Chem. Pharm. Bull.
30(2) 526—533 (1982)

New Methods and Reagents in Organic Synthesis. 19.[1] Synthesis and Rearrangement of α-Acylsulfonyldiazomethanes (α-Diazo-β-ketosulfones)[2]

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(Received July 1, 1981)

Sulfonyldiazomethanes (**1**), as stable and safe substitutes for hazardous diazomethane, have been conveniently acylated with acyl chlorides in the presence of triethylamine in acetonitrile to give α-acylsulfonyldiazomethanes (α-diazo-β-ketosulfones, **3**) in good yields. Investigation of their thermal behavior in the presence of benzyl alcohol has revealed that Wolff rearrangement occurs to give α-sulfonylacetates (**4**). The overall process may provide a new, safe method for the Arndt-Eistert synthesis of α-sulfonylacetates (**4**) from carboxylic acid chlorides.

Keywords——sulfonyldiazomethane; α-diazosulfone; α-acylsulfonyldiazomethane; Wolff rearrangement; Arndt-Eistert synthesis; acylation; benzyl alcohol; diazomethane; α-sulfonylacetate; α-diazo-β-ketosulfone; thermal rearrangement

We have proposed in our preceding papers[1,3,4,5,6] the use of trimethylsilyldiazomethane ($(CH_3)_3SiCHN_2$) in organic synthesis as a stable and safe substitute for hazardous diazomethane. Trimethylsilyldiazomethane has been used efficiently for the Arndt-Eistert synthesis,[3] the homologation of ketones[1,4] and aldehydes,[5] and the preparation of methyl esters.[6] The stability of trimethylsilyldiazomethane to heat and its non-explosive character are due to its pπ-dπ resonance between carbon and silicon.

Sulfonyldiazomethanes (α-diazosulfones, **1**),[7] in general, are known to be stable and non-explosive, because their diazo function is stabilized by the sulfone group owing to its electron-withdrawing character as well as the pπ-dπ resonance. Our recent interest in making hazardous reactions safe led us to investigate the synthetic use of sulfonyldiazomethanes (**1**).

The preparation of the first representative of **1** was accomplished by Strating and van Leusen[8] in 1962, and they established a general method for the preparation of **1**.[7a,9] The chemical properties of sulfonyldiazomethanes (**1**) have been investigated since they are structurally related to acyldiazomethanes (**2**), which are of considerable significance in organic chemistry. α-Acylsulfonyldiazomethanes (α-diazo-β-ketosulfones, **3**), which can be regarded as acyl derivatives of **1** or sulfonyl derivatives of **2**, may have chemical properties of both **1** and **2**, but there are very few reports on their reactivities except for the photolysis[10] and deacylation[11] of **3**.

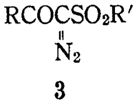
We now describe the preparation of α-acylsulfonyldiazomethanes (**3**) by the acylation of sulfonyldiazomethanes (**1**) and the thermal Wolff rearrangement of α-acylsulfonyldiazomethanes (**3**) in the presence of alcohols. The overall process is depicted in Chart 1, which shows the Arndt-Eistert synthesis of α-sulfonylacetates (**4**) from carboxylic acid chlorides.

$R'SO_2CHN_2$

1

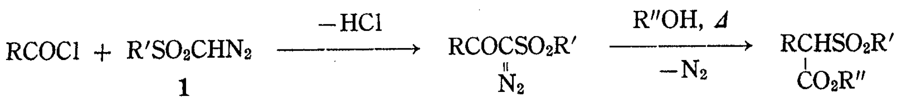
$RCOCHN_2$

2



$$\underset{\substack{\| \\ \mathrm{N_2}}}{\mathrm{RCOCSO_2R'}}$$

3



$$\mathrm{RCOCl} + \underset{\mathbf{1}}{\mathrm{R'SO_2CHN_2}} \xrightarrow{-\mathrm{HCl}} \underset{\substack{\| \\ \mathrm{N_2}}}{\mathrm{RCOCSO_2R'}} \xrightarrow[-\mathrm{N_2}]{\mathrm{R''OH},\ \Delta} \underset{\substack{| \\ \mathrm{CO_2R''}}}{\mathrm{RCHSO_2R'}}$$

3 **4**

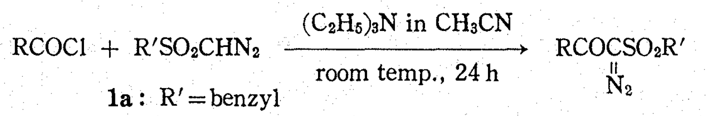
Chart 1

Synthesis of α-Acylsulfonyldiazomethanes

α-Acylsulfonyldiazomethanes (3) were previously prepared[11,12)] by the action of *p*-toluenesulfonyl azide on β-ketosulfones under basic conditions but the yields were not usually high. Since sulfonyldiazomethanes (1) are easily prepared by the method of van Leusen,[7a,8,9)] we thought that the acylation of **1** with carboxylic acid chlorides would be the method of choice to obtain α-acylsulfonyldiazomethanes.

