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Reactions of Hexamethylbenzene Adsorbed on Silica Gel and Florisil with O_3 and with Oxygen Species Formed on Microwave Discharge of O_2

Elazar Zadok, Sarah Rubinraut, Felix Frolow, and Yehuda Mazur*

Department of Organic Chemistry, The Weizmann Institute of Science, Rehovot, Israel

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Microwave discharge of O_2 at low pressure generates O(^{3}P) atoms which, on contact with silica gel or Florisil, combine with O_2 molecules to give O_3. The latter reacts with hexamethylbenzene adsorbed on these solid supports resulting in pentaoxide **4**. Two additional compounds, endo peroxides **2** and **3**, were isolated under these conditions, the former being the product of O_3 and $^1O_2$, and the latter of O_3, $^1O_2$, as well as O(^{3}P), all of which are present in the discharged gases. Conventional short time ozonation of hexamethylbenzene, adsorbed on these inorganic supports, results also in pentaoxide **4**.

Microwave glow discharge of O_2 and CO_2 at low pressure in the presence of He generates O(^{3}P) atoms[1] accompanied by $O_2(^1\Delta_g)$ molecules.[2,3] We have developed a technique by which the discharged gases are transported in a flow system and made to react with organic substrates adsorbed on inorganic supports.[4–6]

When the reactions are performed at 0 °C or higher temperatures, with CO_2/He discharge, O(^{3}P) atoms are the main reacting species, while at lower temperatures (below −60 °C) with O_2/He discharge, O_3 is formed and accumulates on the support. We have recently shown that the latter method may be used for ozonolysis of olefins and is particularly suitable for cleavage of only one bond in aromatic compounds.[6]

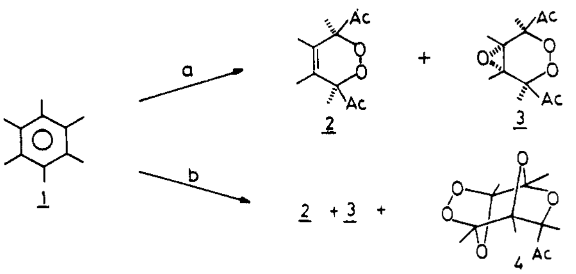
This paper describes the reaction of hexamethylbenzene (**1**) adsorbed on silica gel or Florisil under such ozonolytic conditions. For comparison, we have also ozonized **1** adsorbed on the same supports by conventional ozonation technique.

1 was chosen as a model, since it is known to react readily with ozone in solution, resulting, however, in oxidative cleavage of all three double bonds, to form formic acid, acetic acid, and 2,3-butanedione as the only products.[7]

Results

The reaction procedure consisted of discharging a mixture of He and O_2 (85:15) with microwaves (2450 MHz) at 2 torr in a flow system generated by a vacuum pump.[2,4–6] The discharged gases were passed over 25 mL of magnetically stirred silica gel (Merck 60, 70–200 mesh) or Florisil (Floridin, 100–200 mesh) preadsorbed with **1** (2–2.5% w/w). Ozonations were performed by passing O_3 (3% in O_2) from Welsbach ozonator through a column containing ca. 5 g of the solid support preadsorbed with **1**.[8]

Scheme I[a]



[a] a, He/O_2 discharge, −78 °C, Florisil or SiO_2; b, He/O_2 discharge, −78 °C, vacuum-dried Florisil.

Hexamethylbenzene (**1**) adsorbed on Florisil gave, after a 2-h reaction, 30% conversion to a 2:1 mixture of two symmetrically substituted endo peroxides **2** and **3**, each showing only three separate methyl signals in the ^{1}H NMR (Scheme I). Similar results were obtained when the reaction was performed on substrate adsorbed on silica gel. However, the conversion was larger (80%), the two products **2** and **3** being formed in 1:1 ratio. After longer reaction periods the ratio of **2** to **3** decreased considerably, indicating that **2** is an intermediate in the formation of **3**.

When the reaction was performed on Florisil dried under vacuum at 250 °C, the main product was pentaoxide **4** (50% relative yield), whose ^{1}H NMR (six different methyl signals) indicated loss of the high symmetry of **1**. The two endo peroxides, **2** and **3**, were also formed but in smaller yields (23% and 27%, respectively). Very small amounts (<5%) of pentaoxide **4** were also isolated in the former reactions, performed on supports which had not been previously dried.

