The Acid-Induced Reaction of Aryldiazomethanes with Olefins. Mechanism of Reaction[1a]

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The acid-induced reaction of aryldiazomethanes with olefins gives arylcyclopropanes in addition to olefins and esters. The cyclopropane products are formed stereospecifically and their yields are largest in reactions with olefins which on cation addition give secondary carbonium ion centers. Stereoisomeric mixtures of 3-methyl-4-aryl-2-butyl derivatives from reactions in *cis*- and *trans*-butene were found to arise probably by a preferential cis mode of addition. The use of deuterated acids leads to partial incorporation of deuterium in the cyclopropane adducts while the use of phenyldiazomethane-α-d_1 leads to partial loss of deuterium. The extent of deuterium incorporation is dependent on the strength of the acid used as well as the basicity of the aryldiazomethanes. A carbenoid mechanism of the reaction is proposed.

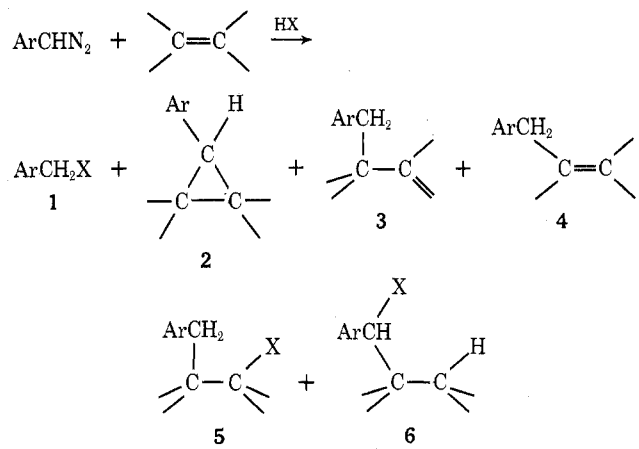
With the possible exception of diphenyldiazomethane, the detailed mechanism of the reactions of diazo compounds with acids is not well understood.[2] Apart from intrinsic interest, the mechanism of the reaction probably embraces the most common method of diazoalkylation used in organic synthesis while the formation of a diazonium ion intermediate makes it an important source of information for the understanding of the deamination of aliphatic amines and of other reactions proceeding by way of diazonium ions.[3] Interest in diazonium ions (or the carbonium ions derived from them) is due to their enhanced reactivity as compared to that of intermediates from solvolytic reactions. Studies of the acid-catalyzed reactions of diazo compounds are usually restricted to the more stable diaryldiazomethanes, diazo ketones, diazoacetic esters, and diazo sulfones. The reaction of the unstable alkyl and dialkyl diazo compounds with very weak acids (*e.g.*, hydroxylic solvents) could only be studied *via* the Bamford–Stevens reaction.[4] In many such reactions a clear distinction between the acid-catalyzed reaction (diazonium ion or carbonium ion intermediates) and the thermal reaction (carbene intermediate) cannot be made. A change in a carbonium ion mode of decomposition to that of a carbenic one has been encountered when a slight modification of the reaction conditions (*e.g.*, solvent change) is made. Thus the sodium salt of cyclopropanecarboxaldehyde tosylhydrazone decomposes in aprotic solvents *via* a carbene intermediate to give mainly cyclobutene, whereas in protic solvents a diazonium ion (or a carbonium ion derived from this) is formed leading to bicyclobutane as product.[5] Deuterium-labeling studies have supported the operation of these dual pathways.[6]

Results and Discussion

The acid-induced decomposition of aryldiazomethanes was studied with a large number of organic and inorganic acids in olefinic solvents. Most strong acids, *e.g.*, HI, HBr, HCl, CF_3COOH, and CCl_3COOH, reacted instantly with phenyldiazomethane at −70° but trifluoroacetic acid was found to be convenient for most of the work, since it has moderate solubility at low temperature in the solvents employed and the products obtained are readily isolable by gas–liquid partition chromatography (glpc). Furthermore, it is advantageous, as will be evident below, to have a relatively poor nucleophile as the trifluoroacetate ion. The major types of products obtained are illustrated in Scheme I and these consist of cyclopropanes, olefins, and esters.

For the series of olefinic solvents of varying nucleophilic strength, the more nucleophilic ones gave a 40–60% yield of a total mixture of cyclopropanes **2**, olefins **3** and **4**, and esters **5** (Table I). The poorly nucleophilic dichloro- and tetrachloroethylenes gave negligible amounts of addition products. The simple ester $ArCH_2X$ (**1**), as expected, is a major product, but the amount of this ester could be reduced somewhat by dilution of the reactants with the olefinic solvent. Likewise, dilution helps to eliminate formation of stilbenes and azines. Among the olefins which react, a marked variation in the distribution of products can also be seen (Table I). It is useful to distinguish the cyclopropane products from the olefins and esters which can be referred to as carbonium ion products. The general trend observed from the data obtained is that olefins which on cation addition would give a primary carbonium ion center did not give addition products, those that would give a secondary carbonium ion gave substantial amounts of cyclopropane adducts, and those that would give a tertiary or allylic carbonium ion gave mainly olefins and esters. While the formation of olefins and esters can readily be attributed to carbonium ion intermediates, cyclopropane formation may well have a different source and the possibility of the intervention of carbenes and carbenoid species has to be considered.

