Michael Addition of Dimethyloxosulphonio-(3-oxocyclohex-1-enyl)methanides to αβ-Unsaturated Compounds: Preparation of Some Vinylcyclopropanes

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Dimethyloxosulphonio-(3-oxocyclohex-1-enyl)methanides reacted with various Michael receptors to produce vinylcyclopropanes.

ALTHOUGH unstabilised oxosulphoniomethanides usually react with Michael receptors to form cyclopropyl ketones,[1-3] reactions of acyl-stabilised oxosulphoniomethanides with the same substrates yield products other than cyclopropane derivatives.[4,5] For instance, dimethyloxosulphoniomethanide reacts with benzylideneacetophenone to form 1-benzoyl-2-phenylcyclopropane exclusively,[1] and dimethyloxosulphonio(ethoxycarbonyl)methanide, which does not react with benzylideneacetophenone,[4] reacts with 1,2-dibenzoylethylene to yield 3-benzoyl-2-ethoxycarbonyl-5-hydroxy-5-phenylthian 1-oxide.[4] In a preliminary communication,[6] we have reported that the dimethyloxosulphoniomethanide (I),[7,] † stabilised by the 3-oxocyclohex-1-enyl group reacted with Michael receptors to give cyclopropane derivatives as in the case of unstabilised oxosulphoniomethanides. We now describe the experimental de-

† Based on our finding[6] that the Michael reaction of (I) provided a convenient route to vinylcyclopropanes, Marino and Kaneko recently prepared other vinylcyclopropanes and applied the reaction to the synthesis of ring-fused cycloheptadienes (J. P. Marino and T. Kaneko, *Tetrahedron Letters*, 1973, 3971, 3975).

[1] E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, 1965, **87**, 1353.

[2] P. T. Izzo, *J. Org. Chem.*, 1963, **28**, 1713; C. Kaiser, B. M. Trost, J. Beeson, and J. Weinstock, *ibid.*, 1965, **30**, 3972; S. R. Landor and N. Punja, *J. Chem. Soc.* (*C*), 1967, 2495.

[3] H. O. House, 'Modern Synthetic Reactions,' Benjamin, California, 1972, p. 719.

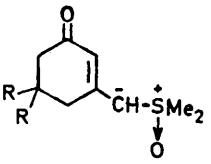
[4] H. Nozaki, D. Tunemoto, S. Matubara, and K. Kondo, *Tetrahedron*, 1967, **23**, 545.

[5] H. König and H. Metzger, *Chem. Ber.*, 1965, **98**, 3733.

[6] Y. Tamura, T. Miyamoto, T. Nishimura, and Y. Kita, *Tetrahedron Letters*, 1973, 2351.

[7] Some reactions of the methanide (Ib) have been reported: (*a*) Y. Tamura, T. Nishimura, J. Eiho, and T. Miyamoto, *Chem. and Ind.*, 1971, 1199; Y. Tamura, T. Miyamoto, T. Nishimura, J. Eiho, and Y. Kita, *J.C.S. Perkin I*, 1974. 102; (*b*) Y. Tamura, T. Miyamoto, J. Eiho, H. Taniguchi, T. Nishimura, and Y. Kita, *ibid.*, p. 105.

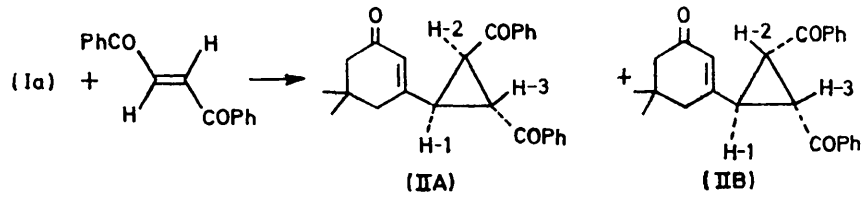
tails of this convenient route to vinylcyclopropane derivatives.



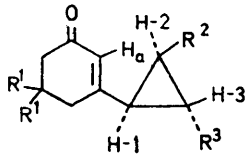
(I) a; R=Me
b; R=H

Treatment of the methanide (Ia) with *trans*-1,2-dibenzoylethylene in tetrahydrofuran under reflux for 1 h yielded two isomeric cyclopropanes (IIA and B) in 59 and 10% yields, respectively. The i.r. (characteristic cyclopropane band [8] at 1015—1020 and enone band at 1650—1685 cm^{-1}), mass [*m/e* 372 (M^+) and 105 (base peak, COPh)], and u.v. spectra [$\lambda_{max.}$ (EtOH) 250 nm (enone)] confirmed the assigned structures. The n.m.r. spectra (90 MHz) of the major (IIa) and the minor isomer (IIb) showed an AMX splitting pattern ($J_{1.2}$ 10·5, $J_{1.3}$ 6·0, $J_{2.3}$ 5·0 Hz) and an AB_2-like pattern, respectively, for the cyclopropane hydrogen atoms. This agrees with the illustrated stereochemistry. The n.m.r. data are shown in the Table.

