Control for Stability of 4-Hydroxyspirohexane. To test the possibility that any of the deamination products might be secondary rearrangement products from the 4-hydroxyspirohexane, the following experiment was done.

Perchloric acid (pH 1.55, 100 mL) was added to a stirred aqueous solution of sodium nitrite (15.35 g, 0.222 mol; plus 25 mL of water). The pH of the resulting solution was found to be 4.65. Then 4-hydroxyspirohexane (0.210 g, 2.14 mmol) was added. The mixture was stirred at room temperature (23 °C) for 40 h. The aqueous reaction mixture was saturated with sodium chloride and extracted with diethyl ether (3 × 100 mL and 1 × 50 mL). The combined ethereal solution was dried over magnesium sulfate. After filtration, the ether was distilled through a 1 ft spiral wire column. VPC on a Carbowax 20M column at 130 °C showed two product peaks in addition to those in the solvent peak region. Peaks corresponding to 3-methylenecyclopentanol and cyclohexanone were not observed. The major product peak had the same retention time as that of the starting alcohol. The retention time of the minor product peak was shorter than those of the major one and cyclohexanone. The two fractions corresponding to the two peaks were collected by VPC (13 mg and 85 mg, respectively). The NMR spectrum (CCl_4 solution) of the major product was identical with that of 4-hydroxyspirohexane. The NMR spectrum (CCl_4 solution) of the minor product showed two symmetrical pairs of multiplets centered at δ 0.96, 1.30, 2.19, and 3.00. The pattern was identical with that of 4-hydroxyspirohexane. However, some other unidentifiable peaks were present with much weaker intensities at δ 0.68 and 0.45 (a symmetrical pair of doublets), 1.56 (singlet), 1.70 (singlet), 4.26 (triplet), 5.20 (multiplet), and 7.86 (singlet). The IR spectrum (CCl_4 solution) of the minor product resembled that of spirohexan-4-one except for the presence of two additional absorptions at 1725 and 1550 cm^{-1}.

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Registry No.—**5**, 21816-24-0; **6**, 20461-31-8; 4-spirohexanecarbonyl chloride, 66036-85-9; 5-spirohexanecarbonyl chloride, 66036-85-9; spirohexane, 157-45-9; oxalyl chloride, 79-37-8; ethyl 4-spirohexanecarboxylate, 66036-86-0; ethyl 5-spirohexanecarboxylate, 66036-86-0; 4-spirohexanecarboxylic acid hydrazide, 66036-87-1; β-naphthyl 4-spirohexanecarbamate, 66036-88-2; β-naphthol, 135-19-3; 5-spirohexanecarboxylic acid hydrazide, 66036-89-3; β-naphthyl 5-spirohexanecarbamate, 66036-88-2; 4-aminospirohexane, 38772-80-4; 4-hydroxyspirohexane, 21816-25-1; 5-aminospirohexane, 38772-81-5; 5-hydroxyspirohexane, 20054-19-7.

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Synthesis of Chlorolium Ion Precursors: Solvolysis of Halobutadienes[1a]

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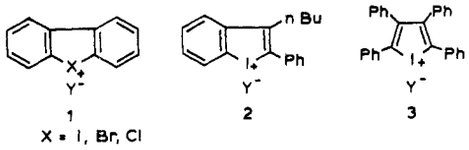
The *E,Z* and *Z,Z* isomers of 1-bromo-4-chloro-1,4-diphenyl-1,3-butadiene, 11*EZ* and 11*ZZ*, specifically deuterated in the 2 and 3 positions, were prepared. Silver-assisted solvolysis of 11*EZ* and 11*ZZ* in acetic acid and 11*EZ* in acetic anhydride gave a mixture of acetates 21*EZ* and 21*ZZ* and acetylene 9*Z*. The *E,E* isomer of 11 where chlorine participation is not possible and (*E*)-1-bromo-1-phenylpropene (29*E*) were solvolyzed in acetic acid with $AgBF_4$ to serve as model compounds. Using 29*E* deuterated in the 2 position, the isotope effect for acetylene formation from the vinyl cation was determined to be 2.0. Analysis of the deuterium distribution in the products from deuterated 11*EZ* led to the conclusion that 24 (in acetic acid) and 30% (in acetic anhydride) of the reaction proceeds through a chlorolium ion (13) intermediate. The isotope effect (k_H/k_D) for the deprotonation of 13 to give 9*Z* is 2.4 (in acetic acid) and 2.2 (in acetic anhydride). Similar results were obtained from the study of the solvolysis of 11*ZZ*. The vinyltriazenes 36*ZZ* from 11*ZZ* and its deuterated analogues were prepared and decomposed in situ with acetic acid. The deuterium content of the products showed that only 1% of the reaction involved a chlorolium ion. Even the vinyltriazene 37*ZZ* prepared from (*Z,Z*)-1-bromo-4-methylthio-1,4-diphenyl-1,3-butadiene showed little evidence (1%) of sulfur capture of the vinyl cation upon decomposition in acetic acid.

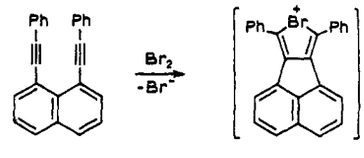
In contrast to the well studied group 7 heteroaromatic compounds furan, thiophene, selenophene, and even tellurophene, the chemistry of the analogous unsaturated halogen heterocycles, the halolium ions, has been little studied. Stable dibenzochlorolium, -bromolium, and -iodolium salts (1) were first prepared by Sandin and Hay.[2] More recently Beringer[3] has reported the synthesis of the benziodolium (2) and



1 2 3

X = I, Br, Cl

tetraphenyliodolium cations (3). A bromolium ion has been proposed by Bossenbroek and Shechter[4] as the intermediate in the bromination of 1,8-bis(phenylethynyl)naphthalene.



We report here the full details[1a] of our work on the ionization of halo- and triazenylbutadienes as a route to the 2,5-diphenylchlorolium ion (4) and related systems.

This approach to the halolium ion (4) involved the use of a halogen to trap a stabilized vinyl cation (5)[5] intramolecu-

4 5

X = Br, Cl

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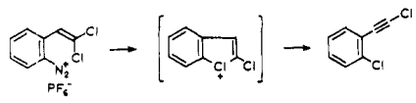
larly. Neighboring halogen is known to interact with carbonium ion centers in aliphatic systems[6] and participation of β-sulfur[7] and iodine[8] has been reported in the solvolysis of vinyl derivatives. The halolium ion (4), being isoelectronic with thiophene, might be aromatic and thus stable enough to be observed.

Olah and Yamada,[9] using a similar approach, have detected the intermediacy of 6 in the thermal decomposition of *o*-

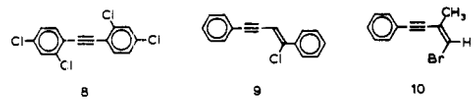


7 6

(β,β-dichloroethenyl)phenyldiazonium fluorophosphate (7).

Results

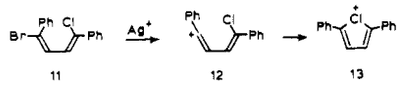
Our initial approach was to generate a vinyl cation by protonation of a suitably substituted phenylacetylene. The acetylenes 8, 9, and 10 were treated with HSO_3F or HSO_3F–



8 9 10

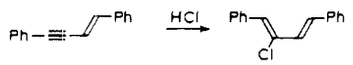
SbF_5. In each case highly colored solutions were formed, whose NMR spectra could not be reconciled with that of the expected halolium ion.

We then concentrated our efforts on the synthesis of 1,4-halobutadienes (11) which could be ionized to yield vinyl cations (12) suitably disposed for capture by neighboring halogen (13). A convenient approach to the desired 1,4-di-

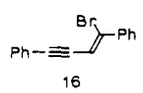


11 12 13

halo-1,4-diphenyl-1,3-butadienes (11), as well as the required deuterium labeled compounds, appeared to be the addition of hydrogen halides to 1,4-diphenyl-1,3-butadiyne or to 1,4-diphenyl-1,3-butenyne (14). In both cases, HCl or HBr addition led to the wrong regioisomer (i.e., 15). Attempted synthesis of 16 by bromination of 14 followed by dehydro-



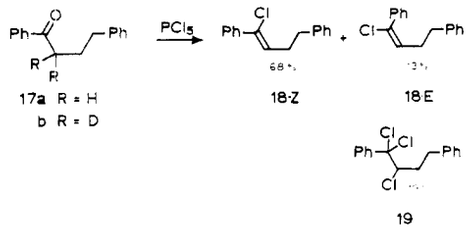
14 15



16

bromination was unsuccessful. Bromine addition to 14 yielded two crystalline products, each of which analyzed for addition of 2 mol of Br_2. Monoaddition products could not be detected. The ratio of the two tetrabromides depended on the brominating agent used.

