with 12 M aqueous HCl, and extracted with CH_2Cl_2. The extract was washed with water, dried, and concentrated. The residue was recrystallized (CCl_4) to give 17 (167 mg). The mother liquor was concentrated. The concentrate was purified by prepartaive TLC (CH$_2$Cl$_)$ to give 17 (19 mg, total yield 71%) and 18 (36 mg, 15%). 18: mp 66.5–67 °C (pentane); IR 3052, 3020, 2974, 1680 (C=O), 1595 (C=C), 1482, 1460, 1398, 1371, 1361, 1325, 1286 (S=O), 1136 (S=O), 1089, 968, 940, 915, 792, 750, 543, 498, 444 cm^{-1}; ^{1}H NMR δ 1.24 (s, 9 H, *t*-Bu), 1.31 (s, 9 H, *t*-Bu), 2.92 (s, 3 H, SO_2Me), 6.24 (s, 1 H, vinyl H); ^{13}C NMR δ 28.0 (q, Me of *t*-Bu), 30.5 (q, Me of *t*-Bu), 37.2 (s, *C*Me$_3$), 43.8 (q, SO_2Me), 44.5 (s, *C*Me$_3$), 124.9 (d, sp^2 C carrying H), 167.5 (s, sp^2 C carrying *t*-Bu), 214.0 (s, C=O); MS (CI) *m/z* 247 (M$^+$ + 1). Anal. Calcd for $C_{12}H_{22}O_3S$: C, 58.50; H, 9.00. Found: C, 58.31; H, 8.85.

$NaHSO_3$-Induced Decomposition of 17. A two-phase mixture of a solution of 17 (66.2 mg, 0.25 mmol) in CH_2Cl_2 (10 mL) and a solution of $NaHSO_3$ (104 mg, 1 mmol) in H_2O (5 mL) was stirred at room temperature for 1.5 h. The two liquid layers were separated. The organic layer was washed with water, dried, and concentrated to give 19 (39.1 mg, 82%): mp 190–191 °C (CCl_4); IR 3064, 3020, 2970, 2876, 1716 (C=O), 1598 (C=C), 1463, 1361, 1304 (S=O), 1245, 1203, 1145 (S=O), 1118, 1097, 1041, 980, 876, 849, 578 cm^{-1}; ^{1}H NMR δ 1.28 (s, 9 H, *t*-Bu), 3.85 (s, 2 H, methylene), 7.35 (s, 1 H, vinyl H); ^{13}C NMR δ 28.2 (q, Me of *t*-Bu), 33.8 (s, *C*Me$_3$), 56.2 (t, methylene), 144.4 (d, sp^2 C carrying H), 157.8 (s, sp^2 C carrying t-Bu), 189.2 (s, C=O); high-resolution MS, calcd for $C_8H_{12}O_3$ 188.0507, found 188.0489.

Thermolysis of 17. Compound 17 (7.5 mg) was heated at 145–150 °C for 20 min in a small test tube. The mixture was purified by preparative TLC (CH_2Cl_2) to give 19 (5.4 mg, 100%).

Reduction of 17 with $NaBH_4$. To a stirred, ice-cooled solution of 17 (131 mg, 0.5 mmol) in MeOH (3 mL) was added $NaBH_4$ (38 mg, 1 mmol). The mixture was warmed to room temperature and was stirred for 4 h. The mixture was then cooled in ice water and was acidified by 12 M aqueous HCl (the pH of the mixture was adjusted to ca. 6–7). The mixture was extracted with Et_2O. The extract washed with water, dried, and concentrated. The residue was recrystallized (CCl_4) to give pure alcohol (114 mg, 93%): mp 161 °C; IR 3488 (OH), 3086, 2964, 1613 (C=C), 1585, 1461, 1396, 1375, 1281 (S=O), 1234, 1213, 1130 (S=O), 1081, 1011, 956, 822, 580 cm^{-1}; ^{1}H NMR δ 1.16 (s, *t*-Bu), 1.38 (s, *t*-Bu), 3.10 (s, 1 H, OH, disappears on addition of D_2O), 3.28 (d, 1 H, methylene, J = 14.3 Hz), 3.85 (d, 1 H, methylene, J = 14.3 Hz), 6.51 (d, 1 H, vinyl H); ^{13}C NMR δ 27.6 (q, Me of *t*-Bu), 32.8 (q, Me of *t*-Bu), 36.8 (s, *C*Me$_3$), 40.1 (s, *C*Me$_3$), 62.8 (t, methylene), 89.6 (s, sp^3 C carrying OH), 130.5 (d, sp^2 C carrying H), 167.5 (s, sp^2 C carrying *t*-Bu). Anal. Calcd for $C_{12}H_{22}O_3S$: C, 58.50; H, 9.00. Found: C, 58.42; H, 8.65.