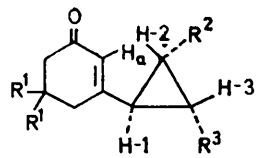
Similarly, a variety of other αβ-unsaturated compounds (benzylideneacetophenone, methyl vinyl ketone, acrylonitrile, methyl acrylate, α-naphthoquinone, and *N*-phenylmaleimide) gave the corresponding vinylcyclopropanes (III)—(XI) in 26—92% yields in reactions with the ylides (Ia and b). The products (IV)—(VII) from methyl vinyl ketone, acrylonitrile, and methyl acrylate were obtained as mixtures of isomers, whose configurations were assigned on the assumption that the vinyl proton (H_a) of isomer (A) resonates downfield of that of isomer (B) owing to the anisotropic effect of the acyl system. Ratios of isomers (A) and (B) were determined by n.m.r. spectroscopy (Table). The products (VIII)—(XI) were assigned configurations of type (B) on the basis of their coupling constants (*J* 3 and 5 Hz), indicating two *trans*-hydrogen atoms.[9]



(IIA) (IIB)



(A)



(B)

Compd.	R¹	R²	R³	Chemical shifts (τ) H_a	H-1	H-2	H-3	Coupling constants (Hz) $J_{1.2}$	$J_{1.3}$	$J_{2.3}$	$\nu_{max.}$ ($CHCl_3$) cm^{-1}	Ratio (A) : (B) [a]
(II) A	Me	COPh	COPh	3·98	7·02	6·27	5·95	10·5	6·0	5·0	1660	6 : 1
(II) B				3·97	6·8—7·0	6·6—6·75					1685—1650	
(III) A	Me	COPh or Ph	Ph or COPh	3·94	7·2—7·5	6·5—6·8					1660—1650	
(III) B				4·09	7·25	6·36 or 6·70	6·70 or 6·36	5·5 or 10·0	10·0 or 5·5	5·5	1665—1650	*b*
(IVA,B)	Me	COMe	H	4·05 and 4·14				*c*			1700, 1660	1 : 9
(VA,B)	H	COMe	H	4·04 and 4·15				*c*			1700, 1660	1 : 19
(VIA,B)	Me	CN	H	3·99 and 4·11				*c*			1660	3 : 7
(VIIA,B)	Me	CO_2Me	H	4·08 and 4·18				*c*			1725, 1655	1 : 19
(VIII)	Me	pdc *		4·04	7·43	7·06	7·06	5·0	5·0		1685—1660	(B)
(IX)	H	pdc *		4·01	7·41	7·01	7·01	5·0	5·0		1690—1660	(B)
(X)	Me	pidc †		4·16	7·54	7·27	7·27	3·0	3·0		1780, 1715, 1665	(B)
(XI)	H	pidc †		4·16	*c*	7·23	7·23	3·0	3·0		1780, 1715, 1665	(B)

[a] Calculated from integration of vinyl proton or methyl proton signals. [b] Could not be determined as (A) or (B) form. [c] Overlapped with other methylene protons.

* *o*-Phenylenedicarbonyl. † Phenyliminodicarbonyl.

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 standard tetramethylsilane; solvent $CDCl_3$).

[8] J. D. Graham and M. T. Rogers, *J. Amer. Chem. Soc.*, 1962, **84**, 2249; P. Bravo, G. Fronza, G. Gaudiano, C. Ticozzi, and M. G. Zubiani, *Tetrahedron*, 1971, **27**, 3563; C. N. R. Rao, 'Chemical Applications of Infrared Group Frequencies,' Methuen, London, 1968.

[9] H. Booth, *Progr. N.M.R. Spectroscopy*, 1969, **5**, 167; L. M. Jackmann and S. Sternhell, 'Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry,' Pergamon, Oxford, 1969.

Mass spectra were obtained with a Hitachi-RMU-6D instrument at 70 eV.

(5,5-*Dimethyl*-3-*oxocyclohex*-1-*enyl*)*dimethyloxosulphoniomethanide* (Ia).—This was prepared in 28% yield from 3-chloro-5,5-dimethylcyclohex-2-enone (15·9 g) and dimethyloxosulphoniomethanide [obtained from sodium hydride (9·10 g, 52·9%) and trimethyloxosulphonium chloride (26·0 g)] in absolute tetrahydrofuran (350 ml) by the same method as described for the preparation of dimethyloxosulphonio-(3-oxocyclohex-1-enyl)methanide.[7a] Recrystallisation from acetone gave pale yellow *crystals*, m.p. 170—171° (decomp.) (Found: C, 61·6; H, 8·4. $C_{11}H_{18}O_2S$ requires C, 61·65; H, 8·45%); $\nu_{max.}$ ($CHCl_3$) 1595 and 1540 cm^{-1}; τ ($CDCl_3$) 4·27 (1H, s, CH=, disappeared gradually on addition of D_2O), 6·12br (1H, s, $W_{\frac{1}{2}}$ 8·0 Hz, CH·S, disappeared on addition of D_2O), 6·60 (6H, s, SMe_2, disappeared on addition of D_2O), 7·80 (2H, s, CH_2), 7·85 (2H, s, CH_2), and 8·94 (6H, s, 2 × Me); $\lambda_{max.}$ (EtOH) 355 nm (log ε 4·67).

