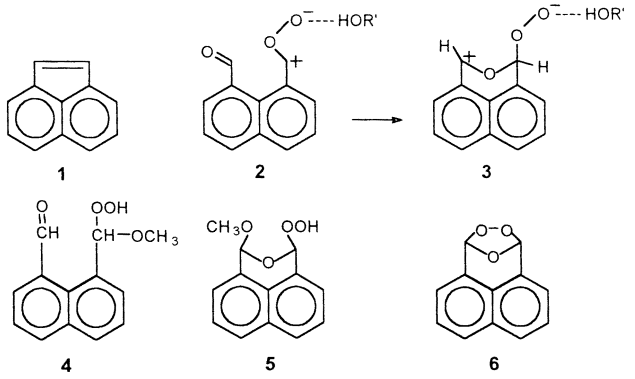
Nonperoxidic Products from the Ozonolyses of Acenaphtylene and 4,5-Methylenephenanthrene

Chi Won Lee and Tae Sung Huh*

Department of Chemistry, The Catholic University of Korea, Puchon 422-743, Korea
Received April 17, 1999

The Ozonolysis of alkenes has attracted attention with regard to mechanism.[1] We were interested in the ozonolysis of acenaphthylene **1** for following reason. The reaction of acenaphtylene **1** in chloroform or carbon tetrachloride[2] has been reported to afford exclusively the polymeric products, while in methanol a solvent-participated product **5** rather than normal product **4** and ozonide **6** were obtained in yields of 69% and 7%, respectively.[3] Ozonolysis reaction of acenaphthylene **1** in methanol revealed a partially anomalous behavior as compared to other olefins. This was explained by an intramolecular reaction between the carbonyl oxide moiety and aldehyde group **2** to give intermediate **3**, which is subsquently trapped by methanol to give **5**.

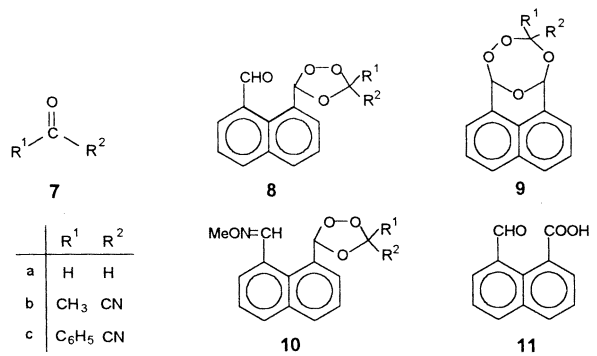


Thus it would be interesting to see if carbonyl oxide intermediate **2** or **3** generated by ozonolysis of acenaphthylene **1** in aprotic solvent could undergo cycloadditions with "foreign" carbonyl compounds **7** to give monoozonide **6**, cross ozonide **8** and tetroxepane **9**.[4,5,6]

In this investigation, we have tried to get answers to these questions by ozonizing acenaphthylene **1** in the presence of added carbonyl compounds **7** and by converting the aldehyde groups of the anticipated ozonides **8** into the less destabilizing methoximino groups as in the case of α-oxo-ozonides.[7] To this end, 1 : 1 mixtures of an acenaphthylene and a carbonyl compound in CH_2Cl_2 were treated with ozone at low temperature, and the cold crude reaction products were immediately admixed with a precooled solution of O-methylhydroxylamine in methanol.[7,8]

