Reaction of Diphenylcyclopropenone with Dimethyloxosulfonium Methylide

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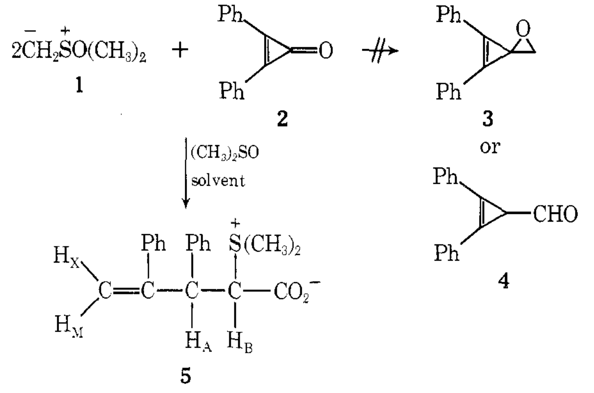
Diphenylcyclopropenone reacts with 2 mol of dimethyloxosulfonium methylide to give the betaine **5**. Structure proof of the betaine is presented and its formation is interpreted in terms of a complex mechanism initiated by conjugate addition of the nucleophilic ylide to the ketone. On heating (135°), **5** gave the isomeric betaine **11** and 2,3-diphenylcyclopent-2-en-1-one (**12**).

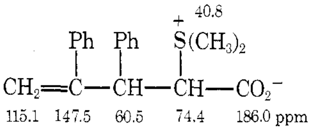
Dimethyloxosulfonium methylide (**1**) is particularly useful for the preparation of aldehydes via the isomeric epoxides.[2,3] Reaction of this ylide with diphenylcyclopropenone (**2**) using dimethyl sulfoxide solvent provided neither the epoxide **3** nor the previously known[4] aldehyde **4**, but the ring-opened betaine **5**, 2-dimethylsulfonio-3,4-diphenylpent-4-enoate.



The structure of **5** is based on the following data. Elemental and mass spectral analysis, including relative abundances of isotope peaks, confirmed the molecular formula $C_{19}H_{20}O_2S$. A styryl group was indicated by the ultraviolet spectrum, which had λ_{max} 210 nm (ϵ 25,450) and 255 (18,850). The infrared spectrum had intense bands at 1540 and 1360 cm^{-1}, characteristic of carboxylate, and the pattern of the 5–6-μ region as well as the long-wavelength diagnostic bands established the presence of one or more phenyl groups. The nuclear magnetic resonance spectrum ($CDCl_3$) exhibited a ten-proton multiplet centered at 7.3 ppm (two phenyl groups), a six-proton singlet at 3.2 ppm [$(CH_3)_2S^+$], and an array of four slightly broadened signals at 4.42 (H_B), 4.73 (H_A), 5.12 (H_M), and 5.58 ppm (H_X). Expansion of the four-proton array and double-resonance technique revealed an uncoupled signal (H_B) and a weakly coupled AMX pattern: J_{AM} = 1.2, J_{AX} = 0.4, and J_{MX} = 1.0 Hz. Chemical shift assignments were established by comparisons with α-methylstyrene, 3,4-diphenylpent-4-enoic acid,[5] and model sulfonium salts.[6] The slight broadening of the H_B signal 4.42 ppm we attribute to a nuclear Overhauser interaction between this proton and the dimethyl protons. This conclusion is based on two observations. (1) Irradiation of the dimethyl signal caused a significant enhancement of the H_B signal. (2) When the NMR spectrum was recorded using dimethyl sulfoxide-d_6 solvent, this signal was similarly enhanced and shifted downfield to 4.95 ppm. In the same solvent the dimethyl signal was shifted to 3.4 ppm. Other signals were not significantly altered by solvent change. Apparently dimethyl sulfoxide solvates the sulfonio group, removing the nuclear Overhauser effect.[7]