The structures of **2**, **3**, and **4** were established by X-ray analysis. Computer drawings of the crystal structures of **2**, **3**, and **4** are shown in Figures 1, 2, and 3, respectively, and their crystallographic data (atomic and bond parameters) are listed in the supplementary material. The unsaturated six-membered ring of endo peroxide **2** in the single crystal has an almost perfect half-chair conformation, as shown in the schematic drawing (Figure 4). The two acetyl groups in 1,4-cis positions are almost symmetrically oriented in respect to the plane bisecting C1–C6 and O3–O4 bonds. The conformation of the six-membered ring of **3** in the single crystal is similar to that of its precursor **2**, the epoxide ring being in an anti configuration to the acetyl substituents. In pentaoxide **4**, the acetyl group is trans to the C1–O9–C4 bridge (Figure 3).

1 adsorbed on Florisil gave, after 2-min ozonation, **4** (40%) and a volatile fraction (23%) consisting mainly of 2,3-butanedione. After longer ozonation periods (5–10 min) the relative yields of **4** and 2,3-butanedione increased. Similar results were obtained when the ozonations were performed on substrate adsorbed on silica gel. In each of

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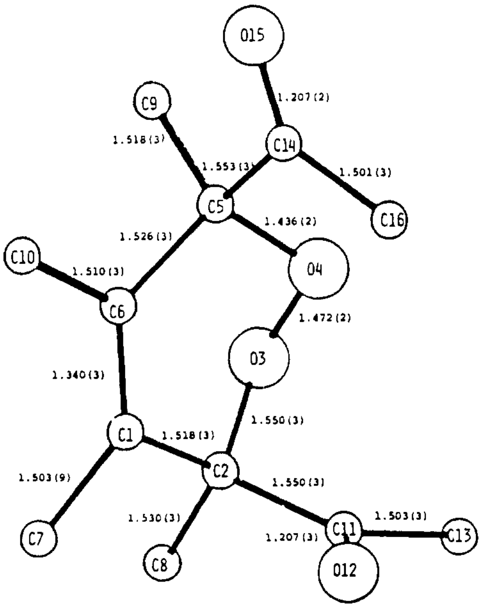


Figure 1. Computer drawing of the structure of endo peroxide 2 and a list of interatomic distances (Å). Selected torsion angles: C(6)-C(1)-C(2), 119.4 (2); C(5)-O(4)-O(3), 107.1 (1); C(4)-C-(5)-C(9), 111.4 (2); O(3)-C(2)-C(1), 109.8 (1); C(11)-C(2)-O(3), 108.0 (1); O(4)-O(3)-C(2), 104.9 (1); C(6)-C(5)-O(4), 110.7 (1); C(5)-C(6)-C(1), 120.5 (2).

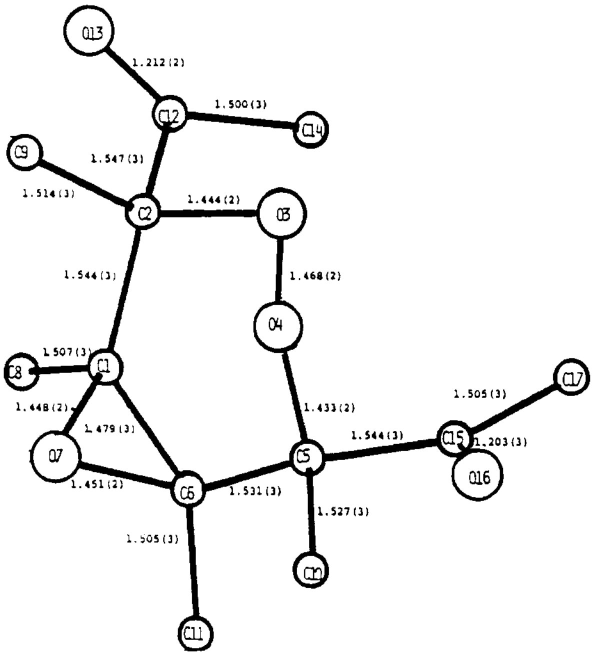


Figure 2. Computer drawing of the structure of epoxy endo peroxide 3 and a list of interatomic distances (Å). Selected torsion angles: C(6)-C(1)-C(2), 118.6 (2); O(3)-C(2)-C(1), 111.0 (1); O(4)-O(3)-C(2), 107.5 (1); C(6)-C(5)-O(4), 109.2 (2); C(5)-C-(6)-C(1), 117.3 (2); C(9)-C(2)-C(1), 110.9 (2); C(12)-C(2)-C(9), 111.5 (2); C(5)-O(4)-O(3), 105.6 (1); C(15)-C(5)-O(4), 106.9 (1); C(15)-C(5)-C(10), 111.7 (2).

these reactions small amounts of 2 (less than 2%) were also identified.