Ozonolyses of acenaphthylene **1** in the presence of carbonyl compounds **7a**, **7b** and **7c** gave ozonide **6** and nonperoxidic product **11** by the flash column chromatography, suggesting that the carbonyl oxide intermediate **2** and **3** can be produced in the course of this reaction. On the basis of the similarity of the ^1H NMR shift values of respective groups of corresponding products of type **6**, **8** and **9**, only ozonides **6** and **8** could be detected by ^1H NMR analysis of the crude ozonolysis products prior to derivatization reactions. However, these cross ozonides **8a** [^1H NMR: δ 5.28 (s, 1H), 5.33 (s, 1H), 6.79 (s, 1H), 10.54 (s, 1H). ^{13}C NMR: δ 94.30, 101.14, 192.87], **8b** [^1H NMR: δ 1.97 (s, 3H), 6.68 (s, 1H), 10.47 (s, 1H). ^{13}C NMR: 32.27, 99.83, 104.35, 117.04, 192.74] and **8c** [^1H NMR: δ 7.02 (s, 1H), 10.42 (s, 1H). ^{13}C NMR: δ 100.98, 105.43, 112.87, 194.06] could not be isolated and decomposed during the attempted isolation. The decomposition product of **8a**, **8b** and **8c** was 8-formyl-1-naphthalenecarboxylic acid **11** as a lactol form, which had been also obtained previously as a product of the ozonolysis of the acenaphthylene **1** in methanol.[2] For derivatization of ozonides **8**, ozonolysis of acenaphthylene **1** in the presence of the carbonyl compounds **7a**, **7b** and **7c** followed by treatment with O-methylhydroxylamine could not produced the correspoonding ozonides **10** (Chart 1).

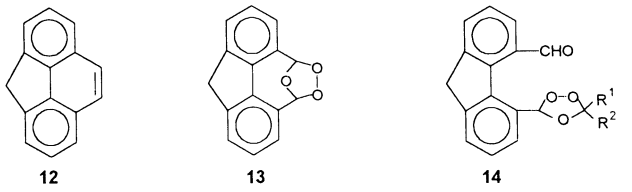
Ozonolyses of 4,5-methylenephenanthrene **12**, which has similar structure of acenaphthylene **1** in the presece of the carbonyl compounds **7a**, **7b** and **7c** gave the monoozonide **13** and nonperoxidic product **16** by the flash column chromatography. On the basis of the similarity of the ^1H NMR shift values of respective groups of corresponding ozonides of type **13**, **14** and **9**, only ozonides **13** and **14** could be detected by ^1H NMR analysis of the crude ozonolysis prod-



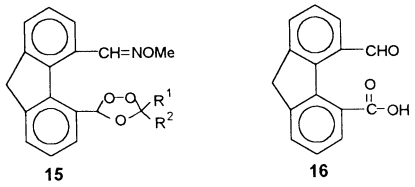
	R^1	R^2	6(%)	8(%)[a]	9(%)	10(%)	11(%)[b]
a	H	H	(16)	50	nd	nd	(50)
b	CH_3	CN	(25)	20	nd	nd	(45)
c	C_6H_5	CN	(25)	25	nd	nd	(60)

[a]Determined in the product mixture by ^1H NMR analysis using CH_2Cl_2 as internal standard. The data in parentheses are the isolated yields. [b]Lactol form. nd = not detected.

Chart 1



12 13 14



15 16

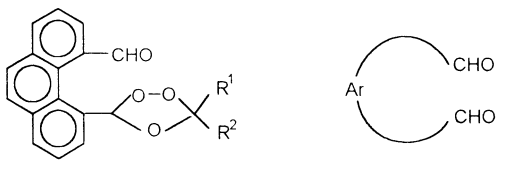
	R^1	R^2	**13**(%)[a]	**14**(%)[a]	**15**(%)[b]	**16**(%)[b]
a	H	H	nd	80 (82)	8	46
b	CH_3	CN	13	80 (70)	12	45
c	C_6H_5	CN	60	10	nd	20

[a]Determined in the product mixture by ^1H NMR analysis using CH_2Cl_2 as internal standard. The data in parentheses are the isolated yields by the recrystallization from cold methylene chloride. [b]Yield of isolated products. nd = not detected.