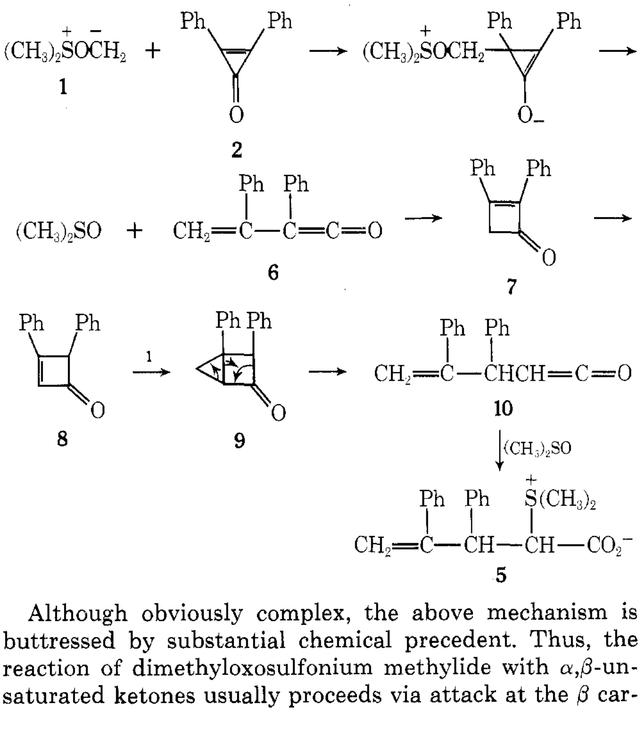
Given the presence of a styryl group, there are six positional isomers of the betaine **5**. Three of the betaines, including **5**, have the dimethyl sulfonio group α to the carboxylate group and the remaining four have a β arrangement. An α arrangement was established by measuring the pK_a of the protonated betaine. The observed pK_a, 2.59, is consistent with an α arrangement.

The structure of the betaine, aside from configuration, was established with finality by its ^{13}C NMR spectrum. Chemical shift assignments, summarized in the following formula, were established by comparison with suitable model compounds.[8] Aromatic carbons had the expected chemical shifts and all carbons had the expected multiplicities.



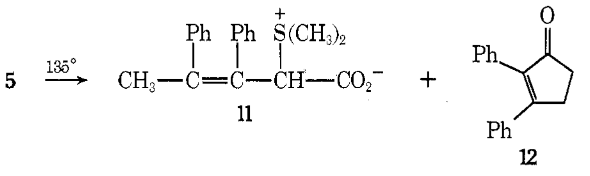
$$\underset{115.1}{CH_2}{=}\underset{147.5}{\overset{Ph}{C}}-\underset{60.5}{\overset{Ph}{CH}}-\underset{74.4}{\overset{\overset{40.8}{\overset{+}{S}(CH_3)_2}}{CH}}-\underset{186.0\ \text{ppm}}{CO_2^-}$$

Mechanism of Formation of 5. Ring-opened products are almost always obtained in the reactions of cyclopropenones with nucleophiles and, depending on the nature of the attacking nucleophile, the apparent mechanisms of these reactions are of varying degrees of complexity.[9] The mechanism summarized in the following scheme provides a chemically plausible rationale for the formation of the betaine.



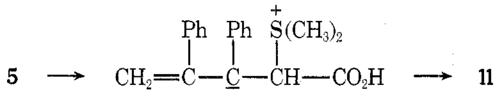
Although obviously complex, the above mechanism is buttressed by substantial chemical precedent. Thus, the reaction of dimethyloxosulfonium methylide with α,β-unsaturated ketones usually proceeds via attack at the β carbon and yields a cyclopropyl ketone.[3] In the present case ring strain would undoubtedly facilitate opening to the vinyl ketene **6**. Jenny and Roberts[10] have shown that vinyl ketenes close rapidly to cyclobutenones, so that conversion of **6** to **7** is predictable. It is clear from the composition of the betaine that it is the product of a diphenylcyclopropenone molecule, two CH_2 units, and a unit of dimethyl sulfoxide. Further, it is necessary at some stage to shift a hydrogen atom. The ylide **1** is probably sufficiently basic to effect isomerization of **7** to **8**, especially in dimethyl sulfoxide. This step accomplishes the required hydrogen shift. Formation of the "housone" **9** is straightforward, and its isomerization to the allyl ketene **10** is analogous to reactions implicated recently in the photochemistry of some cyclopentenones[5] and the thermal-photochemical reactions of some functionalized cyclopropenes.[11] Addition of dimethyl sulfoxide to ketenes appears not to have been reported but the result here, in the addition to the ketene **10**, is similar to the addition reaction of dimethyl sulfoxide with dimethyl acetylenedicarboxylate, in which the oxygen on sulfur is transferred to carbon to yield a dimethylsulfonio enolate betaine.[12]

Thermal Reactions of the Betaine. Attempts to transform the betaine to known compounds by treatment with a variety of bases, acids, and reducing agents were singularly unfruitful. However, in refluxing chlorobenzene (135°) the betaine gave the isomeric betaine **11**, 2-dimethylsulfonio-3,4-diphenylpent-3-enoate (stereochemistry of the double bond not established), and 2,3-diphenylcyclopent-2-en-1-one (**12**).