NaOH-Induced Decomposition of 17. To a stirred solution of 17 (26.2 mg) in EtOH (1 mL) was added aqueous NaOH (0.1 mL of a 1 M solution). The mixture was heated at 58–60 °C for 30 h. The usual workup, followed by purification by preparative TLC (hexane/Et_2O, 1:1) afforded 18 (21.6 mg, 88%).

NaOH-Induced Decomposition of 20. To a stirred solution of 20 (12.3 mg) in EtOH (1.6 mL) was added aqueous NaOH (0.075 mL of a 1 M solution). The mixture was heated at 60 °C for 7 h. Workup in the manner described above gave 18 (12.3 mg, 100%).

Ozonides of Substituted Norbornenes with Exo- and Endo-Positioned Peroxide Bonds

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Ozonolyses of three methyl-substituted norbornenes **1a–c** on polyethylene gave in each case the corresponding ozonide **2** with an endo-positioned peroxide bridge. From **1b**, ozonide **3b** with an exo-positioned peroxide bridge was obtained, too. Thermally and photolytically induced decompositions of the ozonides are described.

Introduction

Ozonides of norbornenes (bicyclo[2.2.1]heptenes) have remained unknown for a long time. Thus, early work on the ozonolysis of norbornene itself in inert solvents resulted in the formation of intractable peroxidic materials,[2a] and it was only very recently that we have been able to prepare the ozonide of norbornene as the first example of its kind by application of the modified ozonolysis on polyethylene.[3] However, due to its instability, this ozonide could not be analyzed by X-ray diffraction and, hence, it remained uncertain whether it has the peroxide bridge in the endo or exo position. Since it is known that the ozonide of 1,2-dimethylcyclopentene is more stable than that of cyclopentene, we have now tried the ozonolysis of the methyl substituted norbornenes **1a–c** on polyethylene with the goal of preparing the corresponding ozonides and assigning them to structures **2** and/or **3**.

Results and Discussion

After treatment of **1a** with ca. 23 molar equiv of ozone on polyethylene at −75 °C, we isolated 16% of unreacted **1a**,[4] 7% of ozonide **2a**, and 12% of the diketone **4a**. The structure of the crystalline ozonide **2a** has been assigned based on a positive peroxide test, correct elemental analysis in conjunction with an [M + 1]$^+$ ion at *m/z* 171 in the CI mass spectrum, and the formation of **4a** as the sole product of reduction with triphenylphosphine. The stereochemical identity, i.e. the endo position of the peroxide group, has been demonstrated by X-ray diffraction, which showed additional salient features: the 1,2,4-trioxolane ring assumes an envelope conformation, in which—in contrast to monocyclic[3] or dispiroozonides[5]—the O atom of the ether

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[2] Bailey, P. S. In *Ozonation in Organic Chemistry*; Academic Press: New York, 1978; Vol. I, (a) p 114, (b) p 142ff.

[3] Griesbaum, K.; Volpp, W.; Greinert, R.; Greunig, H.-J.; Schmid, J.; Henke, H. *J. Org. Chem.* **1989**, *54*, 383.

[4] Incomplete olefin conversions even after using ozone in a large excess are usual in ozonolyses on polyethylene. We assume that it is caused by partial migration of the olefinic substrates into the polymer particles and limited diffusion of ozone into the polymer.

