Quantitative Synthesis and Formation of Cyclopenta[*cd*]pyrene 3,4-Oxide under Simulated Atmospheric Conditions[1]

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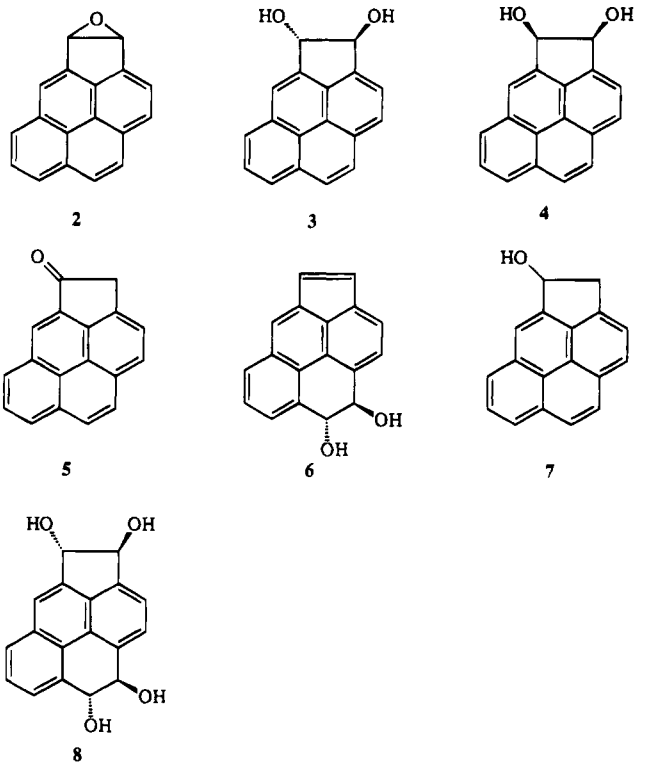
Cyclopenta[*cd*]pyrene 3,4-oxide (**2**) has been synthesized in a one-step, quantitative reaction using dimethyldioxirane. The oxide, or its thermal rearrangement products cyclopenta[*cd*]-pyren-3(4*H*)-one and cyclopenta[*cd*]pyren-4(3*H*)-one, is formed from cyclopenta[*cd*]pyrene (**1**) under simulated environmental conditions. In one case these products are formed when **1** is adsorbed on model particulates and then exposed to the reaction products of tetramethylethylene and ozone in the gas phase.

Introduction

Cyclopenta[*cd*]pyrene (CPP)[2] (**1**) is one of several polycyclic aromatic hydrocarbons (PAH) found in polluted atmospheres, usually bound to soot and other particulate matter (*1*). The mutagenicity of CPP exceeds that of benzo[*a*]pyrene (BaP) (*1*). CPP has also been found to be carcinogenic in mice (*2*). BaP, a known mutagen and carcinogen, is also found in polluted atmospheres and has long been the considered the most notorious of the PAH in such atmospheres. The fact that CPP is more mutagenic than BaP has stimulated research directed at identifying its mutagenic metabolites. It has been predicted that CPP 3,4-oxide (**2**) should be one such mutagenic metabolite of CPP (*3*). This prediction has stimulated efforts to synthesize the oxide as well as improved syntheses of the parent hydrocarbon. In 1979 Gold *et al.* reported the synthesis of CPP 3,4-oxide and confirmed that it is a powerful mutagen (*4*). A different and higher yield synthesis of **2** was reported by McCaustland *et al.* in 1980 (*5, 6*). Sangaiah and Gold have described (*7*) a synthesis of **2** with an improved yield over that in the earlier report from the same group. More recently Tannenbaum and co-workers have reported a new and improved yield (86%) synthesis of **2** (*8*).

