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Evidence for a Carbene–Anion Pair. 1,4-Disubstituted Adamantanes as a Stereochemical Probe[1]

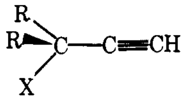
W. J. le Noble,* Der-Ming Chiou, and Y. Okaya

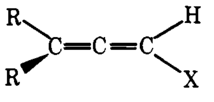
Contribution from the Department of Chemistry, State University of New York, Stony Brook, New York 11794. *Received November 16, 1978*

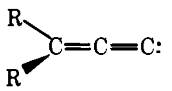
Abstract: A mechanistic investigation is reported of the base-promoted conversion of tertiary propargylic halides into the corresponding solvolysis products and into the isomeric haloallenes. The experiment is basically a stereochemical one. Use is made of the *E* and *Z* isomers of 4-chloro-4-ethynyl-1-phenyladamantane ((*E*)- and (*Z*)-**12**-Cl) and of the corresponding geometric isomers of 5-phenyl-2-chlorovinylideneadamantane ((*E*)- and (*Z*)-**13**-Cl). The proof of configuration in both series **12** and **13** is based on X-ray diffraction; for the **12** series, it is consistent with a study of the NMR spectra measured in the presence of shift reagents, and for the **13** series, with the known stereochemistry of the formation of these compounds. Neutral methanolysis of the **12**-Cl compounds gives completely stereorandom mixtures of methyl ethers; internal return simultaneously gives the isomeric chloroallenes with complete retention in accord with the behavior expected from free carbonium ions and from tight ion pairs, respectively. Base-induced solvolysis of **12**-Cl again gives solvolysis products that are stereochemically random. In *tert*-butyl alcohol containing potassium *tert*-butoxide, the fair yield of isomeric chloroallenes which is produced under these conditions cannot be attributed to neutral heterolysis, yet the formation of these allenes shows a clear bias of at least 30% toward retention. This proves that the intermediate carbenes are paired with the leaving group in such a way as to maintain configuration. Since the fraction of the allenes that obtains via external return of the chloride ion to the free carbene is known approximately, it proved possible to provide a detailed account of the behavior of the pair. The usefulness of the 1,4- (or 2,5-) disubstituted adamantane skeleton in stereochemical investigations is emphasized. It is pointed out that the product distribution at C_2 in the adamantane skeleton is unexpectedly sensitive to phenyl substitution at C_5.

Introduction

Much attention has been lavished by mechanistically oriented chemists on the solvolysis of tertiary propargyl halides **1**-X that simply give the substituted products **1**-OS, as well as minor amounts of the rearrangement products **2**-X. The initial reasons for this interest were, first, that the reaction is promoted by strong base, and second, that this catalysis does not produce much elimination, even with amide anion;[2] both of these observations are rare indeed for tertiary halides.[3] Initial investigations, primarily by Hennion, Shiner, and Hartzler, proved beyond any doubt that the neutral solvolysis is a relatively uneventful carbonium ion reaction, and that the base catalysis involves the acetylide anion that undergoes C–X heterolysis to generate carbene **3**; this intermediate then partitions into the various products including the allenes **2**-X. The latter compounds are subject to the same reaction in reverse to give **1**-OS under more vigorous conditions. The principal evidence that can now be quoted in support of this mechanism includes the following. (a) **4**-Cl (**1**-Cl, R = Me) is subject to base-catalyzed H–D exchange[4] much faster than solvolysis[5] in deuterated media; the same is true of **5**-Cl (**2**-Cl, R = Me), although the exchange to solvolysis ratio is more modest in that case.[6] (b) **4**-Cl and **5**-Cl produce identical mixtures of products if they are solvolyzed under the same basic conditions (e.g., alcohols and ethers in aqueous ethanol).[6,7] (c) If olefinic materials are present, the carbenes can be captured to give cyclopropane adducts.[8]


1-X


2-X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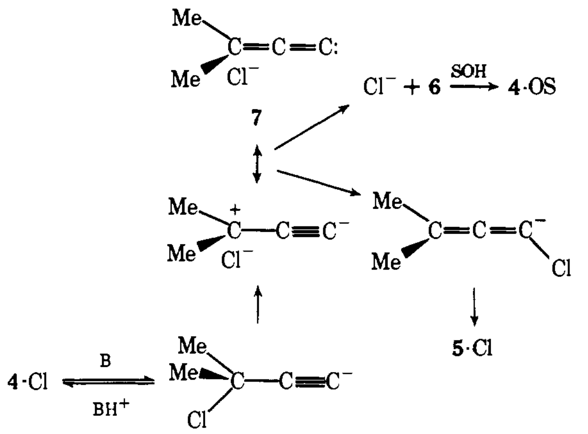
Comparison of the activation volumes of the base-promoted generation of a number of carbenes, however, revealed that the formation of **6** (**3**, R = Me) from either **4**- or **5**-Cl is virtually independent of hydrostatic pressure;[9,10] this type of reaction is normally strongly inhibited by the application of pressure.[11] This observation hinted at a previously unsuspected feature in the reaction; it was proposed[8] that the polarization of the incipient carbene by the leaving group (and hence electrostriction[11]) was the cause of the absence of the volume expansion normally expected. This proposal was subsequently expanded[10] to include a carbene-anion pair **7** as another intermediate, and this pair was held at least partly responsible for the isomerization of **4**-Cl to **5**-Cl that is always observed in these reactions. In other words, the return which produces **2**[6] was suggested to be at least in part internal (Scheme I). The support for this suggestion was that the yield of **5**-Cl increases much less rapidly if the reaction of **4**-Cl is carried out in the presence of added chloride ion than the yield expected on the basis of purely external return; detailed kinetic analysis[10] revealed that the fraction of return that is internal varies from 30 to 85%, depending on the medium.

Scheme I



The phenomena of pairing and of internal return are well known and have produced many dividends in carbonium ion, carbanion, and free-radical chemistry; they are almost unknown in the areas of the other common intermediates of organic chemistry, carbenes among them. A probable reason for this is that stereochemistry has been instrumental in the study of pairing and return with each of the three intermediates mentioned;[12-14] with carbenes this approach is obviously not generally feasible. Happily, carbenes **3** are an exception to this: if a chiral compound **1**-X is used, the leaving group should be able to serve as a configurational anchor as the acetylenic anion

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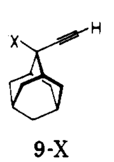
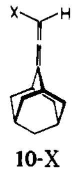
rearranges to the allenic one, while stereorandomization must necessarily result if the planar free carbene is formed.

