Experimental Section

IR spectra (neat film) were recorded on a Perkin-Elmer 521 grating spectrophotometer. UV spectra (ethanol) were recorded on a Perkin-Elmer 350 spectrophotometer; extinction values are given as log ε. NMR (CDCl$_3$ with internal Me$_4$Si) spectra were run on a Varian A-60A. The solvents were removed in vacuo on a rotary evaporator. Kieselgel (SiO$_2$) was used for chromatography. Elemental analyses are within ±0.4% of theory.

Tetrahydro-4-isopropyl-2-[3-(trifluoromethyl)phenyl]-2H-1,4-oxazin-2-ol (7). A stirred solution of 3-(trifluoromethyl)acetophenone (93.5 g, 0.5 mol) in CHCl$_3$ (500 mL) at room temperature was treated dropwise over 1.5 h with a solution of Br$_2$ (80.0 g, 0.5 mol) in CHCl$_3$ (200 mL). The reaction was stirred for 1.5 h after the addition was completed and then the mixture was extracted with H$_2$O (3 × 250 mL) and aqueous NaCl (100 mL), dried (Na$_2$SO$_4$), filtered, and concentrated. The residue was distilled to give 5 (124 g, 92.9%), bp 85–90 °C (1.2 mm) [lit.[8] bp 71–72 (0.25 mm)].

A solution of 5 (26.7 g, 0.10 mol) in toluene (250 mL) was treated with N-isopropylethanolamine (20.6 g, 0.20 mol) and stirred at room temperature for 24 h. The resulting mixture was extracted with 10% aqueous HCl (2 × 250 mL). The combined aqueous extract was cooled with ice, made basic by slow addition of concentrated NH$_4$OH, and extracted with Et$_2$O (2 × 300 mL). The combined Et$_2$O extract was dried (MgSO$_4$), treated with charcoal, filtered, and concentrated to a yellow liquid (25.4 g). This was purified by chromatography on SiO$_2$ (500 g), eluting with toluene–1% Et$_3$N (3.5 L) and with toluene–50% CHCl$_3$–2% Et$_3$N (4 L), taking 500-mL fractions. The product was obtained by combining and concentrating fractions 8–13 to give 7 (18.8 g, 65.1%) as a yellow liquid: IR ν 3420, 1330, 1115 cm^{-1}; UV λ 256 (2.812), 263 (2.826); ^{1}H NMR δ 1.04 (6 H, d, J = 6.5 Hz, 2 × CH$_3$), 2.25–3.03 (5 H, m, 2 × CH$_2$N + CH), 3.63–4.28 (2 H, CH$_2$O), 5.30 (s, 1 H, exchangeable, OH), 7.30–8.07 (4 H, m, aromatic). Anal. Calcd for C$_{14}$H$_{18}$F$_3$NO2: C, 58.12; H, 6.27; N, 4.84. Found: C, 57.62; H, 6.35; N, 4.66.

3,4-Dihydro-4-isopropyl-6-[3-(trifluoromethyl)phenyl]-2H-1,4-oxazine (8). A stirred mixture of 7 (15.5 g, 53.6 mmol),

p-toluenesulfonic acid monohydrate (11.2 g, 58.9 mmol), and benzene (400 mL) was heated at reflux under a Dean–Stark water separator for 2 h. The reaction mixture was cooled to room temperature and extracted with saturated aqueous NaHCO$_3$ (2 × 200 mL). The organic layer was dried (K$_2$CO$_3$/MgSO$_4$), treated with charcoal, filtered, and concentrated to a red-brown liquid which was distilled to give 8 (11.47 g, 79.1%): bp (kugelrohr) 150–155 °C (0.025 mm); IR ν 1640, 1600, 1585, 1115 cm^{-1}; UV λ 243 (3.617), 329 (4.108); ^{1}H NMR δ 1.15 (6 H, d, J = 6.5 Hz, 2 × CH$_3$), 2.92–3.52 (3 H, m, CH$_2$N + CH), 4.18 (2 H, t, J = 5 Hz, CH$_2$O), 6.25 (1 H, s, C=CH), 7.13–7.73 (4 H, m, aromatic). Anal. Calcd for C$_{14}$H$_{16}$F$_3$NO: C, 61.98; H, 5.95; N, 5.16. Found: C, 61.22; H, 5.87; N, 4.94.

