2364 *J. Org. Chem.* **1983**, *48*, 2364-2366

A Convenient Generation of 2,3-Naphthalyne. Linear Annulation of Naphthalene and a New Naphthacene Synthesis

Craig S. LeHoullier and Gordon W. Gribble*

Department of Chemistry, Dartmouth College, Hanover, New Hampshire 03755

Received November 9, 1982

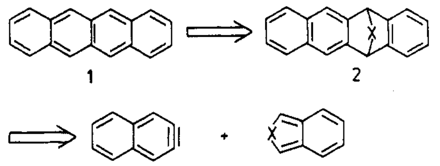
2,3-Naphthalyne (**3**) is conveniently generated by treating 2,3-dibromonaphthalene (**9**) with phenyllithium and is used in a two-step sequence to prepare naphthacene (**1**) and 1,2,3,4-tetrafluoronaphthacene (**17**). Thus, the cycloadditions of **3** with 2-methylisoindole (**13**) and 2-methyl-4,5,6,7-tetrafluoroisoindole (**14**) afford the naphthacenimines **15** and **16**, respectively. Deamination with *m*-chloroperbenzoic acid (for **15**) and dichlorocarbene (for **16**) affords **1** and **17** in 44% and 63% overall yield from **9**, respectively. Similarly, cycloadditions of **3** with furan and *N*-*tert*-butylpyrrole give anthracene, after extrusion of the heteroatom bridge.

In continuation of our syntheses of polycyclic aromatic hydrocarbons using a sequential aryne Diels–Alder cycloaddition/cheletropic bridge extrusion methodology,[1] we projected that the linear arene annulation of naphthalene, via 2,3-naphthalyne (**3**), would result in a very convenient synthesis of the naphthacene (**1**) ring system, illustrated retrosynthetically in Scheme I.

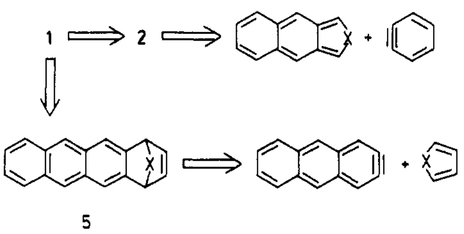
Although a priori this approach to **1** seemed very attractive and more viable than those involving the alternative bond disconnection of **2** or the alternative Diels–Alder cycloadduct **5** (Scheme II), the reported generations of **3** from 3-amino-2-naphthoic acid (by diazotization),[2] from 1-amino-1*H*-naphtho[2,3-*d*]triazole (by lead tetraacetate oxidation),[3] or from mono- and dihalonaphthalenes (by metalation or Grignard formation)[4] either involve a lengthy preparation of the precursor to **3** and/or give the Diels–Alder cycloadduct in poor yield or not at all.

However, the reaction of *o*-dibromoarenes with lithium metal, alkyllithiums, or phenyllithium has been employed several times to generate benzynes[5] and, more recently, bisarynes[6] and hexamethyl-2,3-naphthalyne.[7] In all of these cases excellent yields of Diels-Alder cycloadducts were reported. Therefore, we have investigated the reaction of 2,3-dibromonaphthalene (**9**) with lithium reagents in the presence of heterocyclic dienes (e.g., **4**) as a means with which to effect the strategy shown in Scheme I.

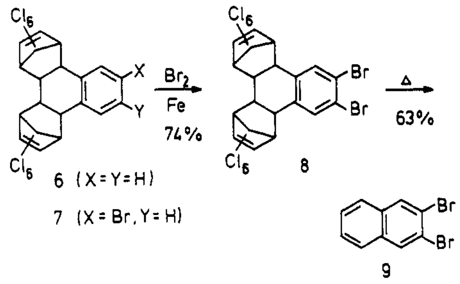
Scheme I



Scheme II



Scheme III



Results and Discussion

Although 2,3-dibromonaphthalene (**9**) has been prepared by several methods,[8,9] the commercial availability of the naphthalene–bis(hexachlorocyclopentadiene) Diels–Alder adduct **6** and its monobromo derivative **7** makes the synthesis[9] of **9** that is outlined in Scheme III the method of choice. Thus, either **6**[9] or **7** (see the experimental section) can be brominated to a single dibromide **8**, which on pyrolysis at 220 °C undergoes a retro-Diels–Alder reaction to afford **9** in 63% yield.

