Pergamon

Tetrahedron Vol. 50, No. 46, pp. 13113-13120, 1994
Elsevier Science Ltd
Printed in Great Britain
0040-4020/94 $7.00+0.00

0040-4020(94)00856-6

Dioxirane Oxidation of (*Z*)-1-Thioaurones, (*E*)-3-Arylidene-1-thiochroman-4-ones and (*E*)-3-Arylidene-1-thioflavan-4-ones

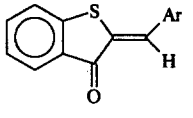
Waldemar Adam,[*,a] Dieter Golsch,[a] Lazaros Hadjiarapoglou,[a] Albert Lévai,[*,b] Csaba Nemes,[b] Tamás Patonay[b]

[a] Institute of Organic Chemistry, University of Würzburg, Am Hubland, D-97074 Würzburg, Germany

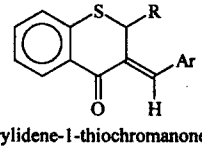
[b] Department of Organic Chemistry, Lajos Kossuth University, H-4010 Debrecen, Hungary

Abstract: The oxidation of the title compounds **1**, **4** and **7** with dimethyldioxirane (DMD) afforded the corresponding sulfoxides **2**, **5** and **8** and/or sulfones **3**, **6** and **9** in good yields (Scheme 1 and 2). Excess dimethyldioxirane gave the sulfones chemoselectively without formation of the epoxides. The epoxidation of the sulfones **6a,b,d** to the respective spiroepoxides **10a,b,d** required the more reactive methyl(trifluoromethyl)dioxirane (TFD) as oxidant.

Previously we have investigated the oxidation of aurones,[1] 3-arylidenechromanones[2] and 3-arylideneflavanones,[3] for which dimethyldioxirane proved to be a convenient oxygen transfer reagent in the preparation of aurone epoxides[1] and *trans* and *cis* spiroepoxides from (*E*)- and (*Z*)-3-arylidenechromanones.[2] We provided a diastereoselective synthesis of *trans,trans* spiroepoxides from (*E*)-3-arylideneflavanones both by isolated dimethyldioxirane and methyl(trifluoromethyl)dioxirane;[3] however, attempted epoxidation of the (*Z*)-3-arylideneflavanones with these two dioxiranes afforded instead the 3-aroylflavones and/or 3-aroylflavanones in low yield.[3] The present paper reports the oxidation of the thio analogues of the above-mentioned oxygen heterocycles with the same oxygen transfer reagents.



(*Z*)-1-thioaurones **1**



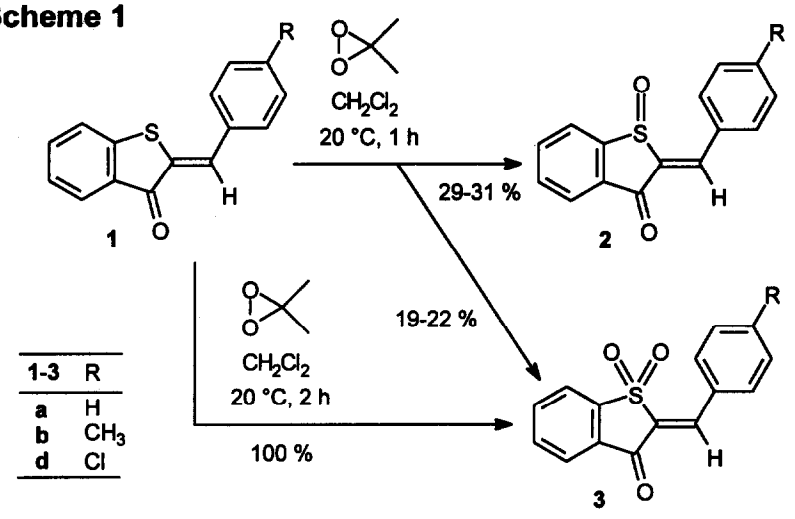
(*E*)-3-arylidene-1-thiochromanones (R = H) **4**
(*E*)-3-arylidene-1-thioflavan-4-ones (R = Ph) **7**