Metabolic activation of **1** by rat liver microsomes has shown that the major metabolite is *trans*-3,4-dihydroxy-3,4-dihydrocyclopenta[*cd*]pyrene (**3**) (*9*). Furthermore, it was also shown that acid catalyzed decomposition of oxide **2** gives the *cis* (**4**) and *trans* CPP 3,4-dihydrodiols and cyclopenta[*cd*]pyren-4(3*H*)-one (**5**) (*9*). The authors conclude that these observations imply that oxide **2** is a major metabolite of CPP. It was subsequently shown that metabolism of **1** by microsomes and cytochrome P-450 from rat liver gave **3** and the *trans*-9,10-dihydrodiol (**6**) of **1** (*10*). More recently additional metabolites of **1** have been identified when mouse and human hepatic microsomal enzymes are used (*11*). Two of these metabolites are the monooxygenated derivatives 4-hydroxy-3,4-dihydro CPP (**7**) and ketone **5**. The previously identified *trans*-3,4-diol **3** was also found to be the major metabolite in these studies. However, the 9,10-diol **6** found in the rat studies was not observed when mouse or human microsomal activation was used. Also included as metabolites were the *cis*-3,4-diol **4**, the diastereomeric tetrols, 3,4,9,10-tetrahydro-*trans*-3,4-dihydroxy-*trans*-9,-10-dihydroxycyclopenta[*cd*]pyrene (**8**), and two metabolites containing three hydroxy groups. Most oxygenated derivatives of **1** have been found to be mutagenic (*12*).



It has long been known that airborne and particulate adsorbed PAH undergo a variety of oxidative transformations in polluted atmospheres (*13, 14*). Furthermore, oxygenated fractions of samples collected in these atmospheres have been found to be carcinogenic or to contain direct acting mutagens (*15–18*). These observations suggest that atmospheric PAH can become activated in the absence of metabolic processes. We have been investigating the possibility that this activation may be accomplished by oxidants produced in reactions of ozone and alkenes, particularly carbonyl oxides and dioxiranes.

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[1] This is paper 26 in the series "Chemistry of Dioxiranes".
[2] Abbreviations: CPP, cyclopenta[*cd*]pyrene; PAH, polycyclic aromatic hydrocarbons; BaP, benzo[*a*]pyrene; EI, electron ionization; APT, attached proton test.

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It has been shown that both carbonyl oxides (*19*–*23*) and dioxiranes (*24*–*31*) are capable of converting PAH to the derived arene oxide, that is, these oxidants can activate PAH.

In this work we describe a one-step, quantitative synthesis of oxide **2**. We also show that **2** is formed under simulated atmospheric conditions involving an ozone–alkene reaction and particulate adsorbed **1**.

Experimental Section

Caution: *Dimethyldioxirane is a hazardous substance which should be synthesized and used in a hood.*

Materials. 1-Acetylpyrene, Oxone (DuPont, $2KHSO_5{\cdot}KHSO_4{\cdot}K_2SO_4$), and silica gel (Merck, 35–70 mesh, 40 Å) were obtained from Aldrich Chemical Co. (Milwaukee, WI) and used as received. Cupric bromide was purchased from J. T. Baker (Phillipsburg, NJ). Hexane (Fisher, Fairlawn, NJ) and methylene chloride (Fisher) were distilled from calcium hydride. Acetone (Fisher) was fractionally distilled over anhydrous potassium carbonate. The dimethyldioxirane solution in acetone was prepared according to the literature procedure (*32*–*34*) and was assayed for dioxirane content using phenyl methyl sulfide and the GLC method.