Scheme I



Further information was obtained from a detailed study of a series of aryldiazomethanes with 2-butene as solvent (Table II). The product distribution in each case is outlined in Scheme I; with *trans*-butene mainly **7**, **9**, and **11** are formed and *cis*-butene gives **8**, **9**, **10a**, and **11** as major products. It may be noted that the cyclopropane formation is completely stereospecific and when syn and anti isomers (**8a** and **8b**, respectively) are possible there appears to be no marked syn stereoselectivity except for the case of the *p*-methoxy substitution. High stereospecificity is also observed in the formation of olefin **10a** from *cis*-butene and **10b** (in low yield) from *trans*-butene. The ester **11**, however, was obtained as unequal mixtures of

Table I
Product Distribution from the Reaction of Phenyldiazomethane with Trifluoroacetic Acid in a Number of Olefinic Solvents[h]

Solvent	Yield,[a] % 2	3	4	5	6
Tetramethylethylene (563-79-1)	1	98 (13395-01-2)		1	
Isobutylene (111-11-7)	2	64 (6683-51-8)	20 (4489-84-3)	14 (51157-52-9)	
cis-Butene (590-18-1)	43.1 (1.0)[b]	21.6 (1647-06-9)	9.6[c]	23.4[d]	2.3
trans-Butene (624-64-6)	56.7 (7653-95-4)	7.5	Trace[e]	28.2[d]	7.5
1-Butene (106-98-9)	36.5 (1.1)[b]	20.5 (1745-16-0)	10.3 (27911-12-2)	28.8 (51157-53-0)	4.9
1,3-Butadiene[f] (106-99-0)			35 (51157-51-8)	65[g]	

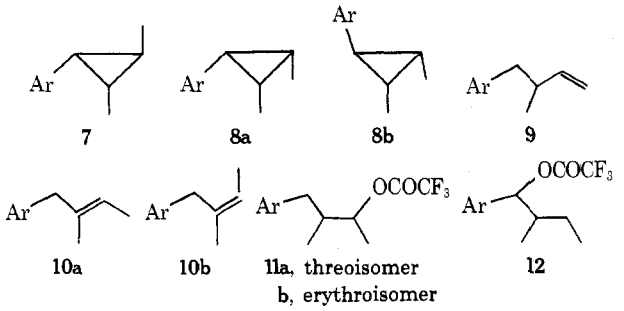
[a] Yields are in per cent of total adducts; benzyl trifluoroacetate is excluded. [b] Syn/anti isomer ratio. [c] Trans isomer **10a**. [d] Threo and erythro isomers. [e] Cis isomer **11b**. [f] 4-$ClC_6H_4CHN_2$ used. [g] Two isomers, 5-*p*-chlorophenyl-3-pent-2-enyl and 5-*p*-chlorophenyl-3-pent-1-enyl trifluoroacetates. [h] Registry numbers are in parentheses.

Table II
Relative Yields[a] of Major Products from the Reaction of Aryldiazomethanes with Trifluoroacetic Acid in 2-Butene[b]

$ArCHN_2$	2-Butene	7	8a	8b	9	10a	11
m-Cl (51157-54-1)	*trans*-	52.7 (51157-55-2)			18.2 (51202-20-1)		29.1 (51157-63-2)
p-Cl (19277-54-4)	*trans*-	59.7 (51157-56-3)			19.6 (51157-59-6)		20.7 (51157-64-3)
H (766-91-6)	*trans*-	61.2			8.1		30.5 (51202-23-4)
p-Me (23304-24-7)	*trans*-	66.0 (51157-57-4)			12.8 (51157-60-9)		21.2 (51157-65-4)
p-MeO (23304-25-8)	*trans*-	72.3 (51157-58-5)			4.6		23.1 (51157-66-5)
m-Cl	*cis*-		14.5 (51259-41-7)	14.7 (51259-45-1)	25.0	16.4 (51157-61-0)	29.4 (51157-67-6)
p-Cl	*cis*-		11.2 (51259-42-8)	15.3 (51259-46-2)	25.0	16.8 (51157-62-1)	31.7 (51157-68-7)
H	*cis*-		22.2 (7653-96-5)	21.9 (25181-26-4)	22.1	9.8	24.0 (51157-69-8)
p-Me	*cis*-		19.4 (51259-43-9)	19.6 (51259-47-3)	23.9	10.0 (51202-22-3)	21.5 (51157-70-1)
p-MeO	*cis*-		52.5 (51259-44-0)	9.0	13.9	3.2	21.5 (51157-71-2)

[a] Yields as determined by glpc are in per cent of the total major addition products listed. Hydride shift ester **12**, not listed in the table, is formed in 2–7% yield. [b] Registry numbers are in parentheses.

threo and erythro isomers, indicating partial stereospecificity.

