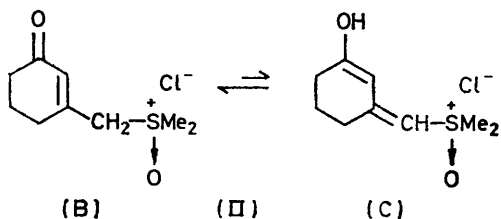
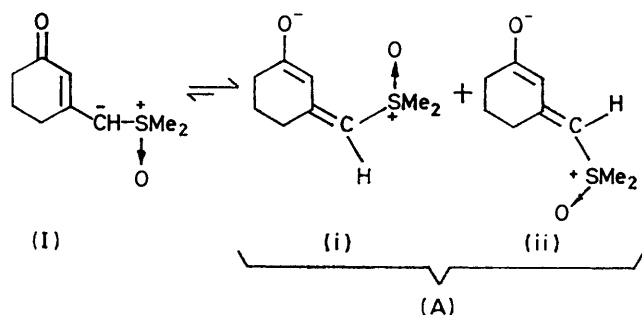


Structure and Some Reactions of Dimethyloxosulphonio-(3-oxocyclohex-1-enyl)methanide

By Yasumitsu Tamura,* Tomohisa Miyamoto, Tadashi Nishimura, Jiro Eiho, and Yasuyuki Kita, Faculty of Pharmaceutical Sciences, Osaka University, Toneyama, Toyonaka, Osaka, Japan

Stable crystalline dimethyloxosulphonio-(3-oxocyclohex-1-enyl)methanide (I) was prepared from 3-chlorocyclohex-2-enone by reaction with dimethyloxosulphonio-methanide. Acylation and alkylation of (I) provided convenient routes to 3-acetyl-cyclohex-2-enone (VI), 3-phenacylcyclohex-2-enone (VII), 3-acetyl-2-methyl-5-(3-oxocyclohex-1-enyl)furan (IX), and 3-(1-iodoethyl)cyclohex-2-enone (X). The structure of the ylide (I) is discussed.

We have briefly reported¹ the structure and several fundamental reactions (acylation and alkylation) of dimethyloxosulphonio-(3-oxocyclohex-1-enyl)methanide (I),† and now give a full account of these experiments.



The ylide (I) was prepared in 58% yield by the reaction of 3-chlorocyclohex-2-enone with dimethyloxosulphonio-methanide at room temperature. It was readily converted by treatment with hydrogen chloride gas in acetone into the corresponding quaternary salt (II), which regenerated (I) on treatment with sodium methoxide. The carbonyl group of (I) absorbs at 1590 and 1535 cm^{-1} in the i.r. spectrum, and at 354 nm in the u.v. spectrum, and the n.m.r. signal of the vinyl proton appears at τ 4.35. Comparison of these values with those of (II) [ν_{max} 1665 and 1630 cm^{-1} ; λ_{max} 229 nm; τ 3.65] shows that the ylidic anion of (I) is largely delocalised over an enone system [betaine form (A)] and the quaternary salt (II) exists in the keto-form (B), which resembles normal cyclohexenones.

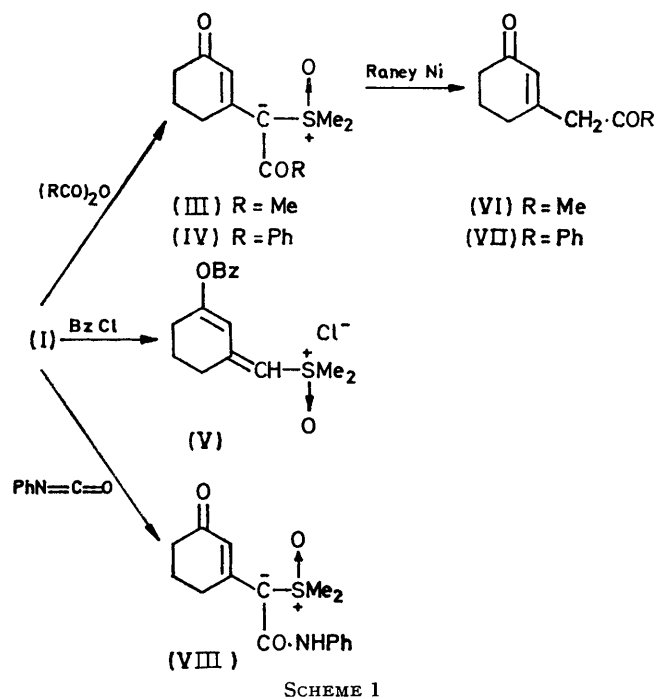
Treatment of (I) with deuterium oxide in chloroform at 34° resulted in deuterium exchange at the α - and γ -positions and exchange of two SCH_3 protons, giving an octadeuterio-derivative. This fast exchange implies

