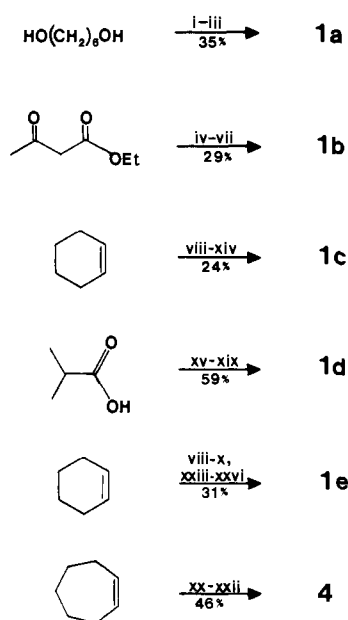


Scheme II



Structure proofs for all adducts were based upon 300-MHz ^1H and ^{13}C NMR analysis and chemical transformations. Each compound gave characteristic fulvene and cyclopentane resonances. When bridgehead hydrogens were present, surprisingly low cis couplings were observed; in **3a** and **3d**, $J_{1,3} = 5.3$ and 5.1 Hz, respectively. These small cis couplings are likely the result of strain and consequent distortions of the central ring, as shown by the more normal couplings found in less strained intermediates.¹¹ The reactions of **3a** or **3d** with 1-(diethylamino)butadiene in benzene proceeded by [6 + 4] cycloadditions to form the tetracyclic dihydroazulenes **7a** and **7d**, in 31% and 66% yield, respectively. The bridgehead couplings, J_{ab} , are 7.9 and 8.2 Hz in these adducts, closer to expectation for cis couplings in such systems.¹¹ The J_{bc} couplings of 5.2 and 6.0 Hz in **7a** and **7d** suggest the trans stereochemistry of these hydrogens, consistent with approach of the dienamine to the less hindered face of **3a** or **3b** in the [6 + 4] cycloadditions. Conversions of **7a** and **7d** to the brilliant blue tetracyclic azulenes **8a** (14%, $J_{ab} = 6.2$ Hz) and **8d** (20%, $J_{ab} = 5.9$ Hz) was effected by refluxing **7a** and **7b** in triglyme in the presence of sulfur. Small cis couplings are observed again in these strained compounds.

Catalytic hydrogenation (5% Pd-C, hexane) of **3a** gave two adducts, **9a** and **10a**, the parent linearly fused tricyclopentanoids, in a 60:40 ratio. These were separated by GLC (SE-30 column). The ^{13}C NMR spectra¹² of each compound gave only six resonances, consistent with C_s or C_2 symmetry. Only the spectra predicted¹³ for the cis-syn-cis and cis-anti-cis structures are consistent with the observed spectra of **9a** and **10a**, respectively. The alternative C_s and C_2 all-trans compounds would be highly strained and give different ^{13}C spectra. Hydrogenation of **6e** gave two adducts, **9b** and **10b** in a 56:44 ratio. ^{13}C spectra excluded the structure which is the epimer of **10b** at C-4, since this epimer

(11) A coupling constant of 12 Hz has been reported for the bridgehead hydrogens in a cis-fused tricyclopentanoid precursor to coriolin: Trost, B. M.; Curran, D. P. *J. Am. Chem. Soc.* **1981**, *103*, 7380.

