Gas-Phase Reactions of 1,2-Dimethylcyclopentene and of 2,6-Heptanedione with Ozone: Unprecedented Formation of an Ozonide by Ozone Treatment of a Diketone

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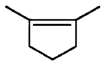
Gas-phase ozonizations of 1,2-dimethylcyclopentene (**1**) and of 2,6-heptanedione (**5**) afforded in each case dimethylcyclopentene ozonide (**2**) in low yields. In the ozonization of **1**, diketone **5** was formed as the single major product, along with nine "abnormal" ozonolysis products which were formed by oxidative cleavage of carbon−carbon single bonds.

Introduction

Gas-phase ozonolyses of olefins are of interest in connection with the role of such reactions in atmospheric chemistry. A large variety of olefins, in particular terpenes[1], which are emitted to the atmosphere from coniferous trees, have been ozonized, and several mechanisms have been proposed for the course of such reactions[2][3][4]. It is a common feature of all results reported that, in contrast to ozonolyses of olefins in solution, peroxidic compounds were either found as minor products or not at all. In particular, ozonides, which are often the major products in liquid-phase ozonolyses, have for a long time only been detected in gas-phase ozonolyses of small acyclic olefins[5], and more recently of cyclic terpenes having exocyclic double bonds[6]. By contrast, bicyclic ozonides derived from ozonolyses of cyclic olefins have not been reported, although a number of terpenes having such structural units have been ozonized. Since it is known, that 1,2-dimethylcyclopentene (**1**) provides the corresponding ozonide **2** in good yields in liquid-phase ozonolyses[7], we have now examined the ozonolysis of **1** in the gas phase.

Results and Discussion

Treatment of **1** with 0.8 molar equivalents of ozone at room temperature in the gas phase gave a product mixture in which, aside from residual **1**, compounds **2** (0.5%), **3** (5%), **4** (1%), **5** (51%), **6** (2%), **7** (3%), **8** (9%), **9** (2%), **10** (5%) and **11** (5%) have been detected by GC analysis in the proportions reported. In addition, the gas chromatogram showed the presence of trace amounts, each, of ca. 20 unknown compounds, and ^{1}H- as well as ^{13}C-NMR analysis showed the presence of **12**. The identifications of the above products are based on coinjections with authentic samples, on GC/MS analyses and on the following additional evidence: a) The GC peak for ozonide **2** disappeared when the reaction mixture was treated with triphenylphosphane (TPP). b) From the combined crude products of several ozonolysis reactions of **1**, the acids **9**−**12** were extracted with aqueous $NaHCO_3$ and identified on the basis of diagnostic signals in the ^{1}H- and/or ^{13}C-NMR spectra of the mixture of acids. c) The neutral products **3**−**8** were isolated or enriched to the extent that they could be unequivocally assigned on the basis of their ^{1}H- and/or ^{13}C-NMR data.



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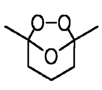

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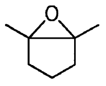

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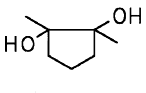

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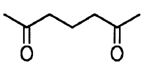

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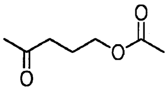

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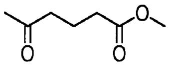

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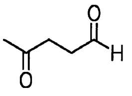

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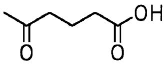

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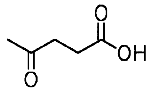

10

CH_3COOH

11

HCOOH

12

It is generally agreed that gas-phase ozonolyses of olefins occur by the Criegee mechanism, though with the difference, that a diradical- rather than a zwitterion-type of carbonyl oxide is produced. Hence, ozonolysis of **1** should provide intermediate **13**, and ozonide **2** could arise from intramolecular cycloaddition of the latter. It was, furthermore, reported that "hot" radical-type carbonyl oxides may be isomerized to dioxiranes, which can undergo several subsequent reactions, including epoxidations and rearrangements to give acids or esters, depending on the nature of the