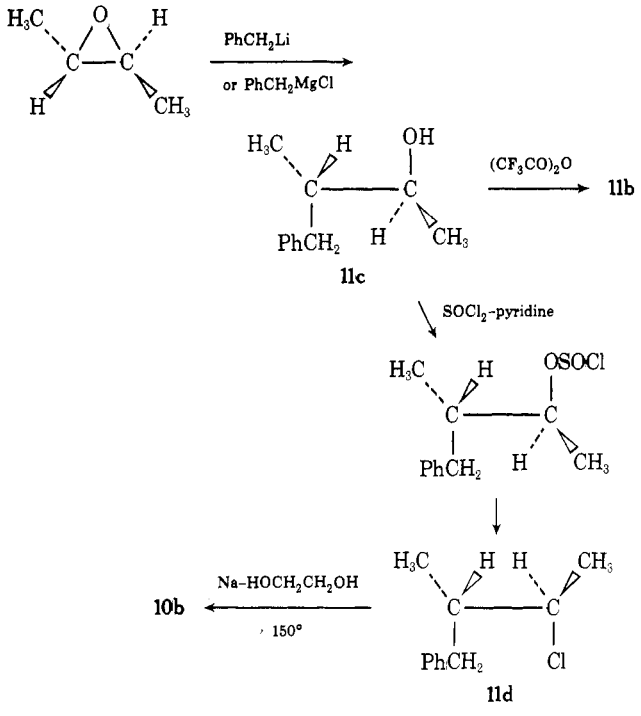


7 8a 8b 9 10a 10b 11a, threoisomer b, erythroisomer 12

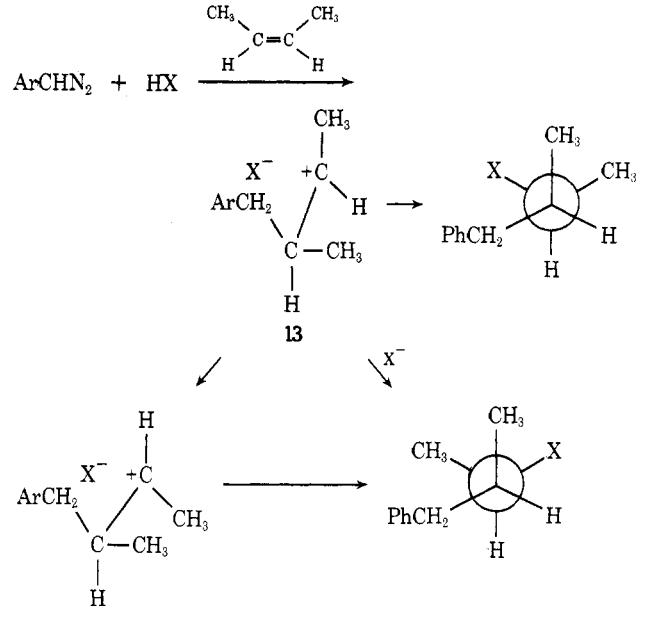
It was of interest to determine the exact stereochemistry of the trifluoroacetate esters (**11**) obtained from the reactions. From each reaction the unequal amounts of the stereoisomers can readily be detected by nmr spectra and the corresponding alcohol or halide derivatives can be separated by glpc. As the relative proportions of product obtained from reaction in *trans*-butene were opposite to those obtained from *cis*-butene, there appears to be a slightly preferred mode (*i.e.*, whether cis or trans) of addition to the olefin. According to the available literature[7] on electrophilic additions to double bonds, one would be led to believe that a trans mode of addition would be preferred for bridged ion intermediates, but on the other hand recent literature has revealed that there are instances of electrophilic cis additions.[8] Although the chemical shifts of the methyl groups of the stereoisomeric esters **11a** and **11b** differ from each other, a direct assignment of stereochemistry based on preferred conformations may not be unambiguous and it was desirable to establish this by direct synthesis as shown in Scheme II.

The key step in this synthesis is a stereospecific epoxide ring opening which has been established to be of trans mode.[9] Thus *trans*-2-butene epoxide reacts with benzyllithium or benzylmagnesium chloride to give the erythro alcohol **11c**, which can subsequently trifluoroacetylated to give **11b**. The conversion of alcohols to chlorides by thionyl chloride in pyridine usually proceeds with inversion[10] and the high stereospecificity obtained in the present chloride **11d** indicates that this case is no exception. The stereospecific synthesis of **11d** also allows the stereochemical identity of olefins **10a** and **10b** to be correctly assigned. Thus trans elimination of **11d** gives the olefin **10b**. The nmr spectra of the olefins also agrees with the above assignment; the methylene protons of **10a** (δ 3.3) have a

Scheme II



Scheme III



broader half-width than those of **10b** (δ 3.2). This follows from the general observation that the long-range coupling constants of allylic protons to the olefinic proton are greater when they are cis to the latter than when they are trans.[11]

The synthesized alcohol **11c** and the corresponding trifluoroacetate **11b** have structures identical with the major product of the acid-catalyzed addition of phenyldiazomethane to *cis*-butene, while the chloride **11d** is identical with the major product obtained from *trans*-butene. The stereochemistry and nmr data for a number of 3-methyl-4-aryl-2-butyl derivatives are given in Table III. The results obtained show that the mode of addition to 2-butene is preferentially cis. Such a result can be accommodated by postulating the formation of an ion pair intermediate **13**, assuming that the rate of collapse of the pair to form the erythro ester **11b** is faster than either diffusion of X^- to the rear side of the carbonium ion or the attack by an external nucleophile (Scheme III).

Deuterium-Labeling Studies. The fate of the acid proton was studied in a series of experiments carried out with deuterated acids. These acids reacted with phenyldiazomethane in olefinic solvents to yield cyclopropane derivatives of which 10–25% were monodeuterated while the carbonium ion products (esters and olefins) contained 60–80% deuterium. No dideuterated compounds were obtained. Although the deuterio acids used contained more than 95% deuterium, much less deuterium was found in the carbonium ion products even if an excess of the acid was used. However, this was not unexpected in view of the fact that protons are continuously generated in the olefin-forming pathway of the reaction. Another reason for the reduction of deuterium incorporation is a deuterium isotope effect of unknown magnitude[12] which would tend to discriminate against the reaction with deuterated acid.

