Addition of Aliphatic Sulfonyl Chlorides to Enamines. Formation of Acyclic Products

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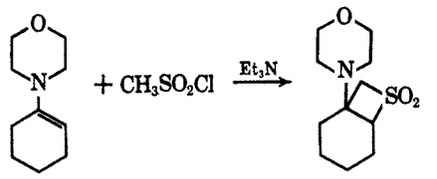
The addition of methanesulfonyl, phenylmethanesulfonyl, and *p*-chlorophenylmethanesulfonyl chloride to 1,3-diphenyl-2-pyrrolidinopropene in the presence of base was studied. The products obtained were not the expected four-membered ring sulfones, but the isomeric acyclic compounds. These findings suggest that the acyclic products formed by ring opening of the initially formed cyclic sulfones. The nmr spectra of the sulfones and sulfides prepared indicate that they have nonequivalent methylene protons due to a nonadjacent asymmetric center.

Aliphatic sulfonyl chlorides undergo cycloaddition to enamines in the presence of base and produce four-membered ring sulfones. Examples are the addition of methanesulfonyl chloride to 1-morpholinocyclohexene,[1] which gave sulfone **1**, and addition of phenylmethanesulfonyl chloride to 1-pyrrolidino-2-methylpropene,[2,3] which afforded compound **2**. Recently the addition of 2-phenylethanesulfonyl[3] and phenylmethanesulfonyl chloride[4] has been reported to give both a cyclic and an acyclic sulfone.



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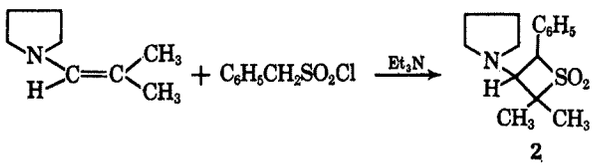

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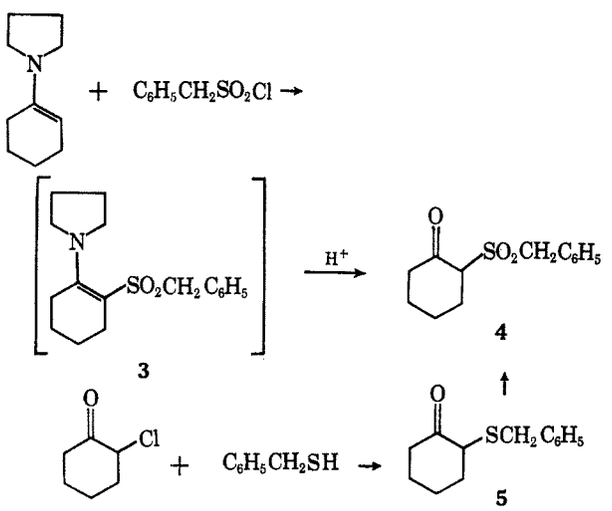
An attempt to extend the addition of phenylmethanesulfonyl chloride to enamines derived from ketones has also yielded acyclic sulfones. Addition of this sulfonyl chloride to 1-pyrrolidinocyclohexene gave, upon hydrolysis, benzyl 2-ketocyclohexyl sulfone (**4**). The adduct was identical with the sulfone obtained from 2-chlorocyclohexanone and phenylmethanethiol. The