Earlier oxidations of 5-methyl-1-thioaurones were performed with sodium hypochlorite, alkaline hydrogen peroxide and *m*-chloroperoxybenzoic acid to afford various oxidized products, *viz.* 1-oxides, 1,1-dioxides, spiroepoxides, 1-oxide spiroepoxides and 1,1-dioxide spiroepoxides.[4] Thus, alkaline hydrogen peroxide oxidation of 3-arylidene-1-thiochroman-4-ones gave spiroepoxides, which were then further oxidized with hydrogen peroxide in acetic acid to the corresponding 1-oxides or 1,1-dioxides.[5] Sulfoxides of 3-arylidene-1-thiochroman-4-ones have been prepared with hydrogen peroxide in acetic acid by Nishio et al.[6] Furthermore, 3-benzylidene-1-thiochroman-4-one 1,1-dioxides were obtained by hydrogen peroxide oxidation in acetic acid. (*E*)- and (*Z*)-3-Arylidene-1-thioflavan-4-ones gave 1,1-dioxides on their oxidation with *m*-chloroperoxybenzoic acid, while both isomers afforded diastereomeric mixtures of epoxides on oxidation with

sodium hypochlorite or alkaline hydrogen peroxide.[8] To our knowledge, 3-arylidene-1-thioflavan-4-one sulfoxides have not yet been described in the literature.

Dimethyldioxirane (as acetone solution)[9] has proved to be a powerful and convenient oxidant both for α,β-unsaturated ketones[1-3,10-12] and sulfur-containing compounds.[13-15] Such oxidations have not been carried out with thioaurones **1** (Scheme 1) and with 3-arylidene-1-thiochroman-4-ones **4** and 3-arylidene-1- thioflavan-4-ones **7** (Scheme 2). These substrates are of interest because they possess both an α,β-unsaturated ketone unit and a thioether functionality, which are susceptible to oxidation by dimethyldioxirane. For this reason, our aim was to investigate the chemoselectivity of this oxidizing agent with the above sulfur-containing α,β-unsaturated ketones.

Scheme 1



1-3	R
a	H
b	CH_3
d	Cl

Solutions of (*Z*)-1-thioaurones **1a,b,d**, (*E*)-3-arylidene-1-thiochroman-4-ones **4a-e** and (*E*)-3-arylidene-1-thioflavan-4-ones **7a-d** in anhydrous CH_2Cl_2 were allowed to react with isolated dimethyldioxirane in acetone (0.07-0.08 M) at ambient temperature. The amount of the dimethyldioxirane administered determined whether either a mixture of the appropriate sulfoxides **2,5,8** and sulfones **3,6,9**, or pure sulfones **3,6,9** were obtained quantitatively (Tables 1 and 2). The sulfoxides and sulfones were separated by column chromatography. In the case of (*Z*)-1-thioaurones **1a,b,d** the originally yellow mixtures of the sulfoxides **2a,b,d** and sulfones **3a,b,d** turned purple on silica gel during the chromatographic separation due to decomposition of the sulfoxides and thus the low yields.

Sulfones **3,6,9** remained unchanged on addition of further amounts of dimethyldioxirane even after two weeks. Thus, dimethyldioxirane affords sulfoxides and/or sulfones of (*Z*)-1-thioaurones, (*E*)-3-arylidene-1-thiochroman-4-ones and (*E*)-3-arylidene-1-thioflavan-4-ones in a chemoselective sulfur oxidation. (*E*)-3-arylidene-1-thiochroman-4-one 1,1-dioxides **6a,b,d** were allowed to react with isolated methyl(trifluoromethyl)dioxirane (0.48-0.63 M) in trifluoroacetone solution to yield spiroepoxides **10a,b,d** (Table 3). However, (*Z*)-1-thioaurone 1,1-dioxides **3a,b,d** and (*E*)-3-arylidene-1-thioflavan-4-one 1,1-dioxides **9a-d** remained unchanged even on treatment with methyl(trifluoromethyl)dioxirane.