Synthesis of 1-Bromo-4-chloro-1,4-diphenylbutadienes. The successful synthesis of 11*EZ* and -*ZZ* started with 1,4-diphenyl-1-butanone (17). Treatment with PCl_5 in refluxing benzene gave the *Z* vinyl chloride (18) in addition to 18*E* and 19 in the ratio indicated by GLC analysis. The crude

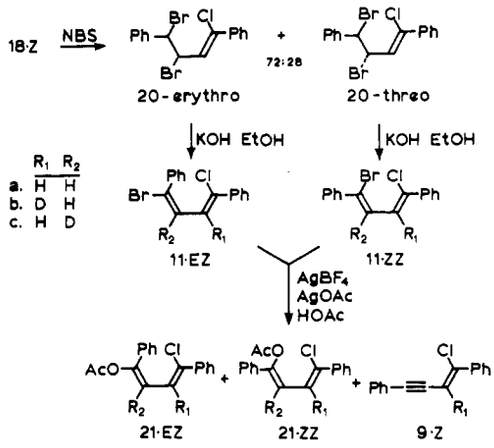


17a R = H
b R = D

18Z 18E

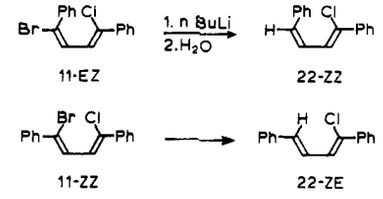
19

Scheme I



product mixture was treated with Zn in AcOH/Et_2O to reduce the trichloride 19 to 18*Z*. The deuterated vinyl chloride needed for mechanistic studies was formed from the deuterated ketone (17b) in an analoguous sequence. The vinyl chloride with the longer GLC retention time on SE-30 was assigned the *Z* configuration about the double bond since it was the major isomer formed (*Z*/*E* = 5) with the vinyl proton coming at δ 6.01 (δ 5.86 for the *E* isomer). This chemical shift difference, as well as the relative GLC retention times, is consistent with a number of related cis and trans isomers that have been observed.[10]

Treatment of 18*Z* with NBS in refluxing CCl_4 (Scheme I) gave sequentially the 3-bromo and 3,4-dibromo (20) compounds. The dibromide product 20 was a 72:28 mixture of erythro and threo diastereomers. The erythro isomer can be crystallized from the mixture in 48% yield and dehydrohalogenated to give 11*EZ*. Pure 11*ZZ* can be isolated by dehydrohalogenation of the crystallization mother liquor. Similar transformations using the deuterated vinyl chloride gave monodeuterated 11b*EZ* and 11b*ZZ* (98 ± 1%, d_1).[11] The stereochemistry of 11*EZ* and 11*ZZ* was proven by conversion to the monolithio compounds. Quenching of the vinyllithium from 11*EZ* with 1,2-dibromoethane gave back 93% isomerically pure 11*EZ* showing that the sequence proceeded with retention.[12,13] On quenching with water, 11*EZ* gave (*Z*,*Z*)-1-chloro-1,4-diphenyl-1,3-butadiene (22*ZZ*) with $J_{3,4}$ = 8 Hz, whereas 11*ZZ* gave the *Z*,*E* isomer (22*ZE*) with $J_{3,4}$ = 16 Hz.

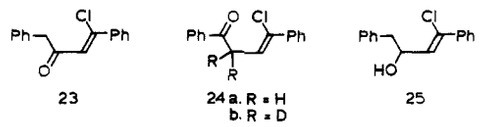


11-EZ 22-ZZ

11-ZZ 22-ZE

The deuterated bromo chlorides (11*b*,*c*) were carried through in an analogous manner. Quenching with hexachloroethane gave the isomeric 1,4-dichloro-1,4-diphenyl-1,3-butadienes. The stereochemical assignments here are unambiguous since the (*Z*,*Z*)-dichloride is symmetric, as shown by both ^1H and ^{13}C NMR, whereas the (*E*,*Z*)-dichloride is not.

The synthetic route of Scheme I was not suitable for the preparation of the deuterated compounds 11c*EZ* and 11c*ZZ*. Ketones 23 and 24 appeared to be potential precursors for these compounds. The alcohol precursor to 23 (25) could be



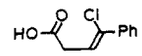
23 24a R = H
b R = D 25

Table I. Products of Silver Assisted Solvolyses of 1-Bromo-4-chloro-1,4-diphenyl-1,3-butadienes

Compd	% yield[a]	(% reaction)[b]	% 21*EZ*[c]	% 21*ZZ*[c]	% 9*Z*[c]	% *D* in 9*Z*
		In Acetic Acid at 118 °C				
11a*EZ*	97	(62)	21	52	27	
11b*EZ*	91	(72)	23	52	25	79
11c*EZ*	96	(63)	25	52	23	56
11a*ZZ*	78	(58)	24	52	24	
11b*ZZ*	75	(57)	22	51	27	83
11c*ZZ*	73	(64)	27	53	20	50
		In Acetic Anhydride at 80 °C				
11a*EZ*	93	(89)	19	53	28	
11b*EZ*	83	(67)	20	52	28	72
11c*EZ*	87	(61)	22	52	26	61

[a] Sum of products and recovered starting material. [b] Extent of reaction as determined by amount of recovered starting material. [c] Product ratios normalized to 100%.

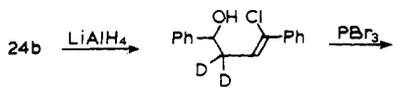
prepared by hydrolysis of the mono-NBS bromination product of 18*Z*, but oxidation of **25** could not be accomplished in acceptable yield using CrO_3, Collins or Jones conditions, or MnO_2. Attempts to prepare **24** from the readily available acid **26** by treatment with phenyllithium gave only low yields.



26

Reaction of the acid chloride of **26** with phenyllithium, $CdCl_2$ and phenyllithium, CuI and phenyllithium, phenylmagnesium bromide, and benzene under Friedel–Crafts conditions met with no better success.

Ketone **24** was prepared from the enol acetates **21**, obtained by silver-catalyzed ionization of **11** (Scheme I). These enol acetates were quite resistant toward both acid and base hydrolysis in refluxing THF–H_2O. Refluxing dioxane–H_2O–CF_3COOH did effect hydrolysis, but these conditions were strenuous enough to cause destruction of the product (**24**). Methyllithium cleaves the enol acetates cleanly to give **24** in 95% yield. This chloro ketone (**24**) was somewhat unstable and was deuterated directly by base-catalyzed exchange in D_2O. Reduction to **27**, conversion to the bromide **28** with PBr_3, and NBS bromination converted **24b** to a 75:25 mixture of erythro and threo dibromides **20**. These were separated and converted



27

28 20

to pure 11c*EZ* and 11c*ZZ* (97 ± 1%, d_1)[11] as described for the undeuterated compounds.

Solvolysis Results. Table I gives the yields of the solvolysis products from 11*EZ* and 11*ZZ* in AcOH and Ac_2O with $AgBF_4$ as catalyst. About 1 equiv of AgOAc was added to the solvolysis solution to remove fluoroboric acid generated by elimination. The stereochemistry of 21*EZ* and 21*ZZ* was assigned with the aid of $Eu(DPM)_3$ shift reagent.[14] The acetylene 9*Z* underwent facile dehydrohalogenation with ethanolic KOH to give 1,4-diphenyl-1,3-butadiyne. The stereochemistry was assigned on the basis of a 70-fold larger rate of elimination compared to 9*E* which was prepared by photochemical isomerization of 9*Z*. Both starting materials (11) and products (9*Z*, 21) were shown to be stereochemically stable and not subject to deuterium exchange under the reaction conditions.

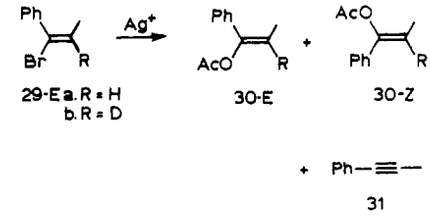
The deuterium content of the acetylene 9*Z* was determined mass spectrometrically and that of the acetates **21** was found by ^1H NMR with deuterium decoupling.

Solvolysis in AcOH or in Ac_2O shows no stereospecificity. The product ratios from 11*EZ* are the same, within experimental error, as those from 11*ZZ*. In AcOH 11*EZ* solvolyzes roughly five times as fast as 11*ZZ*.

The silver-assisted ionization of 11*EZ* and 11*ZZ* was also done in such aprotic solvents as toluene and nitrobenzene using $AgOCOCF_3$. In these cases the products were the acetylene 9*Z* and the *E,Z* and *Z,Z* trifluoroacetates which were formed with partial retention of configuration.[10b] About twice as much acetylene was formed from 11*EZ* as from the *ZZ* isomer. The amount of deuterium isomerization observed in the products from 11b*EZ* in these solvents was roughly the same as what was observed in AcOH with $AgBF_4$. These results were not pursued since the absolute yield of products was quite low.

The intervention of a symmetrical intermediate, the chlorolium ion **13**, in the above solvolyses is evidenced by the observation of substantial deuterium isomerization in the acetylene 9*Z*. Since the deuterium content of 9*Z* is dependent on the position of deuterium in the starting material, some of the acetylene is arising from a nonsymmetrical species, either by deprotonation of the vinyl cation or E_2 elimination of the vinyl bromide. The acetates 21*EZ* and 21*ZZ*, on the other hand, must be derived almost entirely from the ion **12** since only small amounts (2–6%) of deuterium isomerization were detected. Unfortunately, the small amount of scrambling, together with our inability to accurately assess the deuterium distribution in **11c**, makes conclusions drawn from this result somewhat tentative.

(*E*)-1-Bromo-1-phenylpropene (29*E*) was used as a model to determine the β-isotope effect on acetylene formation in the absence of participation. After 15 min in AcOH at 70 °C with $AgBF_4$, the solvolysis of 29*E* was essentially complete



29-E a. R = H b. R = D 30-E 30-Z

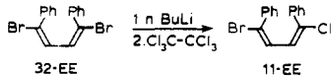
31

(>95%). A rough extrapolation gives about a factor of 10^4 for the rate acceleration of (*E*)-1-bromo-1-phenylpropene (29*E*) over (*E,Z*)-1-bromo-4-chloro-1,4-diphenyl-1,3-butadiene (11*EZ*). Thus the β-chlorovinyl group inductively retards vinyl cation formation. Product studies by GLC (Table II) indicated that k_H/k_D for acetylene formation is 2.0 ± 0.2 in AcOH with $AgBF_4$.