Tetrahydro-4-isopropyl-[3-(trifluoromethyl)phenyl]-2H-1,4-oxazine (1). A mixture of 8 (1.0 g, 3.69 mmol), PtO$_2$ (0.12 g), and AcOH (75 mL) was shaken under a H$_2$ atmosphere for 18 h. The mixture was diluted with 95% EtOH (50 mL), filtered through Celite, and concentrated. The residue was chromatographed on SiO$_2$ (35 g), taking 25-mL fractions and eluting with CHCl$_3$–5.5% MeOH–0.5% Et$_3$N. Fractions 3 and 4 were combined and concentrated to give 1 (0.66 g, 66%): bp 52 °C (0.005 mm); ^{1}H NMR δ 1.07 (6 H, d, J = 6 Hz, 2 × CH$_3$), 1.98–3.10 (5 H, m, 2 × CH$_2$N + NCH), 3.58–4.25 (2 H, m, CH$_2$O), 4.62 (1 H, d, J = 2.5 and 10 Hz, CHO), 7.45–7.78 (4 H, m, aromatic). Anal. Calcd for C$_{14}$H$_{18}$F$_3$NO: C, 61.53; H, 6.64; N, 5.13. Found: C, 61.64; H, 6.76; N, 5.34.

Registry No. 1, 26629-87-8; 5, 2003-10-3; 6, 109-56-8; 7, 75247-59-5; 8, 75232-80-3; 3-(trifluoromethyl)acetophenone, 349-76-8.

Evidence for 1,2-Dehydroadamantane as a Gas-Phase Product in Time-Resolved Field-Ionization Mass Spectrometry of 2-Adamantyl Trifluoroacetate

Gordon Walter Wood* and Bernard T. Kiremire

Department of Chemistry, University of Windsor, Windsor, Ontario, Canada N9B 3P4

James E. Gano and Neil Marron

Department of Chemistry, University of Toledo, Toledo, Ohio 43606

Arnold Falick and Pierre Tecon

Institute of Physical Chemistry, Federal School of Technology, CH-1015 Lausanne, Switzerland

Introduction

Demonstration of 1,2-dehydroadamantane (adamantene) as an intermediate in photolysis of the adamantyl phenylacetates[1] led us to investigate the possibility that the radical ion of this highly strained olefin might be detected in the mass spectrometer. Of particular use in this attempt was the ability of the field-ionization (FI) mass spectrometer to present a time-resolved view of low-energy processes occurring at times as short as 10^{-12} s and thus to isolate unimolecular gas-phase processes with lifetimes approaching this value.[2] A recent report provides evidence for formation of neutral adamantene in a McLafferty rearrangement of 2-(1-adamantyl)cyclohexanone following EIMS[3a] and reviews briefly the complex history of this

---

(8) I. J. Borowitz, H. Parnes, E. Lord, and K. C. Yee, J. Am. Chem. Soc., 94, 6817 (1972).

(1) J. E. Gano and L. Eizenberg, J. Am. Chem. Soc., 95, 972 (1973).
(2) H. D. Beckey, "Principles of Field Ionization and Field Desorption Mass Spectrometry", Pergamon, Oxford, 1977, p 174, and references therein.

Table I. Field-Ionization Mass Spectral Data of 2-Adamantyl Trifluoracetate

m/z	relative intensity	assignment
135	0.2	$C_{10}H_{15}^+$
152	4.3	$C_{10}H_{13}F^+\cdot$
153	0.2	
170	0.5	$C_{10}H_{12}F_2^+\cdot$
194	1.2	adamantyl acetate?
228	0.2	$(M - HF)^+\cdot$
247	0.2	
248	100	M, $(C_{12}H_{15}F_3O_2)^+\cdot$
249	13.4	
250	1.7	

elusive bridgehead compound[3b] which currently defines an important focal point for research into the properties of strained olefins.[3b]

We report here evidence for initial formation of adamantene ion from 2-adamantyl trifluoracetate (I) which decomposes by McLafferty rearrangement in the gas phase following FI. Charge retention by adamantene rather than its complementary product as reported above[3a] is not unexpected in view of the difference in ionization potentials of cyclohexanone enol and trifluoroacetic acid.

