Bzl)-OTcp, 95485-15-7; Z-His(im-Z)-OPcp, 60666-46-8; Z-His(im-Z)-OTcp, 40917-51-9; Z-His(im-Tos)-OPcp, 95485-16-8; Z-His(im-Tos)-OTcp, 95485-17-9; Boc-His(im-DNP)-OPcp, 42290-57-3; Boc-His(im-DNP)-OTcp, 95485-18-0; Z-His(im-Z)-ONP, 20531-27-5; Z-His(im-Tos)-ONP, 95485-19-1; Z-His(tos)-OMe, 95485-21-5; Z-His(Z)-OMe·HCl, 95485-27-1; H-Val-OMe, 4070-48-8; N^{α}-carbobenzoxy-N^{im}-benzyl-L-histidine methyl ester hydrochloride, 95485-20-4; N^{α}-carbobenzoxy-L-histidine hydrazide, 49706-31-2; N^{α}-carbobenzoxy-N^{im}-benzyl-L-histidine hydrazide, 26582-89-8; N^{α}-carbobenzoxy-N^{im}-tosyl-L-histidine hyrazide, 95485-22-6; N^{α}-carbobenzoxy-N^{im}-benzyl-L-histidyl-L-valine methyl ester, 95485-23-7; N^{α},N^{im}-dicarbobenzoxy-L-histidyl-L-valine methyl ester, 95485-24-8; N^{α}-carbobenzoxy-N^{im}-tosyl-L-histidyl-L-valine methyl ester, 95485-25-9; pentachlorophenol, 87-86-5; 2,4,5-trichlorophenol, 95-95-4; N^{α}-(*tert*-butyloxycarbonyl)-N^{im}-benzyl-L-histidine pentachlorophenyl ester, 61266-04-4; N^{α}-(carbobenzoxy)-N^{im}-benzyl-L-histidine, 21929-66-8; N^{α}-(*tert*-butyloxycarbonyl)-N^{im}-2,4-dinitrophenyl-L-histidyl-L-valine methyl ester, 95485-26-0; N^{α},N^{im}-dicarbobenzoxy-L-histidine hydrazide, 95514-76-4.

Ozonolysis of 1-Methylindenes. Solvent, Temperature, and Substituent Electronic Effects on the Ozonide Exo/Endo Ratio

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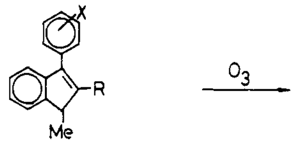
The ozonolyses of 1-methyl-3-aryl-, 1,2-dimethyl-3-aryl-, and 1-methyl-2,3-diarylindenes (**1a–e**, **4a–e**, **7a–e**, **7a′,b′,d′**) in various solvents at several temperatures have been undertaken. The data revealed the following. (a) The ozonolysis of indenes **1c**, **4c**, and **7c** in aprotic solvents yielded in each case a mixture of exo/endo ozonide isomers, the solvent-independent exo/endo ratio being 7:3, 3:2, and 3:7, respectively. In marked contrast, protic solvents exerted a significant influence on the ozonide stereochemistries. (b) The ozonolysis of indene **7c** in methanol at −70 °C afforded a novel methanol-participated product **14** as the major product, whereas the reaction at 20 °C lead to the production of a 72% yield of the expected ozonide isomers **8c**/**9c**. A similar trend was observed for **4c**. From **1c**, however, a more conventional methanol-participated product **10** was obtained along with ozonide isomers **2c**/**3c**. (c) The ozonide exo/endo ratios increased with the decrease of the reaction temperature. The exception was the ozonolysis of **4** in MeOH, in which the reverse trend was observed. (d) The substituent electronic effect can exert a significant influence on the ozonide composition.

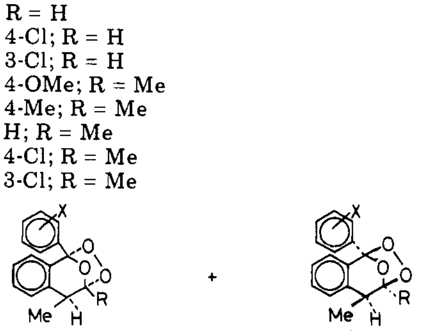
Recently we reported that (a) the ozonolysis of a series of 1-substituted indenes in CCl_4 at 20 °C affords in each case a corresponding mixture of exo/endo ozonide isomers and (b) the steric effects of 1- or 2-substituents play a significant role in determining the ozonide exo/endo ratio.[2] Since there are other factors which could affect the ozonide stereochemistry, we have consequently performed the ozonolysis of 1-methyl-3-aryl-, 1,2-dimethyl-3-aryl-, and 1-methyl-2,3-diarylindenes (**1a–e**, **4a–e**, **7a–e**, **7a′,b′,d′**) in various solvents, including protic ones, and at a series of temperatures. The product yields and ratios of the respective exo/endo isomeric ozonides from each reaction were determined. We anticipated that careful examination of the resulting data could provide further insight into the ozonolysis mechanism.[3,4]

Results

(I) Ozonolysis in Aprotic Solvents. The ozonolysis of 1-methyl-3-phenylindene (**1c**) in hexane, carbon tetrachloride, methylene chloride, acetone, and acetonitrile at 20 °C gave, in each case, a mixture of exo ozonide **2c** and the endo isomer **3c** in isolated yields of around 60%, the exo/endo isomer ratios averaging around 7:3 (Table I and IV). Similarly, the ozonide isomer ratios obtained from the ozonolyses of indenes **1a,b,d–e** in some aprotic solvents were found to vary little with the solvents (eq 1 and Table I). In this series the exo/endo ratio depended on the electronic nature of the substituent X, the ratio varying



1a, X = 4-OMe; R = H
1b, X = 4-Me; R = H
1c, X = R = H
1d, X = 4-Cl; R = H
1e, X = 3-Cl; R = H
4a, X = 4-OMe; R = Me
4b, X = 4-Me; R = Me
4c, X = H; R = Me
4d, X = 4-Cl; R = Me
4e, X = 3-Cl; R = Me



(1)

2a, X = 4-OMe; R = H	**3a**, X = 4-OMe; R = H
2b, X = 4-Me; R = H	**3b**, X = 4-Me; R = H
2c, X = R = H	**3c**, X = R = H
2d, X = 4-Cl; R = H	**3d**, X = 4-Cl; R = H
2e, X = 3-Cl; R = H	**3e**, X = 3-Cl; R = H
5a, X = 4-OMe; R = Me	**6a**, X = 4-OMe; R = Me
5b, X = 4-Me; R = Me	**6b**, X = 4-Me; R = Me
5c, X = H; R = Me	**6c**, X = H, R = Me
5d, X = 4-Cl; R = Me	**6d**, X = 4-Cl; R = Me
5e, X = 3-Cl; R = Me	**6e**, X = 3-Cl; R = Me

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(1) (a) Osaka University. (b) Heriot-Watt University.