(12) ^{13}C NMR (CDCl_3). **9a**: 27.3 (t, C-3,8 or 4,7), 28.4 (t, C-3,8 or 4,7), 31.6 (t, C-2,9), 40.3 (dd, C-11), 47.2 (d, C-1,10), 47.4 (d, C-5,6). **10a**: 26.1 (t, C-3,8), 32.9 (t, C-4,7), 34.0 (t, C-2,9), 40.2 (t, C-11), 44.9 (d, C-1,10), 52.4 (d, C-5,6). **9b**: 20.9 (q, Me), 27.8 (t, C-7), 28.1 (t, C-8), 31.3 (t, C-2,9), 36.0 (d, C-4), 37.6 (t, C-3), 41.0 (dd, C-11), 46.5 (d, C-6), 48.3 (d, C-1,10), 55.3 (d, C-5). **10b**: 19.8 (q, Me), 26.4 (t, C-8), 31.8 (t, C-7), 33.1 (t, C-2), 34.4 (t, C-9), 35.8 (t, C-3), 41.0 (t, C-11), 41.7 (d, C-4), 44.4 (d, C-1), 44.8 (d, C-10), 50.4 (d, C-6); 61.2 (d, C-5). MM2 calculations indicate that **9a** and **10a** have essentially identical heats of formation. **Note Added in Proof**: Syntheses of **9a** and **10a** by alternative routes were recently reported: Kakuchi, K.; Takeuchi, H.; Tobe, Y.; Odaira, Y. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 1613. ^{13}C spectra reported there are the same, to within ± 0.1 ppm, as those reported here.

(13) Whitesell, J. K.; Matthews, R. S. *J. Org. Chem.* **1977**, *42*, 3878.

has been prepared by a different route in Professor Curran's laboratories.^{3b} The spectra¹² confirm the structures shown and establish the stereochemistry of **6e**.

The cis and trans tricyclic compounds **5** were obtained as an inseparable mixture. The chemical shifts of the vinyl protons of the major isomer are essentially identical with those observed for the cis adduct **3**, leading to the tentative conclusion that the major isomer of **5** has the cis stereochemistry.

Synthetic routes to the 6-(ω -formylalkyl)fulvenes, **1a-e** and **4**, involved the sequences listed in Scheme II. Each of these compounds was prepared in excellent overall yields using the commercial reagents given in ref 14.¹⁴⁻²¹ Thus, the substituted linearly fused tricyclopentanoid skeleton can be easily assembled in 4-8 steps from readily available starting materials in 7-39% overall yield by this reaction sequence.

Acknowledgment. We are grateful to the National Institutes of Health for financial support of this research and to Professor Dennis P. Curran for helpful advice.

(14) Reagents and yields. **1a**: (i) PCC, Celite, CH_2Cl_2 , 62%; (ii) C_3H_6 , 35% aqueous CH_3NH_2 , THF,¹⁵ 69%; (iii) PCC, Celite, CH_2Cl_2 , 82%. **1b**: (iv) NaOEt/EtOH ; 4-bromobutyraldehyde ethylene acetal¹⁶, reflux,¹⁷ 76%; (v) decarboxylation, 8% KOH, 1:1 THF/ H_2O , 81%; (vi) C_3H_6 , KOH, $\text{CH}_3\text{OH-THF}$,¹⁸ 52%; (vii) 0.5% HCl, 2:1 THF/ H_2O , 91%. **1c**: (viii) O_3 , $\text{EtOH-CH}_2\text{Cl}_2$ (1:5); $(\text{CH}_3\text{CO})_2\text{O}$, Et_3N ,¹⁹ 70%; (ix) $\text{HOCH}_2\text{CH}_2\text{OH}$, *p*-TsOH, PhH reflux, 95%; (x) LDA, THF, MeI, HMPA, 97%; (xi) DIBAL, toluene, 0 °C,²⁰ 67%; (xii) 1% HCl, 2:1 THF/ H_2O , 99%; (xiii) C_3H_6 , 35% aqueous CH_3NH_2 , THF¹⁵ 68%; (xiv) PCC, CH_2Cl_2 , Celite, 81%. **1d**: (xv) 2 equiv of LDA, THF; 4-bromobutyraldehyde ethylene acetal,¹⁶ HMPA,²¹ 86%; (xvi) LAH, ether, 95%; (xvii) PCC, CH_2Cl_2 , Celite, 90%; (xviii) C_3H_6 , *n*-BuLi, THF, 0 °C, 82%; (xix) 0.2% HCl, 2:1 THF/ H_2O , 99%. **4**: (xx) O_3 , $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$ (5:1); *p*-TsOH; NaHCO_3 ; $(\text{CH}_3)_2\text{S}$, 74%; (xxi) $\text{C}_3\text{H}_5\text{Li}^+$, THF, 0 °C, 64%; (xxii) 0.1 N HCl, 2:1 THF/ H_2O , 99%. **1e**: (xxiii) DIBAL, CH_2Cl_2 , 0 °C, 1h, 89%; (xxiv) PCC, NaOAc, Celite, CH_2Cl_2 , 82%; (xxv) C_3H_6 , BuLi, THF, 0 °C, 71%; (xxvi) 0.06 N HCl, 9:6:1 THF/ H_2O /acetone 89%.

