

Dimethyloxosulfonium 2-(Methylamino)benzoylmethylide. A New Stable Ylide and Its Use in Heterocyclic Syntheses^{1a}

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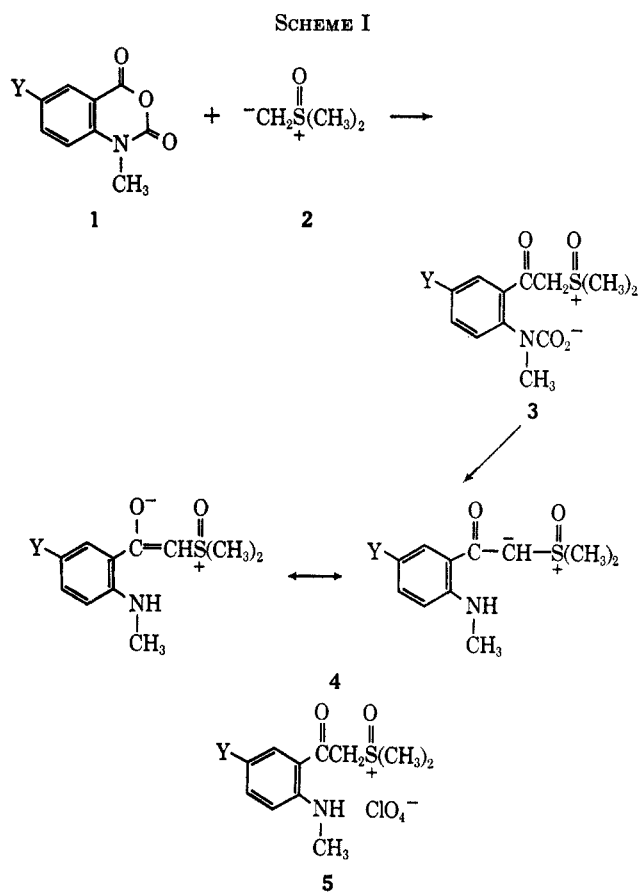
The reaction of *N*-methylisatoic anhydride (**1a**) with dimethyloxosulfonium methylide (**2**) gives dimethyloxosulfonium 2-(methylamino)benzoylmethylide (**4a**), a new, stable ylide which is a useful intermediate for heterocyclic synthesis because of participation in ring closure reactions of the *ortho*-situated methylamino grouping. Reaction of **4a** with triethyl orthoformate gives 1-methyl-3-methylsulfinyl-4(1H)-quinolinone (**9**), which is desulfurized with Raney nickel alloy and alkali to 1-methyl-4(1H)-quinolinone. Triethyl orthoacetate converts **4a** into 1,2-dimethyl-3-methylsulfinyl-4(1H)-quinolinone (**11**). Condensation of **4a** with carbon disulfide in pyridine gives 1-methyl-2-mercapto-4(1H)-quinolinone (**16**). Reaction of **4a** with nitrosobenzene in ethanol gives 1-methylsatin-2-anil (**19**), while with aqueous hydrochloric acid containing sodium chloride, 2-methylamino- α -chloroacetophenone (**22**) is formed. Possible mechanisms for the above reactions are discussed.

Acyl-substituted ylides^{2a-c} $XCH-S^+(=O)(CH_3)_2$ ($X = RC\equiv O$) are derived from the versatile dimethyloxosulfonium methylide^{2a,3} (**2**) by reaction with carboxylic acid derivatives (chlorides, anhydrides, and phenyl esters) or with ketenes. In contrast with **2** itself, these acyl derivatives are isolable and reasonably stable. Other stabilized ylides which have been reported recently have $X = RNHC=O$,^{2b,c} $X = ROOC-C=$,^{2c,d} $X = RSO_2$,^{2e} and $X = ROOC^-$.^{2f} Substitution of both hydrogens of the ylide carbon in **2** by the same electro-negative group has also been reported.^{2b,c,f}

We wish to report the synthesis of dimethyloxosulfonium 2-(methylamino)benzoylmethylide (**4a**) by the reaction of dimethyloxosulfonium methylide (**2**) with *N*-methylisatoic anhydride (**1a**). The presence of the *ortho*-situated methylamino group in **4a** makes this new, isolable, and stable ylide an interesting intermediate for the synthesis of several heterocyclic systems, as described below.

The ylide **4a** is obtained in 70% yield by the reaction of **1a** with **2** (from trimethyloxosulfonium iodide and sodium hydride^{2a}) in DMSO solution for 1 hr at 50–60°. The (presumed) intermediate adduct **3a** can give rise to **4a** by loss of carbon dioxide and a prototropic shift. Carbon dioxide is indeed evolved from the reaction mixture, but its 1:1 adduct with **2**, reported by Corey and Chaykovsky,^{2a} is either not formed or is not stable under these conditions. The yield of **4a** is not increased by the use of more **2**. (See Scheme I.)