(2) Miura, M.; Nojima, M.; Kusabayashi, S.; McCullough, K. J. *J. Am. Chem. Soc.* **1984**, *106*, 2932.

(3) For a recent comprehensive summary of this topic, see: (a) Bailey, P. S. "Ozonation in Organic Chemistry"; Academic Press: New York, Vol. 1, 1978; Vol. 2, 1982. (b) Kuczkowski, R. L. *Acc. Chem. Res.* **1983**, *16*, 42.

(4) The leading references for the ozonolysis in solution: (a) Bailey, P. S.; Ferrell, T. M. *J. Am. Chem. Soc.* **1978**, *100*, 899. (b) Murray, R. W.; Ramachandran, V. *J. Org. Chem.* **1983**, *48*, 813. (c) Murray, R. W.; Su, J.-S. *Ibid.* **1983**, *48*, 817. (d) Bailey, P. S.; Ferrell, T. M.; Rustaiyan, A.; Seyhan, S.; Unruh, L. E. *J. Am. Chem. Soc.* **1978**, *100*, 894. (e) Choe, J.-I.; Kuczkowski, R. L. *Ibid.* **1983**, *105*, 4839. (f) Choe, J.-I.; Srinivasan, M.; Kuczkowski, R. L. *Ibid.* **1983**, *105*, 4703. (g) Reinhardt, H. G.; Doorakian, G. A.; Freedman, H. H. *Ibid.* **1968**, *90*, 5934. (h) Kolsaker, P. *Acta Chem. Scand., Ser. B* **1978**, *B32*, 557.

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Table I. Ozonolysis of 1-Methyl-3-arylindenes 1[a]

	ozonide exo/endo ratio (total ozonide yield,[b] %)					
substit	CCl_4	CH_2Cl_2	MeCN	MeOH[c]	AcOH[c]	HCO_2H[d]
4-OMe	74:26 (57)			86:14 (32)	88:12 (30)	
4-Me	72:28 (60)	76:24 (58)	74:26 (56)	86:14 (40)	82:18 (38)	61:39 (25)
H	66:34 (72)	72:28 (65)	70:30 (65)	85:15 (49)	82:18 (40)	68:32 (36)
4-Cl	59:41 (59)			79:21 (41)	77:23 (39)	72:28 (28)
3-Cl	57:43 (57)	61:39 (56)	59:41 (60)	77:23 (35)	79:21 (32)	79:21 (26)

[a] The reaction was performed at 20 °C. [b] The isolated yield; the ratio of the stereoisomeric ozonides was determined by ^1H NMR spectroscopy after isolation of the ozonides. [c] To obtain a homogeneous solution, CCl_4 (30 vol %) was used as a cosolvent. [d] Ozonolysis was performed in a mixed solvent, HCO_2H and CH_2Cl_2 (1:1).

Table II. Ozonolysis of 1,2-Dimethyl-3-arylindenes 4[a]

	ozonide exo/endo ratio (total ozonide yield,[b] %)					
substit	CCl_4	CH_2Cl_2	MeCN	MeOH[c]	AcOH[c]	HCO_2H[d]
4-OMe	54:46 (83)					
4-Me	59:41 (78)	58:42 (78)	57:43 (78)	60:40 (65)	41:59 (66)	64:36 (72)
H	60:40 (83)	61:39 (80)	58:42 (85)	57:43 (66)	40:60 (66)	62:38 (75)
4-Cl	65:35 (84)					
3-Cl	68:32 (81)	67:33 (83)	67:33 (80)	56:44 (68)	38:62 (72)	51:49 (78)

[a] The reaction was performed at 20 °C. [b] The isolated yield; the exo/endo ratio was determined by ^1H NMR spectroscopy. [c] CCl_4 (30 vol %) was used as a cosolvent. [d] CH_2Cl_2 (50 vol %) was used as a cosolvent.

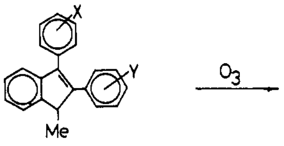
Table III. Ozonolysis of 1-Methyl-2,3-diarylindenes 7[a]

	ozonide exo/endo ratio (total ozonide yield,[b] %)					
substit, X or Y	CCl_4	CH_2Cl_2	MeCN	MeOH[c]	AcOH[c]	HCO_2H[d]
X = 4-OMe	23:77 (89)			47:53 (68)	78:22 (89)	78:22 (82)
Y = 4-OMe	23:77 (85)					
X = 4-Me	27:73 (86)	26:74 (82)	26:74 (85)	47:53 (65)	75:25 (85)	80:20 (83)
Y = 4-Me	28:72 (84)			42:58 (54)	75:25 (88)	79:21 (80)
H	29:71 (93)	29:71 (88)	28:72 (92)	46:54 (72)	76:24 (89)	76:24 (90)
X = 4-Cl	45:55 (91)			42:58 (66)	77:23 (86)	80:20 (85)
Y = 4-Cl	37:63 (95)			46:54 (53)	77:23 (86)	78:22 (83)
X = 3-Cl	49:51 (95)	40:60 (88)	40:60 (89)	44:56 (65)	78:22 (82)	75:25 (80)

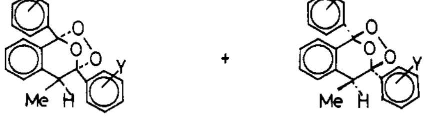
[a] The reaction at 20 °C. [b] The isolated yield; the ratio of the stereoisomeric ozonides was determined by ^1H NMR spectroscopy after the isolation. [c] To obtain a homogeneous solution, CCl_4 (30 vol %) was used as a cosolvent. [d] Ozonolysis was performed in a mixed solvent, HCO_2H and CH_2Cl_2 (1:1).

directly as a function of electron-donating ability of the substituent (Figure 1).