Discussion

In order to explain the results of reactions of 1 adsorbed on solid supports, we assume the participation not only of O_3 but also of $^1O_2$ molecules. The presence of $^1O_2$ in the discharged gases, under our experimental conditions, was shown previously by isolating an endo peroxide from 9,10-dimethylanthracene adsorbed on silica gel or Florisil

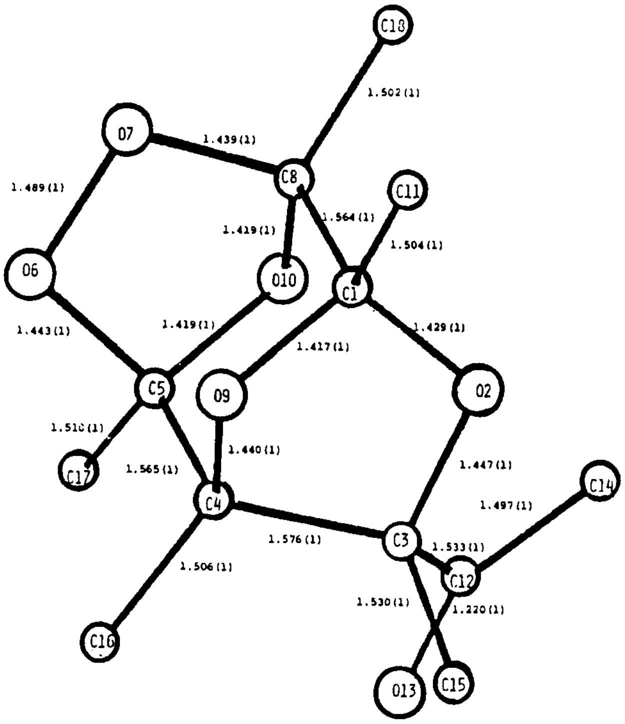


Figure 3. Computer drawing of the structure of pentaoxide 4 and a list of interatomic distances (Å). Selected torsion angles: C(8)-C(1)-O(2), 108.0 (1); O(9)-C(1)-C(8), 107.5 (1); C(3)-O-(2)-C(1), 106.7 (1); O(9)-C(4)-C(3), 98.8 (1); C(8)-O(7)-O(6), 103.6 (1); O(10)-C(8)-C(1), 108.8 (1); C(8)-O(10)-C(5), 100.9 (1); O-(9)-C(1)-O(2), 104.7 (1); C(4)-C(3)-O(2), 102.9 (1); C(12)-C-(3)-C(4), 115.7 (1); C(5)-C(4)-C(3), 111.5 (1); O(9)-C(4)-C(5), 106.0 (1); O(6)-C(5)-C(4), 108.9 (1); O(10)-C(5)-O(6), 102.9 (1); O(7)-O(6)-C(5), 104.5 (1); O(7)-C(8)-C(1), 108.3 (1); O(10)-C-(8)-O(7), 103.0 (1); C(4)-O(9)-C(1), 101.8 (1); O(13)-C(12)-O(13), 118.2 (1).

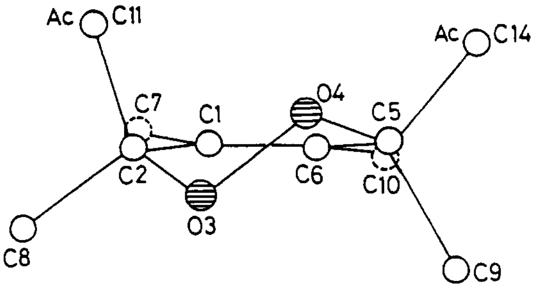
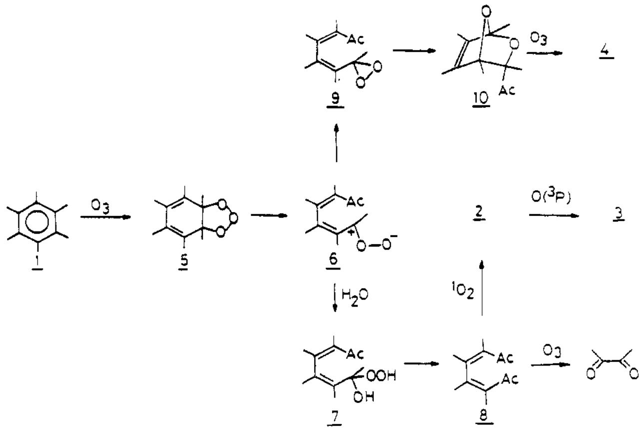


Figure 4. Schematic drawing of the structure of endo peroxide 2 viewed along the axis bisecting C1-C6 and O3-O4 bonds.

