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# Ozonolyses of Selected Vinyl Ethers

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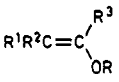
Ozonolyses of the 1-substituted methyl vinyl ethers **5**, **8**, and **16**, bearing bulky substituents, and of the 2-substituted and 2,2-disubstituted methyl vinyl ethers **25** and **30**, respectively, afforded the corresponding ozonides which have been isolated and characterized. In most cases, dry ozonolysis on polyethylene was advantageous over ozonolysis in solution. Ozonolysis of the 1,2,2-trisubstituted vinyl ether **34** gave no ozonide under either conditions.

Since the appearance of the first report[1] on the successful isolation of ozonides **4**, derived from the ozonolysis of acyclic vinyl ethers **1**, a number of investigations have dealt with this subject.[2-5] From the results it can be taken that cleavage of substrates of type **1** occurs predominantly to give fragments **2** and **3** and that in solution and in the absence of added ester fragment **3**, ozonides were only found starting from unsubstituted (i.e. $R^1 = R^2 = R^3 = H$) and from 1-substituted (i.e. $R^1 = R^2 = H$; $R^3$ = alkyl) vinyl ethers as well as from one 2-substituted vinyl ether, viz. from 1-ethoxypropene (i.e. $R^1 = CH_3$; $R^2 = R^3 = H$).[3] By contrast, no ozonides were obtained from all the other examined 2-substituted (i.e. $R^1$ = $>C_1$-alkyl,[4] aryl,[4] or alkoxy;[5] $R^2 = R^3 = H$) and from 2,2-disubstituted (i.e. $R^1$, $R^2$ = alkyl or aryl; $R^3$ = H)[4] vinyl ethers. Furthermore, the ozonide yield obtained in pentane was lower (viz. 3%) starting from a 1-substituted substrate (viz. $R^1 = R^2 = H$; $R^3 = CH_3$; R = Et) than starting from the corresponding unsubstituted substrate (viz. $R^1 = R^2 = R^3 = H$; R = Et), which was obtained in a yield of 9%.[2] It is true that ozonide yields could be raised by performing ozonolyses of vinyl ethers (**1**) in the presence of an excess of the corresponding ester fragment **3**, but this method failed to afford ozonides when applied to most 2-substituted[4,5] and 2,2-disubstituted[4] vinyl ethers. By contrast, ozonolyses of the same 2-substituted and 2,2-disubstituted vinyl ethers on polyethylene did provide the corresponding ozonides.[4] In pursuit of this observation, we have now examined the ozonolysis of vinyl ethers **5**, **8**, **16**, **25**, **30**, and **34** on polyethylene for the reasons given below.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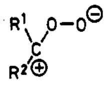
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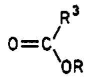
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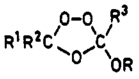
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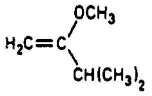
Ozonolysis of **5** was performed in order to assess the effect of a more bulky substituent than $CH_3$ in the 1-position upon the aptitude of ozonide formation. Ozonolysis of **5** on polyethylene provided **6** and **7** in yields of 18% and 24%, respectively. They were characterized by their $^1H$ and $^{13}C$ NMR spectra, and ozonide **6** by reduction with triphenylphosphine to give formaldehyde and methyl isobutyrate. Both **6** and **7** are labile; at room temperature they decomposed in $CDCl_3$ solution within 15 and 8 h, respectively.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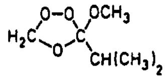
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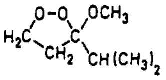
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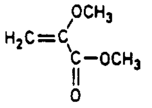
Ozonolysis of **8** was carried out in order to test the dipolarophilicity of a diester (viz. **10**) as opposed to monoesters toward carbonyl oxides in 3 + 2-cycloadditions. Ozonolysis of **8** on polyethylene afforded **11** and **12** in relative proportions of ca. 9:1, as evidenced by $^1H$ NMR analysis, and in isolated yields of 36% and 4%, respectively. Ozonolysis of **8** in pentane, by contrast, gave **11** and **12** in a proportion of ca. 1:1. This indicates that on polyethylene the competition between **8** and **10** for **9** is in favor of **10**, and it supports our view[6] that ozonolysis of olefins on polyethylene favors the formation of ozonides due to the proximity of the initial cleavage products, viz. **9** and **10** in the ozonolysis of **8**. Compounds **11** and **12** were again characterized by their $^1H$ and $^{13}C$ NMR spectra; reduction of **11** by triphenylphosphine gave **10**, as expected. Both **11** and **12** are labile and decomposed within 10 and 5 h, respectively, in $CDCl_3$ at room temperature. A violent explosion occurred when **11** was introduced into a flame.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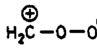
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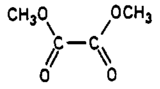
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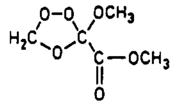
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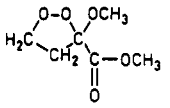
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The facile formation of ozonide **11** indicates that the carbonyl groups in diester **10** are more dipolarophilic than those of monoesters, probably due to mutual activation of the two ester groups in **10**. This concept of mutual activation is supported by the fact that the remaining, apparently nonactivated ester group in ozonide **11** does not undergo cycloaddition with carbonyl oxide **9** to give diozonide **15c**. By contrast, in the ozonolysis of the α,β-unsaturated ketones **13a** and **13b** on polyethylene, diozonides **15a** and **15b** had been formed in yields of 17% and 7%, respectively, via the corresponding monoozonides **14**.[7] Since **15a** and **15b** could be obtained in considerably higher yields from the ozonolyses of the corresponding

