TLC plates were visualized by UV light or iodine. Column chromatography was conducted at medium pressure by utilizing silica gel 60 (E. Merck, 230–400 mesh). All solvents were reagent grade distilled from glass (Burdick and Jackson).

3-Acetyl-5-(2-hydroxybenzoyl)-2-methylfuran (3a). To a chloroform solution (100 mL) of 3-bromochromone (1; 4.50 g, 20 mmol) and acetylacetone (2.0 g, 20 mmol) was added a chloroform solution (10 mL) of DBN (4.96 g, 40 mmol) over a period of 2–3 min. The reaction immediately turned black. After being stirred at room temperature for 1 h, the reaction was quenched by the addition of 5% HCl (100 mL). The organic layer was separated and the aqueous layer extracted with chloroform (2 × 50 mL). The combined chloroform solutions were then dried ($MgSO_4$), and the solvent was removed in vacuo to give 4.1 g of a yellow solid. This material was chromatographed[5] over 200 g of silica gel packed in 10% EtOAc/$CHCl_3$. Fractions of 100 mL each were collected. Fractions 13–17 contained 3.94 g (81%) of **3a**: mp 98–100 °C; IR ($CHCl_3$) ν_{max} 3000 (OH), 1670, 1620 (C=O), 1580, 1560 (C=C), 1350, 1200, 1160 cm^{-1} (C–O/other); NMR ($CDCl_3$) δ 8.12 (dd, 1 H, aromatic, J = 8 and 2 Hz), 7.52 (s, 1 H, furan proton), 7.31–7.62 (m, 1 H, aromatic), 6.80–7.10 (m, 2 H, aromatic), 2.7 (s, 3 H, furan methyl), 2.45 (s, 3 H, methyl ketone); UV (EtOH) λ_{max} 212 (sh) nm (ϵ 18 850) and 304 (13 600). Anal. Calcd for $C_{14}H_{12}O_4$ (mol wt 243.6): C, 68.96; H, 4.96. Found: C, 68.74; H, 4.92.

Ethyl 5-(2-Hydroxybenzoyl)-2-methyl-3-furancarboxylate (3b). To a chloroform solution (100 mL) of 3-bromochromone (1: 2.25 g, 10 mmol) and ethyl acetoacetate (1.30 g, 10 mmol) was added a chloroform solution (5 mL) of DBU (3.04 g, 20 mmol) over a period of 2–3 min. The reaction immediately began to turn bright orange. After being stirred at room temperature for 30 min, the reaction was quenched by the addition of 5% HCl (50 mL). The organic layer was separated and the aqueous layer extracted with chloroform (2 × 50 mL). The combined chloroform solutions were dried ($MgSO_4$), and the solvent was removed in vacuo to give 2.75 g of a yellow oil. This oil was chromatographed over 250 g of silica gel packed in 50% EtOAc/hexane. Fractions of 18 mL were collected. Fractions 35–50 were combined to give 2.48 g (91%) of **3b**: mp 40–42 °C; IR (mull) ν_{max} 2900 (OH), 1720 (ester), 1625 (C=O), 1605, 1585 (C=C), 1275, 1240, 1160, 1100 cm^{-1} (C–O/other); NMR ($CDCl_3$) δ 8.1 (d, 1 H, aromatic J = 8 Hz), 7.53 (s, 1 H, furan proton), 7.3–7.6 (m, 1 H, aromatic), 6.75–7.11 (m, 2 H, aromatic), 4.27 (q, 2 H, OCH_2CH_3, J = 7 Hz), 2.65 (s, 3 H, furan methyl), 1.35 (t, 3 H, OCH_2CH_3, J = 7 Hz). Anal. Calcd for $C_{15}H_{14}O_5$ (mol wt 273.5): C, 65.81; H, 5.11. Found: C, 65.86: H, 5.10.

Ethyl 5-(2-Hydroxybenzoyl)-2-phenyl-3-furancarboxylate (3c). By use of the same procedure as that for **3b**, 2.25 g of 1 afforded 3.5 g of a yellow solid which was chromatographed over 250 g of silica gel packed in 50% EtOAc/hexane. Fractions of 18 mL were collected. Fractions 29–48 were combined to give 2.98 g (89%) of **3c**: mp 103–105 °C; IR (mull) ν_{max} 2900 (OH), 1725 (ester), 1620 (C=O), 1590, 1570, 1520 cm^{-1} (C=C); NMR ($CDCl_3$) δ 8.14 (dd, 1 H, aromatic, J = 8 and 2 Hz), 7.75 (s, 1 H, furan proton), 7.25–7.65 (m, 6 H, aromatic), 6.85–7.10 (m, 2 H, aromatic), 4.33 (q, 2 H, OCH_2CH_3, J = 7 Hz), 1.35 (t, 3 H, OCH_2CH_3, J = 7 Hz). Anal. Calcd for $C_{20}H_{16}O_5$ (mol wt 335.5): C, 71.53; H, 4.76. Found: C, 71.42; H, 4.76.