Optically active tertiary propargyl alcohols **1**-OH and allenic halides **2**-X have been reported,[15] but no resolved halides **1**-X are known. Optically active propargyl benzoates have been prepared,[15a,c] but these undergo acyl rather than alkyl cleavage upon exposure to base.[16] As an alternative, geometric isomers (i.e., cyclic structures) may be used to approach the problem. This avoids resolution, and it has the advantages of a separation by means of standard operations such as crystallization or chromatography, and of analysis by means of a wider range of techniques than just polarimetry. It has the disadvantage that since an equilibrium mixture of the epimers does not necessarily have a 50:50 composition as racemic mixtures do, it is necessary to carry out the reaction with both epimers if one wishes to determine stereoselectivity. As an example, ethynylation of 4-*tert*-butylcyclohexanone followed by reaction with hydrochloric acid should produce a separable pair of epimeric chlorides. The parent cyclohexanone derivative **8**-Cl (**1**-Cl, R,R = $-(CH_2)_5-$) is known, but it and its allenic isomer have a disturbing tendency to form cyclohexene derivatives.[17] In order to escape this problem, the 2,2,6,6-tetramethyl derivative may be considered, but with such highly branched tertiary ethynyl alcohols, all attempts to produce halides **1** to date have yielded only the allenes **2** instead.[18] Alternatively, Bredt's rule may be used to prevent isomerizations to cyclic olefins: this requires the use of derivatives **1** in which both carbons flanking the carbinyl carbon are bridgehead atoms in a polycyclic skeleton. Of the various possibilities[19] that suggest themselves, the 2-adamantyl system seemed particularly attractive: its symmetry suggests that its derivatives will be solids, facilitating purification and enabling one to use X-ray diffraction in the assignment of configuration if need be. Scouting experiments with 2-chloro-2-ethynyladamantane (**9**-Cl) and its allenic isomer **10**-Cl revealed that its behavior with base was normal; i.e., in aqueous methanol containing methoxide ion, **9**-Cl gives **9**-OH and **9**-OMe as well as small amounts of **10**-Cl. In order to produce a suitable pair of stereoisomers, a substituent must be introduced at the 5 position. The substituent chosen was phenyl; the hope was that this choice would optimize melting points, provide ring current effects to help assign configurations, and serve as the UV absorbing group in high-pressure liquid chromatography (LC) separations that might be necessary. It was further anticipated that this system of geometric isomers might equally well serve in other stereochemical problems in which enantiomers are either unavailable or have only small specific rotations.



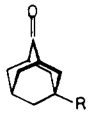
9-X



10-X

Results and Discussion

Configurational Studies. The basic building blocks **11** (R = OH,[20] Cl,[21] Ph[22]) had already been reported; hence reference is made to the Experimental Section for the details of the synthesis, separation, and purification of (*E*)- and (*Z*)-**12**-Cl, -OH, and -OMe, and (*E*)- and (*Z*)-**13**-Cl. All these adamantane derivatives turned out to be solids, as hoped. The X-ray data[1b] provided us with unambiguous proofs of configuration of (*Z*)-**12**-OH, (*E*)-**12**-OMe,[23] both (*E*)- and (*Z*)-**12**-Cl, and (*E*)-**13**-Cl, and showed that the conversions of **12**-OH to **13**-Cl by means of thionyl chloride[24] and to **12**-OMe via base-catalyzed methylation take place with retention of configuration as expected.



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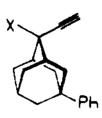
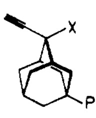
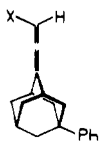


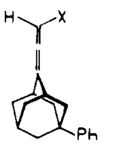
(*E*)-**12**-X



(*Z*)-**12**-X

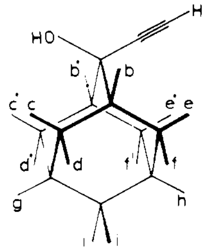


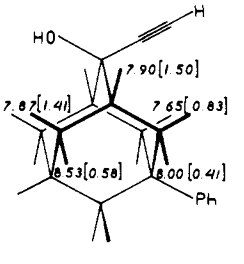
(*E*)-**13**-X

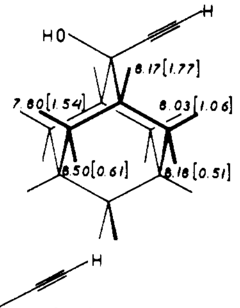


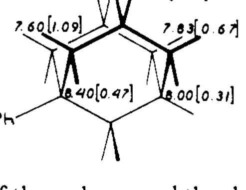
(*Z*)-**13**-X

The X-ray work confirmed our assignments of configuration by means of NMR. Since 1,4-disubstituted adamantanes may become useful in the solution of stereochemical problems and since X-ray diffraction may not always be available or applicable in making such assignments, we record our most salient NMR observations here. The model compound is **9**-OH. Its complex NMR spectrum can be analyzed by means of an application of lanthanide shift reagents,[25] as has been done with adamantan-2-ol,[26] 2-alkyladamantan-2-ols,[27] and some 2,5-dialkyladamantan-2-ols.[22] Our assignments are based on: (a) the known[26-28] increase in chemical shift among the series of doublets corresponding to cc′, ee′, dd′, and ff′, respectively; (b) the geminal pairs, which have J_{gem} = 12-13 Hz, distinguishing them from protons bb′, gg′, and ii′; (c) the fact that protons in 1,3-diaxial positions with respect to the hydroxy group are more deshielded than those in the 1,3-diequatorial locations;[27,28] (d) the experience[29] that a bridgehead phenyl group will deshield β protons by ca. 0.12 ppm, and shield γ hydrogens by 0.03 ppm. The assignments made on this basis are completely consistent with the chemical-shift changes induced by the addition of Eu(fod)$_3$; the spectra with the shift reagent were measured in carbon tetrachloride with 0.33 M substrate, and shift reagent concentrations were varied from 0 to 0.10. The "initial" slopes of the plots were determined as exemplified in Figure 1 (note that $\Delta\tau/\tau \simeq (3\cos^2\theta - 1)K/r^3$, where $K = [LS_n]/[L][S]^n$; L is the lanthanide and S the substrate). The shifts $\Delta\tau/\tau$ decrease in nearly linear fashion at low ρ as expected on this basis. Protons g and h were difficult to locate in all our spectra; the other protons are not especially relevant. The numbers in the structures below summarize all the data; they represent the chemical shifts in τ units and the slopes in the $\Delta\tau/\tau$ plots aré given in parentheses. The assignments on the basis of these slopes and the shifts caused by the phenyl groups are clear and straightforward. It is perhaps









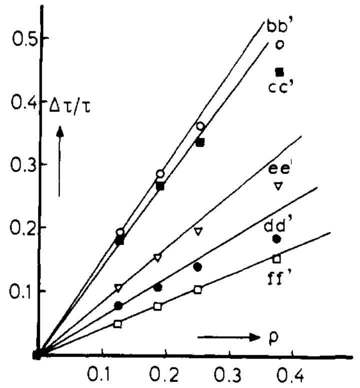


Figure 1. The effect of adding Eu(fod)$_3$ on the various protons in (E)-**12**-OH.

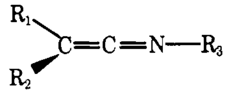
worth pointing out that the decreases in the slopes $\Delta\tau/\tau$ occasioned by the phenyl group are greatest in the Z isomers, which can reasonably be attributed to the greater difficulty of fitting the shift reagent molecule between the hydroxy and phenyl groups.

The assignments of (E)- and (Z)-**12**-Cl are based on the extrapolation that the dd′ protons correspond to the highest field doublet as they do in each of the alcohols: those in the chlorides are at τ 8.32 and 8.20, respectively. The phenyl group again depresses the value more in the Z than in the E compound. Finally, the assignments of the ethers **12**-OMe and the allenic chlorides **13**-Cl can be based on those of their precursors and the known stereochemistry of the reactions of their formation.