The yellow, crystalline stable ylide **4a** melts at 141–143° with only slight decomposition. Its nmr spectrum (DCCl₃) shows an aromatic multiplet between 7.5 and 6.3 ppm, a broad weak signal at 8.2 ppm (N–H), a broad signal at 5.0 ppm (C–H), a singlet at 3.36 ppm (S–CH₃), and a singlet at 2.81 ppm (N–CH₃) (ratio 4:1:1:6:3). The absorptions due to the ylide portion of **4a** are in good agreement with values reported for other stabilized oxosulfonium ylides.² The low carbonyl absorption



band at 1520 cm⁻¹ is likewise consistent with previous observations on related systems.^{2a-c}

Treatment of **4a** with perchloric acid gave a perchlorate salt (**5a**), whose nmr spectrum (DMSO-*d*₆) was similar to the spectrum of **4a** except for a two-proton signal at 6.12 ppm ($-CH_2S^+=O$ in **5a**) instead of the one-proton signal at 5.0 ppm ($-CH-S^+=O$ in **4a**).

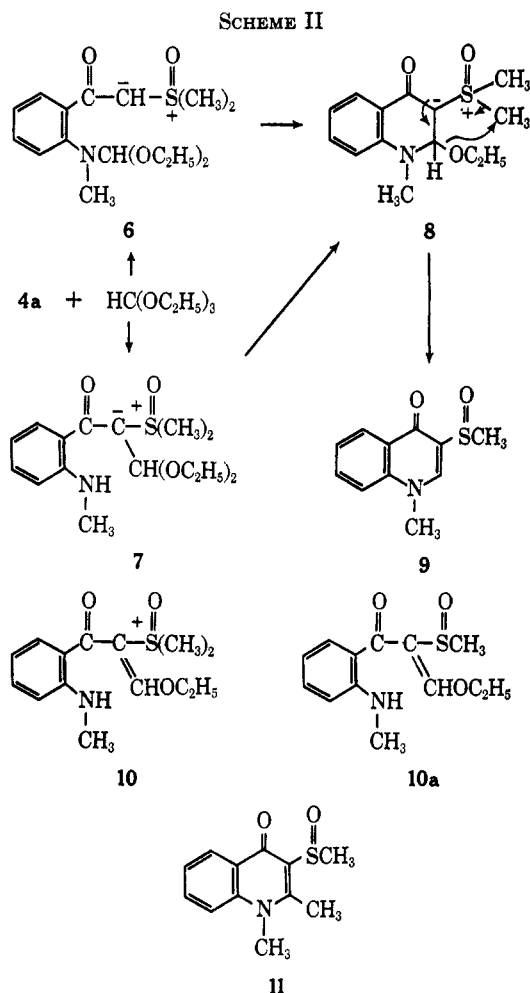
In complete analogy with the above results, reaction of 6-nitro-*N*-methylisatoic anhydride (**1b**) with **2** gave the nitro derivatives **4b** (in 66% yield) and **5b**.

Dimethyloxosulfonium 2-(methylamino)benzoylmethylide (**4a**) is converted to 1-methyl-3-methylsulfinyl-4(1H)-quinolinone (**9**) (see Scheme II) in 90% yield by refluxing with a mixture of triethyl orthoformate and ethanol containing a small amount of acetic acid as catalyst. The nmr spectrum of **9** (DCCl₃) showed a

(1) (a) This work was supported by Research Grant CA-02551 to Princeton University from the National Cancer Institute, National Institutes of Health, Public Health Service. (b) On leave of absence from Groningen University, The Netherlands.

(2) (a) E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **87**, 1353 (1965); **86**, 1640 (1964); (b) H. König and H. Metzger, *Chem. Ber.*, **98**, 3733 (1965); (c) C. Kaiser, B. M. Trost, J. Beeson, and J. Weinstock, *J. Org. Chem.*, **30**, 3972 (1965); (d) J. Ide and Y. Kishida, *Tetrahedron Letters*, 1787 (1966); (e) W. E. Truce and G. D. Madding, *ibid.*, 3681 (1966); (f) H. Nozaki, D. Tunemoto, S. Matubara, and K. Kondo, *Tetrahedron*, **23**, 545 (1967).

(3) For a recent review on sulfur ylides, see A. W. Johnson, "Ylid Chemistry," Academic Press Inc., New York, N. Y., 1966, p 304 ff.



five-proton aromatic multiplet between 8.4 and 7.2 ppm (in which a one-proton singlet for the C-2 hydrogen was discernible at 7.96 ppm) and two three-proton singlets at 3.96 (NCH₃) and 2.89 ppm (SCH₃). Its infrared spectrum showed a carbonyl band at 1615 cm⁻¹, consistent with a 4(1H)-quinolinone structure,⁴ and a sulfoxide S=O band at 1050 cm⁻¹. Reductive desulfurization with Raney nickel alloy and sodium hydroxide in aqueous ethanol⁶ gave 1-methyl-4(1H)-quinolinone, while desulfurization with Raney nickel in aqueous ethanol gave 1-methyl-5,6,7,8-tetrahydro-4(1H)-quinolinone.⁶

Catalytic reduction of 1-methyl-4(1H)-quinolinone with Raney nickel as a catalyst gave the 5,6,7,8-tetrahydro derivative. According to Price, however,⁷ this transformation cannot be effected by the Raney nickel alloy-alkali method,⁵ although the corresponding 3-carboxylic acid is transformed under these conditions to the 5,6,7,8-tetrahydro derivative. It thus appears that an electronegative substituent must be present in the heterocyclic ring for reduction of the benzene moiety to be effected by the Raney nickel alloy-alkali method.

