and the residue was recrystallized from 2-propyl alcohol to give 9.09 g (96%) of a white solid: mp 58–59 °C (lit.[10] 57–59 °C). The spectral data was identical with that previously reported.[10]

Hexakis(phenylthio)benzene (1a). Light yellow solid; Purified by recrystallization from toluene; mp 183–184.5 °C (lit.[17] 182–185 °C) ^{1}H NMR ($CDCl_3$) (200 MHz) δ 7.00 (m, 12 H), 7.14 (m, 18 H). Anal. Calcd for $C_{42}H_{30}S_6$: C, 69.4; H, 4.2. Found: C, 69.3; H, 4.4.

Hexakis(*n*-dodecylthio)benzene (1b). White solid; Purified by recrystallization from a mixture of hexane and acetone; mp 39–41 °C; ^{1}H NMR ($CDCl_3$) (80 MHz) δ 0.96 (t, CH_3, 18 H), 1.27 (complex m, 120 H), 3.02 (t, SCH_2, 12 H). Anal. Calcd for $C_{78}H_{150}S_6$: C, 73.2; H, 11.8; S, 15.0. Found: C, 72.9; H, 11.8; S, 15.2.

Pentakis(ethylthio)benzenethiol (2). Colorless liquid; Purified by preparative HPLC (silica gel: heptane eluent); ^{1}H NMR ($CDCl_3$) (80 MHz) δ 1.15 (overlapping t, CH_3, 15 H), 2.96 (overlapping q, CH_2, 10 H), 6.77 (exchangeable s, SH, 1 H); IR ν 2455 cm^{-1} (SH); MS, *m/z* 410 ($M^{+\cdot}$). Anal. Calcd for $C_{16}H_{26}S_6$: C, 46.8; H, 6.4. Found: C, 47.0; H, 6.4.

1,2,4,5-Tetrakis(ethylthio)benzene (3a). White solid; Purified by recrystallization from 2-propyl alcohol; mp 65–67 °C (lit.[6c,10] 65–67 °C); ^{1}H NMR ($CDCl_3$) (80 MHz) δ 1.31 (t, CH_3, 12 H), 2.94 (q, CH_2, 8 H), 7.19 (s, ArH, 2 H).

1,2,4,5-Tetrakis(*n*-octylthio)benzene (3b). White solid; Purified by recrystallization from 2-propyl alcohol; mp 66–67 °C; ^{1}H NMR ($CDCl_3$) (200 MHz) δ 0.87 (t, CH_3, 12 H), 1.27–1.65 (complex m, 48 H), 2.89 (t, SCH_2, 8 H), 7.17 (s, ArH, 2 H). Anal. Calcd for $C_{42}H_{70}S_4$: C, 69.7; H, 10.8. Found: C, 69.9; H, 10.8.

1,2,4,5-Tetrakis(*n*-dodecylthio)benzene (3c). White solid; Purified by recrystallization from 2-propyl alcohol; mp 72–73.5 °C; ^{1}H NMR ($CDCl_3$) (200 MHz) δ 0.88 (t, CH_3, 12 H), 1.26–1.68 (complex m, 80 H), 2.90 (t, SCH_2, 8 H), 7.18 (s, ArH, 2 H). Anal. Calcd for $C_{54}H_{102}S_4$: C, 73.7; H, 11.7. Found: C, 73.7; H, 11.9.

1,2,4,5-Tetrakis(phenylthio)benzene (3d). White solid; Purified from a mixture of ethyl alcohol and toluene; mp 147–148.5 °C; ^{1}H NMR ($CDCl_3$) (80 MHz) δ 6.81 (s, 2 H), 7.19 (s, 20 H). Anal. Calcd for $C_{30}H_{22}S_4$: C, 70.6; H, 4.3. Found: C, 70.7; H, 4.7.

1,2,4-Tris(phenylthio)benzene (4a). Clear amber liquid; Purified by dry-column chromatography (silica gel; heptane eluent); ^{1}H NMR ($CDCl_3$) (200 MHz) δ 7.35 (dd, 1 H), 7.41 (dd, 1 H), 7.49 (dd, 1 H), 7.71 (complex m, 15 H). Anal. Calcd for $C_{24}H_{18}S_3$: C, 71.6; H, 4.5. Found: C, 71.2; H, 4.6.

1,4-Bis(*n*-dodecylthio)benzene (5). White solid; Purified by recrystallization from 2-propyl alcohol; mp 79–80 °C (lit.[18] 78–79.5 °C); ^{1}H NMR ($CDCl_3$) (200 MHz) δ 0.88 (t, CH_3, 6 H), 1.26–1.62 (complex m, 40 H), 2.90 (t, SCH_2, 4 H), 7.26 (s, ArH, 4 H). Anal. Calcd for $C_{30}H_{54}S_2$: C, 75.2; H, 11.4. Found: C, 74.8; H, 11.4.

(*n*-Dodecylthio)benzene (6). White solid; Purified by recrystallization from ethyl alcohol; mp 33–34 °C (lit.[17b,19] 33–34 °C); ^{1}H NMR ($CDCl_3$) (200 MHz) δ 0.89 (t, CH_3, 3 H), 1.07–1.63 (complex m, 20 H), 2.91 (t, SCH_2, 2 H), 6.99–7.59 (complex m, ArH, 5 H). Anal. Calcd for $C_{18}H_{30}S$: C, 77.6; H, 10.9. Found: C, 77.9; H, 10.5.

Acknowledgment. We wish to thank CIBA-GEIGY Corporation for support and permission to publish this work. S.D.P. thanks Bogdan Piatek for the mass spectra, Timothy Geran for ^{1}H NMR spectra, and Derry Lounsbury for preparation of the manuscript.

(16) Since the product (in most cases) partially separated on standing, the organic phase was not dried.

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Reaction of Amines with Cyclopropylcarbinyl Halides: S_N2' or Solvolysis?[1a]

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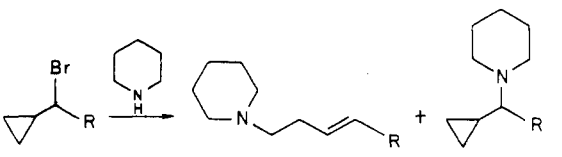
The cyclopropane ring can be opened by amines, under noncationic conditions, and without the requirement of electron-withdrawing groups on the ring. The pedant halide in cyclopropylcarbinyl halides, **1**, provides sufficient activation for the homoallylic ring opening to the corresponding alkenylamine. The substitution reaction of amines with a variety of increasingly sterically hindered halides follows second-order kinetics. This sharply contrasts with the S_N1-like behavior when the halides react with alkoxides in alcohol solvents. It appears that the reaction of **1** with amines proceeds via a homoallylic S_N2' pathway, analogous to Bordwell's description of the S_N2' reaction in allylic systems, rather than via a pathway involving solvent-separated ion pairs.

We have recently reported that cyclopropylcarbinyl halides, **1**, undergo facile substitution on reaction with piperidine to give mixtures of the homoallylic substitution product, **2**, and the direct substitution product, **3**, in good yield.[2] When the alkyl group on the bromine-bearing carbon provided sufficient steric hindrance, the major product of this reaction was **2**, which corresponds to the homoallylic analogue of the well-known S_N2' process observed with allylic halides.[3] Such a S_N2' process is unprecedented for the cyclopropylcarbinyl system. Indeed, only cyclopropane rings activated with two electron-with-



1 **2** **3**

a, R = Me; **b**, R = Et; **c**, R = *n*-Pr; **d**, R = *n*-Bu; **e**, R = *i*-Pr; **f**, R = *t*-Bu

(1) (a) Smith, M. B.; Hrubiec, R. T., presented, in part, at the Thirteenth Northeast Regional Meeting of the American Chemical Society, Hartford, CT, June 27, 1983, *ORGN 149*. (b) Abstracted, in part, from the Ph.D. thesis of R.T.H.