Ethyl 5-(2-Hydroxybenzoyl)-2-[(phenylthio)methyl]-3-furancarboxylate (3d). By use of the same procedure as that for **3b**, 1.0 g of 1 afforded 1.65 g of a yellow oil which was chromatographed over three Merck B columns packed in 50% EtOAc/hexane. Fractions of 18 mL were collected. Fractions 19–22 were combined to give 1.18 (75%) of **3d**: mp 76–77 °C; IR (mull) ν_{max} 3000 (OH), 1720 (ester), 1625 (C=O), 1600, 1520 (C=C), 1285, 1240, 1160 cm^{-1} (C–O/other); NMR ($CDCl_3$) δ 7.95 (dd, 1 H, aromatic, J = 8 and 2 Hz), 7.50 (s, 1 H, furan proton), 6.7–7.4 (m, 8 H, aromatic), 4.47 (s, 2 H, CH_2–S), 4.2 (q, 2 H, OCH_2CH_3, J = 7 Hz), 1.28 (t, 3 H, OCH_2CH_3, J = 7 Hz). Anal. Calcd for $C_{21}H_{18}O_5S$ (mol wt 381.5): C, 66.05; H, 4.71; S, 8.38. Found: C, 65.69; H, 4.84; S, 8.53.

Ethyl 3-(Ethoxycarbonyl)-5-(2-hydroxybenzoyl)-2-furanacetate (3e). By use of the same procedure as that for **3b**, 2.25 g of 1 afforded 3.34 g of a light yellow oil which was distilled [230 °C (0.8 mm Hg)] and then chromatographed over three Merck B columns packed in chloroform. Fractions of 18 mL were collected. Fractions 26–39 contained 1.31 g (38%) of **3e**: mp 81–83 °C; IR ($CHCl_3$) ν_{max} 3000 (OH), 1735, 1715 (ester), 1620 (C=O), 1610, 1530, (C=C), 1300, 1290, 1245, 1085 cm^{-1} (C–O/other); NMR ($CDCl_3$) δ 8.15 (d, 1 H, atomatic, J = 8 Hz), 7.59 (s, 1 H, furan proton), 7.30–7.65 (m, 1 H, aromatic), 6.75–7.12 (m, 2 H, aromatic), 4.30 (q, 2 H, OCH_2CH_3, J = 7 Hz), 4.25 (q, 2H, OCH_2CH_3, J = 7 Hz), 4.18 (s, 2 H, CH_2CO_2Et), 1.32 (t, 3 H, OCH_2CH_3, J = 7 Hz), 1.25 (t, 3 H, OCH_2CH_3, J = 7 Hz). Anal. Calcd for $C_{18}H_{18}O_7$ (mol wt 345.3): C, 62.55; H, 5.21. Found: C, 62.50; H, 5.22.

6,7-Dihydro-2-(2-hydroxybenzoyl)-6,6-dimethyl-4(5*H*)-benzofuranone (3f). To a chloroform solution (50 mL) of 3-bromochromone (1; 2.25 g, 10 mmol) and 5,5-dimethylcyclohexane-1,3-dione (1.40 g, 10 mmol) was added a chloroform solution (5 mL) of DBN (2.48 g, 20 mmol) over a 2–3-min time period. After the reaction was stirred at room temperature for 4 h, the reaction was quenched by addition of 5% HCl (50 mL). The organic layer was separated and the aqueous layer extracted with chloroform (2 × 50 mL). The combined organic solutions were dried ($MgSO_4$), and the solvent was removed in vacuo to give a yellow solid which when chromatographed over 250 g of silica gel packed in 5% CH_3OH/CH_2Cl_2 afforded 1.90 g (67%) of **3f**: mp 100–102 °C; IR (mull) 2900 (OH), 1685 (C=O), 1620 (C=O, hdyrogen bonded), 1585, 1515 (C=C), 1305, 1240, 1165, 895 cm^{-1} (C–O/other); NMR ($CDCl_3$) δ 8.08 (d, 1 H, aromatic, J = 9 Hz), 7.55 (s, 1 H, furan proton), 7.3–7.6 (m, 1 H, aromatic), 6.8–7.15 (m, 2 H, aromatic), 2.90 (s, 2 H, CH_2), 2.45 (s, 2 H, CH_2), 1.20 (s, 6 H, *gem*-dimethyl). Anal. Calcd for $C_{17}H_{16}O_4$ (mol wt 283.6): C, 71.93; H, 5.64. Found: C, 71.67; H, 5.46.