Chart 2

ucts prior to the derivatization reactions. However, these cross ozonides **14a**, **14b** and **14c** could not be isolated and decomposed during the attempted isolation at room temperature. Of these ozonides only **14a** and **14b** could be isolated by the recrystallization of cold methylene chloride, whereas **14c** decomposed during the attempted isolation. The decomposition product of **14a**, **14b** and **14c** was 5-formyl-4-fluorenecarboxylic acid **16**. Ozonolyses of 4,5-methylenephenantrene **12** in the presence of the carbonyl compounds **7a**, **7b** and **7c** followed by treatment with O-methylhydroxylamine could be detected the corresponding ozonides **15** of which only **15a** and **15b** were isolated in the yields shown (Chart 2).

All of the ozonides have been characterized by positive peroxide tests, satisfactory elemental analyses, and their ^1H and ^{13}C NMR spectra. Reductions of ozonides gave corresponding compounds of types **18** and **7** in nearly equimolar amounts.

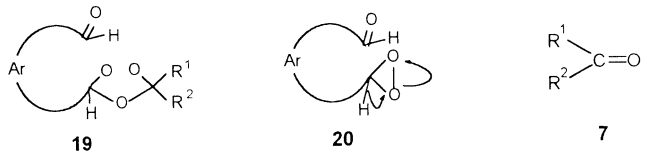


17 18

The results obtained in this study show that carbonyl oxides **2** rather than **3** derived from ozonolyses of acenaphthylene **1** and 4,5-methylenephenanthrene **12** in aprotic solvent can be readily trapped by carbonyl compounds **7** to give cross ozonides **8** and **14** in addition to **6** and **13**. In contrast to the ozonolysis of acenaphthylene **1** in methanol, in these reactions no evidences were found the formation of tetroxepane **9** *via* intermediate **3**. Ozonides **8** and **14** underwent rapid decomposition in solution at room temperature. However, of these ozonides only **14** could be isolated by recrystallization of cold methylene chloride, whereas cross ozonides **8** decomposed during the attemped isolation. Ozonolysis of **1** in the presence of carbonyl compounds **7** followed by derivatizaton with O-methylhydroxylamine did not provide corresponding ozonides **10**. This, together with low yields of **15a** and **15b** indicated that the stability of ozonide does seem to be influenced by the aldehyde group.

However, cross ozonides **17** obtained from the ozonolysis of pyrene in the presence of carbonyl compounds **7** were readily isolated in solution at room temperature.[9] Thus, the stability of ozonide decreased in the order of **17** >**14** > **8**, suggesting that the proximity between ozonide ring and aldehyde group are affect to the stability of ozonide.

The formation of nonperoxidic products **11** and **16** may be explain by cleavage of peroxide bond of labile ozonides **8** and **14** to give diradical or ionic intermediate **19**, by analogy with the postulated course of decomposition of α-oxo-ozonide.[10,11] Further reaction **19** may produce the 1,2-dioxirane **20**, which-in line with postulated reaction of 1,2-dioxiranes[10,11,12,13]-may be converted into **11** and **16**.



19 20 7

Experimental Section

NMR spectra: Brucker AC-300. ^1H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ with TMS as internal references. Chromatographic separations: Flash chromatography on silica gel.

Ozonolyses and Reductions of Ozonides: Unless mentioned otherwise, the following procedure was used: The Ozonolysis reaction was carried out in dichloromethane at –78 °C until the solution turned blue. Residual ozone was flushed out with nitrogen, the solvent was distilled off at room temperature under reduced pressure, and the residue was separated by flash chromatography. Reductions of isolated ozonides were carried out on *ca.* 20-40 mg samples in *ca.* 0.6 mL of $CDCl_3$ with an excess of triphenylphosphine, and the products were analyzed by ^1H NMR spectroscopy.