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(1) Keul, H.; Kuczkowski, R. L. *J. Am. Chem. Soc.* **1984,** *106,* 5370.

(2) For a recent review, see: Kuczkowski, R. L. *Advances in Oxygenated Processes*; JAI Press: Greenwich; CT, 1991; Vol. 3, p1.

(3) Wojciechowski, B. J.; Pearson, W. H.; Kuczkowski, R. L. *J. Org. Chem.* **1989,** *54,* 115.

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(6) Griesbaum, K.; Volpp, W.; Greinert, R.; Greunig, H.-J.; Schmid, J.; Henke, H. *J. Org. Chem.* **1989,** *54,* 383.

(7) Griesbaum, K.; Greunig, H.-J.; Volpp, W.; Jung, I.-Ch. *Chem. Ber.* **1991,** *124,* 947.

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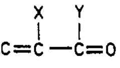
parent olefins, viz. isoprene and 2,3-dimethyl-1,3-butadiene, we have ozonized 2,3-dimethoxy-1,3-butadiene (**16**) in attempt to prepare a sample of diozonide **15c** and assess its stability.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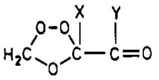
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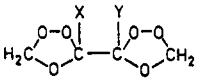
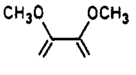

15

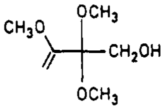
a: X=H; Y=$CH_3$; b: X=Y=$CH_3$; c: X=Y=$OCH_3$

Ozonolysis of diene **16** was first carried out with 0.9 molar equiv of ozone in methanol, in order to determine the direction of cleavage. This resulted in the formation of **8** (24%), **10** (13%), **17** (53%), and **18** (10%), as evidenced by $^1$H NMR analysis. The rationale for this result is that diene **16** undergoes ca. 90% of double bond cleavage and ca. 10% of epoxidation to give **19**, which in turn undergoes ring cleavage with methanol to give **18**. The appearance of **17** as the sole methoxy hydroperoxide indicates, furthermore, that double-bond cleavage occurs selectively in one direction only, viz. by formation of **8** and **9**.


16

$CH_3OCH_2OOH$

17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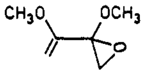
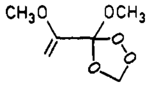

19

Ozonolysis of diene **16** on polyethylene gave 52% of **10**, 17% of **11**, and 31% of **12**. Ozonolysis of **16** in pentane with 2 molar equiv. of ozone gave the same products, albeit in different proportions of 17:23:60. This shows, that—in line with previous experience about the ozonolysis of other conjugated dienes[6]—ozonolysis of **16** on polyethylene gave no monoozonolysis products. The absence of diozonide **15c** in the product mixture is again indicative of the low dipolarophilicity of the ester group in ozonide **11**.