Return during Neutral Solvolysis. As noted above, neutral solvolysis competes with the base-promoted reactions of tertiary propargyl halides, giving the same products. Thus, in any appraisal of the stereochemistry of the base-catalyzed reaction it is necessary to evaluate to what extent the neutral reaction is contributing; this is especially pertinent in this case since tertiary 2-adamantyl esters solvolyze more rapidly than open chain analogues.[30]

(E)- and (Z)-**12**-Cl solvolyze in initially neutral 80% methanol solution at 50 °C at comparable rates (1.2 and 1.7 × 10^{-6} s^{-1}, respectively). In both cases there is almost 60% solvolysis and 40% return to **13**-Cl. The solvolyzed part in both reactions consists of an identical mixture of (E)- and (Z)-**12**-OMe in the ratio of 1:3; the return product is in both instances formed with complete retention. These results are easily accounted for in terms of ion pairs that undergo stereospecific return or dissociate to free carbonium ions; the ions in turn are the source of the methyl ethers. Scouting experiments with the same medium, but now containing significant concentrations of lyate ions, then revealed that neutral *solvolysis* does not offer its base-catalyzed cousin sufficient competition to obscure the stereochemistry of the latter; however, while *return* to form the allenic isomer accounts for 40% of the substrate in the neutral reaction, the same reaction with methoxide ion produces only 3% of this material. For the return reaction, therefore, we had to search for another medium in which this problem does not arise. This medium turned out to be *tert*-butyl alcohol: under conditions in which the base-catalyzed reaction readily occurs, neutral solvolysis and return are completely absent.

Exchange and Epimerization Studies. It will be realized that the successful execution of the entire project rested on one risky assumption: that the allenic anion corresponding to **13**-Cl is neither linear nor capable of rapid isomerization. Cyano-substituted vinyl carbanions are bent;[31] among the ketenimines **14**, rapid epimerization occurs in solution when R$_1$ = Me, R$_2$ = i-Pr, and R$_3$ = Ph ($\Delta G^{\ddagger}$ = 12.2 kcal/mol) and when R$_1$ = R$_3$ = Ph and R$_2$ = i-Pr ($\Delta G^{\ddagger}$ = 9.1 kcal/mol).[32] In the solid phase, **14** is linear when R$_1$ = R$_2$ = PhSO and R$_3$ = Me,[33] but a wide C=N—C angle (150°) occurs when R$_1$ = R$_2$ = PhSO and R$_3$ = Et.[34] Diisopropylcarbodiimide **15** is nonlinear, but inverts rapidly in solution with $\Delta G^{\ddagger}$ = 7 kcal/mol.[35] On the basis of the evidence then available, Shiner and Humphrey[6] expressed the opinion that haloallenic anions would be linear, but we were subsequently encouraged by the fact that N-chloro substitution in amines raises their barrier to inversion.[36]



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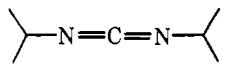

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Our experimental approach was to compare the rates of base-catalyzed H-D exchange and epimerization in (E)-**13**-Cl; the former was followed by means of NMR and the latter by means of LC. At 30 °C in t-BuOD, the rate constant for H-D exchange was found to be about 0.3 M^{-1} s^{-1}, and that of epimerization 4 × 10^{-4} M^{-1} s^{-1}; thus, the latter reaction is some 700 times slower than the former. Clearly, the anions are able to preserve their configurations after the act of proton abstraction.

The rate constant of epimerization corresponds to a free-energy barrier of 22.5 kcal/mol, starting with the parent allenes. In order to evaluate the barrier starting with the allenic anions, we need to know the equilibrium constant for the process:

$$t\text{-BuO}^- + \text{HA} \rightleftharpoons t\text{-BuOH} + \text{A}^-$$

A crude estimate of this number can be made by means of pK_a data in Cram's summary.[37] If we begin with ethylene (pK_a = 36.5) and correct for α-chloro substitution (compare water, pK_a = 16, and hypochlorous acid, 7.5) and for the cumulative double bond (compare ethane, pK_a = 42, and propene, 36 (allylic H)), we have a result of 22 for chloroallene compared to 19 for *tert*-butyl alcohol. This means that the barrier to configuration loss for the anion at 30 °C is 22.5 − 2.3RT(22 − 19) = 18 kcal/mol. The precision of this estimate is, of course, not very great, nor can a mechanism be assigned to the epimerization. Thus, it may be that the anions isomerize via rotation rather than inversion, or via carbene formation and return of the chloride; in fact, it cannot be considered proved that the anions are bent, since exchange *can* take place by a route analogous to the conducted tour mechanism.[38] Our present purpose, however, is not seriously undermined by these possibilities. The exchange rate of **10**-Cl was similar to that of (E)-**13**-Cl; (**9**)-Cl underwent complete exchange upon mixing, as did (Z)-**12**-Cl, the latter without detectible epimerization.

Results in Basic Medium. The results are as follows. As Hennion had found with **4**-Cl,[4] powerful base catalysis occurs (>10^3 by 1 M base). In all of our experiments in methanol, starting with either (E)- or (Z)-**12**-Cl and with or without base, the resulting methyl ethers **12**-OMe always were produced in the same E/Z ratio of 1:3, respectively. Clearly, the two neutral solvolysis reactions produce a common intermediate, i.e., the free carbonium ion, as do the two base-catalyzed reactions, namely, the free carbene. It is tempting to further suppose that a carbonium ion is also the last intermediate on the way to ether formation in the base-promoted case; however, it could also be mere coincidence, with methanol having equal preference for the Z side whether it is approaching the carbene or the carbonium ion.

In the base-catalyzed reaction in *tert*-butyl alcohol, the solvolytic part was not analyzed. It seems likely that both **12**- and **13**-O-t-Bu products are formed as apparently happened in other instances;[39] however, in view of the total randomness of the methanolysis, it did not seem worthwhile to find the conditions necessary for analysis by LC. The return part of the reaction, which amounts to about 35%, shows a clear bias toward retention; thus, when **13**-Cl is obtained from (*E*)-**12**-Cl, it consists of an *E*/*Z* mixture in the ratio of 57:43; if it is obtained from (*Z*)-**12**-Cl, the ratio is 28:72. Both of these ratios are reliable to 1-2%, and are independent of how far the reaction is allowed to progress. It was also shown that neither (*E*)- nor (*Z*)-**12**-Cl epimerizes under these conditions. The selectivity is thus found to be about 30%.[40] It should be emphasized that this is a *minimum figure*, since our earlier kinetic analysis[10] with **4**-Cl had shown contributions from external return to be from 30 to 85%, depending on conditions. Thus, it is even possible that the internal return is in fact stereospecific. Unfortunately, the technique we had used to analyze the return reaction in terms of internal and external contributions could not be applied in the present case, the solubility of chloride salts in pure *tert*-butyl alcohol being too low. Attempts to increase the solubility by adding small amounts of water to the solvent produced large decreases in the yield of **13**-Cl instead. If we assume that the fraction of external return in *tert*-butyl alcohol to the adamantanevinylidenes is 15% as it is in **6**, our observations can be most economically accounted for by the statement that about two-thirds of the pair dissociates to give solvolysis products, and of the remainder, 15% dissociates and returns externally (and randomly), 30% returns stereospecifically (with retention), and 55% equilibrates its stereolabel before undergoing internal return.

In any case, with even the minimum stereoselectivity of the return reaction clearly demonstrating that the reaction must traverse a stage in which the carbene is not yet free, we should now examine whether there is any alternative to proposing a simple pair such as **7**. It should be noted that Jones has argued for a free carbene **16** (**3**, R = phenyl) on the basis of identical product distributions independent of the source of the carbene,[41] and Hartzler has drawn the same conclusion after finding that it makes little difference in the competition of olefins for **3** whether R is methyl or *tert*-butyl.[42] These conclusions are undoubtedly correct (the stereorandomness of the solvolysis products of **12**-Cl falls into the same category), but they pertain to the product forming step and do not rule out an earlier complexed stage.