Methods. ^1H and ^{13}C NMR spectra were obtained at 300 and 75 MHz, respectively, on a Varian XL-300 NMR spectrometer with $CDCl_3$ or acetone-d_6 as solvent unless otherwise stated. All NMR data are reported in ppm or δ values downfield from TMS. The multiplicities of the ^{13}C NMR signals were determined by the attached proton test (APT) pulse sequence. Electron impact mass spectra were recorded (70 eV ionizing voltage) on a Hewlett-Packard 5988A EI quadrupole mass spectrometer connected to a Hewlett-Packard 5890A gas chromatograph fitted with a Hewlett-Packard 12 m × 0.2 mm × 0.33 μm Ultra-1 (cross-linked methyl silicone) column. Infrared spectra were recorded using KBr pellets on a Perkin-Elmer Model 1600 FT-IR spectrometer. Melting points were determined either on a Dynamic Optics AHT 713921 hot-stage apparatus or on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Chromatographic separations on the Chromatotron Model 8924 (Harrison Research) were accomplished using 1–4 mm Kieselgel 60 PF_{254} gypsum plates.

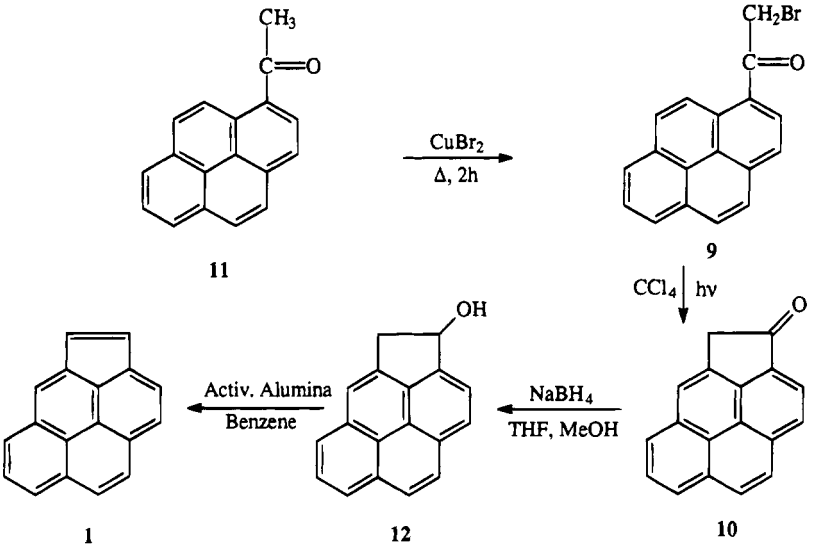
1-(Bromoacetyl)pyrene (9). To a magnetically stirred solution of 1-acetylpyrene (2.0 g, 8.19 mmol) in ethyl acetate (40 mL) and chloroform (40 mL) was added powdered $CuBr_2$ (3.65 g, 16.34 mmol). The reaction mixture was heated to reflux. The dark green color of the reaction mixture began to turn lighter in 15–30 min, and a creamy precipitate formed. A grass green solution was obtained after 2 h. The reaction mixture was filtered to remove the creamy precipitate. The precipitate was washed with CH_2Cl_2, and the washings were mixed with the filtrate. Evaporation of the solvent on the rotary evaporator gave an orange-yellow crystalline solid. The crude product was dissolved in CH_2Cl_2 and the solution treated with activated charcoal. Filtration and evaporation of the solvent gave a canary yellow solid (2.613 g). The ^1H NMR spectrum of the crude product indicated the presence of three compounds: 1-(dibromoacetyl)pyrene, 1-(bromoacetyl)pyrene, and 1-acetylpyrene. Radial chromatography of the solid on a Chromatotron (silica gel plate), using CH_2Cl_2/hexane (1:1) as the eluent, gave 0.290 g of 1-(dibromoacetyl)pyrene (10% yield) and 2.05 g of 1-(bromoacetyl)pyrene (83% yield). In addition, 0.120 g of 1-acetylpyrene (6%) was recovered. The major product was identified as 1-(bromoacetyl)pyrene on the basis of the following data: canary yellow needles, mp 129–131 °C (lit. mp 129–130 °C) (*8*)); IR (KBr, cm^{-1}): 1654 (C=O), 1594, 1582, 1507, 1371, 1260, 1235, 1065, 852, 710, 667, 589; ^1H NMR ($CDCl_3$): δ 4.70 (s, 2 H, -C*H*$_2$Br), 7.95–8.40 (m, 8 H, Ar*H*), 8.95 (d, J = 9.36 Hz, 1 H, Ar*H*-2). These values compare well with those in the literature (*35*). ^{13}C NMR ($CDCl_3$): δ 34.24 (-*C*H$_2$Br), 123.79 (*C*H), 124.48 (*C*H), 124.91 (*C*), 126.36 (*C*H), 126.49 (*C*H), 126.60 (*C*H), 126.65 (*C*H), 126.85 (*C*H), 128.22 (*C*), 130.07 (*C*H), 130.18 (*C*H), 130.31 (*C*), 130.48 (*C*), 134.49 (*C*), 194.32 (-*C*OCH$_2$Br); MS (EI, 70 eV): m/z 324 (^{81}Br-M$^+$) (12), 322 (^{79}Br-M$^+$) (12), 230 (17), 229 (100), 215 (17), 201 (60), 200 (30), 100 (26); calcd for $C_{18}H_{11}BrO$: 323.18. The minor product was identified as 1-(dibromoacetyl)pyrene on the basis of the following data: bright yellow cubes, mp 164–166 °C; IR (KBr, cm^{-1}): 1680 (C=O), 1592, 1502, 1383, 1256, 1214, 1105, 1067, 990, 958, 852, 716, 670, 610, 584; ^1H NMR ($CDCl_3$): δ 6.99 (s, 1 H, -C*H*Br$_2$), 7.90–8.50 (m, 8 H, Ar*H*), 8.71 (d, J = 9.4 Hz, 1 H, Ar*H*-2); ^{13}C NMR ($CDCl_3$): δ 42.77 (-*C*HBr$_2$), 123.61 (*C*H), 124.09 (*C*H), 124.75 (*C*), 125.57 (*C*H), 125.74 (*C*), 126.51 (*C*H), 126.56 (*C*H), 126.72 (*C*H), 126.74 (*C*H), 130.23 (*C*H), 130.70 (*C*), 130.91 (*C*), 134.61 (*C*), 188.62 (-*C*OCHBr$_2$); MS (EI, 70 eV): m/z 404 (6), 402 (M$^+$, 9), 401 (3), 295 (12), 293 (10), 229 (100), 202 (11), 201 (46), 200 (33); calcd for $C_{18}H_{10}Br_2O$: 402.08.