In fact, benzoyl chloride easily reacted with various sulfonyldiazomethanes (**1a**—**d**) at room temperature in the presence of triethylamine in acetonitrile to provide α-benzoylsulfonyldiazomethanes (**3a**—**d**) in good yields. The experimental procedure is quite similar to the acylation of trimethylsilyldiazomethane.[3)] Since benzylsulfonyldiazomethane (**1a**) is very stable and easy to prepare, various carboxylic acid chlorides were allowed to react with **1a** as described above. As summarized in Table I, most of the acylated benzylsulfonyldiazomethanes (3) were obtained in good yields.

TABLE I. Acylation of Sulfonyldiazomethanes



$$\mathrm{RCOCl} + \mathrm{R'SO_2CHN_2} \xrightarrow[\text{room temp., 24 h}]{(\mathrm{C_2H_5})_3\mathrm{N\ in\ CH_3CN}} \mathrm{RCO}\underset{\mathrm{N_2}}{\overset{}{\underset{\|}{\mathrm{C}}}}\mathrm{SO_2R'}$$

1a: R′ = benzyl
1b: R′ = *tert*-butyl
1c: R′ = *p*-tolyl
1d: R′ = *p*-anisyl

3

Compd. No.	R	R′	Yield (%)
3a	Phenyl	Benzyl	87
3b	Phenyl	*tert*-Butyl	82
3c	Phenyl	*p*-Tolyl	80[a)]
3d	Phenyl	*p*-Anisyl	80
3e	*p*-Chlorophenyl	Benzyl	82
3f	*m*-Chlorophenyl	Benzyl	84
3g	*p*-Anisyl	Benzyl	84
3h	α-Naphthyl	Benzyl	82
3i	2-Furyl	Benzyl	87
3j	*trans*-Styryl	Benzyl	29
3k	β-Phenethyl	Benzyl	76
3l	Isopropyl	Benzyl	80
3m	Cyclohexyl	Benzyl	89

a) The reaction time was 43 h.

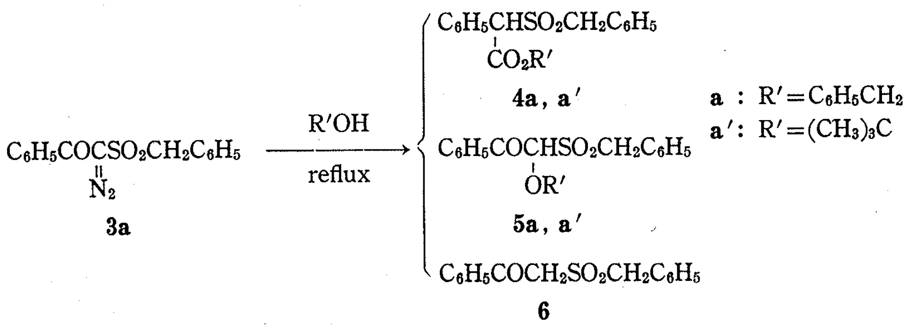
Wolff Rearrangement of α-Acylsulfonyldiazomethanes

In 1967, van Leusen and co-workers[10)] reported that the photolysis of α-acetyl- and α-benzoyl-α-(*p*-tolylsulfonyl)diazomethanes afforded the Wolff rearrangement products in low yields.[13)] Since then, no studies directed to the preparative use of the Wolff rearrangement of α-acylsulfonyldiazomethanes have been reported. Thus we investigated the Wolff rearrangement of α-benzoylsulfonyldiazomethanes (**3a**—**d**). Since the acylated trimethylsilyldiazomethanes easily underwent the Wolff rearrangement in the presence of benzyl alcohol in 2,4,6-trimethylpyridine at 180°C for several minutes,[3)] similar reaction conditions were applied to α-benzoylsulfonyldiazomethanes. In fact, when α-benzoyl-α-(benzylsulfonyl)diazomethane (**3a**) was refluxed in 2,4,6-trimethylpyridine in the presence of benzyl alcohol at 190—200°C for 10 minutes, a Wolff rearrangement product (**4a**) was obtained in 36% yield. However, a benzyl ether (**5a**) and a ketosulfone (**6**) were also formed in 18 and 28% yields, respectively. The reaction intermediate is apparently α-benzoylsulfonylcarbene ($\mathrm{C_6H_5CO\ddot{C}SO_2CH_2C_6H_5}$, **7**), which will insert into the H–O bond of benzyl alcohol to give the benzyl ether (**5a**). The ketosulfone (**6**) can be formed from the carbene (**7**) by the abstraction of hydrogens from benzyl alcohol.[10] The Wolff rearrangement, however, proceeded at much lower temperatures and refluxing in benzene or, preferably, refluxing in toluene afforded the α-sulfonylacetate (**4a**) in good yield, as shown in Table II. When the nucleophile was changed from benzyl alcohol to *tert*-butyl alcohol, the *tert*-butyl ether (**5a′**) was the main product together with some of the α-sulfonylacetate (**4a′**). Interestingly, treatment of **3a** with ethyl alcohol afforded the ketosulfone (**6**) as the sole isolable product.