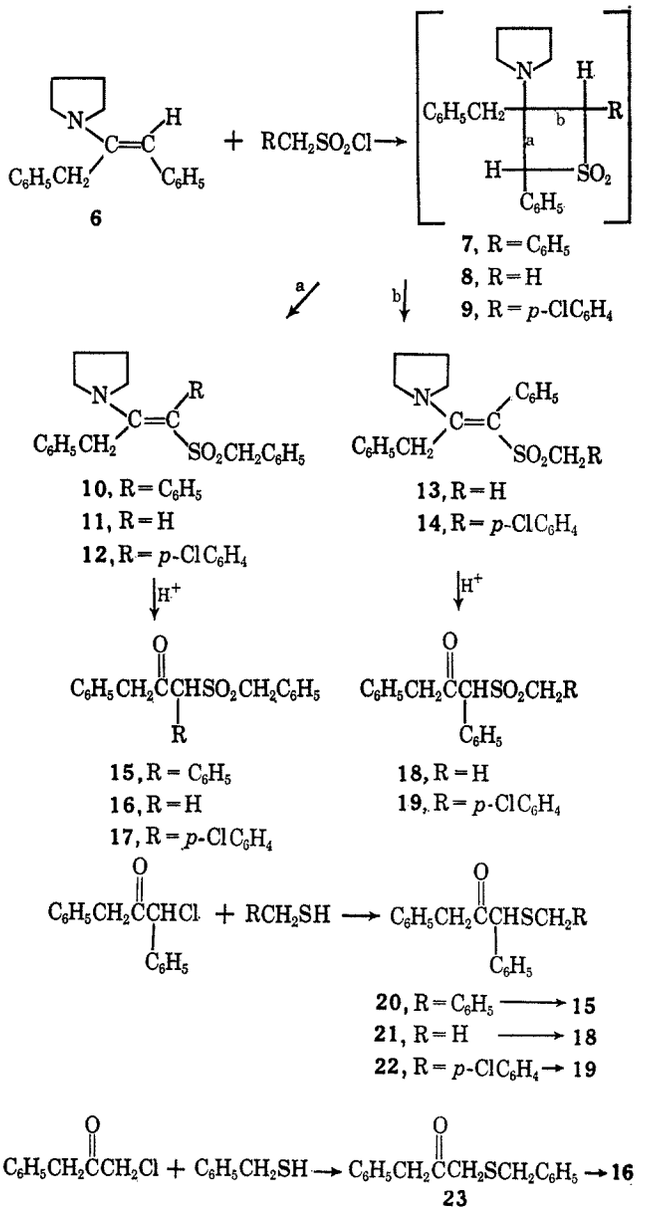


3 **4** **5**

assumed intermediate enamine sulfone, **3**, could not be isolated.

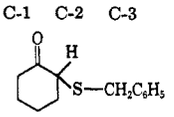
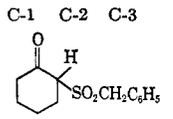
The enamine **6**, prepared from dibenzyl ketone and pyrrolidine, behaved in a similar manner and gave the acyclic enamine sulfone **10**, upon treatment with phenylmethanesulfonyl chloride (Scheme I). Acid hydrolysis of enamine **10** produced keto sulfone **15** which was identical with the compound obtained by oxidation of sulfide **20**.

SCHEME I



(1) G. Stork and I. J. Borowitz, *J. Am. Chem. Soc.*, **84**, 313 (1962).
(2) G. Opitz and H. Adolph, *Angew. Chem.*, **74**, 77 (1962).
(3) G. Opitz, H. Schempp, and H. Adolph, *Ann.*, **684**, 92 (1965).
(4) R. Fusco, S. Rossi, and S. Maiorana, *Chim. Ind.* (Milan), **44**, 873 (1962)

TABLE I[a]