Registry No. 1, 49619-82-1; **2a**, 123-54-6; **2b**, 141-97-9; **2c**, 94-02-0; **2d**, 25907-38-4; **2e**, 105-50-0; **2f**, 126-81-8; **3a**, 71426-02-3; **3b**, 71426-03-4; **3c**, 71426-04-5; **3d**, 71426-05-6; **3e**, 71463-32-6; **3f**, 71426-06-7.

(5) Purification via silica gel chromatography was necessary to remove small amounts of starting materials and more polar impurities formed during the reaction. Attempts to purify the crude reaction by recrystallization (5–20% EtOAc/hexane) either resulted in much lower yields or was completely unsuccessful.

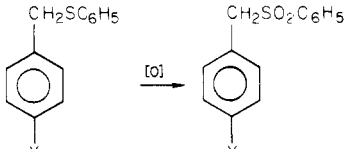
Pummerer Reaction of Para-Substituted Benzylic Sulfoxides

Glen A. Russell* and Joseph M. Pecoraro

Department of Chemistry, Iowa State University, Ames, Iowa 50011

Received February 8, 1979

In the course of a study of the $S_{RN}1$ displacement reaction, a series of para-substituted benzyl phenyl sulfides, sulfoxides, and sulfones were required.[2] We observed that the sulfides **1a–e** can be oxidized to the corresponding



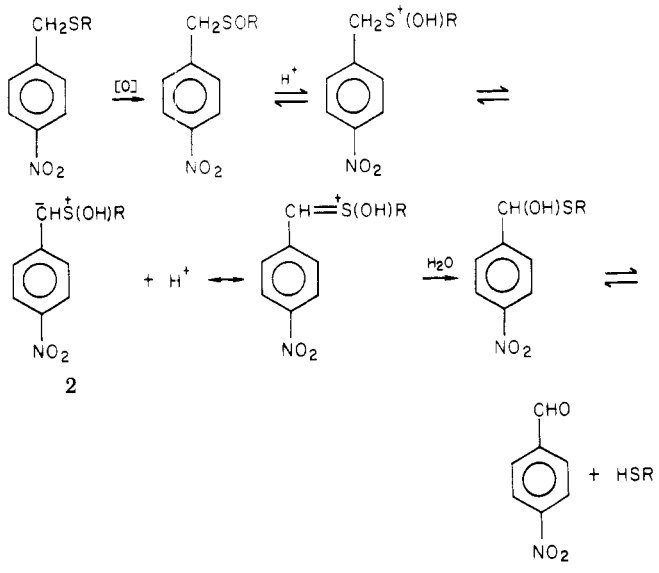
1a, X = CH_3O
b, X = H
c, X = Cl
d, X = CN
e, X = NO_2

sulfones in essentially quantitative yield by the use of 30% hydrogen peroxide in glacial acetic acid. However, oxidation with 30% hydrogen peroxide in a mixture of acetic acid (60%)–water (40%) acidified to 3 M with sulfuric acid, although successful for **1a–d**, led to the Pummerer reaction

(1) R. Pummerer, *Ber. Dtsch. Chem. Ges.*, **42**, 2282 (1909); *ibid.*, **43**, 1401 (1910).
(2) G. A. Russell and J. M. Pecoraro, *J. Am. Chem. Soc.*, **101**, 3331 (1979).

0022-3263/79/1944-3990$01.00/0

Scheme I



of the intermediate sulfoxide from **1e** (or the corresponding *p*-nitrobenzyl methyl sulfide), resulting in a 90% yield of *p*-nitrobenzaldehyde. The *p*-nitro group must facilitate the Pummerer reaction by stabilizing the zwitterionic intermediate **2** (Scheme I). *p*-Nitro-α,α-dimethylbenzyl phenyl sulfide could be oxidized to the sulfone in high yield by treatment with 30% hydrogen peroxide in glacial acetic acid but was stable to refluxing aqueous acetic acid solutions of hydrogen peroxide.