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Ozonolysis of Olefins Adsorbed on Polyethylene: A New Access to Ozonides by Cycloadditions of Carbonyl Oxides to Ketones

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It is well recognized that in the absence of specific electronic, steric, or concentration effects, ketones are too unreactive to undergo intermolecular cycloadditions with carbonyl oxides to form ozonides.¹ As a consequence, ozonolyses of acyclic tetrasubstituted ethylenes in nonparticipating solvents usually do not lead to the corresponding ozonides. A case in point is tetramethylethylene (**1**). It has been reported that upon ozonolysis of **1** in chloroethane² or in pentane³ as solvent, ozonide **4** could not be obtained, i.e., the primary fragments **2** and **3** of the ozone cleavage reaction did not recombine. Recently, it has been shown that cycloadditions of carbonyl oxides with aldehydes, and hence ozonide formation,

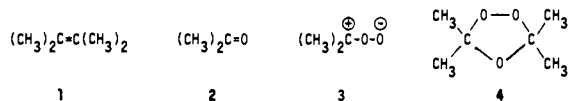
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(3) Story, P.; Burgess, J. *J. Am. Chem. Soc.* **1967**, *89*, 5726.

can be substantially facilitated by the ozonolysis of olefins on silica gel, presumably due to restricted migration of the adsorbed primary cleavage fragments.⁴ However, application of this method to **1** also failed to produce ozonide **4**,⁵ which, thus, has been unknown to now.

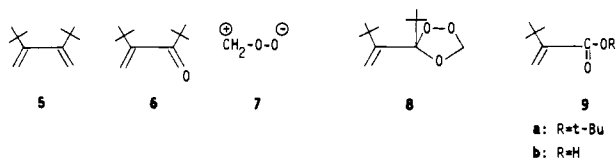
In the present investigation we have performed the ozonolysis of **1** adsorbed on powdered polyethylene (Microthene FN 500,



spherical particles, maximum size 20 μm ; supplier, Serva Feinbiochemica, Heidelberg, FRG). The adsorption of **1** (2.11 g on 60.0 g of polyethylene) was carried out at ambient temperatures and the ozone treatment at -78°C for 4 h with 80 L of a gas stream containing 1.1 mmol of ozone per liter. The products were extracted with diethyl ether at ambient temperatures and the combined extracts were distilled at 15 torr and ambient temperatures. From the distillate, ether was largely removed by a second distillation step at normal pressure, using a 20-cm Vigreux column. The liquid distillation residue contained the ozonide **4** as the single major component, along with residual ether, unreacted **1**, and minor amounts of unidentified products. Separation of the residue by preparative gas chromatography (glass column 0.7 \times 300 cm, 5% OV 101 on Chromosorb G; 80°C) afforded the pure,⁶ colorless liquid ozonide **4**: $^1\text{H NMR}$ (CDCl_3) δ 1.46 (s); $^{13}\text{C NMR}$ (CDCl_3) δ 24.60 (q, $J = 127.6$ Hz), 108.65 (s); IR no absorption in the carbonyl region; CI-MS, m/e (%) 133 (6) ($M + 1$)⁺, 117 (5), 75 (100); yield 130.0 mg (3.9%).