No.	Compd	τ (multiplet), J_{AB}, cps		
	C-1 C-2 C-3	C-1 protons	C-2 protons	C-3 protons
23	$C_6H_5CH_2CO$—CH_2S—$CH_2C_6H_5$	6.21 (s)	6.36 (s)	6.92 (s)
16	$C_6H_5CH_2CO$—CH_2SO_2—$CH_2C_6H_5$	6.09 (s)	5.63 (s)	6.16 (s)
20	$C_6H_5CH_2CO$—CHS—$CH_2C_6H_5$ (C_6H_5)	6.41 (d)[b] 6.38	5.47 (s)	6.49 (s)[c]
15	$C_6H_5CH_2CO$—$CHSO_2$—$CH_2C_6H_5$ (C_6H_5)	6.20 (s)	4.86 (s)	5.40 (d), 13.6 5.63 5.86 (d), 13.6 6.09
21	$C_6H_5CH_2CO$—CHS—CH_3 (C_6H_5)	5.98 (d), 18.0 6.25 6.28 (d), 18.0 6.55	5.40 (s)	8.15 (s)
18	$C_6H_5CH_2CO$—$CHSO_2$—CH_3 (C_6H_5)	6.09 (s)	4.67 (s)	7.17 (s)
22	$C_6H_5CH_2CO$—CHS—$CH_2C_6H_4Cl$-p (C_6H_5)	6.11 (d), 15.0 6.36 6.41 (d), 15.0 6.66	5.50 (s)	6.52 (s)
19	$C_6H_5CH_2CO$—$CHSO_2$—$CH_2C_6H_4Cl$-p (C_6H_5)	6.21 (s)	4.86 (s)	5.48 (d), 13.6 5.71 5.88 (d), 13.6
5		...	...	5.88 (d), 13.6 6.11 6.33 (s)
4		...	6.39 (t), 6.5	5.31 (d), 12.5 5.53 5.64 (d), 12.5

[a] Spectra were measured on a Varian Associates A-60 instrument in deuteriochloroform, with TMS as an internal standard. All areas were in agreement with the assignments made. [b] Resolvable into a pair of AB doublets, J_{AB} = 15.5 cps. [c] Resolvable into a pair of AB doublets, J_{AB} = 13.5. cps.

The addition of methanesulfonyl chloride to the enamine **6** was examined to see if an acyclic product would form. Two enamine sulfones were obtained and their nmr spectra indicated that they were the methyl sulfone **13** and the benzyl sulfone **11**. These products are analogous to those obtained from the addition of ketene to enamines.[5] Acid hydrolysis of enamine **13** gave keto sulfone **18** and compound **11** afforded keto sulfone **16**.

The ketone **18**, obtained by hydrolysis of enamine **13**, was identical with methyl 1,3-diphenyl-2-keto-1-propyl sulfone, prepared by oxidation of sulfide **21**. Similarly, the structure of ketone **16** was established by an independent synthesis from sulfide **23**.

Formation of enamines **13** and **11** from addition of methanesulfonyl chloride to the enamine **6** can best be explained by the initial formation of cyclic sulfone **8**. Under the reaction conditions, compound **8** can cleave at bond a, forming enamine **11**, or at bond b, with the formation of the isomeric enamine **13**. A similar cyclic intermediate may form when phenylmethanesulfonyl chloride is added to enamine **6**. The expected intermediate is unique since cleavage at either bond a or bond b would give the same product (**10**).

The solvent used for sulfene addition reactions has been found to influence the nature of the product[6] (acyclic or cyclic) in one example, and the yield,[7] but not the nature of the product, in another. The effect of various solvents on the reaction of methanesulfonyl chloride with 1,3-diphenyl-2-pyrrolidinopropene was examined, and there was no effect on the nature of the product when the solvent was ether, benzene, or chloroform. The yield of acyclic product did depend upon the solvent, being highest in benzene (92%) and lowest in chloroform (34%). The ratio of the cleavage products (**11** and **13**) also changed with solvent.

In order to determine if phenyl-substituted methanesulfonyl chlorides can form acyclic products from cyclic intermediates, the addition of *p*-chlorophenylmethanesulfonyl chloride to enamine **6** was examined. If compound **9** is formed, then enamine sulfones **12** and **14** may be produced. The initial product was a mixture which could not be purified. The nmr spectrum was consistent with a mixture of compounds **12** and **14**. Acid hydrolysis of this mixture gave another crude product from which keto sulfone **19** was separated. Although isomeric ketone **17** was not isolated, there was evidence for its presence. Elemental analysis of the hydrolysis mixture was correct for the expected composition, and the nmr spectrum was identical with that of ketone **19**, except for a singlet at τ 4.83 and an AB pair of doublets at τ 5.40, 5.65, 5.80, and 6.05. The additional peaks can be assigned to isomer **17**. The integral of this spectrum is also in

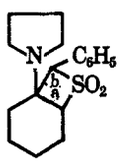
(5) G. A. Berchtold, G. R. Harvey, and G. W. Wilson, Jr., *J. Org. Chem.*, **30**, 2642 (1965).