Cyclopenta[*cd*]pyrene (1). The general procedure described by Cornelisse *et al.* (*35*) was followed. A solution of 1-(bromoacetyl)pyrene (0.750 g, 2.32 mmol) in CCl_4 (850 mL) containing lithium carbonate (1 g) was irradiated with a medium pressure mercury arc lamp through a Pyrex filter for 180 min. Removal of the CCl_4 on the rotary evaporator afforded a dark orange-brown residue. The residue was dissolved in CH_2Cl_2 and filtered through a small column of silica gel (10 g). Evaporation of the CH_2Cl_2 gave an orange-brown residue (0.650 g). ^1H NMR analysis of the crude sample shows the presence of three compounds, 1-(bromoacetyl)pyrene (11%), 1-acetylpyrene (38%), and cyclopenta[*cd*]pyren-3(4*H*)-one (**10**) (52%). Purification of the crude sample on a Chromatotron (silica gel plate) using CH_2Cl_2 as eluent gave cyclopenta[*cd*]pyren-3(4*H*)-one (0.226 g, 40%) as a yellow solid: mp 210–213 °C (lit. mp 201–203 °C (*35*), 213–214 °C (*36*)); ^1H NMR ($CDCl_3$): δ 3.87 (s, 2 H, -CH$_2$-), 7.86 (s, 1 H, Ar*H*), 8.00–8.35 (m, 7 H, Ar*H*); MS (EI, 70 eV): m/z 243 (M + 1, 19), 242 (M$^+$, 100), 214 (60), 213 (57), 121 (10), 106 (44), 105 (14), 93 (14); calcd for $C_{18}H_{10}O$: 242.26. These data compare well with the literature (*36*) values. Reduction of cyclopenta[*cd*]pyren-3(4*H*)-one (0.218 g) with $NaBH_4$ (0.20 g) in a methanol (20 mL) and THF (20 mL) mixture and subsequent dehydration of 3-hydroxy-3,4-dihydrocyclopenta[*cd*]pyrene with basic activated alumina (0.20 g) in dry benzene (150 mL) afforded cyclopenta[*cd*]pyrene as an orange crystalline solid (0.1601 g). Purification of the product on a Chromatotron (silica gel plate) using hexane as eluent gave a pure sample of **1** (0.1314 g, 65%). The ^1H NMR spectrum of this material was identical to that reported in the literature (*36*).