Ozonolysis of diene **16** with ca. 1 molar equiv of ozone in pentane provided **8** (34%), **10** (19%), **11** (1.5%), **20** (1.5%), and **21** (44%), as determined by $^1$H NMR analysis. This shows, that the double bonds in the diene **16** compete favorably with that in **8** and with the carbonyl groups in **8** and **10** for carbonyl oxide **9**. In this respect, the ozonolysis of **16** differs considerably from that of 2,3-dimethyl-1,3-butadiene, which gave predominantly the corresponding monoozonide[8] and diozonide[6] upon treatment with ozone in a molar ratio of 1:1 and 1:2, respectively.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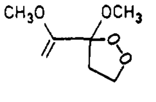
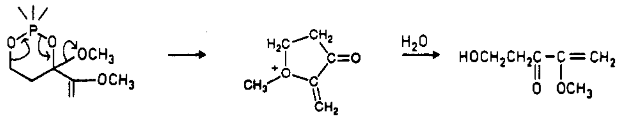

21

Compounds **20** and **21** have been isolated in yields of ca. 1 and 19%, respectively. In $CDCl_3$ solution at room temperature, **20** began to decompose after 20 h, and **21** after 1 day. Reduction with triphenylphosphine gave **8** and formaldehyde from **20**, whereas **21** gave **24** as the sole product. The latter result can be explained by the reaction sequence **21** → **22** → **23** → **24**, starting by insertion of triphenylphosphine into the peroxide bond of **21**. Such an insertion has been postulated previously for the reduction of ozonides with triphenylphosphine,[9] and it has been rendered likely as the cause for an unusual reduction reaction of cyano-substituted ozonides recently.[10]



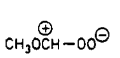
22 23 24

1,2-Dimethoxyethene (**25**) is a special representative of 2-substituted vinyl ethers, since its ozonolysis should provide the methoxy-substituted carbonyl oxide **26**. This has indeed been verified by Kuczkowski and co-workers, who obtained the dimer of **26**, viz. **27**, in the ozonolysis of **25**.[5] The parent ozonide **28**, however, could not be detected, even if the ozonolysis of **25** was carried out in the presence of added methyl formate.[5] By contrast, ozonolysis of **25** on polyethylene in the present investigation gave **28** in 51% selectivity, along with 28% of **27** and of unidentified components. From the product mixture, 8% of *cis*-**28**, 13% of *trans*-**28**, and 8% of *trans*-**27** have been isolated. Ozonides **28** have been assigned on the basis of their $^1$H and $^{13}$C NMR data and by reduction with triphenylphosphine to give methyl formate. The stereochemical assignment is based on the assumption, that—by analogy with other examples[11]—the CH signal in the $^1$H NMR spectrum of the trans isomer appeared at a lower field position ($\delta$ 6.16) than that of the cis isomer ($\delta$ 6.01). Compound *trans*-**27** has been assigned based on the identity of its $^1$H NMR data with those published.[5] Ozonides **28** are rather labile; in $CDCl_3$ they decomposed within 3 days at −30 °C.

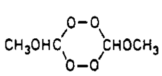
Further evidence for the formation of carbonyl oxide **26** has been provided by Kuczkowski and co-workers[5] by ozonolysis of **25** in the presence of added acetone, which gave ca. 10% of cross ozonide **29**. This result indicates that acetone, despite the notoriously low dipolarophilicity of ketones, is more reactive than methyl formate toward carbonyl oxide **26**. In the present investigation we have tried to generate **29** in a reverse manner, viz. by ozonolysis of the parent substrate **30** and cycloaddition of the expected carbonyl oxide **31** to methyl formate. Indeed, ozonolysis of **30** on polyethylene did afford **29**, but only in a selectivity of ca. 6%, whereas the major peroxidic product with 31% selectivity was ozonide **32**. Additional peroxidic products were **33a** (ca. 1%) and **33b** (17%).

$CH_3OCH{=}CHOCH_3$

25


$CH_3O\overset{\oplus}{C}H{-}OO^{\ominus}$

26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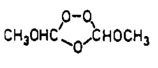
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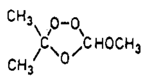
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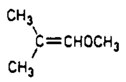
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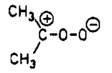
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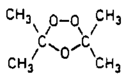
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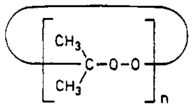
33

a: n=2 b: n=3

To our knowledge, there is no report about the preparation of ozonides by the ozonolyis of acyclic trisubstituted vinyl ethers. Recently, we have succeeded, however, in

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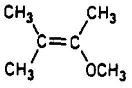
(8) Griesbaum, K.; Keul, H.; Agarwal, S.; Zwick, G. *Chem. Ber.* **1983**, *116*, 409.