Results and Discussion

The FI mass spectrum of I is presented in Table I. It is perhaps worth emphasizing that this "normal" FI spectrum includes ions formed on the anode surface as well as those formed at very short times (ca. 10^{-11} s) after the precursors leave the surface. Under these conditions, the molecular ion is the base peak. There is no evidence of either adamantene (m/z 134) or the corresponding acid product of McLafferty rearrangement (m/z 114). Direct cleavage at the adamantyl ring is the only simple fragment observed (m/z 135, 0.2%). The ions m/z 152 and 170 probably give evidence of fluoride exchange between the acid moiety and the adamantane portion of the molecule. Exchange of fluorine with aromatic hydrogen has been reported.[4]

It may appear surprising that a low-energy fragmentation such as McLafferty rearrangement, which is prominent in low-energy EI mass spectra of esters, is not present after low-energy ionization by FI. However, it should be recalled that whereas EIMS records the ionic products of all reactions that occur in the gas phase within about 10^{-6} s, FIMS records, in addition to ions formed at the anode surface, only those products which are formed in the gas phase after about 10^{-11} s. This latter time is short enough to preclude many rearrangement reactions since they have frequency factors of the same order of magnitude. The time frame between 10^{-11} and 10^{-6} s, which is of considerable interest because it coincides with the rates of several common rearrangements, is accessible through the technique of field-ionization kinetics (FIK). This technique allows one to sample the ions formed by decompositions of a molecular ion at various times after its formation. In this way ions formed less than 10^{-10} s after the molecular ion leaves the field anode may be detected separately. These ions are limited in both energy and time for rearrangement and are therefore likely to correspond closely to original structures. We then undertook to explore this
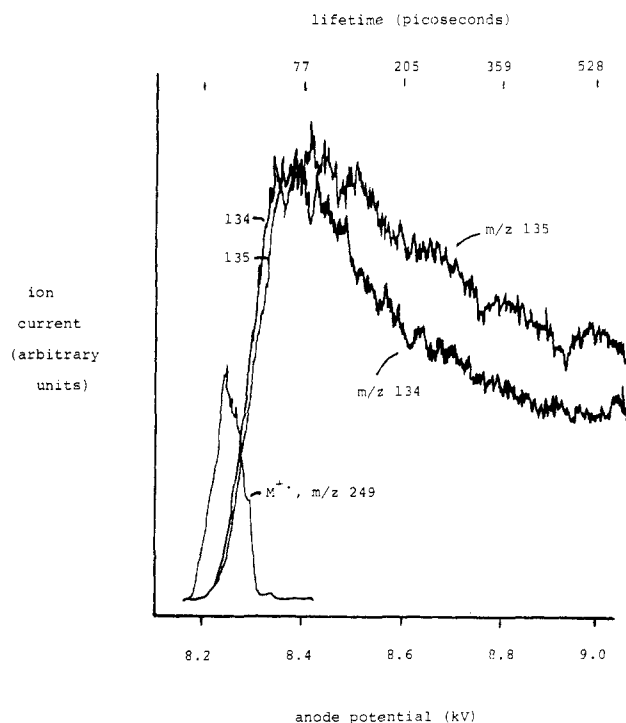

Figure 1. Ion-current profiles at increasing anode potentials for 2-adamantyl-*1-d_1* trifluoracetate. Profile for $M^+\cdot$ is typical of ions formed at anode surface. Profiles for m/z 134 and 135 demonstrate their origin at a distance from the anode (in gas phase).

intermediate region of the time scale by several approaches.

In experiments where the FI spectrum was first scanned at normal anode voltage (nominal 3 kV) and then repeatedly scanned as the anode voltage was increased in steps, all of the ions in the normal spectrum disappeared within a range of 40 V (2937 to 2979 V). At the higher voltage the ion m/z 134 was the only one observed. We interpret this result as evidence that the ions in the normal spectrum are all formed on or near the surface of the anode, whereas the ion m/z 134 is formed in negligible amounts. The latter ion, on the other hand, is formed at significant distance from anode and therefore in the gas phase.

