Table II. Definition of Rearrangement, Isomerization, and Automerization

Molecular formula	Structural formula	Name
Not conserved	Not conserved	Rearrangement
Conserved	Not conserved	Isomerization
Conserved	Conserved	Automerization

thus a particular case of rearrangements, and automerizations a particular case of isomerizations.

Automerizations of carbon atoms evidenced by isotopic labeling were recently reviewed.[9] The thermal automerizations of bullvalene,[10] homotropylidene,[11] etc., were evidenced by nmr spectra. A photochemical automerization of carbon atoms in benzene is plausible in view of recent data.[12]

According to the proposed definitions the benzidine, phenylhydroxylamine, Beckmann, Claisen, and Stevens rearrangements and a few others should be termed isomerizations. Only processes such as the neopentylic, pinacolic, benzilic, Demjanov, Wolff, and Curtius rearrangements, etc., are named in agreement with this definition.

Further work is being done in our laboratory in order to degrade systematically the isomerized anthranilic acid (Vb).[13] The possibility of the isotopic automerization of naphthalene and phenanthrene was mentioned in 1965.[14]

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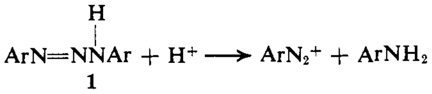
The Generation of Vinyl Cations from Vinyltriazenes

Sir:

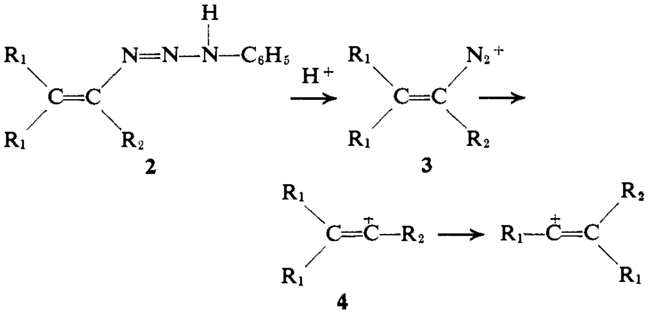
The classical reaction of diaryltriazenes (diazoaminobenzenes) with acid to give aryldiazonium ions[1] suggested to us a potentially convenient way to generate



$$\text{ArN=N}\overset{\text{H}}{\underset{|}{\text{N}}}\text{Ar} + \text{H}^+ \longrightarrow \text{ArN}_2^+ + \text{ArNH}_2$$

1

vinyldiazonium ions[2] from the analogous vinyltriazenes (**2**).[3] This type of intermediate might then lose nitrogen to give the corresponding vinyl cation, a type of species that has been the subject of considerable study by a number of investigators in recent years.[4] The purpose of this note is to report the synthesis of selected vinyltriazenes (**2a–d**)[5] and their reactions with acids to give products that are believed to arise from intermediate vinyl cations.



a, $R_1 = R_2 = C_6H_5$
b, R_1 = *p*-tolyl; $R_2 = C_6H_5$
c, $R_1 = C_6H_5$; $R_2 = CH_3$
d, $R_1 = C_6H_5$; R_2 = H

All triazenes were synthesized by reaction of the appropriate Grignard reagent with phenyl azide.[1] The triazene structure assignments were based on standard criteria[6] plus ozonolysis to ketones to exclude the triazoline structural possibility that could not be excluded by routine methods. All of the triazenes were found to be sensitive to acid, reacting, for example, with acetic acid at room temperature in a matter of seconds with essentially quantitative nitrogen evolution. The products of reaction of **4a–d** with various acids are given in Table I. Points of particular interest are the following.

(1) In all cases, the products are those that would be expected to arise from simple cation formation followed by reaction with nucleophile either before or after rearrangement. Furthermore, the potential generality of this reaction as a synthetic method for producing triarylvinyl derivatives is emphasized by the fact that, even when the conjugate base of the acid is as weakly nucleophilic as the toluenesulfonate ion, 20% of the corresponding vinyl sulfonate is formed.