The ozonolyses of 1,2-dimethyl-3-arylindenes **4a–e** (eq 1 and Table II) and 1-methyl-2,3-diarylindenes **7a-e** **7a′,b′,d′** (eq 2 and Table III) revealed the following. (a) The indenes **4** and **7** yielded the corresponding mixtures of the exo/endo ozonide isomers almost quantitatively. (b) The ozonide isomer ratios observed in the ozonolyses of **4c** and **7c** were ca. 3:2 and 3:7, respectively, irrespective of the solvent. (c) In the ozonolysis of **7a-e**, **7a′,b′,d′**, the exo/endo ratios were found to increase when either of the substituents X or Y became electron withdrawing. Similar



7a, X = 4-OMe; Y = H
7b, X = 4-Me; Y = H
7c, X = Y = H
7d, X = 4-Cl; Y = H
7e, X = 3-Cl; Y = H
7a′, X = H; Y = 4-OMe
7b′, X = H; Y = 4-Me
7d′, X = H; Y = 4-Cl



(2)

8a, X = 4-OMe; Y = H
8b, X = 4-Me; Y = H
8c, X = Y = H
8d, X = 4-Cl; Y = H
8e, X = 3-Cl; Y = H
8a′, X = H; Y = 4-OMe
8b′, X = H; Y = 4-Me
8d′, X = H; Y = 4-Cl

9a, X = 4-OMe; Y = H
9b, X = 4-Me; Y = H
9c, X = Y = H
9d, X = 4-Cl; Y = H
9e, X = 3-Cl; Y = H
9a′, X = H; Y = 4-OMe
9b′, X = H; Y = 4-Me
9d′, X = H; Y = 4-Cl

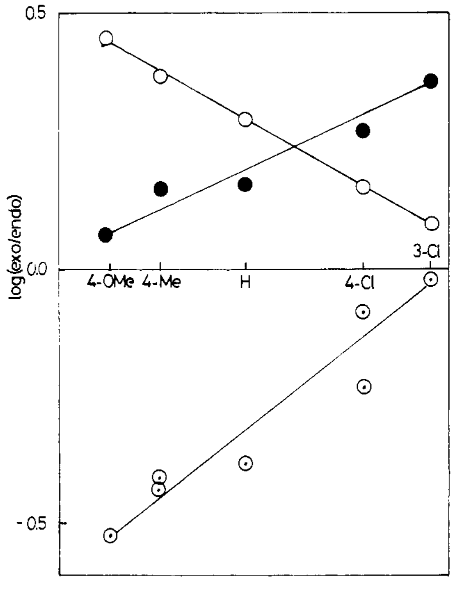


Figure 1. Plots of log (exo/endo) vs. Hammett σ constant in the ozonolysis of **1** (○), **4** (●), and **7** (⊙) in CCl_4.

Table IV. Solvent Effects on the Ozonide Exo/Endo Ratio and Yield[a]

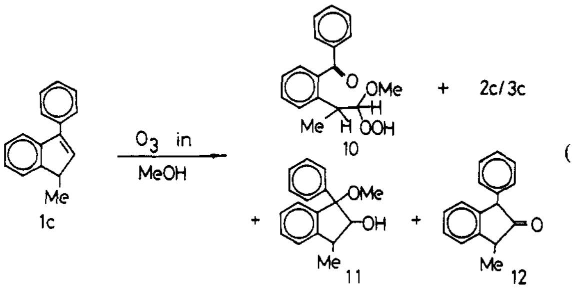
solvent	ozonide exo/endo ratio (total ozonide yield,[b] %) **1c**	**4c**	**7c**
hexane	67:33 (78)	61:39 (74)	31:69 (90)
CCl_4	66:34 (72)	60:40 (83)	29:71 (93)
CH_2Cl_2	72:28 (65)	61:39 (80)	29:71 (88)
acetone	71:29 (66)	61:39 (78)	28:72 (83)
MeCN	70:30 (65)	58:42 (85)	28:72 (92)
$(CH_3)_2CHOH$[c]	75:25 (44)	54:46 (72)	39:61 (82)
EtOH[c]	80:20 (51)	56:44 (72)	42:58 (81)
MeOH[c]	85:15 (49)	57:43 (66)	46:54 (72)
CF_3CH_2OH[d]	90:10 (53)	64:36 (81)	55:45 (81)
AcOH[c]	82:18 (40)	40:60 (66)	76:24 (89)
HCO_2H[d]	68:32 (36)	62:38 (75)	76:24 (90)
$CH_3CH_2CO_2H$[c]	87:13 (32)	49:51 (75)	79:21 (85)

[a] The reaction at 20 °C. [b] The isolated yield; the ratio of the stereoisomeric ozonides was determined by ^1H NMR spectroscopy. [c] To obtain a homogeneous solution, CCl_4 (30 vol %) was used as a cosolvent. [d] CH_2Cl_2 (50 vol %) was used as a cosolvent.

trends were also observed for indenes **4a–e** (Figure 1).