The *p*-nitrobenzyl phenyl or methyl sulfoxides can be formed by oxidation of the sulfides with 1 equiv of *m*-chloroperbenzoic acid in chloroform at −10 °C. Treatment of these sulfoxides with aqueous mineral acid readily brings about the Pummerer reaction, whereas *p*-nitrocumyl phenyl sulfoxide is stable to aqueous acid. Under similar conditions (24-h reflux, 3 M H_2SO_4 in aqueous acetic acid) *p*-methoxybenzyl phenyl sulfoxide gave but a trace of benzaldehyde, *p*-chlorobenzyl phenyl sulfoxide gave 30% of *p*-chlorobenzaldehyde, and *p*-cyanobenzyl phenyl sulfoxide gave 85% of *p*-cyanobenzaldehyde. The ability of acid-strengthening para substituents in benzyl sulfoxides to promote the Pummerer reaction is analogous to the β-carbonyl group in β-keto sulfoxides, wherein the Pummerer reaction occurs readily.[3]

Experimental Section

Substituted benzyl chlorides were reacted with a 200% excess of sodium benzenethiolate[4] or methyl mercaptide[5] in ethanol to yield the sulfides shown in Table I in yields of 63–96%. The benzylic hydrogen atoms in ^{1}H NMR were a singlet at δ 3.60–4.15 (Me_2SO-d_6), depending upon the structure. *p*-Nitro-α,α-dimethylbenzyl phenyl sulfide was formed in a similar fashion in 86% yield: ^{1}H NMR δ 1.75 (s, 6), 7.3 (m, 7), 8.11 (d, 2).

Oxidation of the appropriate sulfides in chloroform at −10 °C for 24 h by 1 equiv of *m*-chloroperbenzoic acid (83% assay) gave the corresponding sulfoxides in 90–95% yield.[6,7] The sulfoxides all had IR absorption at 1030–1055 cm^{-1} except for phenyl *p*-methoxybenzyl sulfoxide which absorbed at 1125 cm^{-1}. The sulfoxides possess diastereotopic benzylic hydrogen atoms which give rise to an AB ^{1}H NMR quartet centered at $(\delta_A + \delta_B)/2$ = 3.95–4.3 (J = 12.7–12.9 Hz) (Me_2SO-d_6), depending on structure.[8]

Oxidation of the sulfides in glacial acetic acid containing an excess of aqueous hydrogen peroxide (30% assay) gave after 45 min of reflux an essentially quantitative yield of the sulfones. The sulfones possessed a benzylic ^{1}H NMR singlet (Me_2SO-d_6) at δ 4.3–4.65 and IR absorptions at 1100 and 1350 cm^{-1}. In a similar fashion *p*-nitro-α,α-dimethylbenzyl phenyl sulfone, mp 82–84 °C, was prepared in 80% yield: ^{1}H NMR (Me_2SO-d_6) δ 1.9 (s, 6), 7.6 (m, 7), 8.1 (d, 2); mass spectrum (70 eV) m/e 305 (M^+).

An alternate procedure applicable to benzyl, *p*-chlorobenzyl, *p*-cyanobenzyl, or *p*-methoxybenzyl phenyl or methyl sulfides involved treatment of the sulfide in a mixture of acetic acid (60%)–water (40%) acidified to 3 M with sulfuric acid. An excess of 30% hydrogen peroxide was added dropwise and the mixture refluxed for 24 h before dilution with water and extraction with chloroform to yield the sulfone.

Pummerer rearrangement of the performed sulfoxides involved refluxing the sulfoxides in acetic acid (60%)–water (40%) acidified to 3 M with sulfuric acid for a period of 24 h followed by GC analysis of the ether-soluble products.