† More recently, it has been shown² that pyrolysis of (I) causes a series of interesting transformations yielding a cyclohepta-1,4-diene derivative.

* Y. Tamura, T. Nishimura, J. Eiho, and T. Miyamoto, *Chem. and Ind.*, 1971, 1199.

that the formal negative charge of (I) is delocalised over the enone system. Under similar conditions, (II) gave a trideuterio-derivative (α - and γ -), perhaps owing to contribution by the enol form (C). The great stability of the ylide (I) is no doubt ascribable to the delocalisation of negative charge. The methine proton of (I) gives rise to a broadened n.m.r. peak ($W_{1/2}$ 9.6 Hz) at τ 6.15, possibly owing to the presence of geometric isomers, (i) and (ii).³

Acylation of the α -carbon atom of (I) with acetic and benzoic anhydrides in tetrahydrofuran (THF) proceeded readily to give the highly stabilised *C*-acetyl (III) and *C*-benzoyl (IV) derivatives in 66 and 53% yield, respectively. In contrast, use of benzoyl chloride in dichloromethane led to the *O*-acyl salt (V) in 68% yield.

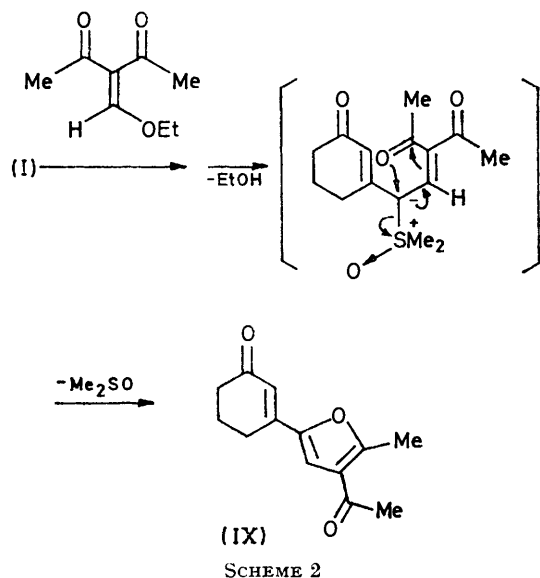


These products were identified from elemental and spectral analyses (see Experimental section). The former is presumably the product of thermodynamic control and the latter of kinetic control. These results

² Y. Tamura, T. Miyamoto, T. Nishimura, and Y. Kita, *Tetrahedron Letters*, 1973, 2351.

³ A. W. Johnson and R. T. Amel, *J. Org. Chem.*, 1969, **34**, 1240.

are consistent with the known ambident behaviour for dimethylsulphonium,³ triphenylphosphonium,⁴ and pyridinium phenacylides.⁵ Desulphurisation of compounds (III) and (IV) with deactivated Raney nickel (W2) in hot ethanol gave 3-acetyl- (VI) and 3-phenacylcyclohex-2-enones (VII) in 85 and 84% yield, respectively. Carbonylation of (I) with phenyl isocyanate in THF gave the ylide (VIII) in 84% yield, which was identified by its characteristic spectral data (see Experimental section). Treatment of (I) with 3-ethoxymethylenepentane-2,4-dione in the absence of solvent at 75° gave a furan derivative (IX) in 22% yield. Structure (IX) was assigned on the basis of spectral evidence: λ_{\max} 316 nm [2-(3-oxoalk-1-enyl)furan]; ν_{\max} (CHCl₃) 1675s and 1655s cm⁻¹ (MeCO·C= and C=C·C=O); τ (CDCl₃) 7.39 (3H, s, =CMe), 7.60 (3H, s, Ac), 3.06 (1H, s, O·C=CH), 3.56br (1H, s, CH=), and 7.2—8.1 (6H, m, 3 × CH₂), m/e 218 (M^+) and 190 (base peak). A possible mechanism for its formation is outlined in Scheme 2.*