Cyclopenta[*cd*]pyrene 3,4-Oxide (2). To a magnetically stirred solution of cyclopenta[*cd*]pyrene (0.0224 g, 0.099 mmol) in acetone (2 mL) was added a solution of 0.088 M dimethyldioxirane in acetone (1.30 mL, 0.114 mmol) at room temperature. As the reaction mixture was stirred at room temperature, the orange color began to fade and gave a pale yellow solution in 1 h. Removal of the acetone on the rotary evaporator gave pale yellow flakes of the oxide (0.024 g, 100% yield). Recrystallization of this material from acetone afforded almost colorless cubes: mp 212–215 °C dec (lit. mp 206–209 °C (*8*), 207–209 °C dec (*4*), 215 °C (*5*)); ^1H NMR (acetone-d_6): δ 5.15 (s, 2 H, *H*-3,4), 8.05 (t, J = 7.73 Hz, 1 H), 8.12 (s, 2 H), 8.18 (dd, J = 7.73, 11.05 Hz, 2 H), 8.27 (dd, J = 7.73, 0.95 Hz, 1 H), 8.31 (s, 1 H), 8.34 (d, J = 7.60 Hz, 1 H): ^{13}C NMR (acetone-d_6): δ 59.13 (-*C*H-, C-3 or C-4), 59.83 (-*C*H-, C-3 or C-4), 123.22 (*C*), 123.61 (*C*H), 124.34 (*C*H), 124.89 (*C*H), 126.31 (*C*H), 127.09 (*C*H), 127.46 (*C*H), 127.54 (*C*H), 128.57 (*C*H), 131.16 (*C*), 131.55 (*C*), 132.62 (*C*), 136.61 (*C*), 136.69 (*C*), 138.89 (*C*); MS (EI, 70 eV): m/z 243 (M + 1, 21), 242 (M$^+$, 100), 214 (91), 213 (74), 187 (10), 121 (14), 106 (64), 105 (23), 93 (19); calcd for $C_{16}H_{10}O$: 242.26. This mass spectrum is actually that of the 4-one (**5**) the thermal rearrangement product of **2**. It is accompanied by a trace amount of the 3-one (**10**) which was identified by comparing its GC retention time with that of authentic **10**.

Reaction of Cyclopenta[*cd*]pyrene, Adsorbed on Silica Gel, with Dimethyldioxirane. Cyclopenta[*cd*]pyrene (9 mg) was dissolved in acetone (10 mL). Silica gel was added to the solution which was stirred (5 s) until the silica gel took up the orange color of the hydrocarbon. The solvent was removed on the rotary evaporator and the silica gel dried with a vacuum