Confirmation of this interpretation was obtained by upward scanning of the accelerating voltage (2 to 3 kV) with the magnet fixed to pass a selected ion (m/z 248 or 134). From these experiments it was shown that FI of I generates an intense ion at m/z 134 in the gas phase and that I-*1-d_1* generates both m/z 134 and 135 on comparable time scales. Subsequent field-ionization kinetic (FIK) experiments on a mass spectrometer with 8-kV accelerating voltage and a potential vs. time calibration derived as previously described[5] corroborated these findings. In Figure 1 are presented the data obtained from this latter instrument. The plot for m/z 249 defines the region for ions generated at the anode surface. In contrast, ions m/z 134 and 135 are generated some time after their precursor leaves the surface as indicated by the horizontal scale at the top of Figure 1. The most reasonable assignment for these ions is that they arise as complementary ions to $CF_3COOH(D)$ in a gas-phase McLafferty rearrangement with charge retention on olefin. The relative abundances of these ions provide evidence that the structure of the charged olefin corresponds to 1,2-dehydroadamantane

(3) (a) H. Schwartz, M. T. Reetz, W. F. Maier, C. Wesdemiotis, I. Chatziiosifidis, and M. Schilling, *Angew. Chem., Int. Ed. Engl.*, **18**, 952 (1979). (b) The second review listed by the preceding authors contains an error; see G. Köbrich, *ibid.*, **12**, 464 (1973).

(4) R. J. Dickinson and D. H. Williams, *J. Chem. Soc., Perkin Trans. 2*, 1363 (1972).

(5) A. M. Falick, P. J. Derrick, and A. L. Burlingame, *Int. J. Mass Spectrom. Ion Phys.*, **12**, 101 (1973).

(adamantene), at least at the rate-determining transition state.

The ratio of CF_3COOD/CF_3COOH loss (m/z 134/m/z 135) is essentially constant at 0.8 over the time interval 140–1320 ps. This value is reasonably taken as the kinetic isotope effect for a McLafferty rearrangement, since it is only marginally greater than the values 0.88 and 0.92 quoted for aliphatic esters.[6] On the other hand, the significant loss of deuterium from the position adjacent to the trifluoracetoxy group rules out major competition from 1,3-elimination processes to form 2,4-dehydroadamantane and/or protoadamantene.[7,8] In the extreme, absence of a deuterium isotope effect would mean that the 25% excess m/z 135 arose from some combination of 1,3-processes. Calculations show that, even at this limit, the sum of such processes is only 10% of the total (90% 1,2-elimination means 45% H and 45% D loss; 10% 1,3-elimination means 10% H loss, from which D/H = 45/55 = 0.8).

Although the above rationale is both reasonable and attractive for its simplicity, it is not conclusive for the following reason. The McLafferty rearrangement is generally believed to occur in a stepwise fashion, with formation of an intermediate after transfer of H. Strictly speaking, it is the structure of the transition state preceding this intermediate that our labeling experiment defines. Our results do not preclude rearrangement of this intermediate prior to loss of $CF_3COOH(D)$ to yield a $C_{10}H_{14}^{+\cdot}$ ion of different structure.

The apparent isotope effect at 8.4 kV is 0.95. It is interesting to speculate that at these very short times (44–110 ps) the decomposing ions may be of sufficiently high energy that the isotope effect is reduced.

In summary, we conclude that the m/z 134 ions generated from ester I, unlike those formed from related olefins and alcohols,[9] are predominantly of the 1,2-dehydroadamantane structure.

Experimental Section

Mass spectra were recorded on a Varian MAT Model CH5 DF spectrometer equipped with an EI/FI/FD source and operating under control of an INCOS Model 2000 data system. Ion source temperature was 50–70 °C for FI measurements. Spectra were recorded at a nominal resolution of 1500 on a scale calibrated with PFK in the EI mode. Normal voltages for FI were anode, 3 kV, cathode, 8 kV. The instrumental setup for the preliminary defocusing experiments is outlined with the results.

FIK results were obtained with a modified double-focusing mass spectrometer of Mattauch–Herzog geometry (DuPont/CEC 21-110B) equipped with a combination FI-EI source and an electrical detection system. Commercial uncoated stainless steel razor blades were used as FI anodes. Curves of ion current vs. blade voltage were recorded on an x–y recorder by setting the magnetic analyzer for a particular ion and varying the blade voltage from 8 to 10 kV.[10]

2-Adamantyl-1-d_1 trifluoroacetate (I) was synthesized from 4-protoadamantanone[11] by reduction with lithium aluminum deuteride,[12] acid rearrangement,[13] and esterification of the resulting 2-adamantanol-1-d_1 with trifluoroacetic anhydride. The product showed the following: NMR ($CDCl_3$) δ 1.7–2.2 (br m);

(6) D. G. I. Kingston, J. T. Bursey, and M. M. Bursey, Chem. Rev., 74, 219 (1974).