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Table I. ^{13}C and ^{1}H NMR Data[a] of 2a, 2b, 2c, and 3b

compd no.	R^1	R^2	^{13}C NMR (δ, ppm in C_6D_6/TMS) C$_6$	C$_1$	C$_2$	C$_5$	nonassigned C atoms
2a	H	H	107.54 s		45.44 d[1]		20.96 q,[2] 25.19 t,[3] 28.23 t[4]
2b	CH_3	H	107.26 s	110.23 s	49.21 s	46.09 d[5]	17.80 q,[6] 20.38 q,[6] 21.62 q,[7] 26.35 t,[8] 34.10 t,[9] 36.53 t[9]
3b	CH_3	H	111.24 s	113.63 s	47.61 s	46.08 d[10]	16.16 q,[11] 18.30 q,[11] 19.72 q,[12] 28.80 q,[8] 34.33 t,[13] 40.03 t[14]
2c[19]	CH_3	CH_3	108.03 s	111.07 s	53.09 s	42.07 d	16.05 q, 19.26 q, 22.00 q, 22.76 q, 23.61 t, 26.11 q, 33.18 t, 56.02 s

compd no.	R^1	R^2	^{1}H NMR (δ, ppm in C_6D_6/TMS) CH_3-C$_6$	CH_3-C$_1$	R^1	H-C$_5$	nonassigned H atoms
2a	H	H	1.32 s		1.16–1.21 m		0.49, 1 H, dt;[20] 1.39, 1 H, dm;[21] 2.02–2.11, 4 H, m
2b	CH_3	H	1.32 s	1.36 s	0.90 s	2.01–2.04 m	0.48, 1 H, dd;[22] 0.89–0.99, 1 H, m; 1.27–1.42, 2 H, m; 2.12–2.34, 2 H, m
3b	CH_3	H	1.19 s	1.20 s	0.79 s	2.85 dm[23]	0.92–1.04, 2 H, m; 1.29–1.46, 1 H, m; 1.62–1.82, 2 H, m; 1.85, 1 H, t[24]
2c[19]	CH_3	CH_3	0.65 s	0.75 s	1.14 s	2.15–2.26 m	1.05–1.14, 1 H, m; 1.34, 3 H, s; 1.35, 3 H, s; 1.35–1.49, 1 H, m; 1.65, 1 H, d;[25] 2.35–2.46, 1 H, m.

[a] Coupling constants *J* (Hz): [1]136.1, [2]126.6, [3]134.2, [4]135.5, [5]139.2, [6]129.2, [7]124.1, [8]137.3, [9]131.0, [10]142.4, [11]128.5, [12]126.0, [13]132.3, [14]136.7, [19]due to decomposition during measurement, no ^{13}C coupling constants could be determined, [20]10.6 and 4.4, [21]10.5 and 3.1, [23]10.8, [24]4.1, [25]10.0.

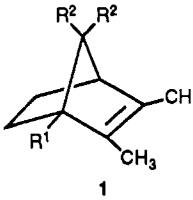
bridge rather than a O atom of the peroxide bond occupies the out of plane position, and the angle C1–O–C6 in the 1,2,4-trioxolane ring is compressed to 100.6°, as opposed to 108.0° in monocyclic[3] and 107.9° in dispiro ozonides,[5] respectively.

After treatment of **1b** with ca. 17 molar equiv of ozone on polyethylene at –75 °C, we isolated 8% of unreacted **1b**,[4] 39% of diketone **4b**, and two liquid ozonides in yields of 16% and 4%. They were shown to be isomers by elemental analyses, by the occurrence of the same $[M + 1]^+$ ion at m/z 185 in the CI mass spectra, and formation of **4b** from either ozonide by reduction with triphenylphosphine. The major isomer exhibited nearly the same ^{13}C NMR chemical shift value for the C_6 atom as ozonide **2a** (Table I); it was therefore tentatively assigned structure **2b**. By contrast, the minor isomer showed its C_6 signal at a lower field position and, hence, it was tentatively assigned structure **3b**. The latter assignment was confirmed by X-ray diffraction, which showed in addition that the 1,2,4-trioxolane ring assumes again an envelope conformation with the ether oxygen in the out of plane position, and that the C1–O–C6 angle was again compressed, viz. to 101.4°.