Scheme 1. Synthesis of Cyclopenta[*cd*]pyrene



pump for 15 min. The silica gel was then packed into a 6 in. reaction tube. Argon was then passed through a freshly prepared solution of dimethyldioxirane in acetone in order to carry the vapors into the reaction tube. The orange color of **1** began to fade immediately, and the silica gel had turned pale yellow in 15–20 min. The vapor was passed for a total of 25 min at room temperature. The silica gel was extracted with acetone (25 mL) to give an orange yellow solution. The solvent was removed on the rotary evaporator to give an orange yellow solid (10 mg). This solid was dissolved in acetone-d_6 for NMR analysis. The NMR spectrum showed a number of new absorptions in these regions: δ 3.50–4.20, 4.50–5.80, and 6.00–6.60 ppm. The NMR spectrum showed the characteristic 5.13 ppm absorption of cyclopent[*cd*]pyrene 3,4-oxide. An intense peak at 4.03 ppm and a smaller one at 3.79 ppm were assigned to cyclopenta[*cd*]pyren-4(3*H*)-one and cyclopenta[*cd*]pyren-3(4*H*)-one, respectively. The spectrum also showed some unreacted **1**. Repeating the experiment for a shorter period (3 min) led to the same results.

Reaction of Cyclopenta[*cd*]pyrene 3,4-Oxide with Silica Gel. Cyclopenta[*cd*]pyrene 3,4-oxide (5–6 mg) was dissolved in acetone-d_6 (0.6 mL) in an NMR tube. To this was added 50–60 mg of silica gel of the type used in the gas phase reaction above. The reaction was monitored by NMR. Within 5–15 min of mixing, the ^{1}H NMR spectrum showed the singlet at 4.07 ppm due to cyclopenta[*cd*]pyren-4(3*H*)-one. As monitoring continued, the 5.15 ppm peak of the epoxide was observed to decrease in intensity as the peak due to the ketone increased in intensity. After 8 h 58% of the epoxide had rearranged. Adding a few drops of $CDCl_3$ led to complete rearrangement of the remaining epoxide. The 4-one product was isolated from the reaction mixture by radial chromatography (silica gel plate, CH_2Cl_2). The product was obtained as orange-yellow needles: mp 220–225 °C (lit. mp 220–222 °C (*4*), 217–219 °C (*5*), 218–220 °C (*11*)); IR (KBr, cm^{-1}): 1715 (C=O), 1636, 1508, 1394, 1132, 888, 834, 684; ^{1}H NMR ($CDCl_3$) δ 4.03 (s, 2 H, -C*H*$_2$-), 7.94 (d, J = 7.70 Hz, 1 H), 8.00–8.10 (m, 3 H), 8.18 (d, J = 7.62 Hz,1 H), 8.26 (d, J = 7.57 Hz, 1 H), 8.44 (s, 1 H). It should be noted that a literature report (*11*) on this compound gives the methylene absorption as δ 5.48. ^{13}C NMR ($CDCl_3$): δ 43.53 (-*C*H$_2$-, C-3), 121.61 (*C*H), 122.96 (*C*H), 125.02 (*C*H), 126.63 (*C*H), 126.70 (*C*H), 127.14 (*C*H), 128.23 (CH), 138.69 (*C*), 130.97 (*C*), 131.29 (*C*), 131.38 (*C*), 137.04 (*C*), 203.32 (*C*=O, C-4); MS (EI, 70 eV): m/z 243 (M + 1, 21), 242 (M$^+$, 100), 214 (99), 231 (78), 187 (11), 121 (21), 106 (98), 105 (32), 93 (27); calcd for $C_{16}H_{10}O$: 242.26.

