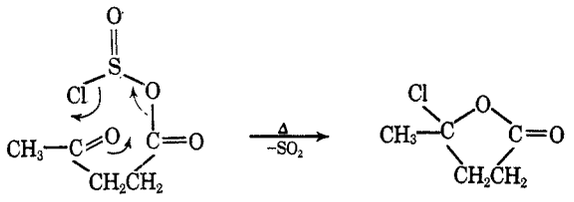
chloride, IV, shown to be entirely cyclic by nmr analysis, is formed by the action of thionyl chloride on levulinic acid or on sodium levulinate, only the cyclic isomer is present.[10] This fact may be explained by assuming a [3.2.1]bicyclic path, as shown below. The mixed anhydride, V, would surely be expected to form from the sodium salt sequence, at least.



V IV

The formation of cyclic acid chloride of *o*-benzoylbenzoic,[11] *o*-acetylbenzoic,[11] and *o*-phthalaldehydic[11] acids may be explained similarly.

Experimental Section[12]

Normal Methyl Levulinate, I.—Esterification of levulinic acid with methanol and hydrogen chloride gave methyl levulinate which had only infrared absorption at 5.85 μ in the carbonyl region even when crude product was examined. The nmr spectrum in CCl_4 showed a singlet at δ = 2.13 ppm (keto CH_3, 3 H), a multiplet at 2.56 ($-CH_2-CH_2-$, 4 H), and a singlet at 3.63 ($-COOCH_3$, 3 H). As the methyl protons of *n* ester ($CH_3-C(=O)-$, 2.13 ppm) and ψ ester (CH_3-C-, 1.56 ppm) are both singlets, the only difference is in the chemical shift (δ).

Pseudo Methyl Levulinate, II.—This ester, bp 95° (15 mm), was prepared pure in 50% yield as described.[6] The nmr spectrum in CCl_4 showed a singlet at δ 1.56 ppm (CH_3-C, 3 H), a multiplet at 2.37 ($-CH_2-CH_2-$, 4 H), and a singlet at 3.29 ($-C-OCH_3$, 3 H). The infrared absorption spectrum showed a strong band at 5.65 μ and no other band in the carbonyl region.

Levulinyl Chloride.—A solution formed by adding 5.0 g of levulinic acid to 30 ml of pure thionyl chloride was allowed to stand for 1 hr at room temperature. The excess thionyl chloride was removed under reduced pressure on a rotary evaporator. The acid chloride thus formed had an nmr spectrum (neat) which consisted of a singlet centered at δ 2.03 ppm (CH_3-C, 3 H), and a multiplet at 2.66 ($-CH_2CH_2-$, 4 H). When vacuum distillation is attempted a certain amount of hydrogen chloride is lost and some angelica lactone is formed.[10] When levulinyl chloride is made by treating dry sodium levulinate with thionyl chloride in ether the acid chloride obtained is identical with that formed directly from the acid.

Levulinic Methylcarbonic Anhydride, III. A.—To a suspension of 5.0 g of dry sodium levulinate in 35 ml of dry ether at 0° was added dropwise a solution of 6.9 g of methyl chlorocarbonate in 10 ml of dry ether. After being stirred for 30 min at 0° and at room temperature for 2 hr the mixture was filtered. The solvent and excess methyl chlorocarbonate were removed under reduced pressure to yield 2.0 g of a colorless liquid which was essentially pure III as judged by the nmr spectrum which consisted of a singlet centered at δ 2.16 ppm ($CH_3-C=O$, 3 H), a multiplet at 2.70 ($-CH_2-CH_2-$, 4 H) and a singlet at 3.86 ($-COO-COOCH_3$, 3 H).

B.—In another experiment a solution of 4.4 g of methyl chlorocarbonate in 10 ml of dry ether was added to a stirred solution at 0° of 5.0 g of levulinic acid in 30 ml of ether. To this solution at 0° was added dropwise a solution of 2.4 g of Dabco[9] in 90 ml of ether during 45 min. After a further 30 min at 0° and 40 min at room temperature, the colorless precipitate was removed by filtration. The solvent was removed under reduced pressure on a rotary evaporator to yield 6.7 g of a colorless liquid which by nmr analysis was estimated to contain 91% of III, 8% of II, and 1% of I.