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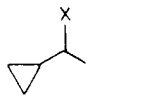
drawing groups had been successfully opened under noncationic conditions.[4] Ring-opening reactions of cyclopropane derivatives under acidic conditions are, of course, well-known.[5]

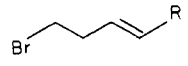
The S_N2 product, **3**, was produced in each case, even from bromides **1e** and **1f**. The increased steric encumbrance of these latter halides should have resulted in a significant encumbrance of the S_N2 process. We therefore questioned whether homoallylic substitution of **1** proceeded via a S_N2' pathway, and wished to explore the possibility of a reaction involving solvent-separated ion pairs, in a S_N1-like pathway. We have now examined this unusual behavior of **1f** in the context of the other halides and in comparison with the reaction of **1** with alkoxides, which appears to proceed via solvolysis. The behavior of **1** with amines when compared to the reaction with alcohols suggested that the former proceeds via a S_N2' pathway and the latter via a S_N1-like pathway. The second-order kinetics exhibited in the reaction of **1** with amines appeared to confirm this premise. We discuss these conflicting pathways and give a full account of this novel homoallylic substitution reaction.[2]

Results

Our initial probe of the reactivity of piperidine with cyclopropylcarbinyl derivatives focused on the ester derivatives **4b** and **4c**, prepared from 1-cyclopropyl-1-ethanol (**4a**) by treatment with the appropriate acid chloride.



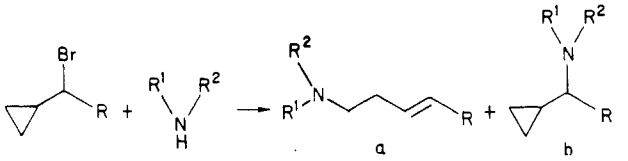
4a, X = OH
b, X = $OCOC_6H_5$
c, X = $OCOC_6H_5$
d, X = Cl



5, R = $-CH(CH_3)_2$
6, R = $-CH_3$

Both **4b** and **4c** were inert to refluxing piperidine. Even reaction at 130 °C for 25 h in a sealed tube gave no substitution products. The unreactive nature of these esters led us to examine the analogous 1-chloro-1-cyclopropylethane, **4d**, prepared from **4a** and hexachloroacetone/triphenylphosphine.[6] Reaction of **4d** with a pedant primary amine in complex alkaloids had been reported several times[7] but only the direct substitution product was formed, in good yield. When **4d** was refluxed in neat piperidine for 72 h, we obtained an 83% yield of the expected 1-cyclopropyl-1-piperidinoethane, **3a**, but also observed 6% of 1-piperidino-3-pentene, (**2a**).[2] Similar results were obtained with the corresponding bromide, **1a**, when a 91% yield of **2a** and **3a** was obtained as an 8:92 mixture.[2] The presence of **2a** encouraged us to examine this reaction with compounds possessing more steric hindrance at the halogen-bearing carbon. By analogy with the well-known S_N2' reaction observed for allylic halides and amines,[3] we anticipated increased amounts of **2** as the steric encumbrance around the bromine-bearing carbon in **1** increased. Since **1a** was more reactive than **4d**, we prepared a series of bromides, **1b–1f**, from the corresponding alcohol and bromine/triphenylphosphine,[8] which gave good yields of **2** and **3** on reaction with piperidine, as shown in Table I.[2] As the steric hindrance in **1** increased, greater amounts of **2**, relative to **3**, were observed, and **1f** gave a 92:8 mixture of **2f** and **3f**, in 95% yield.

Table I. Reactions of 1-Bromo-1-cyclopropylalkanes with Piperidine or Diethylamine

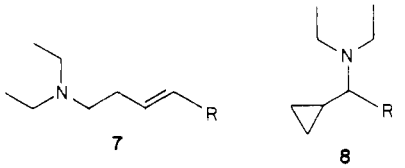


a b

R	R^1, R^2	amine a, %	amine b, %
CH_3	$-CH_2CH_2CH_2CH_2CH_2-$[a]	**2a**, 8	**3a**,[d] 86
	$-CH_2CH_2CH_2CH_2CH_2-$[b]	10	74
	Et, Et[c]	**7a**, 27	**8a**,[d] 34
Et	$-CH_2CH_2CH_2CH_2CH_2-$[a]	**2b**,[d] 35	**3b**,[d] 60
n-Pr	$-CH_2CH_2CH_2CH_2CH_2-$[a]	**2c**,[d] 33	**3c**,[d] 65
n-Bu	$-CH_2CH_2CH_2CH_2CH_2-$[a]	**3d**,[d] 39	**3d**,[d] 45
	$-CH_2CH_2CH_2CH_2CH_2-$[b]	12	66
	Et, Et[c]	**7b**,[d] 46	**8b**,[d] 27
i-Pr	$-CH_2CH_2CH_2CH_2CH_2-$[a]	**2e**,[d] 67	**3e**,[d] 27
	$-CH_2CH_2CH_2CH_2CH_2-$[b]	72	21
	Et, Et[c]	**7c**,[d] 36	**8c**,[d] 9
t-Bu	$-CH_2CH_2CH_2CH_2CH_2-$[a]	**2f**,[d] 88	**3f**, 8
	$-CH_2CH_2CH_2CH_2CH_2-$[b]	73	8
	Et, Et[c]	**7d**,[d] 75	**8d**, 4

[a] *T* = refluxing piperidine. [b] *T* = 25 °C. [c] *T* = refluxing diethylamine. [d] Satisfactory analysis obtained for this compound.

Reactions of **1a**, **1d**, **1e**, and **1f** with diethylamine gave similar results and a mixture of the homoallylic substitution product **7** and the direct substitution product **8** was



7 8

a, R = Me **b**, R = *n*-Bu **c**, R = *i*-Pr **d**, R = *t*-Bu

obtained in each case. As the steric hindrance in **1** increased, the proportion of **7** increased accordingly, as summarized in Table I, and these results are similar to those obtained with piperidine, although the yields are somewhat lower. The reaction of **1a** with diethylamine appears to be anomalous since 34% of **8a** and 27% of **7a** was obtained.

The presence of the direct substitution product **3f** raised doubts that S_N2' was the proper description for reactions of **1** with amines, and we explored reasonable alternatives. Rearrangement of the bromide, **1**, before substitution, or rearrangement of **3**, after substitution, in a reversible process, would also give **2**. Refluxing **1** with piperidine for extended periods of time gave the same ratio of **2:3** and refluxing **3** in piperidine for 12 h, gave no change at all. Shorter reaction times gave similar ratios of **2:3** although the reaction was incomplete. Rearrangement after substitution does not appear to be important.

Rearrangement before substitution could involve thermal opening of the cyclopropane ring, or catalysis by the piperidine hydrobromide formed during the reaction. To

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(8) Hrubiec, R. T.; Smith, M. B. *J. Org. Chem.* **1984**, *49*, 431.

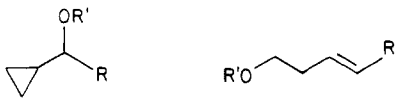
test this premise, **1e** was refluxed in dioxane for 12 h to mimic the temperature conditions in refluxing piperidine and 23.8% of 6-bromo-2-methyl-3-hexene (**5**), was formed via thermal rearrangement. Reaction of **1e** with piperidine hydrobromide in refluxing dioxane for 12 h, however, gave only an additional 3% of **5**. Similar treatment of **1a** led to 1.9% of **6**, and addition of the piperidine hydrobromide gave only 2% of **6**.

It appears that with hindered halides such as **1e** and **1f** and to a lesser extent with **1d**, thermal rearrangement before substitution by the amine can account for some of the **2d**, **2e**, and **2f** which is observed, although the acid-catalyzed ring opening is not a significant process. Since reaction of **1d**, **1e**, or **1f** with piperidine at ambient temperatures also gave significant amounts of **2**, although somewhat less than under reflux conditions, not all of the **2** was formed by thermal rearrangement. The effects of the solvent on this rearrangement are unknown for an amine vs. dioxane, and we can only say that thermal rearrangement is not the exclusive nor major process leading to **2**.