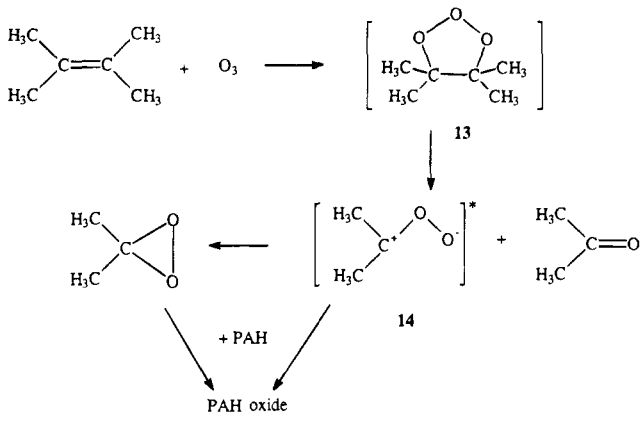
Reaction of Particulate Adsorbed Cyclopent[*cd*]pyrene with the Products of Gas Phase Ozonolysis of Tetramethylethylene. Cyclopenta[*cd*]pyrene (7 mg) was dissolved in acetone (2 mL). Silica gel (2 g) was then added to the solution. The solvent was removed on the rotary evaporator, and the silica gel containing **1** was packed into a small reaction tube. The gas phase reaction procedure was similar to that described (*31*) previously. Tetramethylethylene was carried into the gas phase using an argon stream. This stream was then combined with another carrying an ozone–oxygen mixture (0.16 mmol of O_3 min^{-1}) using a Y connector. The products of the ozone reaction are then carried into the reaction zone containing the particulate adsorbed **1**. This procedure was continued for 30 min at room temperature. The silica gel was removed from the reaction tube and extracted with acetone. The acetone was removed on the rotary evaporator and the residue dissolved in acetone-d_6 for NMR analysis. The NMR spectrum had several absorptions in the δ 5.00–5.20 region. Any peak at δ 5.13 due to the oxide **2** would be masked by these absorptions. A small peak at δ 4.09 is attributed to ketone **5**, a known rearrangement product of **2**. Analysis of the product mixture by GC/MS confirmed the presence of **5** and indicated that a trace amount of cyclopenta[*cd*]pyren-3(4*H*)-one (**10**) was also present. A similar experiment was carried out except that no tetramethylethylene was used. When ozone was passed through the reaction tube, the orange color of **1** was lost immediately. Analysis of the reaction mixture by NMR and GC/MS showed the absence of oxide **2** and ketone **5**.

A similar procedure was followed except that **1** (7 mg) in acetone was adsorbed on Chromosorb 102 (2 g) as model particulate. The ozonolysis reaction stream was passed through the reaction tube for 60 min. Analysis of the product mixture by GC/MS showed the presence of ketones **5** and **10**. In a separate experiment the reaction tube was divided (frit) into two zones. One of these zones contained tetramethylethylene adsorbed on silica gel while the other contained **1** adsorbed on silica gel. Ozone was passed (15 min, room temperature) into the reaction tube so that it encountered the zone containing the tetramethylethylene first. The silica gel containing **1** was removed and extracted with acetone. Analysis of the reaction mixture by GC/MS indicated the presence of ketone **5**.

Results and Discussion

While a number of syntheses of **1** have been reported (*6, 7, 35–44*), we found it convenient to modify an existing synthesis (*35, 38*) in such a way that a less expensive starting material is used. Thus 1-acetylpyrene was converted to 1-(bromoacetyl)pyrene using cupric bromide. The latter compound was then photolyzed to give ketone **10**, as previously described. The remainder of the synthesis follows literature precedents (Scheme 1). The oxidation of **1** to oxide **2** was accomplished by using an

Scheme 2. Formation of PAH Oxides *via* Ozone-Derived Oxidants



acetone solution of dimethyldioxirane. This procedure gives the oxide in quantitative yield in a very convenient manner. The highest yield previously reported is 86% (*8*).