When either liquid obtained as described in A and B above was heated at 120–140° for 2 hr, the evolution of carbon dioxide was about quantitative. On analysis of the products by nmr the products were shown to consist of 91–93% II and the remainder, I.

(10) J. A. Helberger [*Ann.*, **522**, 269 (1936)] used no spectrographic proofs of structure.

(11) M. Rensen, *Bull. Soc. Chim. Belges*, **70**, 77 (1961).

(12) Every experiment and preparation described herein was repeated at least once by each co-worker. Nmr spectra were determined on a Varian A-60 spectrometer with tetramethylsilane (TMS) as internal standard. δ values are given in parts per million downfield from the TMS signal (0 ppm).

Cleavage of β-Keto Sulfones by Pyrrolidine

J. J. LOOKER

Research Laboratories, Eastman Kodak Company, Rochester, New York 14650

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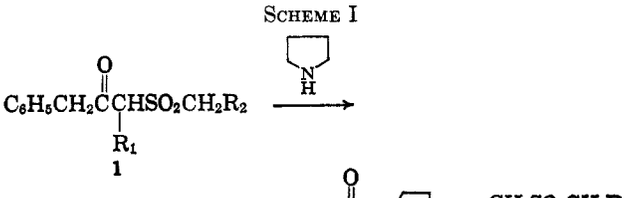
β-Keto sulfones can be obtained by a variety of reactions.[1-4] One reaction of these compounds which has not been investigated is enamine formation. We have found that, under normal conditions of enamine synthesis, β-keto sulfones cleave into an amide and a sulfone. For example, β-keto sulfone **1a** is converted by heating with pyrrolidine into *p*-chlorobenzyl benzyl sulfone (**2a**) and 1-(phenylacetyl)pyrrolidine. In a similar manner, the other acyclic β-keto-sulfones (Ib–d) are cleaved in good yield; **1c** and **1d** afford the same sulfone **2c** (Scheme I).

SCHEME I



1a, R_1 = C_6H_5; R_2 = *p*-ClC_6H_4 **2a**, R_1 = C_6H_5; R_2 = *p*-ClC_6H_4
b, R_1 = R_2 = C_6H_5 **b**, R_1 = R_2 = C_6H_5
c, R_1 = H; R_2 = C_6H_5 **c**, R_1 = H; R_2 = C_6H_5
d, R_1 = C_6H_5; R_2 = H

Two cyclic β-keto sulfones, containing the carbonyl group in the ring, also underwent cleavage: the product contains both the amide and the sulfone functions. Benzyl 2-ketocyclopentyl sulfone (**3a**) is converted to **4a** in high yield. The corresponding six-membered ring ketone, **3b**, is converted in cleavage product **4b** if water is not removed from the reaction mixture, and into enamine **5b** if it is removed. Either product can be isolated in about 50% yield. None of the other examples studied gave any isolable enamine. The nmr spectrum of enamine **5b** established the position of the double bond (τ 5.05 triplet, J = 3.0 cps, vinyl proton). Upon hydrolysis, this enamine was readily converted to the starting ketone **3b**. (See Scheme II.)

Formation of these products can be explained by attack of the base at the carbonyl carbon atom with formation of intermediate **7**, which has two modes of reaction: it can lose water and form enamine **5b** (Scheme III), or it can lose a carbanion and form compound **4b** upon

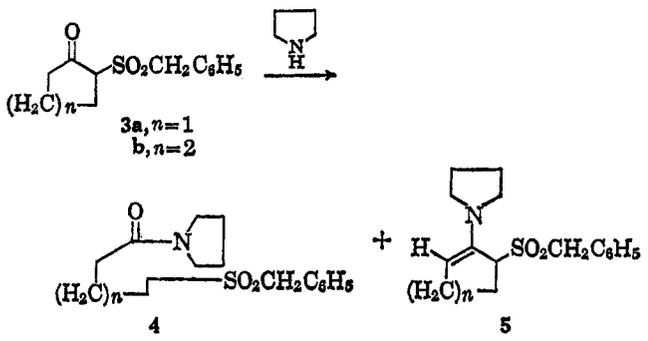
(1) W. E. Truce and R. H. Knospe, *J. Am. Chem. Soc.*, **77**, 5063 (1955).