(4) N. J. McCorkindale, *Tetrahedron*, **14**, 223 (1961).

(5) (a) D. Papa, E. Schwenk, and B. Whitman, *J. Org. Chem.*, **7**, 587 (1942); (b) D. Papa, E. Schwenk, and H. F. Ginsberg, *ibid.*, **16**, 253 (1951); (c) E. Schwenk, D. Papa, H. Hankin, and H. F. Ginsberg, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p 742.

(6) Our evidence does not exclude the 1-methyl-2-methylsulfinyl-4(1H)-quinolinone structure, but it is hard to design a reasonable reaction scheme which would explain its formation. Equal difficulty is experienced in proposing a reasonable route to the corresponding isomeric structure (1,3-dimethyl-2-methylsulfinyl-4(1H)-quinolinone) for **11** (*vide infra*).

(7) J. R. Price, *Australian J. Sci. Res.*, **2A**, 272 (1949).

It follows that reductive removal of the methylsulfinyl grouping in **9** under these conditions must be rapid, for otherwise concomitant reduction of the benzene ring might have been expected.

Oxidation of sulfoxide **9** with hydrogen peroxide gave, as expected, 1-methyl-3-methylsulfonyl-4(1H)-quinolinone. Its nmr spectrum was similar to that of compound **9** and showed (DMSO-*d*₆) singlets at 8.48 (C₂ H), 3.85 (NCH₃), and 3.13 ppm (SO₂CH₃). The infrared spectrum of the sulfone exhibited the characteristic SO₂ bands at 1150 and 1295 cm⁻¹.

The ylide carbon in acyl-stabilized oxosulfonium methylides still retains nucleophilic properties, although to a lesser extent than in **2** itself.^{2b} Thus the first step in the reaction of **4a** with triethyl orthoformate (protonated by the acetic acid employed as catalyst)⁸ may lead either to **6** or to **7** (there being no *a priori* basis for judging the relative nucleophilicities of the -NHCH₃ vs. the ylide CH-S⁺(=O)(CH₃)₂ groupings). The second step could then be the formation of the cyclic ylide **8** either by nucleophilic attack by the ylide carbon on the very reactive aminoacetal grouping in **6**⁹ or by cyclization of acetal **7**. Aromatization of **8** by elimination of ethyl methyl ether¹⁰ would then lead to **9**, the observed product.¹¹ This mechanistic interpretation provides a reasonable explanation for the unusual formation of a sulfoxide (**9**) from the oxosulfonium ylide **4a**.¹²

Similarly, **4a** and triethyl orthoacetate in the presence of a small amount of acetic acid as catalyst gave 1,2-dimethyl-3-methylsulfinyl-4(1H)-quinolinone (**11**) in 87% yield.¹³ As in compound **9**, the carbonyl stretching band in **11** appears at low frequency (1625 cm⁻¹); the sulfoxide S=O band appears at 1025 cm⁻¹. Its nmr spectrum (DCCl₃) shows an aromatic multiplet between 8.3 and 7.1 ppm and singlets at 3.75 ppm (NCH₃) and at 3.04 and 2.87 ppm (SCH₃ and CCH₃, or *vice versa*) (ratio 4:3:3:3). Compound **11** apparently undergoes partial rearrangement or decomposition upon recrystallization either from benzene or acetone (in the presence of air). The melting point, originally 179–181°, becomes indistinct (130–175°), additional absorptions in the infrared spectrum appear around 3400 and 1550 cm⁻¹ and new, ill-defined signals appear in the higher field region of the nmr spectrum. The origin of these changes has not been elucidated.

Reaction of dimethyloxosulfonium 2-(methylamino)-benzoylmethylide (**4a**) with carbon disulfide in pyridine solution gives a light yellow compound which, on the basis of the following evidence, is assigned the structure 1-methyl-2-mercapto-4(1H)-quinolinone (**16**). A weak, broad -SH band at 2550 cm⁻¹ and a carbonyl band at 1625 cm⁻¹ are distinguishing features of its

(8) For a discussion and pertinent references, see E. C. Taylor and W. A. Ehrhart, *J. Org. Chem.*, **28**, 1108 (1963).

(9) H. Meerwein in "Methoden der organischen Chemie," Houben-Weyl, Vol. 6/3, Thieme Verlag, Stuttgart, 1965, pp 259 ff.

