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Silver-Promoted Conversion of Cyclopropene to Allylic Products

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Abstract: Cyclopropene **1**, passed in a He stream through a gas chromatography column containing firebrick impregnated with a saturated solution of $AgNO_3$ in glycerol, reacted to give acrolein **6** (6%) and allyl nitrate **7** (20%). The products were identified by GC, MS, IR, and ^1H NMR. A mechanism is proposed to explain the reactions.

The occurrence and mechanisms of metal-mediated cyclopropene reactions are of continuing interest.[1] Although substituted cyclopropenes have been observed to undergo intriguing ring-opening oxidation and solvolysis reactions in the presence of transition metals such as Ag^+ cation[2-4] and Cu^{2+} cation,[5] comparable chemistry has not been reported for cyclopropene itself (**1**), which is an unstable gas at room temperature.[6] Cyclopropene was quantitatively removed from N_2 when the mixture was passed into an aqueous silver nitrate solution, but the product was characterized as a gummy polymeric material.[6]

In order to quantitate the nitrogenase-catalyzed reduction products of cyclopropene, it was required to separate **1** from one of its reaction products, cyclopropane.[7] Gas chromatography (GC) columns containing firebrick impregnated with ethylene glycol or glycerol solutions of $AgNO_3$ were known to separate mixtures of small alkanes and alkenes very effectively,[8] and it was found that cyclopropane and cyclopropene were easily resolved by GC on firebrick treated with a saturated solution of $AgNO_3$ in glycerol.[7] Cyclopropene did not emerge from this column, and larger injected quantities caused the appearance of an unknown peak at very long retention time relative to C_3 hydrocarbons. We now report that this peak, collected by preparative GC and analyzed by GC, MS, IR and ^1H NMR, consists of a mixture of acrolein **6** and allyl nitrate **7**, thus providing the first evidence that the parent cyclopropene molecule can undergo Ag^+-promoted reactions analogous to those previously described for aryl-substituted cyclopropenes.[3]

RESULTS AND DISCUSSION

Reaction of Cyclopropene with $AgNO_3$-Glycerol. In order to analyze the gas phase products formed from reduction of **1** by nitrogenase[7] or in model studies of this enzyme,[9] a GC column containing acid-washed firebrick impregnated with a saturated solution of $AgNO_3$ in glycerol, having a short section of Porapak N at the end of the column, was used to separate ethane (internal standard), propene, and cyclopropane. No peak corresponding to cyclopropene (70 nmol injected) was seen, but when the Porapak N section was removed or moved to the beginning of the column, a broad peak eluted with a retention time 11-13x longer than that of ethane. The unknown peak was isolated using the $AgNO_3$-glycerol GC column preparatively, providing a clear, colorless, volatile liquid with an acrid odor.

IR, MS, ^1H NMR and GC Analyses of the Unknown Peak. The IR spectrum of the eluted liquid in $CDCl_3$ displayed strong, sharp bands at 1275 and 1640 cm^{-1} (nitrate ester, $\nu_{O\text{-}NO_2}$).[10] Other significant features of the IR spectrum were: a shoulder at 1660 cm^{-1} (alkene), a strong band at 850 cm^{-1} (alkene), a sharp band at 1695 cm^{-1} ($\nu_{C=O}$ for α,β-unsaturated aldehydes), and finally, weak bands at 2890, 2775, and 2770 cm^{-1} (aldehydic $\nu_{C\text{-}H}$). The MS data of the unknown showed molecular ions for $C_3H_5NO_3$ **7** (m/e 103) and possibly C_3H_4O **6** (m/e 56), which were identified by a peak match program. Other fragments were detected at m/e 27 (vinyl), 41 (allyl), 46 (NO_2^+), and 29 (CHO^+); larger molecular weight fragments were not observed. Acrolein **6** and allyl nitrate **7** were therefore tentatively identified as the major components of the unknown mixture.

The structures were confirmed by a ^1H NMR spectrum of the product mixture in $CDCl_3$, which displayed a multiplet at δ 9.67-9.83 ppm (1.0 H, a), multiplets at 6.43-6.60 ppm (2.8 H, b), a doublet at δ 5.00 ppm (7.3 H, c), multiplets at 5.30-5.75 ppm (8.0 H, d), and multiplets at 5.75-6.43 ppm (3.6 H, e). The proton assignment based on peak chemical shifts, multiplicity and integration (assuming a ratio of ~ 3.6:1 of **7**:**6**) is shown in Fig. 1.

A peak with the same retention time as authentic allyl nitrate was observed from the injection of the eluted mixture, after storage at ambient temperature, into a boiling point GC column (OV-101). Although no peak was detected for acrolein, a polymeric material was observed in the sample, consistent with the known instability of acrolein.[11]

Preparation and Analysis of a Synthetic Allyl Nitrate-Acrolein Mixture. As only small amounts of the product mixture were recovered by preparative GC (see below), the components of the unknown mixture were not analyzed separately. Instead, authentic allyl nitrate and acrolein were mixed in a molar ratio of 3.6:1 (based on the NMR data) and analyzed for comparison. The synthetic mixture exhibited IR and ^1H NMR spectra very similar to those obtained for the cyclopropene products (data not shown), confirming our identification of the latter as **7** and **6**.

Fig. 1. ^1H NMR Peak Assignment for Cyclopropene Products.

We estimate that the total yield of **6** and **7** in the GC reaction was on the order of 26%.[12] This yield does not take into account possible interception of the cation **3** by the glycol to give an allyl glycerol ether product analogous to solvolysis products formed with substituted cyclopropenes.[13] Such a product, and also any polymeric product, would presumably be retained on the GC column, and thus not be detected in our analysis.