The other α-benzoylsulfonyldiazomethanes (**3b**—**d**) also underwent the thermal Wolff rearrangement under similar reaction conditions to give α-sulfonylacetates (**4b**—**d**) in good to moderate yields, as shown in Table III.

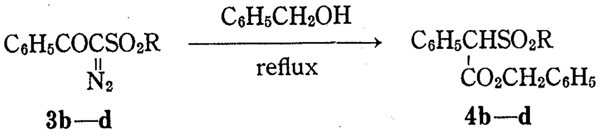
The use of acetonitrile as a solvent for the Wolff rearrangement is worthy of comment. The rearrangement occurred in refluxing acetonitrile to give α-sulfonylacetates (**4**), but con-

Table II. Wolff Rearrangement of α-Benzoyl-α-(benzylsulfonyl)diazomethane (**3a**)



Run	R′OH	Reaction		Yield (%) of		
		Solvent	Time (h)	4	5	6
1	$C_6H_5CH_2OH$	2,4,6-Trimethylpyridine	10 min	36	18	28
2	$C_6H_5CH_2OH$	Benzene	4	23	8	—
3	$C_6H_5CH_2OH$	Benzene	64	66	33	—
4	$C_6H_5CH_2OH$	Toluene	4	92	7	—
5	$(CH_3)_3COH$	2,4,6-Trimethylpyridine	73	27	54	—
6	CH_3CH_2OH	2,4,6-Trimethylpyridine	7	—	—	67

Table III. Wolff Rearrangement of α-Benzoylsulfonyldiazomethanes (**3b**—**d**)

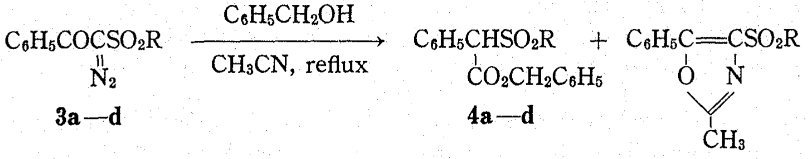


Run	Starting material	R	Reaction		Product	Yield (%)
			Solvent	Time (h)		
1	**3b**	*tert*-Butyl	2,4,6-Trimethylpyridine	10 min	**4b**	64[a]
2	**3b**	*tert*-Butyl	Benzene	22.5	**4b**	91
3	**3b**	*tert*-Butyl	Toluene	5	**4b**	95
4	**3c**	*p*-Tolyl	2,4,6-Trimethylpyridine	10 min	**4c**	46
5	**3c**	*p*-Tolyl	Benzene	20	**4c**	74
6	**3c**	*p*-Tolyl	Toluene	2	**4c**	82
7	**3d**	*p*-Anisyl	2,4,6-Trimethylpyridine	10 min	**4d**	39
8	**3d**	*p*-Anisyl	Benzene	24	**4d**	34
9	**3d**	*p*-Anisyl	Toluene	1	**4d**	41

a) Accompanied by α-benzyloxy-α-(*tert*-butylsulfonyl)acetophenone (8%) and α-(*tert*-butylsulfonyl)acetophenone (15%).

siderable amounts of sulfonyloxazole derivatives (**8**) were formed, as shown in Table IV. When the thermal rearrangement of **3a** in acetonitrile was carried out without benzyl alcohol, the sulfonyloxazole (**8a**) was obtained together with dibenzylsulfone. The sulfonyloxazoles (**8**) are presumably formed from the intermediary α-benzoylsulfonylcarbenes by 1,3-dipolar addition to acetonitrile.[14] A part of the α-benzoylsulfonylcarbene (**7**) derived from **3a** may undergo the Wolff rearrangement to give benzylsulfonyl phenyl ketene which would ultimately yield dibenzylsulfone.