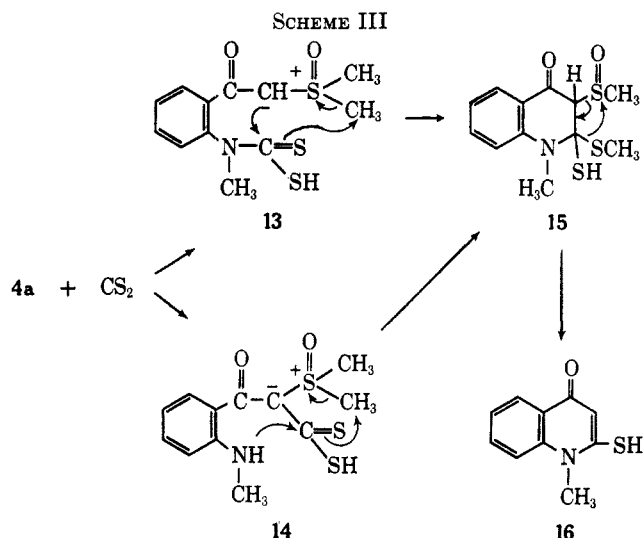
(10) Although aromatization is depicted as intramolecular and concerted, there is no present evidence to exclude a two-step process proceeding via elimination of ethoxide from **8** to give the dimethyloxosulfonium salt corresponding to **9**, followed by loss of methyl to solvent. No attempt was made to isolate ethyl methyl ether from the reaction mixture.

(11) Other sequences of reactions (e.g., **7** → **10** → **8** → **9**, or **7** → **10a** (via **10**?) → **9**) are also possible.

(12) Another example, the formation of C₆H₅CH(NHC₂H₅)CH₂SOCH₃ from benzalaniline and **2**, has been reported (H. König, H. Metzger, and K. Seelert), *Chem. Ber.*, **98**, 3724 (1965); see also ref 2a.

(13) The formation of **11** from **4a** supports the conclusion that the carbon atom at position 2 in **9** originates from triethyl orthoformate and not, by some unspecified reaction, from one of the S-methyl groups in **4a**.

infrared spectrum. Its nmr spectrum (DMSO- d_6) shows an aromatic multiplet between 7.9 and 7.0 ppm, a singlet at 6.89 ppm (C_3 H), a broad band at 11.15 ppm (SH), and a singlet at 3.97 ppm (NCH_3) (ratio 4:1:1:3). Reductive desulfurization with Raney nickel alloy and alkali⁵ gives 1-methyl-4(1H)-quinolinone. In contrast to the reaction of **4a** with ortho esters, this reaction with carbon disulfide results in the loss of the sulfoxide grouping. We propose the reaction course depicted in Scheme III to account for this unexpected re-



sult. The reaction presumably is initiated by nucleophilic addition of either the methylamino grouping or the ylide carbon to carbon disulfide (**4a** \rightarrow **13** or **14**). Subsequent ring closure, with transfer of one of the dimethyloxosulfonium methyl groups to S (**13** or **14** \rightarrow **15**) does not, however, result in aromatization (as in the conversion of **8** to **9**, Scheme I). The loss of dimethyl disulfide S-oxide¹⁴ from **15** (rather than hydrogen sulfide) may be favored because of the formation of a S-S bond in the elimination step. The conversion of **13** (or **14**) into **16** may be considered in effect as a synchronous insertion of the dithiocarbamic acid $=S$ into the SCH_3 bond.

Utilization of **4a** as an intermediate for the formation of an indole derivative is conceivable as a result of intramolecular nucleophilic attack of the methylamino group at the protonated ylide carbon (**17**), with expulsion of DMSO (Scheme IV).¹⁵ The resulting product, N-methylindoxyl (**18**), which has not been reported, might be expected to be oxidized readily to N,N'-dimethyl indigo,¹⁶ a reaction characteristic of indoxyls.¹⁷ We assume that some N,N'-dimethyl indigo is indeed formed from **4a** via **18**, because of the observation of a small blue spot in thin layer chromatograms of **4a** following recrystallization from hot ethanol. Further-

more, when **4a** is refluxed with nitrosobenzene in ethanol solution, 1-methylisatin-2-anil¹⁸ (**19**) is formed in 61% yield. Acid hydrolysis of **19** gives N-methylisatin¹⁸ (**20**) in 57% yield. The anil **19** is presumably formed by direct condensation of N-methylindoxyl (**18**) with nitrosobenzene, since a similar reaction of indoxyl itself with nitrosobenzene has been described.¹⁹ It is also possible, however, that **4a** may react first with nitrosobenzene to give an oxazirane²⁰ (**21**), which can also give rise to **19** as shown. The usual reluctance of oxaziranes to undergo nucleophilic ring opening²¹ would be expected to be decreased in **21** because of the carbonyl substituent.

Intermolecular nucleophilic displacement of DMSO from **17** has also been observed.²² Reaction of **4a** with aqueous hydrochloric acid containing sodium chloride afforded 2-methylamino- α -chloroacetophenone (**22**).