To investigate the effect of temperature on ozonide stereochemistry, the ozonolyses of indenes **1b**,**c**,**e**, **4b**,**c**,**e** and **7b**,**c**,**e** in methylene chloride were performed at the lower temperatures, −30 °C and −70 °C (Table V). In all the ozonolyses of **1**, **4**, and **7**, increased proportions of more thermodynamically stable exo ozonides **2**, **5**, and **8** were obtained at the lower temperatures (Figure 2).[5]

(II) Ozonolysis in Alcoholic Solvents. The ozonolyses of 1-methyl-3-arylindenes **1a–e** in alcoholic solvents gave the following (Tables I and IV). First, ozonolysis of **1c** in methanol afforded the methanol-participated product **10**, together with the ozonide exo/endo isomers **2c**/**3c**, the partial-cleavaged product **11**, and 1-methyl-3-phenyl-2-indanone (**12**) (eq 3). Second, the **2c**/**3c** ratio increased with the increase of the solvent E_T values: 2-propanol (75:25) < ethanol (80:20) < methanol (85:15) < trifluoroethanol (TFE) (90:10).[6] Moreover, these exo/endo ratios were noted to be significantly larger than those observed in the ozonolysis in aprotic solvents (ca. 7:3). Third, the ozonide exo/endo ratio observed in the ozonolysis of **1a–e** in methanol increased as the substituent became increasingly electron donating (Table I). Finally, in all cases the ozonide exo/endo ratio increased at lower reaction temperatures (Table V). As a result of accumulated solvent, temperature, and substituent effects, the reactions of **1b**,**c** in methanol at −70 °C gave exclusively the exo ozonides **2b**,**c**.



(3)

Table V. Temperature Effects on the Ozonide Exo/Endo Ratio and Yield

indene	solvent	temp, °C	ozonide exo/endo ratio[a]	total ozonide yield,[b] %
1b	CH_2Cl_2	20	76:24	58
1b	CH_2Cl_2	−70	89:11	54
1c	CH_2Cl_2	20	72:28	65
1c	CH_2Cl_2	−30	79:21	70
1c	CH_2Cl_2	−70	87:13	68
1e	CH_2Cl_2	20	61:39	56
1e	CH_2Cl_2	−70	71:29	58
4b	CH_2cl_2	20	58:42	78
4b	CH_2Cl_2	−70	67:33	74
4c	CH_2Cl_2	20	61:39	80
4c	CH_2Cl_2	−30	65:35	80
4c	CH_2Cl_2	−70	69:31	80
4e	CH_2Cl_2	20	67:33	83
4e	CH_2Cl_2	−30	73:27	79
7b	CH_2Cl_2	20	26:74	82
7b	CH_2Cl_2	−70	40:60	82
7c	CH_2Cl_2	20	29:71	88
7c	CH_2Cl_2	−30	39:61	90
7c	CH_2Cl_2	−70	44:56	91
7e	CH_2Cl_2	20	40:60	88
7e	CH_2Cl_2	−70	53:47	86
1b	MeOH[c]	20	86:14	40
1b	MeOH[d]	−70	100:0	40
1c	MeOH[c]	20	85:15	49
1c	MeOH[d]	−70	100:0	42
1e	MeOH[c]	20	77:23	35
1e	MeOH[d]	−70	88:12	32
4b	MeOH[c]	20	60:40	65
4b	MeOH[d]	−70	60:40	35
4c	MeOH[c]	20	57:43	66
4c	MeOH[d]	−70	52:48	33
4e	MeOH[c]	20	56:44	68
4e	MeOH[d]	−70	48:52	21
7b	MeOH[c]	20	47:53	65
7b	MeOH[d]	−70	69:31	35
7c	MeOH[c]	20	46:54	72
7c	MeOH[d]	−70	59:41	28
7e	MeOH[c]	20	44:56	65
7e	MeOH[d]	−70	48:52	21

[a] The ratio was determined by ^1H NMR spectroscopy after the isolation. [b] The isolated yield. [c] CCl_4 (30 vol %) was used as a cosolvent. [d] In a mixed solvent, MeOH–CH_2Cl_2 (1:1).

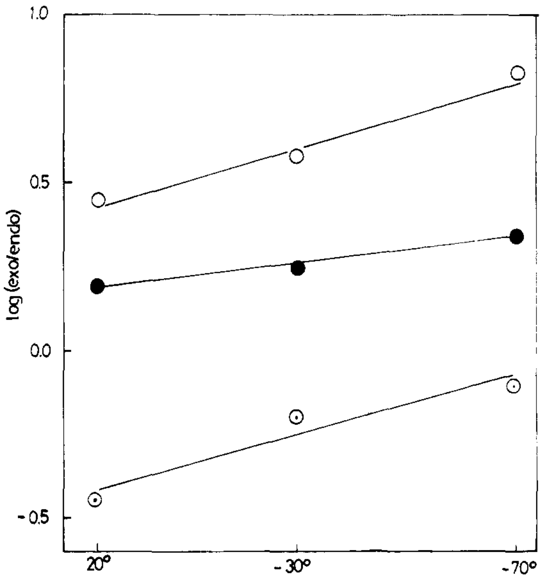


Figure 2. Plots of the log (exo/endo) vs. $1/T$ in the ozonolysis of **1c** (○), **4c** (●), and **7c** (⊙) in CH_2Cl_2.

The ozonolysis of 1-methyl-2,3-diphenylindene (**7c**) in 2-propanol, ethanol, methanol, or TFE at 20 °C afforded in each case a mixture of **8c** and **9c** in good yield (Table IV).[7,8] The **8c**/**9c** ratio was increased with the increase of the solvent E_T value: 2-propanol (39:61) < ethanol

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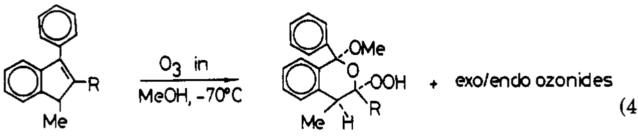
[5] Miura, M.; Ikegami, A.; Nojima, M.; Kusabayashi, S.; McCullough, K. J.; Nagase, S. *J. Am. Chem. Soc.* **1983**, *105*, 2414.

[6] (a) Reichardt, C. "Solvent Effects in Organic Cheimistry"; Verlag Chemie Weinheim: New York, 1979. (b) Bentley, T. W.; Schleyer, P. v. R. "Advances in Physical Organic Chemistry"; Gold, V., Bethell, D., Eds; Academic Press: New York, 1977; Vol. 14.