Scheme 2

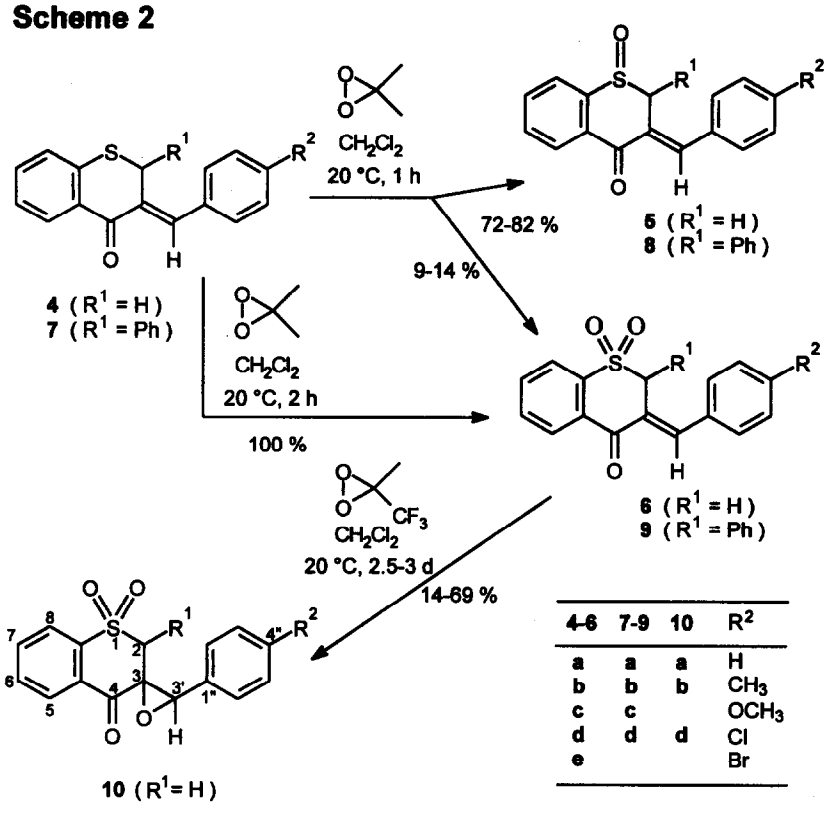


Table 1. Sulfur Oxidation of (*Z*)-1-Thioaurones **1a,b,d** by Dimethyldioxirane (DMD)

Sub-strate	R	DMD[a] (Equiv.)	Sulf-oxide[b]	Yield (%)	mp (°C)	Sulf-one[c]	Yield (%)	mp (°C)
1a	H	1.3	**2a**	29	157-158	**3a**	19	164-165
1b	CH_3	1.4	**2b**	29	174-176	**3b**	22	186-187
1d	Cl	1.4	**2d**	31	197-198	**3d**	21	233-235

[a] In acetone at 20°C for 1 h. - [b] When 2.2 equiv. of DMD were used, the sulfones **3** were obtained quantitatively. - [c] Sulfones **3a,b** were reisolated on treatment with excess DMD (added in 24-h intervals) even after two weeks.

The structure assignment of sulfoxides **2,5,8,** sulfones **3,6,9** and spiroepoxides **10** rests on their characteristic C=O, C=C, SO or SO_2 IR bands (Table 4). The structures of sulfoxides and sulfones were

further corroborated by their ^{1}H NMR spectra in which the methine proton signals (singlets) between 8.10 and 8.64 ppm are characteristic for each molecules.

Chemical shifts and coupling constants of the 2-H protons of substances **5**, **6**, **8**, **9** and **10** are also shown in Table 4. In analogy to the *trans* spiroepoxides obtained from (*E*)-3-arylidenechromanones,[2] the 4.59-4.65 ppm chemical shift value of the 3'-H proton of spiroepoxides **10** corresponds to a *trans* spiroepoxide structure. This assignment was further corroborated by NOE measurements.