Table III
Stereochemistry and Nmr[a] Data of 3-Methyl-4-aryl-2-butyl Derivatives $ArCH_2CH(Me)CH(Me)X$ from the Acid-Catalyzed Reactions of Aryldiazomethanes with 2-Butene[d]

Reactants	Ar	X	Threo isomer %[b]	Threo δ(3-Me)	Threo δ(1-Me)	Erythro isomer %[b]	Erythro δ(3-Me)	Erythro δ(1-Me)
trans-Butene + CF_3COOH (76-05-1)	H	CF_3COO	80	0.89	1.22	20	0.88	1.36
cis-Butene + CF_3COOH	H	CF_3COO	30	0.89	1.22	70	0.88	1.36
trans-Butene + HCl (7647-01-0)	H	Cl	95 (51157-72-3)	0.97	1.54	5	1.00	1.49
cis-Butene + HCl	H	Cl	19.5	0.97	1.54	80.5 (51157-73-4)	1.00	1.49
trans-Butene + HBr (10035-10-6)	H	Br	93.5 (51157-74-5)	1.02	1.77	6.5	1.03	1.73
cis-Butene + HBr	H	Br	11.5	1.02	1.77	88.5 (51157-75-6)	1.03	1.73
$PhCH_2CH(Me)COMe$ + $(i\text{-}PrO)_3Al$ (2550-27-8) (555-31-7)	H	OH	50 (1499-63-4)	0.85	1.22	50 (1499-64-5)	0.88	1.22
trans-Butene + CF_3COOH	*p*-Cl	CF_3COO	70	0.88	1.35	30	0.95	1.35
cis-Butene + CF_3COOH	*p*-Cl	CF_3COO	40	0.88	1.35	60	0.95	1.35
cis-Butene + CF_3COOH	*m*-Cl	CF_3COO	35	0.88	1.33	65	0.93	1.33
cis-Butene + CF_3COOH	*p*-Me	CF_3COO	45	0.87	1.33	55	0.95	1.33
cis-Butene + CF_3COOH	*p*-MeO	OH[c]	20 (51157-76-7)	0.78	1.14	80 (51157-77-8)	0.82	1.14

[a] Chemical shifts from approximately 15% solutions in carbon tetrachloride in parts per million downfield from internal tetramethylsilane standard. [b] Per cent of threo or erythro isomer as estimated by glpc or nmr spectrum. [c] From the saponified reaction mixture. [d] Registry numbers are in parentheses.

Table IV
A Comparison of the Deuterium Content of Cyclopropanes from the Reactions of Aryldiazomethanes with Deuterated Acids in Various Olefin Solvents

$ArCHN_2$	Acid	Solvent	Syn/anti isomer ratio	% Cyclopropane-d_1[a]
$PhCHN_2$	CF_3COOD	*trans*-Butene		29 ± 2
$PhCHN_2$	CF_3COOD	*cis*-Butene	1.0	28 ± 2
$PhCHN_2$	CF_3COOD	1-Butene	1.1	23 ± 2
$PhCHN_2$	CF_3COOD	Tetramethylethylene		17 ± 1
$PhCHN_2$	CF_3COOD	Tetramethylethylene and *trans*-butene[b]		20 ± 2[c] (24 ± 1)
$PhCHN_2$	CF_3COOD	*cis*-Butene and CH_2Cl_2[b]	0.83	24 ± 1
$PhCHN_2$	CF_3COOD	*cis*-Butene and tetrahydrofuran[b]	1.5	19 ± 1
$PhCHN_2$	$CH_2ClCOOD$	*cis*-Butene	0.97	27 ± 2
$PhCHN_2$	CCl_3COOD	*cis*-Butene	0.89	29 ± 1
$PhCHN_2$	DCl	*cis*-Butene	1.7	14 ± 2
$PhCHN_2$	DBr	*cis*-Butene	1.9	30 ± 1
$PhCHN_2$	DI	*cis*-Butene	2.3	44 ± 2
$PhCHN_2$	DCl	*trans*-Butene		16 ± 2
$PhCHN_2$	DBr	*trans*-Butene		29 ± 1
$PhCHN_2$	DI	*trans*-Butene		46 ± 1
m-$ClC_6H_4CHN_2$	CF_3COOD	*cis*-Butene	0.9	32 ± 2
p-$ClC_6H_4CHN_2$	CF_3COOD	*cis*-Butene	0.7	
p-$MeC_6H_4CHN_2$	CF_3COOD	*cis*-Butene	0.97	20 ± 1
p-$MeOC_6H_4CHN_2$	CF_3COOD	*cis*-Butene	5.7	6 ± 1
$PhCDN_2$	CF_3COOD	*trans*-Butene		85 ± 3
$PhCDN_2$	CF_3COOD	*cis*-Butene		83 ± 4
$PhCDN_2$	HCOOH	*cis*-Butene		80 ± 1

[a] Ratio of per cent cyclopropane-d_1 to per cent olefin-d_1, multiplied by 100. Values are from the mean of duplicate runs and errors given are average mean deviations from mass spectral intensity data. [b] 1:1 ratio by volume. [c] Determined on the adduct to tetramethylethylene; that in parentheses is for the adduct to *trans*-butene.

Although the deuterium content of the products varied slightly in every experiment, it was found that the ratio of the percentage of deuterated cyclopropane to that of the deuterated carbonium ion products was constant for the same acid and this ratio can therefore be used as a measure of the deuterium incorporation in the cyclopropane. Table IV shows the results for a number of reactions. It is clear that there is incorporation of deuterium from the acid into the cyclopropane but the extent is less than 50%, the exact value being dependent on the acid and diazo compound used. Similar results (Table IV) are obtained from experiments using phenyldiazomethane-α-d; in these cases there is incorporation of 15–20% protons from the acid into the cyclopropane product.