TABLE IV. Wolff Rearrangement of α-Benzoylsulfonyldiazomethanes (**3a**—**d**) in Acetonitrile



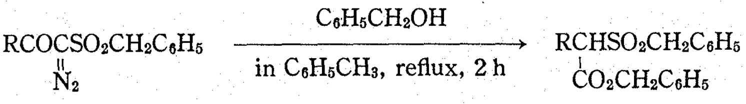
3a—**d** **4a**—**d** **8a**—**c**

Run	Starting material	R	Reaction time (h)	Yield (%)	
				4	8
1	**3a**	Benzyl	66	**4a** (41)	**8a** (59)
2	**3a**	Benzyl	60	—[a]	**8a** (63)
3	**3b**	*tert*-Butyl	62	**4b** (62)	**8b** (24)
4	**3c**	*p*-Tolyl	48	**4c** (33)	**8c** (24)
5	**3d**	*p*-Anisyl	45	**4d** (37)	—[b]

[a] Benzyl alcohol was not used. Dibenzylsulfone was obtained in 36% yield.
[b] The oxazole derivative could not be isolated.

The above experiments on α-benzoylsulfonyldiazomethanes (**3a**—**d**) revealed that the Wolff rearrangement of α-acylated sulfonyldiazomethanes (**3e**—**m**) proceeds smoothly in refluxing toluene in the presence of benzyl alcohol. Indeed, when **3e**—**m** were refluxed in toluene together with benzyl alcohol for 2 h, the thermal Wolff rearrangement efficiently occurred to give α-sulfonylacetates (**4e**—**m**) in good yields. The results are summarized in Table V.

TABLE V. Wolff Rearrangement of α-Acyl-α-(benzylsulfonyl)diazomethanes



$$\underset{\underset{\displaystyle N_2}{\|}}{RCOCSO_2CH_2C_6H_5} \xrightarrow[\text{in } C_6H_5CH_3\text{, reflux, 2 h}]{C_6H_5CH_2OH} \underset{\underset{\displaystyle CO_2CH_2C_6H_5}{|}}{RCHSO_2CH_2C_6H_5}$$

3e—**m** **4e**—**m**

Compd. No.	R	Yield (%)
4e	*p*-Chlorophenyl	70
4f	*m*-Chlorophenyl	54
4g	*p*-Anisyl	82
4h	α-Naphthyl	83
4i	2-Furyl	59[a]
4j	*trans*-Styryl	73[b]
4k	β-Phenethyl	66
4l	Isopropyl	86
4m	Cyclohexyl	96

[a] Reflux for 16 h. [b] Reflux for 6 h.

Since acylation of benzylsulfonyldiazomethane (**1a**) followed by the Wolff rearrangement of the resulting α-acylated benzylsulfonyldiazomethanes (**3**) proceeds smoothly and conveniently, the overall process provides a new, safe method for the Arndt-Eistert synthesis of α-sulfonylacetates (**4**) from carboxylic acid chlorides.

Experimental

General experimental procedures employed are essentially the same as described in our previous paper.[1,3] All the crystalline products were recrystallized from either diethyl ether or diethyl ether–hexane. Benzylsulfonyldiazomethane (**1a**) was prepared as described below, according to one of the general methods for the preparation of sulfonyldiazomethanes.[9] Other sulfonyldiazomethanes (**1b**—**d**) were prepared as described by van Leusen and Strating.[9,15]

***N*-(Benzylsulfonylmethyl)urethane**——Prepared by the known method,[16] which we slightly modified as follows. To a solution of sodium sulfite heptahydrate (100.9 g, 0.4 mol) in water (200 ml) was added benzylsulfonyl chloride (38.8 g, 0.2 mol) and sodium bicarbonate (33.6 g, 0.4 mol) at 70—80°C during 2 h. The mixture was stirred at 70—80°C for 24 h, cooled, and acidified with formic acid to pH 3. Ethyl carbamate (35.6 g, 0.4 mol) and 35% formalin (130 ml, 1.6 mol) were added to the acidified mixture (which contained precipitates), and the whole was stirred at 60°C for 24 h. The precipitates were collected, washed with water, and dried to give *N*-(benzylsulfonylmethyl)urethane (37.6 g, 73%); mp 115—117°C (from ethanol) (lit.[16] mp 114.5—115°C).