(9) Charles, J.; Fliszár, S. *Can. J. Chem.* **1970**, *48*, 1309.

(10) Griesbaum, K.; Huh, T.-S.; Gutsche, S.-H. *Tetrahedron Lett.* **1990**, *31*, 3299.

(11) Kolsaker, P. *Acta Chem. Scand.* **1965**, *19*, 223.

preparing representatives of this class of ozonides in a roundabout way, viz. by substitution of the acetoxy group of **35b** by alkoxy groups, e.g. by the methoxy group to give **35a**.[12] Since **35a** turned out to be a stable compound, we have now tried to generate it from the parent substrate **34**. However, ozonolysis of **34** in pentane or on polyethylene gave no detectable amounts of ozonide **35a**, but only acetone, methyl acetate, peroxide **33b**, and additionally ozonide **32** on polyethylene. This, in conjunction with the results obtained above, confirms the previous experience, that methyl acetate is a weaker dipolarophile than methyl formate.



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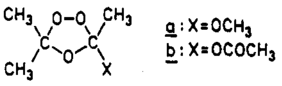

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## Experimental Section

**General Methods.** Ozonolyses on polyethylene have been carried out by a procedure which has been published in detail.[12] Loading of polyethylene with substrates was performed according to the method for volatile liquids for **5**, **25**, and **30**, and according to the method for nonvolatile compounds for **8**, **16** and **34**, using diethyl ether as solvent. Unless mentioned otherwise, ozone treatment was carried out at –75 °C, using a $O_3/O_2$ gas stream of 20 L/h containing 1.1 mmol of $O_3$/L, and the products were extracted from polyethylene with diethyl ether and concentrated in a rotary evaporator at room temperature and 15–20 Torr. The residues were separated by flash chromatography[13] on silica gel, using water-cooled glass columns.

**Ozonolysis of 5 on Polyethylene.** When 0.6 g (6.0 mmol) of **5**[14] on 45 g of polyethylene was ozonized for 3 h, one obtained 0.66 g of a liquid residue. Separation (42 g of silica gel; pentane/diethyl ether, 50:1) afforded 160 mg (18%) of **6** and 200 mg (24%) of **7**.

**3-Isopropyl-3-methoxy-1,2,4-trioxolane (6):** colorless liquid; $^1$H NMR ($CDCl_3$, TMS, –20 °C) $\delta$ 1.03 (d, $J$ = 6.8 Hz, 6 H), 2.16 (sept, $J$ = 6.9 Hz, 1 H), 3.41 (s, 3 H), 5.02 (d, $J$ = 0.9 Hz, 1 H), 5.44 (d, $J$ = 0.9 Hz, 1 H); $^{13}$C NMR ($CDCl_3$, TMS, –20 °C) $\delta$ 17.13, 34.40, 50.06, 95.07, 122.18.

**3-Isopropyl-3-methoxy-1,2-dioxolane (7):** colorless liquid; $^1$H NMR ($CDCl_3$, TMS, –20 °C) $\delta$ 0.98 (d, $J$ = 6.8 Hz, 3 H), 1.01 (d, $J$ = 6.9 Hz, 3 H), 2.26 (sept, $J$ = 6.8 Hz, 1 H), 3.30 (s, 3 H), ABXY system with $\delta_A$ 2.34, $\delta_B$ 2.54, $\delta_X$ 4.03, and $\delta_Y$ 4.28, $J_{AB}$ = 12.54, $J_{AX}$ = 7.79, $J_{AY}$ = 6.13, $J_{BX}$ = 7.97, $J_{BY}$ 4.37, $J_{XY}$ = 7.71 Hz; $^{13}$C NMR ($CDCl_3$, TMS, –20 °C) $\delta$ 18.29, 29.13, 41.09, 48.79, 69.92, 111.06.

**Reduction of 6.** A mixture containing one drop of **6** and triphenylphosphine in 1 mL of $CDCl_3$ was kept at room temperature for 2 h. $^1$H NMR analysis showed the presence of methyl isobutyrate ($\delta$ 1.17, d, $J$ = 7.05 Hz; 2.56, sept; 3.67, s) and of formaldehyde ($\delta$ 9.74) in molar ratio of 1:0.8.