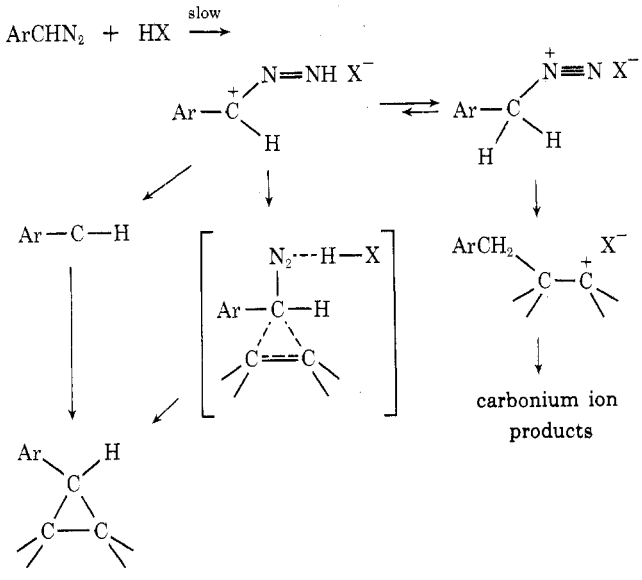
A rapid preequilibrium reaction between phenyldiazomethane and the acid may be excluded from the fact that an isolated sample of benzyl trifluoroacetate from the reaction of the diazo compound with deuteriotrifluoroacetic acid contained only the monodeuterated compound. Likewise the absence of dideuterated olefins and other esters demonstrates the same point. Preequilibration with acid, however, can occur with some diazo compounds, *e.g.*, diazomethane[13] and diazo esters.[14] Diazonium ions are probably important intermediates in these reactions; in fact, the direct observation by nmr spectroscopy of an aliphatic diazonium ion has been reported.[15] Proton exchange of a diazo compound with acid is governed by the stability of the diazonium ion formed as compared to that of the carbonium ion formed by the subsequent loss of nitrogen. Aryldiazomethanes in this respect would be similar to diazobutane[16] in that the reaction with deuterated acids yields only the monodeuterated ester. It follows that, if diazonium ions are intermediates in these reactions, their formation rather than the step involving loss of nitrogen is rate determining.

It is also of interest to compare the extent of deuterium incorporation in the cyclopropane product from the reactions of a series of aryldiazomethanes with deuterated acids. The results obtained (Table IV) show that there is a dependence of the deuterium incorporation on the nature of the acid used and on the substituent of the diazo compound. Theory has shown that in reactions involving proton transfer, *e.g.*, acid–base reaction, the nature of the transition state is very much dependent on the acid or base strength.[17] Thus in such reactions the extent of proton transfer in the transition state will vary according to the strength of both the acid and the base. The present experimental results are in agreement with this observation. Among the halogen acids the stronger acid cause a greater deuterium incorporation in the cyclopropane, although the carboxylic acids do not seem to cause much change. The latter result could be due to the small range of acidity or perhaps to the nature of the deprotonating counterions. Since the increase in acid strength can alter the deuterium content, a corresponding effect should be observed by changing base strength in the diazo compound (Table IV). Increasing base strength by substitution of p-methoxy group leads to very little deuterium incorporation.

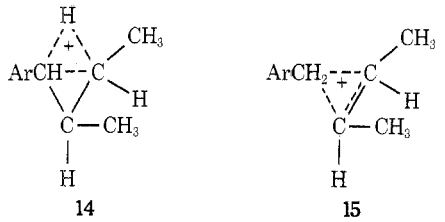
Mechanism of Cyclopropane Formation. Any mechanism formulated must be able to accommodate the following summary of experimental observations: (a) product distribution, (b) predominant cyclopropane formation only from olefins capable of forming secondary carbonium ions, (c) stereospecific cyclopropanation, (d) preferred syn mode of cyclopropanation, the extend being dependent on solvent and acid used, (e) partial incorporation of deuterium into cyclopropanes, (f) partial loss of deuterium in cyclopropane formation from phenyldiazomethane-α-d, and (g) dependence of the degree of deuterium incorporation in the cyclopropane on strength of acid as well as the basicity of the diazo compound.

First one may consider whether carbonium ions, which are clearly responsible for the formation of esters and olefins, are also responsible for the formation of cyclopropanes. Instances of cyclopropane formation *via* carbonium ions are known, but these are usually intramolecular reactions.[6,18] The open carbonium ion or ion pair **13** that

Scheme IV



yields stereoisomeric esters **11a** and **11b** is an unlikely intermediate, since unlike the esters the cyclopropanes are formed stereospecifically. It is of interest to consider whether protonated cyclopropane intermediates **14** and **15**