(7) Th. Kuster and J. Seibl, Org. Mass Spectrom., 11, 458 (1976).

(8) E. M. Engler and P. von R. Schleyer in "Alicyclic Compounds", W. Parker, Ed., Butterworth, London, 1973, Vol 5, p 244.

(9) Z. Majerski, G. Karlović, S. Digaš, and D. Stefanović, Org. Mass Spectrom., 12, 37 (1977).

(10) A. M. Falick and A. L. Burlingame, J. Am. Chem. Soc., 97, 1525 (1975).

(11) W. H. Lunn, J. Chem. Soc. C, 2124 (1970).

(12) D. Lenoir, R. D. Hall, and P. von R. Schleyer, J. Am. Chem. Soc., 96, 2138 (1974).

(13) D. Lenoir and P. von R. Schleyer, J. Chem. Soc. D, 941 (1970).

IR ($CHCl_3$) 1780, 1235, 1185 cm^{-1}; appropriate displacement of the FI mass spectrum shown in Table I.


Palladium-Catalyzed Triethylammonium Formate Reductions. 3.[1] Selective Reduction of Dinitroaromatic Compounds

Marc O. Terpko and Richard F. Heck*

Department of Chemistry, University of Delaware, Newark, Delaware 19711

The palladium-catalyzed triethylammonium formate reduction of mononitroaromatics has been reported previously.[1] Since publication of these results, we have had

$$ArNO_2 + 3Et_3NH^+ \; ^-O_2CH \xrightarrow{Pd}$$
$$ArNH_2 + 3CO_2 + 2H_2O + 3Et_3N$$
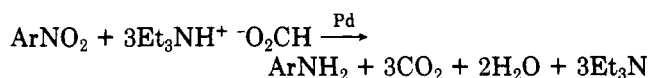
occasion to employ the reaction to selectively reduce one of two nitro groups in dinitroaromatic compounds. The reductions generally proceeded in good yield. Since the method offers advantages over other methods available we carried out a brief study of its scope. The results are reported herein.

Catalytic hydrogenation is apparently not a generally useful method for partially reducing dinitroaromatic compounds to nitroamines. Most often, hydrogen sulfide or variations of this reagent (Zinin reduction) or stannous chloride is used. Which reagent is selected depends upon the compound being reduced and (sometimes) which isomer, if more than one is possible, is desired. In general, the sulfide reagents and stannous chloride both prefer to reduce the less hindered nitro group. Important exceptions, however, occur with dinitrophenols, dinitrophenolic ethers, and dinitroaniline derivatives which tend to undergo reduction with sulfide reagents at the nitro group ortho to the oxygen or amine substituent,[2] while stannous chloride still prefers to reduce the least hindered nitro group. Iron and acetic acid recently were shown to selectively reduce some dinitroaromatics also, but examples with ortho heteroatoms were not studied.[3]

Results and Conclusions

A series of ten dinitroaromatic compounds was studied, employing 4.3 mol of formic acid per mole of dinitro compound (43% excess). The most reactive compounds were reduced in the presence of acetonitrile as solvent to improve the selectivity. Other compounds were reduced with only a small excess of triethylamine as solvent. The compounds successfully reduced are listed in Table I. The products usually were isolated by filtration to remove the catalyst followed by distillation under reduced pressure or by concentration and crystallization or chromatography. Yields of nitroamines ranged from 49 to 92% in nine of the ten examples. The reduction of 2,4-dinitroanisole gave

(1) Paper 2 in the series: N. A. Cortese and R. F. Heck, J. Org. Chem., 42, 3491 (1977). Paper 4 in the series: J. R. Weir, B. A. Patel, and R. F. Heck, J. Org. Chem., companion paper in this issue.

(2) H. K. Porter, Org. React., 20, 455 (1973).

(3) D. S. Wulfman and C. F. Cooper, Synthesis, 924 (1978).