(6) G. Opitz and H. Schempp, *Z. Naturforsch.*, **196**, 78 (1964).

(7) W. E. Truce and P. N. Son, *J. Org. Chem.*, **30**, 71 (1965).

agreement with the proposed mixture. It can be concluded that phenylmethanesulfonyl chlorides can also form acyclic products from cyclic intermediates.

The adduct **24**, which may form from phenylmethanesulfonyl chloride and 1-pyrrolidinocyclohexene, would give a ring-expanded product from cleavage at bond a.



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However, only ketone **4** (cleavage at b) was isolated from hydrolysis of this reaction mixture. The nmr spectrum of the crude product showed that only ketone **4** and 1-(phenylmethanesulfonyl)pyrrolidene were present. Ketene also failed to give a ring-expanded product with a cyclohexanone enamine.[5]

Table I contains the nmr data for the aliphatic protons of the five sulfides and the corresponding sulfones which were prepared. Some of these compounds contain methylene groups with nonequivalent protons, as shown by the appearance of an AB pair of doublets. Sulfone **16** and sulfide **23** have no center of asymmetry, and their spectra indicate equivalent methylene groups (singlets). The remaining eight compounds have an asymmetric center (C_2), and six of these have at least one methylene group which exhibits an AB pattern. The presence of a nonadjacent asymmetric center has been found to cause methylene protons to be nonequivalent in sulfinic esters,[8] steroids,[9] and substituted N, N,-dimethylbenzylamines,[10] and may be the reason for nonequivalence in these sulfones and sulfides.

Experimental Section

Reaction of Phenylmethanesulfonyl Chloride with 1-Pyrrolidinocyclohexene.—A solution of 24 g (0.16 mole) of 1-pyrrolidinocyclohexene[11] and 16 g (0.16 mole) of triethylamine in 200 ml of benzene was stirred while a solution of 30 g (0.16 mole) of phenylmethanesulfonyl chloride in 200 ml of benzene was added dropwise. The mixture was stirred for 3 hr at room temperature. The solid was collected, washed with benzene, and discarded.

The filtrate was concentrated and dissolved in 200 ml of 1,2-dimethoxyethane containing 200 ml of 3 *N* hydrochloric acid. The solution was heated at reflux for 1 hr, and concentrated. The residue was taken up in benzene, washed with water, and dried, concentrated, and recrystallized from ethanol to give 26 g of crude product, mp 94–98°. Upon distillation, 23 g (57%) of keto sulfone **4** was obtained: bp 180° (0.10 mm), mp 98–100°. A mixture melting point with the authentic sample was not depressed.

The original ethanol filtrate was concentrated and recrystallized from ethanol to give 0.33 g of 1-(phenylmethanesulfonyl)-pyrrolidine, mp 75–76°. The nmr spectrum showed peaks at τ 2.68 s (phenyl), 5.80 s (benzylic), 6.7–7.0 m (pyrrolidino), 8.1–8.4 m (pyrrolidino) in an area ratio of 5:2:4:4. A sample prepared as already described[12] melted at 93–94°. Recrystallization of the 75–76° material from ethanol in the presence of a crystal of the material which boiled at 93–94° caused it to melt at 93–94°.

The nmr spectrum of the crude hydrolysis product showed only keto sulfone **4** and 1-(phenylmethanesulfonyl)pyrrolidine (8%). Vapor phase chromatography also showed the presence of only these two compounds.