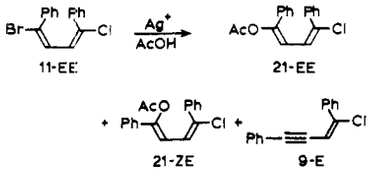
Table II. Silver Assisted Solvolysis of (*E*)-1-Bromo-1-phenylpropene in AcOH with $AgBF_4$ at 70 °C

	% 30*E*	% 30*Z*	% 31	k_H/k_D
29a*E*	28	49	23	
29b*E*	34	53	13	2.0 ± 0.2

The solvolysis of 11*EE*, for which intramolecular capture by chlorine is not possible, was also examined. This compound was prepared from (*E*,*E*)-1,4-dibromo-1,4-diphenyl-1,3-butadiene (32*EE*).[13] In AcOH the products consisted of the

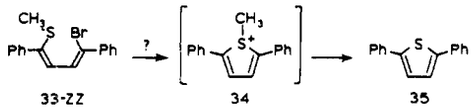


acetates 21*ZE* and 21*EE* and the acetylene 9*E* in a ratio of 72:18:10.



A Test for Sulfur Participation: Vinyl Triazene Decomposition. The low degree of participation by neighboring chlorine during silver-assisted solvolyses of 11*ZZ* and 11*EZ* made it desirable to examine a system in which the neighboring group has greater nucleophilicity.

A suitable substrate was (*Z*,*Z*)-1-bromo-4-methylthio-1,4-diphenyl-1,3-butadiene (33*ZZ*), prepared from 32*ZZ* via the monolithio compound.[13] A number of stable *S*-alkyl thiophenium salts (including 34) have been isolated. They

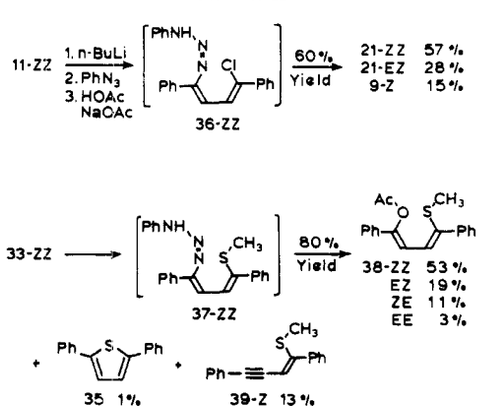


undergo dealkylation under solvolytic conditions,[15] so the product of participation would be the stable 2,5-diphenylthiophene 35.

The usual conditions for silver-assisted solvolysis failed to ionize the bromide 33*ZZ* probably because of silver complexation with the sulfur. After 1 h in refluxing AcOH with $AgBF_4$, starting material was recovered along with 25% of 33*ZE*.

Acid treatment of vinyl triazenes has been reported as a route to vinyl cations.[16] They are prepared by treatment of organometallics with phenyl azide. For the present study the vinyl triazenes 36*ZZ* and 37*ZZ* were prepared as shown in Scheme II. They could not be isolated but were decomposed directly by addition of the reaction mixture to acetic acid.

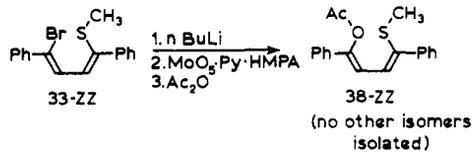
Scheme II



The equations above show the products isolated by preparative thin-layer chromatography. The triazene 36*ZZ* gave similar product distribution to that found for the solvolysis of 11a*ZZ*. However, when the deuterated dienes 11b*ZZ* and 11c*ZZ* were converted to triazenes and these treated with acetic acid the acetylenic product 9*Z* was not derived primarily from the chlorolium ion 13, as for the silver assisted solvolyses, since it was formed with little deuterium scrambling. Starting with 11b*ZZ* (97.5% d_1), the acetylene 9*Z* contained 96% deuterium, and from 11c*ZZ* (97% d_1), 11% deuterium (compare this with 83 and 50% for the silver-assisted solvolysis of 11*ZZ*, Table I). In contrast to the solvolysis, the enol acetate products showed no evidence for deuterium scrambling (<2%). There is clearly only a very small amount of chlorolium ion formed in this reaction.

The methylthio-substituted triazene 37*ZZ* gave an enol acetate 38*ZZ* as the major product, together with lesser quantities of 38*EZ*, 38*ZE*, and 38*EE*, the latter two having been formed by isomerization at the vinyl sulfide double bond. Only a trace amount of 2,5-diphenylthiophene was formed, identified by comparison with authentic material prepared according to the procedure of Böttcher and Bauer.[17]

The stereochemistry of 38*ZZ* was determined by comparison with material prepared by oxidation of the vinyllithium derivative with MoO_5·Py·HMPA.[18] The assignment of stereochemistry to the remaining acetates (38*EZ*, 38*ZE*, and 38*EE*) is tentative. First of all, 38*ZZ* is isomerized to 38*ZE* on

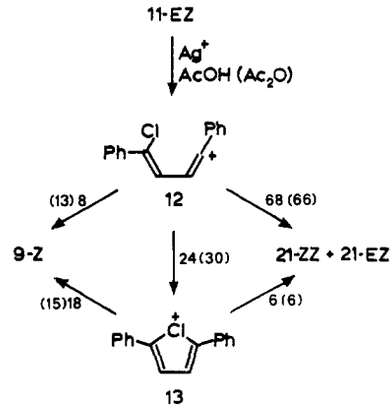


exposure to light. It has been our experience that all of the vinyl sulfides are readily isomerized even by ambient room lighting and that isomerization occurs at the vinyl sulfide double bond (for example, 33*ZZ* isomerizes to 33*ZE*; conversion of bromo to hydrogen with retention of configuration via the corresponding lithium reagents showed that the two compounds had the same configuration at the vinyl bromide double bond). Second, one of the vinyl proton chemical shifts usually moves upfield as a *Z* double bond is changed to an *E* double bond, with the *EE* isomer having both protons upfield compared to the *ZZ* isomer. For example, the dibromides 32*ZZ* and 32*EE* have chemical shifts at δ 7.30 and 6.63.[13] A number of other examples can be found among the chemical shifts reported in the Experimental Section.

Discussion

Our data have led us to propose the mechanistic Scheme III for the silver-assisted ionization of 11*EZ*. Yields refer to

Scheme III



100% of isolated products. Assuming that the isotope effect for the direct elimination (**12** → **9*Z***) is 2.0 as determined in our model compound **29*E***, we find[19] that in AcOH 24% of the solvolysis proceeds through the chlorolium ion (**13**) with k_H/k_D for **13** → **9*Z*** of 2.4 ± 0.2. In Ac_2O 30% of **13** is formed and k_H/k_D is 2.2.

The interpretation of these data is not crucially dependent on the assumption of isotope effects for the elimination **12** → **9*Z***. If this isotope effect is 1.0, then the amount of chlorolium ion in AcOH only changes from 24 to 27%, and the isotope effect for **13** → **9*Z*** becomes 2.8. The observation of lower acetylene yields from **11c** in all cases is consistent with an isotope effect of about 2 for the deprotonation of **12**. The kinetic analysis of the two routes to **9*Z*** cannot simultaneously give values for both isotope effects unless the decrease in yield of **9*Z*** between **11a** (or **11b**) and **11c** is used. Unfortunately, the yields are not sufficiently accurate or reproducible to do this.

The solvolysis of **11*ZZ*** in AcOH gives essentially the same product distribution as does **11*EZ***. In the case of **11*ZZ***, however, slightly less of the acetylene is formed via the symmetrical intermediate. In order to obtain the same isotope effect for deprotonation of **12** during the solvolysis of **11*ZZ*** as was obtained from **11*EZ***, it is necessary for the remainder of the elimination reaction to proceed with an isotope effect of 2.6 instead of 2.0 as used for **11*EZ***. Since E_2 elimination is a commonly observed pathway for vinyl halide solvolysis when hydrogen is trans to the leaving group, we assume that a small contribution from this process is present. It is this contribution which results in the higher isotope effect and higher yield for the nonchlorolium ion portion of the elimination. Analyzing the yields and deuterium distribution for **11*ZZ*** according to the mechanistic scheme, we find that 20% of the reaction proceeds via the chlorolium ion **13**, of which 14% appears as acetylene, and, tentatively, 6% as acetate.

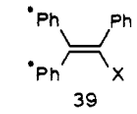
The solvolysis of **11*EE***, for which participation of chlorine is not possible, gives products consistent with the above mechanism. In AcOH only 10% of acetylene **9*E*** is formed along with 90% of acetates. This is comparable to the amount of acetylene **9*Z*** that comes from direct elimination via the vinyl cation **12** in our mechanistic scheme. Although other products were not detected, a complication here is the possible intermediacy of a spirophenonium ion.

The results of the triazene decomposition give a rather different pattern. Analysis of the deuterium distribution in the acetylenes by the same procedure as used for the silver-assisted solvolyses[19] gave the following results, assuming an isotope effect (k_H/k_D) of 2.4 for deprotonation of the chlorolium ion: acetylene **9*Z*** from **11b*ZZ*** was derived to the extent of only 5 ± 2% from chlorolium ion; from **11c*ZZ*** 16 ± 2% came from chlorolium ion. The isotope effect for formation of acetylene from open ion could not be accurately determined (k_H/k_D = 1–5).

Since about 15% of the triazene decomposition leads to acetylene, the above results demonstrate that between 0.5 and 1.0% of the reaction goes via chlorolium ion, as compared with 20% during the silver-assisted solvolysis of **11*ZZ***.