Ozonide **4** is unusually stable. Heating of **4** in CDCl_3 at 80°C did not lead to a change in the $^1\text{H NMR}$ spectrum within 36 h. At ambient temperatures reduction of **4** occurred only slowly with sodium iodide in acetic acid and not at all within 3 days with dimethyl sulfide or with triphenylphosphine. At 80°C **4** was slowly reduced by triphenylphosphine to give acetone (**2**).

Trisubstituted and 1,1-disubstituted ethylenes are usually cleaved such that disubstituted carbonyl oxides and aldehydes are formed as primary fragments and hence ozonide formation is possible in most cases. Recently we have found, however, that diene **5** is cleaved in the opposite direction, providing **6** and **7** as



the primary fragments.⁷ In line with this, ozonolysis of **5** in pentane did not give the monoozonide **8**. Therefore, we have tried the ozonolysis of **5** on polyethylene under conditions similar to those described above for the ozonolysis of **1** (1.12 g of **5** on 44.2 g of polyethylene, ozone treatment at -78°C for 2 h with 40 L of a gas stream containing 1.2 mmol of ozone per liter). The products were extracted from polyethylene with pentane and the pentane was distilled off. Column chromatographic separation of the residue on silica gel afforded among other products in ca. 30% yield the colorless, liquid ozonide **8**: $^1\text{H NMR}$ (CDCl_3) δ 1.05 (s, 9 H), 1.18 (s, 9 H), 5.00 (s, 1 H), 5.26 (s, 1 H), 5.28 (s, 1 H), 5.35 (s, 1 H); IR only a weak absorption in the carbonyl region due to partial decomposition; CI-MS, m/e (%) 215 (78) ($M + 1$)⁺, 185 (94), 168 (43) ($M - \text{CH}_2\text{O}_2$)⁺, 131 (100) ($M - \text{C}_6\text{H}_{11}$)⁺.

Ozonide **8** is thermally unstable. At ambient temperatures it was converted into a mixture of **9a,b**, formaldehyde, and isobutene. This conversion is catalyzed by silica gel, and hence the isolation

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(7) Volpp, W., unpublished results.

of **8** by column chromatography is affected. Reduction of **8** by triphenylphosphine afforded the expected ketone **6**.

The foregoing results show that the ozonolysis of olefins on polyethylene opens a new route to types of ozonides which are otherwise not accessible. It is noteworthy in this respect, that, as it had been reported for **1**,⁵ the ozonolysis of **5** adsorbed on silica gel did not afford ozonide **8** either.⁷ It appears, thus, that polyethylene has properties that are very conducive to ozonide formation. This view is confirmed by recent results of our continuing investigations, which are aimed at the preparation of hitherto not accessible classes of ozonides.

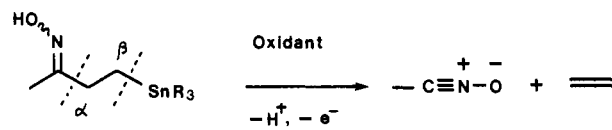
Oxidative Fragmentation of β -Stannyl Oximes: Stereospecific Formation of Unsaturated Nitrile Oxides

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New versions of fragmentation reactions have been recently devised and envisioned as versatile synthetic methodology with high stereochemical controllability,¹ utilizing organosilyl² or organostannyl³ functions. In connection with our recent work on silicon-directed Beckmann fragmentations,^{2ab} we became interested in oxidative reactions of β -silyl oximes. However, only known reactions at the oxime group were observed, such as formation of ketones and vicinal acetoxy-nitroso compounds.⁴ Since the oxidation of oximes is known to form stable iminoxyl radicals,⁵ we have chosen a β -stannyl group as a directing group to cause easily radical fission or transmetalation rather than a silyl group. We report here a new homolytic fragmentation of β -stannyl oximes by oxidation with lead tetraacetate (LTA). Selective formation of nitrile oxides and subsequent intramolecular cycloaddition are described. In addition, a direct cyclization between N-O and C-Sn from *Z* oximes has also been discovered.



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