Table 2. Sulfur Oxidation of (*E*)-3-Arylidene-1-thiochroman-4-ones **4a-e** and (*E*)-3-Arylidene-1-thioflavan-4-ones **7a-d** by Dimethyldioxirane (DMD)

Sub-strate	R^1	R^2	DMD[a] (Equiv.)	Sulf-oxide[b]	Yield (%)	mp [Lit. mp] (°C)	Sulf-one[c]	Yield (%)	mp [Lit. mp] (°C)
4a	H	H	1.3	**5a**	75	88-90 [99][6]	**6a**	14	164-166 [176][7]
4b	H	CH_3	1.3	**5b**	73	136-138 [142][6]	**6b**	13	156-158
4c	H	OCH_3	1.2	**5c**	78	130-132	**6c**	10	140-142
4d	H	Cl	1.2	**5d**	76	147-149 [148][6]	**6d**	10	166-167
4e	H	Br	1.3	**5e**	72	132-134 [134][6]	**6e**	12	149-150
7a	Ph	H	1.2	**8a**	82	157-159	**9a**	9	142-144
7b	Ph	CH_3	1.3	**8b**	74	174-175	**9b**	11	190-191
7c	Ph	OCH_3	1.3	**8c**	77	174-176	**9c**	11	199-200
7d	Ph	Cl	1.3	**8d**	81	160-162	**9d**	13	183-185

[a] In acetone at 20°C for 1 h. - [b] When 2.2 equiv. of DMD were used, the sulfones **6** and **9** were obtained quantitatively. - [c] Sulfones **6a,b** and **9a,b** were reisolated on treatment with excess DMD (added in 24-h intervals) even after two weeks. -

Table 3. Oxidation of (*E*)-3-Arylidene-1-thiochroman-4-one 1,1-dioxides **6a,b,d** with Methyl(trifluoromethyl)dioxirane[a] (TFD)

Sub-strate	R^1	R^2	TFD (Equiv.)	Temp. (°C)	Time (d)	Epoxide	Yield (%)	mp [Lit. mp] (°C)
6a	H	H	2.5	20	2.5	**10a**	31	151-152 [170-171][5]
6b	H	CH_3	3.0	20	3	**10b**	14	186-187
6d	H	Cl	3.0	20	3	**10d**	69	207-208 [203-205][5]

[a] In all cases, TLC showed considerable decomposition of the starting material and/or product.

