

Infrared spectra were recorded on a Nicolet Impact 410 FT-IR spectrophotometer. Band positions are given in reciprocal centimeters (cm^{-1}) and relative intensities are listed as: br (broad), s (strong), m (medium), or w (weak).

Thin layer chromatography (TLC) was performed on 0.25 mm Merck silica-coated glass plates, with the compounds being identified in one or more of the following manners: UV (254 nm, unless otherwise specified), iodine. Flash chromatography was performed according to the procedure of Still⁵ using thick-walled glass columns and Merck Silica Gel 60 (230-400 Mesh). All solvents were distilled from calcium chloride before use unless noted otherwise. Tetrahydrofuran (THF), diethyl ether (Et_2O), and hexanes were distilled from sodium/benzophenone ketyl. All reagents were distilled, recrystallized, or chromatographed prior to use unless otherwise noted.

Glassware used in the reactions described below was dried in an oven at 120 °C overnight (12 hours) and assembled under an inert atmosphere of nitrogen, or flame-dried under vacuum and then cooled under nitrogen.

O-Methoxycarbonyl cyanohydrin 3. The solution of tributyltin cyanide (22 mg, 0.07 mol) in dried acetonitrile (5 mL) was added methyl cyanofornate (160 mg, 1.86 mmol) and hydrocinnamaldehyde (200 mg, 1.49 mmol) in sealed tube at room temperature. The reaction mixture was stirred at 80 °C for 2.5 h. The reaction mixture was extracted with EtOAc (3×50 ml) after evaporated acetonitrile in the rotavapor. The organic layer was dried (Na_2SO_4), and concentrated *in vacuo* to give crude solid. Purification by flash chromatography (25% EtOAc/hexane) afforded 239 mg (79%) of methyl cyanofornate **3**. Rf 0.67, 25% EtOAc/hexane; IR (neat) 3060 (m), 2960 (s), 2930 (m), 2890 (m), 2210 (w), 1760 (s), 1700 (s), 1490 (s); ^1H NMR (CDCl_3): 2.34-2.23 (m, 2H), 2.86 (t, 2H, $J=7.7$), 3.88 (s, 3H), 5.15 (t, 1H, $J=6.8$), 7.34-7.18 (m, 5H).

Formylated cyanohydrin 5. IR (neat) 2940 (s), 2920 (s), 2840 (s), 2190 (w), 1760 (s), 1440 (s); ^1H NMR (CDCl_3): 0.86 (t, 3H, $J=6.41$), 1.25-1.53 (m, 12H), 1.86-1.94 (m, 2H), 3.83 (s, 3H), 5.17 (t, 1H, $J=6.72$).

Formylated cyanohydrin 7. IR (neat) 3000 (m), 2930 (s), 2860 (s), 2300 (w), 1760 (s), 1430 (s), 1270 (s); ^1H NMR (CDCl_3): 0.90 (t, 3H, $J=6.59$), 1.29-1.60 (m, 18H), 1.89-2.03 (m, 6H), 3.86 (s, 3H), 5.20 (t, 1H, $J=6.74$), 5.32-5.37 (m, 2H).

Formylated cyanohydrin 9. IR (neat) 3040 (m), 3020 (m), 2940 (w), 2840 (w), 2270 (w), 1770 (s), 1580 (s); ^1H NMR (CDCl_3): 3.88 (s, 3H), 6.23 (s, 1H), 7.02-7.42 (m, 9H).

Formylated cyanohydrin 11. IR (neat) 3060 (m), 3030 (s), 2990 (m), 2940 (s), 2960 (w), 2270 (w), 1760 (s), 1560 (s); ^1H NMR (CDCl_3): 3.88 (s, 3H), 6.24 (s, 1H), 7.01-7.52 (m, 9H).

Formylated cyanohydrin 13. IR (neat) 3040 (m), 3010 (m), 3000 (m), 2960 (s), 2200 (w), 1770 (s), 1500 (m), 1410 (s); ^1H NMR (CDCl_3): 3.85 (s, 3H), 6.25 (s, 1H), 7.40-7.55 (m, 5H).