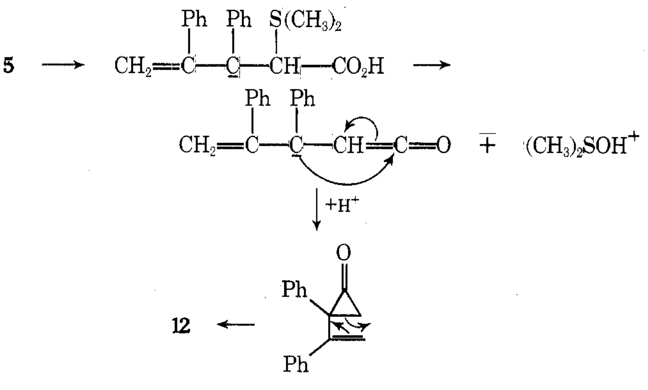
The structure of the isomeric betaine was established by means of analytical and spectroscopic data. The cyclopentenone has been known for some time,[13] although its structure was in question for many years until it was established with the aid of ultraviolet spectroscopy.[14] Our analysis of its NMR spectrum confirms the structure.

The origin of the isomeric betaine is mechanistically straightforward.



$$5 \longrightarrow CH_2{=}\underset{Ph}{C}{-}\underline{\underset{Ph}{C}}{-}\underset{\overset{+}{S}(CH_3)_2}{CH}{-}CO_2H \longrightarrow 11$$

The origin of the cyclopentenone is more complex. The following tentative mechanism is suggested.



Experimental Section

Melting points were determined on a Fisher-Johns apparatus and are uncorrected. Uv spectra were recorded with a Beckman DB-GT spectrophotometer using methanol solvent; ir spectra were recorded on a Wilks Hilger-Watts Infragraph; proton NMR spectra were recorded at 60 MHz on a Varian T60-A spectrometer and at 30 MHz on a Varian EM-300 spectrometer; chemical shifts are relative to internal tetramethylsilane at δ 0. ^{13}C NMR spectra were recorded on a Jeol FX-60 instrument using dimethyl sulfoxide-d_6 solvent; chemical shifts are relative to tetramethylsilane at δ 0. Mass spectra were obtained from Morgan-Schaffer, Montreal, Canada. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, N.Y.

2-Dimethylsulfonio-3,4-diphenylpent-4-enoate (5). A stirred solution of trimethyloxosulfonium iodide[2] (1.76 g, 8 mmol) in 10 ml of dry dimethyl sulfoxide (DMSO) at 10° under nitrogen was treated with 5 ml of 1.6 *M* *n*-butyllithium in hexane (Foote Mineral Co.). After 10 min 2,3-diphenylcyclopropenone[15] (1.03 g, 5 mmol) in 10 ml of dry DMSO was added in one portion. The mixture was stirred for 3 hr at 50–55°, then cooled and diluted with water (50 ml), and the mixture was shaken with 1:1 benzene–hexane (50 ml). The organic layer was separated, washed five times with water, dried ($MgSO_4$), and filtered. Evaporation of the filtrate gave a glassy solid (1.01 g) which was recrystallized from benzene–hexane to give **5** (0.44 g), colorless microcrystals: mp 129–131°; mass spectrum *m/e* (rel intensity, ion) 312 (0.7, M^+), 234 [16, $M^+ - (CH_3)_2SO$], 119 (100). The $M^+ + 1$ and $M^+ + 2$ peaks had, respectively, intensities of 25.6 and 8.7 relative to M^+ at 100; calculated intensities for $C_{19}H_{20}O_2S$ are $M^+ + 1$, 21.7 and $M^+ + 2$, 6.9. Additional spectroscopic data are discussed in the text. The pK_a of the protonated betaine in 20% H_2O–80% EtOH, determined by standard technique,[16] was 2.59.