Benzyl 2-Ketocyclohexyl Sulfide (5).—A solution of 13.2 g (0.10 mole) of α-chlorocyclohexanone in 10 ml of ethanol was added dropwise to a stirred solution of 12.4 g (0.10 mole) of α-toluenethiol and 4.2 g (0.10 mole) of sodium hydroxide in 50 ml of ethanol. The mixture was stirred and heated at reflux for 15 min after the initial evolution of heat had stopped. The solvent was removed and the residue was poured into 200 ml of water. The organic layer was extracted into methylene chloride. The extract was washed with water, dried, concentrated, and distilled: yield 14.9 g (68%) of sulfide **5**, bp 108° (0.1 mm).

Anal. Calcd for $C_{13}H_{16}OS$: C, 71.0; H, 7.3; S, 14.5. Found: C, 70.6; H, 7.4; S, 14.6.

The 2,4-dinitrophenylhydrazone melted at 144–145°.

Benzyl 2-Ketocyclohexyl Sulfone (4).—Oxidation of 10.0 g of benzyl 2-ketocyclohexyl sulfide with hydrogen peroxide[13] gave 2.4 g (21%) of sulfone **4** after recrystallization from heptane–ethanol, mp 99–100°.

Anal. Calcd for $C_{13}H_{16}O_3S$: C, 61.9; H, 6.4; S, 12.7. Found: C, 61.6; H, 6.6; S, 12.4.

The 2,4-dinitrophenylhydrazone melted at 219–220°.

1,3-Diphenyl-2-pyrrolidinopropene (6).—Water was removed by azeotropic distillation from a solution of 30.9 g (0.14 mole) of dibenzyl ketone and 20.0 g (0.28 mole) of pyrrolidine in 100 ml of benzene. The solvent was removed and the residue was distilled under reduced pressure. An oil was obtained, bp 130–150° (0.05 mm), which, upon redistillation, gave 18.0 g (52%) of the enamine, bp 142° (0.02 mm).

Anal. Calcd for $C_{13}H_{21}N$: C, 86.7; H, 8.1; N, 5.3. Found: C, 86.4; H, 8.5; N, 4.9.

The nmr spectrum has peaks at τ 2.8–3.0 m (phenyl), 4.65 s (vinyl), 6.15 s (benzyl), 6.8–7.1 m (pyrrolidino), and 8.1–8.4 m (pyrrolidino) in an area ratio of 10:1:2:4:4.

Reaction of Phenylmethanesulfonyl Chloride with 1,3-Diphenyl-2-pyrrolidinopropene.—A solution of 3.8 g (0.020 mole) of phenylmethanesulfonyl chloride in 100 ml of ether was added dropwise, with stirring, to a solution of 2.1 g (0.021 mole) of triethylamine and 5.0 g (0.020 mole) of 1,3-diphenyl-2-pyrrolidinopropene in 50 ml of ether. The mixture was stirred at room temperature for 1 hr and at reflux for an additional hour. The precipitate was collected (it was completely water soluble) and the filtrate was concentrated, leaving a solid which, when recrystallized from ethanol, gave 4.5 g (56%) benzyl 1,3-diphenyl-2-pyrrolidino-1-propenyl sulfone (**10**), mp 162–163°.

Anal. Calcd for $C_{26}H_{27}NO_2S$: C, 74.6; H, 6.5; N, 3.4; S, 7.7. Found: C, 74.2; H, 6.3; N, 3.0; S, 7.6.

The nmr spectrum has peaks at τ 2.7–2.8 m (phenyl), 5.82 s (benzylic), 6.17 s (benzylic), 7.1–7.4 m (pyrrolidino), 8.4–8.7 m (pyrrolidino) in an area ratio of 15:2:2:4:4.