SCHEME 2

Alkylation of the ylide (I) was performed with methyl iodide in the absence of solvent at room temperature. An unstable product, 3-(1-iodoethyl)cyclohex-2-enone (X), was obtained in 86% yield. Structure (X) was deduced from spectral data: τ (CDCl₃) 3.90 (1H, s, CH=), 8.00 (3H, d, J 7 Hz, Me), 5.09 (1H, q, J 7 Hz, CHI), and 7.2—8.2 (6H, m, 3 × CH₂); ν_{\max} (CHCl₃) 1660 and 1610 cm⁻¹ (conjugated enone); and established by conversion with zinc-ethanol into the known 3-ethylcyclohex-2-enone (XI).⁷ The formation of (X) is reasonably explained in terms of attack by iodide ion

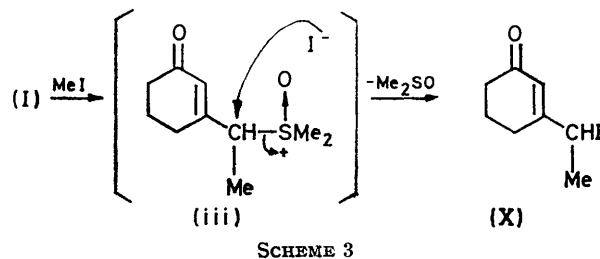
* An analogy with this type of reaction is found in the transformation of a diacetylvinylaminide into a 4-acetyl-5-methylisoxazole.⁶

⁴ P. A. Chopard, R. J. G. Searle, and F. H. Devitt, *J. Org. Chem.*, 1965, **30**, 1015.

⁵ F. Kröhnke, *Ber.*, 1935, **68B**, 1177.

⁶ Y. Tamura, Y. Miki, Y. Sumida, and M. Ikeda, *J.C.S. Perkin I*, 1973, 2580.

on the initially formed salt (iii) with subsequent liberation of dimethyl sulphoxide.⁸



SCHEME 3

EXPERIMENTAL

I.r. spectra were recorded with a Hitachi-G2 spectrometer, u.v. spectra with a Hitachi-124 spectrophotometer, and n.m.r. spectra with a Hitachi-R20A spectrometer {internal standards tetramethylsilane (in CDCl₃) or sodium 2,4-disilapentane-1-sulphonate [in H₂O, D₂O, or (CD₃)₂SO]}. Mass spectra were obtained with a Hitachi-RMU-6D instrument at 70 eV.