To mimic the conditions in diethylamine, **1a** and **1e** were refluxed in THF for 60 h but less than 2% of **6** or **5** were observed, and thermal isomerization is not significant at this temperature. When **1e** was refluxed with diethylamine hydrobromide in THF for 60 h, less than 2% of **5** was observed. Bromide **1a**, however, under similar conditions gave 31.8% of **6**. Clearly, a significant amount of **2a** arises via ring opening, induced by diethylamine hydrobromide before substitution, and probably accounts for the anomalously high amount of **2a**. Inexplicably, piperidine hydrobromide does not affect **1e** or **1a**, and **1e** was unaffected by diethylamine hydrobromide. It has been suggested that diethylamine hydrobromide (pK_a = 10.93) is slightly more acidic than piperidine hydrobromide (pK_a = 11.22).[9] This may account for the anomalous behavior of **1a**, but it does not explain the insensitivity of the other halides, and a completely satisfactory explanation of this phenomenon is not now available.

We have also initiated the cationic ring opening reaction of **1**, to compare with our results for the amines. Reaction of **1d** with zinc bromide in refluxing THF for 1 h, gave products consistent with a cationic intermediate. We assume formation of the cyclopropylcarbinyl cation, with subsequent facile rearrangement. The reaction with amines was significantly slower, gave a different product distribution, and was clearly a function of the steric impedance of the halide. This seems to militate against a cationic species.

A preliminary examination of the reaction of **1a**, **1d**, **1e**, and **1f** with alkoxides gave what appeared to be surprising results, as shown in Table II. Two observations are significant: (a) the reaction was remarkably insensitive to the steric environment of **1**, in contrast to the reactions of amines; and (b) the direct substitution product, **9** or **11**,

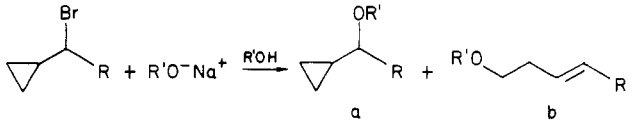


9 R' = Me
11 R' = *n*-Pr

10 R' = Me
12 R' = *n*-Pr

a, R = Me; **b**, R = Et; **c**, R = *n*-Pr
d, R = *n*-Bu; **e**, R = *i*-Pr; **f**, R = *t*-Bu

Table II. Reaction of 1-Bromo-1-cyclopropylalkanes with Sodium Methoxide or Sodium *n*-Propoxide



R	R′	ether a, %	ether b, %
CH_3	CH_3	**9a**,[b] 42	**10a** 18
	n-Pr	**11a**,[b] 47	**12a** 43
n-Bu	CH_3	**9d**,[b] 76	**10d** –[a]
	n-Pr	**11d**,[b] 78	**12d** –[a]
t-Bu	CH_3	**9f**,[b] 75	**10f** –[a]
	n-Pr	**11f**,[b] 71	**12f** 21

[a] Not detected by VPC/MS or ^1H NMR. [b] Satisfactory analysis obtained for this compound.

predominates in each case. We believe the results in Table II point to a solvent-separated ion pair intermediate, in an S_N1-like process and stands in sharp contrast to the reactions of piperidine and diethylamine.

Confirmation of the S_N2'-like behavior of the amines came from a kinetic study of piperidine and diethylamine with **1a** and **1e**. In each case, the unreacted amine was titrated with hydrochloric acid, after the method of Young.[10] The results for **1a** with diethylamine and for **1e** with diethylamine and piperidine are shown in Figure 1. The linear plot of 1/[1] as a function of time (s) indicates that these reactions follow second-order kinetics, at least through three half-lives. An analysis of Figure 1 indicated that for **1a** and piperidine, $k = 1.21 \times 10^{-5}$ ($t_{1/2} = 5.76 \times 10^4$); for **1e** and piperidine, $k = 4.42 \times 10^{-6}$ ($t_{1/2} = 1.57 \times 10^5$); and for **1e** and diethylamine, $k = 1.87 \times 10^{-6}$ ($t_{1/2} = 3.70 \times 10^5$). The reaction of **1a** with diethylamine, however, did not show linearity in this plot and does not follow second-order kinetics. This is not surprising since, as discussed above, **1a** reacts with diethylamine hydrobromide in a competitive ring opening process which would give rise to a complex kinetics scheme. The other halides are unaffected by the amine salts and give good correlations in Figure 1. We take this as strong evidence for the bimolecular nature of the reaction with amines, in support of our proposed S_N2' pathway.

Discussion

In our preliminary report[2] we suggested that a S_N2' reaction analogous to the ion-pair mechanism of Bordwell[11] could account for the results observed with piperidine and **1**. The presence of **3f** and **6d** from **1**, however, complicated this view. The terms S_N2 and S_N2' can imply direct substitution at the halogen-bearing carbon and similar attack on the ring, with concomitant expulsion of the halide, or in Bordwell's view,[11] reaction via an ion pair. Ionization leads to solvent-separated ion pairs in an S_N1-like process involving a cyclopropylcarbinyl cation with subsequent rearrangement to give **2**. The second-order kinetics observed with amines on reaction with **1** strongly favors the S_N2' pathway. A S_N2 process on the "neopentyl-like" **1f**, however, would be extremely slow but a cyclopropylcarbinyl cation intermediate is not consistent with the observed products or kinetics. It is known that cyclopropylcarbinyl cations give mixtures of closed-ring product, **13**, the open-chain product, **14**, and also cyclobutane de-

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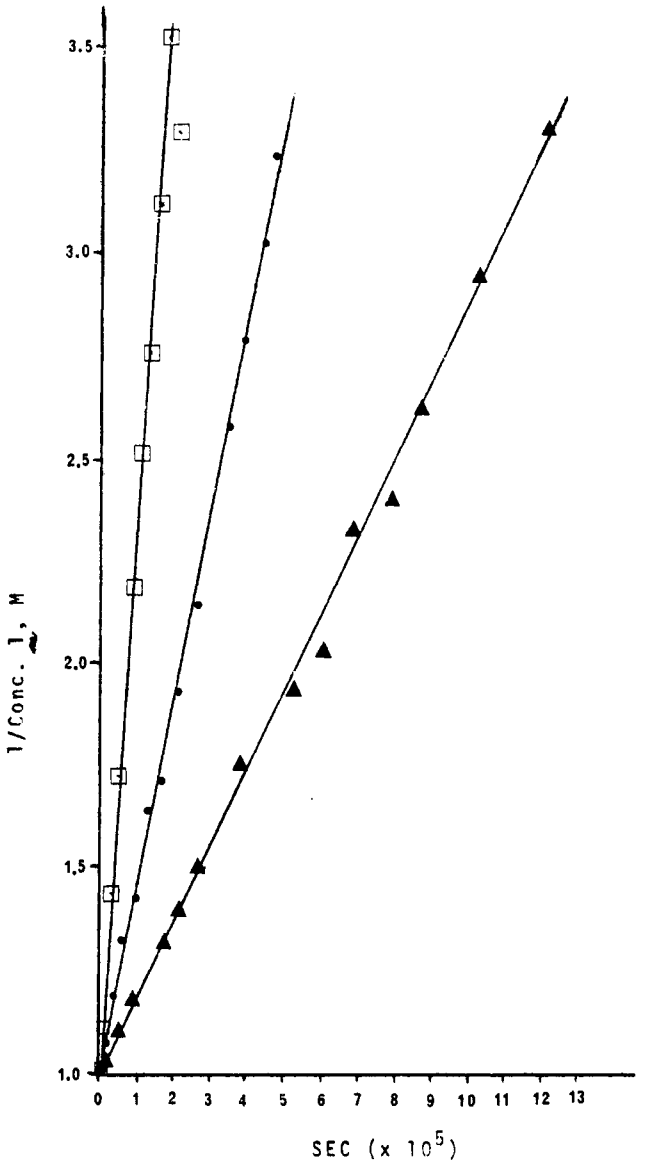
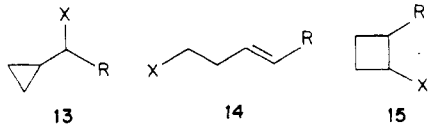