As part of our continuing program aimed at identifying atmospheric processes which are capable of activating PAH in a manner which mimics metabolic processes, we then studied the reaction of **1** with gas phase dimethyldioxirane. This reaction is carried out under simulated atmospheric conditions. Hydrocarbon **1** is adsorbed on a model particulate and then exposed to dimethyldioxirane which has been carried into the gas phase using an argon stream. In this case the first model particulate used was silica gel which was packed into a reaction tube after adsorption of **1**. Following exposure to dimethyldioxirane, the silica gel is removed from the reaction tube and extracted with a solvent, and the products are analyzed by NMR and GC/MS. In this experiment the product mixture contained oxide **2**, as well as ketones **5** and **10**. We have shown *via* a separate experiment that silica gel promotes rearrangement of oxide **1** to ketone **5** when the reaction occurs at room temperature. At higher temperatures, such as those present during a GC/MS experiment, for example, the oxide is converted to a mixture of ketones **5** and **10**. This latter point is important in interpreting the results of the next experiment in which the silica gel adsorbed **1** is exposed to a reaction stream containing the products of reaction of ozone and tetramethylethylene. In this case multiple NMR absorptions in a critical region make it impossible to determine whether any **2** is present in the reaction mixture. However, ketones **5** and **10**, which we believe are derived from thermal rearrangement of **2** under these conditions, could be detected. The ozonolysis product stream is quite hot because of the great exothermicity of the reaction. This process was repeated using Chromosorb 102 as the model particulate. Again, the product mixture contained ketones **5** and **10**, indicating that oxide **2** had been formed.

Our interpretation of these results is based on our previously described (*31*) proposal in which we suggest that ozonolysis of the tetramethylethylene proceeds in the usual manner (Scheme 2) to give unstable trioxolane (**13**). This intermediate then decomposes to the carbonyl oxide (**14**) and acetone. The exothermicity of the reaction means that **14** is formed in an energy-rich form, which we postulate leads to cyclization to the isomeric dimethyldioxirane. In this connection it is worth recalling that the parent dioxirane has been synthesized by ozonolysis of ethylene. The process is believed to involve cyclization of the carbonyl oxide (*45*). Similar observations have been made in liquid phase ozonolyses (*29*, *46*). While both carbonyl oxides (*19–23*) and dioxiranes (*24–31*) are capable of giving the oxide **2**, we believe that the dioxirane is the most likely oxidant in these cases because of its greater reactivity. It is important to note that when a similar experiment is run with ozone alone, no evidence for ketones **5** and **10** can be found. Reaction occurs under these circumstances, but it is confined to direct reaction of ozone with **1**. It is clear then that the oxide-forming oxidant is not ozone, but an oxidant derived from the ozone–tetramethylethylene reaction. We have further tested this hypothesis by running a modified version of the ozonolysis experiment. In this case the tetramethylethylene is adsorbed on silica gel and packed into the reaction tube in a separate zone from that containing **1** adsorbed on silica gel. Ozone is passed into the reaction tube so that it encounters the zone containing tetramethylethylene first. Under these conditions **1** is converted to ketone **5**, presumably *via* oxide **2**. These conditions confine most of the reaction heat to the ozonolysis zone so that the oxide is not exposed to the higher temperatures required to form **10**. The oxide-forming oxidant is carried into the second reaction zone and converts **1** into **2**.

These experiments involving ozone simulate atmospheric conditions in several different ways. The use of gas phase dimethyldioxirane, as well as the use of the reaction stream containing the ozonolysis products of tetramethylethylene, along with particulate adsorbed **1**, simulates a common condition in polluted atmospheres in which particulate adsorbed PAH are exposed to a variety of oxidants. The experiment with the separately adsorbed **1** and tetramethylethylene simulates a related situation in which the oxidant source is also present in an adsorbed manner. Urban atmospheres frequently contain high concentrations of ozone as a result of photochemical smog. These same atmospheres also contain a variety of alkenes as well as PAH in the vapor or particulate adsorbed form. These are the conditions which we have attempted to simulate. Our results suggest that ozone-derived oxidants are good candidates for the atmospheric oxidants which cause activation of PAH in the absence of metabolic processes and the consequent formation of mutagens and carcinogens in these atmospheres.

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