Scheme II. Suggested Mechanism for the Oxidation of Hexamethylbenzene with Oxygen Species Produced in He/O_2 Discharge at −78 °C



by using Hg vapours to trap $O(^3P)$ atoms.[5]

The suggested mechanism (Scheme II) for the formation of **2**, **3**, and **4** involves O_3 attack on **1** leading to a primary ozonide **5** which cleaves to the carbonyl–oxide **6**. These two functions do not undergo the expected combination to ozonide, but instead, the carbonyl oxide function reacts with water present on the solid support,[9] resulting in hydroxy hydroperoxide **7** which decomposes to H_2O_2 and diacetyl derivative **8**. We have shown recently that water intervenes in the ozonation of unsaturated olefins adsorbed on silica gel, interfering with the formation of ozonides and leading instead to carbonyl compounds.[9]

The diacetyl derivative possessing an activated *cis*-1,3-diene function undergoes cycloaddition with $^1O_2$ present in the discharged gases to give endo peroxide **2**. The latter reacts further with $O(^3P)$ also present in these gases, yielding **3**. This last step accounts for the fact that, after prolonged reaction periods, the ratio of **2** to **3** decreases considerably.

On vacuum-dried Florisil the reaction takes a different course: the amount of products **2** and **3** derived from hydrolytic decomposition of carbonyl oxide **6** diminishes and, instead, pentaoxide **4** is formed. A possible mechanism for its formation involves interconversion of carbonyl oxide **6** to dioxirane derivative **9** (Scheme II). Addition of both oxygen atoms to the double bond adjacent to the carbonyl group from the same side, results in bicyclic ketal **10**, having the acetyl group in an endo orientation. The second molecule of ozone attacks the double bond of **10** from the antiside to the acetyl group leading to a molozonide, whose stereospecific rearrangement results in pentaoxide **4**. Interconversion of carbonyl oxide to dioxirane function was postulated previously to explain the formation of unusual ozonation products.[10]

Our assumption that pentaoxide **4** is a product of **1** and O_3 was also corroborated by its isolation in high yields in the conventional ozonation of **1** adsorbed on solid supports.[8] This ozonolysis also leads to 2,3-butanedione which is the product of further ozonolysis of diacetyl derivative **8** (Scheme II). The absence of 2,3-butanedione in the microwave ozonations may be explained by the efficient trapping of **8** by $^1O_2$ present in the discharged gases.

Experimental Section

Melting points are uncorrected. Infrared spectra were taken on Perkin Elmer 457A or on Nicollet MX-1 spectrophotometers. ^1H NMR spectra were taken on Varian FT-80A (80 MHz) or on Bruker HFX-10 (90 MHz) spectrometers and ^{13}C NMR spectra on a Bruker WH-90 (22.63 MHz) spectrometer. MS spectra were measured with a Finnigan GC-MS 4000 spectrometer. Separations were performed on a SE-54 capillary column (0.25-μm film thickness, 30 m, i.d. 0.24 mm).

Microwave discharge reactions were performed on **1** (0.25 g, 1.54 mmol) preadsorbed from CH_2Cl_2 on Florisil (Floridin, 100–200 mesh) or on silica gel (Merck 60, 70–100 mesh) (25 mL) and evaporated to dryness on a rotatory evaporator under reduced pressure. Microwaves were generated by using a Kiva MPG-4 generator (2450 MHz, 100 W) and transmitted to the discharge cavity with an air-cooled antena. The reaction vessel consisted of an 8-cm diameter closed petri dish, 15 mm height, connected to a 15-mm diameter quartz inlet tube in which the discharged gases were passed.[5] The outlet of the reaction vessel was connected via a diaphragm manometer and a liquid nitrogen trap to the vacuum pump. The mixture of gases submitted to the discharge consisted of O_2 and He (15:85) at a total flow rate of 0.7 L/min and total pressure of 2 torr. The solid support containing the substrate was magnetically stirred with a specially designed magnet driven in orbit. All reactions were performed in a thermostatic bath.

