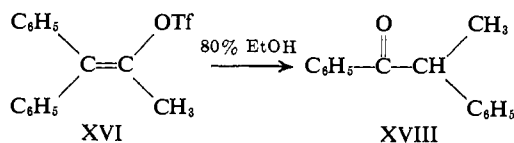
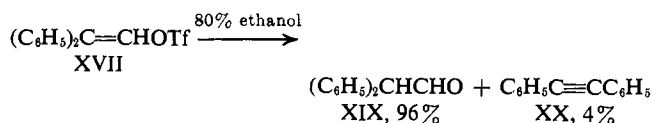


$(\text{H}_5)_2\text{C}=\text{C}^+\text{CH}_3 \rightarrow \text{C}_6\text{H}_5\text{C}^+=\text{C}(\text{CH}_3)\text{C}_6\text{H}_5$ . Solvolysis of XVI in 80% ethanol (followed by ether hydrolysis) gave almost exclusively the rearranged ketone, XVIII. As far as we are aware, this is the first example



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. Meltoni, 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.

(17) National Science Foundation Predoctoral Fellow, 1968-1970.

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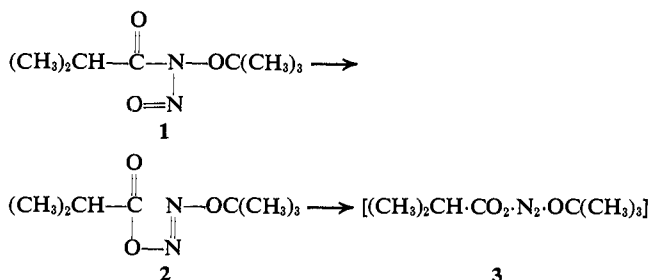
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## Thermal Decomposition of N-Nitrosohydroxylamines. IV. Nuclear Polarization of Products

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).

The intermittent nmr spectra of these solutions show, in addition to the decreases in starting material signals (2: *t*-butyl singlet,  $\delta$  1.45; isopropyl doublet,  $\delta$  1.31) and increases in the signals associated with the products listed in Table I, a strong emission signal from chloroform, which becomes the most intense peak (negative) in the spectrum after about 200 sec. Such emission peaks are now expected from diamagnetic compounds formed from radical precursors.<sup>3,4</sup>

Table II summarizes the effects of additives on the emission. Cyclohexene increases the yield of chloroform while decreasing the emission intensity. *t*-Amyl-

**Table II.** Chloroform Emission Sensitivity to Additives<sup>a</sup>

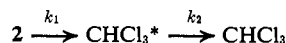
Additive	$E_{\max}^b$	$A_{\infty}^c$	$V^3$
None	1.90	0.008	240
Cyclohexene (0.5 M)	1.75	0.040	44
Cyclohexene (1.9 M)	0.89	0.063	14
Cyclohexene (2.8 M)	0.46	0.050	9
<i>t</i> -Amylthiol (1.9)	0.	0.008	0

<sup>a</sup> Starting hyponitrite approximately 0.25 M. <sup>b</sup> Intensity of chloroform emission signal at its maximum in units of molar concentration of normal chloroform. <sup>c</sup> Intensity of final chloroform absorption signal in units of molar concentration.

thiol completely destroys the emission, though chloroform is still a product in comparable yield. Thus, polarization resulting from a trichloromethyl-diamagnetic donor complex appears unlikely. When the starting material was deuterated in the methyl positions (96%), the emission intensity was reduced to 20%. These observations indicate that the emission signal is due to reaction between isopropyl-trichloromethyl radical pairs with a primary isotope effect of ca. 4.

The observed polarization could be explained by the simplified models originally put forth<sup>3</sup> if the chloroform arose from a hydrogen atom transfer from a radical in which the protons were previously polarized. However, the major isopropyl radical product (isopropyl chloride) shows only very weak enhanced absorption in both members of the methyl doublet. Addition of bromine or carbon tetrabromide diverts these radicals to the bromide, which still does not show emission. Fairly strong emission peaks were observed at the position corresponding to the methyl doublet of propylene. However, this product is consumed during the reaction so that the identification is complicated in this case.