The reaction of **9** with various lithium reagents in the presence of simple heterocyclic dienes that follows is efficient and reproducible. Treatment of a tetrahydrofuran (THF) solution of **9** and excess furan at 0 °C with 1 equiv of phenyllithium gave the desired epoxyanthracene **10** in 72% yield. The structure of **10** is supported by spectral data, by its melting point, and by the conversion to anthracene. Thus, hydrogenation of **10** using Olah's proce-

---

[1] (a) Gribble, G. W.; Allen, R. W.; Anderson, P. S.; Christy, M. E.; Colton, C. D. *Tetrahedron Lett.* **1976**, 3673. (b) Gribble, G. W.; Allen, R. W.; LeHoullier, C. S.; Eaton, J. T.; Easton, N. R., Jr.; Slayton, R. I.; Sibi, M. P. *J. Org. Chem.* **1981**, *46*, 1025. (c) Gribble, G. W.; Kelly, W. J.; Sibi, M. P. *Synthesis* **1982**, 143. (d) LeHoullier, C. S.; Gribble, G. W. *J. Org. Chem.* **1983**, *48*, 1682.

[2] (a) Fieser, L. F.; Haddadin, M. J. *Can. J. Chem.* **1965**, *43*, 1599. (b) Wilcox, C. F., Jr.; Talwar, S. S. *J. Chem. Soc. C* **1970**, 2162. (c) Zimmerman, H. E.; Bender, C. O. *J. Am. Chem. Soc.* **1970**, *92*, 4366. (d) Sugihashi, M.; Kawagita, R.; Otsubo, T.; Sakata, Y.; Misumi, S. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 2836. (e) Thummel, R. P.; Cravey, W. E.; Nutakul, W. *J. Org. Chem.* **1978**, *43*, 2473.

[3] (a) Barton, J. W.; Jones, S. A. *J. Chem. Soc. C* **1967**, 1276. (b) Rees, C. W.; Storr, R. C. *Ibid.* **1969**, 765.

[4] (a) Ward, E. R.; Pearson, B. D. *J. Chem. Soc.* **1959**, 1676. (b) Ward, E. R.; Marriott, J. E. *Ibid.* **1963**, 4999. (c) Huisgen, R.; Zirngibl, L. *Chem. Ber.* **1958**, *91*, 1438.

[5] (a) Wittig, G.; Pohmer, L. *Chem. Ber.* **1956**, *89*, 1334. (b) Gilman, H.; Gorsich, R. D. *J. Am. Chem. Soc.* **1957**, *79*, 2625. (c) Wolthuis, E. *J. Org. Chem.* **1961**, *26*, 2215. (d) Wolthuis, E.; Bossenbroek, B.; DeWall, G.; Geels, E.; Leegwater, A. *Ibid.* **1963**, *28*, 148. (e) Hart, H.; Teuerstein, A. *Synthesis* **1979**, 693.

[6] (a) Sy, A.; Hart, H. *J. Org. Chem.* **1979**, *44*, 7. (b) Hart, H.; Lai, C.; Nwokogu, G.; Shamouilian, S.; Teuerstein, A.; Zlotogorski, C. *J. Am. Chem. Soc.* **1980**, *102*, 6649. (c) Hart, H.; Shamouilian, S.; Takehira, Y. *J. Org. Chem.* **1981**, *46*, 4427.

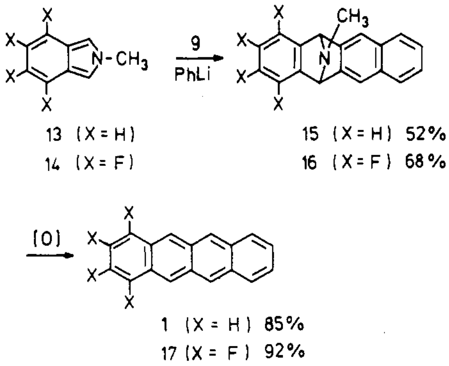
[7] (a) Hart, H.; Ruge, B. *Tetrahedron Lett.* **1977**, 3143.

[8] (a) Kenner, J.; Ritchie, W. H.; Wain, R. L. *J. Chem. Soc.* **1937**, 1526. (b) Hodgson, H. H.; Hathway, D. E. *Ibid.* **1945**, 841. (c) Pearson, B. D. *Chem. Ind.* **1960**, 899.

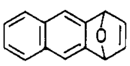
[9] Danish, A. A.; Silverman, M.; Tajima, Y. A. *J. Am. Chem. Soc.* **1954**, *76*, 6144.