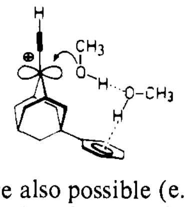
There are two additional suggestions in the literature that carbenes **3** may be complexed. Patrick et al.[43] found changes in olefin selectivity by factors of about two if an equivalent amount of 18-crown-6 was added, and concluded that the carbene must be complexed with the cation. The fact that the reactions were carried out in heterogeneous fashion invalidates any comparison with homogeneous reaction mixtures such as were employed in the present experiments; however, apart from that caveat, it seems possible that the carbene-anion pair is in turn complexed with a cation. The authors also do not seem to have considered the possibility that the crown ether may have complexed with the positive carbon of the carbene itself, with the linear three-carbon chain protruding into the cavity of the crown ether. Such complexation has been postulated and strongly supported for diazonium cations by Izatt.[44] Finally, Craig has studied α-CH insertion reactions of monoalkylvinylidenecarbenes into primary alcohols.[45] He argued that the carbene carbon is complexed with the alcohol by a hydrogen bond, but conceded that a carbene-anion pair could explain his data equally well. It seems that none of these views expressed in the literature adequately explain our present data.

It is, of course, also possible to suppose that the acetylenic anions rearrange to the allenic ones in a concerted and hence stereospecific manner, bypassing the carbene stage altogether. Before the advent of the Woodward-Hoffmann rules, this possibility had to be seriously considered, for example, in the closely related allylic carbonium ion rearrangements; however, even at that stage, this alternative was effectively demolished by Winstein, who showed that the neutral allylic chlorides must first dissociate,[46] and that the characteristics of a concerted reaction were only observable in such 3,3-shifts as occur in allylic azides.[47] To resurrect this possibility here and now is therefore to consider a mechanism for which there is no precedent in spite of a diligent and thorough search.

With the present instance as the only one of a carbene reaction apparently requiring the paired intermediate to interpret available data, we cannot yet really appraise the importance of this observation. With pairs having been detected and then exploited in both ionic and free-radical dissociation, the notion that a carbene should initially be paired with the group whose departure produced it has ample precedent. Pairing of an ion with a neutral molecule has in fact been demonstrated in at least one other case, that of the phenyl cation with nitrogen.[48] There is a possibility, even a likelihood, that such pairs are always the first product of all dissociation reactions in condensed phases; the question that only further work can answer is whether such insights can stimulate chemical manipulation of these reactions, and provide rationales for apparently aberrant behavior in some. It seems possible, for example, that there is a connection between the observations described here and the so-called carbenoids that have been encountered so many times.[49] On the other hand, carbenes **3** may be unique in that they have pronounced zwitterionic character; this is evident, for instance, from the dipole moment, calculated[50] to be 4.0 D, and from its nucleophilic behavior; thus $\rho = +0.52$ in the C-H insertion reaction in benzyl alcohol.[51] Our present position is that the solvolytic carbene reaction studied here, accompanied as it is by a return product providing a handle for a mechanistic study, has been shown to go through a paired stage; the possibility that such a stage is present in other or even all carbene reactions must therefore be considered. It is perhaps of interest to reflect, in retrospect, that the first hint at this phenomenon was an unexpectedly small effect of pressure on a rate constant!

A final comment needs to be made concerning the *E*/*Z* product distributions in the stereorandom reactions. In 1,4-disubstituted cyclohexanes in which one substituent is as bulky as a phenyl group, this moiety is expected to occupy an equatorial position and not to have any direct steric or electronic interaction with the other substituent. Thus, the NMR spectra of 4-*tert*-butyl substituted cyclohexanes are often used to help evaluate the equatorial-axial equilibrium of the rapidly reverting ring system without the *tert*-butyl group. In compounds **12**, the 5-phenyl group is necessarily equatorial to all three six-membered rings represented there and the 2 substituents are necessarily axial to one ring and equatorial to the other. We expected, therefore, that the *E* and *Z* isomers to be encountered in our work should have equal, or very nearly equal, populations in a mixture of stereorandom composition. Surprisingly, however, the mixtures generated in several reactions depart quite far from this equality.

Thus, as noted, when either (*E*)- or (*Z*)-**12**-Cl is treated with methanol, the solvolysis product is a 1:3 mixture (*E* to *Z*) of methyl ethers: the methanol favors, if anything, the more hindered side of the carbonium ion. We propose a hydrogen bonded complex such as **17** to explain this observation, but other combinations are also possible (e.g., a single methanol molecule, edge- rather than face-bonded solvent, and so on). There are a few other instances of such remote effects.[52] We



hope to study a number of 5-substituted 2-adamantane derivatives in order to learn how sound it is to suppose that there are indeed no direct steric or electronic interactions in 1,4-disubstituted cyclohexanes.

Experimental Section

Instrumentation. Use was made of a Perkin-Elmer Model 137 infrared spectrophotometer, a Varian EM-360 60-MHz instrument for ^{1}H NMR (Me_4Si as internal standard; chemical shifts are reported in parts per million (τ)), a Hewlett Packard 5980-A for low-resolution and an AEI MS-30 for high-resolution mass spectra, a Perkin-Elmer 900 gas chromatograph, and a Waters Associates ALC/GPC liquid chromatograph. The melting points are uncorrected.

Syntheses. 5-Hydroxy-, 5-chloro-, and 5-phenyladamantan-2-one were prepared as described in the literature.[53]

2-Ethynyladamantan-2-ol (9-OH). A 1-L, three-necked flask, equipped with a mechanical stirrer and cooled in a dry ice-acetone mixture, is charged with 400 mL of liquid ammonia. A stream of dry acetylene is rapidly passed through the vigorously stirred liquid ammonia; 6.90 g (0.300 mol) of sodium is added in 1 h. The flow of acetylene is then reduced and 30.0 g (0.200 mol) of 2-adamantanone is added gradually over a period of 1 h. The reaction mixture is allowed to stand at dry ice temperature for 7 h. The flow of acetylene is stopped, and the reaction mixture is flushed with nitrogen and allowed to reach room temperature for 8 h to permit the evaporation of the ammonia. The solid residue is treated with 250 g of ice-water, acidified with 50% sulfuric acid, and extracted with three portions of 200 mL of ether. The ethereal solution is washed twice with 200-mL portions of saturated aqueous sodium chloride and dried over magnesium sulfate; after filtration and evaporation of the solvent, 32.4 g of white solid is obtained. After recrystallization from hexane, 24.9 g (70%) of 2-ethynyladamantan-2-ol is obtained as a white solid: mp 102-104 °C. Further recrystallization from hexane give pure **9**-OH: mp 105-106 °C; ^{1}H NMR ($CDCl_3$) τ 7.45 (1 H, C$\equiv$CH), 7.70-8.53 (m, 15 H); IR (KBr) μ 2.81 (s, OH), 2.91 (s, $\equiv$C—H), 3.40 (s, C—H), 4.77 (vw, C$\equiv$C). Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.92; H, 9.05.