Ozonolysis of 1 and 7a: Ozonolysis of 0.46 g (3.0 mmol) of **1** and 1 mL of **7a** (freshly prepared by pyrolysis of paraformaldehyde) in 50 mL of dichloromethane, followed by distillation of the solvent under reduced pressure gave a solid residue. This residue dissolved in 20 mL of dichloromethane and the white precipitate was collected by filtration and recrystallization from dichloromethane gave 0.30 g (1.5 mmol, 50%) of **11**. From the filtrate, 0.1 g (0.48 mmol, 16%) of colorless precipitate **6** was isolated by flash chromatography (silica gel, solvent : dichloromethane/n-pentane – 1 : 1).

8-Formyl-1-naphthalenecarboxylic acid 11 (lactol

form). Colorless needle crystal; mp 167168 °C (Lit.[2-14], 167-168 °C); ^{1}H NMR: δ 4.62 (d, J = 6 Hz, 1H), 6.94 (d, J = 6 Hz, 1H), 7.64-7.74 (m, 3H), 7.99 (d, J = 4 Hz, 1H), 8.18 (d, J = 4 Hz, 1H), 8.47 (d, J = 4 Hz, 1H). ^{13}C NMR: 96.29, 119.28, 125.46, 127.12, 127.34, 128.12, 128.92, 129.12, 130.24, 132.14, 134.85, 164.61. **IR** (KBr/tablet): γ 3300, 1710, 1140.

Acenaphthylenemonoozonide (6). Colorless crystal; mp 102-103 °C (Lit.,[11] 102-105 °C). ^{1}H NMR: δ 6.69 (s, 2H), 7.47 (m, 4H), 7.86 (d, J = 3 Hz, 2H). ^{13}C NMR: δ 101.03, 122.12, 125.24, 126.28, 128.87, 131.69, 132.76.

Reduction of 6 with TPP gave 1,8-naphthalenedialdehyde: δ 10.48 (s, 2H).

Ozonolysis of 1 and 7b: Ozonolysis of 0.46 g (3.0 mmol) of **1** and 0.42 g (6 mmol) of pyruvonitrile **7b** in 50 mL of dichloromethane, followed by distillation of the solvent under reduced pressure gave a solid residue. This residue dissolved in 20 mL of dichloromethane and the precipitate was collected by filtration and recrystallized from dichloromethane gave 0.27 g (1.35 mmol, 45%) of **11**. From the filtrate, 0.15 g (0.75 mmol, 25%) of colorless solid **6** was isolated by flash chromatography (silica gel, solvent : dichloromethane/pentane = 1 : 1).

Ozonolysis of 1 and 7c: Ozonolysis of 0.46 g (3.0 mmol) of **1** and 0.79 g (6 mmol) of benzoyl cyanide **7c** in 50 mL of dichloromethane, followed by distillation of the solvent under reduced pressure gave a solid residue. This residue dissolved in 20 mL of dichloromethane and the precipitate was collected by filtration and recrystallized from dichloromethane gave 0.36 g (1.80 mmol, 60%) of **11**. From the filtrate, 0.15 g (0.75 mmol, 25%) of colorless solid **6** was isolated by flash chromatography (silica gel, solvent : dichloromethane/pentane = 1 : 1).

Ozonolysis of 12 and 7a. Ozonolysis of 0.57 g (3.0 mmol) of **12** and 1 mL of **7a** (freshly prepared by pyrolysis of paraformaldehyde) in 50 mL of dichloromethane the reaction mixture was kept at room temperature for 1 h., followed by distillation of the solvent under reduced pressure gave a solid residue. This residue dissolved in 20 mL of dichloromethane and the precipitate was collected by filtration and recrystallization from dichloromethane gave 0.33 g (1.38 mmol, 46%) of **16**.

After evaporation of the solvent from the cold reaction mixture directly, the residue was recrystallized with cold dichloromethane to give 0.62 g (2.46 mmol, 82%) of **14a**.