***N*-(Benzylsulfonylmethyl)-*N*-nitrosourethane**——Prepared as described in the literature.[9]

Benzylsulfonyldiazomethane (1a)——To alumina (300 g) suspended in diethyl ether (600 ml) was added *N*-(benzylsulfonylmethyl)-*N*-nitrosourethane (28.6 g, 0.1 mol) in methylene chloride (150 ml) at 0°C.[15] The mixture was stirred well for 2 h at 0°C, and the solution was decanted from the alumina. Diethyl ether (400 ml) and methylene chloride (200 ml) were added to the alumina, and the mixture was stirred for 2 h at 0°C, then the solution was decanted off. This work-up was repeated twice more. The combined decanted solutions were filtered and evaporated to dryness *in vacuo* to give benzylsulfonyldiazomethane (**1a**, 13.65 g, 70%), mp 96.5—99°C (lit.[9] mp 98—99°C).

Acylation of Sulfonyldiazomethanes——General Procedure: To a mixture of a sulfonyldiazomethane (**1**, 5.0 mmol) and triethylamine (557 mg, 5.5 mmol) in acetonitrile (50 ml) was added dropwise an acyl chloride (5.5 mmol) at 0°C or at room temperature. The mixture was stirred at room temperature for 24 h, then concentrated *in vacuo*. The residue was purified by silica gel (90—200 g) column chromatography with hexane–ethyl acetate (10—7: 1) to give an α-acylated sulfonyldiazomethane (**3**). The results are summarized in Tables I and VI.

TABLE VI. Analytical and Spectral Data for α-Acylsulfonyldiazomethanes (3)

Compd. No.	mp (dec) (°C)	Formula	Analysis (%) Calcd (Found)			IR $\nu_{\max}^{\text{Nujol}}$ cm^{-1}			NMR(CDCl$_3$) δ (ppm) CH$_2$SO$_2$ (2H, s)
			C	H	N	N$_2$	CO	SO$_2$	
3a	83.5—84.5	$C_{15}H_{12}N_2O_3S$	59.99 (60.09	4.03 3.96	9.33 9.59)	2120	1645	1340 1155	4.72
3b	132—133	$C_{12}H_{14}N_2O_3S$	54.12 (53.69	5.30 5.28	10.52 10.47)	2120	1660	1320 1125	1.48(9H, s, $(CH_3)_3C$)
3c	101—103	$C_{15}H_{12}N_2O_3S$	59.99 (60.15	4.03 3.98	9.33 9.33)	2120	1655	1335 1150	2.44 (3H, s, CH_3)
3d	108.5—110	$C_{15}H_{12}N_2O_4S$	56.95 (56.78	3.83 3.70	8.86 8.60)	2120	1650	1340 1150	3.86 (3H, s, CH_3O)
3e	114.5—116	$C_{15}H_{11}ClN_2O_3S$	53.82 (53.74	3.31 3.15	8.37 8.68)	2140	1640	1340 1150	4.72
3f	110—112	$C_{15}H_{11}ClN_2O_3S$	53.82 (53.91	3.31 3.15	8.37 8.47)	2120	1650	1330 1155	4.70
3g	94—96	$C_{16}H_{14}N_2O_4S$	58.17 (58.39	4.27 4.19	8.48 8.62)	2120	1650	1340 1140	4.72
3h	128—129	$C_{19}H_{14}N_2O_3S$	65.13 (65.04	4.03 3.97	7.99 8.39)	2140	1640	1345 1160	4.82
3i	121—122.5	$C_{13}H_{10}N_2O_4S$	53.79 (53.89	3.47 3.35	9.65 9.93)	2140	1635	1335 1140	4.68
3j	109.5—111	$C_{17}H_{14}N_2O_3S$	62.56 (62.52	4.32 4.18	8.58 8.87)	2160	1650	1340 1155	4.56
3k	58—60	$C_{17}H_{16}N_2O_3S$	62.18 (62.43	4.91 4.98	8.53 8.77)	2120	1655	1340 1150	4.38
3l	80.5—81.5	$C_{12}H_{14}N_2O_3S$	54.12 (53.88	5.30 5.20	10.52 10.86)	2120	1655	1330 1140	4.60
3m	67.5—69	$C_{15}H_{18}N_2O_3S$	58.80 (59.01	5.92 5.95	9.14 9.11)	2120	1655	1330 1145	4.56

Wolff Rearrangement of α-Benzoyl-α-(benzylsulfonyl)diazomethane (3a) in 2,4,6-Trimethylpyridine——(a) With Benzyl Alcohol (Run 1 in Table II): A mixture of **3a** (150 mg, 0.5 mmol), benzyl alcohol (2 ml), and 2,4,6-trimethylpyridine (2 ml) was refluxed at 190—200°C in a preheated oil bath for 10 min, then concentrated *in vacuo* to remove benzyl alcohol and 2,4,6-trimethylpyridine. The residue was chromatographed over silica gel (30 g) with hexane–ethyl acetate (10: 1). The first fraction to be eluted contained a mixture (103 mg) of **4a** and **5a** (2: 1), the ratio of which was determined by nuclear magnetic resonance (NMR) spectroscopy. The yields of **4a** and **5a** were 36 and 18%, respectively. The second fraction to be eluted containing **6** (39 mg, 28%).