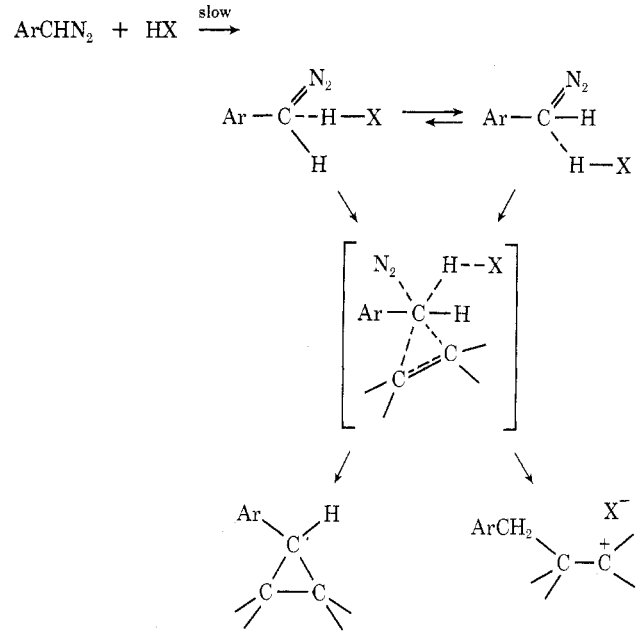


14 **15**

are involved. Evidence for protonated cyclopropane intermediates is well documentated;[19] the formation of the 1,3-hydride shift ester **12** in the present case may be directly attributed to the edge-protonated species **14.** However, the low yield of this ester makes this intermediate unlikely to be of great significance in cyclopropane formation. The incorporation of less than 50% deuterium in the cyclopropane product when the reaction is carried out with deuterated acid further excludes the possibility of this species. Moreover, except for perhaps the simplest unsubstituted protonated cyclopropane, edge-protonated cyclopropanes are of little importance owing to unfavorable 1,2-dialkyl interactions.[19] The species **14** in this system is therefore at most the transition state to the formation of the hydride shift ester **12.** Nonstereospecific formation of esters **11a** and **11b** argues against the symmetrical 1,2-bridged (or corner-protonated) intermediate **15,** while unique deuterium incorporation in the cyclopropane also rules it out. In fact, the incorporation of considerably less deuterium in the cyclopropane adducts than in the esters and olefins is the single most convincing evidence ruling out all the carbonium ion intermediates. If the intermediate precursor of the cyclopropane adducts is the same as that of the other carbonium ion products, the cyclopropanes should contain at least half the deuterium content of the other products even without considering the deuterium isotope effect. Estimates made of this isotope effect for deprotonation of bridged ions are in the order of three,[19a] in which case the cyclopropane should be expected to contain very much more deuterium. So, whereas the other products can be supposed to arise from discrete carbonium ions, the same cannot be true for the cyclopropane adduct.

Mechanisms not involving acid catalysis need not be considered; *e.g.*, thermolysis of aryldiazomethanes in solution to free carbenes does not occur at room temperature and would be less likely at the low temperatures of the experiments. Under the reaction conditions the diazo compounds are completely stable and reactions occur only after the introduction of acid. 1,3-Dipolar addition of the diazo compound to olefin is excluded for the same reasons.

Scheme V



The present results can be accommodated by mechanisms involving a slow proton transfer from the acid to the diazo compound. However, the complete transfer is slow or comparable with the rate of subsequent reactions. This is reasonable, since one might expect the reactivity of phenyldiazomethane to be intermediate to that of diazomethane and diphenyldiazomethane. Plausible mechanisms are illustrated in Schemes IV and V. In the former scheme, protonation at nitrogen is considered to be important in cyclopropane formation but it is difficult to decide whether the carbon or the nitrogen atom will first be protonated. It is clear, however, from the presence of deuterium in the cyclopropane product that protonation of the carbon has to take place at some stage. The formation of a free carbene is unlikely for a number of reasons. For reactions with *cis*-butene the syn/anti ratios of the cyclopropane adducts (Table IV) are not only different from those reported for free arylcarbenes[20] but they also change with the nature of acid or solvent used. These marked variations in syn stereoselectivity is usually indicative of carbenoid behavior rather than free carbene. Carbene formation from diazonium ions has been looked for but has not been found.[19,21] Without the carbene pathway Scheme IV can explain most of the experimental observations. However, it is difficult to explain why the use of tetramethylethylene or isobutylene as solvents should lead to low yields of cyclopropane adducts (Table I) even though the deuterium incorporation remains similar (Table IV).

Scheme V can explain the present experimental results adequately.[22] Partial deuterium incorporation from deuterated acids is possible from this mechanism and the extent of this deuterium incorporation will be dependent on the nature of both the acid and the diazo compound as observed. It is apparent that the transition state is carbenoid in character and in fact resembles that postulated for many of the known carbenoid reactions.[20] It may be noted that syn stereoselectivity is likely in this transition, espe-

cially with a *p*-methoxy substituent where maximum effect of the π-cloud participation would be possible.[20] The scheme also accounts for the predominance of carbonium ion products when tetramethylethylene or isobutylene are used as solvents as compared to butene solvents, since it is logical to expect that a change from secondary to tertiary carbon centers should favor more carbonium ion character than carbenoid character. Finally, it may be noted that the present system need not be considered as a unique case of acid-catalyzed cyclopropanation of olefins by diazo compounds not involving discrete carbenes or carbonium ions, but that it is one example of general behavior of diazo compounds toward Lewis acids or metal halides[20] and of the less well defined "protonic catalysis" observed in several Bamford–Stevens reactions.[4-6]

Experimental Section

General. Infrared spectra were obtained using a Beckman IR-7 spectrophotometer. ^{1}H nmr spectra were obtained in carbon tetrachloride solutions using a Varian A-60 spectrometer with chemical shifts reported in parts per million (δ) downfield from internal tetramethylsilane. Mass spectra were obtained using an AEI MS-9 instrument.