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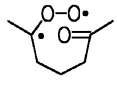
substituents[3]. Hence, epoxide **3** could have been formed by reaction of **1** with ozone and/or with the dioxirane **14**, while esters **6** and **7** could have been formed by rearragement of **14**, possibly via intermediate **15**. The formation of diol **4** can be explained by reaction of **3** with water, which is known to be formed in gas-phase reactions of ozone with hydrocarbons. The formation of diketone **5** as the single major product is in line with the experience, that gas-phase ozonolyses of olefins lead predominantly to the corresponding carbonyl fragments.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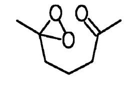
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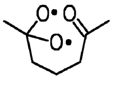
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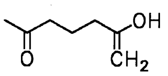
For the formation of the abnormal ozonolysis products **8**–**12**, having less carbon atoms than substrate **1**, we have assumed the enols of **5** as precursors: Ozonolysis of enol **16** can produce acid **9** and the "hot" carbonyl oxide **17**, which – as has been reported previously[2] – can be converted into formic acid (**12**). Similarly, ozonolysis of enol **18** can afford **8**, **10** and **11.**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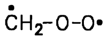
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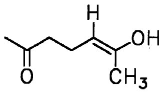
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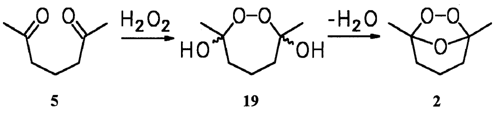
To test this hypothesis, we have treated **5** with ozone at the elevated temperature of 45°C in order to assure gas-phase conditions. GC analysis showed indeed the formation of **8** (0.3%), **9** (0.8%), **10** (1%) and **11** (1.3%), and ^{1}H-NMR analysis showed the presence of **12**. To our surprise, however, the presence of ozonide **2** (0.8%) was also indicated by GC analysis. This was confirmed by the isolation of **2** and its characterization by ^{1}H-NMR spectroscopy and by reduction with TPP to give **5**.

The unprecedented formation of an ozonide by ozone treatment of a diketone introduces a new aspect to organic ozone chemistry and may have implications for the area of atmospheric ozone chemistry. Since gas-phase reactions of ozone with hydrocarbons are accompanied by the formation of OH radicals[8], which can subsequently form H_2O_2, it appeared feasible, that ozonide **2** may have been formed by addition of H_2O_2 to **5** via **19** as an intermediate. In the liquid phase, such a reaction of **5** has indeed been realized, but it was reported that the conversion of **19** into **2** required the presence of the strong dehydrating reagent P_2O_5[9]. In preliminary experiments, we have shown that **2** was indeed formed from H_2O_2 and **5** in the gas phase at 45°C. Experiments are underway to test the scope of this reaction with other di- and also monocarbonyl compounds.



5 **19** **2**

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Experimental Section

General: The substrates **1**[10] and **5**[11] and authentic samples of the not commercially available compounds **2**[12], **3**[13], **4**[14a], **6**[14b], **7**[14c], and **8**[15], have been prepared by published procedures and were of > 98% purity. NMR spectra were obtained in $CDCl_3$ with TMS as internal reference with a Bruker AC 250 instrument. GC analyses were performed with a Hewlett-Packard 5890A instrument, using the following conditions: Column: 50 m, fused silica, phenyl-5%-methylsilicone SE 54; 50°C for 10 min, then 50–180°C at 7°C/min; injector temperature 200°C. GC/MS analyses (EI): Hewlett-Packard system 5985B; GC conditions as above. HPLC separations: Merck Hitachi chromatograph 655 A 11; column: LiChrosorb Si 60, 25 cm, pentane/ether, 70:30. All ozonization reactions were carried out in a 6-l two-neck round-bottom flask, equipped with a septum on one neck and a connection to a vacuum line on the other neck.