Hydrolysis of Benzyl 1,3 Diphenyl-2-pyrrolidino-1-propenyl Sulfone (10).—A solution of 2.0 g of benzyl 1,3-diphenyl-2-pyrrolidino-1-propenyl sulfone in 50 ml of tetrahydrofuran and 50 ml of 3 *N* hydrochloric acid was heated at reflux for 45 min and the tetrahydrofuran was distilled. The aqueous layer was extracted with methylene chloride and the organic layer was washed with water, dried, and concentrated. The solid residue was recrystallized from ethanol: yield 1.5 g (83%), mp 123–124°. A mixture melting point with an authentic sample of benzyl 1,3-diphenyl-2-keto-1-propyl sulfone (**15**), prepared as described below, was not depressed. A crystalline form melting at 112–113° was also obtained. These forms could be interconverted by seeding.

Reaction of Methanesulfonyl Chloride with 1,3-Diphenyl-2-pyrrolidinopropene.—A solution of 13.0 g (0.053 mole) of 1,3-diphenyl-2-pyrrolidinopropene and 5.5 g (0.055 mole) of triethylamine in 150 ml of ether was stirred while a solution of 6.1 g (0.053 mole) of methanesulfonyl chloride was added dropwise. The solid was collected after 24 hr. The filtrate was concentrated and the residue recrystallized from ethanol. With careful fractionation, 0.94 g (5%) of methyl 1,3-diphenyl-2-pyrrolidino-1-propenyl sulfone (**13**), mp 170–171°, and 2.3 g (13%) of benzyl 3-phenyl-2-pyrrolidino-1-propene (**11**), mp 132–133°, were obtained.

(8) J. W. Wilt and W. J. Wagner, *Chem. Ind.* (London), 1389 (1964).

(9) J. N. Shoolery and M. T. Rogers, *J. Am. Chem. Soc.*, **80**, 5121 (1958). See also L. M. Jackman, "Application of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press Inc., New York, N. Y., 1959, p 102.

(10) J. C. Randall, J. J. McLeskey, III, P. Smith, and M. E. Hobbs, *J. Am. Chem. Soc.*, **86**, 3229 (1964).

(11) S. Hünig, E. Benzing, and E. Lucke, *Chem. Ber.*, **90**, 2833 (1957).

(12) O. Martensson and E. Nilsson, *Acta Chem. Scand.*, **14**, 1151 (1960).

(13) A. Pomeranty and R. Conor, *J. Am. Chem. Soc.*, **61**, 3386 (1939).

Anal. Calcd for $C_{20}H_{23}NO_2S$: C, 70.4; H, 6.8; N, 4.1; S, 9.4. Found for isomer **13**: C, 70.2; H, 6.8; N, 3.9; S, 9.5. Found for isomer **11**: C, 70.5; H, 6.7; N, 3.9; S, 9.6.

The nmr spectrum of the methyl sulfone **13** had peaks at τ 2.7–2.8 m (aromatic), 5.50 s (benzylic), 7.1–7.3 m (pyrrolidino), 7.3 s (methyl), and 8.4–8.7 m (pyrrolidino) in an area ratio of 12:2:2:3:2. The ultraviolet spectrum had peaks at $\lambda_{max}^{CH_3CN}$ 264 mμ (log ϵ 3.96) and 303 mμ (log ϵ 3.98). The nmr spectrum of the benzyl sulfone **11** had peaks at τ 2.7–2.8 M (aromatic), 5.34 s (olefinic), 5.92 s and 6.19 s (benzylic), 6.7–7.0 m and 8.0–8.3 m (pyrrolidino) in an area ratio of 12:1:2:2:2:2. The ultraviolet spectrum had a peak at $\lambda_{max}^{CH_3CN}$ 268 mμ (log ϵ 4.32).