Aryldiazomethanes were prepared as described by Closs and Moss[20] and were stored at low temperature in pentane solution. Authentic samples of variously substituted phenylcyclopropanes were prepared as reported.[20] Olefinic solvents (gases) were Phillips pure reagent or Matheson reagent grade. Liquid olefin solvents were Phillips pure grade and were chromatographed through alumina before use.

Deuterated Acids. Deuteriotrifluoroacetic, trichloroacetic, and monochloroacetic acids were prepared by the reaction of their respective anhydrides with 99.5% deuterium oxide. Deuterium iodide, bromide, and chloride gases were generated from phosphorus triiodide, tribromide, and trichloride, respectively, and 99.5% deuterium oxide.

Phenyldiazomethane-α-d_1. This was prepared by direct exchange of phenyldiazomethane with deuterium oxide.[16,23] A 0.7 *M* solution of phenyldiazomethane in tetraglyme was well stirred at 10° with a 10-molar excess of deuterium oxide after addition of sufficient sodium methoxide to give a base concentration of 2 *M*. After 4 hr the diazo compound was extracted into pentane and chilled to −30° to remove solids, and the solvents were evaporated under reduced pressure. One such exchange reaction provided a product with an isotopic purity of greater than 90% (nmr).

General Procedure. A typical reaction was conducted under a blanket of nitrogen in a 100-ml three-neck flask carrying a Dry Ice condenser. About 30 ml of olefin was introduced or condensed into the flask. Aryldiazomethane (10 mmol) in about 15 ml of pentane or precooled olefin solvent was added in small portions into the reaction flask. Simultaneously, trifluoroacetic acid solution in pentane or precooled olefinic solvent was added dropwise to decolorize the diazo compound solution, which was stirred magnetically. The reaction was instantaneous and the addition of the acid was stopped when the color of the diazo compound was just discharged. It was advantageous to keep the concentration of the diazo compound low in the reaction mixture to reduce the formation of azines. In the case of halogen acids a slow stream of the dry gases was passed directly into the flask.

After the reaction was completed the solvents were evaporated and the products were analyzed by the following methods: (i) alumina chromatography followed by preparative glpc, (ii) short-path distillation under reduced pressure followed by preparative glpc, or (iii) saponification in aqueous methanolic alkali followed by alumina chromatography and preparative glpc. The most useful column for separation of the reaction products was a mixed column made of 10% QF-1 and 20% SF-96 on Chromosorb W (20 ft × 0.25 in.). Other columns of various lengths were made with Silicone SF-96, Silicone 710, Silicone QF-1, Carbowax 20M, and ethylene glycol succinate as liquid phases.

Analysis and Characterization of Reaction Products. Product yields were estimated by glpc on the crude reaction mixtures. Cyclopropane adducts, isolated by preparative glpc, were characterized by comparison of their spectra (ir, nmr, and mass) and glpc retention times with those of authentic samples obtained in earlier studies.[20] Other products isolated by preparative glpc were characterized by their ir, nmr, and mass spectra. Authentic samples of several compounds formed in low yields were also synthesized for identification. An approximately equal mixture of *threo*- and *erythro*-**4-phenyl-3-methyl-2-butanol** was prepared by the method described previously,[24] and the mixture was trifluoroacetylated using trifluoroacetic anhydride. The characteristic nmr absorptions of these and related compounds are listed in Table III.

1-Phenyl-2-methylbutanol was synthesized following the method of Warrick and Saunders[25] and the trifluoroacetate derivative was prepared using trifluoroacetyl chloride at 10°: ir (CCl_4) 5.6 (s), 8.15 (s), 8.55 (s), 8.7 μ (s); nmr (CCl_4) δ 0.75–2.05 (m, 9 H), 5.35–5.75 (~q, 1 H), 7.30 (s, 5 H); mass spectrum *m/e* 260 (M^+). The spectra and glpc retention times of this ester were identical with those of the product **12** isolated from the trifluoroacetic acid induced reaction of phenyldiazomethane with 2-butene.

1-Phenyl-3-pentyl Trifluoroacetate. 1-Phenyl-1-penten-3-one[27] (15 g) was hydrogenated at 2 atm with 5% Pd/C catalyst for 4 hr at 40° to give the saturated ketone [10 g, 67% yield, bp 69–73° (0.5 mm)]. The latter on reduction with $LiAlH_4$ gave 1-phenyl-3-pentanol (9 g, 90% yield), 2 g of which when treated with a slight excess of trifluoroacetic anhydride yielded the desired trifluoroacetate [3.2 g, 94% yield, bp 92–94° (0.05 mm)]: ir (CCl_4) 5.6 (s), 8.1 (s), 8.5 μ (s); nmr (CCl_4) δ 0.90 (t, J = 7 Hz, 3 H), 1.45–2.1 (m, 4 H), 2.4–2.8 (m, 2 H), 4.95 (t of t, J = 6 Hz, 1 H), 7.11 (s, 5 H); mass spectrum *m/e* 260 (M^-). The compound has spectra and glpc retention times identical with those of the product type **5** from the trifluoroacetic acid catalyzed reaction of phenyldiazomethane in 1-butene.

erythro-**3-Methyl-4-phenyl-2-butanol (11c).** *trans*-2-Butene oxide[28] was prepared from *trans*-2-butene by HOCl addition followed by KOH treatment. The epoxide (5 g, 0.07 mol) on treatment with benzylmagnesium chloride[29] gave the desired alcohol (6.3 g, 55% yield). The use of benzyllithium[30] instead of the Grignard reagent also gave the same product in 79% yield.