Acknowledgment. financial support was provided by the Institute of Basic Science of Changwon National University and R&D Promotion Center for Agriculture, Forestry and Fishery.

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Ozonolyses of Vinyl Triflates

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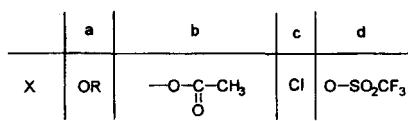
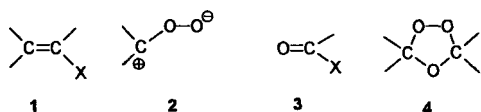
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Received August 22, 1997

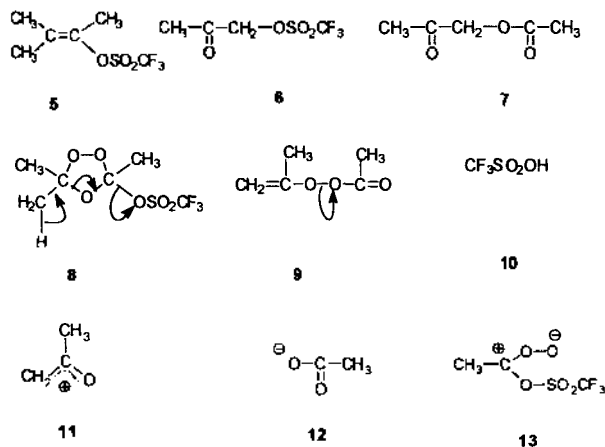
Olefins which bear electronegative substituents in a vinylic position such as **1a**¹, **1b**² or **1c**³ are preferentially cleaved by ozone to give fragments of types **2** and **3**. Due to the low dipolarophilicity of acid derivatives such as **3a-3c**, cycloadditions of fragments of types **2** and **3** to give ozonides of type **4** are disfavored. Hence, it is not surprising that ozonolyses of substrates of types **1a**¹, **1b**² and **1c**³ afford the corresponding ozonides in low yield or not at all,

depending on the nature of the substituents at the double bonds of **1a-1c**. In the present work we were interested in the behavior of vinyl triflates towards ozone since, to our knowledge, such reactions have not been reported. Since it was apparent from previous work,⁷ that ozonolysis of olefinic substrates on polyethylene is a more suitable technique than ozonolysis in solution, the ozonolyses of **5** and **14** were carried out on polyethylene.



Ozonolysis of **5** on polyethylene at -75°C afforded a mixture of **6** (16%), **7** (8%), acetone (20%) and acetic acid (56%) in the relative proportions reported in parenthesis, as determined by ^1H NMR spectroscopy. Compounds **6** and **7** have been isolated and characterized of their ^1H NMR, MS and GC- t_{R} data.

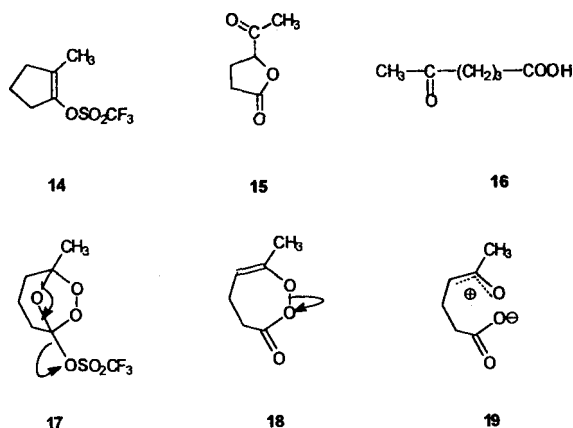
The formation of the abnormal ozonolysis products **6** and **7** can be rationalized by the intermediacy of ozonide **8** which undergoes spontaneous fragmentation in the sense indicated by the arrows and initiated by elimination of the good leaving group trifluoromethanesulfonate. In accord with the known instability of vinylic peroxides, the ensuing peroxide **9** undergoes further fragmentation to give **11** and **12**. Finally, trapping of **11** by **10** or by **12** affords the abnormal ozonolysis products **6** and **7**, respectively. This reaction course is analogous to that postulated for the formation of **7** in the ozonolysis of 2-chloro-3-methyl-2-butene.⁵ The formation of the other ozonolysis products, viz. acetone and acetic acid can be explained by cleavage of **5** by ozone to give acetone and carbonyl oxide **13**, followed by solvolysis of the latter by adventitious amounts of water to give acetic acid.