The main features of the reactions reported here are the following: the silver-assisted solvolysis of the *ZZ* and *ZE* isomers of the bromochlorodiene **11** in both acetic acid and acetic anhydride leads to 20–30% of chlorolium ion intermediate. The decomposition in acetic acid of the chloro- and methylthiotriazenes (**37**, **38**) leads to only about 1% of products derived from intramolecular capture of vinyl cation by the heteroatom.

The significantly different results obtained for the silver-assisted solvolyses and vinyltriazene decompositions would not appear to be explainable solely on the basis of different temperatures and somewhat different solvent for the two reactions. A direct comparison between vinyl cations generated by solvolyses or by triazene decomposition has been made by Lee and Ko.[20] The decomposition of radio-labeled triphenylvinyltriazene **39a** led to no detectable 1,2-phenyl rearrangement, whereas the silver-assisted acetolysis (**39b**) gave



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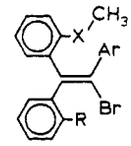
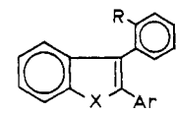
(a) X = N=NNHPh
(b) X = Br

7% of rearranged material. This result would appear to parallel our observation. However, these workers also examined the tri-*p*-anisylvinyl system and found 38% rearrangement from the triazene and only 20% from AgOAc/HOAc solvolysis of the bromide. The vinyl cations in the anisyl series are enormously more stabilized than in the phenyl, and this could obviously contribute to the difference in behavior.

While participation (anchimeric assistance) by remote nucleophilic substituents has been rare for vinyl systems, intramolecular capture of vinyl cations has been observed frequently.[21,22] Particularly pertinent to the present study are the reactions reported by Taniguchi et al.[22] in which β-ortho-substituted aryl vinyl cations were generated either by solvolysis in ethanol or silver-assisted ionization of **40** (R = H, XCH_3) in acetic acid. These reactions gave exclusively the products (**41**) of intramolecular captures. The much higher



40 X = O, S, NCH_3



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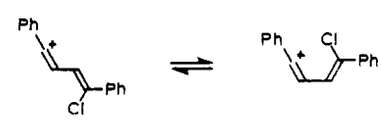
degree of cyclization here when compared with our system is somewhat surprising but can be rationalized on the basis that favorable conformations for the vinyl cation derived from **40** have the nucleophilic XCH_3 group in a suitable position to attack the carbonium ion center.

A satisfactory explanation for all features of the solvolytic reactions described in this paper has not been developed. In view of the probable high stability of the chlorolium and especially thiophenium ions, we had anticipated substantial or exclusive formation of cyclized intermediates. Instead, only minor amounts were observed even with the normally very strongly participating CH_3S group.

A possible explanation of these unexpected results may lie in the conformations of the 1,4-diphenyl-1,3-butadiene precursors and the vinyl cations derived from them. If the barrier to rotation interconverting cisoid and transoid conformations of the vinyl cation were higher than the activation barrier for solvent capture or deprotonation, then the amount of chlorolium or thiophenium ion formed would be a function of the fraction of cisoid ion (B) generated and not necessarily a reflection of the thermodynamic stability of the aromatic heterocycle or vinyl cation lifetime which must surely differ



A ⇌ B

greatly between acetic acid and acetic anhydride as solvent. Furthermore, the ratio of A to B could well favor A much more strongly in the triazene reactions because of the lower temperature and different nature of the leaving group in this reaction. The difficulty encountered with an explanation of this type is that even if attack of solvent on the cation is diffusion

controlled, the barrier to rotation would still have to be significant ($\Delta G^{\ddagger} \approx 4$–6 kcal/mol)[23] to prevent rotational equilibrium. It is not, however, unreasonable to assume that the rotation barrier is higher in the vinyl cation than in the butadiene.

A possibility that cannot be completely ruled out is that the formation of chlorolium ion in the silver-assisted solvolysis is not a vinyl cation reaction at all but rather an addition–elimination pathway initiated by silver complexation of the olefin. Such a process has been observed by Sonoda, Kobayashi and Taniguchi[22c] for systems like **40** (X = S) but which lack the aryl substituent on the α carbon and hence cannot be proceeding through vinyl cations. A mechanism such as this should have resulted in especially facile silver-assisted solvolysis of the methylthio compound **33***ZZ* because such a mechanism involves nucleophilic participation. In actuality, **33***ZZ* was unaffected by the conditions which sufficed for ionization of the bromochlorodienes **11**.

Experimental Section

Nuclear magnetic resonance spectra were obtained on a Varian A-60A, Jeol MH-100, or Varian XL-100 spectrometer. Infrared spectra were obtained on a Beckman IR-8 or Perkin-Elmer IR-267 spectrophotometer and mass spectra were obtained on an AEI MS-902 spectrometer. Unless specified otherwise, NMR and IR spectra were measured in CCl_4 solution. A 5 ft × 0.125 in. column of 3% SE-30 on 100/120 Varaport 30 was used for analytical GLC. Preparative GLC was done on a 0.25 × 3 in. column of 20% SE-30 on 60/80 Chromosorb W, AW-DMCS.

2,2′,4,4′-Tetrachlorodiphenylacetylene (8) was prepared according to the procedure of Fieser[24] starting with 2,4-dichlorobenzaldehyde: mp 131–132 °C; NMR δ 7.14 (dd, J = 8.3, 2.4 Hz, 1 H), 7.40 (d, J = 2.4 Hz, 1 H), 7.41 (d, J = 8.3 Hz, 1 H). Anal. Calcd for $C_{14}H_6Cl_4$: C, 53.21; H, 1.91. Found: C, 53.19; H, 2.06.

(*Z*)- and (*E*)-1-Bromo-4-phenyl-2-methyl-1-buten-3-yne (10). A 10.9-g (25 mmol) portion of bromomethyltriphenylphosphonium bromide was stirred in 40 mL of anhydrous ether under N_2 while a mixture of 4 mL (3.4 g, 40 mmol) of dry piperidine and 16 mL of a 2.3 M solution of phenyllithium (37 mmol) in 70:30 benzene–ether was added dropwise. After being stirred for 20 min, a solution of 3.6 g (25 mmol) of 1-phenyl-1-butyn-3-one in an equal volume of anhydrous ether was added dropwise with cooling. The solution was stirred at room temperature 30 min and allowed to stand for 15 min. The solution containing the product was decanted from the precipitated phosphine oxide. The precipitate was washed with two 100-mL portions of ether. The combined washes and decanted solution were filtered and washed with two 100-mL portions of 2 N HCl, 100 mL of 5% Na_2CO_3, and two 100-mL portions of saturated NaCl. The solution was dried with Na_2SO_4 and the solvent was evaporated. The crude product was chromatographed on silica gel, eluting with pentane. Incomplete separation of the *Z* and *E* isomers was achieved. The more rapidly eluting isomer A (0.39 g) gave: NMR δ 2.02 (d, J = 1.6 Hz, 3 H), 6.60 (q, J = 1.6 Hz, 1 H), 7.2–7.5 (m, 5 H); IR 2210, 2185, 1590 cm^{-1}. Anal. Calcd for $C_{11}H_9Br$: m/e 219.9888. Found: m/e 219.9897. The slower moving isomer B gave: NMR δ 2.01 (d, J = 1.4 Hz, 3 H), 6.33 (q, J = 1.4 Hz, 1 H), 7.2–7.6 (m, 5 H); IR 2215, 2185, 1600 cm^{-1}. Anal. Calcd for $C_{11}H_9Br$: m/e 219.9888. Found: m/e 219.9890. In addition 1.24 g of a mixture of isomers was obtained. The total yield was 1.81 g (33%).

1,4-Diphenyl-1-butanone (17a). To the Grignard reagent prepared from 90.2 g (0.46 mol) of 3-bromo-1-phenylpropane, 11.2 g (0.46 mol) of magnesium, and 350 mL of ether was added 42.1 g (0.409 mol) of benzonitrile during 10 min. The reaction mixture was refluxed for 16 h, 150 mL of 5 N HCl was added slowly, and the mixture was steam distilled to remove unreacted benzonitrile. The product was taken up in ether and washed with 5% Na_2CO_3 solution and saturated NaCl solution. After drying (Na_2SO_4), solvent was removed and the product was crystallized from pentane, giving 77.6 g (85% yield), mp 55–56 °C (lit.[25] 56–57 °C).

(*Z*)-1-Chloro-1,4-diphenyl-1-butene (18*Z*). 1,4-Diphenyl-1-butanone (**17a**) (15.0 g, 67 mmol) was added to 42.5 g of PCl_5 (204 mmol) in 800 mL of benzene and the mixture was refluxed for 1 h. About 400 g of the ice was added to the solution and it was stirred vigorously until the ice melted. The benzene layer was then washed with 5% Na_2CO_3 and saturated NaCl solutions and chromatographed on 150 g of silica gel. The crude product is a mixture of three main components: 68% of (*Z*)-1-chloro-1,4-diphenyl-1-butene (**18*Z***), NMR δ 2.5–3.0 (m, 4 H), 6.01 (t, J = 6.4 Hz, 1 H), 7.0–7.5 (m, 10 H); 13% of (*E*)-1-chloro-1,4-diphenyl-1-butene (**18*E***), NMR δ 2.1–2.9 (m, 4 H), 5.86 (t, J = 7.6 Hz, 1 H), 6.9–7.3 (m, 10 H); and 19% of 1,1,2-trichloro-1,4-diphenylbutane (**19**), NMR δ 1.9–3.0 (m, 4 H), 4.28 (dd, J = 4.8, 1.1 Hz, 1 H), 6.9–7.7 (m, 10 H), mp 49–54 °C. Crystallization afforded pure **18*Z*** and **19**. The two isomers of **18** can be separated preparatively by GLC at 175 °C. The retention times are for **18*E*** 14.1 min and for **18*Z*** 19.9 min.