Dimethyloxosulphonio-(3-oxocyclohex-1-enyl)methanide (I).—To a stirred solution of dimethyloxosulphoniomethanide⁹ [prepared from sodium hydride (9.10 g, 52.9%) and trimethyloxosulphonium chloride (26.0 g)] in THF (300 ml), cooled in ice, 3-chlorocyclohex-2-enone (13.0 g) in absolute THF (60 ml) was added in portions during 30 min. The mixture was stirred at room temperature for an additional 20 h, then cooled in an ice-salt bath; the precipitate was filtered off, washed with ether, and extracted with hot ethyl acetate (10 × 500 ml). Evaporation of the combined extracts *in vacuo* gave the ylide (I) (10.8 g, 58%), which was washed with cold acetone and recrystallised (from acetone) to give pale yellow crystals, m.p. 157—157.5° (decomp.) (Found: C, 57.85; H, 7.55. C₉H₁₄O₂S requires C, 58.05; H, 7.6%); ν_{\max} (KCl) 1575 and 1520 cm⁻¹; ν_{\max} (CHCl₃) 1590 and 1535 cm⁻¹; τ (CDCl₃) 4.35 (1H, s, CH=), 6.15br (1H, s, $W_{\frac{1}{2}}$ 9.6 Hz, CH-S), 6.63 (6H, s, SMe₂), and 7.5—8.3 (6H, m, 3 × CH₂); λ_{\max} (EtOH) 354 nm (log ϵ 4.18); M^+ 186; pK_a 8.25 [μ 0.1 (KCl) solution]. The ylide (I) was also obtained from the corresponding quaternary salt (II) (45 mg) by treatment with sodium methoxide (20 mg) in methanol (10 ml) at room temperature overnight. The solution was concentrated *in vacuo*, chloroform was added to the residue with cooling, and insoluble solids were filtered off. Evaporation of the filtrate *in vacuo* followed by trituration with acetone gave the sulphoxonium ylide (I) (35 mg, 93%).

Dimethyloxo-(3-oxocyclohex-1-enylmethyl)sulphonium Chloride (II).—The ylide (I) (5.0 g) was dissolved in hot acetone (900 ml). Dry hydrogen chloride was bubbled through the solution cooled in ice-water and the resulting crystals were collected. More crystals were obtained by adding ether (2 l) to the filtrate (total yield 5.70 g, 95%). Recrystallisation from methanol-benzene gave needles, m.p. 111.5—112° (decomp.) (Found: C, 48.6; H, 7.0. C₉H₁₅ClO₂S requires C, 48.55; H, 6.8%); ν_{\max} (KCl) 1665 and 1630 cm⁻¹; τ (H₂O) 3.65br (1H, s, CH=), 4.99br (2H, s, CH₂S), 6.13 (6H, s, SMe₂), and 7.2—8.1 (6H, m, 3 × CH₂);

⁷ G. F. Woods, P. H. Griswold, jun., B. H. Armbrecht, D. I. Blumenthal, and R. Plapinger, *J. Amer. Chem. Soc.*, 1949, **71**, 2028.

⁸ H. König and H. Metzger, *Chem. Ber.*, 1965, **98**, 3733.

⁹ E. J. Corey and M. Chaykovski, *J. Amer. Chem. Soc.*, 1965, **87**, 1353.

τ (D_2O) 3.65 (1H, t, J 1.5 Hz, CH=, disappeared gradually), 6.13 (6H, s, SMe_2), and 7.2—8.1 (6H, m, $3 \times CH_2$); λ_{max} (EtOH) 229 (log ϵ 4.01) and 352 nm (4.00); λ_{max} (H_2O) 232 (log ϵ 4.17) and 348 nm (3.03).

1-Dimethyloxosulphonio-2-oxo-1-(3-oxocyclohex-1-enyl)-propanide (III).—A suspension of the ylide (I) (2.0 g) and acetic anhydride (1.17 g) in dry THF (150 ml) was stirred at room temperature for 20 h. The solution was evaporated *in vacuo* and the residue was passed through a short column of alumina with chloroform. Concentration of the yellow fraction followed by trituration of the residue with ether gave the hygroscopic *acetyl derivative* (III) (1.73 g, 66%). Recrystallisation from benzene-ether afforded pale yellow needles, m.p. 102—103° (Found: C, 57.45; H, 7.0. $C_{11}H_{16}O_3S$ requires C, 57.9; H, 7.05%); ν_{max} ($CHCl_3$) 1640 and 1525 cm^{-1} ; τ ($CDCl_3$) 4.06 (1H, s, CH=), 6.45 (6H, s, SMe_2), 7.92 (3H, s, Ac), and 7.3—8.2 (6H, m, $3 \times CH_2$); λ_{max} (EtOH) 235 (log ϵ 3.91), 257 (3.80), and 335 nm (3.76).