Experimental Section²³

Dimethyloxosulfonium 2-(Methylamino)benzoylmethylide (4a) and Perchlorate (5a).—A solution of dimethyloxosulfonium methylide²⁴ was prepared from sodium hydride (12.0 g of a 50% dispersion in mineral oil, 0.25 mole) and trimethyloxosulfonium iodide (55.0 g, 0.25 mole) in 250 ml of anhydrous dimethylsulfoxide²⁴ in a 1-l. vessel equipped with two pressure-equalizing dropping funnels. A solution of N-methylisatoic anhydride²⁶ (35.4 g, 0.20 mole) in 300 ml of anhydrous DMSO was added in 5 min to the magnetically stirred solution of dimethyloxosulfonium methylide. By the time addition was complete, CO_2 evolution had commenced vigorously. After heating at 50–60° for 1 hr, the cooled mixture was poured into 3 l. of ice-water and the solution was saturated with NaCl and extracted five times with dichloromethane. The combined extracts were dried over Na_2SO_4 and concentrated *in vacuo* to give a greenish oil which was dissolved in dichloromethane (75 ml). Slow addition of diethyl ether (250 ml) caused crystallization of the yellow ylide (31.7 g, 0.14 mole) (70%), mp 138–141°. The melting point was raised to 141–143° (slight decomposition) upon crystallization from dichloromethane-diethyl ether.

Anal. Calcd for $C_{11}H_{16}NO_2S$: C, 58.64; H, 6.71; N, 6.22; S, 14.23. Found: C, 58.40; H, 6.88; N, 6.11; S, 14.05.

A mixture of perchloric acid (70% in water, 10 ml) and ethanol (30 ml) was added to a hot solution of dimethyloxosulfonium 2-(methylamino)benzoylmethylide (1.0 g) in ethanol (80 ml), under nitrogen. Rapid chilling resulted in crystallization of the yellow perchlorate (1.35 g, 92%), mp 130–132° dec.

Anal. Calcd for $C_{11}H_{16}ClNO_6S$: C, 40.55; H, 4.95; Cl, 10.89; N, 4.30; S, 9.85. Found: C, 40.56; H, 4.85; Cl, 11.48; N, 4.39; S, 10.18.

Dimethyloxosulfonium 2-Methylamino-5-nitrobenzoylmethylide (4b) and Perchlorate (5b).—In similar fashion to the preparation of **4a** described above, the 5-nitro derivative was obtained from 1.20 g of sodium hydride (50% dispersion in mineral oil, 0.025 mole), 5.50 g of trimethyloxosulfonium iodide (0.025 mole) in 25 ml of anhydrous DMSO, and 4.44 g (0.020 mole) of

(18) R. Pummerer, *Chem. Ber.*, **44**, 338 (1911).

(19) R. Pummerer and M. Goettler, *ibid.*, **42**, 4269 (1909).

(20) Oxaziranes have been proposed as possible intermediates in the formation of nitrones from a number of sulfonium ylides and nitrosobenzene (ref 3, p 338).

(21) For a review of oxazirane chemistry, see W. D. Emmons in "The Chemistry of Heterocyclic Compounds," Vol. 19, A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, p 624.

(22) A similar reaction has been reported by König and Metzger.^{2b}

(23) All reactions were carried out under nitrogen; furthermore, nitrogen was bubbled through all reaction mixtures for 30 min prior to heating. Microanalyses were performed by the Spang Microanalytical Laboratory, Ann Arbor, Mich. Infrared spectra were determined on a Perkin-Elmer grating spectrophotometer, Model 237B, from samples milled in Nujol. Nmr spectra were taken on a Varian A-60 A instrument in the indicated solvents, with absorptions measured in parts per million downfield from internal TMS. Melting points are uncorrected.

(24) Anhydrous DMSO (Matheson Coleman and Bell) was stored over Molecular Sieves (Linde, Type 5A) and used without further distillation.

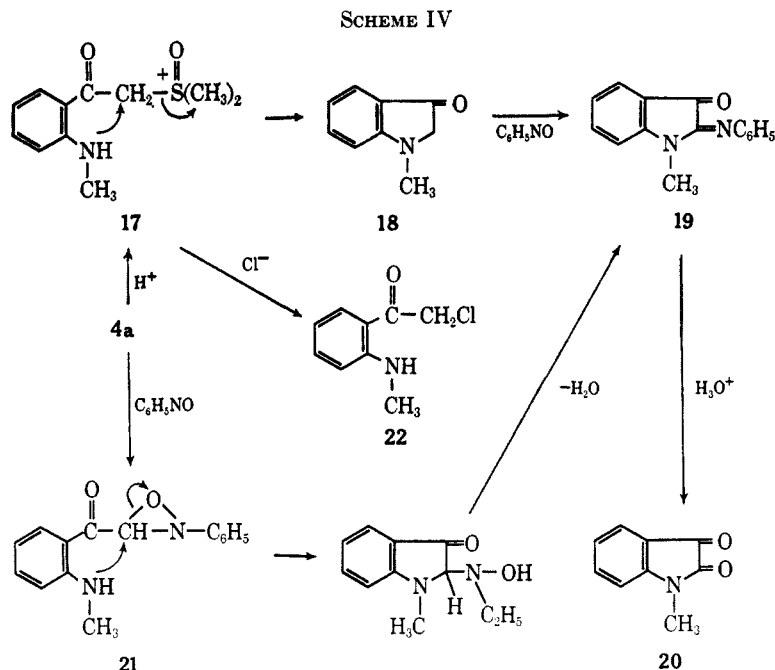
(25) From J. T. Baker Chemical Co., Phillipsburg, N. J.