**Ozonolysis of 8 on Polyethylene.** When 0.77 g (6.6 mmol) of **8**[15] on 45 g of polyethylene was ozonized for 3 h, one obtained 788 mg of a liquid residue. $^1$H NMR analysis showed the presence of **11** and **12** in relative proportions of 9:1, along with **8** and **10**. Separation of the residue (80 g of silica gel; pentane/diethyl ether, 2.3:1) gave 32 mg of a mixture of **8**, **10**, and **11** (fraction 1), 410 mg of a mixture of **10** and **11** (fraction 2), 70 mg of a mixture of **10** and **12** (fraction 3), and 180 mg of **10** ($\delta$ 3.91, s). From the combined fractions 1 and 2 one obtained 392 mg (36%) of **11**, and from fraction 3 one obtained 43 mg (4%) of **12** by distillation at room temperature and $10^{-2}$ Torr and collection of product at 0 °C.

**3-(Carboxymethyl)-3-methoxy-1,2,4-trioxolane (11):** colorless liquid; $^1$H NMR ($CDCl_3$, TMS, –20 °C) $\delta$ 3.56 (s, 3 H), 3.88 (s, 3 H), 5.30 (d, $J$ = 1.47 Hz, 1 H), 5.59 (d, $J$ = 1.46 Hz, 1 H); $^{13}$C NMR ($CDCl_3$, TMS, –20 °C) $\delta$ 50.80 (q, $J$ = 146.24 Hz), 53.56 (q, $J$ = 148.56 Hz), 96.18 (dd, $J$ = 167.45 and 175.43 Hz), 113.49 (s), 163.46 (s).

**Reduction of 11.** A solution of 39 mg of **11** in 2 mL of $CDCl_3$ was admixed with 47 mg of triphenylphosphine. $^1$H NMR analysis after 1 h showed the presence of **10** ($\delta$ 3.91) and of formaldehyde ($\delta$ 9.74) in a ratio of ca. 1:0.8.

**3-(Carboxymethyl)-3-methoxy-1,2-dioxolane (12):** colorless liquid; $^1$H NMR ($CDCl_3$, TMS) $\delta$ 3.42 (s, 3 H), 3.85 (s, 3 H), ABXY system with $\delta_A$ 2.86, $\delta_B$ 2.93, $\delta_X$ 4.15, $\delta_Y$ 4.21, $J_{AB}$ = 12.50, $J_{AX}$ = 7.55, $J_{AY}$ = 7.48, $J_{BX}$ = 7.57, $J_{BY}$ = 4.30, $J_{XY}$ = 7.61 Hz; $^{13}$C NMR ($CDCl_3$, TMS, –20 °C) $\delta$ 47.07 (t, $J$ = 135.67 Hz), 53.08 (q, $J$ = 148.24 Hz), 54.32 (q, $J$ = 144.08 Hz), 69.93 (ddt, $J$ = 151.38, 148.61, 2.76 Hz), 105.35 (s), 166.88 (s).

**Ozonolysis of 16 in Methanol.** A solution of 500 mg (4.39 mmol) of **16**[16] in 35 mL of methanol was treated with 0.9 molar equiv of ozone at –30 °C. The product was concentrated in vacuo at room temperature to leave 550 mg of a residue. $^1$H NMR analysis showed the presence of **8** (24%; $\delta$ 3.67), **10** (13%; $\delta$ 3.91), **17** (53%; $\delta$ 3.50), and **18** (10%; $\delta$ 3.25). Separation of the residue (80 g of silica gel; pentane/diethyl ether, 4:1) gave 86 mg (17%) of **8**, 147 mg (43%) of **17** ($\delta$ 3.50, s, 3 H; 4.98, s, 2 H; 9.19, s, 1 H),[17] 49 mg (7%) of **18**, and 40 mg of a mixture consisting of **8**, **10**, and **17**.

**2,3,3-Trimethoxy-4-hydroxy-1-butene (18):** colorless liquid; $^1$H NMR ($CDCl_3$, TMS) $\delta$ 3.25 (s, 6 H), 3.62 (s, 3 H), 3.69 (d, $J$ = 5.69 Hz, 2 H), 4.36 (d, $J$ = 2.16 Hz, 1 H), 4.67 (d, $J$ = 2.20 Hz, 1 H); $^{13}$C NMR ($CDCl_3$, TMS) $\delta$ 49.05 (q, $J$ = 142.91 Hz), 55.20 (q, $J$ = 144.13 Hz), 61.31 (t, $J$ = 146.07 Hz), 86.57 (dd, $J$ = 156.42 and 164.93 Hz), 100.72 (s), 158.09 (s); El-MS $m/z$ (relative intensity) 131 (100) $(M - OCH_3)^+$.