0022-3263/83/1948-2364$01.50/0 © 1983 American Chemical Society

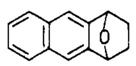
Scheme IV



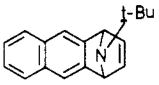
dure[10] gave 11 in 95% yield after recrystallization. This was dehydrated to anthracene under the usual conditions[5a] (HCl/EtOH).



10



11



12

A similar sequence with *N-tert*-butylpyrrole[11] gave anthracenimine 12 in 78% yield. This compound showed in the ^{1}H NMR spectrum the characteristic[1b] AA′XX′ pattern at 4.90 and 6.75 ppm for the bridgehead and vinyl protons, respectively. Deamination[1a] of 12 with *m*-chloroperbenzoic acid (*m*-CPBA) (CH_2Cl_2, 25 °C) gave anthracene in 86% yield.

Our attention now turned to the synthesis of naphthacenes by use of this methodology. Thus, treatment of 9 with phenyllithium in the presence of 2-methylisoindole (13)[12a] or 2-methyl-4,5,6,7-tetrafluoroisoindole (14)[12b] gave the anticipated naphthacenimines, 15 and 16, in 52% and 68% yield, respectively (Scheme IV). Imine 15 with *m*-CPBA was smoothly transformed into naphthacene (1), in 85% yield. A similar reaction with 16 gave 1,2,3,4-tetrafluoronaphthacene (17) in low yield. However, our[1b] alternative deamination procedure using dichlorocarbene, generated under phase-transfer conditions, gave 17 in 92% yield.

In summary, the facile generation of 2,3-naphthalyne (3) from 2,3-dibromonaphthalene (9) has been used to synthesize naphthacenes from available[12] isoindoles.

Experimental Section

Melting points were determined with a Mel-Temp Laboratory Devices apparatus and are uncorrected. Elemental analyses were performed by Atlantic Microlabs, Atlanta, GA. Infrared spectra were recorded on a Perkin-Elmer 599 instrument. ^{1}H NMR spectra were obtained with a Hitachi Perkin-Elmer R-24 spectrometer and ^{13}C NMR spectra were measured on a JEOL FX60Q Fourier-transform NMR spectrometer. Tetramethylsilane was the internal reference. Woelm alumina was used for column chromatography and thin-layer chromatography was performed on precoated (0.2 mm) silica gel 60 F_{254} plastic sheets (E. Merck). Phenyllithium was standardized by titration against 2,5-dimethoxybenzyl alcohol.[13] Tetrahydrofuran was distilled from sodium/benzophenone. All reactions were performed in oven-dried (130 °C) glassware under nitrogen.

10,11-Dibromo-1,2,3,4,5,6,7,8,13,13,14,14-dodecachloro-1,4,4a,4b,5,8,8a,12b-octahydro-1,4;5,8-dimethanotriphenylene (8). To a magnetically stirred and refluxing suspension of 10-bromo-1,2,3,4,5,6,7,8,13,13,14,14-dodecachloro-1,4,4a,4b,5,8,-8a,12b-octahydro-1,4;5,8-dimethanotriphenylene (7; 10 g, 0.013 mol; Aldrich Chemical Co.) and Fe powder (0.05 g) in 1,1,2,2-tetrachloroethane (20 mL) was added dropwise a solution of Br_2 (4.15 g, 0.026 mol) in 1,1,2,2-tetrachloroethane (5 mL) over 1 h. The mixture was refluxed for an additional 2 h and then allowed to cool slightly. The warm solution was treated with 10% aqueous sodium thiosulfate (2 × 100 mL) and then washed with H_2O (2 × 50 mL) and dried (Na_2SO_4). The resulting golden solution was diluted with MeOH (20 mL) and stored at 10 °C for 48 h to deposit 8.1 g (74%) of 8 as colorless crystals: mp 221–222 °C (lit.[9] mp 220–222 °C).

2,3-Dibromonaphthalene (9). This was prepared in 63% yield from 8 (on a 40-g batch) by the reported[9] procedure: mp 139–140 °C (lit.[9] mp 139–140 °C; ^{1}H NMR ($CDCl_3$) δ 7.6 (m, 4 H), 8.15 (s, 2 H); IR (KBr) 1575 (s), 1490 (s), 1430 (s), 1310 (s), 1200 (s), 950 (s), 890 (s), 860 cm^{-1} (m).