The chromatographed crude product was dissolved in 100 mL of ether and 10 mL of acetic acid, and this solution was stirred with 4.4 g of zinc dust for 1 h to dehalogenate the 1,1,2-trichloro-1,4-diphenylbutane. Excess zinc was filtered; acetic acid was removed by extraction with $NaHCO_3$ solution. After drying (Na_2SO_4) and evaporation of the solvent, the residue was crystallized from 150 mL of pentane in dry ice, yielding 10.5 g (65%) of **18*Z***, mp 25–26 °C. Anal. Calcd for $C_{16}H_{15}Cl$: m/e 242.0862. Found: m/e 242.0866.

(*Z*)-1-Chloro-3,4-dibromo-1,4-diphenyl-1-butene (20). A suspension of 11.1 g (62 mmol) of *N*-bromosuccinimide in 125 mL of CCl_4 containing 6.9 g (28 mmol) of the vinyl chloride **18*Z*** was refluxed for 22 h. If reaction was not complete, more *N*-bromosuccinimide and a small amount of benzoyl peroxide were added and reflux was continued. The succinimide was filtered and the solvent was evaporated. The residue was dissolved in ether and washed with ice cold 5% NaOH and saturated NaCl solution. The solution was dried and solvent was removed. NMR shows the presence of erythro and threo dibromides in a 72:28 ratio. Two crystallizations from dichloromethane–pentane yielded 5.48 g (48%) of the erythro isomer, mp 126–127 °C. The mother liquor had erythro/threo 18:82. Erythro dibromide: NMR δ 5.14 (d, J = 10 Hz, 1 H), 5.61 (t, J = 10 Hz, 1 H), 6.42 (d, J = 10 Hz, 1 H), 7.2–7.8 (m, 10 H). Anal. Calcd for $C_{16}H_{13}Br_2Cl$: C, 47.97; H, 3.27. Found: C, 48.03; H, 3.21. Threo dibromide: NMR δ 5.25 (d, J = 6, 1 H), 5.62 (dd, J = 6, 10 Hz, 1 H), 6.22 (d, J = 10 Hz, 1 H), 7.2–7.7 (m, 10 H).

(*E,Z*)-1-Bromo-4-chloro-1,4-diphenyl-1,3-butadiene (11*EZ*). Crystalline erythro dibromide (3.42 g) was heated with stirring at 55 °C for 0.5 h with 50 mL of absolute ethanol containing 7 mL of a 1.5 N ethanolic KOH solution. The reaction mixture was poured into ether and acidified (0.05 N HCl) water. The ether layer was washed with saturated NaCl solution and dried (Na_2SO_4). Removal of solvent gave an oil which was dissolved in pentane and allowed to crystallize, giving 2.22 g (81%) of **11*EZ***: mp 50–51 °C; NMR δ 6.64 (d, J = 11 Hz, H_3), 7.32 (d, J = 11 Hz, H_2), 7.1–7.6 (m, 11 H). Anal. Calcd for $C_{16}H_{12}BrCl$: C, 60.12; H, 3.79. Found: C, 60.11; H, 3.85.

(*Z,Z*)-1-Bromo-4-chloro-1,4-diphenyl-1,3-butadiene (11*ZZ*). The oily mother liquor from the dibromide crystallization (2.32 g of 18/82 erythro/threo) was stirred at room temperature for 3 h with 30 mL of ethanol containing 5.5 mL of 1.5 N ethanolic KOH solution. The reaction mixture was worked up as for **11*EZ***, and the product was crystallized from ether–pentane and from ethanol, giving 0.72 g (35%) of **11*ZZ***: mp 107.5–108.0 °C; NMR δ 7.24 (d, J = 11 Hz, H_3), 7.38 (d, J = 11 Hz, H_2), 7.1–7.8 (m, 12 H). Anal. Calcd for $C_{16}H_{12}BrCl$: C, 60.12; H, 3.79. Found: C, 60.22; H, 3.84.

(*Z,Z*)- and (*Z,E*)-1-Chloro-1,4-diphenyl-1,3-butadienes (22). To a solution of 50 mg (0.16 mmol) of **11*EZ*** or **11*ZZ*** dissolved in 1 mL of ether under nitrogen at 0 °C was added 0.10 mL (0.24 mmol) of 2.37 M *n*-butyllithium solution. After 10 min, 0.5 mL of methanol was added, and the solution was poured into ether and water. The ethereal layer was washed with saturated NaCl solution and solvent was removed. From **11*ZZ*** the (*Z,E*)-chlorodiene is obtained: mp 111–112 °C (lit.[26] 114–5 °C); NMR δ 6.60 (d, J = 16 Hz, H_4), 6.91 (d, J = 11 Hz, H_2), 7.0–7.7 (m, 11 H). From **11*EZ***, the (*Z,Z*)-chlorodiene is obtained: NMR AB part of ABX pattern, δ 6.63 (J_{AB} = 11 Hz, J_{AX} = 0, H_A), 6.68 (J_{AB} = 11 Hz, J_{BX} = 8 Hz, H_B), 7.0–8.0 (m, 11 H). Anal. Calcd for $C_{16}H_{13}Cl$: m/e 240.0706. Found: m/e 240.0707.

To confirm that the metallation–protonation sequence proceeds with retention of configuration, a metallation as above was carried out using **11*EZ***, and the organolithium was treated with 1,2-dibromoethane. The product was 93% isomerically pure **11*EZ*** by GLC analysis.

(*Z,Z*)- and (*E,Z*)-1,4-Dichloro-1,4-diphenyl-1,3-butadienes. To a solution of 80 mg (0.25 mmol) of **11*ZZ*** in 2 mL of ether under nitrogen at 0 °C was added 0.20 mL (0.26 mmol) of 1.19 M *n*-butyllithium solution. After 10 min 71 mg (0.30 mmol) of solid hexachloroethane was added and stirring was continued for 10 min. The solution was poured into a separatory funnel containing ether and saturated aqueous $NaHCO_3$. After the $NaHCO_3$ wash the ethereal layer was washed with saturated NaCl and dried (Na_2SO_4). The solvent was removed yielding (*Z,Z*)-1,4-dichloro-1,4-diphenyl-1,3-butadiene identical to that prepared previously:[13] ^{13}C NMR δ_{Me_4Si} ($CDCl_3$) 137.60 (s, ipso), 136.25 (s, 1), 129.18 (d, para), 128.50 (d, meta), 126.58

(d, ortho), 129.6 (d, 2).

The *E,Z* isomer was prepared in an analogous manner from 11*EZ*: NMR δ 6.71, 7.05 (ABq, J = 11 Hz, 2 H), 7.1–7.6 (m, 10 H); ^{13}C NMR δ_{Me_4Si} ($CDCl_3$) 137.40 (s, ipso), 137.13 (s, ipso'), 136.87 (s, 1), 134.21 (s, 4), 129.30 (d, para'), 129.22 (d, ortho), 128.90 (d, para), 128.39 (d, meta, meta'), 126.39 (d, ortho'), 125.48 (d, 2), 121.23 (d, 3).

1,4-Diphenyl-1-butanone-*2,2-d* (17b). A solution of 15.0 g of 1,4-diphenyl-1-butanone and 0.3 g of $NaOCH_3$ in 70 mL of dry tetrahydrofuran and 15 mL of D_2O was refluxed for 4 h and poured into 200 mL of ether and 200 mL of water. The aqueous layer was extracted with 2 × 100 mL of ether, and the combined ethereal extracts were washed with saturated NaCl solution and dried (Na_2SO_4). The solvent was removed and the extent of deuteration was checked mass spectrometrically. Four deuterations as above, followed by crystallization from hexane, gave 14.5 g (97% yield) of ketone, 98.8% d_2.

(*E,Z*)- and (*Z,Z*)-1-Bromo-4-chloro-1,4-diphenyl-1,3-butadiene-*3-d* (11b*EZ* and 11b*ZZ*). 1,4-Diphenyl-1-butanone-*2,2-d_2* was converted to the isomeric deuterated dienes as for the undeuterated compounds. In the first step (treatment with PCl_5) 30% of the 1,1-dichloro-1,4-diphenylbutane-*2,2-d_2* is formed (less than 5% of this compound is formed in the undeuterated series). Treatment with zinc to remove 1,1,2-trichloro-1,4-diphenylbutane converted the dichloride to 1,4-diphenylbutane, and hence only 11% yield of the deuterated vinyl chloride was obtained.

Compounds 11b*EZ* and 11b*ZZ* were each 98 ± 1% d_1 (mass spectra). The NMR spectrum showed no detectable proton absorption at the chemical shift of H_3.

Preparative Silver-Assisted Solvolysis of 11*EZ*. A mixture of 5.6 g (17.5 mmol) of 11*EZ*, 3.0 g of AgOAc, 5.7 g of $AgBF_4$, 5 mL of acetic anhydride, and 100 mL of acetic acid was refluxed for 45 min. The bulk of the acetic acid was distilled under vacuum and 200 mL of 2:1 ether–pentane and 50 mL of saturated NaCl solution were added. The mixture was stirred for 10 min and filtered through celite. The organic layer was washed with 5% Na_2CO_3 (2×) and saturated NaCl solutions and dried (Na_2SO_4). Solvent was removed and the residue was adsorbed on 25 g of silica gel and chromatographed on 250 g of silica gel. The column was eluted first with pentane and then with increasing amounts of ether in pentane up to 7.5% ether. Unreacted 11*EZ* was eluted first followed by the acetylene 9*Z*. Pure acetylene fractions were combined and crystallized from pentane: mp 81–82 °C, NMR δ 6.41 (s, 1 H), 7.1–7.7 (m, 10 H); IR ($CHCl_3$) 2188 cm^{-1}. Anal. Calcd for $C_{16}H_{11}Cl$: C, 80.50; H, 4.65. Found: C, 80.57; H, 4.76.