Benzoyl(dimethyloxosulphonio)-(3-oxocyclohex-1-enyl)-methanide (IV).—A suspension of the ylide (I) (1.0 g) and benzoic anhydride (1.22 g) in dry THF (70 ml) was stirred for 20 h. Work-up as above gave the *benzoyl derivative* (IV) (0.827 g, 53%). Recrystallisation from acetone-hexane gave pale yellow crystals, m.p. 134—135.5° (Found: C, 66.25; H, 6.35. $C_{16}H_{18}O_3S$ requires C, 66.2; H, 6.25%); ν_{max} ($CHCl_3$) 1640, 1580, and 1505 cm^{-1} ; τ ($CDCl_3$) 2.2—2.75 (5H, m, Bz), 3.97 (1H, s, CH=), 6.34 (6H, s, SMe_2), and 7.5—8.4 (6H, m, $3 \times CH_2$); λ_{max} (EtOH) 235 (log ϵ 4.18), 290 (3.88), and 342 nm (4.04).

The Enol Benzoate (V) of Dimethyloxo-(3-oxocyclohex-1-enylmethyl)sulphonium Chloride.—A mixture of the ylide (I) (500 mg) and benzoyl chloride (396 mg) in dichloromethane (60 ml) was stirred at room temperature for 3 h. Concentration of the mixture *in vacuo* gave crystals, which were washed with acetone to give the *benzoate* (V) (610 mg, 68%). Recrystallisation from acetone-dichloromethane gave needles, m.p. 136.5—137° (Found: C, 58.25; H, 5.9. $C_{16}H_{18}ClO_3S$ requires C, 58.8; H, 5.85%); ν_{max} (KCl) 1725, 1635, and 1230 cm^{-1} ; τ ($CDCl_3$) 1.75—1.95 [2H, m, COC(CH=)CH], 2.2—2.5 (3H, m, aromatic), 2.57 (1H, s, CH=), 2.78 (1H, s, CH=), 5.67 (6H, s, SMe_2), and 7.1—8.1 (6H, m, $3 \times CH_2$); λ_{max} (EtOH) 242 (log ϵ 3.08), and 280 nm (3.43).

3-Acetyl-cyclohex-2-enone (VI).—A suspension of Raney nickel (W2) (5 g) [deactivated by refluxing in acetone (100 ml) for 1 h] and the acetyl derivative (III) (500 mg) in ethanol (60 ml) was stirred at 55° for 0.5 h. An insoluble solid was filtered off and washed with hot ethanol (4 \times 50 ml). The combined filtrates were concentrated *in vacuo*, and the residue was extracted with hot hexane (3 \times 50 ml). Evaporation of the combined extracts *in vacuo* gave 3-acetyl-cyclohex-2-enone (VI) as a yellow oil (282 mg, 85%). Distillation under reduced pressure gave a pale yellow liquid, b.p. 85—90° (bath temp.) at 0.04—0.08 mmHg (Found: C, 70.6; H, 7.9. $C_9H_{12}O_2$ requires C, 71.0; H, 7.95%); ν_{max} ($CHCl_3$) 1722 and 1667 cm^{-1} ; τ ($CDCl_3$) 4.07br (1H, s, CH=), 6.64 (2H, s, $CH_2 \cdot CO$), 7.80 (3H, s, Ac), and 7.4—8.2 (6H, m, $3 \times CH_2$); λ_{max} (EtOH) 238 nm (log ϵ 4.09); M^+ 152.

3-Phenacylcyclohex-2-enone (VII).—The benzoyl deriv-

ative (IV) (500 mg) was treated with deactivated Raney nickel (W2) as for the preparation of (VI). Extraction with hot hexane followed by concentration *in vacuo* gave 3-phenacylcyclohex-2-enone (VII) (310 mg, 84%) as needles, m.p. 73.5—74° (Found: C, 78.45; H, 6.6. $C_{14}H_{14}O_2$ requires C, 78.5; H, 6.6%); ν_{max} (KCl) 1675 and 1655 cm^{-1} ; ν_{max} ($CHCl_3$) 1695 and 1665 cm^{-1} ; τ ($CDCl_3$) 1.9—2.15 [2H, m, COC(CH=)CH-], 2.3—2.7 (3H, m, aromatic), 4.02br (1H, s, CH=), 6.09 (2H, s, CH_2CO), and 7.4—8.3 (6H, m, $3 \times CH_2$); λ_{max} (EtOH) 246 (log ϵ 4.44), 280sh (3.19), and 290sh nm (3.09).