Figure 1. Plot of 1/[1] vs. time (s) for the reaction of a 1 M solution of **1a** with piperidine (□), **1e** with piperidine (●), and **1e** with diethylamine (▲).

rivatives, **15**.[5] We did not observe cyclobutane derivatives in any reaction of **1** with piperidine or diethylamine. Also, **13** is often a major product of solvolysis reactions involving cyclopropylcarbinyl cations, depending on the solvent.[5] It is noteworthy that the reaction with alkoxides gave primarily analogues of **13**, whereas the amine products were



a function of the halide structure. Indeed, the insensitivity to steric impediment exhibited by the alkoxides compared to the clear and predictable dependance shown by the amines in a second-order reaction is the best evidence against a solvolysis pathway for the amines. As the steric hindrance in **1** increased, the amount of **2** increased proportionally, clearly mimicking S_N2' behavior, suggesting a *tight ion pair* intermediate with little cationic character. Presumably, such an ion pair could account for the small amounts of **3f** or **7d**, if some solvent separation occurred.

It is also clear that a portion, *but not all*, of **2e** and **2f** arises via thermal rearrangement of **1e** to **5** or **1f** to 6-bromo-2,2-dimethyl-3-hexene. The facile formation of **2** in piperidine at ambient temperatures is proof that the S_N2'-like process occurs, independent of the thermal rearrangement. Also, **1b–1f** were essentially unaffected by piperidine hydrobromide or diethylamine hydrobromide, and such acid catalyzed rearrangement does not significantly contribute to formation of **2**. Only for **1a** was a large amount of **2a** formed via rearrangement, apparently induced by the diethylamine hydrobromide. The decreased amounts of **2** at ambient temperatures, when compared to refluxing piperidine, may be the true measure of the extent of thermal rearrangement in this system.

A normal S_N2 type mechanism explains the production of **3** from **1a–1d**, and one could, therefore, invoke classical S_N2' pathways for the formation of most of the observed **2a–2d**. It is only when the S_N2 mechanism breaks down that the S_N2' path is in question. Our results suggest that the reaction of amines with **1** is governed by the same mechanistic considerations involved in reactions of allylic halides with amines. The apparently anomalous behavior of **1f** can be explained by a small amount of solvent separation of the intermediate tight ion pair, leading to increased amounts of the rearrangement product. It appears, therefore, that Bordwell's mechanistic description of the S_N2' pathway[11] explains the results we have observed with **1**, and we conclude that cyclopropylcarbinyl halides react with amines via a S_N2/S_N2' pathway rather than via solvent-separated ion pairs in an S_N1 process. Some thermal rearrangement occurs to give **2** or **7** but the ion-pair pathway is probably responsible for most of the **2** and **3** which is produced, via Bordwell's definition of S_N2' rather than the classical concerted or "bridging" mechanism previously suggested.[3,12]

Experimental Section

All ^1H NMR spectra were recorded with a Varian Associates EM-360 instrument at 60 MHz, a Bruker-90 instrument at 90 MHz, or an IBM-WP-200-SY instrument at 200 MHz, in ppm, downfield from tetramethylsilane. The IR spectra were recorded using a Perkin-Elmer IR-283 instrument and reported in cm^{-1}. The mass spectra were recorded on a HP-5987 VPC/MS instrument using a 30-m SE-54 capillary column. We have recently shown that the cyclopropylcarbinyl moiety controls the fragmentations of **1**, **3**, **8**, **9**, and **11** in the mass spectrum.[13] Analytical VPC was accomplished on a PE-3920-B flame-ionization gas chromatograph using a 7-m, 20% SE-30/Anakrom A column. All boiling points and melting points, determined with a Thomas-Hoover apparatus, are uncorrected. The elemental analyses were performed by MicAnal, Tucson, Arizona.

The requisite halides, **1a–1f** were prepared by methods we have recently described.[6,8] The dioxane-d_8, mesitoyl chloride, 2,6-dichlorobenzoyl chloride, 1-cyclopropyl-1-ethanol, piperidine, *N,N*-diethylamine, hexachloroacetone, bromine, and $CHCl_3$ were obtained from Aldrich. Sodium metal was obtained from Alfa. Anhydrous methanol and *n*-propyl alcohol were obtained from Baker and dried over molecular sieves before distillation under argon. Ethanol-free $CHCl_3$ was obtained by passing reagent grade $CHCl_3$ through a column of activity I alumina (EM reagents). The piperidine, *N,N*-diethylamine, and pyridine were distilled from KOH and stored under argon.

General Procedure for Reaction of Amines and 1-Halo-1-cyclopropylalkanes. A solution of 0.50 g of the 1-cyclopropyl-1-haloalkane in 10 mL of amine (piperidine or diethylamine) was stirred at reflux or at ambient temperature for the indicated time. On cooling, the solution was treated with 6 mL of 15% aqueous KOH, extracted with 3 × 20 mL of ether, and dried (Na_2SO_4), and the ether and unreacted amine were removed under reduced pressure. The resultant oil was distilled, in vacuo,

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(13) Smith, M. B.; Hrubiec, R. T. *Org. Mass Spectrom.* **1984**, *19*, 649.

and the distillate analyzed for product distribution via analytical VPC and VPC/MS. The samples for ^1H NMR and elemental analyses were obtained via preparative VPC.

Reaction of 1-Bromo-1-cyclopropylethane (1a). (a) With Piperidine (Reflux). Reaction of 0.50 g (3.35 mmol) of **1a** for 12 h at reflux gave 0.48 g of a colorless oil, bp 67–70 °C (11 mmHg) which contained 0.04 g (0.26 mmol, 8%) of 1-(3-pentenyl)-piperidine (**2a**)[14] [^1H NMR ($CDCl_3$) δ 1.32–2.00 (m, 8 H), 2.10–3.10 (m, 9 H), and 5.15–5.30 (m, 2 H); mass spectrum, m/z (relative intensity) 153 (1) and 98 (100)] and 0.44 g (2.87 mmol, 86%) of 1-(1-cyclopropylethyl)-1-piperidine (**3a**)[15] [^1H NMR ($CDCl_3$) δ 0.10–0.75 (m, 4 H), 1.1 (d, 3 H, J = 6.1 Hz), 1.23–1.82 (brd m, 7 H), and 2.22–3.00 (m, 5 H); mass spectrum, m/z (relative intensity) 153 (15), 138 (100), and 112 (55)]. Anal. Calcd for $C_{10}H_{19}N$: C, 78.37; H, 12.49; N, 9.14. Found: C, 78.55; H, 12.39; N, 9.43.

(b) With Piperidine (Ambient Temperatures). Reaction of 0.50 g (3.35 mmol) of **1a** for 25 h at ambient temperatures gave 0.43 g of a colorless oil which contained 0.05 g (0.33 mmol, 10%) of **2a** and 0.38 g (2.48 mmol, 74%) of **3a**.

