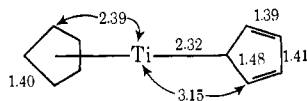


Figure 1. The pmr spectra of  $(C_5H_5)_4Ti$  at several temperatures. The intermediate spectra were run at higher gain.

volume of  $2345 \text{ \AA}^3$  and  $Z = 6$  give  $\rho_{\text{calcd}}$  of  $1.31 \text{ g/cm}^3$  (the great reactivity of the compound prevented us from determining the density experimentally). The integrated intensities of 1205 reflections, including 384 Friedel pairs (*i.e.*, 821 Laue-independent reflections), within the sphere  $\theta \leq 65^\circ$  were measured on a General Electric XRD-5 manual diffractometer using nickel-filtered copper radiation and a  $\theta$ - $2\theta$  scan technique. The structure was solved by a combination of Patterson, Fourier, and least-squares calculations. At the present stage of refinement, by using isotropic temperature factors and the space group  $P6_322$ , the conventional  $R$  factor is 0.139. Though further refinement is needed for meaningful discussion of the finer details, the structure unambiguously contains  $(h^1-C_5H_5)_2(h^5-C_5H_5)_2Ti$  molecules lying on twofold axes. The following average distances (in angstroms with esd's of  $\sim 0.02 \text{ \AA}$ ) are pertinent.



The pmr spectra<sup>10</sup> at several temperatures in  $C_6D_6$  solution are shown in Figure 1. The two lines at lower temperatures are due to the fluxional  $h^1-C_5H_5$  rings ( $\tau$  4.12) and the  $h^5-C_5H_5$  rings ( $\tau$  4.82). Studies at lower temperatures are being conducted in other solvents to examine the  $h^1-C_5H_5$  rearrangement process. As the temperature rises, these two lines

(10) The peak marked X, which has been erroneously attributed<sup>8b</sup> to  $(C_5H_5)_2Ti$ , is due to  $(C_5H_5)_2TiCl$ . This molecule, presumably  $(h^5-C_5H_5)_2(h^1-C_5H_5)TiCl$  is also fluxional, and a broad study of this and other  $(C_5H_5)_2TiX$  molecules is in progress.

collapse and merge, clearly proving that ring interchange occurs. The Arrhenius parameters are  $E_a = 16.1 \pm 0.3 \text{ kcal/mol}$  and  $\log A = 13.5 \pm 0.5$ .

The relatively facile occurrence of  $(h^1-C_5H_5)-(h^5-C_5H_5)$  interchange in this compound may be attributed to the formal 16-electron configuration, which means that the metal atom possesses an empty orbital. This orbital can be employed in binding two rings which are initially  $(h^5-C_5H_5)$  and  $(h^1-C_5H_5)$  in an equivalent fashion, very likely similar to the binding of the two non- $(h^1-C_5H_5)$  rings in  $(C_5H_5)_3MoNO$ , thus affording a suitable, low-energy transition state.<sup>11</sup>

(11) This work was supported by the National Science Foundation and the Petroleum Research Fund.

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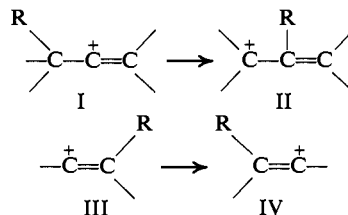
Received April 25, 1970

### Rearrangements Involving Simple Vinyl Cations Generated by Solvolysis<sup>1</sup>

Sir:

One of the best indications of the intermediacy of carbonium ions in a reaction is the observation of rearranged products. Although excellent evidence has been presented that the solvolysis of simple alkyl substituted vinyl triflates can in some cases lead to vinyl cations,<sup>2</sup> we wished to confirm this conclusion by studying the behavior of substrates expected to give rise to rearrangement.

