylene **21** to silylene **25** before trapping. In addition to **23**, adduct **24**[9] was formed in 18% yield. Although it is possible that **24** arises from isomerization of **23**, we favor a route involving intramolecular C–H insertion by silylene **25** to afford silabicyclo[1.1.0]butane **26** followed by ring opening to allylsilylene **27**, which is trapped by DMBD to afford adduct **24**.

The strikingly similarity of products and yields from silylenes **9**, **20**, and **21** suggests that in the absence of traps they merge on the same energy surface. At this time the only clues as to the nature of this surface are the trapping of cyclobutasilylenes **12** and **25** from **8** and **19**, respectively. One possible route for interconversion is presented in Scheme III. Currently, we are probing these reactions through chemical trapping, labeling, and direct generation of the proposed intermediates.

Acknowledgment. Support of this research by the National Science Foundation is gratefully acknowledged.

Registry No. 8, 83268-89-7; **10**, 83268-90-0; **13**, 83268-91-1; **18** (isomer 1), 83268-92-2; **18** (isomer 2), 83268-93-3; **19**, 83268-94-4; **22** (isomer 1), 83268-95-5; **22** (isomer 2), 83268-96-6; **23**, 83268-97-7; **24**, 83268-98-8; cyclopropyllithium, 3002-94-6; bis(trimethylsilyl)dichlorosilane, 5181-42-0; sodium methoxide, 124-41-4; 2,3-dimethyl-1,3-butadiene, 513-81-5.

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(8) **18**: Although a ca. 1:1 mixture of *cis*- and *trans*-**18** was used in these experiments, they could be separated by preparative GC. *trans*-**18**: ^{1}H NMR ($DCCl_3$) δ 0.20 (s, 18 H), 1.89 (d, $J = 6$ Hz, 3 H), 3.48 (s, 3 H, OMe), 5.78 (d, $J = 18$ Hz, 1 H), 6.16 (d of q, $J = 18$, 6 Hz, collapses to d, $J = 18$ Hz, with $h\nu$ at δ 1.89, 1 H). *cis*-**18**: ^{1}H NMR ($DCCl_3$) δ 0.16 (s, 18 H), 1.81 (d. of d, $J = 7$, 1 Hz, 3 H), 3.41 (s, 3 H, OMe), 5.46 (d of q, $J = 14$, 1 Hz, 1 H), 5.41 (center of overlapped d of q, $J = 14$, 7 Hz, 1 H). Calcd for $C_{10}H_{26}OSi_3$ (M^+, 26%) *m/e* 246.1292, measured (from cis, trans mixture) *m/e* 246.1299. **19**: ^{1}H NMR ($CDCl_3$) δ 0.24 (s, 18 H), 1.96 (d, 2 H, $J = 8$ Hz), 3.48 (s, 3 H, OMe), 4.73–5.14 (m, 2 H, $=CH_2$), 5.51–6.28 (m, 1 H, $=CHCH_2-$); calcd for $C_{10}H_{26}OSi_3$ (M^+, 0.2%) *m/e* 246.1292, measured *m/e* 246.1291.

(9) *trans*-**22**: (17%) ^{1}H NMR ($DCCl_3$) δ 0.22 (s, 9 H), 1.57 (br s, 4 H), 1.77 (br s, 6 H), 1.89 (d, $J = 6$ Hz), 5.72 (d, $J = 18$ Hz), 6.10 (d of q, $J = 18$, 6 Hz). *cis*-**22**: (12%) ^{1}H NMR ($DCCl_3$) δ 0.16 (s, 9 H), 1.61 (br s, 4 H), 1.74 (br s, 6 H), 1.77 (d of d, $J = 7$, 1 *hz*. 3 H), 6.43 (center of overlapped d of q, $J = 7$, 14 Hz, 1 H), 5.59 (d of q, $J = 14$, 1 Hz, 1 H). Calcd for $C_{12}H_{24}Si_2$ (M^+, 70%, from cis/trans mixture) *m/e* 224.1417, measured 224.1415). **23**: ^{1}H NMR ($DCCl_3$) δ 0.05 (s, 9 H), 0.77–1.47 (m, 5 H), 1.55 (br s, 4 H allylic CH_2), 1.73 (br s, 6 H allylic Me); CMR ($DCCl_3$) δ −3.71, 15.09, 17.85, 19.15, 19.26, 24.0, 27.17, 130.31, 130.80; calcd for $C_{12}H_{24}Si_2$ (M^+, 43%), *m/e* 224.1417, measured *m/e* 224.1414. **24**: ^{1}H NMR ($DCCl_3$) δ 0.13 (s, 9 H), 1.44 (br s, 4 H, sharpens with $h\nu$ at δ 4.14), 1.71 (br s, 6 H), 1.81 (br d, 2 H, $J = 4$ Hz, collapses to br s with $h\nu$ at δ 4.14), 4.14 (m, 1 H, SiH, collapses to s with $h\nu$ at δ 1.71–1.81), 5.22 (d, 1 H, $J = 3$ Hz), 5.47 (overlapped d of t, $J = 3$, 2 Hz. 1 H, collapses to d with $h\nu$ at 1.81; calcd for $C_{12}H_{24}Si_2$ (M^+, 11%) *m/e* 224.1417. measured 224.1420.