***N*-*tert*-Butylpyrrole.** This was prepared in 45% yield (on a 50-g batch) by the reported[11] procedure: bp 70 °C (30 torr) (lit.[11] bp 68 °C (30 torr)); ^{1}H NMR ($CDCl_3$) δ 1.35 (s, 9 H), 6.07 (m, 2 H), 6.72 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 30.4, 54.0, 107.2, 116.9; IR (neat) 2995 (s), 1490 (s), 1375 (s), 1270 (s), 1230 (m), 1080 (m), 955 (m), 720 (s), 640 cm^{-1} (m).

1,4-Epoxy-1,4-dihydroanthracene (10). To a magnetically stirred solution of 9 (1.0 g, 3.5 mmol) and furan (20 mL, 0.27 mol) in dry THF (25 mL) under N_2 at 0 °C was added dropwise phenyllithium (1.90 M in cyclohexane; 2.0 mL, 3.8 mmol). The resulting brown solution was stirred at 25 °C for 1 h and then was preadsorbed onto activity III basic Al_2O_3. Column chromatography over activity III basic Al_2O_3 (Et_2O) gave 0.48 g (72%) of 10 as a colorless solid: mp 164–165 °C (lit.[3b] mp 164–165 °C); ^{1}H NMR ($CDCl_3$) δ 5.80 (s, 2 H), 6.95 (s, 2 H), 7.60 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ 81.7, 118.4, 125.9, 127.9, 131.8, 141.5, 144.0; IR (KBr) 1290 (m), 980 (m), 875 (s), 850 (s), 760 (s), 705 (s), 640 cm^{-1} (m).

1,4-Epoxy-1,2,3,4-tetrahydroanthracene (11). To a magnetically stirred suspension of 10 (0.15 g, 0.77 mmol), 10% Pd/C (10 mg), and MeOH (20 mL) under N_2 at 25 °C was added oven-dried, crushed Mg turnings (0.1 g, 3.9 mmol). The mixture was stirred at 25 °C overnight and then poured into cold 3 N HCl (20 mL) and extracted with CH_2Cl_2 (3 × 50 mL). The extract was dried (Na_2SO_4) and evaporated in vacuo to afford 11 as a white solid. Recrystallization from hexane gave 0.14 g (95%) of 11 as colorless flakes: mp 140–141 °C; ^{1}H NMR ($CDCl_3$) δ 1.5 (m, 2 H), 2.1 (m, 2 H), 5.5 (m, 2 H), 7.6 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ 24.8, 78.8, 116.7, 125.5, 128.0, 132.8, 143.9; IR (KBr) 1300 (m), 1010 (m), 970 (s), 880 (s), 850 (s), 825 (s), 750 cm^{-1} (s).

Anal. Calcd. for $C_{14}H_{12}O$: C, 85.68; H, 6.16. Found: C, 85.48; H, 6.19.

Anthracene from 11. A magnetically stirred solution of 11 (0.030 g, 0.15 mmol) in absolute EtOH (5 mL) was treated with HCl gas for 5 min and then refluxed for 2 h. The mixture was poured into H_2O (20 mL) and extracted with CH_2Cl_2 (2 × 25 mL). The organic extract was dried and evaporated in vacuo to afford 0.03 g (ca. 100%) of anthracene: mp 216–217 °C, identical (IR, TLC, UV) to a commercial sample.

11-*tert*-Butyl-1,4-dihydroanthracen-1,4-imine (12). This reaction was carried out as described for 10, employing the following materials: 9 (2.0 g, 7 mmol), *N-tert*-butylpyrrole (8.6 g, 70 mmol), THF (50 mL), and phenyllithium (1.80 M in cyclohexane, 4.0 mL, 7 mmol). The usual workup and chromatography gave 1.35 g (78%) of 12 as a pale-yellow solid. Recrystallization from hexane gave pure 12 as colorless needles: mp 95–96 °C; ^{1}H NMR ($CDCl_3$) δ 1.00 (s, 9 H), 4.90 (m, 2 H), 6.75 (m, 2 H), 7.40 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ 29.6, 53.0, 65.7, 118.0, 125.3, 127.6, 132.0, 142.2, 147.5; IR (KBr) 2980 (m), 1365 (m), 1285 (s), 1210

---

[10] Olah, G. A.; Prakash, S. G. K.; Arvanaghi, M.; Bruce, M. R. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 92.

[11] Lightner, D. A.; Pak, C.-S. *J. Org. Chem.* **1975**, *40*, 2724.

[12] (a) Zeeh, B.; Konig, K. H. *Synthesis* **1972**, 45. (b) Priestley, G. M.; Warrener, R. N. *Tetrahedron Lett.* **1972**, 4295.