5-Formyl-4-fluorene-4-carboxylic acid (16). Colorless crystal; mp 139141 °C (Lit.[15], 140-142 °C); ^{1}H NMR (acetone-d_6): δ 3.95 (s, 2H), 7.11-7.76 (m, 6H), 10.14 (s, 1H). ^{13}C NMR (acetone-d_6): δ 37.23, 127.23-131.75{m}, 170.00, 190.38. - **IR** (KBr/tablet): γ 3000 (broad), 1730. Anal. Calcd. for $C_{15}H_{10}O_3$ (238.2): C 75.64, H 4.23; found C 75.68, H 4.25.

5-(1,2,4-Trioxolan-3-yl)fluorene-4-carbaldehyde (14a). Colorless crystal; mp 100-102 °C; ^{1}H NMR: 4.01 (s, 2H), 5.30 (s, 1H), 5.40 (s, 1H), 6.35 (s, 1H), 7.45-7.86 (m, 6H), 10.44 (s, 1H). ^{13}C NMR: δ 37.73, 95.62, 101.45, 126.75-145.90 (m), 193.04. Anal. Calcd. for $C_{16}H_{12}O_4$ (268.3): C 71.63, H 4.51; found C 71.44, H 4.65.

5-(1,2,4-Trioxolan-3-yl)fluorene-4-carbaldehyde-O-methyloxime (15a). Colorless liquid: ^{1}H NMR: δ 3.82 (s, 3H), 3.94 (s, 2H), 5.31 (s, 1H), 5.39 (s, 1H), 6.37 (s, 1H), 7.22-8.25 (m, 6H), 8.68 (s, 1H). ^{13}C NMR: δ 37.74, 62.19, 96.00, 101.34, 125.23-145.15 (m), 150.78. Anal. Calcd. for $C_{17}H_{15}O_4N$(297.3): C 68.68, H 5.09; found C 68.83, H 4.97.

Reduction of 14a with TPP gave 4,5-methylenephenanthrene-8,9-di-carbaldehyde [^{1}H NMR: δ 3.91 (s, 2H), 10.07 (s, 2H). - ^{13}C NMR: δ 37.46, 190.99.]

Ozonolysis of 12 and 7b: Ozonolysis of 0.57 g (3.0 mmol) of **12** and 0.42 g (6 mmol) of pyruvonitrile **7b** in 50 mL of dichloromethane, followed by distillation of the solvent under reduced pressure gave a solid residue. This residue dissolved in 20 mL of dichloromethane and the precipitate was collected by filtration and recrystallized from dichloromethane gave 0.32 g (1.35 mmol, 45%) of **16**. From the filtrate, 0.09 g (0.39 mmol, 13%) of **13** was isolated by flash chromatography (silica gel, solvent : dichloromethane/pentane = 1 : 1).

After evaporation of the solvent from the cold reaction mixture directly, the residue was recrystallized with cold dichloromethane to give 0.64 g (2.11 mmol, 70%) of **14a**.

The reaction mixture of the ozonolysis was admixed with a solution of 0.5 g (6 mmol) of O-methylhydroxylamine and 1 mL of pyridine in 10 mL of methanol was precooled to −20 °C, and the mixture was kept at low temperature for several days. Then, the solvent was evaporated at room temperature and reduced pressure, the residue was admixed with water, and the mixture was extracted with ether. The extract was sequentially washed with 2 M aqueous hydrochloric acid and an aqueous solution of sodium bicarbonate, dried $MgSO_4$, filtered, and concentrated by evaporation of the solvent at room temperature and reduced pressure. From this residue 0.12 g (0.36 mmol, 12%) of **15b** was isolated (silica gel, n-pentane/ether = 20 : 1).

4,5-Methylenephenanthrenemonoozonide (13). Colorless crystal; mp 141-142 °C (Lit.[15], 141-143 °C) : ^{1}H NMR: δ 3.94 (s, 2H), 6.46 (s, 2H), 7.247.59 (m, 6H). ^{13}C NMR: δ 37.56, 104.26, 125.85, 126.67, 127.40, 132.48, 139.96, 144.36. The data are identical to those reported.[15]

Reduction of 13 with TPP gave 4,5-methylenephenanthrene-8,9-di- carbaldehyde.