Table 4. Spectral Data of Sulfoxides, Sulfones and Epoxides

	Molecular Formula[a]	Molecular mass	IR (KBr) ν (cm^{-1})	^1H NMR ($CDCl_3$/TMS) δ (ppm), *J* (Hz)
2a	$C_{15}H_{10}O_2S$	254.3	1692 (C=O), 1596 (C=C), 1026 (S=O)	8.33 (s, 1H, =CH-)
2b	$C_{16}H_{12}O_2S$	268.3	1692 (C=O), 1598 (C=C), 1024 (S=O)	8.29 (s, 1H, =CH-)
2d	$C_{15}H_9ClO_2S$	288.8	1690 (C=O), 1602 (C=C), 1028 (S=O)	8.26 (s, 1H, =CH-)
3a	$C_{15}H_{10}O_3S$	270.3	1708 (C=O), 1596 (C=C), 1294, 1156 (SO_2)	[b]
3b	$C_{16}H_{12}O_3S$	284.3	1700 (C=O), 1592 (C=C), 1298, 1150 (SO_2)	[b]
3d	$C_{15}H_9ClO_3S$	304.8	1698 (C=O), 1602 (C=C), 1302, 1150 (SO_2)	[b]
5a	$C_{16}H_{12}O_2S$	268.3	1670 (C=O), 1596 (C=C), 1044 (S=O)	4.31 (d, 1H, $^2J_{ax,eq}$ = 12.5, 2-H_{eq}), 4.70 (d, 1H, $^2J_{ax,eq}$ = 12.5, 2-H_{ax}), 8.22 (s, 1H, =CH-)
5b	$C_{17}H_{14}O_2S$	282.4	1660 (C=O), 1590 (C=C), 1044 (S=O)	4.30 (d, 1H, $^2J_{ax,eq}$ = 12.5, 2-H_{eq}), 4.73 (d, 1H, $^2J_{ax,eq}$ = 12.5, 2-H_{ax}), 8.19 (s, 1H, =CH-)
5c	$C_{17}H_{14}O_3S$	298.4	1662 (C=O), 1594 (C=C), 1050 (S=O)	4.32 (d, 1H, $^2J_{ax,eq}$ = 12.2, 2-H_{eq}), 4.77 (d, 1H, $^2J_{ax,eq}$ = 12.2, 2-H_{ax}), 8.17 (s, 1H, =CH-)
5d	$C_{16}H_{11}ClO_2S$	302.8	1668 (C=O), 1598 (C=C), 1042 (S=O)	4.32 (d, 1H, $^2J_{ax,eq}$ = 12.7, 2-H_{eq}), 4.56 (d, 1H, $^2J_{ax,eq}$ = 12.7, 2-H_{ax}), 8.12 (s, 1H, =CH-)
5e	$C_{16}H_{11}BrO_2S$	347.2	1670 (C=O), 1604 (C=C), 1042 (S=O)	4.31 (d, 1H, $^2J_{ax,eq}$ = 12.7, 2-H_{eq}), 4.54 (d, 1H, $^2J_{ax,eq}$ = 12.8, 2-H_{ax}), 8.10 (s, 1H, =CH-)
6a	$C_{16}H_{12}O_3S$	284.3	1672 (C=O), 1606 (C=C), 1314, 1150 (SO_2)	4.65 (s, 2H, 2-H), 8.21 (s, 1H, =CH-)
6b	$C_{17}H_{14}O_3S$	298.4	1666 (C=O), 1582 (C=C), 1312, 1152 (SO_2)	4.68 (s, 2H, 2-H), 8.20 (s, 1H, =CH-)
6c	$C_{17}H_{14}O_4S$	314.4	1666 (C=O), 1588 (C=C), 1316, 1148 (SO_2)	4.70 (s, 2H, 2-H), 8.20 (s, 1H, =CH-)
6d	$C_{16}H_{11}ClO_3S$	318.8	1674 (C=O), 1592 (C=C), 1310, 1154 (SO_2)	4.61 (s, 2H, 2-H), 8.12 (s, 1H, =CH-)
6e	$C_{16}H_{11}BrO_3S$	363.2	1680 (C=O), 1588 (C=C), 1318, 1150 (SO_2)	4.59 (s, 2H, 2-H), 8.11 (s, 1H, =CH-)
8a	$C_{22}H_{16}O_2S$	344.4	1662 (C=O), 1592 (C=C), 1046 (S=O)	6.08 (s, 1H, 2-H), 8.64 (s, 1H, =CH-)
8b	$C_{23}H_{18}O_2S$	358.5	1660 (C=O), 1588 (C=C), 1042 (S=O)	6.08 (s, 1H, 2-H), 8.61 (s, 1H, =CH-)
8c	$C_{23}H_{18}O_3S$	374.5	1662 (C=O), 1588 (C=C), 1042 (S=O)	6.08 (s, 1H, 2-H), 8.60 (s, 1H, =CH-)
8d	$C_{22}H_{15}ClO_2S$	378.9	1670 (C=O), 1598 (C=C), 1048 (S=O)	6.00 (s, 1H, 2-H), 8.55 (s, 1H, =CH-)
9a	$C_{22}H_{16}O_3S$	360.4	1660 (C=O), 1588 (C=C), 1320, 1148 (SO_2)	5.81 (s, 1H, 2-H), 8.39 (s, 1H, =CH-)
9b	$C_{23}H_{18}O_3S$	374.5	1662 (C=O), 1588 (C=C), 1316, 1148 (SO_2)	5.82 (s, 1H, 2-H), 8.38 (s, 1H, =CH-)
9c	$C_{23}H_{18}O_4S$	390.5	1658 (C=O), 1588 (C=C), 1312, 1148 (SO_2)	5.82 (s, 1H, 2-H), 8.36 (s, 1H, =CH-)
9d	$C_{22}H_{15}ClO_3S$	394.9	1668 (C=O), 1592 (C=C), 1318, 1148 (SO_2)	5.73 (s, 1H, 2-H), 8.34 (s, 1H, =CH-)
10a	$C_{16}H_{12}O_4S$	300.3	1688 (C=O), 1330, 1156 (SO_2)	3.42 (d, 1H, $^2J_{ax,eq}$ = 14.5, 2-H_{eq}), 4.00 (d, 1H, $^2J_{ax,eq}$ = 14.4, 2-H_{ax}), 4.65 (s, 1H, 3'-H)
10b	$C_{17}H_{14}O_4S$	314.4	1694 (C=O), 1332, 1156 (SO_2)	3.46 (d, 1H, $^2J_{ax,eq}$ = 14.3, 2-H_{eq}), 3.98 (d, 1H, $^2J_{ax,eq}$ = 14.3, 2-H_{ax}), 4.62 (s, 1H, 3'-H)
10d	$C_{16}H_{11}ClO_4S$	334.8	1694 (C=O), 1326, 1168 (SO_2)	3.34 (d, 1H, $^2J_{ax,eq}$ = 14.3, 2-H_{eq}), 4.02 (d, 1H, $^2J_{ax,eq}$ = 14.3, 2-H_{ax}), 4.59 (s, 1H, 3'-H)