Two types of rearrangements involving vinyl cations are possible: (1) *to* the double bond (I  $\rightarrow$  II) and (2) *across* the double bond (III  $\rightarrow$  IV). We present here examples of both types in strain-free systems.<sup>5</sup>



The solvolysis of *t*-butylvinyl triflate (V) in aqueous ethanol was shown to give *t*-butylacetylene as the major product, but 10–15% of 2,3-dimethylbutadiene as well as rearranged alcohols and ethers were also obtained.<sup>3</sup> Similar products are found after acetolysis. Those products were formulated<sup>3</sup> as arising from a vinyl cation rearrangement.<sup>6</sup>

We have now excluded an alternative rearrangement course involving addition-elimination.<sup>7</sup> As indicated

(1) Paper IV in a series on the preparation and solvolysis of vinyl triflates.<sup>2-4</sup>

(2) P. J. Stang and R. H. Summerville, *J. Amer. Chem. Soc.*, **91**, 4600 (1969).

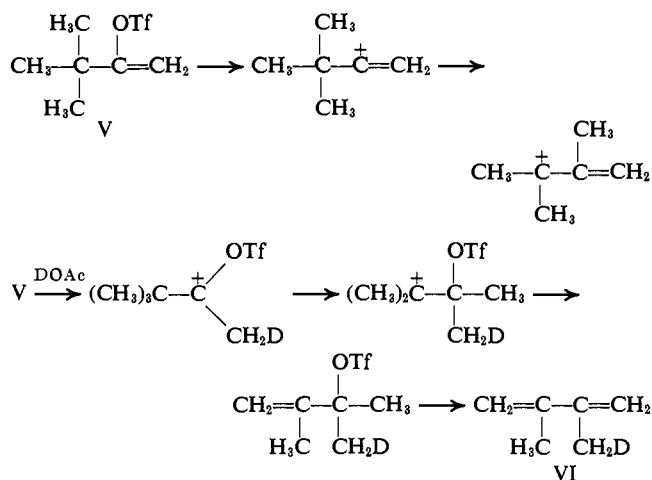
(3) A. G. Martinez, M. Hanack, R. Summerville, P. v. R. Schleyer, and P. J. Stang, *Angew. Chem.*, in press.

(4) T. E. Dueber, P. J. Stang, W. D. Pfeifer, R. H. Summerville, M. Imhoff, P. v. R. Schleyer, K. Hummel, S. Bocher, C. E. Harding, and M. Hanack, *ibid.*, in press.

(5) Rearrangements have recently been observed in the  $Ag^+$ -catalyzed reactions of 1-iodo-1-cyclopropylpropene-1 by D. R. Kelsey and R. G. Bergman, *J. Amer. Chem. Soc.*, **92**, 228 (1970).

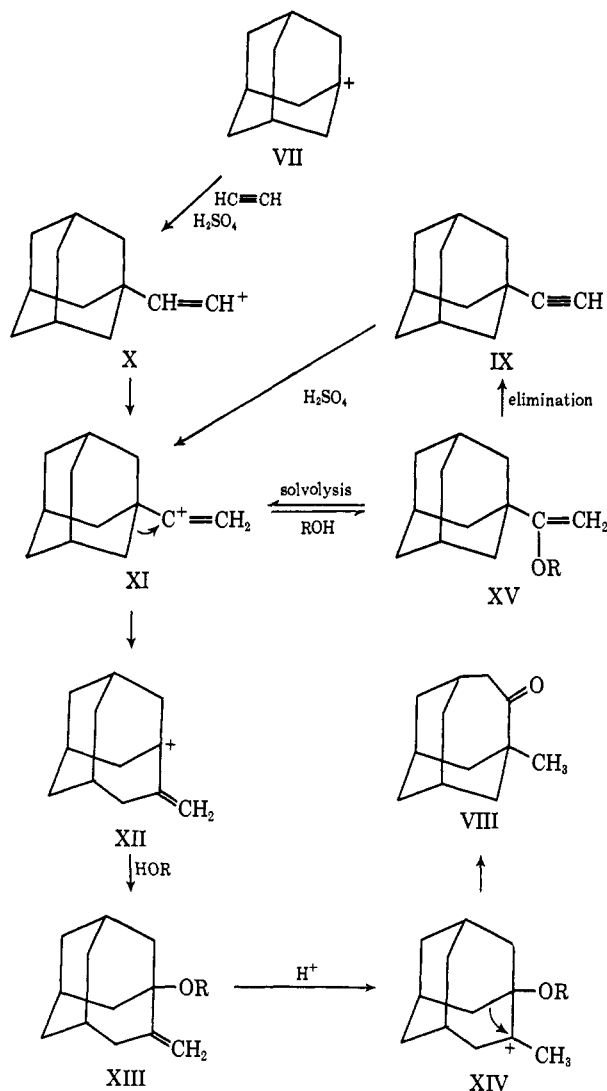
(6) *Cf.* the reaction of sulfuric acid with *t*-butyl acetylene: K. Griesbaum and Z. Rehman, *J. Amer. Chem. Soc.*, in press.