2-Chloro-2-ethynyladamantane (9-Cl). A 25-mL flask containing a magnetic stirring bar and 8.50 mL of concentrated hydrochloric acid is maintained at 5 to 10 °C, while a mixture of 2.23 g (0.02 mol) of calcium chloride and 0.021 g (0.21 mmol) of hydroquinone is added. This mixture is warmed to room temperature, and 3.51 g (0.020 mol) of **9**-OH (mp 102-104 °C) is added over a period of 10 min. A condenser is attached and the mixture is heated to 65-70 °C for 40 min with vigorous stirring. It is then allowed to cool and extracted with ether (3 × 20 mL). The ethereal solutions are combined and washed with 5% aqueous sodium bicarbonate (2 × 20 mL). After drying over anhydrous sodium sulfate, filtration, and rotary evaporation of the solvent, 3.85 g of light brown oil is obtained. This oil is applied to a silica gel column (3.5 × 60 cm) and eluted with a 20:80 (v/v) mixture of hexane and benzene. Portions of 25 mL are collected; **9**-Cl is found in fractions 9 through 18 (2.40 g; 62%). Recrystallization from methanol yields white crystals of **9**-Cl: mp 65.0-66.0 °C; ^{1}H NMR ($CDCl_3$) τ 7.22 (s, 1 H, C$\equiv$CH), 7.53-8.43 (m, 14 H); IR (benzene) μ 2.96 (s, $\equiv$C—H), 3.45 (s, C—H), 4.77 (vw, C$\equiv$C), 11.35 (s), 12.23 (vs), 13.45 (s). Anal. Calcd for $C_{12}H_{15}Cl$: C, 74.01; H, 7.77; Cl, 18.21. Found: C, 73.81; H, 7.88; Cl, 18.07.

Fractions 15 to 20 contain an unidentified light brown oil, fractions 24-32 contain a mixture of the unidentified compound and **10**-Cl, fractions 33 to 41 have **10**-Cl, and fractions 51 to 126 contain 0.50 g (10%) of adamantylideneacetaldehyde: ^{1}H NMR ($CDCl_3$) τ 0.0 (d, J = 8 Hz), 4.15 (d, J = 8 Hz).

Chlorovinylideneadamantane (10-Cl). To a 100-mL flask containing a stirring bar and a solution of 5.30 g (0.030 mol) of **9**-OH in 50 mL of freshly distilled anhydrous ether, 3.67 mL (0.045 mol) of freshly distilled anhydrous pyridine is added. A 25-mL addition funnel is attached which contains a solution of 2.17 mL (0.030 mol) of freshly distilled thionyl chloride in 10 mL of anhydrous ether, and the flask is placed into an ice bath. The thionyl chloride solution is added over a period of 2 h with vigorous stirring. The assembly is allowed to stand in the ice bath for another hour. The reaction mixture is filtered, and the white solid is washed with 10 mL of anhydrous ether. The ethereal solution is washed with 3% hydrochloric acid (2 × 50 mL) and with 5% sodium bicarbonate (2 × 50 mL). The resulting clear solution is dried over anhydrous magnesium sulfate. After filtration and rotary evaporation of the solvent, 4.90 g of white solid is obtained. The crude product is crystallized from a mixture of ethanol and water to give 2.67 g (46%) of **10**-Cl (mp 54-57 °C).

The product so obtained is applied to a silica gel (60-200 mesh) column and eluted with dry benzene; 25-mL fractions are collected. After evaporation of the solvent, **10**-Cl is found in fractions five to ten. Recrystallization from methanol yields pure white **10**-Cl: mp 56.0-58.0 °C; ^{1}H NMR ($CDCl_3$) τ 4.12 (s, 1 H, C=C=CHCl), 7.41 (br s, 2 H), 8.00-8.20 (m, 12 H); IR (KBr) μ 5.10 (m, C=C=C), 13.40 (vs, C=C=CHCl), 13.70 (vs, C=C=CHCl). Anal. Calcd for $C_{12}H_{15}Cl$: C, 74.01; H, 7.77; Cl, 18.21. Found: C, 73.81; H, 7.89; Cl, 18.40.

2-Methoxy-2-ethynyladamantane (9-OMe). Sodium hydride dispersed in oil (0.67 g of 58% (w/w), Alfa Products) is placed in a 50-mL, three-necked flask containing a stirring bar. The oil used for dispersion is removed by washing with pentane (3 × 4 mL). Nitrogen is introduced and 15 mL of dry THF is added to the solid. An addition funnel is attached as well as a condenser which leads to a mercury outlet. A solution of 2.62 g (15 mmol) of **9**-OH and 2.10 g (15 mmol) of methyl iodide in 15 mL of dry THF is discharged into the addition funnel. The sodium hydride suspension is heated to 45 °C with an oil bath and the THF solution is added over a period of 40 min. The reaction mixture is kept at 45-50 °C for another 30 min. The solution is allowed to cool; then 10 mL of water is used to destroy the excess sodium hydride. The resulting mixture is poured into a separatory funnel and extracted three times with 20 mL of ether. The ethereal solutions are combined, washed with saturated sodium chloride solution (2 × 15 mL), and dried over anhydrous sodium sulfate. After filtration, the solvent is evaporated to yield 2.91 g of light yellow liquid which upon distillation under reduced pressure gives 2.13 g (75%) of colorless **9**-OMe: bp 57.0-58.0 °C at 0.1 mm; ^{1}H NMR ($CDCl_3$) τ 6.66 (s, 3 H, -OCH_3), 7.50 (s, 1 H, $\equiv$CH), 7.70-8.60 (m, 14 H): IR (CCl_4) μ 2.94 (m, $\equiv$C—H), 3.45 (s, C—H), 4.74 (vw, C$\equiv$C); mass spectrum m/e 190.1348; calcd for $C_{13}H_{18}O$, 190.1358.

5-Phenyl-2-ethynyladamantan-2-ol (12-OH). Liquid ammonia (250 mL) is discharged into a 500-mL, three-necked flask equipped with a mechanical stirrer and cooled in dry ice. A rapid stream of dry acetylene is passed through the vigorously stirred ammonia; meanwhile, 3.20 g (0.139 mol) of sodium metal is added over a period of 1 h. When the blue color produced during the addition of the sodium metal has disappeared, the gas flow rate is reduced and 3.32 g (14.7 mmol) of 5-phenyladamantan-2-one is added. The mixture is allowed to stand at −78 °C for 7 h while the acetylene gas delivery continues. Then the ammonia is allowed to evaporate, water (110 mL) is slowly added to dissolve the residue, and the resulting solution is neutralized with 10% sulfuric acid and extracted with ether (3 × 50 mL). The ethereal solutions are combined, washed with saturated sodium chloride solution, and dried over anhydrous potassium carbonate. The solvent is evaporated to give 3.55 g of white solid of crude 5-phenyl-2-ethynyladamantan-2-ol. The crude product is applied to a 3.5 × 50 cm column with alumina (obtained from Fisher Scientific Co.; activity grade 1; 80-200 mesh) and eluted, first with a 20:80 (v/v) mixture of hexane and methylene chloride (3 L) and then with a 20:80 (v/v) mixture of hexane and chloroform (2 L). The first fraction, 0.44 g of white solid, is found to be 5-phenyladamantan-2-one. The second fraction is 2.88 g (90%) of **12**-OH as a white solid: ^{1}H NMR ($CDCl_3$) τ 2.57-2.93 (m, 5 H, phenyl H), 7.45 (s, 1 H), 7.48-8.65 (m, 14 H). Analysis of this solid with a Varian Aerograph Model 1400 GC with a 15% Carbowax 20 M-Chromosorb W column (10 ft × 1/8 in. o.d.), helium flow rate 40 mL/min, and a column temperature programmed to rise from 100 to 180 °C at a rate of 8 °C/min, shows the solid to contain two compounds, (E)- and (Z)-**12**-OH, with retention times of 165 and 178 min, respectively. The ratio of E to Z is about 2:1. Fractional recrystallization of the mixture from cyclohexane gives 0.36 g of pure (E)-**12**-OH: mp (hexane) 97.5-98.5 °C; ^{1}H NMR ($CDCl_3$) τ 2.57-2.85 (m, 5 H, phenyl H), 7.45 (s, 1 H, $\equiv$CH), 7.45-8.53 (m, 14 H); mass spectrum m/e (relative intensity) 252 (100%, M^+), 253 (20.7%, M + 1), 254 (1.8%, M + 2).