Direct Observation of the Special Salt Effect: Picosecond Dynamics of Ion Pair Exchange

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Received April 14, 1982

Salt effects are frequently observed in organic reactions that involve ion pair intermediates. Winstein[1] observed that the effect of added $LiClO_4$ on the rate of solvolysis of *threo*-3-*p*-anisyl-2-butyl *p*-bromobenzenesulfonate was an initial rate increase that could not be explained solely in terms of an ionic strength effect. The observation of this special salt effect led him to postulate two different types of ion pair intermediates, contact and solvent separated. Winstein proposed that the special salt effect resulted from the prevention of return to the contact ion pair from the solvent-separated form. This mechanism has received substantial support,[2] but its elucidation has been based on indirect observations. On the other hand, it has been reported[3] that the rate of ion pair exchange is not highly sensitive to ion pair structure. This observation indicates that the mechanism of the special salt effect should involve interception of both contact- and solvent-separated ion pair forms. To data there has been no direct experimental determination of the rates of formation of salt contact ion pairs from initially formed organic ion pairs. We have used picosecond absorption spectroscopy to determine the rate of ion pair exchange. By examining the rate of interception of organic contact and solvent-separated ion pairs by sodium contact ion pairs (NaI) and sodium solvent separated ion pairs ($NaClO_4$), we will show that the rate of interception is dependent on ion pair structure. Our results support, in part, Winstein's proposed mechanism for the special salt effect.

The picosecond absorption spectrometer has been previously described.[4] Transient absorption spectra for the photoreduction of 0.2 M benzophenone by 1.0 M *N*,*N*-diethylaniline (DEA) in the presence of 0.5 M $NaClO_4$ in acetonitrile are shown in Figure 1. We have recently reported[4] that in the absence of salt, photolysis results in a rapid electron transfer forming the solvent-separated ion pair consisting of the amine radical cation and the benzophenone radical anion (λ_{max} 720 nm). These species diffuse together within 300 ps following photolysis to form a contact ion pair (λ_{max} 690 nm). In the present study, the absorption maximum of the radical anion of benzophenone (λ_{max} 695 nm) indicates the formation of the amine contact ion pair (Figure 1A) at 200 ps following photolysis. From 500 ps to 10 ns, the absorption

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(1) (a) Winstein, S.; Robinson, G. *J. Am. Chem. Soc.* **1958**, *80*, 169. (b) Winstein, S.; Clippinger, E.; Fainberg, A.; Robinson, G. *Ibid.* **1954**, *76*, 2597.

(2) (a) Fainberg, A.; Winstein, S. *J. Am. Chem. Soc.* **1956**, *78*, 2767. (b) Fainberg, A.; Robinson, G.; Winstein, S. *Ibid.* **1956**, *78*, 2777. (c) Winstein, S.; Clippinger, E. *Ibid.* **1956**, *78*, 2784. (d) Jenny, E.; Winstein, S. *Helv. Chim. Acta* **1958**, *41*, 807.

(3) (a) Grunwald, E.; Puar, M. *J. Am. Chem. Soc.* **1967**, *89*, 6842. (b) Crampton, M.; Grunwald, E. *Ibid.* **1971**, *93*, 2987. (c) Crampton, M.; Grunwald, E. *Ibid.* **1971**, *93*, 2990.

(4) Simon, J. D.; Peters, K. S. *J. Am. Chem. Soc.* **1981**, *103*, 6403. Fiber optics were used to obtain transient absorption spectra at 5, 10, 50, and 250 ns following photolysis.

0002-7863/82/1504-6142$01.25/0