Further elution gave 2.8 g (53%) of a mixture of enol acetates 21*EZ* and 21*ZZ*, with the early fractions being pure 21*EZ* and the last fractions pure 21*ZZ*. Each isomer was crystallized from pentane. 21*EZ*: mp 66–67 °C; NMR δ 2.17 (s, 3 H), 6.58, 6.84 (ABq, J = 11 Hz, H_2, H_3), 7.1–7.7 (m, 10 H); IR ($CHCl_3$) 1775 cm^{-1}. Anal. Calcd for $C_{18}H_{15}ClO_2$: C, 72.36; H, 5.06. Found: C, 72.35; H, 5.04. 21*ZZ*: mp 97–98 °C; NMR δ 2.26 (s, 3 H), 6.81, 6.91 (ABq, J = 11 Hz, H_3, H_2), 7.1–7.7 (m, 10 H); IR 1770 cm^{-1}. Anal. Calcd for $C_{18}H_{15}ClO_2$: C, 72.36; H, 5.06. Found: C, 72.42; H, 4.97.

The stereochemistry of 21*EZ* and 21*ZZ*, as well as the identity of the protons H_2 and H_3, was assigned with the aid of Eu(DPM)$_3$ using the method developed by Kelsey.[14] For 21*EZ* ΔOAc/ΔH_2 was 1.3 and ΔOAc/ΔH_3 was 2.0. For 21*ZZ* ΔOAc/ΔH_2 was 2.2 and ΔOAc/ΔH_3 was 1.6. These values were compared to those found for (*E*)- and (*Z*)-1-acetoxy-1-phenylpropene. For the *E* isomer ΔOAc/ΔH was 1.4 and for the *Z* isomer ΔOAc/ΔH was 2.2.

(*Z*)-4-Chloro-1,4-diphenyl-3-buten-1-one (24a*Z*). To a solution of 16 mL of 2.0 M methyllithium (32 mmol) in 100 mL of ether at 0 °C was added a solution of 2.6 g (8.7 mmol) of mixed enol acetates 21*EZ* and 21*ZZ* in 10 mL of ether. The solution was stirred for 10 min at 0 °C, 1.5 mL of ethyl acetate was added, and the reaction mixture was poured into ice water. The organic layer was washed with saturated NaCl solution and dried and solvent was evaporated. The crude solid is pure by NMR analysis but is somewhat unstable and was used without purification. Crystallization from ether–pentane gives a yellow solid: mp 74–75 °C, NMR δ 4.01 (d, J = 6 Hz, 2 H), 6.62 (t, J = 6 Hz, 1 H), 7.1–7.8 (m, 8 H), 7.93 (dd, J = 9, 2 Hz, 2 H); IR ($CHCl_3$) 1680 cm^{-1}.

Anal. Calcd for $C_{16}H_{13}ClO$: C, 74.85; H, 5.10. Found: C, 74.85; H, 5.09.

(*E,Z*)- and (*Z,Z*)-1-Bromo-4-chloro-1,4-diphenyl-1,3-butadiene-*2-d* (11a*EZ* and 11c*ZZ*). A solution of 2.3 g (9.0 mmol) of (*Z*)-4-chloro-1,4-diphenyl-3-buten-1-one in 10 mL of dichloromethane was stirred with 209 mg of Na_2CO_3 in 5 mL of D_2O for 20 h. The organic layer was separated and dried (Na_2SO_4) and solvent was evaporated. The extent of deuteration was checked by NMR. This procedure was repeated three more times, giving 2.2 g of dideuterated ketone, 95% deuterated at the 2 position.

A solution of 2.1 g (8.1 mmol) of (*Z*)-4-chloro-1,4-diphenyl-3-buten-1-one-*2,2-d_2* in 20 mL of ether was added at 0 °C to 100 mL of ether containing 0.320 g (8 mmol) of $LiAlH_4$. The solution was stirred at 25 °C for 1 h and then transferred to a solution of 4 g of NH_4Cl in 100 mL of ice water. The ether portion was washed with saturated NaCl solution and dried (Na_2SO_4) and solvent was removed. The residue was chromatographed on 100 g of silica gel using 10–20% ether–pentane as eluant, giving 1.7 g of (*Z*)-4-chloro-1,4-diphenyl-3-buten-1-ol-*2,2-d_2*. The NMR spectrum of the undeuterated material, prepared as above, was δ 2.3 (bs, 1 H), 2.77 (t, J = 7 Hz, 2 H), 4.78 (t, J = 7 Hz, 1 H), 6.19 (t, J = 7 Hz, 1 H), 7.1–7.6 (m, 10 H). In the deuterated compound the multiplet at 3.1 was absent, and the triplets at δ 4.59 and 6.05 appeared as broad singlets.

The alcohol prepared above (1.6 g, 6.1 mmol) was converted to the bromide ((*Z*)-1-bromo-4-chloro-1,4-diphenyl-3-butene-*2,2-d_2*) by stirring for 13 h in 40 mL of ether containing 0.7 mL of PBr_3. Water was added, and the ethereal layer was washed with saturated $NaHCO_3$ and NaCl solutions and dried (Na_2SO_4). The solvent was removed and the residue was dissolved in 25 mL of CCl_4 and chromatographed rapidly on 8 g of silica gel, giving 1.6 g of bromide. The undeuterated compound, prepared as above, had NMR δ 3.2 (m, 2 H), 5.02 (t, J = 7.2 Hz, 1 H), 6.08 (t, J = 6.8 Hz, 1 H), 7.0–7.8 (m, 10 H). In the deuterated compound the multiplet at δ 3.2 was absent, and the triplets at δ 5.02 and 6.08 were broad singlets.

The deuterated bromide prepared above (1.6 g, 4.9 mmol) was refluxed in 50 mL of CCl_4 for 17 h with 2.6 g (15 mmol) of *N*-bromosuccinimide and 12 mg of benzoyl peroxide. NMR analysis showed 75% conversion to dibromides. The bromination was continued by refluxing for 11 h in CCl_4 with 1.0 g of *N*-bromosuccinimide and 11 mg of benzoyl peroxide. NMR analysis showed a 75:25 mixture of erythro–threo dibromides. These were separated and converted to pure (*E,Z*)- and (*Z,Z*)-1-bromo-4-chloro-1,4-diphenyl-1,3-butadiene-*2-d* (97 ± 1% d_1) as described for the undeuterated compounds.

Solvolysis of (*E,Z*)-1-Bromo-4-chloro-1,4-diphenyl-1,3-butadiene. In AcOH. To 31 mg of 11*EZ*, 22.9 mg of AgOAc, and 38.3 mg of $AgBF_4$ was added 2 mL of AcOH containing 0.1 mL of Ac_2O. The mixture was refluxed for 4.5 h and cooled and 2.0 mL of a CCl_4 solution containing 1.10 mg/mL of di-*n*-butyl phthalate was added. The contents of the flask were added to a stirred flask containing 20 mL each of 5% Na_2CO_3 solution, saturated NaCl solution, ether, and pentane. After 15 min the mixture was filtered through celite, the organic layer was washed with 5% Na_2CO_3 solution and dried, and solvent was removed. The residue was dissolved in 3 mL of CCl_4 and analyzed by GLC at 185 °C. Response factors were determined using standard mixtures. Retention times for 9*Z*, 11*EZ*, 21*EZ*, 11*ZZ*, and 21*ZZ* were 4.2, 6.6, 8.2, 10.0, and 11.2 min, respectively. In the case of the deuterated isomers the reaction mixture was examined by NMR (Varian XL-100 with noise-modulated deuterium decoupling) to determine the extent of scrambling in the acetates (the vinyl protons were all well separated sharp singlets). The vinylacetylene was separated either by TLC or preparative GLC at 200 °C and analyzed for deuterium content by mass spectrometry. Analyses of three aliquots of a sample from solvolysis of 11b*EZ* (one purified by TLC, the second crystallized after the purification, and a third collected by GLC) were 78.5, 79.2, and 78.6% deuterium.

In Ac_2O. The solvolysis procedure was generally the same, except that the solvent was Ac_2O containing 1% AcOH, and the reaction was kept at 80 °C in a thermostated bath for 8–12 h.

Solvolysis of (*Z,Z*)-1-Bromo-4-chloro-1,4-diphenyl-1,3-butadiene (11*ZZ*). To 11.0 mg of 11*ZZ*, 5.6 mg of AgOAc, and 17.7 mg of $AgBF_4$ was added 2 mL of AcOH containing 0.1 mL of Ac_2O. The mixture was refluxed with stirring under N_2 for 12 h. Workup was the same as for the *E,Z* isomer. The crude product mixture was separated by preparative TLC into hydrocarbon and acetate fractions. Two milliliters of CCl_4 solution containing 1.988 mg of di-*n*-butyl phthalate was added to each fraction. Each fraction was analyzed by GLC. The estimated errors for the determination of the product yields are ±1% for 11*EZ* and ±2% for 11*ZZ*. This variation in yield is caused by decomposition during the reaction. The errors are larger for 11*ZZ* because of longer reaction time. The analysis of the products from the deuterated compounds was the same as for the *E,Z* isomer.

(*E*)-1-Phenyl-1-propene. Propiophenone was reduced to 1-phenyl-1-propanol with $LiAlH_4$. The alcohol was eliminated by distillation from $NaHSO_4$.[27] The olefin was obtained in 78% yield, pure by NMR and greater than 95% isomerically pure.