(b) With *tert*-Butyl Alcohol (Run 5 in Table II): A mixture of **3a** (300 mg, 1 mmol), *tert*-butyl alcohol (5 ml), and 2,4,6-trimethylpyridine (2 ml) was refluxed for 73 h. *tert*-Butyl alcohol was added 4 times (5 ml each) during the reaction. The reaction mixture was concentrated and diluted with chloroform. The chloroform solution was washed with 1 N hydrochloric acid and saturated aqueous sodium chloride, and dried over magnesium sulfate. The solution was evaporated to dryness, and the residue was chromatographed over silica gel (16 g) with hexane–ethyl acetate (10: 1) to give a mixture (279 mg) of **4a′** and **5a′** (1: 2 by NMR measurement). The yields of **4a′** and **5a′** were 27 and 54%, respectively. Silica gel column chromatography of the mixture with hexane–diethyl ether (15: 1) afforded pure samples of **4a′** from the first fraction and **5a′** from the second fraction.

(c) With Ethyl Alcohol (Run 6 in Table II): A mixture of **3a** (601 mg, 2 mmol), ethyl alcohol (4 ml), and 2,4,6-trimethylpyridine (2 ml) was refluxed for 7 h, then concentrated. The residue was dissolved in chloroform, and washed with 1 N hydrochloric acid. The mixture was dried over magnesium sulfate and evaporated to dryness to give a solid residue, which was washed with hexane–diethyl ether to give **6** (368 mg, 67%).

Runs 2—4 in Table II were carried out as described below in the general procedure for the Wolff rearrangement of 3 in toluene. Analytical and spectral data for **4a**, **4a′**, **5a**, **5a′**, and **6** are summarized in Table VII.

Wolff Rearrangement of α-Benzoyl-α-(*tert*-butylsulfonyl)diazomethane (3b)——(a) In 2,4,6-Trimethylpyridine (Run 1 in Table III): A mixture of **3b** (133 mg, 0.5 mmol), benzyl alcohol (2 ml), and 2,4,6-trimethylpyridine (2 ml) was refluxed at 190—200°C in a preheated oil bath for 10 min, and concentrated *in vacuo* to remove benzyl alcohol and 2,4,6-trimethylpyridine. The crude residue was purified by silica gel preparative layer chromatography (PLC) with hexane–ethyl acetate (2: 1). A mixture (125 mg) of **4b** and α-benzyloxy-α-(*tert*-butylsulfonyl)acetophenone was obtained from the *Rf* 0.4 layer. The ratio of **4b** and the latter was 25: 3 as judged by NMR measurement (64 and 8% yields, respectively).

α-(*tert*-Butylsulfonyl)acetophenone (18 mg, 15%) was obtained from *Rf* 0.2 layer; IR $\nu_{\text{max}}^{\text{Nujol}}$ cm^{-1}: 1680, 1300, 1120. NMR δ ppm (in $CDCl_3$): 1.52 (9H, s, $(CH_3)_3C$), 4.64 (2H, s, CH_2), 7.4—8.3 (5H, m, aromatic H).

(b) In Benzene or Toluene (Run 2 or 3 in Table III): The reactions were carried out as described below in the general procedure for the Wolff rearrangement of 3 in toluene. The analytical and spectral data for **4b** are shown in Table VII.

TABLE VII. Analytical and Spectral Data for the Products derived from α-Benzoylsulfonyldiazomethanes (3a—d)

Compd. No.	mp (°C)	Formula	Analysis (%) Calcd (Found)		IR $\nu_{\text{max}}^{\text{Nujol}}$ cm^{-1}		NMR ($CDCl_3$) δ (ppm)			
			C	H	CO	SO_2	CH_2SO_2 (2H)a)	CH (1H, s)	OCH_2 (2H)a)	Others
4a	86—87	$C_{22}H_{20}O_4S$	69.46 (69.28	5.30 5.20)	1730	1320 1155	4.11, 4.53	4.98	5.20, 5.32	—
4a′	114—114.5	$C_{19}H_{22}O_4S$	65.87 (65.66	6.40 6.49)	1730	1325 1135	4.09, 4.59	4.84	—	1.52 (9H, s, $(CH_3)_3C$)
5a	132—133	$C_{22}H_{20}O_4S$	69.46 (69.20	5.30 5.16)	1675	1310 1130	4.26, 4.50	5.51	4.74, 4.88	—
5a′	126—127	$C_{19}H_{22}O_4S$	65.87 (65.93	6.40 6.45)	1670	1325 1110	4.31, 4.53	5.76	—	1.24 (9H, s, $(CH_3)_3C$)
6	110—112	$C_{15}H_{14}O_3S$	65.67 (65.26	5.14 4.99)	1690	1305 1145	4.40 (2H, s)	—	—	4.56 (2H, s, CH_2CO)
4b	104.5—105.5	$C_{19}H_{23}O_4S$	65.68 (65.61	6.67 6.44)	1740	1305 1115	—	5.18	5.06, 5.20	1.28 (9H, s, $(CH_3)_3C$)
4c	125—126	$C_{22}H_{20}O_4S$	69.46 (69.37	5.30 5.35)	1730	1325 1145	—	5.12	5.06, 5.21	2.38 (3H, s, CH_3)
4d	116—117	$C_{22}H_{20}O_5S$	66.64 (66.56	5.09 4.88)	1730	1325 1150	—	5.12	5.10, 5.26	3.84 (3H, s, CH_3O)