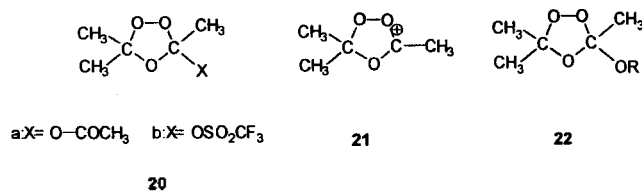
Ozonolysis of **14** on polyethylene at -78°C afforded a mixture of **15** (6%), **16** (21%), acetic acid (41%) and formic acid (10%) in the relative proportions given in parenthesis, as determined by ^1H NMR spectroscopy. The structural assignments of these products have also been confirmed by their ^1H NMR, MS and GC- t_{R} data.

For the mode of formation of products **15** and **16**, we assume a reaction path which is analogous to that proposed for the formation of **6** and **7** in the ozonolysis of **5**: Ozonolysis of **14** leads in part to ozonide **17**, which undergoes immediate fragmentation to give **10** and **18**. Subsequent fragmentation of the vinylic peroxide **18** leads to

zwitterion **19**, which by intra-molecular reaction affords lactone **15**. The formation of ketoacid **16** is explained by ozone cleavage of **14** to give **10** in addition to **16**. The formation of the major product acetic acid and of minor amounts of formic acid is indicative of abnormal cleavage reactions.



A comparison of the results obtained in the present study with those obtained in the ozonolysis of vinylic acetates is in line with the known differences in the behavior could be ascribed to the leaving group ability between acetate and triflate. Since ozonide **20a** turned out to be stable at room temperature,² whereas at temperatures above 40°C it eliminates the acetoxy group, as evidenced by trapping of the ensuing ozonide cation **21** with alcohols to give the corresponding alkoxy substituted ozonides **22**.³ By contrast, similar attempts for the experimental proof of the intermediacy of cation **21** in the elimination of the triflate group from the postulated ozonide **21b** failed. We assume, that due to the enhanced leaving aptitude of the triflate group, ozonide **21b** undergoes elimination immediately after its formation.



Experimental

General methods. ^1H NMR spectra were recorded on a Bruker WM 250 and mass spectra on a Hewlett-Packard GC/MS 5985B instrument. GC analyses were carried out under the following conditions; a) Shimadzu GC-6A instrument; column 0.3×3 m, cyanoethylmethyl-silicone(NiSi); 60°C to 180°C at $4^\circ\text{C}/\text{min}$. b) Hewlett-Packard instrument 5880; 50 m capillary column SE 54; 50°C to 180°C at $7^\circ\text{C}/\text{min}$.

Ozonolysis reactions on polyethylene were performed according to a published procedure.⁹ The substrates were loaded on polyethylene in a stream of nitrogen according to the procedure for low boiling materials.⁹

Ozonolysis of 3-methyl-2-butene-2-yl-triflate (5). Ozonolysis of 730 mg (3.35 mmol) of **5**¹⁰ on 65 g of polyethylene at -75°C was carried out for 6 h. Then the

loaded polyethylene was evacuated at room temperature and 10^{-2} Torr and the products were passed through a series of three traps kept at 0 °C, -20 °C and -78 °C. The trap kept at 0 °C contained 27 mg (4%) of **6**; the trap kept at -20 °C contained additional **6** (7%; $\delta=2.28$) as well as **7** (11%; $\delta=4.66$), acetone (21%; $\delta=2.18$) and acetic acid (58%; $\delta=2.10$) in the relative proportions reported in parenthesis, as determined by ^1H NMR spectroscopy. Separation of this mixture by flash chromatography (silica gel; n-pentane/diethyl ether, in a volumetric ratio of 10:1) gave 12 mg (3%) of **7**. The assignments of the above mentioned products were in each case **11**, **12** confirmed by the comparison of their ^1H NMR data with those of reported^{11,12}; the identity of the non-isolated products acetone and acetic acid was additionally confirmed by their GC- t_R data.