(7) P. E. Peterson and J. M. Indelicato, *ibid.*, **90**, 6515 (1968); **91**



above, such a process in DOAc should lead to deuterium incorporations in the 2,3-dimethyl-1,3-butadiene product (VI). However, in fact, no such deuterium incorporation was found for the latter.

The interaction of the 1-adamantyl cation (VII) with acetylene in sulfuric acid leads to the interesting product, 3-methyl-4-homoadamantanone (VIII).<sup>8</sup> VIII



6194 (1969); W. M. Schubert and G. W. Barfknecht, *ibid.*, 92, 207 (1970); *cf.*, Z. Rappoport, T. Bässler, and M. Hanack, *ibid.*, in press.

Table I. Products of Solvolysis of 1-Adamantylvinyl Triflate (XV, R = Tf)<sup>a</sup>

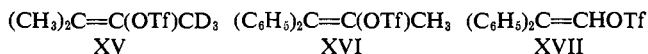
Solvent	% IX	% methyl 1-adamantyl ketone XV <sup>b</sup>	% XIII <sup>b</sup>	% VIII
60% aq ethanol	~90	~10		Trace
HOAc (OAc <sup>-</sup> )	76	7	17	
90% CF <sub>3</sub> CH <sub>2</sub> OH	21	7		72
90% TFE (lutidine)	25	7	69	

<sup>a</sup> These reactions were carried out in the 70–85° range to completion. Products were shown to be stable to the reaction conditions. <sup>b</sup> R is related to the solvent used.

was also formed by the treatment of 1-adamantylacetylene (IX) with sulfuric acid.<sup>9</sup> Bott<sup>8,9</sup> formulated these processes as involving two vinyl cation rearrangements, X → XI and XI → XII.<sup>10</sup> Support for this suggested mechanism is found in the solvolysis of 1-adamantylvinyl triflate (XV, R = Tf).<sup>4</sup>

The results (Table I) show a marked dependence on the solvent used. In 60% aqueous ethanol and in buffered acetic acid elimination (probably E2)<sup>2</sup> predominated, but in the latter solvent an appreciable amount of rearranged acetate (XIII, R = Ac) formed. The behavior in less basic solvent, 90% CF<sub>3</sub>CH<sub>2</sub>OH, was instructive. Rearranged products predominated; under buffered conditions the major products were XIII (R = CH<sub>2</sub>CF<sub>3</sub> and R = H), but when the liberated CF<sub>3</sub>SO<sub>3</sub>H was not neutralized these compounds rearranged further to VIII. There must be considerable driving force for transformations of type 1 (I → II), since the increase in ring strain in going from the adamantane (XI) to the homoadamantane (XII) skeleton does not prevent the rearrangement from occurring.<sup>13</sup>

We have sought rearrangements of type 2 (III → IV) using the substrates XV–XVII.<sup>4</sup>



Deuterated XV was used in order to detect products of the possible methyl migration,  $(\text{CH}_3)_2\text{C}=\text{C}^+\text{CD}_3 \rightleftharpoons \text{CH}_3\text{C}^+=\text{C}(\text{CH}_3)\text{CD}_3$ . However, in 80% CH<sub>3</sub>OD–20% D<sub>2</sub>O, in pyridine–D<sub>2</sub>O, and in 60% CD<sub>3</sub>COCD<sub>3</sub>–40% D<sub>2</sub>O, 73–82% of  $(\text{CH}_3)_2\text{C}=\text{C}(\text{O}_2\text{CCD}_3)\text{CD}_3$  and 18–27%  $(\text{CH}_3)_2\text{C}=\text{C}=\text{CD}_2$  formed, but, within the limits of nmr detection, no rearrangement was observed. The same negative result was obtained with buffered CD<sub>3</sub>COOD, where the major product (80%) was  $(\text{CH}_3)_2\text{C}=\text{C}(\text{O}_2\text{CCD}_3)\text{CD}_3$ .