a) AB type quartet (J=12—14 Hz), unless otherwise stated.

Wolff Rearrangement of α-Benzoyl-α-(*p*-tolylsulfonyl)diazomethane (3c)——(a) In 2,4,6-Trimethylpyridine (Run 4 in Table III): The reaction and work-up were carried out as described for the Wolff rearrangement of **3b**. The crude residue was purified by column chromatography over silica gel with hexane–ethyl acetate (9: 1) to give **4c** (46%).

(b) In Benzene or Toluene (Run 5 or 6 in Table III): The reactions were carried out as described below in the general procedure for the Wolff rearrangement of 3 in toluene. The analytical and spectral data for **4c** are shown in Table VII.

Wolff Rearrangement of α-Benzoyl-α-(*p*-anisylsulfonyl)diazomethane (3d)——(a) In 2,4,6-Trimethylpyridine (Run 7 in Table III): The reaction and the work-up were carried out as described for the Wolff rearrangement of **3b**. The crude residue was purified by column chromatography over silica gel with hexane–ethyl acetate (9: 1) to give **4d** (39%).

(b) In Benzene or Toluene (Run 8 or 9 in Table III): The reactions were carried out as described below in the general procedure for the Wolff rearrangement of 3 in toluene. The analytical and spectral data for **4d** are shown in Table VII.

Wolff Rearrangement of α-Benzoyl-α-(benzylsulfonyl)diazomethane (3a) **in Acetonitrile**——(a) With Benzyl Alcohol (Run 1 in Table IV): A mixture of **3a** (150 mg, 0.5 mmol) and benzyl alcohol (108 mg, 1 mmol) in acetonitrile (25 ml) was refluxed for 66 h. The mixture was concentrated and benzyl alcohol was removed *in vacuo*. The residue was separated by PLC on silica gel with hexane–ethyl acetate (2: 1) to give **4a** (78 mg, 41%, *Rf* 0.4) and the oxazole (**8a**, 92 mg, 59%, *Rf* 0.2). The analytical and spectral data for the oxazole (**8a**) are shown in Table VIII.

TABLE VIII. Analytical and Spectral Data for the Oxazoles (**8**)

Compd. No.	mp (°C)	Formula	Analysis (%) Calcd (Found) C	H	N	IR $\nu_{\max}^{\text{Nujol}}$ cm^{-1} SO$_2$	NMR (CDCl$_3$) δ (ppm) CH$_3$(3H, s)	Others
8a	45—48	$C_{17}H_{15}NO_3S$	65.16 (64.91	4.82 4.52	4.47 4.48)	1330 1150	2.54	4.48 (2H, s, CH$_2$)
8b	139.5—141	$C_{14}H_{17}NO_3S$	60.19 (60.26	6.13 6.29	5.01 5.04)	1305 1130	2.56	1.36 (9H, s, (CH$_3$)$_3$C)
8c	136—137.5	$C_{17}H_{15}NO_3S$	65.16 (65.02	4.82 5.16	4.47 4.23)	1325 1150	2.46	2.40 (3H, s, CH$_3$)

TABLE IX. Analytical and Spectral Data for α-Sulfonylacetates (**4e—m**)