**Ozonolysis of 16 on Polyethylene.** When 0.735 g (6.45 mmol) of **16** on 56 g of polyethylene was ozonized for 6 h at –30 °C, one obtained 0.87 g of a liquid residue. $^1$H NMR analysis showed the presence of **10** (52%), **11** (17%), and **12** (31%). Separation of the residue (80 g of silica gel; pentane/diethyl ether, 2.3:1) gave 365 mg (48%) of **10**, 117 mg of a mixture consisting of **10** and **11**, and 173 mg of a mixture consisting of **10** and **12**. From these mixtures, 51 mg (5%) of **11** and 136 mg (13%) of **12** were isolated by distillation of the respective mixture at room temperature and $10^{-2}$ Torr and collection at 0 °C. Compounds **10**, **11**, and **12** have been identified on the basis of their $^1$H and $^{13}$C NMR spectra.

**Ozonolysis of 16 in Pentane with 2 Molar Equiv of Ozone.** A solution of 1.57 g (13.77 mmol) of **16** in 70 mL of pentane was treated with 2 molar equiv of ozone at –30 °C to give 600 mg of an unidentified colorless solid. The supernatant solution was removed and concentrated in vacuo at room temperature to leave 1.21 g of a liquid residue. $^1$H NMR analysis showed the presence of **10**, **11**, and **12** in a molar ratio of 17:23:60. Separation of the residue (100 g of silica gel; pentane/diethyl ether, 2.3:1) gave 315 mg (20%) of **10**, 280 mg of a mixture consisting of **10** and **11**, and 375 mg of a mixture consisting of **10** and **12**. From these mixtures, 260 mg (12%) of **11** and 307 mg (14%) of **12** were isolated by distillation in vacuo and $10^{-2}$ Torr and collection at 0 °C. Compounds **10**, **11**, and **12** have been identified by their $^1$H and $^{13}$C NMR spectra.

**Ozonolysis of 16 in Pentane with 1 Molar Equiv of Ozone.** A solution of 2.04 g (17.89 mmol) of **16** in 90 mL of pentane was treated with 1 molar equiv of ozone at –30 °C. The product was concentrated in vacuo at room temperature to leave 1.94 g of a liquid residue. $^1$H NMR analysis showed the presence of **8** (34%), **10** (19%), **11** (1.5%), **20** (1.5%), and **21** (44%). Separation of the residue (150 g of silica gel; pentane/diethyl ether, 2.3:1) gave 11 mg (0.4%) of **20** and 544 mg (19%) of **21**, along with unreacted **16** and mixtures of **8** and **21** as well as **10** and **12**.

**3-Methoxy-3-(1-methoxyethenyl)-1,2,4-trioxolane (20):** colorless liquid; $^1$H NMR ($CDCl_3$, TMS) $\delta$ 3.53 (s, 3 H), 3.67 (s, 3 H), 4.33 (d, $J$ = 2.94 Hz, 1 H), 4.80 (d, $J$ = 2.97 Hz, 1 H), 5.23 (d, $J$ = 1.28 Hz, 1 H), 5.54 (d, $J$ = 1.30 Hz, 1 H); $^{13}$C NMR ($CDCl_3$, TMS, –20 °C) $\delta$ 50.61, 55.81, 86.04, 95.84, 115.96, 154.82.

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**Reduction of 20.** A solution of 40 mg of **20** in 1 mL of CDCl$_3$ was admixed with 60 mg of triphenylphosphine. $^1$H NMR analysis after 1 h showed the presence of **8** ($\delta$ 3.67, s) and of formaldehyde ($\delta$ 9.75, s) in a molar ratio of 1.25:1.0.