1-Methyl-2,2-diphenylvinyl triflate (XVI) should be much more prone to rearrangement. Not only should phenyl be a better migrating group than methyl, but rearrangement would lead to a more stable ion, (C<sub>6</sub>-

(8) K. Bott, *Tetrahedron Lett.*, 1747 (1969); T. Sasaki, S. Eguchi, and T. Toru, *Chem. Commun.*, 780 (1968).

(9) K. Bott, *ibid.*, 1349 (1969).

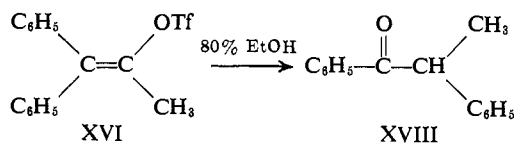
(10) We believe the last step, XIV → VIII, is better formulated as a degenerate type homoadamantane rearrangement,<sup>11</sup> rather than a methyl migration.<sup>12</sup>

(11) P. v. R. Schleyer, E. Funke, and S. Liggero, *J. Amer. Chem. Soc.*, 91, 3965 (1969); J. E. Nordlander, F. Y.-H. Wu, S. P. Jindal, and J. B. Hamilton, *ibid.*, 91, 3962 (1969).

(12) P. v. R. Schleyer, *Angew. Chem., Int. Ed. Engl.*, 8, 529 (1969).

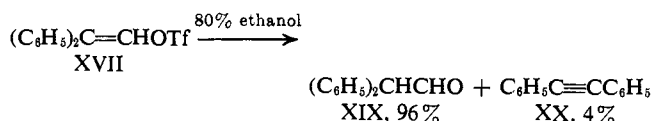
(13) Solvolysis of 1-adamantylmethylcarbonyl brosylate does not give any rearranged product in a variety of solvents (M. Imhoff and S. Liggero, unpublished observations), *cf.* S. H. Liggero, R. Sustmann, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, 91, 4571 (1969), and references therein cited.

$\text{H}_5\text{C}=\text{C}^+\text{CH}_3 \rightarrow \text{C}_6\text{H}_5\text{C}^+=\text{C}(\text{CH}_3)\text{C}_6\text{H}_5$ . Solvolysis of XVI in 80% ethanol (followed by ether hydrolysis) gave almost exclusively the rearranged ketone, XVIII. As far as we are aware, this is the first example



of carbon migration across a double bond of a vinyl cation generated by solvolysis.<sup>14</sup>

A final study was carried out with 2,2-diphenylvinyl triflate, XVII. This "primary" triflate proved to be very unreactive; in 80% ethanol there was only 93% reaction in 110 hr at 125°. In 90% aqueous acetone at 75° for 3 weeks, only 60% reaction was observed. In the latter solvent the only product was the unrearranged aldehyde  $(\text{C}_6\text{H}_5)_2\text{CHCHO}$  (XIX). In 80% ethanol, the same aldehyde was by far the major product, but 4% of tolan (XX) was present in the reacted material. It may be that XVII reacts chiefly by an addition-



elimination mechanism rather than by forming the unstable "primary" cation,  $(\text{C}_6\text{H}_5)_2\text{C}=\text{CH}^+$ . By using more advantageous (e.g.,  $\text{H}_2\text{SO}_4$  in the postulated rearrangement,  $\text{X} \rightarrow \text{XI}$ ) conditions, we hope to observe a greater percentage of rearrangement.