(2) The reactions are accompanied by more or less rearrangement, the amount of rearrangement being consistent with the reaction involving a vinyl cation intermediate. For example, triazene **2b**, in pure acetic acid, gives about 20% rearranged product (to 80% unrearranged). However, when potassium acetate is added, as the vinyl cation intermediate would predict, rearrangement is suppressed. In fact, in the presence

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(1) *Cf.* H. Zollinger, "Azo and Diazo Chemistry," Interscience Publishers, Inc., New York, N. Y., 1961, Chapter 8.

(2) For an elegant study of the diazotization of selected primary vinylamines with isoamyl nitrite and nitrosyl chloride to give products that probably arise from intermediate vinyldiazonium ions, see D. Y. Curtin, J. A. Kampmeier, and B. R. O'Connor, *J. Am. Chem. Soc.*, **87**, 863 (1965).

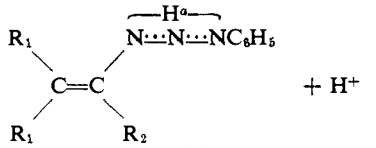
(3) The reaction of acid with aliphatic triazenes has also been studied and found to give products expected from aliphatic diazonium ions. See, for example, E. M. White and H. Scherrer, *Tetrahedron Letters*, **21**, 758 (1961), and ref 1.

(4) For a very thorough review of vinyl cations, see P. E. Peterson and J. E. Duddey, *J. Am. Chem. Soc.*, **88**, 4990 (1966).

(5) The position of the proton is not known. For conceptual convenience, it is placed next to the phenyl.

(6) With the exception of 2c, which was too unstable to yield to normal analytical techniques, all new compounds gave acceptable analyses.

Table I. Vinyltriazenes and Products of Reaction with Acid



Compd	R_1	R_2	Acid	Products (% yield)
2a	C_6H_5	C_6H_5	HOAC	$(C_6H_5)_2C{=}C(C_6H_5)(OAc)$ (100)
2a	C_6H_5	C_6H_5	C_6H_5OH	$(C_6H_5)_2C{=}C(C_6H_5)(OC_6H_5)$ (65) $(C_6H_5)_2CHCOC_6H_5$ (35)
2a	C_6H_5	C_6H_5	*p*-Toluenesulfonic acid hydrate	$(C_6H_5)_2C{=}C(C_6H_5)(OSO_2$-*p*-tolyl) (20) $(C_6H_5)_2CHCO(C_6H_5)$ (80)
2b	*p*-Tolyl	C_6H_5	HOAC	(*p*-tolyl)$_2C{=}C(C_6H_5)(OAc)$ (80)[b] (*p*-tolyl)$(C_6H_5)C{=}C$(*p*-tolyl)(OAc) (20)[b]
2b	*p*-Tolyl	C_6H_5	HOAc[d]	(*p*-tolyl)$_2C{=}C(C_6H_5)(OAc)$ (100)
2c	C_6H_5	CH_3	HOAc[e]	$(C_6H_5)_2C{=}C(CH_3)(OAc)$ (5)[b] $(C_6H_5)(CH_3)C{=}C(C_6H_5)(OAc)$[c] (86)[b]
2d	C_6H_5	H	HOAc	$(C_6H_5)_2C{=}CH(OAc)$ (0) $(C_6H_5)HC{=}C(C_6H_5)(OAc)$[f,g] (9)
2d	C_6H_5	H	HOAc[d]	$(C_6H_5)_2C{=}CH(OAc)$ (0) $(C_6H_5)HC{=}C(C_6H_5)(OAc)$[f,g] (16)