[a] Satisfactory microanalyses obtained: C ±0.18, H ±0.09. - [b] The olefinic proton (=CH-) is overlapped by the aromatic protons.

These sulfur oxidations are not limited to aryl-substituted thioaurones **1**. This is shown in Scheme 3 for the oxidation of vinyl sulfides **12a,b** (Table 5) to their sulfoxides **13a,b** and sulfones **14a,b**. Also in these cases the sulfur atom is chemoselectively oxidized without epoxidation of the C-C double bond. By adjusting the stoichiometry of the DMD oxidant, cleanly the sulfoxides **13** (one equivalent DMD) or the sulfones **14** (three equivalents DMD) may be obtained.

Scheme 3

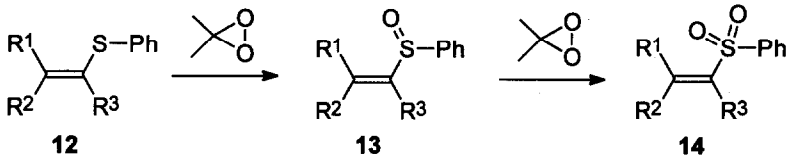
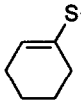


Table 5. Dimethyldioxirane (DMD) Oxidation of Enol Thiol Ethers

Vinyl Sulfide	Temp. (°C)	Time (h)	Equiv. of DMD	Product	Yield (%)
 **12a**	-35	1	1	sulfoxide **13a** [16a]	81
			3	sulfone **14a** [16b]	91
 **12b**	-40	5	1	sulfoxide **13b** [16c]	67
		3.5	3	sulfone **14b** [16d]	62

[a] In CH_2Cl_2 / acetone. - [b] Yield of isolated, pure product after silica gel column chromatography.

In summary, we have described a chemoselective dimethyldioxirane oxidation of (*Z*)-1-thioaurones **1**, (*E*)-3-arylidene-1-thiochroman-4-ones **4** and (*E*)-3-arylidene-1-thioflavan-4-ones **7** to afford the corresponding sulfoxides **2,5,8** and/or sulfones **3,6,9**. Also the vinyl sulfides **12** are chemoselectively oxidized by DMD either to the sulfoxides **13** or sulfones **14**. Moreover, the sulfones **6** of the (*E*)-3-arylidene-1-thiochroman-4-ones **4** have been converted to their previously unknown *trans*-spiroepoxides **10** on treatment with methyl-(trifluoromethyl)dioxirane, which constitute unprecedented epoxidations of highly deactivated double bonds.