(2) E. W. Truce, W. W. Banister, and R. H. Knospe, *J. Org. Chem.*, **27**, 2821 (1962).

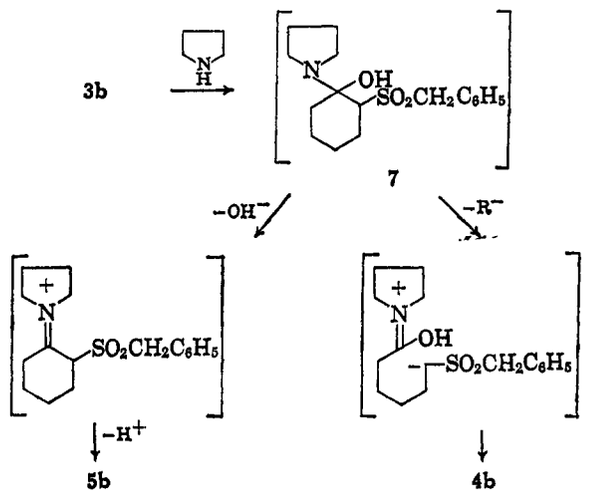
(3) H. Becker and G. A. Russell, *ibid.*, **28**, 1896 (1963).

(4) J. J. Looker, *ibid.*, in press.

SCHEME II



SCHEME III



proton transfer. Loss of the carbanion is undoubtedly favored by the presence of the stabilizing sulfone group.

Experimental Section

Benzyl 2-Ketocyclopentyl Sulfone (3a).—The sulfone was prepared analogously to the cyclohexyl[4] sulfone and, after recrystallization from ethanol, melted at 94–95° (74%). The nmr spectrum has peaks at τ = 2.5–2.7 (m, phenyl), 5.16, 5.40, 5.62, 5.86 (AB, J = 14.0 cps, benzylic), 6.3–6.6 (m, $CHSO_2$), and 7.4–8.3 ppm (m, remaining protons) in an area ratio of 5:2:1:6.

Anal. Calcd for $C_{12}H_{14}O_3S$: C, 60.5; H, 5.9; S, 13.4. Found: C, 60.4; H, 6.1; S, 13.2.

Cleavage of Acyclic β-Keto Sulfones with Pyrrolidine.—The β-keto sulfone was heated under reflux for 1 hr with a solution of 10 g of pyrrolidine in 200 ml of benzene. The sulfone was obtained by concentration of the solution and was recrystallized from ethanol. The ethanol filtrate, upon concentration, was found to contain 1-(phenylacetyl)pyrrolidine and identified by comparison of its infrared spectrum and gas chromatographic retention time with those of an authentic sample.[5] It was isolated by distillation in 62% yield from cleavage of **1a**. Each sulfone was identified by comparison of its infrared spectrum with that of authentic material; mixture melting points were not depressed. See Table I for weights and yields.

TABLE I

β-Keto sulfone[4]	g (mole)	Sulfone	Yield, %
1a	5.0 (0.012)	**2a**	98
1b	3.4 (0.0093)	**2b**	100
1c	2.2 (0.0076)	**2c**	70
1d	0.40 (0.0014)	**2d**	58

Cleavage of Cyclic β-Keto Sulfones.—By using the procedure described for cleavage of acyclic β-keto sulfones, 1.0 g (0.0040 mole) of benzyl 2-ketocyclohexyl sulfone[4] was converted into 0.55 g (43%) of amide **4b**, mp 112–113°. It was isolated by recrystallization of the reaction mixture from ligroin–benzene.

Anal. Calcd for $C_{17}H_{25}NO_3S$: C, 63.1; H, 7.8; N, 4.3; S, 9.9. Found: C, 63.0; H, 7.5; N, 4.2; S, 9.8.

The nmr spectrum had peaks at τ = 2.65 (s, phenyl), 5.82 (s, benzylic), 6.5–6.7 (m, pyrrolidino), 7.20–7.3 (t, J = 7 cps, CH_2 adjacent to SO_2), and 7.8–8.5 ppm (overlapping multiplets, remaining protons) in an area ratio of 5:2:4:2:12.