Reaction of Methanesulfonyl Chloride with 1,3-Diphenyl-2-pyrrolidinopropene. Solvent Study.—The reaction was repeated as described on a 0.010-mole scale, with diethyl ether, benzene, and chloroform as solvents. After standing for 24 hr at 25°, the solid was collected from the diethyl ether and benzene solutions and discarded. The filtrates were concentrated and crystallized with ligroin–ether. The chloroform solution was concentrated and the residue dissolved in benzene. After filtration, the solution was treated as just described. The resulting solids were shown by nmr and tlc to be mixtures of only compounds **13** and **11**. The composition of the mixtures was determined by ultraviolet analysis.

The results are recorded in Table II.

TABLE II

Solvent	Yield (%)	Mp, °C	Ratio of **13**:**11**
Et_2O	2.3 g (70)	80–110	1:1
Benzene	3.0 g (92)	85–100	1.5:1
Chloroform	1.1 g (34)	95–115	0.6:1

Hydrolysis of Methyl 1,3-Diphenyl-2-pyrrolidino-1-propenyl Sulfone (13).—The procedure described for the hydrolysis of benzyl 1,3-diphenyl-2-pyrrolidino-1-propenyl sulfone was used to convert 0.8 g of methyl 1,3-diphenyl-2-pyrrolidino-1-propenyl sulfone into 0.7 g (100%) of methyl 1,3-diphenyl-2-keto-1-propyl sulfone (**18**), mp 98–99°. A mixture melting point with the authentic sample was not depressed.

Hydrolysis of Benzyl 3-phenyl-2-pyrrolidino-1-propenyl Sulfone (11).—The procedure described for the hydrolysis of benzyl 1,3-diphenyl-2-pyrrolidino-1-propenyl sulfone was used to convert 2.2 g of benzyl 3-phenyl-2-pyrrolidino-1-propenyl sulfone into 1.36 g (70%) of benzyl 3-phenyl-2-keto-1-propyl sulfone (**16**), mp 138–139°. A mixture melting point with the authentic sample was not depressed.

Reaction of *p*-Chlorophenylmethanesulfonyl Chloride with 1,3-Diphenyl-2-pyrrolinopropene.—The procedure for the addition of phenylmethanesulfonyl chloride was repeated, with 12.5 g (0.050 mole) of 1,3-diphenyl-2-pyrrolidinopropene, 11.3 g (0.050 mole) of *p*-chlorophenylmethanesulfonyl chloride[14] (mp 93–94°, reported mp 85°), and 5.1 g (0.051 mole) of triethylamine. Benzene was used as a solvent. The solid was removed by filtration and the filtrate was concentrated. Solid was obtained which could not be purified by recrystallization from ethanol, always melting from 160 to 170°. The nmr spectrum had peaks at τ 2.7–2.9 m (phenyl), 5.98 s (benzylic), 6.11 s (benzylic), 7.1–7.3 m (pyrrolidino), and 8.4–8.7 m (pyrrolidino) in an area ratio of 14:2:2:4:4. These values are in agreement with a mixture of enamine sulfones **12** and **14**.

The product was hydrolyzed to the ketone by the method described for hydrolysis of benzyl 1,3-diphenyl-2-pyrrolidino-1-propenyl sulfone (**10**) and afforded 17 g of crude material, mp 90–115°. Upon recrystallization from ethanol, the solid melted at 110–127°. Subsequent recrystallizations gave 1.1 g (7%) of keto sulfone (**19**). A mixture melting point with an authentic sample was not depressed.

(14) C. L. Jackson and J. F. White, *Am. Chem. J.*, **2**, 158 (1880).

The nmr spectrum of the mixture, mp 110–127°, was the same as that of keto sulfone **19** (Table I) with an overlapping singlet (τ 4.83) and an overlapping AB pair of doublets (τ 5.40, 5.65, 5.80, and 6.05). The areas are the same as those in the spectrum of compound **19**.

Anal. Calcd for $C_{22}H_{19}ClO_3S$: C, 66.3; H, 4.8; Cl, 8.9; S, 8.0. Found: C, 66.4; H, 5.0; Cl, 8.6; S, 8.1.