After treatment of **1c** with ca. 16 molar equiv of ozone on polyethylene at –75 °C, we isolated 18% of unreacted **1c**,[4] 17% of **4c**, and only 1% of a solid ozonide. It was assigned structure **2c** based on its $[M + 1]^+$ ion at m/z 213 in the CI mass spectrum, on its reduction with triphenylphosphine to give **4c**, and on the fact that in the ^{13}C NMR spectrum the signals of the C_6 and C_1 atoms appeared in the same range as those of **2b** rather than those of **3b**. Due to its thermal instability (see below), ozonide **2c** was not amenable to X-ray diffraction or elemental analysis.

As neat substances, ozonides **2a**, **2b**, and **3b** were stable at room temperature, whereas **2c** decomposed within a few hours. Decomposition of **2c** in C_6D_6 at room temperature was complete within 6 h and afforded in 98% selectivity diketone **4c**. By contrast, decomposition of **2a** in $CDCl_3$ at 40 °C and of **2b** and **3b** in C_6D_6 at 55 °C gave mixtures of acetic acid, the corresponding diketones **4** and monoketones **5** + **6** in roughly equal proportions and combined selectivities of ca. 93–95%, along with 5–8% of ca. equal parts of acetic anhydride and the corresponding compound **7**. It is noteworthy that the decomposition of the exo isomer **3b** was complete within ca. half of the time (18 h) of that required for the complete decomposition of the endo isomer **2b** (40 h). Photolysis of **2a**, **2b**, and **3b** at ca. –10 °C in pentane gave the same products as thermolysis did, albeit in slightly different ratios.

The formation of products **5**–**7** can be rationalized by homolytic cleavage of the peroxide bonds in **2a**, **2b**, and **3b** to give diradicals of type **8** as common intermediates: Scission of one of the marked bonds in **8** may lead to the formation of **5** and **6** and acetic acid in a reaction sequence, which we had proposed previously for the decomposition of the ozonide of norbornene.[3] Scission of both marked bonds in **8** leads to the formation of acetic anhydride and a cyclopentane-1,3-diyl radical, which is eventually converted into **7**. Precedents for the latter course of reaction, viz. elimination of an anhydride moiety from bicyclic and tricyclic ozonides during thermal and photochemical decomposition reactions have been reported, too.[2b] There is no plausible explanation for the formation of products **4**, which could account for the fate of the third oxygen atom in the ozonolysis of norbornenes **1** or in the decomposition of ozonides **2** and **3**.



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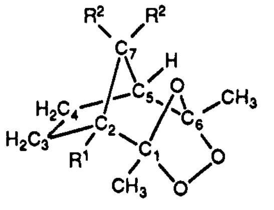

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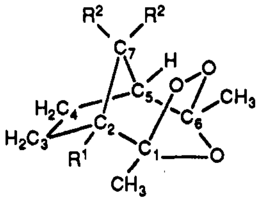

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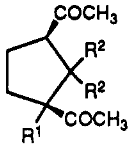

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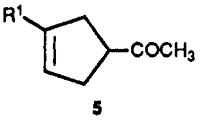

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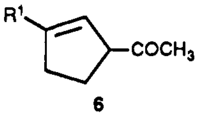

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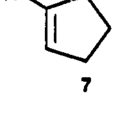

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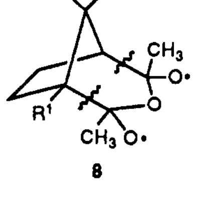

8

	a	b	c
R^1	H	CH_3	CH_3
R^2	H	H	CH_3

Finally, it should be mentioned that in the ozonolysis of substrates **1a**–**c** in pentane, only **1b** resulted in the formation of ozonides, viz. 10% of **2b** and 2% of **3b**,

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(5) Griesbaum, K.; Krieger-Beck, P.; Beck, J. *Chem. Ber.* **1991**, *124*, 391.

whereas **1a** and **1c** gave only intractable peroxidic materials. These results underline the utility of the ozonolysis of olefins on polyethylene as a versatile method for the preparation of otherwise nonaccessible ozonides.