Interconversion of Acrolein and Allyl Nitrate. The injection of an authentic sample of either one of the products (acrolein or allyl nitrate) on the $AgNO_3$-glycerol column did not result in the formation of the other product (<5%, ^1H NMR, data not shown). We conclude that neither product is formed through a secondary reaction of the other on the GC column.

We propose a mechanism similar to those already suggested for other cyclopropenes[2-4] to explain the reaction products (Scheme 1), assuming that glycerol is involved in the reaction. Formation of the allylic argentiocarbonium ion **3** (or an equivalent form) might occur either by an attack of Ag^+ on the cyclopropene π

bond (path a), followed by a rapid ring opening of the transient cyclopropyl cation **2**, or by an attack of Ag^+ on the cyclopropene σ bond (path b) with simultaneous ring opening. Nucleophilic attack of the nitrate ion on **3** would form **5** which loses Ag^+ to give allyl nitrate **7**. Similar attack of glycerol (ROH) on **3** would produce the ether-like intermediate **4**, followed by loss of the alkyl moiety and metallic silver (consistent with the observation that the $AgNO_3$ column blackened on repeated injections of cyclopropene), to give acrolein **6**. The latter process is depicted as being assisted by an electon-donating nucleophile (Nu) such as a glycerol OH group.

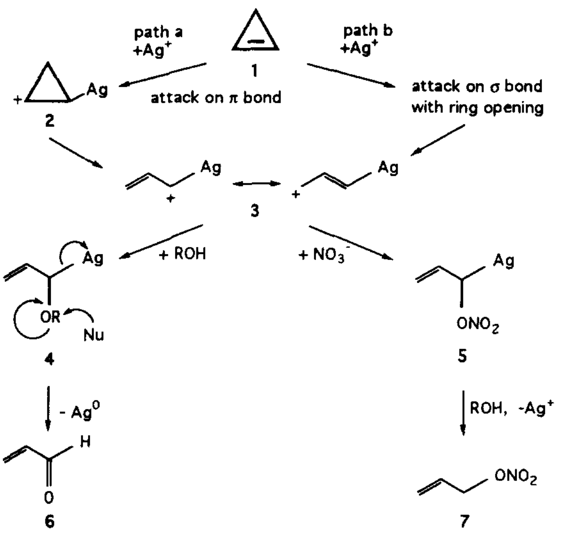
EXPERIMENTAL DETAILS

General Methods and Reagents. Preparative GC to isolate the unknown mixture was carried out at 55°C on a Varian 2400 GC equipped with a flame ionization detector (FID) and a 1:90 gas effluent splitter, using a glass column (0.48 cm x 122 cm) filled with firebrick (Chromosorb P, acid-washed, 80-100 mesh) impregnated with $AgNO_3$-saturated glycerol.[8] The ends of the column (within the hot injector and detector blocks) contained Chromosorb P only to minimize thermal decomposition. Samples were 10 mL of **1**, 0.57 atm in Ar to 1 atm. Ethane (C_2H_6) was used as internal standard, and peaks were integrated electronically. Analysis of the acrolein and allyl nitrate control samples was carried out at 45°C using a stainless steel column (0.32 cm x 183 cm) filled with 15% OV-101 on 100-200 mesh Chromosorb G-HP packing. Purification of acrolein and allyl nitrate standards was performed at 110°C using a boiling point separation column operated in a Varian 3700 GC (thermoconductivity detector). Fragmentation pattern MS data was obtained on a Dupont 21/492 mass spectrometer operated by the California Institute of Technology Analytical Services. A high resolution exact match fit (± 0.003 mass units) was also obtained for the two product parent ions. ^1H NMR spectra were obtained at 60 MHz (Varian A-60) or 250 MHz (Bruker AC-250). IR spectra were recorded on a Perkin Elmer 281 spectrometer.

$CDCl_3$ (99.96%) was from Mallinckrodt or Merck, Sharpe and Dome. Acetonitrile (>99%), vinyl chloride, and *p*-xylene were obtained from Matheson, Coleman and Bell. $CaCl_2$ and anhydrous ether were reagent grade (Mallinckrodt). $AgNO_3$ (99+%) was from Aldrich or Mallinckrodt. Acrolein (Aldrich; toxic, handle carefully) was separated from its stabilizer (hydroquinone) by preparative GC (boiling point column).

Synthesis of Cyclopropene 1. Cyclopropene was prepared by the method of Closs and Krantz[14] and purified by trap-to trap distillation followed by low temperature-low pressure fractional distillation using a previously described method.[7, 15, 16] Cyclopropene was stable to GC analysis using a Porapak N column under conditions similar to those used with the $AgNO_3$ column.

Synthesis of Authentic Allyl Nitrate 7. Allyl nitrate was prepared by an adaptation of the method of Pattison and Brown.[17] To acetonitrile (3.72 mol, dried for 5 h over anhydrous $CaCl_2$) was added $AgNO_3$ (0.60 mol) with vigorous stirring. Allyl chloride (0.50 mol) was then added causing a strong reflux and the formation of a white precipitate. After additional refluxing with gentle heating, the cooled mixture was filtered and the precipitate was washed with dried *p*-xylene (20-30 mL) and anhydrous ether (10 mL). The combined filtrate and washes were distilled with a Vigreux column, giving the allyl nitrate fraction at 110-111°C. (CAUTION: potential explosion hazard: use blast shield and due precautions.) The distillate was further purified from residual *p*-xylene by preparative GC (boiling point column). In one case, the xylene was omitted and the product (bp ~ 50°C at 100 torr) was fractionally distilled using a water pump.



Scheme 1

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