(Z)-**12**-OH can be obtained in pure form by either of the following two methods: (1) elution of 2.10 g of the E/Z mixture, recovered from the fractional recrystallization, with a 70:30 (v/v) mixture of carbon tetrachloride and chloroform through a 78 × 3.5 cm o.d. column with aluminum oxide (Merck) and collection of the eluent in 25-mL portions for 191 fractions. Fractions 171 to 180 are found (analysis by GLC) to contain a total of about 5 mg of 95% pure (Z)-**12**-OH (and 5% E isomer), which upon recrystallization from n-hexane gives pure

(*Z*)-**12**-OH as a white solid. Fractions 121 to 170 all contain mixtures of (*E*)- and (*Z*)-**12**-OH, the composition increasing in *Z* isomer as the fraction number increases. (2) The second method for obtaining pure (*Z*)-**12**-OH is by high-pressure liquid chromatography (LC): elution of the *E*/*Z* mixture with a 50:50 (v/v) mixture of hexane and methylene chloride through a 2-ft μ-porasil column ($^1/_4$ in. o.d.). The retention times of (*E*)- and (*Z*)-**12**-OH are 85.5 and 101.5 min, respectively. Pure (*Z*)-**12**-OH is characterized as follows: mp (*n*-hexane) 89.0–89.5 °C; ^{1}H NMR (CDCl$_3$) τ 2.60–2.90 (m, 5 H, phenyl H), 7.45 (s, 1 H, ≡CH), 7.45–8.43 (m, 14 H); mass spectrum *m/e* (relative intensity) 252 (100%, M$^+$), 253 (18%, M + 1), 254 (2%, M + 2).

2-Chloro-5-phenyl-2-ethynyladamantane (12-Cl). Zinc chloride (54.4 g, 0.40 mol) is added to 24.0 mL (0.29 mol) of vigorously stirred concentrated hydrochloric acid at 0 °C. The mixture is warmed to room temperature, and a solution of 1.948 g (7.7 mmol) of **12**-OH in 12.0 mL of benzene is gradually added. The reaction mixture is left at room temperature for 20 min and extracted with chloroform (3 × 50 mL); the organic solutions are combined, washed with saturated sodium chloride solution (2 × 50 mL), and dried over magnesium sulfate. After filtration and rotary evaporation of the solvent, one obtained 2.23 g of light brown oil. This oil is applied to a silica gel column (200 g) and eluted, first with a 10:90 (v/v) mixture of hexane and benzene (420 mL) and then with an 80:20 (v/v) mixture of benzene and chloroform (240 mL). The first product eluted is 1.18 g (56%) of light yellow oil, which solidifies in the freezer after several days. ^{1}H NMR reveals that it contains **12**-Cl and a trace of **13**-Cl. The second fraction is 0.05 g of white solid. The ^{1}H NMR spectrum shows doublets at τ −0.05 and 4.15, and this compound is tentatively identified as 5-phenyladamantylideneacetaldehyde. The crude **12**-Cl as obtained above is then eluted through a 20 × 1.5 cm silica gel column with hexane. The white solid obtained is subjected to fractional crystallization from hexane to give 0.120 g of pure (*Z*)-**12**-Cl: mp 91.0–92.0 °C; ^{1}H NMR (CDCl$_3$) τ 2.61–2.93 (m, 5 H, phenyl H), 7.22 (s, 1 H, ≡CH), 7.32–8.30 (m, 13 H); mass spectrum *m/e* (relative intensity) 270 (100%, M$^+$), 272 (34.4%, M + 2). Pure (*E*)-**12**-Cl is obtained by LC. The mixture as recovered from the fractional recrystallization is eluted with dry hexane through a 2-ft μ-porasil ($^1/_4$ in. o.d.) LC column; (*E*)- and (*Z*)-**13**-Cl and (*Z*)- and (*E*)-**12**-Cl appear in that order. After collection and recrystallization from hexane, pure (*E*)-**12**-Cl shows the following characteristics: mp 92.5–93.0 °C; ^{1}H NMR (CDCl$_3$) τ 2.57–2.85 (m, 5 H, phenyl H), 7.22 (s, 1 H, ≡CH), 7.32–8.37 (m, 13 H); mass spectrum *m/e* (relative intensity) 270 (100%, M$^+$), 272 (34.4%, M + 2).

(*E*)-5-Phenyl-2-chlorovinylideneadamantane ((*E*)-13-Cl). A solution of 160.0 mg (0.634 mmol) of 95% pure (*E*)-**12**-OH (and 5% (*Z*)-**12**-OH) and 0.072 mL (0.893 mmol) of pyridine in 10 mL of freshly distilled dry ether is placed into a 50-mL, round-bottomed flask. An addition funnel is attached, and a solution of 0.052 mL (0.721 mmol) of freshly distilled thionyl chloride in 10 mL of ether is discharged into the addition funnel. While the adamantanol–pyridine solution is maintained at 0 °C and stirred vigorously, the thionyl chloride solution is added over a period of 80 min, after which the reaction mixture is left to stand at 0 °C for 2 more h. The reaction mixture is filtered and the solid is washed with 5 mL of dry ether. The organic solution is washed with 3% hydrochloric acid (2 × 10 mL) and with 5% sodium bicarbonate solution (2 × 10 mL). After we dried the solution over anhydrous sodium sulfate and evaporated the solvent, 170.1 mg of a light yellow oil was obtained. This oil is applied to a 15 × 1.5 cm column with silica gel (J. T. Baker) and eluted with hexane (100 mL) to give 80.5 mg (93%) of (*E*)-**13**-Cl as a white solid. Unreacted (*E*)-**12**-OH is recovered by washing the column with methylene chloride. The product is dissolved in carbon tetrachloride and the solution is subjected to LC analysis (for conditions, see the purification of (*E*-**12**-Cl); the analysis shows that the composition is 93% (*E*)- and 7% (*Z*)-**13**-Cl. Recrystallization of this mixture from methanol gives 34.5 mg of (*E*)-**13**-Cl as a white solid: mp 64.0–65.0 °C; ^{1}H NMR (CDCl$_3$) τ 2.63–2.93 (m, 5 H, phenyl H), 4.06 (s, 1 H, C=C=CHCl), 7.23 (br s, 2 H), 7.67–8.20 (m, 11 H); mass spectrum *m/e* (relative intensity) 270 (100%, M$^+$), 272 (32%, M + 2).

