(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-$d_1$ trifluoracetate (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 trifluoracetic anhydride. The product showed the following: NMR ($CDCl_3$) $\delta$ 1.7–2.2 (br m); IR ($CHCl_3$) 1780, 1235, 1185 $cm^{-1}$; appropriate displacement of the FI mass spectrum shown in Table I.

**Acknowledgment.** We thank the Natural Sciences and Engineering Council of Canada for financial support.

**Registry No.** 2-Adamantyl trifluoroacetate, 34909-02-9; 1,2-dehydroadamantane, 39257-33-5.

(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. Karlovič, S. Digaš, and D. Stefanovič, *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).

# 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*

*Received April 22, 1980*

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

$$ArNO_2 + 3Et_3NH^+ {}^-O_2CH \xrightarrow{Pd} ArNH_2 + 3CO_2 + 2H_2O + 3Et_3N$$

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).

0022-3263/80/1945-4992$01.00/0 

Table I. Palladium-Catalyzed Triethylammonium Formate Reductions of Dinitroaromatic Compounds

| compd reduced | conditions (solvent) | product (% yield) | mp, °C (lit. mp, °C) |
|---|---|---|---|
| $1,3\text{-}(O_2N)_2C_6H_4$ | 1 h, 100 °C | $3\text{-}O_2NC_6H_4NH_2$ (77) | 113–114 (114)[a] |
| $2,4\text{-}(O_2N)_2C_6H_3CH_3$ | 1 h, 100 °C | $2\text{-}O_2N\text{-}4\text{-}H_2NC_6H_3CH_3$ (92) | 77–78 (78–79)[b] |
| $2,6\text{-}(O_2N)_2C_6H_3CH_3$ | 20 min, 100 °C | $2\text{-}O_2N\text{-}6\text{-}H_2NC_6H_3CH_3$ (76) | 87–88 (91.5)[c] |
| $3,4\text{-}(O_2N)_2C_6H_3CH_3$ | 1 h, 100 °C | $4\text{-}O_2N\text{-}3\text{-}H_2NC_6H_3CH_3$ (55) | 109–110 (109)[d] |
| $3,5\text{-}(O_2N)_2C_6H_3CO_2CH_3$ | 1 h, 100 °C | $3\text{-}O_2N\text{-}5\text{-}H_2NC_6H_3CO_2CH_3$ (65) | 159–160 (160)[e] |
| $2,2'\text{-}(O_2NC_6H_4)_2$ | 1 h, 100 °C | $2\text{-}H_2NC_6H_4C_6H_4NO_2\text{-}2'$ (75) | 64–65 (64.0–64.5)[f] |
| $2,4\text{-}(O_2N)_2C_6H_3OH$ | 5 min, reflux ($CH_3CN$) | $2\text{-}H_2N\text{-}4\text{-}O_2NC_6H_3OH$ (57) | 141–142 (142–143)[g] |
| $2,4\text{-}(O_2N)_2C_6H_3OCH_3$ | 5 min, reflux ($CH_3CN$) | $2\text{-}H_2N\text{-}4\text{-}O_2NC_6H_3OCH_3$ (24) | 117.0–117.5 (118)[h] |
| $2,4\text{-}(O_2N)_2C_6H_3NH_2$ | 10 min, reflux ($CH_3CN$) | $1,2\text{-}(H_2N)_2\text{-}4\text{-}O_2NC_6H_3$ (49) | 198–199 (198)[i] |
| $2,4\text{-}(O_2N)_2C_6H_3NHCOCH_3$ | 5 min, reflux ($CH_3CN$) | $2\text{-}H_2N\text{-}4\text{-}O_2NC_6H_3NHCOCH_3$ (56) | 204–205 (205)[j] |

[a] A. W. Hofmann and J. S. Muspratt, *Ann. Chim. (Paris)*, **57**, 219 (1845). [b] E. Noelting and A. Collin, *Chem. Ber.*, **17**, 263 (1884). [c] E. Noelting, *ibid.*, **37**, 1024 (1904). [d] J. Kenner and M. Parkin, *J. Chem. Soc.*, 858 (1920). [e] A. Herre, *Chem. Ber.*, **28**, 596 (1895). [f] G. M. Badger and W. F. H. Sasse, *J. Chem. Soc.*, 4 (1957). [g] K. Auwers and H. Röhrig, *Chem. Ber.*, **30**, 995 (1897). [h] R. Meldona, G. H. Woolcott, and E. W. Ray, *J. Chem. Soc.*, **69**, 1330 (1896). [i] E. Heim, *Chem. Ber.*, **21**, 2305 (1888). [j] M. A. Phillips, *J. Chem. Soc.*, 1409 (1930).

only 24% monoamine. We could not isolate pure reduction products from 2,4-dinitrophenyl acetate or from 2,4,6-trinitrotoluene. The triethylammonium formate reductions reduce the least hindered nitro group in 2,4-dinitrotoluene (the 4-nitro group) but the more hindered, ortho, nitro group in 2,4-dinitrophenol, 2,4-dinitroanisole, 2,4-dinotroaniline, and 2,4-dinitroacetanilide. Thus, the formate reductions parallel the sulfide and not the stannous chloride reductions of dinitro compounds.

The triethylammonium formate reductions proceed in yields comparable to those reported for sulfide reductions. The formate reductions are more convenient to work up and the use of toxic hydrogen sulfide or compounds which evolve hydrogen sulfide is avoided.