Experimental Section

General Methods. GLC analyses condition 1: glass column, 0.3 × 50 cm, 2.5% methylsilicone OV-101, 60–180 °C at 4 °C/min. Condition 2: same as condition 1, but 50–180 °C at 4 °C/min. Condition 3: 50-m capillary column, 5% phenylmethyl silicone SE 54, 50–180 °C at 7 °C/min. HPLC separations: column 4.4 × 20.8 cm LiChrosorb Si 60, gradient elution program with pentane/diethyl ether (95:5 for 20 min and 90:10 for 20 min) at 12 mL/min.

General Procedures. (a) Preparation of Substrates 1a–c. Substrate **1c** has been prepared by a published procedure.[6] The same procedure has been applied for the synthesis of **1a** and **1b**, which had previously been prepared by other methods.[7,8] Thus, **1a** has been obtained in 7.2% yield by converting bicyclo[2.2.1]heptan-2-one into bicyclo[2.2.1]heptane-2,3-dione,[9] and, proceeding according to ref 6, **2b** has been obtained in 11.3% yield from 1-methylbicyclo[2.2.1]heptan-2-one[10] and **1c** has been obtained in 12.4% yield from 1,7,7-trimethyl[2.2.1]heptan-2-one by following the same sequence of reaction steps and isolation by flash chromatography[11] (column 4 × 60 cm, 300 g of silica gel 60; *n*-pentane).

(b) Ozonolyses on polyethylene have been carried out by a procedure that has been published in detail.[3] The loading of the substrates was carried out by the variant for solid olefins using pentane as a solvent. All ozonolyses were performed at −75 °C. The products were extracted from polyethylene with 400 mL of diethyl ether and concentrated in a rotary evaporator at room temperature at ca. 15–20 Torr. The residues were separated by flash chromatography: water cooled glass columns, 2 × 60 cm, 75 g of silica gel 60; mixtures of *n*-pentane/diethyl ether, followed by diethyl ether.

Ozonolysis of 1a on Polyethylene. When 1.1 g (9.0 mmol) of **1a** on 70 g of polyethylene was ozonized for 10.5 h (23 molar equiv of ozone), one obtained 1.2 g of a liquid residue. Separation by flash chromatography (750 mL of *n*-pentane/diethyl ether, 25:1) gave 0.17 g (16%) of **1a**, 0.10 g (7%) of **2a**, and 0.15 g (12%) of **4a**; GLC t_R = 6.65 min (condition 1).

1,4-Dimethyl-2,3,9-trioxatricyclo[4.2.1.1^{5,8}]decane (2a): colorless solid; mp 25 °C; CI-MS *m/z* (%) 171 (25) [M + 1]$^+$. Anal. Calcd for $C_9H_{14}O_3$: C, 63.51; H, 8.24. Found: C, 63.84; H, 8.14.

***cis*-1,3-Diacetylcyclopentane (4a)**: colorless oil; ^{1}H NMR ($CDCl_3$, TMS) δ 1.83–1.94 (m, 4 H), 2.00–2.14 (m, 2 H), 2.18 (s, 6 H), 2.88–2.96 (m, 2 H); ^{13}C NMR ($CDCl_3$, TMS) δ 27.62, 28.05, 30.33, 51.67, 209.25; EI-MS *m/z* (%) 154 (13) M$^+$, 43 (100) $(CH_3CO)^+$; GLC t_R = 18.65 min (condition 3). The above data are identical with those of an authentic sample.[12]

Ozonolysis of 1b on Polyethylene. When 2.3 g (16.9 mmol) of **2b** on 79 g of polyethylene was ozonized for 14.5 h (17 molar equiv of ozone) one obtained 2.4 g of a liquid residue. Separation by flash chromatography (600 mL of *n*-pentane/diethyl ether, 30:1) gave 0.18 g (8%) of **1b**, 0.63 g of a mixture of **2b** and **3b**, and 1.1 g (39%) of **4b**. HPLC separation of the mixture of ozonides gave 0.49 g (16%) of **2b** and 0.12 g (4%) of **3b**.

***endo*-1,4,5-Trimethyl-2,3,9-trioxatricyclo[4.2.1.1^{5,8}]decane (2b)**: colorless liquid; mp ca. −30 °C; CI-MS *m/z* (%) 185 (100) [M + 1]$^+$; GLC t_R = 11.26 min (condition 2). Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.19; H, 8.75. Found: C, 65.23; H, 8.63.