(42:58) < methanol (46:54) < TFE (55:45). When the ozonolysis of **7c** in methanol was performed at −70 °C, however, the previously unidentified class of solvent-derived product **14** was obtained in 58% yield, together with the expected ozonides **8c** and **9c** (eq 4). The structure of **14** has been unambiguously determined by X-ray analysis.[9] Since ozonides **8c** and **9c** were stable under the ozonolysis conditions, the solvent-derived product **14** was considered to be the primary product from the ozonolysis of **7c** in methanol. In the ozonolyses of **7b,c,e** at −70 °C, the exo/endo ozonide ratios decreased with the increase of electron-donating ability of the substituents, whereas no significant substituent effect had been observed in the reactions at 20 °C. As previously found, lowering of the reaction temperature seems to result in the formation of increased proportion of the exo isomer (Table V). The ozonolysis of 1,2-dimethyl-3-phenylidene (**4c**) in methanol at −70 °C also gave the novel methanol-participated product **13** in 28% yield along with the expected ozonides **5c** and **6c** (eq 4).



(4)

4c; R=Me
7c; R=Ph

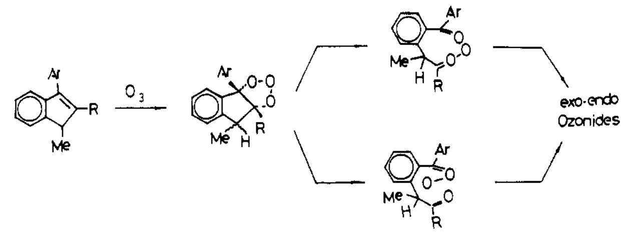
13; R=Me
14; R=Ph

(III) Ozonolysis in Acidic Solvents. Product data for the ozonolysis of indenes **1a–e** in acidic solvents are listed in Tables I and IV and are summarized as follows. First, the yields of the exo/endo ozonides were significantly lower than those obtained from the corresponding reactions in aprotic solvents. Second, the ozonide stereochemistry does vary with solvent; the exo/endo ratio increased in the order formic acid (68:32) < acetic acid (82:18) < propionic acid (87:13). Finally, in the ozonolyses of indenes **1a–e** in acetic acid, the substituent X exerted only a small effect on the ozonide stereochemistry. A large substituent effect was apparent for reactions in formic acid, where the exo/endo ratio increased as the substituent became more electron withdrawing. This trend was the inverse of that observed in the ozonolysis in the aprotic solvents.

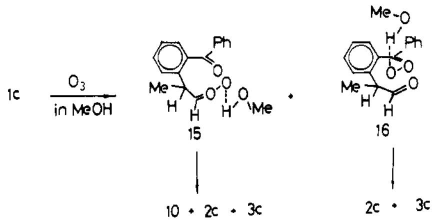
The ozonolyses of indenes **4a–e** in the acidic solvents revealed the following (Tables II and IV). First, the reaction gave a mixture of the isomeric ozonides **5**/**6** in a similar yield to that obtained from the ozonolysis in aprotic solvents. Second, the solvent-dependent **5c**/**6c** ratios increased in the order acetic acid (2:3) < propionic acid (1:1) < formic acid (3:2). Finally, the ozonolysis of indenes **4b,c,e** in acetic acid provided the substituent-independent exo/endo ozonide pairs. In formic acid, however, the exo/endo ratio decreased with the increase of electron-withdrawing ability of the substituent in contrast to that observed in the ozonolysis in aprotic solvents.

The ozonolyses of the series of 1-methyl-2,3-diarylindenes **7a–e**, **7b′**, and **7d′** in acetic acid or formic acid at 20 °C gave the corresponding mixtures of exo/endo ozonide isomers in good yields (Table III); the exo/endo ratios ca. 4:1 being almost insensitive to the nature of the substituents X or Y. Moreover, this high exo/endo ratio was in marked contrast to the exo/endo ratio ca. 3:7 obtained from the ozonolysis in aprotic solvents.

Scheme I



Scheme II



Discussion

Since the three-step Criegee mechanism is widely regarded as important for liquid-phase ozonolysis reactions,[2,3] we have, therefore, attempted to rationalize our results within this framework (Scheme I). Of the possible intermediates generated on ozonolysis of indenes, the corresponding carbonyl oxides would certainly be the most polar functionalities and consequently likely to interact strongly with the reaction solvent. Such interactions could reasonably be expected to give rise to observable solvent effects.

For the ozonolyses of indenes **1**, **4**, and **7** in nonparticipating, aprotic solvents such as hexane, carbon tetrachloride, methylene chloride, and acetonitrile, the total yields of the exo/endo ozonides and their respective relative compositions were largely insensitive to solvent polarity. This suggests that solvation of the carbonyl oxides by these solvents has little effect on the course of the entropically favored intramolecular recombination of the carbonyl/carbonyl oxide fragments which leads to the exo/endo ozonides.[10]

Although ozonolysis of 1-methyl-3-phenylindene (**1c**) in methanol at 20 °C does afford the solvent-derived product **10**,[11] the corresponding ozonides **2c**/**3c** remain the major isolable product (49%) (eq 3). The isomer ratio does, however, change significantly in favor of the exo isomer, **2c**/**3c** 85:15 (cf. **2c**/**3c** ratio of 66:34 in carbon tetrachloride). It is conceivable that in a polar solvent such as methanol, solvation of the zwitterionic carbonyl oxide moieties of intermediates **15** and **16** (Scheme II))could alter the steric requirements in the transition states leading to ozonide formation and hence introduce a further element of stereoselectively. While such arguments are somewhat tentative, it is notable that ozonolysis of **1c** in methanol at −70 °C affords the corresponding ozonide in similar yield as above (42%) but exclusively as the exo isomer.

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[7] Ozonolyses of 2,3-diphenylindene,[8a] certain tetra-, penta-, and hexasubstituted cyclobutenes,[5g] and 1,2-disubstituted indenes[8b] produced ozonides even in participating solvents.