Oxidation of 1 with He/O_2 Discharge. (a) On Silica Gel. **1** (0.25 g) adsorbed on silica gel (25 mL) was reacted with He/O_2 discharge at −78 °C for 2 h. Elution with ether and chromatography (silica gel, 15% ether in hexane) afforded starting material (0.04 g, 0.25 mmol 16%), **2** (0.14 g, 0.62 mmol 40%), **3** (0.15 g, 0.62 mmol 40%), and pentaoxide **4** (0.01 g, 0.04 mmol <4%) (for spectral data see c). **2**: mp 66–67 °C (ether–hexane); ^1H NMR ($CDCl_3$, Me_4Si) δ 1.44 (s, 6 H), 1.69 (s, 6 H), 2.17 (s, 6 H); IR ($CHCl_3$) ν 2921, 2852, 1723, 1654, 1422, 1356, 1220, 1107, 860, 773 cm^{-1}; MS (CI), *m/e* 227 ($M^+ + 1$, 3), 167 ($M^+ + 1 - AcOH$, 20), 141 ($M^+ + 1 - 2Ac$, 20), 125 ($CH_3\overline{C(CH_3)C(CH_3)C(CH_3)}$-$\overline{CO}^+H$, 100). Anal. ($C_{12}H_{18}O_4$) C, H. **3**: mp 110–111 °C (ether–hexane); ^1H NMR ($CDCl_3$, Me_4Si) δ 1.35 (s, 6 H), 1.46 (s, 6 H), 2.20 (s, 6 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 15.91, 16.07, 25.89 (6 CH_3), 63.11 (C1 and C6), 88.14 (C2 and C5); IR ($CHCl_3$) ν 2995, 2945, 1723, 1559, 1446, 1383, 1358, 1235, 1180, 1078, 875, 774 cm^{-1}; MS (CI), *m/e* 243 ($M^+ + 1$, 100), 141 (95). Anal. ($C_{12}H_{18}O_5$) C, H.

(b) **On Florisil.** **1** adsorbed on Florisil was reacted and worked up as in a. Chromatography resulted in **2** and **3** (20% and 10%, respectively) and traces of **4**.

(c) **On Dried Florisil.** **1** was adsorbed on Florisil (dried at 250 °C, 0.01 mmHg for 24 h) and reacted for 2 h at −78 °C. Isolation and chromatography afforded starting material (0.15 g, 0.92 mmol, 60%), **2** (0.03 g, 0.13 mmol, 9%), **3** (0.04 g, 0.17 mmol, 11%), and **4** (0.08 g, 0.13 mmol, 20%): mp 100–101 °C (ether–hexane); ^1H NMR ($CDCl_3$, Me_4Si) δ 1.26 (s, 3 H), 1.35 (s, 3 H), 1.39 (s, 3 H), 1.42 (s, 3 H), 1.46 (s, 3 H), 2.41 (s, 3 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 14.83, 16.13, 17.10, 18.50, 24.06, 27.08 (6 CH_3), 89.49 and 92.51 (C3 and C4), 105.99, 110.20 and 110.74 (C1, C5 and C8), 211.67 (C=O); IR (KBr) ν 2975, 2925, 1690, 1435, 1415, 1375, 1350, 1305, 1180, 1080, 995, 940, 920, 880, 855 cm^{-1}. Anal. ($C_{12}H_{18}O_6$) C, H.

Ozonation of 1 at −78 °C on Silica Gel or Florisil. Stream of O_3 produced by Welsbach ozonator (3% in O_2) was passed through silica gel (10 mL) preadsorbed with **1** (0.1 g, 0.62 mmol) for 2 min at −78 °C. Elution (ether) and chromatography afforded starting material (0.037 g, 37%), pentaoxide **4** (0.064 g, 0.25 mmol, 40%), and a volatile fraction (0.039 g, 23%), which consisted mainly of 2,3-butanedione, identified according to its ^1H NMR (δ 2.33, s) and UV (ether, λ_{max} 419 and λ_{sh} 435 nm). Similar results were obtained by using Florisil as the solid support.

X-ray Crystallography. Transparent clear crystals of good quality of **2**, **3**, and **4** were optically centered on a CAD-4 diffractometer. The intensities of all reflections were measured according to the $w - \theta$ technique by using a scan range of 0.8 deg, and constant scan speed of 6 deg per min. All structures were solved by the direct-phase determination. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were found on difference Fourier maps and refined isotropically.

Registry No. **1**, 87-85-4; **2**, 96616-72-7; **3**, 96616-73-8; **4**, 96632-98-3; O_2, 7782-44-7; O, 17778-80-2; O_3, 10028-15-6; silica, 7631-86-9; Florisil, 1343-88-0; 2,3-butanedione, 431-03-8.

Supplementary Material Available: Tables containing atom coordinates, anisotropic temperature factors, hydrogen atom coordinates, bond lengths, and bond angles for **2**, **3**, and **4** (7 pages). Ordering information is given on any current masthead page.

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