[13] Winkle, M. R.; Lansinger, J. M.; Ronald, R. C. *J. Chem. Soc., Chem. Commun.* **1980**, 88.

(s), 885 (s), 850 (m), 815 (s), 750 (s), 710 (s), 610 cm^{-1} (m).

Anal. Calcd for $C_{18}H_{19}N$: C, 86.70; H, 7.68; N, 5.62. Found: C, 86.57; H, 7.68; N, 5.60.

Anthracene from 12. To a magnetically stirred solution of **12** (0.1 g, 0.4 mmol) in CH_2Cl_2 (10 mL) at 25 °C was added *m*-CPBA (0.06 g, 0.4 mmol). The resulting aqua solution was stirred at 25 °C for 1 h and then preadsorbed onto activity III basic Al_2O_3. Chromatography over activity III basic Al_2O_3 (hexane) gave 0.06 g (86%) of anthracene: mp 217–218 °C, identical (IR, TLC, UV, mmp 217–218 °C) to a commercial sample.

13-Methyl-5,12-dihydronaphthacen-5,12-imine (15). This reaction was carried out as described for **10**, employing the following materials: **9** (1.0 g, 3.5 mmol), 2-methylisoindole (**13**;[12a] 1.5 g, 0.01 mol), THF (25 mL), and phenyllithium (1.80 M in cyclohexane; 2.0 mL, 3.5 mmol). The usual workup and chromatography gave 0.47 g (52%) of **15** as a tan solid. Recrystallization from hexane gave the analytical sample: mp 168–169 °C; ^{1}H NMR ($CDCl_3$) δ 2.25 (s, 3 H), 5.00 (s, 2 H), 7.1 (m, 6 H), 7.65 (s, 4 H); ^{13}C NMR ($CDCl_3$) δ 36.4, 72.3, 120.6, 121.6, 125.6, 125.8, 127.7, 132.3, 144.0, 147.1; IR (KBr) 2980 (w), 2960 (w), 1450 (w), 1270 (w), 940 (m), 885 (m), 780 (s), 740 (s), 700 (s), 695 (s), 640 cm^{-1} (m).

Anal. Calcd for $C_{19}H_{15}N$: C, 88.68; H, 5.88; N, 5.44. Found: C, 88.50; H, 5.91; N, 5.45.

13-Methyl-1,2,3,4-tetrafluoro-5,12-dihydronaphthacen-5,12-imine (16). This reaction was carried out as described for **10**, employing the following materials: **9** (1.0 g, 3.5 mmol), 2-methyl-4,5,6,7-tetrafluoroisoindole; (**14**;[12b] 1.5 g, 7.4 mmol), THF (25 mL), and phenyllithium (1.80 M in cyclohexane; 2.0 mL, 3.5 mmol). The usual workup and chromatography gave 0.78 g (68%) of **16** as white flakes. Recrystallization from hexane gave the analytical sample: mp 186–187 °C; ^{1}H NMR ($CDCl_3$) δ 2.30 (s, 3 H), 5.35 (s, 2 H), 7.5 (m, 2 H), 7.75 (s, 4 H); ^{13}C NMR ($CDCl_3$) δ 36.2, 69.4, 120.9, 126.3, 127.9, 132.3, 141.3; IR (KBr) 2960 (w), 1500 (s), 1280 (s), 1205 (m), 1190 (m), 1100 (m), 1050 (s), 955 (m), 760 (s), 745 cm^{-1} (m).

Anal. Calcd for $C_{19}H_{11}NF_4$: C, 69.30; H, 3.37; N, 4.25. Found: C, 69.39; H, 3.55; N, 4.14.

Naphthacene (1). To a magnetically stirred solution of **15** (0.08 g, 0.3 mmol) in MeCN (25 mL) at 25 °C was added *m*-CPBA (0.05 g, 0.3 mmol). The resulting solution was refluxed for 2 h, during which time a green fluorescence developed and an orange solid appeared. The mixture was cooled and filtered to afford 0.06 g (85%) of **1** as orange flakes: mp 356–357 °C, identical (IR, TLC, UV, mmp 356–357 °C) to a commercial sample.