5-(5-Cyano-5-methyl-1,2,4-trioxolan-3-yl)fluorene-4-carbaldehyde (14b). Colorless liquid: ^{1}H NMR: δ 1.97 (s, 3H), 3.93 (s, 2H), 6.34 (s, 1H), 10.17 (s, 1H). ^{13}C NMR: δ 21.67, 3765, 100.51, 104.22, 117.13, 125.12-146.00 (m), 192.52. Anal. Calcd. for $C_{18}H_{13}O_4N$ (307.3): C 70.35, H 4.26; found C 70.22, H 4.37

5-(5-Cyano-5-methyl-1,2,4-trioxolan-3yl)fluorene-4-carbaldehyde-O-methyloxime (15b). Colorless crystal; mp 103-104 °C; ^{1}H NMR: δ 2.00 (s, 3H), 3.91 (s, 2H), 4.02 (s, 3H), 6.66 (s, 1H), 7.24-7.95 (m, 6H), 8.65 (s, 1H). ^{13}C NMR: δ 21.68, 37.76, 62.34, 100.25, 104.02, 117.13, 150.01. Anal. Calcd. for $C_{19}H_{16}O_4N_2$ (336.4): C 67.84, H 4.79; found C 68.07, H 4.74.

Ozonolysis of 12 and 7c: Ozonolysis of 0.57 g (3.0

mmol) of **12** and 0.79 g (6 mmol) of benzoyl cyanide **8c** in 50 ml of dichloromethane, followed by distillation of the solvent under reduced pressure gave a solid residue. This residue dissolved in 20 ml of dichloromethane and the precipitate was collected by filtration and recrystallized from dichloromethane gave 0.14 g (0.6 mmol, 20%) of **16**. From the filtrate, 0.42 g (1.8 mmol, 60%) of **13** was isolated by flash chromatography (silica gel, solvent: dichloromethane/pentane = 1 : 1).

Acknowledgment. This work supported by the grant of (966-0302-003-2) from Korea Science and Engineering Foundation (KOSEF).

References

1. Bailey, P. S. *Ozonation in Organic Chemistry*; Academic Press: New York, 1982; Vol. II, p 6.
2. Callighan, R. H.; Tarker, H. F.; Wilt M. H. *J. Org. Chem.* **1961**, *26*, 1375.
3. Sugimoto, T.; Nojima, M.; Kusabayashi, S. *J. Org. Chem.* **1990**, *55*, 12, 3816.
4. Griesbaum, K.; Liu, X.; Kassiaris, A.; Scherer, M. *Liebigs Ann.* **1997**, 1381.
5. Kawamura, S.; Yamakoshi, H.; Nojima, M. *J. Org. Chem.* **1996**, *61*, 5953.
6. Lee, J. Y.; Lee, C. W.; Huh, T. S. *Bull. Korean Chem. Soc.* **1998**, *19*, 11, 1244.
7. Griesbaum, K.; Dong, Y. *J. Org. Chem.* **1997**, *62*, 6129.
8. Griesbaum, K.; Ball, V. *Tetrahedron Lett.* **1994**, *35*, 1163.
9. Lee, C. W.; Huh, T. S. To be submitted for publication.
10. Griesbaum, K.; Greunig, H. -J.; Volpp, W.; Jung I. -C. *Chem. Ber.* **1991**, *124*, 947.
11. Griesbaum, K.; Liu, X.; Henke, H. *J. Org. Chem.* **1998**, *63*, 1086.
12. Du, X.; Houk, K. N. *J. Org. Chem.* **1998**, *63*, 6480.
13. Murray, R. W. *Chem. Rev.* **1989**, *89*, 1187.
14. Stille, J. K.; Foster, R. T. *J. Org. Chem.* **1963**, *28*, 2703.
15. Yoshida, M.; Kadokura, A.; Minabe, M.; Suzuki, K. *Tetrahedron*, **1979**, *35*, 2237.