Ozonization of 1,2-Dimethylcyclopentene (**1**): The 6-l flask was evacuated to 10^{-2} Torr at room temp., the vacuum line was closed and 20 mg[16] (0.21 mmol) of the liquid substrate **1** was injected through the septum. After 30 min, 170 ml of an O_3/O_2 mixture, containing 1 mmol of O_3/l, was injected from a gas syringe within ca. 1 min. After a reaction time of 10 min, the flask was cooled in an ice/water bath, and subsequently flushed with nitrogen for 20 min to remove volatiles, which were condensed by passing the nitrogen stream through a trap kept at −50°C. The 6-l flask was rinsed with ether and the combined ether solutions from several experiments were concentrated by distilling off the ether at room temp. and reduced pressure to leave a liquid residue. GC and GC/MS analysis showed that the cold trap contained a mixture of **1**, **3** and **4**, and the liquid residue contained **2** and **5** – **11** in the proportions reported above. ^{1}H- and ^{13}C-NMR analysis showed that the liquid residue contained **12**, too. The liquid residue was dissolved in ether and extracted with an aqueous solution of sodium bicarbonate. The ether phase was concentrated by evaporation of ether and the concentrate was separated by HPLC to give the following compounds in the purities given in parentheses: **5** (88%), **6** (76%), **7** (24%) and **8** (12%). The aqueous extract was acidified, extracted with ether and the ether was distilled off to leave a residue which according to ^{1}H-NMR analysis contained the following compounds in the proportions given in parentheses: **9** (14%), **10** (34%), **11** (33%) and **12** (19%). Products **2**–**12** were assigned based on the identity of the properties reported below with those of authentic samples or with data reported in the literature.

1,5-Dimethyl-6,7,8-trioxabicyclo[3.2.1]octane (**2**): GC: t_R = 16.2 min. – GC/MS; *m/z* (%): 144 (2) $[M]^+$, 128 (1) $[M - O]^+$, 112 (9) $[M - O_2]^+$, 97 (5), 85 (2), 71 (4), 43 (100).

1,5-Dimethyl-6-oxabicyclo[3.1.0]hexane (**3**): GC: t_R = 9.5 min. – GC/MS; *m/z* (%): 112 (14) $[M]^+$, 97 (13) $[M - CH_3]^+$, 71 (14), 69 (16), 55 (16), 43 (100), 41 (25), 39 (19).

trans-1,2-Dihydroxy-1,2-dimethylcyclopentane (**4**): GC: t_R = 18.6 min. – GC/MS; *m/z* (%): 130 (1) $[M]^+$, 112 (22), 97 (25), 71 (22), 69 (14), 58 (17), 57 (13), 55 (11), 43 (100), 41 (13).

2,6-Heptanedione (**5**): GC: t_R = 20.5 min. – GC/MS; *m/z* (%): 128 (4) $[M]^+$, 95 (5), 85 (4), 71 (9), 58 (17), 43 (100). – ^{1}H NMR (88% purity): δ = 1.83 (quint, *J* = 7.1 Hz, 2 H), 2.14[17] (s, 6 H), 2.48 (t, *J* = 7.1 Hz, 4 H). – ^{13}C NMR: δ = 17.78, 29.86, 42.49, 208.19.

4-Oxopentyl Acetate (**6**): GC: t_R = 21.5 min. – GC/MS; *m/z* (%): 144 (1) $[M]^+$, 101 (4), 87 (5), 84 (4), 61 (6), 58 (7), 43 (100). – ^{1}H NMR (76% purity): δ = 1.93 (quint, *J* = 6.9 Hz, 2 H), 2.05[17] (s, 3 H), 2.17 (s, 3 H), 2.54 (t, *J* = 7.2 Hz, 2 H), 4.12 (t,

J = 6.4 Hz, 2 H). – ^{13}C NMR: δ = 20.61, 22.66, 29.64, 39.65, 63.36, 170.66, 207.19. – Ref.[18]: ^{1}H NMR ($CDCl_3$, TMS): δ = 1.90 (t), 2.03 (s), 2.15 (s), 2.53 (t), 4.05 (t).

Methyl 5-Oxohexanoate (**7**): GC: t_R = 21.7 min. – GC/MS; m/z (%): 144 (2) $[M]^+$, 113 (17), 101 (6), 87 (5), 85 (11), 74 (22), 59 (25), 55 (18), 43 (100). – ^{1}H NMR (24% purity): δ = 1.89 (quint, J = 7.2 Hz, 2 H), 2.15 (s, 3 H), 2.35 (t, J = 7.2 Hz, 2 H), 2.52 (t, J = 7.2 Hz, 2 H), 3.67[17] (s, 3 H). – ^{13}C NMR: δ = 18.40, 29.18, 32.41, 41.70, 50.79, 172.86, 207.04.