## Experimental Section

**Materials.** Triethylamine (Aldrich) was stored over Davison 4-Å molecular sieves and otherwise used as received. The 97% formic acid (Aldrich) also was used as received. The 10% palladium on charcoal was a product of Matheson Coleman and Bell. *m*-Dinitrobenzene, 2,4-dinitrotoluene, and 2,4,6-trinitrotoluene were products of the Eastman Kodak Company and the 2,6- and 3,4-dinitrotoluenes were from Aldrich.

2,4-Dinitrophenol, mp 112–113 °C,[4] and 2,4-dinitroanisole, mp 86.5–87.8 °C,[5] were prepared by published procedures. 2,4-Dinitrophenyl acetate, mp 70–71 °C, was obtained by acetylation of the phenol with acetic anhydride. 2,4-Dinitroacetanilide, mp 121–122 °C, was produced by acetylation of 2,4-dinitroaniline (Aldrich) with acetic anhydride. Methyl 3,5-dinitrobenzoate, mp 111–112 °C, was obtained from 3,5-dinitrobenzoyl chloride (Fisher) and methanol.

**General Procedure for Selective Reduction of Dinitroaromatics. Compounds without Hydroxyl, Alkoxyl, Ester, Amino, or Acetamido Substituents.** In a 50-mL three-necked round-bottomed flask equipped with a reflux condenser and a stirrer was placed 10 mmol of the dinitro compound, 0.11 g of 10% palladium on carbon and 6 mL of triethylamine (45 mmol). The mixture was heated to boiling and while stirring 1.6 mL of 97% formic acid (43 mmol) was added dropwise over a period of a few minutes. The mixture was then boiled for 20 min to 1 h. The progress of the reduction was followed by TLC on alumina with chloroform as the eluant. Reactions were terminated after disappearance of the starting material. After the reaction mixture was cooled, methylene chloride was added and the catalyst was removed by filtration. The solvent and excess triethylamine were removed under reduced pressure and the residues were either distilled (*o*-nitroaniline, 2-nitro-4-aminotoluene, and 4-nitro-2-aminoanisole), chromatographed on alumina (4-nitro-3-aminotoluene, methyl 3-nitro-5-aminobenzoate, and 4-nitro-1,2-phenylenediamine), or recrystallized directly (2-nitro-6-aminotoluene, 2-nitro-2'-aminobiphenyl, 4-nitro-2-amino-phenol, and 4-nitro-2-aminoacetanilide).

**Compounds with Hydroxyl, Alkoxyl, Ester, Amino, or Acetamido Substituents.** The same quantities as in the above procedure were used except that 5 mL of acetonitrile was added initially and the formic acid was added dissolved in 5 additional mL of acetonitrile. The formic acid solution was added dropwise over a period of 15 min to a stirred solution of the dinitro compound, cooled to 15 °C in a cold water bath. After the addition, the mixture was quickly heated to boiling for 5–10 min and then cooled. Products were isolated as in the above procedure.

**Acknowledgment** is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

**Registry No.** 1,3-Dinitrobenzene, 99-65-0; 2,4-dinitrotoluene, 121-14-2; 2,6-dinitrotoluene, 606-20-2; 3,4-dinitrotoluene, 610-39-9; methyl 3,5-dinitrobenzoate, 2702-58-1; 2,2'-dinitrobiphenyl, 2436-96-6; 2,4-dinitrophenol, 51-28-5; 2,4-dinitroanisole, 119-27-7; 2,4-dinitroaniline, 97-02-9; 2,4-dinitroacetanilide, 610-53-7; *m*-nitroaniline, 99-09-2; 2-nitro-4-aminotoluene, 89-62-3; 2-nitro-6-aminotoluene, 603-83-8; 4-nitro-3-aminotoluene, 578-46-1; methyl 3-nitro-5-aminobenzoate, 23218-93-1; 2-nitro-2'-aminobiphenyl, 35883-86-4; 4-nitro-2-aminophenol, 99-57-0; 4-nitro-2-aminoanisole, 99-59-2; 4-nitro-1,2-phenylenediamine, 99-56-9; 4-nitro-2-aminoacetanilide, 53987-32-9; palladium, 7440-05-3.

(4) J. A. Moore and D. L. Dalrymple, "Experimental Methods in Organic Chemistry", 2nd ed., W. B. Saunders Co., Philadelphia, PA, 1976, p 197.

(5) B. M. Bogoslovski and L. M. Tsil'man, *Org. Chem. Ind.*, **6**, 445 (1939); *Chem. Abstr.*, **34**, 2360 (1940).

# Stereochemisty of Ciliarin, Zexbrevin, and Their Relatives[1]

Pratish K. Chowdhury, Ram P. Sharma, and Gopalakrishna Thyagarajan

*Regional Research Laboratory, Jorhat 785 006, Assam, India*

Werner Herz* and Serengolam V. Govindan

*Department of Chemistry, The Florida State University, Tallahassee, Florida 32306*

*Received July 17, 1980*

In connection with our work on the tagitinins we have reported the conversion of tagitinin A (1) to **2a** and **3a**.[2,3]

(1) Work at the Florida State University was supported in part by a grant (CA-13121) from the U.S. Public Health Service through the National Cancer Institute.

(2) Baruah, N. C.; Sharma, R. P.; Madhusudanan, K. P.; Thyagarajan, G.; Herz, W.; Murari, R. *J. Org. Chem.* **1979**, *44*, 1831.

(3) To eliminate continuing confusion about how to indicate the correct stereochemistry of these and related heliangolide derivatives, we redraw our earlier formulas in accordance with previously recommended rules[4] so that reentrant angles at tetrahedral ring carbon atoms are shown only when this corresponds to reality. For the 3,10-ethers this results in a change at C-3 (from vertex to reentrant) and for heliangolides in general in a change at C-6 (from reentrant to vertex).

0022-3263/80/1945-4993$01.00/0 