(*Z*)-5-Phenyl-2-chlorovinylideneadamantane ((*Z*)-13-Cl). The procedure is the same as in the preparation of (*E*)-**13**-Cl; 73.4 mg (0.291 mmol) of the mixture of 18% (*E*)- and 82% (*Z*)-**12**-OH is treated with pyridine (0.44 mmol) and thionyl chloride (0.32 mmol). LC analysis before passage through the silica gel column shows that the **13**-Cl obtained is 16% *E* and 84% *Z*. Pure (*Z*)-**13**-Cl is obtained by means of LC. (*Z*)-**13**-Cl is a white solid: mp 101.5–102.5 °C; ^{1}H NMR (CDCl$_3$) τ 2.66–3.00 (m, 5 H, phenyl H), 4.14 (s, 1 H, C=C=CHCl), 7.23 (br s, 2 H), 7.70–8.20 (m, 11 H); mass spectrum, *m/e* (relative intensity) 270 (100%, M$^+$), 272 (33.9%, M + 2).

(*E*)-2-Methoxy-5-phenyl-2-ethynyladamantane ((*E*)-12-OMe). A 50-mL, three-necked flask containing a magnetic bar is charged with 0.108 g of 56% (w/w) sodium hydride dispersed in oil. The oil is removed by washing twice with 1.00 mL of dry pentane. Nitrogen is introduced and 10 mL of dry THF is added. A condenser is attached, as is an addition funnel which contains a solution of 0.504 g (2.00 mmol) of compound **12**-OH (88% *E* and 12% *Z*) and 0.287 g (2.02 mmol) of methyl iodide in 10 mL of dry THF. The temperature of the sodium hydride suspension is kept at 45–50 °C, and the addition is carried out over a period of 20 min. The reaction mixture is allowed to stand at the same temperature for another 40 min; then it is cooled to room temperature, and 10 mL of water is added dropwise to destroy the remaining sodium hydride. The resulting solution is extracted with ether (3 × 10 mL); the ethereal solution is washed with saturated sodium chloride solution (2 × 10 mL) and dried over anhydrous sodium sulfate. After filtration and rotary evaporation of the solvent, 0.542 g of light brown oil is obtained. This oil is eluted from a silica gel column with 450 mL of a 95:5 (v/v) mixture of hexane and ether, and then with 1500 mL of a 90:10 (v/v) mixture of hexane and ether. The first product obtained is 0.263 g of white solid **12**-OMe (96%); GLC shows the ratio of *E* to *Z* to be 88:12. Fractional recrystallization of this mixture from hexane produces pure (*E*)-**12**-OMe: mp 70.5–71.5 °C; ^{1}H NMR (CDCl$_3$) τ 2.60–2.93 (m, 5 H, phenyl H), 6.58 (s, 3 H, -OCH$_3$), 7.47 (s, 1 H, ≡CH), 7.50–8.57 (m, 13 H); mass spectrum *m/e* (relative intensity) 266 (100%, M$^+$), 267 (18.6%, M + 1). The second fraction is 0.246 g of white solid; ^{1}H NMR and GLC both show it to be **12**-OH with an *E*/*Z* ratio of 90:10.

(*Z*)-5-Phenyl-2-methoxy-2-ethynyladamantane ((*Z*)-12-OMe). The same procedure is used as in the preparation of (*E*)-**12**-OMe; 20.1 mg (0.080 mmol) of the (*Z*)-alcohol (>99% pure) is treated with 5.0 mg of 56% oil-dispersed sodium hydride (0.10 mmol) and 11.2 mg (0.08 mmol) of methyl iodide. Some additional methyl iodide is added to the reaction mixture to compensate for loss during reaction. After evaporation of the methyl ether, the resulting mixture shows that about 30% of the alcohol has been converted to **12**-OMe, of which 99% proved to be *Z*. The recovered **12**-OH also contains more than 99% of the *Z* isomer. Pure (*Z*)-**12**-OMe has the following characteristics: mp 61.0–61.5 °C; ^{1}H NMR (CDCl$_3$) τ 2.63–2.90 (m, 5 H, phenyl H), 6.62 (s, 3 H, -OCH$_3$), 7.47 (s, 1 H, ≡CH), 7.60–8.45 (m, 13 H); mass spectrum *m/e* 266.1648; calcd for $C_{19}H_{22}O$, 266.1665.

Configurational Analyses. An NMR tube is carefully charged with 10.11 mg (4.01×10^{-5} mol) of (*E*)-**12**-OH. Carbon tetrachloride (0.25 mL) with a small amount of tetramethylsilane is added, and the ^{1}H NMR spectrum of the solution is recorded. Known volumes of 0.100 M Eu(fod)$_3$ in carbon tetrachloride are added to the solution by the use of a syringe, and the ^{1}H NMR spectrum is recorded each time. The final volume of the solution is assumed to be equal to the sum of the volumes of the carbon tetrachloride originally present (0.25 mL) and that of the Eu(fod)$_3$ solution added; the concentrations of (*E*)-**12**-OH and Eu(fod)$_3$ are then calculated on that basis. Similar experiments are carried out with compounds **9**-OH and (*Z*)-**12**-OH.

The X-ray analyses were carried out with single crystals of (*Z*)-**12**-OH, (*E*)- and (*Z*)-**12**-Cl, (*E*)-**13**-Cl, and (*E*)-**12**-OMe; the diffraction data were obtained on an Enraf–Nonius CAD-4 diffractometer with monochromatized Cu Kα radiation. The computations were carried out on a PDP 11/45 and the Structure Determination Package.[1b]

Solvolysis Studies. Solvents. The drying of *tert*-butyl alcohol[54] and of methanol[55] has been reported. The aqueous alcohols used in the solvolysis are all prepared from the dry alcohols and deionized water. The fraction of alcohol contained in the aqueous alcohol is described by volume; for example, "80% methanol" means the methanol and water are mixed in the volume ratio of 80 to 20.

Bases. Potassium *tert*-butoxide in *tert*-butyl alcohol is prepared by adding potassium metal to dry *tert*-butyl alcohol.[54,56] The potassium hydroxide in aqueous alcohol is prepared by dissolving solid potassium hydroxide in aqueous alcohol. The precise concentrations of the bases are determined by titration with standardized hydrochloric acid with the help of a pH meter. The hydrochloric acid in turn is standardized with potassium biphthalate.

Analytical Methods. The quantitative analysis of (*E*)- and (*Z*)-

12-Cl and (*E*)- and (*Z*)-**13**-Cl in solvolysis is done by means of LC with pentamethylbenzene as internal standard; the amounts of each compound are obtained by comparing the area of each LC peak with the area of the internal standard. The peaks are carefully cut out and weighed. The results obtained are reproducible within ±5%. The conditions are: column, 2-ft μ-porasil (¼ in. o.d.); solvent, dry hexane; solvent flow rate, 0.8 mL/min; detector, differential UV, 254 nm. Base-line separation is achieved. The retention times of pentamethylbenzene, (*E*)-**13**-Cl, (*Z*)-**13**-Cl, (*Z*)-**12**-Cl, and (*E*)-**12**-Cl are 27, 74, 79, 109, and 140 min, respectively. Correct identification is assured by co-injecting the sample with authentic compounds; calibration was achieved by means of mixtures of known composition.