**3-Methoxy-3-(1-methoxyethenyl)-1,2-dioxolane (21):** colorless liquid; $^1$H NMR (CDCl$_3$, TMS) $\delta$ 3.27 (s, 3 H), 3.64 (s, 3 H), 4.24 (d, $J = 2.77$ Hz, 1 H), 4.51 (d, $J = 2.79$ Hz, 1 H), ABXY system with $\delta_A$ 2.78, $\delta_B$ 2.79, $\delta_X$ 4.15, $\delta_\gamma$ 4.31 and $J_{AB} = 6.97$, $J_{AX} = 7.07$, $J_{AY} = 6.79$, $J_{BX} = 7.47$, $J_{BY} = 7.19$, $J_{XY} = 6.51$ Hz; $^{13}$C NMR (CDCl$_3$, TMS, −20 °C) $\delta$ 46.71 (t, $J = 153.60$ Hz), 50.43 (q, $J = 143.11$ Hz), 55.10 (q, $J = 144.21$ Hz), 69.80 (ddt, $J = 150.37$, 147.67, and 2.54 Hz), 84.38 (dd, $J = 164.72$ and 157.55 Hz), 106.06 (s), 156.32 (s).

**Reduction of 21.** When a solution of 260 mg of **21** in 10 mL of CDCl$_3$ was admixed with a solution of 432 mg of triphenylphosphine in 30 mL of CDCl$_3$, a vigorous reaction occurred, as evidenced by heating of the sample. $^1$H NMR analysis after 1 day showed that **21** had completely disappeared and that methanol and **24** had been formed. The mixture was concentrated in vacuo at room temperature, and the residue was separated (15 g of silica gel; pentane/diethyl ether, 2.3:1) to give 118 mg (56%) of **24**.

**2-Methoxy-3-oxo-5-hydroxy-1-pentene (24):** colorless liquid; $^1$H NMR (CDCl$_3$, TMS) $\delta$ 2.94 (t, $J = 5.48$ Hz, 2 H), 3.66 (s, 3 H), 3.90 (t, $J = 5.45$ Hz, 2 H), 4.53 (d, $J = 2.83$ Hz, 1 H), 5.25 (d, $J = 2.83$ Hz, 1 H); $^{13}$C NMR (CDCl$_3$, TMS) $\delta$ 40.26 (t, $J = 126.52$ Hz), 56.43 (q, $J = 144.68$ Hz), 57.75 (tt, $J = 144.16$ and 3.78 Hz), 91.29 (dd, $J = 164.21$ and 160.02 Hz), 158.32 (s), 197.78 (s); IR (film) 3400 (broad; OH), 1720 (C═O) cm$^{-1}$; EI-MS $m/z$ (%) 130 (8) $[M]^+$, 86 (87) $[M - CH_3CH{=}O]^+$, 73 (43) $[COCH_2CH_2OH]^+$, 57 (100) $[CH_2{=}COCH_3]^+$, 44 (3) $[CH_3CH{=}O]^+$, 43 (85) $[CH_3CO]^+$.

**Ozonolysis of 25 on Polyethylene.** When 451 mg (5.13 mmol) of **25** on 40 g of polyethylene was ozonized for 3 h, one obtained 378 mg of a liquid residue. $^1$H NMR analysis showed the presence of *cis*-**27** (13%; $\delta$ 5.93, s),[5] *trans*-**27** (15%; $\delta$ 6.08, s),[5] *cis*-**28** (20%), and *trans*-**28** (31%). Separation of the residue (20 g of silica gel; pentane/diethyl ether, 17:1) gave 85 mg (8%) of *trans*-**27** ($^1$H NMR $\delta$ 3.65, s, and 6.08, s; mp 64–65 °C; lit.[5] mp 66 °C), 79 mg (8%) of *cis*-**28**, and 128 mg (13%) of trans-**28**.

***cis*-3,5-Dimethoxy-1,2,4-trioxolane (*cis*-28):** colorless liquid; $^1$H NMR (CDCl$_3$, TMS) $\delta$ 3.52 (s, 6 H), 6.01 (s, 2 H); $^{13}$C NMR (CDCl$_3$, TMS, −20 °C) $\delta$ 52.01 (qd, $J = 143.17$ and 2.64 Hz), 114.73 (ddq, $J = 203.89$, 5.03, and 3.15 Hz).

***trans*-3,5-Dimethoxy-1,2,4-trioxolane (*trans*-28):** colorless solid; mp 39–41 °C; $^1$H NMR (CDCl$_3$, TMS) $\delta$ 3.41 (s, 6 H), 6.16 (s, 2 H); $^1$H NMR (CDCl$_3$, TMS, −20 °C) $\delta$ 51.79 (qd, $J = 143.17$ and 2.64 Hz), 112.76 (ddq, $J = 198.86$, 5.03, and 3.78 Hz).