Anal. Calcd for $C_{19}H_{20}O_2S$: C, 73.04; H, 6.45; S, 10.27. Found: C, 72.92; H, 6.34; S, 10.46

Thermal Isomerization of 5 to 11 and Fragmentation to 12. A solution of **5** (43 mg) in chlorobenzene (10 ml) was refluxed for 24 hr under nitrogen. Evaporation of the solvent gave a yellow, glassy solid which was triturated with warm ether. An insoluble crystalline fraction (A) was filtered from the soluble fraction (B).

Fraction A. The Isomeric Betaine 11. The filtered solid (10 mg), mp 155–159°, was recrystallized twice from ethyl acetate to give **11** as colorless crystals: mp 158–160°; uv 210 nm (ϵ 18,400), 260 (18,400); ir (KBr) 1530, 1390, 1205, 1140, 1035, 900, 800, 770, 750, 715, 705, and 690 cm^{-1}; NMR ($CDCl_3$, 30 MHz) δ 7.05 (m, 10, 2 phenyls), 4.45 (s, 1, methine H), 3.33 [s, 6, $(CH_3)_2S^+$], and 2.30 (s, 3, vinyl CH_3).

Anal. Calcd for $C_{19}H_{20}O_2S$: C, 73.04; H, 6.45; S, 10.27. Found: C, 73.25; H, 5.6.39; S, 10.54.

Fraction B. 2,3-Diphenylcyclopent-2-en-1-one (12). The soluble fraction was evaporated to dryness and the residue (26 mg) was crystallized from ligroin containing a small amount of ether to give **12** as colorless crystals: mp 93–94° (lit.[13] mp 92°); NMR ($CDCl_3$, 30 MHz) δ 7.2 (s, 10, 2 phenyls), 2.3–2.4 (m, A_2B_2 symmetry, 4, $-CH_2CH_2-$); uv identical with that reported by Allen and Van Allan.[14] The 2,4-dinitrophenylhydrazone had mp 227–228° (lit.[13] mp 228°).

Acknowledgments. We thank Mr. Joseph Lewandowski for pK_a measurements, Ms. Barb Erwine of Varian Associates for excellent NMR spectra, and Mr. Kokichi Ishibitsu of Jeol for invaluable ^{13}C NMR spectra. We are grateful to Mr. Joseph R. De Filippis for many stimulating discussions.

Registry No.—**1**, 5367-24-8; **2**, 886-38-4; **5**, 54446-68-3; **11**, 54446-69-4; **12**, 4258-40-6.

References and Notes

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Preparation and Reactions of α-Lithiobutanesultams

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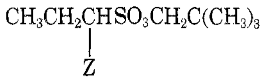
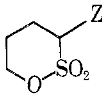
Metalations of *N*-methyl- and *N*-phenylbutanesultam were conveniently effected by means of *n*-butyllithium in THF–hexane at 25° to give α-lithio salts which were condensed with representative electrophiles to afford α-substituted derivatives in good to excellent yields. The electrophiles studied included benzyl chloride, various aldehydes and ketones, methyl benzoate, and benzonitrile. Several reactions with lithio-*N*-methylbutanesultam did not proceed in a predictable manner. Thus, this salt with benzonitrile and chalcone surprisingly afforded a primary enamine and an aminosultone, respectively, rather than the expected ketosultams. Also, this salt and aldehydes gave analytically pure β-hydroxysultams with melting point ranges of up to 30°. Metalation of *N*-methylbutanesultam was also effected by sodium amide in liquid ammonia.