The analysis of (*E*)- and (*Z*)-**12**-OMe is done by GLC. The amounts of each are obtained by comparing the peak areas with that of the internal standard (pentamethylbenzene); the peaks are carefully cut out and weighed. Reproducible results are obtained (±5%). The GLC conditions are: column, 6 ft × ⅛ in. o.d., 3% diethylene glycol succinate on Chromosorb W (HP, 80/100); helium flow rate, 25 mL/min; injector temperature, 190 °C; column temperature, initially at 90 °C for 8 min, then programmed to rise to 172 °C at 6 °C/min, and kept at 172 °C until the analysis is finished. Partial separation of (*E*)- and (*Z*)-**12**-OMe is achieved. The retention times of pentamethylbenzene and (*E*)- and (*Z*)-**12**-OMe are 4.6, 31.0, and 31.6 min, respectively. Qualitative identification is assured by co-injecting the sample with authentic compounds. Calibration was achieved by means of mixtures of known composition.

The quantitative analyses of **9**-Cl, **10**-Cl, and **9**-OMe are done by GLC, with decalin as internal standard. The method used to obtain the quantities of these compounds is similar to the one used for (*E*)- and (*Z*)-**12**-OMe. Reproducible results are obtained (±3%). The GLC conditions are: column, 6 ft × ⅛ in o.d., 3% apiezon L on Chromosorb W (HP, 80/100); injector temperature, 120 °C; column temperature, 8 min at 80 °C, then programmed to rise to 120 °C at 8 °C/min, and kept at 120 °C until the analysis is finished; helium flow rate, 25 mL/min. Base-line separation is achieved. The retention times of decalin, **9**-OMe, **9**-Cl, and **10**-Cl are 7.6, 20.5, 24.8, and 30.5 min, respectively.

Hydrogen–Deuterium Exchange Study. The following description illustrates the procedure used in the H–D exchange study. **10**-Cl (29.2 mg, 0.15 mmol) is carefully weighed and put into an NMR tube through a small funnel; 0.50 mL of dry *tert*-butyl alcohol-*O-d* which contains a small amount of benzene to serve as internal standard, is added. Spectra are taken and the aromatic and allenic proton signals are integrated. It shows there is no noticeable change in the ratio of aromatic and allenic proton signals after 10 min. Potassium *tert*-butoxide in *tert*-butyl alcohol-*O-d* is added with a syringe so as to make the base concentration 10^{-2} M. The tube is shaken for a few seconds and put back into the magnetic cavity; periodic integration is carried out and the areas of aromatic and allenic proton signals are compared. Similar experiments are done with **9**-Cl, (*Z*)-**12**-Cl, and (*E*)-**13**-Cl. For the latter two, the phenyl protons in the compounds serve as internal standard.

Solvolysis of (*E*)- and (*Z*)-13-Cl in *t*-BuOK/*t*-BuOH. The following description illustrates the procedure used. Carefully weighed (1.95 mg) (*E*)-**13**-Cl is put into a small tube through a small funnel and cooled in an ice bath; 2.40 mL of 3.0×10^{-3} M potassium *tert*-butoxide in *tert*-butyl alcohol is added. The tube is quickly sealed and placed into a thermostat. After being shaken for a few minutes, the reaction mixture is allowed to stand in the thermostat for various periods of time. The reaction is quenched with 10 g of ice–water, neutralized with 0.1 N sulfuric acid with the help of a pH meter, and extracted with methylene chloride (4 × 10 mL); the methylene chloride solution is washed with distilled water (2 × 15 mL) and then dried over anhydrous sodium sulfate. After filtration and rotary evaporation of the solvent, internal standard (pentamethylbenzene) is added and the solution is analyzed with LC.

Basic Solvolysis of 9-Cl and 12-Cl in *t*-BuOK/*t*-BuOH. The following description is illustrative. (*Z*)-**12**-Cl (5.57 mg, 2.06×10^{-5} mol) is carefully weighed into a 10-mL flask. Dry *tert*-butyl alcohol (3.20 mL, measured at 30.4 °C) is added to dissolve the solid. The flask is covered with a glass stopper and placed into a thermostat at 30.4 ± 0.1 °C. After 10 min, 1.80 mL of 1.10×10^{-2} M *t*-BuOK in *t*-BuOH (also measured at 30.4 °C) is quickly introduced and the reaction mixture is then left in the thermostat for 40 min, quenched with a mixture of 10 g of ice-water and 5 mL of *tert*-butyl alcohol, and neutralized with 0.1 N sulfuric acid with the help of a pH meter. The resulting solution is extracted with methylene chloride (4 × 10 mL). The organic solution thus obtained is washed with water (2 × 15 mL) and dried over anhydrous sodium sulfate. After evaporation of the solvent, internal standard solution is added and the solution is subjected to LC analysis.

Basic Solvolysis of (*Z*)-13-Cl in KOH/80% *t*-BuOH with Added Chloride Ion. The following procedure is used to carry out the solvolysis of (*Z*)-**13**-Cl in tenfold excess KOH in 80% *tert*-butyl alcohol under the influence of added chloride ion. (*Z*)-**13**-Cl (2.05 mg, 7.57×10^{-6} mol) is carefully weighed into a small tube. This tube is put into an ice bath and 2.50 mL of a solution of 3.00×10^{-1} M in potassium chloride and 3.00×10^{-2} M in potassium hydroxide in 80% *tert*-butyl alcohol is added. The tube is quickly sealed and placed into a thermostat held at 50.4 ± 0.1 °C. The tube is shaken for a few minutes and left to stand for 12 h. The reaction mixture is quenched with 10 g of a mixture of ice and water, and neutralized with 0.1 N sulfuric acid; the resulting solution is extracted with methylene chloride (4 × 10 mL). After being washed with water (2 × 15 mL), the organic solution is dried over anhydrous sodium sulfate. After filtration and rotary evaporation of the solvent, internal standard solution is added to the residue and the resulting solution is analyzed with LC. This experiment was done in the presence of zero-, one-, and tenfold excesses of chloride ion, and in KOH/80% MeOH.

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Thione Photochemistry. Adamantanethione as a Model for Singlet π,π^* Hydrogen Abstraction[1,2]

K. Y. Law and P. de Mayo*

Contribution from the Photochemistry Unit, Department of Chemistry, University of Western Ontario, London, Ontario, N6A 5B7, Canada.

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Abstract: The S_2 (π,π^*) reaction of adamantanethione with alkanes has been shown to involve hydrogen abstraction and a radical pair. Depending on the viscosity of the medium most of the reaction occurs by radical combination within the solvent cage, but a small percentage escapes to be trapped by ground-state thione. The cage products are thiols and alkyl 2-adamantyl sulfides, while the products of escape are the latter sulfide and 2-adamantyl disulfide. The latter is a measure of the amount of escape from the cage as is also the formation of cross products in the irradiation in a cyclohexane–cyclohexane-d_{12} mixture; good agreement is obtained for the value of the cage effect (ca. 90%). Evidence is provided that any chain sequence deriving from the escaping radicals must be short and, with approximations, rate constants for product formation of 6.7×10^7 and 6.3×10^7 $M^{-1}\,s^{-1}$ are obtained for cyclohexane and cyclopentane, respectively.

Of known photochemical reactions hydrogen abstraction has been surely one of the most intensively investigated. Most studies have centered on the photochemistry of the carbonyl function, where it has clearly been established that the $^3(n,\pi^*)$ state is usually the active function both in aliphatic and aromatic systems.[3] More recently, after some discussion, the corresponding singlet has been shown to behave similarly both inter- and intramolecularly.[4] The $^3(\pi,\pi^*)$ state, on the other hand, unmixed with (n,π^*) is unreactive, or at least over an order of magnitude less so,[5] at least as far as aromatic ketones are concerned:[5a] the corresponding singlets are presumably too short lived for detection in this reaction. We are aware of

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