***exo*-1,4,5-Trimethyl-2,3,9-trioxatricyclo[4.2.1.1^{5,8}]decane (3b)**: colorless liquid; mp ca. 5 °C; CI-MS *m/z* (%) 185 (100) [M + 1]$^+$; GLC t_R = 11.26 min (condition 2). Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.19; H, 8.75. Found: C, 65.61; H, 8.44.

***cis*-1,3-Diacetyl-1-methylcyclopentane (4b)**: colorless oil; ^{1}H NMR (C_6D_6, TMS) δ 0.84 (s, 3 H), 0.98–1.09 (m, 1 H), 1.18–1.27 (m, 1 H), 1.41–1.55 (m, 1 H), 1.65–1.70 (m, 1 H), 1.70 (s, 3 H), 1.79 (s, 3 H), 1.88–1.96 (m, 1 H), 2.19–2.27 (m, 1 H), 2.31–2.45 (m, 1 H); ^{13}C NMR (C_6D_6, TMS) δ 24.11, 24.65, 27.51, 27.85, 35.66, 38.01, 51.18, 55.68, 207.09, 209.53; EI-MS, *m/z* (%) 168 (6) M$^+$, 43 (100) $(CH_3CO)^+$; GLC t_R = 19.47 min (condition 3). Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.28; H, 9.50.

Ozonolysis of 1c on Polyethylene. When 2.0 g (12.2 mmol) of **1c** on 75 g of polyethylene was ozonized for 9.5 h (16 molar equiv of ozone), 2.2 g of a liquid residue was obtained. Separation of the latter by flash chromatography (750 mL of *n*-pentane/diethyl ether, 20:1) gave 0.35 g (18%) of **1c**, 0.02 g (1%) of **2c**, and 0.40 g (17%) of **4c**.

1,4,5,10,10-Pentamethyl-2,3,9-trioxatricyclo[4.2.1.1^{5,8}]decane (2c): colorless solid; mp 30 °C; CI-MS *m/z* (%) 213 (100) [M + 1]$^+$.

***cis*-1,3-Diacetyl-1,2,2-trimethylcyclopentane (4c)**: colorless liquid: ^{1}H NMR ($CDCl_3$, TMS) δ 0.76 (s, 3 H), 1.17 (s, 3 H), 1.36 (s, 3H), 1.43–1.55 (m, 1 H), 1.67 –1.83 (m, 1 H), 2.15 (s, 3 H), 2.16 (s, 3 H), 2.16–2.26 (m, 1 H), 2.39–2.56 (m, 1 H), 2.98 (t, *J* = 10.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$, TMS) δ 20.58, 21.23, 22.28, 23.75, 28.60, 31.68, 32.42, 46.40, 60.25, 61.17, 209.42, 211.88; GLC t_R = 23.20 min (condition 3). The above data are identical with those obtained from an independently prepared sample of **4c**.[6]

Reductions of Ozonides 2a, 2b, 3b, and 2c with Triphenylphosphine. Solutions of 10 mg of each ozonide in 1 mL of C_6D_6 were admixed with triphenylphosphine in a NMR tube. The tubes were sealed and kept for 40 h at 30 °C (**2a**) and for 40 h (**2b**), 12 h (**3b**), and 5 h (**2c**) at room temperature. ^{1}H NMR and GLC analysis showed in each case the presence of the corresponding *cis*-diacetyl compound **4** as the sole reduction product.

Thermal Decomposition of Ozonides 2a, 2b, 3b, and 2c in Solution. Solutions containing 75 mg of **2a** in 1 mL of $CDCl_3$, 70 mg of **2b** in 1 mL of C_6D_6, 70 mg of **3b** in 1 mL of C_6D_6, and 60 mg of **2c** in 1 mL of C_6D_6, respectively, were sealed in NMR tubes and kept at the temperatures mentioned below. The progress of the decomposition was monitored by NMR analysis. After completion, the products were quantitatively assessed by GLC analysis (condition 3).

Decomposition of 2a for 40 h at 55 °C gave 32% of **4a** (t_R = 18.67 min), 28% of **5a** (t_R = 10.53 min), 2% of **7a** (t_R = 6.05 min), 33% of acetic acid (t_R = 6.23 min), and 4% of acetic anhydride (t_R = 7.15 min).