1,2-Dibromo-1-phenylpropane. (*E*)-1-Phenyl-1-propene was treated with Br_2 in CCl_4 at 0 °C.[10b] The crystalline residue after evaporation of the CCl_4 is a mixture of diastereomers erythro–threo about 5:1. The erythro isomer can be crystallized to purity, mp 66–67

°C. Erythro: NMR δ 2.04 (d, J = 6 Hz, 3 H), 4.54 (dq, J = 11, 6 Hz, 1 H), 5.00 (d, J = 11 Hz, 1 H), 7.37 (m, 5 H). Threo: NMR δ 1.65 (d, J = 7 Hz, 3 H), 5.17 (d, J = 5 Hz, 1 H) in the mixture.

(*E*)-1-Bromo-1-phenyl-1-propene (29*E*). *erythro*-1,2-dibromo-1-phenylpropane was dehydrohalogenated with alcoholic KOH at 55 °C to give 91% of (*E*)-1-phenyl-1-propene, 1% of (*Z*)-1-phenyl-1-propene, and 8% of 2-bromo-1-phenyl-1-propene. The vinyl bromide was stored in dry ice at −78 °C because it isomerized in the freezer at −20 °C.

The 2-deuterated bromide was made in an analogous manner starting with deuterated propiophenone.

Solvolysis of (*E*)-1-Bromo-1-phenyl-1-propene in AcOH. A mixture of 19 mg of **29*E***, 23 mg of AgOAc, 48 mg of $AgBF_4$, 1 mL of AcOH, and 0.1 mL of Ac_2O was stirred in a sealed tube at 70 °C for 0.5 h. The reaction mixture was worked up and analyzed by GLC. The relative retention times were 3.4 min for **31**, 5.9 min for **29*E***, 7.4 min for **30*E***, and 8.4 min for **30*Z*** with the temperature programmed at 4 °C per min 40–100 °C.

Photochemical Isomerization of 9*Z* to 9*E*. A solution of 70 mg of **9*Z*** in 3 mL of cyclohexane was irradiated with a Hanovia high-pressure Hg lamp through Pyrex for 0.5 h. GLC analysis showed a 56:44 ratio of *E*/*Z* isomers. The two isomers were separated by preparative TLC. The *E* isomer was eluted slightly faster with pentane: NMR δ 6.28 (s, 1 H), 7.2–7.5 (m, 8 H), 7.9–8.1 (m, 2 H); IR 2182 cm^{-1}. Anal. Calcd for $C_{16}H_{11}Cl$: *m/e* 238.0549. Found: *m/e* 238.0551.

Elimination of a Mixture of 9*Z* and 9*E*. Relative Rates. A 74-mg mixture of **9*Z*** and **9*E***, 21:79, was stirred at room temperature in 5 mL of EtOH containing 0.5 mL of 1.5 N KOH in EtOH. After 58 h 97% of the *Z* isomer and only 7% of the *E* isomer had been converted to diphenyldiacetylene. This gives a relative rate of elimination k_Z/k_E = 66. 1,4-Diphenylbutenyne (30 mg) was used as a standard in the GLC analysis.

(*E,E*)-1-Bromo-4-chloro-1,4-diphenyl-1,3-butadiene (11*EE*). To 15 mL of ether was added 0.04 mL of *n*-butyllithium (1.58 M in hexane) followed by 0.367 g (1.0 mmol) of (*E,E*)-1,4-dibromo-1,4-diphenyl-1,3-butadiene (**32*EE***).[13] After the solid had dissolved, the solution was cooled to 0 °C and 0.76 mL of *n*-butyllithium was added dropwise with magnetic stirring. After 3 min 263 mg(1.1 mmol) of hexachloroethane was added, the cooling bath was removed, and after 10 min the reaction was worked up. The solid was crystallized from hexane: 227 mg; 71% yield; mp 108–9 °C. Anal. Calcd for $C_{16}H_{12}BrCl$: *m/e* 317.9811. Found: *m/e* 317.9808.

Solvolysis of (*E,E*)-1-Bromo-4-chloro-1,4-diphenyl-1,3-butadiene. To 0.133 g of **11*EE***, 0.489 g of $AgBF_4$, and 0.065 g of AgOAc was added 8 mL of AcOH and 0.4 mL of Ac_2O. The mixture was stirred at reflux for 75 min. After the usual workup, the products were partially separated by preparative TLC. The plate was eluted with 5% ether–pentane three times. The solvolysis was run to 70% completion and the recovered yield was 68%. The volatile products consisted of 10% **9*E***, separated from starting material by GLC, and two acetates. The minor acetate, **21*EE***, 18% of the product mixture, was separated from **21*ZE*** by GLC: mp 68–69 °C (hexane); NMR δ 2.08 (s, 3 H), 5.98, 6.58 (Abq, J = 11.9 Hz), 7.1–7.6 (m, 10 H); IR 1766 cm^{-1}. Anal. Calcd for $C_{18}H_{15}ClO_2$: *m/e* 298.0760. Found: *m/e* 298.0758. The major acetate, **21*ZE***, comprised 72% of the product mixture: mp 71–2 °C (hexane); NMR δ 2.29 (s, 3 H), 6.30, 6.52 (ABq, J = 11.6 Hz), 7.0–7.5 (m, 10 H); IR 1768 cm^{-1}. Anal. Calcd for $C_{18}H_{15}ClO_2$: *m/e* 298.0760. Found: *m/e* 298.0756. The structure of the acetates was confirmed by cleavage to the ketone, **24a*E***, with methyllithium; mp 27–30 °C; NMR δ 3.68 (d, J = 7.5 Hz, 2 H), 6.30 (t, 7.5 Hz, 1 H), 7.2–7.6 (m, 8 H), 7.84 (dd, J = 8, 2.5 Hz, 2 H); IR 1685 cm^{-1}. Anal. Calcd for $C_{16}H_{13}ClO$: *m/e* 256.0655. Found: *m/e* 256.0653.

Preparation and Solvolysis of the Vinyltriazene (36*ZZ*) from 11*ZZ*. To a stirred flask under nitrogen containing 2 mL of ether was added 0.03 mL of *n*-butyllithium solution (1.65 M) followed by 149 mg (0.47 mmol) of **11*ZZ***. The solution was cooled to −10 °C and 0.31 mL of *n*-butyllithium solution (0.51 mmol) was added dropwise. After a few minutes 66 mg (0.56 mmol) of phenyl azide was added dropwise causing the solution to turn deep-red in color. After 5 min this solution was added with a syringe to a stirred flask containing 20 mL of AcOH and 1 mL of Ac_2O. The AcOH solution was poured into a separatory funnel containing 25 mL of ether, 25 mL of pentane, and 50 mL of 0.5 N HCl solution. The organic layer was washed three times with 50 mL of water followed by 5% Na_2CO_3 solution and saturated NaCl solution. The organic layer was dried (Na_2SO_4) and solvent was removed. The crude product mixture was separated by preparative TLC with 5% ether–pentane elution yielding in order of increasing polarity: fraction 1, 4 mg of **11*ZZ*** (3%); fraction 2, 25 mg, an 8:3 mixture of **22*ZE*** (15%) and **9*Z*** (6%); fraction 3, 16 mg of **21*EZ*** (12%); fraction 4, 33 mg of **21*ZZ*** (24%). The overall recovery was 60%.

Preparation and Solvolysis of the Vinyltriazene (37*ZZ*) from 33*ZZ*.[13] To a stirred flask under nitrogen containing 3 mL of ether was added 0.03 mL of *n*-butyllithium solution (1.65 M) followed by 302 mg (0.91 mmol) of **33*ZZ***. The solution was cooled to −10 °C and 0.62 mL of *n*-butyllithium solution (1.02 mmol) was added dropwise. After a few minutes 128 mg (1.08 mmol) of phenyl azide was added dropwise (deep-red color). After 5 min this solution was added by syringe to a stirred flask containing 40 mL of AcOH, 2 mL of Ac_2O, and 0.35 g of NaOAc (0.1 M NaOAc solution). The workup was as described above for the solvolysis of the triazene from **11*ZZ***. The results were similar when NaOAc was omitted from the AcOH quench. The crude product mixture was purified by preparative TLC with 5% ether–pentane elution three times. The overall recovery was 80%. Four fractions were removed from the plate in order of increasing polarity:

Fraction 1, 10 mg, containing a 1:1 mixture of 1,4-diphenylbutadiene (3%) and (*Z,E*)-1-methylthio-1,4-diphenyl-1,3-butadiene (2%) (NMR δ 2.01 (s, 3 H), 6.54 (d, J = 10.7 Hz, H_2), 6.55 (d, J = 15.8 Hz, H_4), 7.0–7.6 (m, 11 H)) was identical to the material prepared by lithiation of **33*ZZ*** and quenching with water.

Fraction 2, 25 mg, was mainly 39*Z* (11%) containing a small amount of **35** (1%). This fraction was further separated by preparative TLC elution with pentane four times to yield in order of decreasing polarity 22 mg of **39*Z*** (NMR δ 2.14 (s, 3 H), 5.94 (s, 1 H), 7.2–7.6 (m, 10 H), IR 2180 cm^{-1}. Anal. Calcd for $C_{17}H_{14}S$: *m/e* 250.0816. Found: *m/e* 250.0815) and **35** which was purified by preparative GLC to yield 2 mg, mp 151–152 °C (lit.[17] mp 153–154 °C). This material also had identical TLC R_f and GLC retention time with authentic 2,5-diphenylthiophene (**35**). Anal. Calcd for $C_{16}H_{12}S$: *m/e* 236.0660. Found: *m/e* 236.0656.