Acetonitrile (**6**). Colorless solid, mp 45-46 °C (lit.¹¹ mp 44-45 °C); ^1H NMR (CDCl_3 , TMS): $\delta=2.28$ (s, 3H), 4.92 (s, 2H); EI-MS (%) $m/e=207$ (100) ($M+1$)⁺.

Acetoxyacetone (**7**). ^1H NMR (CDCl_3 , TMS): $\delta=2.17$ (s, 3H), 2.18 (s, 2H), 4.66 (s, 2H); EI-MS (%) $m/e=116$ (13) M^+ .

Acetone. ^1H NMR (CDCl_3 , TMS): $\delta=2.18$ (s); EI-MS (%) $m/e=58$ (34) M^+ ; GC- $t_R=2.59$ min (condition a).

Acetic acid. ^1H NMR (CDCl_3 , TMS): $\delta=2.10$ (s); EI-MS (%) $m/e=60$ (31) M^+ ; GC- $t_R=8.73$ min (condition a).

Ozonolysis of 1-methyl-2-cyclopentenyltriflate (14). Ozonolysis of 780 mg (3.39 mmol) of **14** on 65 g of polyethylene at -78 °C was carried out for 6 h, and the products were collected as described above. The trap kept at -78 °C contained 318 mg of a colorless liquid, which was composed of acetic acid (60%; $\delta=2.09$; EI-MS: $m/e=60$, M^+) and formic acid (40%; $\delta=8.03$; EI-MS: $m/e=46$, M^+).

The residual products on polyethylene were isolated by extraction with diethyl ether and subsequent removal of the solvent at room temperature and reduced pressure to leave 412 mg of a colorless liquid residue. ^1H NMR analysis showed the presence of **15** (25%; $\delta=2.31$, s) and **16** (75%; $\delta=2.16$, s) in the relative proportions reported in parenthesis. The assignments of **15**¹³ and **16**¹⁴ were confirmed by comparison of their ^1H NMR, data with those of reported.

5-Acetylbutyrolactone (15). ^1H NMR (CDCl_3 , TMS): $\delta=2.50$ - 2.61 (m, 4H), 2.31 (s, 3H), 4.79-4.85 (m, 1H); EI-MS (%) $m/e=128$ (15) M^+ ; GC- $t_R=14.97$ min (condition b).

5-Oxohexanoic acid (16). ^1H NMR (CDCl_3 , TMS): $\delta=1.90$ (quint, $J=7.1$ Hz, 2H), 2.16 (s, 3H), 2.43 (t, $J=7.1$ Hz, 2H), 2.56 (t, $J=7.1$ Hz, 2H); EI-MS (%) $m/e=130$ (2) M^+ ; GC- $t_R=16.28$ min (condition b).

This work was supported by the Catholic University of Korea Research Fund in the fiscal year of 1997.

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pH Dependence of Electrochemical Behaviors of Methylene Blue on Self-Assembled Monolayers

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Received August 27, 1997

Spectroscopic¹⁻³ and electrochemical⁴⁻⁶ properties of methylene blue (MB) have been widely studied mainly due to its specific interaction with deoxyribonucleic acid (DNA). The driving force of these works is based on the fact that small and planar organic molecules can be used for analytical, diagnostic, and therapeutic purposes⁷ since the probe molecule is electroactive and specifically bound to double-strand-

ed DNA molecules.

Important studies on the electrochemical behaviors of MB have been performed by Chevalet *et al.*⁴⁻⁶ a decade ago. They addressed, from the voltammetric results, that the insoluble reduction product, a mixed valence salt of the leucomethylene blue (LMB) and its cation radical (LMB^{•+}), forms two polymorphic conductive structures on Au and Pt