Decomposition of 2b for 40 h at 55 °C gave 22% of **4b** (t_R = 19.49 min), 39% of **5b** + **6b** (common t_R = 12.47 min), ca. 1% of **7b** (t_R = 6.58 min), 34% of acetic acid, and 2% of acetic anhydride.

Decomposition of 3b for 18 h at 55 °C gave 26% of **4b**, 42% of **5b** + **6b**, 2% of **7b**, 27% of acetic acid, and 2% of acetic anhydride.

Decomposition of 2c for 6 h at room temperature gave 98% of **4c** (t_R = 23.25 min).

Photolytic Decomposition of Ozonides 2a, 2b, and 3b in Solution. Solutions containing 0.20 g of **2a**, 0.27 g of **2b**, and 0.27 g of **3b**, respectively, in 22 mL of *n*-pentane, each, were irradiated with a mercury high pressure lamp at −20 °C. Then the mixtures were concentrated to ca. 10 mL by removal of pentane at ca. 18 Torr and room temperature, and the residues were submitted to GLC analysis (condition 3). Finally, the remaining pentane was removed and the residues were separated by flash chromatography (column 1.5 × 30 cm, ca. 20 g of silica gel; ca. 300 mL of pentane/diethyl ether, 30:1, followed by diethyl ether).

Photolysis of 2a for 7.5 h gave 0.19 g of a liquid residue from which 60 mg (30%) of ozonide **2a**, 14 mg (8%) of **4a**, and 30 mg (23%) of **5a** have been isolated. GLC analysis of the enriched mixture showed additionally the peaks of **7a** (t_R = 6.07 min; ca. 3%), acetic acid (t_R = 6.22 min; 25%), and acetic anhydride (t_R = 7.16 min; 4%).

4-Acetylcyclopentene (5a): ^{13}C NMR ($CDCl_3$, TMS) δ 28.09, 34.94, 49.81, 128.82, 209.58; MS *m/z* (%) 110 (41) M$^+$, 95 (46) $[M - CH_3]^+$, 67 (100) $[M - CH_3CO]^+$.

Photolysis of 2b for 9 h gave 0.18 g of a liquid residue from which 120 mg (45%) of ozonide **2b**, 12 mg (5%) of **4b**, and 26 mg

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(14%) of a mixture of **5b** and **6b** have been isolated. GLC analysis of the enriched mixture showed additionally the peaks of **7b** (t_R = 6.60 min; identical with that of purchased **7b**; 2%), acetic acid (t_R = 6.23 min; 18%), and acetic anhydride (t_R = 7.16 min; 4%).

Mixture of 4-acetyl-1-methylcyclopentene (5b) and 3-acetyl-1-methylcyclopentene (6b): colorless liquid; ^{1}H NMR ($CDCl_3$, TMS) δ 1.70 (s), 1.78 (s), 2.12 (s), 2.16 (s), 2.24–2.48 (m), 2.48–2.58 (m), 3.26 (quint), 3.49–3.61 (m), 5.19–5.23 (m), 5.32–5.36 (m); ^{13}C NMR ($CDCl_3$, TMS) δ 16.23, 16.52, 26.22, 27.71, 28.04, 35.31, 36.51, 38.97, 50.78, 59.71, 122.32, 122.37, 138.73, 144.51, 209.89, 209.93; GLC t_R = 12.49 min. Anal. Calcd for $C_8H_{12}O$: C, 77.38; H, 9.74. Found: C, 77.14; H, 9.63.

Photolysis of 3b for 9 h gave 0.17 g of a liquid residue from which 53 mg (20%) of **3b**, 50 mg (20%) of **4b**, and 31 mg (17%) of a mixture of **5b** and **6b** have been isolated. GLC analysis of the enriched mixture showed additionally the peaks of **7b** (2%), acetic acid (20%), and acetic anhydride (5%).