Table I. Para-Substituted Benzyl Sulfides, Sulfoxides, and Sulfones (p-$XC_6H_4CH_2S(O)_nR$)

		mp, °C		
R	X	n = 0	n = 1	n = 2 (lit. mp)
CH_3	H	liq	53-55	125-127 (125-127)[a]
C_6H_5	H	40-41	124-126	144-145 (147-148)[b]
CH_3	NO_2	69-71	101-102	162-166 (167-168)[c]
C_6H_5	NO_2	74-75	153-155	205-206 (209.5-210.5)[b]
CH_3	Cl	liq	*d*	120-122 (120-122)[a]
C_6H_5	Cl	79-80	162-164	190-193 (189-191)[b]
C_6H_5	CN	74-75	73-76	205-209 (208-210)[b]
C_6H_5	CH_3O	83-85	*d*	139-140 (140-141)[e]

[a] T. R. Lewis and S. Archer, *J. Am. Chem. Soc.*, **73**, 2109 (1951). [b] B. B. Jarvis and J. C. Saukautis, *ibid.*, **95**, 7708 (1973). [c] C. K. Ingold, E. H. Ingold, and F. R. Shaw, *J. Chem. Soc.*, 813 (1928). [d] Obtained as oils. [e] B. R. Brown and M. R. Shaw, *J. Chem. Soc., Perkin Trans. 1*, 2036 (1974).

Registry No. **1a**, 5023-67-6; **1b**, 831-91-4; **1c**, 7693-30-3; **1d**, 51229-54-0; **1e**, 7703-38-0; benzyl methyl sulfide, 766-92-7; *p*-nitrobenzyl methyl sulfide, 51392-53-1; *p*-chlorobenzyl methyl sulfide, 5925-82-6; benzyl methyl sulfoxide, 824-86-2; benzyl phenyl sulfoxide, 833-82-9; *p*-nitrobenzyl methyl sulfoxide, 15733-10-5; *p*-nitrobenzyl phenyl sulfoxide, 17530-84-6; *p*-chlorobenzyl methyl sulfoxide, 24176-68-9; *p*-chlorobenzyl phenyl sulfoxide, 17530-80-2; *p*-cyanobenzyl phenyl sulfoxide, 71426-19-2; *p*-methoxybenzyl phenyl sulfoxide, 71426-20-5; benzyl methyl sulfone, 3112-90-1; benzyl phenyl sulfone, 3112-88-7; *p*-nitrobenzyl methyl sulfone, 61081-34-3; *p*-nitrobenzyl phenyl sulfone, 34063-53-1; *p*-chlorobenzyl methyl sulfone, 5925-80-4; *p*-chlorobenzyl phenyl sulfone, 51229-56-2; *p*-cyanobenzyl phenyl sulfone, 51229-59-5; *p*-methoxybenzyl phenyl sulfone, 55539-39-4; sodium benzenethiolate, 930-69-8; sodium methyl mercaptide, 5188-07-8; benzyl chloride, 100-44-7; *p*-nitrobenzyl chloride, 100-14-1; *p*-chlorobenzyl chloride, 104-83-6; *p*-cyanobenzyl chloride, 874-86-2; *p*-methoxybenzyl chloride, 824-94-2; *p*-nitro-α,α-dimethylbenzyl phenyl sulfide, 15013-24-8; *p*-nitro-α,α-dimethylbenzyl phenyl sulfone, 70951-74-5; *p*-nitrobenzaldehyde, 555-16-8; *p*-methoxybenzaldehyde, 123-11-5; *p*-chlorobenzaldehyde, 104-88-1; *p*-cyanobenzaldehyde, 105-07-7.

(3) G. A. Russell and G. J. Mikol, *Mech. Mol. Migr.*, **1**, 157–207 (1968).
(4) W. R. Waldrin and E. E. Reid, *J. Am. Chem. Soc.*, **45**, 2399 (1923).
(5) H. Plieninger, *Chem. Ber.*, **83**, 265 (1950).
(6) L. A. Paquette, *J. Am. Chem. Soc.*, **86**, 4085 (1964).
(7) G. A. Russell and L. A. Ochrymowycz, *J. Org. Chem.*, **35**, 2106 (1970).
(8) M. Nishio, *Chem. Pharm. Bull. Jpn.*, **15**, 1609 (1967); *ibid.*, **17**, 262 (1969).

4-Imino-4,5-dihydro-1,2λ^6-3-oxathiazol-2-ones. Ring-Opening Cycloaddition Reactions with Maintenance of the Ring Size

Gerrit L'abbé,* Chih-Chou Yu, and Suzanne Toppet

Department of Chemistry, University of Leuven, Celestijnenlaan 200F, B-3030 Heverlee, Belgium

Received May 22, 1979

Many cycloaddition reactions where heterocycles are transformed into other heterocycles of the same size but with a different skeleton involve elimination of a good leaving group. Examples of this are the mesoionic