We conclude that rearrangements involving vinyl cations are likely to be quite common, especially if conditions (and substrates) are chosen which minimize side reactions (concerted elimination and addition-elimination).<sup>7</sup> The use of the exceedingly reactive triflate leaving group<sup>2-4,15</sup> continues to facilitate the study of vinyl cations.<sup>1</sup>

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(14) Cf. a recent case of sulfur migration, G. Capozzi, G. Melloni, G. Modena, and U. Tonellato, *Chem. Commun.*, 1520 (1969).

(15) T. M. Su, W. F. Sliwinski, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **91**, 5386 (1969), and references therein cited; W. M. Jones and D. D. Maness, *ibid.*, **91**, 4314 (1969); R. C. Bingham, W. F. Sliwinski, and P. v. R. Schleyer, *ibid.*, **92**, 3471 (1970); S. A. Sherrod, R. G. Bergman, G. J. Gleicher, and D. Morris, *ibid.*, **92**, 3469 (1970).

(16) National Institutes of Health Postdoctoral Fellow, 1969-1970.

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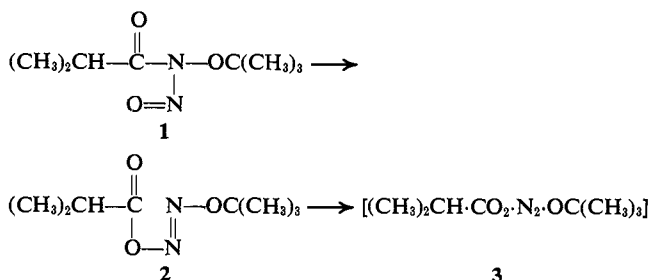
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## Thermal Decomposition of N-Nitrosohydroxylamines. IV. Nuclear Polarization of Products

Sir:

Recent work in these laboratories<sup>1</sup> has demonstrated that the rearrangement and decomposition of N-nitrosohydroxylamines can serve as a low-temperature source of acyloxy-alkoxy radical pairs. The present report deals with this reaction starting with N-isobutyryl-N-nitroso-O-*t*-butylhydroxylamine, 1.



Solutions of this compound were obtained by the published procedure.<sup>1</sup> The rearrangement  $1 \rightarrow 2$  is very rapid, such that the spectral characteristics of these solutions indicate almost complete rearrangement to hyponitrite (2: infrared carbonyl absorption at  $1797 \text{ cm}^{-1}$ , nitroso absorption absent), in spite of precautions against warming prior to spectral measurements. A rapid rearrangement in this case is expected, by analogy with the behavior of other nitrosoamides.<sup>2</sup>

The decomposition step is also more rapid than that observed for the corresponding N-acetyl compound<sup>1</sup> ( $k_{1 \rightarrow 3} \sim 7 \times 10^{-3} \text{ sec}^{-1}$  at ambient A-60 nmr temperature, carbon tetrachloride solvent). The products obtained from the overall reaction in carbon tetrachloride are listed in Table I. Notably absent

**Table I.** Products of Decomposition of 2 in Carbon Tetrachloride at Room Temperature

Product	Mol/mol of 2 <sup>a</sup>
Nitrogen	0.90
Carbon dioxide	0.90
Isopropyl <i>t</i> -butyl ether	0.08
Isopropyl chloride	0.64
<i>t</i> -Butyl alcohol	0.43
Acetone	0.26
Isobutylene chlorohydrin	0.19
1,1,1,3-Tetrachlorobutane	~0.06
Chloroform	0.03

<sup>a</sup> Yields of nongaseous products are by quantitative nmr. Product identification and quantitative analysis of gaseous products are by mass spectrometry. Methyl chloride, methane, and propene are detected in trace amounts in the gaseous products.

is the corresponding *t*-butyl perester. This and the rapid rate of decomposition suggest that the reaction, in this case, is a concerted process giving an isopropyl-*t*-butoxy radical pair, separated by a carbon dioxide and a nitrogen molecule, in a single synchronous step.

(1) T. Koenig and M. Deinzer, *J. Amer. Chem. Soc.*, **88**, 4518 (1966); **90**, 7014 (1968); submitted for publication.

(2) R. Huisgen, *Justus Liebigs Ann. Chem.*, **574**, 171 (1951); R. Huisgen and H. Reimlinger, *ibid.*, **599**, 161 (1956).