1,2,3,4-Tetrafluoronaphthacene (17). To a magnetically stirred solution of **16** (0.03 g, 0.09 mmol) in $CHCl_3$ (10 mL) at 25 °C under N_2 was added 50% aqueous NaOH (2 drops) and benzyltriethylammonium chloride (5 mg). The resulting mildly exothermic reaction was stirred at 25 °C overnight, during which time the solution became orange with a green fluorescence. The solution was partitioned between 3 N HCl (20 mL) and $CHCl_3$ (50 mL). The organic layer was washed with H_2O, dried (K_2CO_3), and evaporated in vacuo to afford **17** as an orange solid. Recrystallization from benzene–hexane afforded 0.025 g (92%) of **17** as orange needles: mp 263–264 °C; IR (KBr) 1590 (m), 1490 (s), 1385 (m), 1100 (m), 1000 (m), 990 (m), 890 (m), 810 (m), 790 (m), 730 cm^{-1} (s); UV (benzene) λ_{max} 473, 443, 416, 392, 295, 278 nm.

Anal. Calcd for $C_{18}H_8F_4$: C, 72.01; H, 2.69. Found: C, 71.84; H, 2.82.

Acknowledgment. This investigation was supported by PHS Grant CA-24422, awarded by the National Cancer Institute, DHEW, and in part by Grant CH-200 from the American Cancer Society and by Merck Sharp and Dohme Research Laboratories.

Registry No. 1, 92-24-0; 3, 19873-31-5; 7, 80789-65-7; 8, 6710-98-1; 9, 13214-70-5; 10, 22187-13-9; 11, 85894-21-9; 12, 85894-22-0; 13, 33804-84-1; 14, 38053-09-7; 15, 85894-23-1; 16, 85908-81-2; 17, 29525-05-1; *N-tert*-butylpyrrole, 24764-40-7; furan, 110-00-9; anthracene, 120-12-7.

Acidolysis of Ozonides. An ab Initio Study

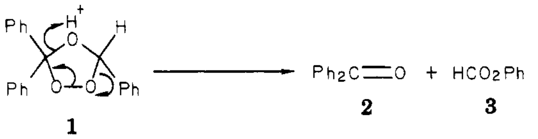
Masahiro Miura,[1a] Shigeru Nagase,*[1b] Masatomo Nojima,*[1a] and Shigekazu Kusabayashi[1a]

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita,
Osaka 565, Japan, and Department of Chemistry, Faculty of Education, Yokohama National University,
Hodogaya-ku, Yokohama 240, Japan

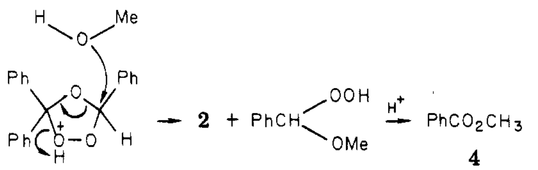
Received September 21, 1982

As the model species of the intermediates which may participate in the acidolysis of ozonides, seven species **14–20** have been investigated with the ab initio SCF–MO method at the split-valence 4-31G level. On the basis of both the relative stabilities and the charge distributions of these species, we have attempted to provide insight into the apparently complicated experimental observations.

Acidolysis of ozonides (1,2,4-trioxolanes) has been found to proceed by several pathways, depending on the structure of ozonides and reaction conditions.[2] The following examples discovered by us[3-6] illustrate this situation. (a) The reaction of triphenylethylene ozonide (**1**) in methylene chloride gave equimolar proportions of benzophenone (**2**) and phenyl formate (**3**) (eq 1),[3] while in methanol its reaction afforded methyl benzoate (**4**) (via α-methoxybenzyl hydroperoxide) along with **2** (eq 2).[4] The former reaction seems to proceed via heterolytic cleavage of the C–O bond of the ether bridge. Probably C–O bond fission of the



(1)



(2)

---

[1] (a) Osaka University. (b) Yokohama National University.

[2] Bailey, P. S. "Ozonation in Organic Chemistry"; Academic Press: New York, 1978; Vol. 1; *Ibid.*, 1982, Vol. 2.

[3] Miura, M.; Nojima, M. *J. Am. Chem. Soc.* **1980**, *102*, 288.

[4] Miura, M.; Nojima, M.; Kusabayashi, S. *J. Chem. Soc., Perkin Trans. 1* **1980**, 2909.

[5] Miura, M.; Nojima, M.; Kusabayashi, S.; Nagase, S. *J. Am. Chem. Soc.* **1981**, *103*, 1789.

[6] Miura, M.; Ikegami, A.; Nojima, M.; Kusabayashi, S.; McCullough, K. J.; Nagase, S. *J. Am. Chem. Soc.* **1983**, *105*, 2414.

0022-3263/83/1948-2366$01.50/0 © 1983 American Chemical Society