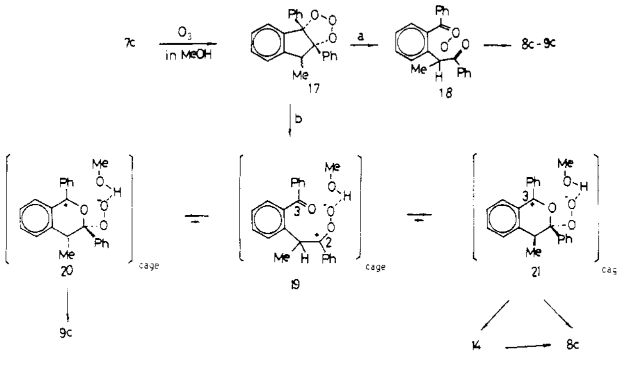
[8] (a) Bailey, P. S. *Chem. Ber.* **1954**, *87*, 993. (b) Criegee, R.; De Bryn, P.; Lohaus, G. *Justus Liebigs Ann. Chem.* **1953**, *583*, 19.

[9] McCullough, K. J.; Nojima, M.; Miura, M.; Fujisaka, T.; Kusabayashi, S. *J. Chem. Soc., Chem. Commun.* **1984**, 35.

[10] In the ozonolysis of acyclic alkenes in aprotic solvents, however, remarkable solvent effects have been observed. Some typical examples are that (a) in th eozonolysis of a series of parasubstituted methyl cinnamates, the yield and the ratio of the cis–trans isomeric ozonides are the marked function of the solvent polarity,[4h] and that (b) polar solvents greatly decrease the ozonide yield from *trans*-1,2-di-*tert*-butylethylene, in most cases to zero, even at −78 °C or lower.[4b,c]

[11] Fliszár, S.; Belzecki, C.; Chylinska, J. B. *Can. J. Chem.* **1967**, *45*, 221.

Scheme III

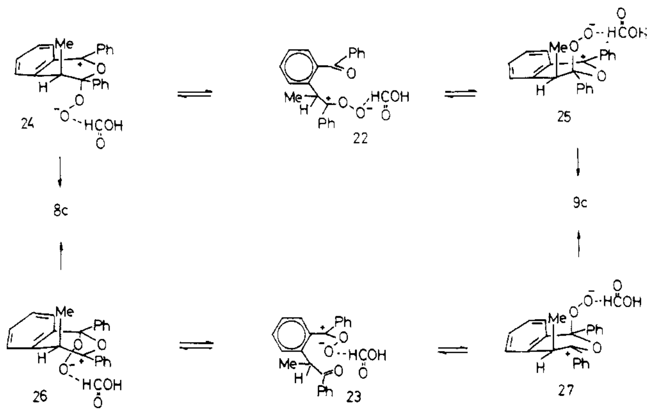


The ozonolysis of the trisubstituted indene **7c** in methanol at 20 °C gives mainly the corresponding ozonides **8c**/**9c** in slightly reduced but high yield with an isomer ratio of almost 1:1 (cf. **8c**/**9c** 1:3 in nonparticipating solvents). In addition, small quantities of a solvent derived product were also observed. When the ozonolysis of **7c** was repeated at −70 °C, this latter product was obtained as the major isolable product (58%) and subsequently shown by X-ray crystallography to have the relative stereochemistry depicted in formula **14**.[9] A plausible mechanism for the transformation **7c** → **8c** + **9c** + **14** based on scission pathways (a and b) of the primary ozonide **17** is outlined in Scheme III.

Since solvent-participated products uniquely attributable to intermediate **18** were not observed, it is presumed that only ozonides **8c** and **9c** are produced via scission pathway a. The absence of conventional solvent-participated products derived from **19** indicates that intramolecular partial-capture of the carbonyl oxide moiety by the adjacent carbonyl group oxygen atom in **19** affording the cyclized forms **20** and **21** must be substantially faster than the intermolecular nucleophilic attack by methanol at C-2. Moreover, reference to the molecular structure of **14** shows that it is specificially related to intermediate **21** rather than **20**, which must preferentially undergo cyclization to the corresponding endo ozonide **9c**.

The markedly different solvent-derived products obtained from indenes **1c** and **7c** can be accounted for in terms of differences in substitution pattern between the substrates and solvent effects, particularly at low temperature. Clearly, the additional phenyl group at C-2 in **7c** should hinder nucleophilic attack by methanol on the carbonyl oxide moiety of **19**, inhibiting the formation of the corresponding α-methoxy hydroperoxide, and also retard the complete recombination of the carbonyl/carbonyl oxide pair in **19** to form ozonides. Examination of molecular models together with the crystal structure of **14** suggests that **21** might preferentially adopt a half-chair conformation, puckered at C-3, with the cis methyl and phenyl groups axial and equatorial, respectively, to minimize gauche interactions and the peroxy moiety axial. Both the peroxy group and methanol may subsequently compete for capture of the incipient carbenium ion at C-3. At lower temperatures, when the solvent cage is likely to be more structured and hence tighter, cyclization of the solvated species **21** would be severely hindered, thereby rendering solvent capture as the favored process. To account for the observed stereochemistry of **14**, it requires that nucleophilic attack by methanol occurs exclusively from the sterically least hindered face, possibly with assistance from the neighboring peroxy group. Since solvent effects are likely to be less important at room temperature, intramolecular cyclization of **21** to give the exo ozonide **8c** should predominate.

Scheme IV



Ozonolyses of indenes **7** in aprotic solvents generally give rise to the thermodynamically less-stable endo ozonide **9** as the major product in each case (Table III and ref 2). Conversely, when the reactions are repeated in acidic solvents, the exo/endo ratios attain values close to 3:1 which are apparently independent of the nature of aryl-group substituents. Although these latter ratios are similar to the observed equilibrium ratios,[2] it has been found that the exo/endo ozonides, once formed, do not interconvert simply in the presence of weak organic acids. It seems more likely that in the acidic media the carbonyl oxide groups would interact strongly with the solvent or may possibly even be protonated. As outlined in Scheme IV, the open-chain carbonyl/carbonyl oxide pairs **22** and **23** could cyclize reversibly prior to the final ring-closure which results in irreversible formation of the ozonides. The equilibrium must lie toward the cyclized forms **24** and **26** to account for the relative preponderance of the exo isomer obtained under these conditions.