A solution of 8.5 g (0.034 mole) of benzyl 2-ketocyclohexyl sulfone in 300 ml of benzene containing 30 ml of pyrrolidine was heated at reflux for 16 hr and the water was separated. Concentration and addition of absolute ethanol caused a solid to separate which was recrystallized from ethanol to give 4.8 g (46%) of enamine **5b**, mp 95–96°. From the filtrate was obtained 0.6 g (6%) of amide **4b**. On standing a few minutes open to the air, the enamine was hydrolyzed to the starting ketone.

Anal. Calcd for $C_{17}H_{23}NO_3S$: C, 67.0; H, 7.6; N, 4.6; S, 10.5. Found: C, 66.8; H, 7.3; N, 4.3; S, 10.8.

The nmr spectrum had peaks at τ = 2.65 (s, phenyl), 5.05 (t, J = 3.0 cps, olefinic), 5.62 and 5.64 (benzylic, AB), 6.08 (m, allylic adjacent to SO_2), and 6.5–8.3 ppm (m, remaining overlapping peaks) in an area ratio of 5:1:2:1:14.

A 4.8-g (0.020 mole) portion of benzyl 2-ketocyclopentyl sulfone (**3a**) was cleaved by each of the procedures described for β-keto sulfone **3b**. When the reaction time was 1 hr, amide **4a** was obtained in 67% yield upon recrystallization of the product from benzene, mp 125–126°. With a 16-hr reaction time and water separation, 4.8 g (80%) of the amide was isolated. Enamine **5a** was not isolated from the filtrates.

Anal. Calcd for $C_{16}H_{23}NO_3S$: C, 62.1; H, 7.5; N, 4.5; S, 10.4. Found: C, 61.9; H, 7.8; N, 4.3; S, 10.6.

The nmr spectrum of amide **4a** had peaks at τ = 2.57 (s, phenyl), 5.75 (s, benzylic), 6.4–6.7 (m, pyrrolidino), 7.10 (t, J = 8.0 cps, CH_2SO_2), 7.73 (t, J = 6.0 cps, CH_2CO), and 8.0–8.3 ppm (m, remaining protons) in an area ratio of 5:2:4:2:2:8.

Hydrolysis of Enamine 5b.—A solution of 0.50 g (0.0016 mole) of the enamine in 10 ml of 1,2-dimethoxyethane and 10 ml of 3 *N* hydrochloric acid was heated on a steam bath for 30 min and concentrated. The residue was extracted into ether, washed with water, dried, and concentrated to give 0.39 g (100%) of benzyl 2-ketocyclohexyl sulfone, mp 100–101°. A mixture melting point with an authentic sample[4] was not depressed.

Preparation of Sulfones.—*p*-Chlorobenzyl benzyl sulfide was prepared from 8.0 g (0.050 mole) of α,*p*-dichlorotoluene, 6.2 g (0.050 mole) of α-toluenethiol, 50 ml of ethanol, and 2.0 g (0.050 mole) of sodium hydroxide, bp 154° (0.1 mm), 8.7 g (62%).

Anal. Calcd for $C_{14}H_{13}ClS$: C, 67.5; H, 5.3; Cl, 14.3; S, 12.9. Found: C, 67.6; H, 5.2; Cl, 14.6; S, 13.2.

Oxidation of 2.5 g of this sulfide with potassium permanganate gave 2.2 g (98%) of sulfone **2a**, mp 168–169° (lit.[6] mp 167–168°).

Benzyl methyl sulfone was prepared (65%) by potassium permanganate oxidation of the corresponding sulfide,[7] mp 125–126° (lit.[8] mp 127°).

Dibenzyl sulfone was prepared (78%) by potassium permanganate oxidation of the corresponding sulfide, mp 150–151° (lit.[8] mp 150°).

Acknowledgment.—The author is grateful to Dr. T. H. Regan for the nmr spectra.

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C^{14} Tracer Studies in the Wallach Transformation

LYELL C. BEHR AND EDWARD C. HENDLEY

Hand Chemical Laboratory, Mississippi State University, State College, Mississippi

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In the Wallach transformation azoxybenzene is converted into 4-hydroxyazobenzene (among other prod-