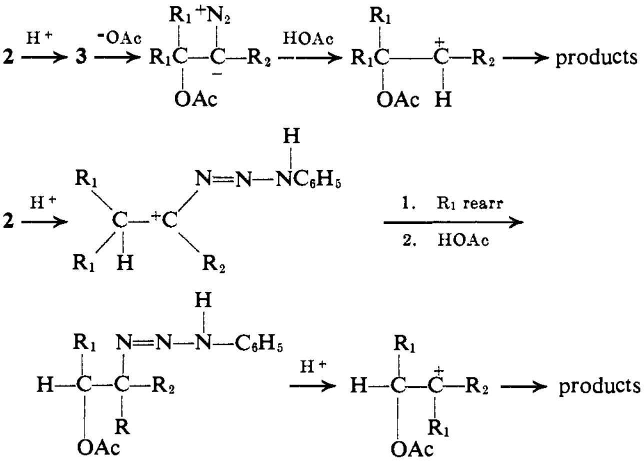
[a] Position of hydrogen is unknown. [b] Determined by ozonolysis. Models indicated essentially quantitative ozonolysis. [c] Unknown stereochemistry. [d] Containing 10 molar equiv of added potassium acetate. [e] Synthetic difficulties prevented more detailed study. [f] Mixture of isomers. [g] Predominant products were diphenylacetylene and deoxybenzoin. A more detailed discussion of these products will be presented in a following paper.

of 10 molar equiv it is completely eliminated. Furthermore, generation of the less stable vinyl cation **4c** from reaction of the triazene **2c** with acetic acid gave almost completely rearranged product, and generation of the least stable cation **4d** (if it is a discrete intermediate) gave exclusively rearranged acetates, even in the presence of added potassium acetate. This order of rearrangement finds precedence in aliphatic counterparts where it has been found that diazotization of 1,2,2-triphenylethylamine gives only 23% rearrangement,[7] whereas diazotization of 2,2-diphenylethylamine[8] and 2,2-diphenyl-2-alkylethylamines[8,9] give rearranged products exclusively.

(3) The mixture of vinyl acetates resulting from reaction of **2d** with acetic acid invariably contained a predominance of the isomer that is believed to have the two phenyl rings *cis*. This observation is not only consistent with a vinyl cation intermediate (possibly resulting simply from a steric effect of the phenyl ring that is held in the plane of the approaching nucleophile) but is in accord with the surprisingly large amount of *cis*-1,2-diphenylvinyl chloride observed by Curtin, *et al.*,[2] in the reaction of the same vinyl cation with chloride ion.

(4) Finally, in all cases the material balance of the reactions was essentially complete. For example, the reaction of **2a** with acetic acid gave triphenylvinyl acetate quantitatively (aniline appeared as acetanilide from traces of acetic anhydride in the solvent), **2c** gave 91% of a mixture of vinyl acetates with about 9% of α-phenylpropiophenone, etc. In no case was any disubstitution product observed.[10]

All of the results mentioned above are consistent with a reaction *via* the vinyl cation (or, possibly, the vinyl equivalent of the S_N2 intermediate) although none actually demands such an intermediate. However, all alternative mechanisms that we have been able to think of have serious weaknesses. The two most likely alternatives are β addition of a nucleophile to give a diazoalkane which could then react with acid to give products,[11] and an addition–elimination mechanism that involves β addition of a proton to the triazene (which is essentially an enamine) followed by a variety of steps to give rearranged and unrearranged products. The most glaring weakness in both mechanisms is the total absence of disubstituted products since both mechanisms require, at some point, a cation with a neighboring acetoxy group (in the latter mechanism, this is required only for rearranged products), a type of intermediate that would certainly be expected to give disubstitution products. More subtle arguments against these types of mechanisms include unrealistic competition between rearrangement of aryl *vs.* acetoxy, inconsistent rearrangement of aryl *vs.* acetoxy from one system to the next, and total absence of diphenylacetaldehyde when triazene **2d** is decomposed with aqueous



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(10) Selected vicinal diacetates were independently shown to be stable to reaction conditions.

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acid. All of these arguments will be fully delineated in a forthcoming paper.

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Preparation of Bis(fluoroxy)difluoromethane, $CF_2(OF)_2$

Sir:

The known existence of $CF_2(OF)_2$ as established by Thompson[1] of the 3M Company together with a knowledge of the usefulness of cesium fluoride as an aid to the formation of hypofluorites, as established by Ruff and Lustig,[2] suggested the possibility of preparing $CF_2(OF)_2$ by the fluorination of carbon dioxide. The procedure was tried and found to be very effective.