Ozonolysis of 1a in Pentane. A solution of 0.30 g (2.5 mmol) of **1a** in 30 mL of pentane was ozonized at −5 °C until it turned blue, flushed with nitrogen, and warmed up to room temperature. The solution was decanted from precipitated semisolid material, and pentane was removed at room temperature and ca. 18 Torr to leave 0.33 g of a liquid residue. ^{1}H and ^{13}C NMR and GC/MS analyses of the latter showed only the presence of **4a**. By flash chromatography (column 2 × 60 cm, 40 g of silica gel; 400 mL of pentane/diethyl ether, 25:1, followed by diethyl ether) 0.17 g (46%) of **4a** was isolated. It was identified by GLC (t_R = 18.69 min, condition 3) and ^{13}C NMR analysis ($CDCl_3$, TMS; δ 27.62, 28.05, 30.33, 51.67, 209.25).

Ozonolysis of 1b in Pentane. In the same way as described above, 0.36 g (2.7 mmol) of **1b** in 40 mL of pentane was ozonized at −20 °C to give 0.38 g of a liquid residue. Separation by flash chromatography (column 2 × 60 cm, 40 g of silica gel; 400 mL of pentane/diethyl ether, 30:1, followed by diethyl ether) gave 60 mg (12%) of a mixture of **2b** and **3b**, and 200 mg of **4b**. HPLC separation of the mixture of ozonides gave 50 mg (10%) of **2b** and 10 mg (2%) of **3b**.

Ozonolysis of 1c in Pentane. In the same way as described above, 0.28 g (1.7 mmol) of **1c** in 40 mL of pentane was ozonized at −5 °C to give 0.30 g of a liquid residue, from which 0.15 g (45%) of **4c** was isolated by flash chromatography (column 2 × 60 cm, 30 g of silica gel; 250 mL of pentane/diethyl ether, 20:1, followed by diethyl ether).

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Supplementary Material Available: Tables of atomic positional parameters and equivalent isotropic thermal parameters, bond distances and angles, and anisotropic thermal parameters and ORTEP views for **2a** and **3b** structure determinations (10 pages). Ordering information is given on any current masthead page.

Domino Reactions. One-Pot Preparation of Fluoreno[2,3,4-*ij*]isoquinoline Derivatives from Conjugated Ketene Imines

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Iminophosphoranes **4**, derived from ethyl α-azido-2-(allyloxy)-3-methoxycinnamates, react with ketenes to give the corresponding ketene imines, which by thermal treatment at 150–160 °C undergo a consecutive electrocyclic ring closure/Claisen rearrangement/second ring closure/double aromatization process to give isoquinoline derivatives **7** and/or the previously unknown fluoreno[2,3,4-*ij*]isoquinolines **9** in moderate yields. Similarly, iminophosphoranes **14** derived from ethyl α-azido-2,3-disubstituted–4–(allyloxy)cinnamates reacted with diphenyl ketene to give the intermediate ketene imines, which at 150–160 °C undergo a cascade of pericyclic reactions to give the isoquinolines **15** and the pentacyclic compounds **16** in moderate yields.

Conjugated heterocumulenes exhibit a rich chemistry of unusual synthetic promise.[1] Cycloaddition reactions of such unsaturated heterocumulenic systems as ketenes, isocyanates, isothiocyanates, and carbodiimides provide an attractive entry to a variety of carbocycles and heterocycles. However, the chemistry of conjugated ketene imines has received limited attention. Only the preparation and some intra- and intermolecular reactions have been reported: *N*-arylvinyl ketene imines react with electron-deficient dienes in all-carbon Diels–Alder reactions, while their reactions with electron-rich ynamines afford quinoline derivatives by cycloaddition across the aza diene system.[2] Similar observations have been made on the reaction of *N*-arylvinyl ketene imines with thiobenzophenones.[3] *N*-Vinyl ketene imines react with diphenyl ketene to give 2*H*–1,3–oxazine derivatives.[4] In this case the unsaturated ketene imine acts as a 2-aza diene, which cycloadds to the C=O bond of the ketene.

We have recently shown that thermal treatment of β-arylvinyl carbodiimides provide an efficient annulation route to highly substituted isoquinolines and 1,9-diazaphenalene derivatives.[5] In our original version of this annulation strategy, the unsaturated carbodiimide is generated by aza-Wittig-type reactions of iminophosphoranes derived from ethyl α-azido-2-(allyloxy)-3-

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