(14) We did not attempt to isolate dimethyl disulfide S-oxide, or its disproportionation products, from this reaction mixture. The intermediacy of a four-membered transition state (or even intermediate) in the aromatization step is conceivable.

(15) The comparable formation of a furan ring system from *o*-hydroxyaldehydes and dimethyloxosulfonium methylide (**2**) has been reported recently by B. Holt and P. A. Lowe, *Tetrahedron Letters*, 683 (1966).

(16) L. Ettinger and P. Friedländer, *Chem. Ber.*, **45**, 2074 (1912).

(17) For reviews on indoxyl chemistry, see P. L. Julian, E. W. Meyer, and H. C. Printy in "Heterocyclic Compounds," Vol. 3, R. C. Elderfield, Ed., John Wiley and Sons, Inc., New York, N. Y., 1952, p 186; W. C. Sumpter and F. M. Miller in "The Chemistry of Heterocyclic Compounds," Vol. 8, A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1954, p 163.



6-nitro-N-methylisatoic anhydride²⁶ in 20 ml of DMSO. The greater insolubility of the product allowed isolation without extraction. After the reaction was complete, the cooled reaction mixture was poured into 500 ml of ice-water and the yellow precipitate was collected after stirring for 30 min. The crude product (3.98 g) was crystallized from a mixture of DMSO (70 ml) and ethanol (550 ml) to give 3.54 g (0.013 mole, 66%) of yellow needles, mp 214–215° dec.

Anal. Calcd for $C_{11}H_{14}N_2O_4S$: C, 48.88; H, 5.22; N, 10.37; S, 11.86. Found: C, 48.64; H, 5.30; N, 10.04; S, 12.26.

The perchlorate **5b** was obtained as described above for **5a**. The product was obtained in 93% yield in the form of yellow needles, which became green at 190–195° and decomposed about 197°.

Anal. Calcd for $C_{11}H_{13}ClN_2O_8S$: C, 35.63; H, 4.08; Cl, 9.56; N, 7.55; S, 8.65. Found: C, 36.01; H, 4.25; Cl, 9.64; N, 7.56; S, 8.55.

1-Methyl-3-methylsulfonyl-4(1H)-quinolinone (9).—A mixture of dimethyloxosulfonium 2-(methylamino)benzoylmethylide (**4a**) (1.80 g, 0.008 mole), triethyl orthoformate (20 ml), absolute ethanol (20 ml), and acetic acid (0.75 ml, 0.012 mole) was refluxed for 5 hr; the solution was concentrated *in vacuo* to about 15 ml, cooled to 0°, and the white solid collected by filtration and washed with ether; yield, 1.59 g (0.0072 mole) (90%); mp 169–171°. Recrystallization from benzene–hexane raised the melting point to 169.5–171.5°.

Anal. Calcd for $C_{11}H_{11}NO_2S$: C, 59.70; H, 5.01; N, 6.33; S, 14.49. Found: C, 59.59; H, 4.92; N, 6.38; S, 14.48.

Desulfurization of 1-Methyl-3-methylsulfonyl-4(1H)-quinolinone (9) with Raney Nickel Alloy.—Raney nickel alloy (3.5 g) was added in small portions in the course of 6 hr to a stirred, refluxing solution of 1-methyl-3-methylsulfonyl-4(1H)-quinolinone (0.50 g) in a mixture of 35 ml of 10% sodium hydroxide and 20 ml of ethanol. The reaction mixture was concentrated *in vacuo* in order to remove the ethanol and was extracted five times with dichloromethane. After drying over anhydrous sodium sulfate, the extract was concentrated to dryness. The solid residue (270 mg, mp 129–136°) was shown by tlc to consist of two main components, one of which was identified as 1-methyl-4(1H)-quinolinone by comparison with an authentic sample.²⁷ The other unidentified component was shown by tlc not to be 1-methyl-5,6,7,8-tetrahydro-4(1H)-quinolinone (*vide infra*). The crude product, after crystallization from benzene, afforded 110 mg (31%) of pure 1-methyl-4(1H)-quinolinone, mp 149–151°, which was identical (mixture melting point, infrared and nmr spectra) with an authentic sample prepared by methylation of 4(1H)-quinolinone.²⁷

Raney Nickel Desulfurization of 1-Methyl-3-methylsulfonyl-4(1H)-quinolinone (9).—A stirred mixture of 1-methyl-3-methylsulfonyl-4(1H)-quinolinone (1.00 g), about 18 g of wet Raney nickel,²⁸ and 50 ml of ethanol was heated on a steam bath for 5 hr. The reaction mixture was extracted overnight (Soxhlet) with additional ethanol (200 ml) and the extracts were concentrated to dryness. The solid residue was extracted five times with dichloromethane, the dichloromethane was evaporated, and the residue was dissolved in water (20 ml). Addition of 100 ml of saturated aqueous picric acid solution gave a yellow picrate which, after recrystallization from methanol, weighed 1.15 g (65%), mp 248–250° dec. This material was identical (mixture melting point, infrared spectrum) with an authentic sample of the picrate of 1-methyl-5,6,7,8-tetrahydro-4(1H)-quinolinone prepared as described by Price⁷ (obtained by decarboxylation of the corresponding 3-carboxylic acid) and also with a sample prepared by reduction of 1-methyl-4(1H)-quinolinone with Raney nickel by the procedure described above.