Experimental Section

All reagents were of commercial purity. Potassium monoperoxy sulfate, the triple salt $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$, was received as a generous gift from Peroxid-Chemie GmbH (München, Germany). The solvents were purified by following standard literature methods. Analytical TLC plates and silica gel for column chromatography were purchased from Merck. Melting points were taken on a Reichert Thermovar

hot-stage apparatus. Microanalyses were performed in-house on a Carlo Erba 1106 CHN Analyzer. IR spectra were measured on a Perkin-Elmer 16 PC spectrometer, ^{1}H NMR spectra were acquired on a Bruker WP 200 SY (200 MHz) spectrometer.

Dimethyldioxirane[17a] (as acetone solution) and methyl(trifluoromethyl)dioxirane[17b] (as trifluoroacetone solution) were prepared as described, and their peroxide content was determined iodometrically.

Sulfur Oxidation by Dimethyldioxirane; General Procedure:

Dimethyldioxirane in acetone (0.07-0.08 M), stored over molecular sieves (4 Å) at -20 °C, was rapidly added to solutions of the particular sulfur-containing substrate (1.22-2.92 mmol) in dry CH_2Cl_2 (10 mL). The reaction progress was monitored by the peroxide test (KI / HOAc) and additional batches of dimethyldioxirane solution were administered until complete consumption (TLC) of the starting compound. The solvent was removed at reduced pressure (ca. 25°C / 20 Torr) and the residue was submitted to column chromatography [hexane : acetone (8:2 v/v) and hexane : ethyl acetate (7:3 v/v) as eluents] to yield the corresponding sulfoxides and sulfones. When the dimethyldioxirane addition was continued until only one product could be detected, removal of the solvent afforded the corresponding sulfones quantitatively.

Epoxidation of the Sulfones 6 by Methyl(trifluoromethyl)dioxirane; General Procedure:

The dioxirane in trifluoroacetone (0.48-0.63 M) was added rapidly to a stirred solution of the particular sulfone (0.63-0.70 mmol) in dry CH_2Cl_2 (15 mL) under an oxygen gas atmosphere. The stirring was continued for 12 h and a new batch of methyl(trifluoromethyl)dioxirane (0.5 equiv.) solution was rapidly added. The dioxirane (0.5 equiv.) addition was continued in 12-h intervals until ca. 90 % conversion (monitored by TLC) of the starting sulfone **6** was obtained. The solvent was removed under reduced pressure (ca. 25°C / 20 Torr) and the residue was submitted to column chromatography [chloroform : hexane (6:4 v/v) as eluent] to yield the epoxides **10**.

Acknowledgement

The work in Debrecen was sponsored by the Hungarian Research Foundation (Grant No. OTKA T7459) and by the European Communities (COST Project ERBCIPECT 926003 8385), for which our gratitude is expressed. The work in Würzburg was supported by the Deutsche Forschungsgemeinschaft (SFB 347 "Selektive Reaktionen Metall-aktivierter Moleküle") and the Fonds der Chemischen Industrie. Technical assistance of Mrs. M. Nagy is highly appreciated. C.N. thanks the UNIVERSITAS Foundation of the Hungarian Commercial Bank (Debrecen, Hungary) for a doctoral fellowship.