Fraction 3, 159 mg, contained three thio acetates: 38*ZZ* 42%, **38*EZ*** 15%, **38*EE*** 2%. This mixture was further separated by preparative TLC, elution with 7.5% ether–pentane four times, to yield, in order of decreasing polarity, pure **38*ZZ*** which was crystallized from ether–pentane: mp 121–122 °C; NMR δ 2.03 (s, 3 H), 2.23 (s, 3 H), 6.54, 7.18 (ABq, J = 11 Hz, 2 H), 7.3–7.7 (m, 10 H); IR 1770 cm^{-1}. Anal. Calcd for $C_{19}H_{18}O_2S$: C, 73.52; H, 5.84. Found: C, 73.59; H, 5.88. This thio acetate was identical by NMR to that formed in 20% yield by treatment of **33*ZZ*** sequentially with *n*-butyllithium (−78 °C), MoOPH (−78 °C), and Ac_2O (−78 to 25 °C). No other isomeric thio acetate was detected in this oxidation of the vinyllithium derivative. Preceding **38*ZZ*** on the plate, **38*EZ*** was eluted: NMR δ 2.02 (s, 3 H), 2.15 (s, 3 H), 6.60, 6.80 (ABq, J = 11 Hz, 2 H), 7.2–7.6 (m, 10 H); IR 1767 cm^{-1}. Anal. Calcd for $C_{19}H_{18}O_2S$: *m/e* 310.1027. Found: *m/e* 310.1033. The minor isomer, **38*EE***, could not be obtained in pure form and was eluted along with **38*ZZ***. It was tentatively identified as the *E,E* isomer in the NMR spectrum of the mixture having an AB quartet at δ 5.84, 6.22 (J = 11.5 Hz).

Fraction 4, 24 mg, 9%, contained a fourth thio acetate, **38*ZE***: NMR δ 2.19 (s, 3 H), 2.30 (s, 3 H), 6.23, 6.31 (ABq, J = 11 Hz, 2 H), 7.0–7.6 (m, 10 H); IR ($CHCl_3$) 1760 cm^{-1}. Anal. Calcd for $C_{19}H_{18}O_2S$: *m/e* 310.1027. Found: *m/e* 310.1033. Photolysis of **38*ZZ*** gave this isomer (**38*ZE***).

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Registry No.—**8,** 65943-09-1; **9*E***, 65943-10-4; **9*Z***, 52516-81-1; **10*E***, 65943-11-5; **10*Z***, 65943-12-6; **11a*EZ***, 52516-75-3; **11a*ZZ***, 52516-76-4; **11a*EE***, 65943-13-7; **11b*EZ***, 65943-14-8; **11b*ZZ***, 65943-15-9; **11c*EZ***, 65943-16-0; **11c*ZZ***, 65943-17-1; **17a,** 5407-91-0; **17b,** 65943-18-2; **18*Z***, 52516-77-5; **18*E***, 65943-19-3; **19,** 65943-20-6; *erytho*-**20,** 52516-78-6; *threo*-**20,** 65943-21-7; **21a*EZ***, 52516-80-0; **21a*EZ***, 52516-79-7; **21*EE***, 65943-22-8; **21*ZE***, 65943-23-9; **22*ZE***, 14533-17-6; **22*ZZ***, 65943-24-0; **23,** 65943-25-1; **24a*Z***, 65942-93-0; **24a*E***, 65943-08-0; **24b*Z***, 65942-94-1; **27,** 65942-95-2; **28,** 65942-96-3; **29a*E***, 31076-47-8; **29b*E***, 65942-97-4; **30a*E***, 7642-42-4; **30a*Z***, 13266-91-6; **31,** 673-32-5; **32*EE***, 7641-45-4; **33*ZZ***, 55373-72-3; **33*ZE***, 65942-98-5; **35,** 1445-78-9; **36*ZZ***, 65943-06-8; **37*ZZ***, 65969-55-3; **38*ZZ***, 65942-99-6; **38*EE***, 65943-00-2; **38*EZ***, 65943-01-3; **38*ZE***, 65943-02-4; **39*Z***, 65943-03-5; 1-phenyl-1-butyn-3-one, 1817-57-8; 3-bromo-1-phenylpropane, 637-59-2; (*Z,Z*)-1,4-dichloro-1,4-diphenyl-1,3-butadiene, 55373-69-8; (*E,Z*)-1,4-dichloro-1,4-diphenyl-1,3-butadiene, 65943-04-6; 1,1-dichloro-1,4-diphenylbutane-2,2-d_2, 65943-05-7; (*E*)-1-phenyl-1-propene, 873-66-5; propiophenone, 93-55-0; 1-phenyl-1-propanol, 93-54-9; *erythro*-1,2-dibromo-1-phenylpropane, 21087-19-4; *threo*-1,2-dibromo-1-phenylpropane, 21087-20-7; (*Z,E*)-1-methylthio-1,4-diphenyl-1,3-butadiene, 65943-07-9; 1,4-diphenylbutadiene, 886-65-7.

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$$\%\ \text{D in } \mathbf{9}Z \text{ from } \mathbf{11b} = \frac{k_c}{k_c + k_{eH}}\left(\frac{R}{R+1}\right) + \frac{k_{eH}}{k_c + k_{eH}} = \left(\frac{1}{P_H + 1}\right)\left(\frac{R}{R+1}\right) + \frac{P_H}{P_H + 1}$$

$$\%\ \text{D in } \mathbf{9}Z \text{ from } \mathbf{11c} = \frac{k_c}{k_c + k_{eD}}\left(\frac{R}{R+1}\right) = \left(\frac{1}{P_D + 1}\right)\left(\frac{R}{R+1}\right)$$

where $R = k_H/k_D$ for deprotonation of chlorolium ion **13**; k_c = rate constant for **12** → **13**; k_{eH} = rate constant for **12** → **9Z**, k_{eD} = rate constant for **12** → **9Z** where **12** is deuterated; $P_H = k_{eH}/k_c$ and $P_D = k_{eD}/k_c$; and $P_H/P_D = k_{eH}/k_{eD}$, which is the isotope effect for deprotonation of vinyl cation **12**. To solve these equations, it is necessary to assume a value for either R or P_H/P_D. Once the equation is solved, the fraction of **9Z** formed from chlorolium ion is given by $1/(1 + P_H)$.
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Synthetic and Kinetic Studies on Tricarbonates and Dicarbonates[1]

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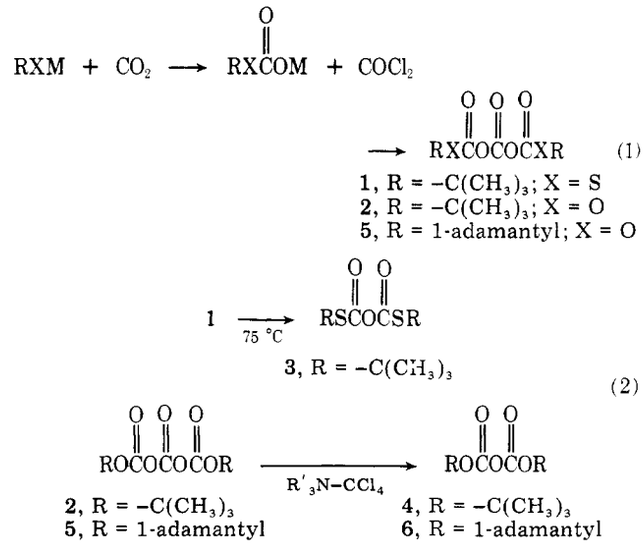
The synthesis and properties of di-1-adamantyl tricarbonate (**5**), dicarbonate (**6**), and monocarbonate (**7**) are described. The kinetics of the thermal conversion of **6** to **7** have been measured and the activation parameters determined. Some systematic errors in the previously reported kinetics of the tri- and dicarbonates **1**, **2**, **3**, and **4** are corrected and the mechanisms of the thermal reactions are discussed. Some substituted phenoxycarbonyl derivatives of amino acids, prepared from *tert*-butyl aryl dicarbonates, are described.

In earlier studies,[3-7] the preparation and reactions of a hitherto unknown class of compounds, the di-*tert*-butyl tricarbonates **1** and **2**, were described, along with convenient syntheses of the corresponding dicarbonates **3** and **4**. The utility of the latter for preparing *t*-BOC and thio-*t*-BOC derivatives of amino acids was pointed out;[8] the oxygen dicarbonate[4] has been widely adopted for this purpose,[9] and the reagent is commercially available[10] as well as readily synthesizable in the laboratory.[7,8] The present paper reports further studies on the novel tricarbonates and on other carbonate derivatives.

Di-1-adamantyl tricarbonate (**5**) was prepared as a pure crystalline compound from the sodium salt of 1-adamantanol as shown in eq 1. When heated to approximately 110 °C, **5** melted with decomposition to yield approximately 75% of 2 equiv of carbon dioxide and a mixture of di-1-adamantyl dicarbonate (**6**) and di-1-admantyl carbonate (**7**). Subsequent heating of this mixture above 150 °C led to the formation of only the monocarbonate **7** and 2 equiv of carbon dioxide. Attempts to effect the thermal stepwise transformation of **5** to **6** to **7** were not successful, although a variety of solvents and temperatures was utilized. Thermal decomposition of **5** always led to a mixture of **6** and **7** in addition to carbon dioxide. However, as was the case with **2**, reaction of **5** with a tertiary base in carbon tetrachloride gave solely the corresponding dicarbonate **6** (eq 2).

Examination of the decomposition of pure dicarbonate **6** at approximately 170 °C indicated that the monocarbonate



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