In a typical run, 0.298 g (6.78 mmoles) of carbon dioxide and 1.03 g (27.1 mmoles) of fluorine were condensed together from a 2310-ml glass vacuum line into a heavy-walled, 9-ml Monel metal bomb which contained 7.80 g of dry cesium fluoride at about −196°. The salt was used directly from a bottle of the "99% pure" compound by Alfa Inorganics, Inc. It was pulverized in a drybox and placed in the bomb which was then filled with gaseous fluorine under pressure and allowed to stand at room temperature for 1 day. The fluorine was then removed. After addition of the above amounts of carbon dioxide and fluorine, the bomb was closed and placed in a safety shield consisting of a piece of heavy-walled pipe. It warmed slowly and remained at room temperature for 3 days. The gases were then transferred to the vacuum line and found to have a volume corresponding to 20.1 mmoles (theory, 20.3 mmoles). When the gas was pumped slowly through a U-trap cooled by liquid nitrogen (−196°), fluorine was removed, and the material, which condensed in the trap, upon evaporation had a volume of 6.72 mmoles (theory, 6.78 mmoles) of gas. Fractional codistillation[3] gave one peak, indicating that the compound was pure. Successive fractions taken by evaporation had vapor densities expressed as molecular weights of 120.0, 119.2, and 120.8 (theory for $CF_2(OF)_2$, 120.0).

The reaction described above showed each molecule of product to contain (like CO_2) one atom of carbon. When a similar run was made using an excess of carbon dioxide, the fluorine was completely consumed, and substantially no material volatile at −196° remained in the bomb. This meant that oxygen was not produced and that a molecule of product (on the average) contained two atoms of oxygen. The product had the same volume as the carbon dioxide used in the process. Fractional codistillation separated the product into two fractions. Infrared spectra showed one to be carbon dioxide, and the other to be the same new compound that was produced by the reaction involving an excess of fluorine. Two moles of fluorine was consumed for every mole of product formed in the first reaction. This evidence clearly established the reaction to be

$$\mathrm{CO_2 + 2F_2 \xrightarrow[25^\circ]{CsF} CO_2F_4}$$

The compound was not observed to freeze when chilled. It was a liquid at −183° and a glassy material, or very viscous liquid, at −196°. It reacted vigorously with an aqueous solution of potassium iodide liberating iodine. The infrared spectrum of the gas as observed through silver chloride windows using a Beckman IR-10 spectrometer had absorption bands (in μ) at 7.84 (vs), 8.01 (vs), 8.22 (vs), 8.30 (vs), 8.43 (vs), 10.6 (m), 10.7 (m), 10.8 (m), 10.9 (m), 11.0 (m), 14.5 (m), and 15.2 (m). Several weaker bands were also present.

The fluorine-19 nmr spectrum was obtained with a Varian Associates high-resolution, 40-Mc, nuclear magnetic resonance spectrometer with a Model No. V-4311 fixed-frequency radio frequency transmitter using $CFCl_3$ as an external standard. Two triplets of equal area were observed, centering at chemical shifts (from $CFCl_3$) of −155 and 88.5 ppm. The coupling constant, J, had a value of 39 cps. This spectrum is consistent with the structure $CF_2(OF)_2$.

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Rearrangement as a Criterion for Triple Bond Participation in the Formolysis of Acetylenic Brosylates

Sir:

The intramolecular participation of an acetylenic bond with a center of developing positive charge, generated by the loss of a negative leaving group in a solvolysis reaction, leads, if classically described, to a vinylcarbonium ion. The possible intermediacy of such ions in a variety of reactions has received recent attention.[1]

Positive evidence for triple bond participation in a solvolysis reaction would be a rate acceleration[2] or the formation of rearrangement products involving the acetylenic bond.[2,3] Examples of rate acceleration are few, and their interpretation is complicated by the uncertainty in the magnitude of the inductive rate-retarding effect exerted by the acetylene group.[2] Several examples of rearrangements are known, all from closely related systems: sulfonate solvolysis in formic, acetic, or trifluoroacetic acids.[2,3] Thus, 3-pentyn-1-yl brosylate, heated at 60° for 17 days in formic acid buffered with sodium formate, gave 2-methylcyclobutanone and a trace of methyl cyclopropyl ketone as well as the normal solvolysis product.[3a]

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