Experimental Section

General Procedures. ^{1}H NMR spectra were obtained with a JNM-PS-100 spectrometer in $CDCl_3$. MS data were obtained with a Hitachi RMU-6H spectrometer and infrared spectra with a Hitachi 215 spectrometer. Ozonolyses were carried out with use of a Nippon Ozone Model 0-1-2 ozonator. All melting points are not corrected.

Preparation of Indenes. 1-Methyl-3-phenylindene (**1c**), 1,2-dimethyl-3-phenylidene (**4c**), and 1-methyl-2,3-diarylindenes **7a**,**a′**,**c**–**d**,**d′** were prepared by the methods previously reported.[2] 1-Methyl-3-arylindenes **1a**,**b**,**d**,**e**, 1,2-dimethyl-3-arylindenes **4a**,**b**,**d**,**e**, and 1-methyl-2,3-diarylindenes **7b**,**e** were obtained from the reactions of corresponding indanones with 3- or 4-substituted phenylmagnesium bromides. Melting points of **7b** and **7c** were 119–120 °C and 84–85 °C, respectively. The indenes **1a**,**b**,**d**,**e** and **4a**,**b**,**d**,**e** were obtained as oils. 1-Methyl-2-(4-methylphenyl)-3-phenylindene (**7b′**) was prepared by the reaction of 2-(4-methylphenyl)-3-phenylindenone with methylmagnesium iodide followed by treatment with 57% HI in refluxing acetic acid; mp 138–139 °C (from ethanol–benzene).

Ozonolysis in Carbon Tetrachloride. The procedure has been described previously.[2] Configurations of ozonide exo–endo pairs were determined as described before.[2,5] The physical properties of ozonides **2c**, **3c**, **5c**, **6c**, **8a**,**a′**,**c**,**d**,**d′**, and **9a**,**a′**,**c**–**d**,**d′** were previously reported.[2,5] Melting points (°C) of the aryl derivatives after recrystallization from methanol were **2a**, 90–93; **3a**, 144–146; **2b**, 83–84; **3b**, 151–152; **2d**, 142–143; **3d**, 154–155; **2e**, 104–106; **3e**, 130–132; **5a**, 98–100; **6a**, 65–68; **5b**, 118–119; **6b**, 73–74; **5d**, 101–102; **6d**, 79–80; **5e**, 127–128; **6e**, 143–145; **8b**, 139–141; **9b**, 131–132; **8e**, 148–149; and **9e**, 145–146. The exo/endo ratios were determined by comparing the peak areas of C-1 hydrogens of the isolated exo–endo ozonide isomers in ^{1}H NMR spectra.

Ozonolysis of 1-Methyl-3-phenylindene (1c) in MeOH. To a solution of **1c** (1.034 g, 5 mmol) in $MeOH-CCl_4$ (20 mL, 7:3 v/v) was passed a slow stream of ozone (1 molar equiv) at 20 °C. After conventional workup, the neutral products were column chromatographed on silica gel. The first fraction (elution with benzene–hexane, 7:3) contained a mixture of **2c** and **3c** (622 mg, 49%), the **2c**/**3c** ratio being 85:15. From the second fraction (elution with benzene), 1-methyl-3-phenyl-2-indanone[5] was obtained (30 mg, 3%). From the third fraction, 1-(2-benzoylphenyl)propionaldehyde[5] (40 mg, 3%) was obtained. The fourth fraction contained the unidentified polymeric products (150 mg). The ^{1}H NMR spectrum of the polymeric products indicated the absence of methoxy groups. The fifth fraction (elution with ether–benzene, 1:99) contained the partial-cleavaged product **11** (120 mg, 8%): an oil; ^{1}H NMR δ 1.41 (d, 3 H, J = 6.5 Hz), 2.81 (bs, 1 H, exchangeable with D_2O), 3.09 (s, 3 H), 3.15 (m, 1 H), 3.59 (d, 1 H, J = 8.0 Hz), 7.19–7.55 (m, 9 H); MS, m/e 254 (M$^+$); IR 3500, 1445, 1120, 1070 cm^{-1}. From the final fraction (elution with ether–benzene, 1:9), the hydroperoxide **10** (81 mg, 6%) was obtained: an oil; ^{1}H NMR δ 1.26 (d, 3 H, J = 8.0 Hz), 3.50 (m, 1 H), 3.52 (s, 3 H), 4.81 (d, 1 H, J = 6.5 Hz), 7.26–7.70 (m, 9 H), 9.62 (bs, 1 H, exchangeable with D_2O); IR 3300, 1660, 1450, 1320, 1300, 1195 cm^{-1}. Treatment of **10** with catalytic amounts of $ClSO_3H$ in methanol at 20 °C for 24 h gave quantitatively methyl 1-(2-benzoylphenyl)propinate.[5]

The ozonolysis of **1c** in a mixed solvent MeOH–CH_2Cl_2 (20 mL, 1:1 v/v) at −70 °C (1 molar equiv of ozone), followed by column chromatography on silica gel, afforded **2c** (542 mg, 42%), 1-(2-benzoylphenyl)propionaldehyde (29 mg, 2%), **11** (130 mg, 9%), and **10** (81 mg, 6%), along with the unidentified polymeric products (130 mg).

Ozonolysis of 1c in AcOH. Indene **1c** (1.034 g, 5 mmol) was ozonized in a mixed solvent AcOH–CCl_4 (20 mL, 7:3 v/v) by passing 1 equiv of ozone through the solution. The mixture was poured onto aqueous $NaHCO_3$ and extracted with ether. The products were separated by column chromatography on silica gel. Elution with benzene–hexane (1:1) gave a mixture of **2c** and **3c** (508 mg, 40%). From the second fraction (elution with benzene) was obtained 1-methyl-3-phenyl-2-indanone as an oil (37 mg, 3%). The third fraction contained 1-(2-benzoylphenyl)propionaldehyde (65 mg, 6%). From the fourth fraction were obtained the unidentified polymeric products, which did not contain acetoxy groups (180 mg). From the final fraction (elution with ether–benzene, 1:9) was obtained 1-acetoxy-1-phenyl-3-methylindan-2-ol as an oil (52 mg, 3%): ^{1}H NMR δ 1.34 (d, 3 H, J = 7.0 Hz), 2.02 (s, 3 H), 2.82 (bs, 1 H, exchangeable with D_2O), 3.42 (quintet, 1 H, J = 7.0 Hz), 5.38 (d, 1 H, J = 7.0 Hz), 7.10–7.90 (m, 9 H); IR 3400, 1740 cm^{-1}.