(c) With *N,N*-Diethylamine. Reaction of 0.50 g (3.35 mmol) of **1a** for 66 h at reflux gave 0.29 g of a colorless oil, bp 62–64 °C (27 mmHg) which contained 0.13 g (0.92 mmol, 27%) of *N,N*-diethyl-3-pentenylamine (**7a**)[16] [^1H NMR ($CDCl_3$) δ 1.00 (t, 6 H, J = 6.0 Hz), 1.48–1.75 (m, 3 H), 1.80–2.83 (m, 4 H), 2.50 (q, 4 H, J = 6.0 Hz), and 5.10–5.45 (m, 2 H); mass spectrum, m/z (relative intensity) 141 (1) and 96 (100)] and 0.16 g (1.13 mmol, 34%) of *N,N*-diethyl-1-cyclopropylethylamine (**8a**) [^1H NMR ($CDCl_3$) δ 0.10–0.78 (m, 4 H), 0.98 (t, 6 H, J = 6.0 Hz), 1.0–1.3 (m, 1 H), 1.06 (d, 3 H), and 2.23–2.76 (m, 5 H); mass spectrum, m/z (relative intensity) 141 (20), 126 (100), and 100 (61)]. Anal. Calcd for $C_9H_{19}N$: C, 76.53; H, 13.56; N, 9.92. Found: C, 76.37; H, 13.95; N, 9.72.

Reaction of 1-Chloro-1-cyclopropylethane (4d). Reaction of 0.50 g (4.78 mmol) of **4d** with 8 mL of dry piperidine for 20 h at relfux gave, after workup as described for **1a**, 0.65 g of a colorless oil, bp 69–71 °C (12 mmHg), which contained 0.61 g (3.98 mmol, 83%) of **3a** and 0.04 g (0.26 mmol, 6%) of **2a**.

Reaction of 1-Bromo-1-cyclopropylpropane (1b). With Piperidine. Reaction of 0.50 g (3.07 mmol) of **1b** for 12 h at reflux gave 0.49 g of a colorless oil, bp 80–83 °C (10 mmHg), which contained 0.18 g (1.08 mmol, 35%) of 1-(3-hexenyl)piperidine (**2b**) [^1H NMR ($CDCl_3$) δ 0.92 (t, 3 H), 1.4–1.7 (bd m, 6 H), 1.94–2.2 (m, 4 H), 2.3–2.7 (m, 6 H), and 5.30–5.49 (m, 2 H); mass spectrum, m/z (relative intensity) 167 (1) and 98 (100). Anal. Calcd for $C_{11}H_{21}N$: C, 78.97; H, 12.65; N, 8.37. Found: C, 78.97; H, 12.95; N, 8.31] and 0.31 g (1.85 mmol, 60%) of 1-(1-cyclopropyl-propyl)piperidine, **3b** [^1H NMR ($CDCl_3$) δ 0.15–0.65 (m, 4 H), 0.89 (t, 3 H), 1.13–1.74 (brd m, 9 H), and 1.98–2.76 (m, 5 H); mass spectrum, m/z (relative intensity) 167 (3), 138 (100), and 126 (12). Anal. Calcd for $C_{11}H_{21}N$: C, 78.97; H, 12.65; N, 8.37. Found: C, 79.02; H, 12.91; N, 8.60].

Reaction of 1-Bromo-1-cyclopropylbutane (1c). With Piperidine. Reaction of 0.50 g (2.82 mmol) of **1c** for 14 h at reflux gave 0.50 g of a colorless oil, bp 85–87 °C (6 mmHg), which contained 0.17 g (0.94 mmol, 33%) of 1-(3-heptenyl)piperidine (**2c**) [^1H NMR ($CDCl_3$) δ 0.91 (t, 3 H), 1.3–1.7 (br d m, 8 H), 1.93–2.22 (m, 4 H), 2.3–2.75 (m, 6 H), and 5.36–5.49 (m, 2 H); mass spectrum, m/z, (relative intensity): 181 (1) and 98 (100). Anal. Calcd for $C_{12}H_{23}N$: C, 79.49; H, 12.79; N, 7.72. Found: C, 79.47; H, 13.04; N, 7.64], and 0.33 g (1.82 mmol, 65%) of 1-(1-cyclopropylbutyl)piperidine (**3c**) [^1H NMR ($CDCl_3$) δ 0.29–0.78 (m, 4 H), 0.89 (t, 3 H), 1.3–1.7 (brd m, 9 H), and 2.25–2.7 (m, 5 H); mass spectrum, m/z (relative intensity): 181 (2), 140 (10), and 138 (100). Anal. Calcd for $C_{12}H_{23}N$: C, 79.49; H, 12.79; N, 7.72. Found: C, 79.42; H, 12.86; N, 7.82].

Reaction of 1-Bromo-1-cyclopropylpentane (1d). (a) With Piperidine (Reflux). Reaction of 0.50 g (2.62 mmol) of **1d** for 14 h at reflux gave 0.43 g of a colorless oil, bp 90–92 °C (2 mmHg) which contained 0.20 g (1.01 mmol, 39%) of 1-(3-octenyl)piperidine (**2d**) [^1H NMR ($CDCl_3$) δ 0.90 (t, 3 H), 1.3–1.7 (br d m, 10 H), 1.9–2.2 (m, 4 H), 2.3–2.7 (m, 6 H), and 5.33–5.48 (m, 2 H); mass spectrum, m/z (relative intensity) 195 (1) and 98 (100). Anal. Calcd for $C_{13}H_{25}N$: C, 79.93; H, 12.90; N, 7.17. Found: C, 80.14; H, 12.60; N, 7.12.] and 0.23 g (1.18 mmol, 45%) of 1-(1-cyclopropylpentyl)piperidine (**3d**) [^1H NMR ($CDCl_3$): δ 0.03–0.74 (m, 4 H), 0.90 (t, 3 H), 1.26–1.83 (br d m, 11 H), and 2.31–2.78 (m, 5 H); mass spectrum, m/z (relative intensity) 195 (2), 154 (5), and 138 (100). Anal. Calcd for $C_{13}H_{25}N$: C, 79.98; H, 12.90; N, 7.17. Found: C, 80.05; H, 13.04; N, 7.41.].

(b) With Piperidine (Ambient Temperatures). Reaction of 0.50 g (2.62 mmol) of **1d** for 63.5 h at ambient temperatures gave 0.40 g of a colorless oil which contained 0.06 g (0.31 mmol, 12%) of **2d** and 0.34 g (1.74 mmol, 66%) of **3d**.

(c) With *N,N*-Diethylamine. Reaction of 0.50 g (2.62 mmol) of **1d** for 64.5 h at reflux gave 0.35 g of a colorless oil, bp 57–58 °C (3 mmHg) which contained 0.22 g (1.20 mmol, 46%) of *N,N*-diethyl-3-octenylamine (**7b**)[16] [^1H NMR ($CDCl_3$) δ 0.89 (t, 3 H), 0.92 (t, 6 H), 1.15–1.65 (m, 4 H), 1.82–2.1 (m, 4 H), 2.2–2.9 (m, 6 H), and 5.1–5.4 (m, 2 H); mass spectrum, m/z, (relative intensity): 183 (2) and 86 (100). Anal. Calcd for $C_{12}H_{25}N$: C, 78.62; H, 13.74; N, 7.64. Found: C, 78.55; H, 14.03; N, 7.28.] and 0.13 g (0.71 mmol, 27%) of *N,N*-diethyl-1-cyclopropylpentylamine (**8b**) [^1H NMR ($CDCl_3$) δ 0.15–0.60 (m, 4 H), 0.89 (t, 3 H), 0.92 (t, 6 H), 1.1—1.7 (m, 6 H), and 2.15–2.9 (m, 5 H); mass spectrum, m/z (relative intensity) 183 (2), 142 (11), and 126 (100). Anal. Calcd for $C_{12}H_{25}N$: C, 78.62; H, 13.74; N, 7.64. Found: C, 78.56; H, 13.96; N, 7.42.].