4-Oxopentanal (**8**): GC: t_R = 12.3 min. – GC/MS; m/z (%): 100 (0.1) $[M]^+$, 72 (14), 57 (7), 43 (100), 29 (26). – ^{1}H NMR (12% purity): δ = 2.21[17] (s, 3 H), 2.77 (s, 4 H), 9.81 (s, 1 H). – ^{13}C NMR: δ = 29.76, 35.53, 37.45, 200.33, 206.29.

5-Oxohexanoic Acid (**9**): GC: t_R = 27.5 min. – GC/MS; m/z (%): 130 (0.3) $[M]^+$, 112 (8), 70 (5), 60 (5), 45 (15), 43 (100), 42 (15), 41 (9). – ^{1}H NMR (14% purity): δ = 1.90 (quint, J = 7.1 Hz, 2 H), 2.16[17] (s, 3 H), 2.40 (t, J = 7.2 Hz, 2 H), 2.55 (t, J = 7.2 Hz, 2 H). – ^{13}C NMR: δ = 18.51, 29.78, 32.88, 42.23, 179.00, 208.24.

4-Oxopentanoic Acid (**10**): GC: t_R = 23.4 min. – GC/MS; m/z (%): 116 (2) $[M]^+$, 101 (2), 73 (3), 56 (18), 55 (8), 45 (12), 43 (100). – ^{1}H NMR (34% purity): δ = 2.21[17] (s, 3 H), 2.60–2.65 (m, 2 H), 2.74–2.79 (m, 2 H). – ^{13}C NMR: δ = 27.79, 29.72, 37.71, 178.25, 206.58.

Acetic Acid (**11**): GC: t_R = 6.3 min. – GC/MS; m/z (%): 60 (34) $[M]^+$, 45 (100), 43 (98), 29 (11), 15 (19). – ^{1}H NMR (33% purity): δ = 2.10[17] (s). – ^{13}C NMR: δ = 20.63, 177.85.

Formic Acid (**12**): ^{1}H NMR (19% purity): δ = 8.05[17] (s). – ^{13}C NMR: δ = 165.69.

Ozonization of 2,6-Heptanedione (**5**): The solid diketone **5** (100 mg; 0.8 mmol) was placed in the 6-l flask, the flask was cooled with liquid nitrogen, evacuated to 10^{-1} Torr and completely submersed in a water bath, which was kept at 45°C. After **5** was volatilized, 500 ml of a O_3/O_2 mixture was added as described above, and the mixture was kept at 45°C for 2 d. Then, the flask was removed from the bath, filled with nitrogen and rinsed with ether. From the combined ether solution of several runs, ether was distilled off, the residue was examined by GC and GC/MS analysis and subsequently separated by the HPLC method to afford ozonide **2**: ^{1}H NMR (70% purity): δ = 1.50 (s, 6 H), 1.58–1.90 (m, 5 H), 2.10–2.30 (m, 1 H)[19].

Reduction of **2**: A sample of **2** in ca. 0.5 ml of $CDCl_3$ was admixed with triphenyl phosphane in an NMR tube. ^{1}H-NMR analysis after ca. 30 min showed the presence of **5** as the sole product of reduction.

Reaction of 1,6-Heptanedione (**5**) *with H_2O_2 in the Gas Phase*: A few drops of 35% aqueous H_2O_2 and a few grains of **5** were placed in a 500-ml round-bottom flask. The flask was cooled with liquid nitrogen, evacuated to 10^{-2} Torr and placed into a water bath kept at 45°C for 12 h. The flask was removed from the bath, filled with nitrogen, rinsed with ether and the ether was distilled off at room temp. and reduced pressure. ^{1}H-NMR analysis showed the presence of **2** (δ = 1.50, s, CH_3) and of **5** (δ = 2.14, s, CH_3) in a ratio of ca. 1:5.

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[16] In reactions, which were carried out with 40 mg of **1**, the mixture became hazy immediately after ozone was injected and, hence, exclusive gas-phase ozonolysis of **1** could not be assured at such concentrations.

[17] Signal used for the determination of the proportion of the compound in the mixture of **5–8** and in the mixture of **9–12**, respectively.

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