3-Methyl-4-phenyl-2-butyl Chloride. The reaction of 3-methyl-4-phenyl-2-butyl alcohol with thionyl chloride in pyridine using the procedure described by Vogel[31] gave a 15% yield of a mixture of threo and erythro chlorides and a 50% yield of 3-methyl-4-phenyl-2-butene (cis and trans isomers). The threo and erythro stereoisomers were separated by preparative glpc using an ethylene glycol succinate column. The spectra and glpc retention times of these compounds were identical with those isolated from the reaction of phenyldiazomethane with HCl in *cis*- and *trans*-butene solvents. *threo*-**3-Methyl-4-phenyl-2-butyl chloride (11d)** was obtained similarly from *erythro*-3-methyl-4-phenyl-2-butyl alcohol (**11c**) and the product was shown by glpc to be at least 97% stereospecific.

3-Methyl-4-phenyl-2-butene (10b). *threo*-3-Methyl-4-phenyl-2-butyl chloride (**11d,** 500 mg) was stirred with 3.5 ml of 0.4 *M* Na–ethylene glycol at 150° for 3 hr. After addition of 2 ml of water the solution was extracted five times with 12-ml pentane portions. Evaporation of the solvent and preparative glpc gave 16% of the desired pure olefin **10b.** The product was at least 95% stereospecifically cis from the nmr spectrum. The terminal olefin **9** was also isolated in 11% yield.

Determination of Deuterium Content. The estimation of the percentage of deuterated compounds was carried out by mass spectrometry on samples purified by glpc. The reaction products readily gave molecular ion peaks for intensity measurements. The cyclopropane derivatives also gave small $M^+ - 1$ peaks but these may be eliminated by using lower ionizing voltage (10–15 eV). Measurements were also made using the $M^+ - 15$ peak (corresponding to the loss of a methyl group) and this provides an independent check on the measurements based on the molecular ions.

In a typical reaction using phenyldiazomethane, deuteriotrifluoroacetic acid, and *trans*-butene, the cyclopropane adduct was found to be 18% monodeuterated while the carbonium ion products contained 65% d_1. The use of an excess of deuterated acid increased the amount of deuterium incorporation in all products, but the ratio of the per cent cyclopropane-d_1 product to per cent ester-d_1 or olefin-d_1 product remained constant. These and other results are presented in Table IV.

Control Experiments. To show that the carbonium ion products do not arise from cyclopropanes, a sample of 1-phenyl-2,3-dimethylcyclopropane prepared previously[20] was stirred with trifluoroacetic acid in *cis*-2-butene under the same reaction conditions. No other peaks were detected by glpc other than the original cyclopropanes.

To show that cyclopropanes do not exchange deuterium of the acid a sample of reaction products was subjected to vigorous stir-

ring in *cis*-butene saturated with deuteriotrifluoroacetic acid. The cyclopropane product when isolated was found to contain negligible amounts of deuterium (<1%).

To show that there is no preequilibrium and exchange of deuterium of the acid and the diazo compound, phenyldiazomethane was treated with an excess of deuteriotrifluoroacetic acid in pentane solution. The benzyl trifluoroacetate was isolated and was found to contain no dideuterated product. Olefins were found not to react with the deuterated acids under the reaction conditions.[32]

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Registry No.—5-*p*-Chlorophenylpent-2-enyl trifluoroacetate, 51157-78-9; 5-*p*-chlorophenyl-3-pent-1-enyl trifluoroacetate, 51157-79-0.

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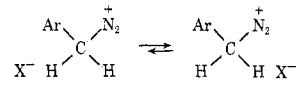

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Allene Epoxidation. The Isolation of Reactive Intermediates from Hindered Allenes[1a]

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The peracid oxidation of several highly hindered allenes has resulted in the isolation of allene oxides and 1,4-dioxaspiro[2.2]pentanes (spiro dioxides), and the chemistry of these sequentially formed products has been explored. Allene **1** yields spiro dioxide **2**, which readily isomerizes to oxetanone **3** and unsaturated ketone **4**. The addition of acetic acid to **2** gives **5**. Allene **8** yields labile allene oxide **19**, which spontaneously isomerizes to cyclopropanone **11**. Remarkably stable **11** is photochemically or thermally decarbonylated to **12**. Sodium methoxide cleaves **11** to **13** and **14**; acid treatment gives rearranged ketones **15** and **16**. In the presence of excess oxidant, **8** is transformed to oxetanone **22** and oxacyclopentanone **23**, presumably *via* a transient spiro dioxide intermediate. Allene **25** leads to stable allene oxide **26**, which is converted to its geometric isomer **28** by irradiation or heating. Thermolysis converts either **26** or **28** to **29** and **30**. Rearrangement of **26** to **29** is also effected by BF_3. Further peracid oxidation of **26** gives dioxidation products **27**, **31**, and **32** *via* labile spiro dioxide **33**. Allene **36** gives allene oxide **37** and dioxidation products **39** and **40**. Acid or heat transforms **36** to ketone **38**. Ozone converts allene **8** to cyclopropanone **11** and also effects the oxidation of allene **25** to spiro dioxide **33**.

Recent work on the epoxidation of allenes has provided a reasonably detailed understanding of this rather complex reaction.[2-4] Several interesting species have been implicated as reactive intermediates in this process, including allene oxides, cyclopropanones, and 1,4-dioxaspiro[2.2]pentanes. In the present study, the oxidation of sever-