Reaction of 1-Bromo-1-cyclopropyl-2-methylpropane (1e). (a) With Piperidine (Reflux). Reaction of 1.0 g (5.65 mmol) of **1e** for 12.5 h at reflux gave 1.0 g of a colorless oil, bp 80–83 °C (8 mmHg) which contained 0.69 g (3.81 mmol, 67%) of 1-(5-methyl-3-hexenyl)piperidine (**2e**) [^1H NMR ($CDCl_3$) δ 0.96 (dd, 6 H, J = 1.8, 6.2 Hz), 2.28–2.95 (m, 8 H), and 2.00–2.78 (m, 6 H); mass spectrum, m/z (relative intensity) 181 (1) and 98 (100). Anal. Calcd for $C_{12}H_{23}N$: C, 79.49; H, 12.79; N, 7.72. Found: C, 79.52; H, 13.05; N, 7.49.] and 0.28 g (1.54 mmol, 27%) of 1-(1-cyclopropyl-2-methylpropyl)piperidine (**3e**) [^1H NMR ($CDCl_3$) δ 0.15–0.62 (m, 4 H), 0.93 (d, 6 H), 1.18-1.8 (m, 8 H), and 2.0–2.8 (m, 5 H); mass spectrum, m/z, relative intensity): 181 (1), 140 (3), and 138 (100). Anal. Calcd for $C_{12}H_{23}N$: C, 79.49; H, 12.79; N, 7.72. Found: C, 78.96; H, 12.74; N, 7.74.].

(b) With Piperidine (Ambient Temperatures). Reaction of 1.0 g (5.65 mmol) of **1e** for 70 h at ambient temperatures gave 0.96 g of a colorless oil which contained 0.74 g (4.08 mmol, 72%) of **2e**; and, 0.22 g (1.21 mmol, 21%) of **3e**.

(c) With *N,N*-Diethylamine. Reaction of 0.5 g (2.82 mmol) of **1e** for 66.5 h at reflux gave 0.21 g of a colorless oil, bp 54–56 °C (5 mmHg) which contained 0.17 g (1.00 mmol, 36%) of *N,N*-diethyl-5-methyl-3-hexenylamine (**7c**) [^1H NMR ($CDCl_3$) δ 0.97 (d, 6 H, J = 6.2 Hz), 0.92–1.15 (t, 6 H), 1.8–2.3 (m, 1 H), 2.3–2.7 (m, 8 H), and 5.02–5.3 (m, 2 H); mass spectrum, m/z (relative intensity) 169 (2) and 86 (100). Anal. Calcd for $C_{11}H_{23}N$: C, 78.03; H, 13.69; N, 8.27. Found: C, 77.87; H, 13.97; N, 8.18.] and 0.04 g (0.24 mmol, 9%) of *N,N*-diethyl-1-cyclopropyl-2-methylethylamine (**8c**) [^1H NMR ($CDCl_3$) δ 0.12–0.62 (m, 4 H), 0.92 (d, 6 H), 0.96 (t, 6 H), 1.2–1.9 (m, 2 H), 2.21–3.04 (m, 5 H); mass spectrum, m/z (relative intensity) 169 (1), 128 (3), and 126 (100). Anal. Calcd for $C_{11}H_{23}N$: C, 78.03; H, 13.69; N, 8.27. Found: C, 77.91; H, 13.98; N, 7.87.].

Reaction of 1-Bromo-1-cyclopropyl-2,2-dimethylpropane (1f). (a) With Piperidine (Reflux). Reaction of 0.50 g (2.62 mmol) of **1f** for 14 h at reflux gave 0.49 g of a colorless oil which contained 0.45 g (2.30 mmol, 88%) of 1-(5,5-dimethyl-3-hexenyl)piperidine (**2f**) [^1H NMR ($CDCl_3$) δ 1.0 (s, 9 H), 1.28–1.73 (m, 8 H), 2.14–2.55 (m, 6 H), and 5.21–5.48 (m, 2 H); mass spectrum, m/z (relative intensity) 195 (1) and 98 (100). Anal. Calcd for $C_{13}H_{25}N$: C, 79.93; H, 12.90; N, 7.17. Found: C, 79.81; H, 13.18; N, 7.08.] and 0.04 g (0.20 mmol, 8%) of 1-(1-cyclopropyl-2,2-dimethylpropyl)piperidine (**3f**) [^1H NMR ($CDCl_3$) δ 0.30–0.70 (m, 4 H), 0.99 (s, 9 H), 1.15–1.8 (br d m, 7H), and 2.3–2.8 (m, 5 H); mass spectrum, m/z (relative intensity) 195 (1), 154 (1), and 138 (100).].

All attempts to isolate a pure sample of **3f** resulted in mixtures of **2f** and **3f** and identification of the latter is based on ^1H NMR and mass spectral analysis.

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(15) Houser, R. W.; Witzel, B. E.; Shen, T-Y Ger. Patent 2 363 608; *Chem. Abstr.* **1974**, *81*, *105269v*.
(16) Tiollais, R.; Bouget, H.; Huet, J.; Odeye, M., *C. R. Acad. Sci., Ser. C* **1967**, *264*, 1662.

(b) With Piperidine (Ambient Temperatures). Reaction of 0.5 g (2.62 mmol) of **1f** for 102 h at ambient temperatures gave 0.40 g of a colorless oil which contained 0.36 g (1.84 mmol, 70%) of **2f** and 0.04 g (0.20 mmol, 8%) of **3f**.

(c) With *N,N*-Diethylamine. Reaction of 0.5 g (2.62 mmol) of **1f** for 70 h at reflux gave 0.38 g of a colorless oil, bp 56–58 °C (3 mmHg) which contained 0.36 g (1.96 mmol, 75%) of *N,N*-diethyl-5,5-dimethyl-3-hexenylamine (**7d**) [^{1}H NMR ($CDCl_3$): δ 0.92 (s, 9 H), 0.88–1.07 (t, 6 H), 2.18–2.72 (m, 8 H), and 4.93–5.17 (m, 2H); mass spectrum, *m/z*, (relative intensity) 183 (1) and 86 (100). Anal. Calcd for $C_{12}H_{25}N$: C, 78.62; H, 13.74; N, 7.64. Found: C, 78.55; H, 14.13; N, 7.69.] and 0.02 g (0.11 mmol, 4%) of *N,N*-diethyl-1-cyclopropyl-2,2-dimethylpropylamine (**8d**) [^{1}H NMR ($CDCl_3$) δ 0.2–0.65 (m, 4 H), 0.92 (t, 6 H), 0.98 (s, 9 H), and 2.15–2.7 (m, 5H); mass spectrum, *m/z*, (relative intensity) 192 (2) and 126 (100).].

All attempts to isolate a pure sample of **8d** resulted in mixtures of **7d** and **8d**, and the identification of the latter is based on ^{1}H NMR and mass spectral analysis.

5-Bromo-2-pentene (6). (a) From 1a in Neat Dioxane. When 0.005 g (0.034 mmol) of **1a** was refluxed in 0.5 mL of dioxane-d_8 for 12 h, analysis of the signals at 5.3–5.4 ppm by ^{1}H NMR revealed **1a** with less than 2% rearrangement to 5-bromo-2-pentene, **6**.

(b) From 1a in Neat THF. When 0.14 g (0.94 mmol) of **1a** was refluxed in 2.5 mL of dry THF for 60 h, analysis of the oil remaining after removal of solvents showed **1a** with less than 1% of rearrangement to **6**, had occurred.

(c) From 1a and Piperidine Hydrobromide in Dioxane. When 0.0332 g (0.222 mmol) of **1a** was refluxed in 0.8 mL of dioxane-d_8 with 0.0369 g (0.222 mmol) of piperidine hydrobromide[17a], 3.4 % of **6** was observed by ^{1}H NMR analysis, the remainder being **1a**.

(d) From 1a and Diethylamine Hydrobromide in THF. When 0.3700 g (2.30 mmol) of **1a** was refluxed in 3.0 mL of dry THF with 0.3538 g (2.30 mmol) of diethylamine hydrobromide[17b] for 60 h, removal of solvents and analysis by ^{1}H NMR showed 31.8% of **6** had been formed, with the remainder being **1a**.