REFERENCES

1. Adam, W.; Hadjiarapoglou, L.; Lévai, A. *Synthesis* **1992**, 436.
2. Adam, W.; Halász, J.; Lévai, A.; Nemes, C.; Patonay, T.; Tóth, G. *Liebigs Ann. Chem.*, in press.
3. Nemes, C.; Lévai, A.; Patonay, T.; Tóth, G.; Boros, S.; Halász, J.; Adam, W.; Golsch, D. *J. Org. Chem.* **1994**, *59*, 900.
4. a) Réamonn, L.S.S.; O'Sullivan, W.I. *J. Chem. Soc. Chem. Commun.* **1976**, 642. - b) Réamonn, L.S.S.; O'Sullivan, W.I. *J. Chem. Soc. Chem. Commun.* **1976**, 1012. - c) Réamonn, L.S.S.; O' Sullivan, W.I. *J. Chem. Soc., Perkin Trans. 1* **1980**, 1194.
5. Hofmann, H.; Westernacher, H. *Chem. Ber.* **1969**, *102*, 205.
6. Nishio, M.; Ichiume, K.; Ito, T.; Koeda, T.; Shibata, U. *Japan Patent* 70 26,099 (1970); *Chem. Abstr.* **1970**, *73*, 130890h.
7. Nambara, T.; Takemori, Y.; Okamoto, S. *Yakugaku Zasshi* **1961**, *81*, 1.; *Chem. Abstr.* **1961**, *55*, 12397.
8. Beirne, J.J.; O'Sullivan, W.I. *Proc. R. Ir. Acad.* **1977**, *77b*, 331, 337.
9. a) Murray, R.W. in *Modern Models of Bonding and Delocalization*; Liebmann, J.F.; Greenberg, A., Eds.; VCH Publishers: New York, 1988; p. 311. - b) Adam, W.; Curci, R.; Edwards, J.O. *Acc. Chem. Res. 1989, 22*, 205. - c) Murray, R.W. *Chem. Rev.* **1989**, *89*, 1187. - d) Curci, R. In *Advances in Oxygenated Processes;* Baumstark, A.L., Ed.; JAI Press: Greenwich, 1990; Vol. 2, p. 1. - e) Adam, W.; Hadjiarapoglou, L. *Top. Curr. Chem.* **1993**, *164*, 45. - f) Adam, W.; Hadjiarapoglou, L.; Curci, R.; Mello, R. In *Organic Peroxides;* Ando, W., Ed.; Wiley: New York, 1993; p. 195.
10. Adam, W.; Hadjiarapoglou, L.; Smerz, A. *Chem. Ber.* **1991**, *124*, 227.
11. Adam, W.; Hadjiarapoglou, L.; Nestler, B. *Tetrahedron Lett.* **1990**, *31*, 331.
12. Adam, W.; Bialas, J.; Hadjiarapoglou, L.; Patonay, T. *Synthesis*, **1992**, 49.
13. a) Adam, W.; Haas, W.; Lohray, B.B. *J. Am. Chem. Soc. 1991,* **113**, 6202. - b) Adam, W.; Chan, Y.Y.; Cremer, D.; Gauss, J.; Scheutzow, D.; Schindler, M. *J. Org. Chem.* **1987**, *52*, 2800. - c) Adam, W.; Golsch, D. *Chem. Ber.* **1994**, *127*, 1111.
14. Murray, R.W.; Jeyaraman, R.; Pillay, M.K. *J. Org. Chem.* **1987**, *52*, 746.
15. Clennan, E.L.; Yang, K. *J. Org. Chem.* **1993**, *58*, 4504.
16. a) Parham, W.E.; Edwards, L.D. *J. Org. Chem.* **1968**, *33*, 4150. - b) Akasaka, T.; Misawa, Y.; Goto, M.; Ando, W. *Tetrahedron Lett.* **1989**, *45*, 6657. - c) De Lucchi, O.; Marchioro, G.; Modena, G. *J. Chem. Soc., Chem. Commun.* **1984**, 513. - d) Trost, B.M.; Braslau, R. *J. Org. Chem.* **1988**, *53*, 532.
17. a) Adam, W.; Bialas, J.; Hadjiarapoglou, L. *Chem. Ber.* **1991**, *124*, 2377. - b) Mello, R.; Fiorentino, M.; Sciacovelli, O.; Curci, R. *J. Org. Chem.* **1988**, *53*, 3890.

(*Received in Germany* 24 *August* 1994; *revised* 26 *September* 1994; *accepted* 28 *September* 1994)