Preparation of Sulfides 20, 21, and 22.—A mixture of one molar equivalent of α-chlorodibenzyl ketone,[15] one molar equivalent of mercaptan, two molar equivalents of 2,6-lutidine, and 50 ml of acetonitrile or benzene per 0.05 mole of mercaptan was heated at reflux for 24 hr. The solid was collected and discarded. The filtrate was concentrated, taken up in benzene, washed with dilute hydrochloric acid and water, dried, and concentrated. The product crystallized when ligroin was added and was recrystallized from this solvent.

20.—Benzyl 1,3-diphenyl-2-keto-1-propyl sulfide was obtained from phenylmethanethiol (0.030 mole): 5.5 g (55%), mp 53–54°.

Anal. Calcd for $C_{22}H_{20}OS$: C, 79.5; H, 6.1; S, 9.7. Found: C, 79.2; H, 6.1; S, 9.7.

21.—Methyl 1,3-diphenyl-2-keto-1-propyl sulfide was obtained with methanethiol (0.050 mole): yield 11 g (86%), mp 67–68°.

Anal. Calcd for $C_{16}H_{16}OS$: C, 75.0; H, 6.3; S, 12.5. Found: C, 74.8; H, 6.4; S, 12.6.

22.—*p*-Chlorobenzyl 1,3-diphenyl-2-keto-1-propyl sulfide was obtained from *p*-chlorophenylmethanethiol[16] (0.030 mole): yield 5.5 g (50%), mp 51–52°.

Anal. Calcd for $C_{22}H_{19}ClOS$: C, 72.0; H, 5.2; Cl, 9.7; S, 8.7. Found: C, 72.2; H, 5.5; Cl, 9.8; S, 8.6.

Benzyl 3-Phenyl-2-keto-1-propyl Sulfide (23).—A 7.0-g (0.042 mole) portion of benzyl chloromethyl ketone[17] was added dropwise to a solution of 5.2 g (0.042 mole) of phenylmethanethiol and 1.7 g (0.042 mole) of sodium hydroxide in 25 ml of ethanol. The mixture was heated for 15 min on a steam bath, poured into 200 ml of water, and extracted into methylene chloride. The extract was washed with water, dried, concentrated, and distilled to give 9.3 g (87%) of the sulfide, bp 142° (0.06 mm).

Anal. Calcd for $C_{16}H_{16}OS$: C, 75.0; H, 6.3; S, 12.5. Found: C, 75.3; H, 6.4; S, 12.8.

Preparation of Sulfones 15, 18, 19, and 16.—These compounds were prepared by oxidation of the corresponding sulfides with potassium permanganate[18] and recrystallized from ethanol.

15.—Benzyl 1,3-diphenyl-2-keto-1-propyl sulfone had mp 123–124° (21%).

Anal. Calcd for $C_{22}H_{20}O_3S$: C, 72.5; H, 5.5; S, 8.8. Found: C, 72.3; H, 5.6; S, 8.8.

18.—Methyl 1,3-diphenyl-2-keto-1-propyl sulfone had mp 98–99° (45%).

Anal. Calcd for $C_{16}H_{16}O_3S$: C, 66.6; H, 5.6; S, 11.1. Found: C, 66.2; H, 5.2; S, 11.2.

19.—*p*-Chlorobenzyl 1,3-diphenyl-2-keto-1-propyl sulfone had mp 135–136° (65%).

Anal. Calcd for $C_{22}H_{19}ClO_3S$: C, 66.3; H, 4.8; Cl, 8.9; S, 9.0. Found: C, 66.0; H, 5.1; Cl, 9.2; S, 8.0.

16.—Benzyl 3-phenyl-2-keto-1-propyl sulfone had mp 138–139° (78%).

Anal. Calcd for $C_{16}H_{16}O_3S$: C, 66.6; H, 5.6; S, 11.1. Found: C, 67.0; H, 6.0; S, 10.7.

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