6-Bromo-2-methyl-3-hexene (5). (a) From 1e in Neat Dioxane. When 0.007 g (0.04 mmol) of **1e** was refluxed in 0.5 mL of dioxane-d_8 for 12 h, analysis of the signals at 5.3–5.4 ppm by ^{1}H NMR showed 23.8% of 6-bromo-2-methyl-3-hexene (**5**) had been formed, the remainder being **1e**.

(b) From 1e in Neat THF. When 0.12 g (0.68 mmol) of **1e** was refluxed in 2.5 mL of dry THF for 60 h, analysis of the oil remaining after removal of the solvents showed **1e** and less than 1% of rearrangement had occurred.

(c) From 1e and Piperidine Hydrobromide in Dioxane. When 0.0215 g (0.121 mmol) of **1e** was refluxed for 12 h in 0.8 mL of dioxane-d_8 with 0.0202 g (0.122 mmol) of piperidine hydrobromide,[17a] 26.8% of **5** was found, the remainder being **1e**.

Similarly, when 0.0508 g (0.287 mmol) of **1e** was stirred in dioxane-d_8 with 0.0476 g (0.287 mmol) of piperidine–hydrobromide for 12 h, **1e** was observed with less than 1% of **5**.

(d) From 1e and Diethylamine Hydrobromide in THF. When 0.6373 g (3.60 mmol) of **1e** was refluxed in 3.0 mL of dry THF with 0.5440 g (3.60 mmol) of diethylamine hydrobromide[17b] for 60 h, removal of solvents and analysis by ^{1}H NMR showed 31.8% of **5** had been formed, the remainder being **1e**.

General Procedure for Reaction of 1-Bromo-1-cyclopropylalkanes with Sodium Alkoxides. Sodium metal was added to the appropriate alcohol. On dissolution, the 1-bromo-1-cyclopropylalkane (**1**) was added and the mixture heated to reflux. The reaction was cooled, diluted with 10 mL of ether, and filtered, and the solvents were removed under reduced pressure. The resultant oil was analyzed by analytical VPC and VPC/MS, and the samples for NMR and elemental analyses were obtained via preparative VPC.

Reaction of 1-Bromo-1-cyclopropylethane (1a). (a) With Sodium Methoxide. Reaction of 0.25 g (1.68 mmol) of **1a** with 0.09 g (1.67 mmol) of sodium methoxide in 4.2 mL of dry methanol for 6 h gave 0.25 g of a colorless oil which contained 0.03 g (0.30 mmol, 18%) of 1-methoxy-3-pentene, **10a**[18] [^{1}H NMR ($CDCl_3$) δ 2.86 (d, 3 H), 3.38–3.56 (t, 3 H), 3.86 (s, 3 H), and 5.24–5.30 (m, 2 H); mass spectrum, *m/z* (relative intensity) 85 (100), 72 (36), and 59 (2)] and, 0.07 g (0.70 mmol, 42%) of 1-cyclopropyl-1-methoxyethane (**9a**) [^{1}H NMR ($CDCl_3$) δ 0.14–0.60 (m, 4 H), 1.28 (d, 3 H), 3.4–3.51 (m, 1 H), and 3.86 (s, 3 H). Anal. Calcd for $C_6H_{12}O$: C, 71.95; H, 12.08. Found: C, 69.56; H, 11.79.].

(b) With Sodium *n*-Propoxide. Reaction of 0.25 g (1.68 mmol) of **1a** with 0.09 g (1.10 mmol) of sodium *n*-propoxide in 4.0 mL of dry *n*-propyl alcohol for 2 h gave 0.84 g of a colorless oil which contained 0.06 g (0.47 mmol, 43%) of 1-*n*-propoxy-3-pentene (**12a**) [^{1}H NMR ($CDCl_3$) δ 0.91 (t, 3 H, J = 7.4 Hz), 1.2–1.7 (m, 4 H), 1.64 (d, 3 H, J = 4.9 Hz), 3.3–3.7 (m, 4 H), and 5.3–5.6 (m, 2 H); mass spectrum, *m/z* (relative intensity) 99 (84), 73 (30), 69 (15), 55 (20), 43 (100), 41 (23)] and 0.07 g (0.52 mmol, 47%) of 1-(*n*-propoxy)-1-cyclopropylethane (**11a**) [^{1}H NMR ($CDCl_3$) δ 0.3–0.68 (m, 4 H), 0.91 (m, 3 H, J = 7.3 Hz), 1.20 (d, 3 H, J = 6.2 Hz), 1.2–1.5 (m, 3 H), and 3.2–3.7 (m, 3 H); mass spectrum, *m/z* (relative intensity) 113 (100), 71 (63), 69 (78), 58 (25), 43 (37), and 41 (37). Anal. Calcd for $C_8H_{16}O$: C, 74.94; H, 12.58. Found: C, 75.04; H, 12.78.].

Reaction of 1-Bromo-1-cyclopropylpentane (1d). (a) With Sodium Methoxide. Reaction of 0.25 g (1.31 mmol) of **1d** with 0.07 g (1.30 mmol) of sodium methoxide in 4.2 mL of dry methanol for 6.5 h gave 0.16 g of a colorless oil which contained 0.14 g (0.98 mmol, 76%) of 1-methoxy-1-cyclopropylpentane (**9d**): ^{1}H NMR ($CDCl_3$) δ 0.2–0.65 (m, 4 H), 0.91 (distinct t, 3 H), 1.15–2.00 (m, 7 H), 3.6–3.85 (m, 1 H), and 3.78 (s, 3 H); mass spectrum, *m/z*, (relative intensity) 85 (100) and 45 (12). Anal. Calcd for $C_9H_{18}O$: C, 76.00; H, 12.76. Found: C, 76.18; H, 13.04.

(b) With Sodium *n*-Propoxide. Reaction of 0.25 g (1.31 mmol) of **1d** with 0.07 g (0.85 mmol) of sodium *n*-propoxide in 3.0 mL of dry *n*-propyl alcohol for 1 h gave 0.34 g of a colorless oil which contained 0.113 g (0.66 mmol, 78%) of 1-*n*-propoxy-1-cyclopropylpentane (**11d**): ^{1}H NMR ($CDCl_3$) δ 0.2–0.7 (m, 4 H), 0.93 (distinct, 6 H), 1.1–1.9 (m, 7 H), and 3.2–3.8 (m, 3 H); mass spectrum, *m/z* (relative intensity): 113 (100), 71 (92), 69 (20), 43 (25), and 41 (12). Anal. Calcd for $C_{11}H_{22}O$: C, 77.58; H, 13.02. Found: C, 77.60; H, 13.16.

Reaction of 1-Bromo-1-cyclopropyl-2,2-dimethylpropane (1f). (a) With Sodium Methoxide. Reaction of 0.25 g (1.31 mmol) of **1f** with 0.071 g (1.31 mmol) of sodium methoxide in 3.0 mL of dry methanol for 6 h gave 0.2 of a colorless oil which contained 0.14 g (0.98 mmol, 75%) of 1-cyclopropyl-1-methoxy-2,2-dimethylpropane (**9f**): ^{1}H NMR ($CDCl_3$) δ 0.07–0.78 (m, 4 H), 0.97 (s, 9 H), 1.13–1.5 (m, 1 H), 3.3 (d, 1 H), and 3.35 (s, 3 H); mass spectrum, *m/z* (relative intensity) 85 (100), 55 (15), and 41 (6). Anal. Calcd for $C_9H_{18}O$: C, 76.00; H, 12.76. Found: C, 75.87; H, 13.04.