It has long been known that hydrogen atoms α to sulfonyl-containing functional groups are sufficiently acidic that they can be ionized by basic reagents to afford the corresponding carbanionic derivatives. For example, sulfonate esters like **1** have been converted to anions like **1′** by alkali metal amides in ammonia.[2] Similarly, sultones like **2** have been metalated by *n*-butyllithium in THF–hexane at −78° to give α-lithio salts like **2′**.[3] Various sulfonamides have likewise been metalated. Thus, bromosulfonamides **3** give sultams **4** via **3′** upon treatment with *n*-butyllithium in THF–hexane at −70°.[4] Sulfonamide **5** has even been *gem*-dimetalated by this same base at 25° to give **5″**.[5]

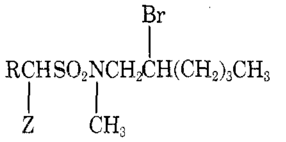


$\mathrm{CH_3CH_2}\underset{\displaystyle \mathrm{Z}}{\underset{|}{\mathrm{C}}}\mathrm{HSO_3CH_2C(CH_3)_3}$

1, Z = H
1′, Z = K

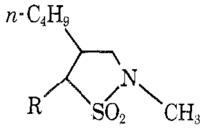


2, Z = H
2′, Z = Li

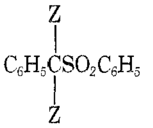


$\mathrm{R}\underset{\displaystyle \mathrm{Z}}{\underset{|}{\mathrm{C}}}\mathrm{HSO_2}\underset{\displaystyle \mathrm{CH_3}}{\underset{|}{\mathrm{N}}}\mathrm{CH_2}\overset{\displaystyle \mathrm{Br}}{\overset{|}{\mathrm{C}}}\mathrm{H(CH_2)_3CH_3}$

3, Z = H; R = H or CH_3
3′, Z = Li; R = H or CH_3



4
(R = H or CH_3)

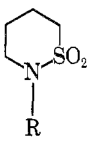


$\mathrm{C_6H_5}\overset{\displaystyle \mathrm{Z}}{\overset{|}{\underset{\displaystyle \mathrm{Z}}{\underset{|}{\mathrm{C}}}}}\mathrm{SO_2C_6H_5}$

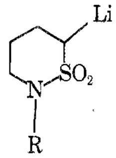
5, Z = H
5″, Z = Li

In contrast, there appear to be no reports of metalation of α hydrogens of sultams. This is somewhat surprising not only because of the above work on open-chain sulfonamides but also because sultams are more resistant to ring opening then are sultones. In light of the latter, in fact, sultams should be capable of being metalated at temperatures more convenient than those necessary for metalation of sultones. Moreover, once formed, α-lithiosultams should be more stable than α-lithiosultones. That such is the case is illustrated in this paper, which describes successful metalations of *N*-methyl- and *N*-phenylbutanesultam and subsequent reactions of the resulting carbanions with electrophiles.

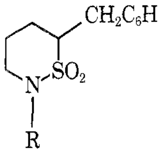
First, *N*-methylbutanesultam (**6**) was converted to its α-lithio salt (**6′**) at 25° by *n*-butyllithium in THF–hexane in only 10 min as evidenced by deuteration with deuterium oxide to give **6-α-*d***, in a yield of 95–100%. Anion **6′** was also alkylated by benzyl chloride to afford the corresponding alkyl derivative **8** in a yield of 65%. Likewise, anion **7′** was prepared from *N*-phenylbutanesultam (**7**) and *n*-butyllithium. Alkylation of **7′** by benzyl chloride gave **9** in a yield of 70%.



6, R = CH_3
7, R = C_6H_5

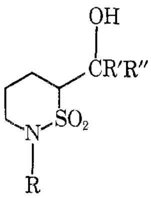


6′, R = CH_3
7′, R = C_6H_5



8, R = CH_3
9, R = C_6H_5

Next, anions **6′** and **7′** were condensed with various aldehydes and ketones to afford β-hydroxysultams. Thus, treatment of **6′** with benzophenone, benzaldehyde, and anisaldehyde gave **10**, **11**, and **12** in yields of 91, 80, and 86%, respectively. Similar condensations of **7′** with these same compounds afforded **13**, **14**, and **15** in yields of 86, 63, and 78%, respectively.



10, R = CH_3; R′ = R″ = C_6H_5
11, R = CH_3; R′ = C_6H_5; R″ = H
12, R = CH_3; R′ = p-$CH_3OC_6H_4$; R″ = H
13, R = R′ = R″ = C_6H_5
14, R = R′ = C_6H_5; R″ = H
15, R = C_6H_5; R′ = p-$CH_3OC_6H_4$; R″ = H

Incidentally, an attempt was made to prepare anions **6′** and **7′** by the interaction of the sultams and sodium amide in liquid ammonia. In the case of **6**, anion **6′** (M = Na) was