1-Methyl-3-methylsulfonyl-4(1H)-quinolinone.—Hydrogen peroxide (30% in water, 5 ml) was added to a solution of 1-methyl-3-methylsulfonyl-4(1H)-quinolinone (4.42 g) in a mixture of 20 ml of acetic acid and 5 ml of acetic anhydride. After standing at room temperature for 3 days, the solution was treated with charcoal, filtered, and the filtrate added to 400 ml of ice-water to give 3.61 g (76%) of colorless sulfone, mp 225–227°. The analytical sample, mp 225.5–227.5°, was crystallized from ethanol.

Anal. Calcd for $C_{11}H_{11}NO_2S$: C, 55.67; H, 4.67; N, 5.90; S, 13.51. Found: C, 55.55; H, 5.02; N, 5.83; S, 13.39.

1,2-Dimethyl-3-methylsulfonyl-4(1H)-quinolinone (11).—A mixture of dimethyloxosulfonium 2-(methylamino)benzoylmethylide (5.40 g, 0.024 mole), triethyl orthoacetate (90 ml), absolute ethanol (30 ml), and acetic acid (3 ml) was refluxed for 3 hr. The finely divided crystalline precipitate which formed upon cooling was collected by filtration, washed with ether, and dried to give 4.87 g (0.0207 mole, 87%) of the sulfoxide, mp 179–181°. It was used without further purification both for the elemental analysis and for spectral determinations, since recrystallization from either benzene or acetone resulted in changes in composition which are not understood (see text).

Anal. Calcd for $C_{12}H_{13}NO_2S$: C, 61.23; H, 5.69; N, 5.95; S, 13.62. Found: C, 61.35; H, 5.60; N, 5.90; S, 13.70.

1-Methyl-2-mercapto-4(1H)-quinolinone (16).—Carbon disulfide (40 ml) was added to a solution of dimethyloxosulfonium 2-(methylamino)benzoylmethylide (3.60 g, 0.016 mole) in dry pyridine (40 ml) under nitrogen. The reaction mixture, which became red almost instantly, was stirred for 17 hr, the solvents were removed *in vacuo*, and the pasty residue was pressed upon a porous plate to give 2.1 g of a crude solid. Crystallization from

(26) From Maumee Chemical Co., Toledo, Ohio.

(27) J. A. C. Allison, J. T. Braunholtz, and F. G. Mann, *J. Chem. Soc.*, 403 (1954); see also ref 4.

(28) From W. R. Grace and Co.

methanol (300 ml) gave 1.10 g (0.00576 mole, 36%) of yellow crystals, mp $\sim 260^\circ$ dec.

Anal. Calcd for $C_{10}H_9NOS$: C, 62.78; H, 4.75; N, 7.32; S, 16.76. Found: C, 62.59; H, 5.10; N, 7.22; S, 16.74.

Desulfurization of 1-Methyl-2-mercapto-4(1H)-quinolinone (16) with Raney Nickel Alloy.—Raney nickel alloy (3.0 g) was added in small portions in the course of 5 hr to a stirred, boiling solution of 1-methyl-2-mercapto-4(1H)-quinolinone (500 mg, 0.0026 mole) in a mixture of 10% sodium hydroxide (30 ml) and ethanol (15 ml). Water (50 ml) was added and most of the ethanol removed by concentration of the solution to about half its volume. The aqueous layer was saturated with sodium chloride and extracted five times with dichloromethane while the solid residue was extracted overnight with dichloromethane. The combined extracts were dried over anhydrous sodium sulfate and concentrated to dryness to give 0.34 g of a solid which consisted of two major components by tlc. As with the Raney nickel alloy reduction of compound 9 described above, one component was 1-methyl-4(1H)-quinolinone, while the other unidentified component was shown not to be 1-methyl-5,6,7,8-tetrahydro-4(1H)-quinolinone. The crude product (0.34 g) was purified by chromatography (Florisil and ethyl acetate-methanol 1:1) to give 0.24 g (0.0015 mole, 57%) of 1-methyl-4(1H)-quinolinone, which was identical with an authentic sample²⁷ as judged by a mixture melting point determination, by comparison of infrared and nmr spectra, and by tlc.

1-Methylisatin-2-anil (19).—A solution of dimethyloxosulfonium 2-(methylamino)benzoylmethylide (450 mg, 0.002 mole) and nitrosobenzene (430 mg, 0.004 mole) in absolute ethanol (40 ml) was refluxed for 1 hr, excess ethanol was removed, and the resulting red oil was dissolved in chloroform and passed through a column of Florisil. Evaporation of the eluate gave a

red solid which was crystallized from 100 ml of petroleum ether (bp 60–70°) to give 300 mg (61%) of the anil as dark red needles, mp 129.5–131° (lit.¹⁸ mp 132°).