**Reduction of 28.** A solution of *cis*- and *trans*-**28** in CDCl$_3$ was admixed with a solution of triphenylphosphine in CDCl$_3$ and kept at room temperature for 2 days. $^1$H NMR analysis showed the signals of methyl formate at $\delta$ 3.77 (d, $J = 0.8$ Hz) and $\delta$ 8.06 (q, $J = 0.8$ Hz).

**Ozonolysis of 30 on Polyethylene.** Compound **30** (972 mg, 11.3 mmol) (prepared by elimination of methanol from 1,1-dimethoxy-2-methylpropane;[18] $\delta$ 1.54, 1.60, 3.53, 5.74) on 80 g of polyethylene was ozonized for 4 h. Then, the mixture was evacuated at room temperature and $10^{-2}$ Torr, and the products were collected in two consecutive cold traps kept at −30 °C (trap 1) and at −78 °C (trap 2), respectively. $^1$H NMR analysis showed that the product of trap 1 (130 mg of colorless liquid) contained 53% of **29** ($\delta$ 1.65, s), 11% of **33a** ($\delta$ 1.35, s and 1.80, s), and 4% of **33b** ($\delta$ 1.46, s), along with methyl formate and acetone; the product of trap 2 (737 mg, colorless liquid) contained 20% of **32** ($\delta$ 1.47, s),[6] along with methyl formate, acetone, and unreacted **30**. Separation of the product from trap 1 (15 g of silica gel; pentane/diethyl ether, 30:1) gave 14 mg (ca. 1%) of **29** and 10 mg (0.6%) of **33a**.

**3-Methoxy-5,5-dimethyl-1,2,4-trioxolane (29):** colorless liquid; $^1$H NMR (CDCl$_3$, TMS) $\delta$ 1.49 (s, 3 H), 1.65 (s, 3 H), 3.45 (s, 3 H), 5.97 (s, 1 H); $^{13}$C NMR (CDCl$_3$, TMS, −20 °C) $\delta$ 21.7, 24.4, 52.1, 109.9, 112.8. The data are consistent with those reported.[5]

**Ozonolysis of 34 on Polyethylene.** Compound **34** (870 mg, 8.4 mmol) on 73 g of polyethylene was ozonized for 7 h. Then, the mixture was evacuated at room temperature and $10^{-2}$ Torr, and the products were collected in two consecutive cold traps kept at −40 °C (trap 1) and at −75 °C (trap 2), respectively. $^1$H NMR analysis showed that the product of trap 1 (230 mg, colorless liquid) contained 58% of **32** ($\delta$ 1.47, s),[6] along with acetone and methyl acetate, and the product of trap 2 (413 mg, colorless liquid) contained acetone and methyl acetate. Separation of the product from trap 1 by PGC (glass column, 0.7 × 540 cm, 5% methylsilicone OV 101 on Chromosorb G; 80 °C) gave 103 mg (9%) of ozonide **32**. It was identified on the basis of the identity of its $^1$H and $^{13}$C NMR and its MS data with those reported.[6]

After evacuation was completed, the residual polyethylene was extracted with ether, the extract was concentrated, and from the residue 15 mg (0.8%) of **33b** was isolated by column chromatography (60 g of silica gel; pentane/diethyl ether, 10:1).

**Ozonolysis of 34 in Pentane.** A solution of 430 mg (4.2 mmol) of **34** in 30 mL of pentane was ozonized to completion at −75 °C. $^1$H NMR analysis of the concentrated crude product showed the presence of acetone (18%), methyl acetate (60%), and **33b** (22%), to the exclusion of the expected ozonide **35a**.

**Supplementary Material Available:** 250-MHz $^1$H NMR spectra of compounds **6**, **7**, **11**, **12**, **18**, **20**, **21**, **24**, *cis*-**28**, *trans*-**28**, and **29** (11 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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# Ambident Behavior of Ketone Enolate Anions in S$_N$Ar Substitutions on Fluorobenzonitrile Substrates

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2,6-Difluorobenzonitrile was found to be a suitable substrate for studying carbon versus oxygen nucleophilic attack by enolate anions of weakly acidic ketones. The influence of the nucleophile structure and the solvent are investigated. The charge control character of the reaction and the influence of the substrate are discussed.

In the course of studies in the field of aromatic nucleophilic substitution reactions with ketone enolate anions,[1] we had occasion to carry out an S$_N$Ar reaction[2] between 2,6-difluorobenzonitrile (**1a**) and the anion derived

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