Dimethyloxosulphonio-(3-oxocyclohex-1-enyl)(phenylcarbamoyl)methanide (VIII).—A suspension of the ylide (I) (372 mg) and phenyl isocyanate (262 mg) in dry THF (15 ml) was stirred at room temperature for 2 h. Collection of the resulting crystals followed by washing with dry THF gave the phenylcarbamoyl derivative (VIII) (510 mg, 84%). Recrystallisation from acetone gave crystals, m.p. 138.5—140° (decomp.) (Found: C, 63.0; H, 6.4; N, 4.85. $C_{16}H_{19}NO_3S$ requires C, 62.95; H, 6.25; N, 4.6%); ν_{max} (KCl) 3370, 1610, 1595, 1590, and 1500 cm^{-1} ; τ [(CD_3)₂SO] 0.92br (1H, s, NH), 2.3—3.1 (5H, m, aromatic), 4.19 (1H, s, CH=), 6.41 (6H, s, SMe_2), and 7.4—8.3 (m, $3 \times CH_2 + Me_2SO$).

3-Acetyl-2-methyl-5-(3-oxocyclohex-1-enyl)furan (IX).—A mixture of the ylide (I) (186 mg) and 3-ethoxymethylpentane-2,4-dione (156 mg) was heated at 75° for 20 min. The resulting dark-brown oil was subjected to preparative t.l.c. (alumina-chloroform) to give two bands. Extraction of that of lower R_F with chloroform gave the *furan derivative* (IX) (50 mg, 22%). Recrystallisation from carbon tetrachloride gave pale yellow crystals, m.p. 127—129° (Found: C, 71.45; H, 6.45. $C_{13}H_{14}O_3$ requires C, 71.55; H, 6.45%); λ_{max} (EtOH) 227 (log ϵ 4.10) and 316 nm (4.38).

3-(1-Iodoethyl)cyclohex-2-enone (X).—A mixture of the ylide (I) (310 mg) and methyl iodide (10 ml) was stirred at room temperature for 2 days, then evaporated *in vacuo*, and the residue was purified by preparative t.l.c. (silica gel; benzene-ethyl acetate, 1 : 1) to give 3-(1-iodoethyl)cyclohex-2-enone (X) (360 mg, 86%) as a heat-labile oil [an attempt to distil at 40° (bath temp.) and 7 mmHg caused decomposition, giving iodine, which was used for the next reaction without further purification.

3-Ethylcyclohex-2-enone (XI).—A suspension of 3-(1-iodoethyl)cyclohex-2-enone (X) (360 mg) and an excess of zinc powder in ethanol (30 ml) was stirred at room temperature for 2 days, then filtered, and concentrated *in vacuo*. The residue was purified by passing through a column of silica gel with benzene-ethyl acetate to give 3-ethylcyclohex-2-enone (XI) (100 mg). Distillation under reduced pressure gave an oil, b.p. 104° (bath temp.) at 12 mmHg (55 mg, 30%); ν_{max} ($CHCl_3$) 1660 and 1620 cm^{-1} ; τ ($CDCl_3$) 4.10 (1H, s, CH=), 7.4—8.4 (8H, m, $3 \times CH_2$, $CH_2 \cdot C=$), and 8.90 (3H, t, J 7.5 Hz, Me), identical with an authentic specimen (i.r. and n.m.r. spectra). The 2,4-dinitrophenylhydrazone, precipitated from ethanol, gave red needles, m.p. 160—161° (from ethanol) (lit.,⁷ 159—160°) (Found: C, 55.25; H, 5.15; N, 18.3. Calc. for $C_{14}H_{16}N_4O_4$: C, 55.25; H, 5.3; N, 18.4%).

[3/1675 Received, 7th August, 1973]