The anil (500 mg) was hydrolyzed by heating under reflux for 1 hr in 50 ml of 2 N hydrochloric acid.¹⁸ Cooling and neutralization of the solution with sodium bicarbonate resulted in the separation of crude 1-methylisatin (140 mg, 41%), which melted at 127–130° after recrystallization from water. The compound was identical with an authentic sample of 1-methylisatin by a mixture melting point determination, by comparison of infrared spectra, and by tlc.

2-Methylamino- α -chloroacetophenone (22).—Dimethyloxosulfonium 2-(methylamino)benzoylmethylide (1.00 g, 0.00444 mole) was stirred in a mixture of 150 ml of saturated sodium chloride solution and 5 ml of 2 N hydrochloric acid for 3 hr. The reaction mixture was then extracted overnight with dichloromethane, the extract dried over anhydrous sodium sulfate, and concentrated *in vacuo*. The residue was chromatographed over a large column of silica gel with chloroform. Elution of the first yellow band and evaporation of the chloroform eluate provided 300 mg (37%)²⁹ of yellow crystalline 2-methylamino- α -chloroacetophenone, mp 81–82.5°. The infrared spectrum showed an N–H band at 3340 cm^{-1} and a C=O band at 1650 cm^{-1} . The nmr spectrum (DCl_3) exhibited a three-proton doublet at 2.90 ppm ($J = 5$ cps) (NCH_3), a two-proton singlet at 4.59 ppm (CH_2), and a four-proton aromatic multiplet between 6.5 and 7.8 ppm. The N–H signal was not observed.

Anal. Calcd for $C_9H_{10}ClNO$: C, 58.86; H, 5.49; Cl, 19.35; N, 7.63. Found: C, 58.92; H, 5.51; Cl, 19.30; N, 7.58.

(29) No attempt was made to find optimum conditions for this reaction.

A New Rearrangement of Sulfonium Ylides

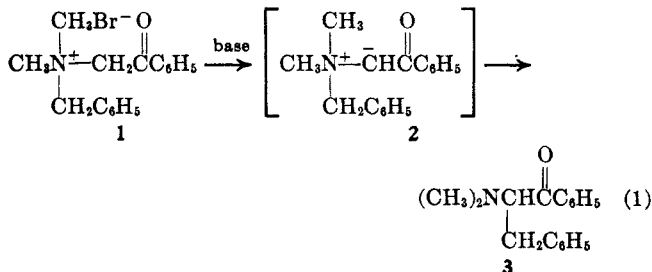
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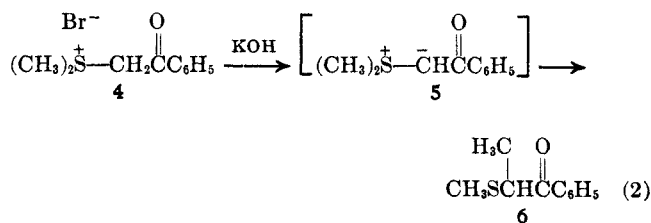
Alkyl- or arylmethylphenacylsulfonium ylides rearrange in boiling water to produce α -(alkyl- or arylthio)-methoxystyrenes rather than alkyl or aryl α -methylphenacyl sulfides as expected by a Stevens rearrangement. Alternate reactions occur under these conditions depending upon the structure of the S-ylides including alkyl migration, elimination, or hydrolysis. S-ylides stabilized by two carbonyl groups do not react under the above conditions. The newly discovered molecular rearrangement and alternative reactions of S-ylides are discussed in terms of ylide structure and mechanism.

The Stevens rearrangement¹ of ammonium salts (*e.g.*, 1) has been extensively studied. This electrophilic, intramolecular 1,2 rearrangement presumably involves an intermediate ylide (2). An example of the reaction, outlined in eq 1, leads to amine (3).



Sulfonium salts similarly rearrange, *via* ylides, to sulfides.² For example, Bohme and Krause³ report that dimethylphenacylsulfonium bromide (4), refluxed with an equivalent of 1 N potassium hydroxide

for 5 hr, gave methyl α -methylphenacyl sulfide (6) *via* the ylide 5 (eq 2). The product 6 was characterized



by synthesis of authentic material from α -bromopropiophenone and methyl mercaptan and by oxidation to the sulfone.³

In the course of a study of S-ylide chemistry this base rearrangement of dimethylphenacylsulfonium bromide was repeated as described by Bohme and Krause. The molecular weight and analysis of the product oil, bp 95° (1 mm), do indeed correspond to $C_{10}H_{12}OS$, but the infrared and nmr spectra (Table I) suggest α -(methylthio)methoxystyrene (7) rather than methyl α -methylphenacyl sulfide (6).⁴ The product

(1) (a) H. E. Zimmerman, "Molecular Rearrangements," P. deMayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p 378. (b) M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, p 279.

(2) T. Thompson and T. S. Stevens, *J. Chem. Soc.*, **55**, 69 (1932).

(3) H. Bohme and W. Krause, *Chem. Ber.*, **82**, 426 (1949).

(4) K. W. Ratti and A. N. Yao, *J. Org. Chem.*, **31**, 1689 (1966).