The present reacting system may be treated as a simple two-step process



in which  $k_1$  is the rate constant for destruction of 2 and  $k_2$  is the rate constant for relaxation of the chloroform.<sup>5</sup> The measured values of  $k_1$  and  $k_2$  are both ca.  $7 \times 10^{-3} \text{ sec}^{-1}$ . These give an integrated enhancement factor of three times that measured at the maximum, or 600–700. This appears to exceed the the-

oretical limit for doublets,<sup>6</sup> using the original simplified models.

These observations are not consistent with the original dipolar relaxation models put forth.<sup>3</sup> They can be explained as being the result of a polarization mechanism similar to that recently proposed by Closs<sup>7</sup> if it is postulated that the positive nuclear spin subgroups of the triplet trichloromethyl-isopropyl pairs are transformed to disproportionation product more rapidly than the low nuclear spin subgroups, thus leading to emission from those products. The isopropyl radicals separating from such encounters would then be enriched in the low nuclear spin substates and would give enhanced absorption. The relatively short relaxation time and long time for formation of the isopropyl chloride would both lead to a weaker enhancement in absorption in the methyl doublet of this product.

It should also be noted that the products obtained from decomposition of 2 show different behavior than those obtained from decomposition of diacyl peroxides.<sup>4</sup> The methyl chloride produced from several hyponitrites, including 2, shows emission, while that from acetyl peroxide shows enhanced absorption. Also, isopropyl chloride from diisobutyl peroxide in hexachloroacetone<sup>4</sup> shows emission-absorption in the methyl doublet, while that from 2 shows only enhanced absorption. Further studies of products derived from the same formal radicals, obtained in different ways, should prove helpful in elucidating the mechanisms of these polarizations.

**Acknowledgment.** This work was supported by grants from the National Science Foundation.

(6) Professor H. Ward has communicated to us privately that he has also observed an enhancement factor greater than 650 for chloroform formation.

(7) G. Closs, *J. Amer. Chem. Soc.*, **91**, 4552 (1969). This model has since been extended to cover energy polarization: G. L. Closs, private communication.

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### Structure of Dichlorotris(triphenylphosphine)dycopper(I)-Benzene, a Chloride-Bridged Dimer Containing both Three- and Four-Coordinate Copper

Sir:

There has been extensive interest in the preparation and study of copper(I) complexes of the type  $L_n\text{Cu}_m\text{X}_m$ , where L is a monodentate tertiary group Vb ligand and X is a halide ion.<sup>1,2</sup> Solid compounds of composition  $L_3\text{CuX}$ ,  $L_3\text{Cu}_2\text{X}_2$ ,  $L_2\text{CuX}$ , and  $\text{LCuX}$  are all known. At least two members of this series, chlorotris(diphenylmethylphosphine)copper(I)<sup>3</sup> and tetrameric iodo-triethylarsinecopper(I),<sup>4</sup> have been studied by X-ray diffraction and shown to contain copper atoms in a distorted tetrahedral environment. Complexes of general

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(2) W. T. Reichle, *Inorg. Nucl. Chem. Lett.*, **5**, 981 (1969).

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(3) R. G. Lawler, *J. Amer. Chem. Soc.*, **89**, 5519 (1967); H. Fischer and J. Bargon, *Accounts Chem. Res.*, **2**, 110 (1969).

(4) R. Kaptein, *Chem. Phys. Lett.*, **2**, 261 (1968).

(5) The measured value for the relaxation time of chloroform at infinite dilution in carbon disulfide is ca. 300 sec: T. L. Pendred, A. M. Pritchard, and R. E. Richards, *J. Chem. Soc.*, 1009 (1966).