Compd. No.	mp (°C)	Formula	Analysis (%) Calcd (Found) C	H	IR $\nu_{\max}^{\text{Nujol}}$ cm^{-1} CO	SO$_2$	NMR(CDCl$_3$) δ (ppm) CH$_2$SO$_2$ (2H)$^{a)}$	CH (1H, s)	CO$_2$CH$_2$ (2H)$^{b)}$
4e	96.5—98	$C_{22}H_{19}ClO_4S$	63.69 (63.66	4.62 4.58)	1730	1305 1125	4.13, 4.50	4.92	5.14, 5.28
4f	85.5—86	$C_{22}H_{19}ClO_4S$	63.69 (63.67	4.62 4.75)	1740	1305 1125	4.17, 4.57	4.88	5.20, 5.32
4g	108.5—110	$C_{23}H_{22}O_5S$	67.30 (67.07	5.40 5.16)	1730	1315 1130	4.05, 4.45	4.88	5.14, 5.26
4h	169—170.5	$C_{26}H_{22}O_4S$	72.54 (72.94	5.15 4.80)	1730	1315 1130	4.21, 4.63	5.80	5.12, 5.28
4i	120—121	$C_{20}H_{18}O_5S$	64.85 (64.87	4.99 4.72)	1730	1320 1140	4.22, 4.56	5.20	5.30(s)
4j	93.5—95	$C_{24}H_{22}O_4S$	70.91 (71.06	5.45 5.54)	1735	1325 1125	4.31, 4.51	4.62 (d, J=9 Hz)	5.30(s)
4k	79—81	$C_{24}H_{24}O_4S$	70.56 (70.62	5.92 5.70)	1740	1320 1125	4.11, 4.33	3.70 (t, J=6 Hz)	5.20 (t, J=12 Hz)
4l	64—66	$C_{19}H_{22}O_4S$	65.87 (65.91	6.40 6.60)	1745	1305 1120	4.16, 4.53	3.61 (d, J=6 Hz)	5.22(s)
4m	63—65	$C_{22}H_{26}O_4S$	68.37 (68.08	6.78 6.65)	1730	1310 1135	4.16, 4.40	3.63 (d, J=6 Hz)	5.20(s)

a) AB type quartet (J=14—16 Hz).
b) AB type quartet (J=12 Hz), unless otherwise stated.

(b) Without Benzyl Alcohol (Run 2 in Table IV): The reaction was carried out by method (a) but without benzyl alcohol. The residue was purified by PLC on silica gel with hexane–ethyl acetate (1: 1) to give a mixture (144 mg) of **8a** and dibenzylsulfone (35: 20 by NMR measurement). The yields of **8a** and dibenzylsulfone were 63 and 36%, respectively. Dibenzylsulfone, mp 148—150.5°C, IR $\nu_{\max}^{\text{Nujol}}$ cm^{-1}: 1300, 1130. NMR δ ppm (in $CDCl_3$): 4.12 (4H, s, $CH_2 \times 2$), 7.40 (10H, s, aromatic H). *Anal.* Calcd for $C_{14}H_{14}O_2S$: C, 68.26; H, 5.73. Found: C, 68.20; H, 5.58.

Wolff Rearrangement of α-Benzoyl-α-(*tert*-butylsulfonyl)diazomethane (3b) in Acetonitrile (Run 3 in Table IV)——The reaction was carried out by method (a) for the Wolff rearrangement of **3a** in acetonitrile. The residue was separated by silica gel column chromatography with hexane–ethyl acetate (9: 1) to give **4b** (62%) in the first fraction. The second fraction to be eluted contained the oxazole (**8b**, 24%).

Wolff Rearrangement of α-Benzoyl-α-(*p*-tolylsulfonyl)diazomethane (3c) in Acetonitrile (Run 4 in Table IV)——The reaction was carried out as above, and the residue was separated by PLC on silica gel with hexane–ethyl acetate (2: 1) to give **4c** (33%, *Rf* 0.3) and **8c** (24%, *Rf* 0.2).

Wolff Rearrangement of α-Benzoyl-α-(*p*-anisylsulfonyl)diazomethane (3d) in Acetonitrile (Run 5 in Table IV)——The reaction was carried out as above, and the residue was purified by PLC on silica gel with hexane–ethyl acetate (2: 1) to give **4d** (37%, *Rf* 0.4).

Wolff Rearrangement of α-Acyl-α-(benzylsulfonyl)diazomethanes (3) in Toluene——General Procedure: A mixture of an α-acyl-α-(benzylsulfonyl)diazomethane (0.5 mmol) and benzyl alcohol (108 mg, 1 mmol) in toluene (25 ml) was refluxed for 2 h. The solvent was evaporated off and the benzyl alcohol was removed *in vacuo*. The residue was purified by washing with hexane, PLC on silica gel (hexane–ethyl acetate), or column chromatography over silica gel (hexane–ethyl acetate) to give an α-benzylsulfonyl acetate. Analytical and spectral data for **4e—m** are summarized in Table IX.

Acknowledgement The authors wish to thank Miss Mie Sahashi of our Laboratory for her able assistance in the preparative work.

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