(b) With Sodium *n*-Propoxide. Reaction of 0.25 g (1.31 mmol) of **1f** with 0.07 g (0.85 mmol) of sodium *n*-propoxide in 3.0 mL of dry *n*-propyl alcohol for 4 h gave 0.03 g (0.18 mmol, 21%) of 2,2-dimethyl-6-*n*-propoxy-3-hexene (**12f**) [^{1}H NMR ($CDCl_3$) δ 0.91 (t, 3 H), 0.96 (s, 9 H), 1.35–1.73 (m, 6 H), 3.1–3.6 (m, 4 H), 5.3–5.46 (m, 2 H); mass spectrum, *m/z* (relative intensity) 141 (25), 97 (15), 95 (20), 73 (47), 69 (32), 55 (9), 43 (100), and 41 (25)] and 0.103 g (0.60 mmol, 71%) of 2,2-dimethyl-1-*n*-propoxy-1-cyclopropylpropane (**11f**) [^{1}H NMR ($CDCl_3$) δ 0.09–0.83 (m, 4 H), 0.92 (t, 3 H), 0.96 (s, 9 H), 1.38–1.70 (m, 3 H), 3.1–3.5 (t, 2 H), and 3.34 (d, 1 H); mass spectrum, *m/z* (relative intensity) 114 (7), 113 (100), 71 (92), 69 (18), 55 (8), 43 (23), and 41 (13). Anal. Calcd for $C_{11}H_{22}O$: C, 77.58; H, 13.02. Found: C, 77.70; H, 13.22.].

1-Cyclopropyl-1-ethanol 2,6-Dichlorobenzoate (4b). A solution of 11.8 g (56.3 mmol) of 2,6-dichlorobenzoyl chloride in 20 mL of ethanol-free $CHCl_3$ was added, at 0 °C, to a solution of 4.3 g (53.0 mmol) of 1-cyclopropyl-1-ethanol (**4a**) in 5 mL of pyridine and 10 mL of ethanol-free $CHCl_3$, over a period of 1 h. The solution was stirred for 11.5 h and quenched with 20 mL of water. The organic phase was washed with 2 × 50 mL of water, 50 mL of 10% HCl, and 50 mL of 5% aq. $NaHCO_3$, and dried ($MgSO_4$), and the solvents were removed under reduced pressure. Distillation gave a colorless oil [bp, 160–180 °C (20 mmHg)] which

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was dissolved in 50 mL of ether and cooled to 0 °C. A stream of ammonia gas was passed through the solution for 10 min, the solids were filtered, and the filtrate was washed with 50 mL of 10% aqueous HCl, 80 mL of saturated ammonium chloride, and 2 × 50 mL of water. The solution was dried ($MgSO_4$) and the solvents were removed under reduced pressure. Distillation of the oily residue gave 7.8 g (30.1 mmol, 57%) of **4b**: bp 178–180 °C (20 mm/Hg) [lit.[19] bp 130–133 °C (1 mmHg)]; ^1H NMR ($CDCl_3$) δ 0.20–0.80 (m, 4 H), 0.80–1.45 (m, 1 H), 1.50 (d, 3 H, J = 6.0 Hz), 4.15–4.80 (m, 1 H), and 7.15 (s, 3 H); IR (neat, film) 3085, 3020, 3000–2880, 1735, 1580, 1565, 1435, 1280, 1150, 1050, 930, 850, 800, and 780 cm^{-1}.

A total of 2.60 g (10.0 mmol) of **4b** in 10 mL of piperidine was heated for 25 h in a sealed tube at 130 °C. On cooling, some piperidine hydrobromide was filtered, and the filtrate was dissolved in 30 mL of 10% HCl solution and washed with ether. The aqueous phase was basified with NaOH and extracted with 3 × 100 mL of ether. The ether extracts were dried (Na_2SO_4) and filtered, and the solvents were removed under reduced pressure. The resulting oil contained piperidine but no trace of substitution products.

1-Cyclopropyl-1-ethanol 2,4,6-Trimethylbenzoate (4c). A solution of 6.3 g (77.6 mmol) of **4a** in 5 mL of pyridine and 15 mL of ethanol-free $CHCl_3$ was added to 20 mL of a solution of 14.3 g (78.3 mmol) of mesitoyl chloride[20] in ethanol-free chloroform, at 0 °C. The solution was stirred at ambient temperature for 13 h and quenched with 20 mL of water. The organic phase was washed with 2 × 50 mL of water, 50 mL of 10% aqueous HCl, and 50 mL of 5% aqueous $NaHCO_3$. The solution was dried ($MgSO_4$), and the solvents were removed under reduced pressure. Distillation of the resultant oil through a 15-cm Vigreux column gave 14.4 g (62.0 mmol, 80%) of **4c**: bp, 160–162 °C (7 mmHg) [lit.[19] bp 145–147 °C (2 mmHg)]; ^1H NMR ($CDCl_3$) δ 0.20–0.75 (m, 4 H), 0.75–1.30 (m, 1 H), 1.37 (d, 3 H, J = 6.0 Hz), 2.23 (s, 9 H), 4.10–4.73 (m, 1 H), and 6.65 (s, 2 H); IR (neat, film): 3080, 3020, 3000–2865, 1725, 1615, 1450, 1270, 1170, 1085, 1050, 930, and 850 cm^{-1}.

Subsequent reaction of 2.30 g (9.90 mmol) of **4c** with 10 mL of piperidine at 130 °C for 25 h gave, after the workup described for **4b**, an oil containing piperidine but no trace of substitution products.

Kinetic Studies of 1 with Amines. A total of 14.903 g (0.1 mol) of **1a** and 8.515 g (0.1 mol) of piperidine; or 17.709 g (0.1 mol) of **1e** and 8.515 g (0.1 mol) of piperidine; or 17.709 g (0.1 mol) of **1e** and 7.314 g (0.1 mol) of diethylamine was dissolved in 100 mL of dry benzene and heated at 55 °C in an oil bath. At intervals 2.0 mL of each solution was removed via syringe and titrated with 0.1 N HCl solution with a methyl orange indicator, following the method of Young.[10] Each reaction was allowed to proceed through three half-lives and the data is presented in Figure 1. A similar experiment with **1a** and diethylamine failed to give data from which a straight-line plot could be made.

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Leaving Group and Solvent Effects on S_N1 Reactions of Adamantyl Substrates. Contributions from Electrostatic, Electrophilic, and Lipophilic Effects

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Solvolytic rate constants are reported for reactions of 1-adamantyl picrate, 2-adamantyl trifluoromethanesulfonate (triflate), and 2-adamantyl perchlorate in binary aqueous mixtures of ethanol, methanol, acetone, trifluoroethanol, and hexafluoroisopropyl alcohol. Logarithms of solvolysis rates for various compositions of a binary mixture (aqueous ethanol, methanol, or acetone) are correlated with the solvent ionizing power (e.g., logarithms of solvolysis rates for 2-adamantyl tosylate). Variations in slopes of the correlations for picrates are attributed primarily to electrostatic effects—more extensive delocalization of negative charge in the anionic leaving group reduces the sensitivities of the solvolyses to changes in solvent ionizing power. The discussion includes previous work on chlorides, bromides, and iodides. Deviations from the correlation lines for aqueous alcohol mixtures provide a measure of electrophilic assistance in acidic and fluorinated solvents. Triflates may be the only exceptions to the general pattern that electrophilic assistance by carboxylic acid solvents depends on the electronegativity of the atom(s) of the leaving group on which charge develops. Only triflates show similar deviations for fluorinated alcohol solvents. Perchlorates and picrates show enhanced reactivities in high percentage acetone/water mixtures, but it is suggested from a plot of Y_I vs. Y_{Pic} that lipophilic effects may not cause these deviations.

Both 1-adamantyl (**1**) and 2-adamantyl (**2**) substrates react by S_N1 reactions,[1] and the rates of solvolysis of sulfonates show almost identical responses to changes in solvent ionizing power.[2] The tertiary adamantyl tosylate (**1**, X = OTs) reacts about 10^5 times faster than the secondary tosylate (**2**, X = OTs).[2-4] Consequently it is possible to examine systematically leaving group and solvent effects over a wide range of solvolytic reactivity, using the adamantyl framework as a relatively constant alkyl group. To aid such studies, the experimentally accessible range of reactivity has been extended to conductimetric studies of relatively rapid reactions (t < 1 s) of sparingly soluble substrates,[2,5] which can be studied con-

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