Ozonolysis of 1-Methyl-2,3-diphenylindene (7c) in MeOH at −70 °C. To a solution of indene **7c** (1.41 g, 5 mmol) in methanol (15 mL)–CH_2Cl_2 (15 mL) was added dry oxygen containing 2% ozone at a speed of 50 L/h for 30 min (2 equiv of ozone). The mixture was poured into ice-cold aqueous potassium dihydrogen phosphate, and the products were extracted with ether. The organic layer was speparated and dried over anhydrous magnesium sulfate, and the solvent was removed under vacuum. The crude products were triturated with ether–hexane to give a white solid (**14**, 1.05 g, 58%): mp 155–157 °C (from ethyl acetate–hexane); IR (KBr) 3375 cm^{-1}; ^{1}H NMR δ 1.03 (d, 3 H, J = 7.5 Hz), 3.34 (q, 1 H, J = 7.5 Hz), 3.46 (s, 3 H), 7.00–7.80 (m, 14 H), 8.96 (s, 1 H, exchangeable with D_2O). Anal. Calcd for $C_{23}H_{22}O_4$: C, 76.22; H, 6.12. Found: C, 76.19; H, 6.10. The ^{1}H NMR spectrum of the residue indicated the existence of considerable amounts of the isomeric ozonides **8c**/**9c**. The signals attributable to other methanol-participated products were not detected. The column chromatography on silica gel gave first a mixture of **8c** and **9c** in a yield of 30% (495 mg), followed by elution of 1-(2-benzoylphenyl)ethyl phenyl ketone[5] (80 mg, 5%).

Ozonolysis of 1,2-Dimethyl-3-phenylindene (4c) in MeOH at −70 °C. Indene **4c** (1.10 g, 5 mmol) was ozonized in a mixed solvent, MeOH–CH_2Cl_2 (20 mL, 1:1 v/v) at −70 °C for 20 min (1.3 equiv of ozone molecule). After workup, the crude products were triturated with ether–hexane to afford the hydroperoxide **13** (426 mg, 28%): mp 136–137 °C (from benzene–hexane); IR 3335 cm^{-1}; ^{1}H NMR δ 1.42 (d, 3 H, J = 7.5 Hz), 1.64 (s, 3 H), 3.16 (q, 1 H, J = 7.5 Hz), 3.43 (s, 3 H), 6.90–7.75 (m, 9 H), 9.08 (s, 1 H, exchangeable with D_2O). Anal. Calcd for $C_{18}H_{20}O_4$: C, 71.98; H, 6.68. Found: C, 71.98; H, 6.68.

The column chromatography of the mother liquor on silica gel gave 33% yield of a mixture of 52% **5c** and 48% **6c**, followed by elution of 1-(2-benzoylphenyl)ethyl methyl ketone (120 mg, 10%): an oil; IR 1720, 1660 cm^{-1}; ^{1}H NMR δ 1.30 (d, 3 H, J = 6.5 Hz), 1.96 (s, 3 H), 3.97 (q, 1 H, J = 6.5 Hz), 7.20–7.83 (m, 9 H).

Registry No. **1a**, 95532-75-5; **1b**, 81706-99-2; **1c**, 22360-62-9; **1d**, 95532-76-6; **1e**, 95532-77-7; **2a**, 95532-78-8; **2b**, 95532-79-9; **2c**, 84810-14-0; **2d**, 95532-80-2; **2e**, 95532-81-3; **3a**, 95588-49-1; **3b**, 95588-50-4; **3c**, 84847-60-9; **3d**, 95588-51-5; **3e**, 95588-52-6; **4a**, 95532-82-4; **4b**, 95532-83-5; **4c**, 42842-58-0; **4d**, 95532-84-6; **4e**, 95532-85-7; **5a**, 95532-86-8; **5b**, 95532-87-9; **5c**, 89619-58-9; **5d**, 95532-88-0; **5e**, 95532-89-1; **6a**, 95588-53-7; **6b**, 95588-54-8; **6c**, 89675-13-8; **6d**, 95588-55-9; **6e**, 95588-56-0; **7a**, 89619-42-1; **7a′**, 89619-43-2; **7b**, 95532-90-4; **7b′**, 95532-91-5; **7c**, 51310-25-9; **7d**, 89619-44-3; **7d′**, 89619-45-4; **7e**, 95532-92-6; **8a**, 89619-65-8; **8a′**, 89619-66-9; **8b**, 95532-93-7; **8b′**, 95532-94-8; **8c**, 84810-15-1; **8d**, 89619-67-0; **8d′**, 89619-68-1; **8e**, 95532-95-9; **9a**, 89707-69-7; **9a′**, 89675-20-7; **9b**, 95671-31-1; **9b′**, 95588-57-1; **9c**, 84847-61-0; **9d**, 89675-21-8; **9d′**, 89675-22-9; **9e**, 95588-58-2; **10**, 95532-96-0; 14, 89619-71-6.

1,3-Oxathiole-2-thiones from the Reaction of Carbon Disulfide with Zwitterionic Iodonium Compounds

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We have synthesized 1,3-oxathiole-2-thiones from the reaction of zwitterionic iodonium compounds with carbon disulfide. The reaction is shown to be photochemical and possible pathways are discussed.

Zwitterionic iodonium compounds (ZIC) are relatively unfamiliar polyvalent iodine compounds, the chemistry of which has recently been reviewed.[1] The majority of ZIC contain two C–I bonds and may be divided into (a) aryliodonium ylides of active methylene compounds[2] (**1**) where the negative charge is dispersed over a system of neighboring bonds usually belonging to keto groups or enolized 1,3-dicarbonyl heterocycles[3] and (b) aryl(oxidoaryl)-

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