1,2-*Dibenzoyl*-3-(5,5-*dimethyl*-3-*oxocyclohex*-1-*enyl*)*cyclopropane* (IIA and B).—A suspension of the methanide (Ia) (428 mg) and *trans*-1,2-dibenzoylethylene (472 mg) in dry tetrahydrofuran (20 ml) was refluxed for 1 h. Evaporation *in vacuo* gave yellow crystals. Recrystallisation from ethanol afforded colourless *crystals* (IIA) (422 mg, 56%), m.p. 171·5—172° (Found: C, 80·5; H, 6·45. $C_{25}H_{24}O_3$ requires C, 80·6; H, 6·5%); $\lambda_{max.}$ (EtOH) 250 nm (log ε 4·50); *m/e* 372 (M^+), 267, 105, and 77. Evaporation of the mother liquors from the recrystallisation gave an oil, which was subjected to preparative t.l.c. (silica gel–chloroform), giving the isomer (IIB) (81 mg, 10%) along with more (IIA) (22 mg, 3%). Recrystallisation of (IIB) from ethanol–n-hexane gave colourless *crystals*, m.p. 137—138° (Found: C, 80·35; H, 6·45%); $\lambda_{max.}$ (EtOH) 250 nm (log ε 4·67); *m/e* 372 (M^+), 267, 105, and 77.

1-*Benzoyl*-2-(5,5-*dimethyl*-3-*oxocyclohex*-1-*enyl*)-3-*phenylcyclopropane* (IIIA and B).—A suspension of the methanide (Ia) (428 mg) and benzylideneacetophenone (416 mg) in ethanol (20 ml) was refluxed for 10 h and then cooled in ice–water. The *cyclopropane* (IIIA) (384 mg, 55%) was collected and recrystallised from ethanol; m.p. 168—170·5° (Found: C, 83·45; H, 6·9. $C_{24}H_{24}O_2$ requires C, 83·7; H, 7·0%); *m/e* 344 (M^+), 239, 105, and 77. Evaporation of the filtrate followed by preparative t.l.c. (silica gel–chloroform) gave the *cyclopropane* (IIIB) (146 mg, 21%) along with more (IIIA) (82 mg, 11%). Recrystallisation of (IIIB) from n-hexane gave crystals, m.p. 91—91·5° (Found: C, 83·85; H, 7·05%); *m/e* 344 (M^+), 239, 105, and 77.

1-*Acetyl*-2-(5,5-*dimethyl*-3-*oxocyclohex*-1-*enyl*)*cyclopropane* (IV).—A mixture of the methanide (Ia) (214 mg) and methyl vinyl ketone (210 mg) was heated at 110° for 5 min in the absence of solvent. The excess of methyl vinyl ketone was removed *in vacuo*, and the residue was dissolved in chloroform (40 ml), washed with water, and dried ($MgSO_4$). Concentration, and distillation of the residual oil at 120—125° (bath temp.) and 0·08 mmHg gave a slightly yellow oil (190 mg, 92%), a mixture of (IVA) and (IVB) in the ratio 1 : 9. Preparative g.l.c. (SE-30; 1 m; 110°) gave an analytically pure sample [(Found: C, 75·6; H, 8·75. Calc. for $C_{13}H_{18}O_2$: C, 75·7; H, 8·8%); *m/e* 206 (M^+)], which did not show any signals due to material other than (IVA and B) in its n.m.r. spectrum.

1-*Acetyl*-2-(3-*oxocyclohex*-1-*enyl*)*cyclopropane* (V).—A mixture of the methanide (Ib) (372 mg) and methyl vinyl ketone (420 mg) was heated at 110° for 5 min. Work-up as described for (IV) gave a slightly yellow oil (V) (221 mg, 62%), b.p. 120—130° (bath temp.) at 0·09 mmHg. An analytical sample was obtained by preparative g.l.c. (SE-30; 1 m; 110°) (Found: C, 74·1; H, 7·95. Calc. for $C_{11}H_{14}O_2$: C, 74·15; H, 7·9%).

2-(5,5-*Dimethyl*-3-*oxocyclohex*-1-*enyl*)*cyclopropane*-1-*carbonitrile* (VI).—A suspension of the methanide (Ia) (428 mg) and acrylonitrile (1·06 g) in dry tetrahydrofuran (20 ml) was refluxed for 3 h. The mixture was concentrated *in vacuo* and the residue was subjected to preparative t.l.c. (silica gel–chloroform). The cyclopropane was obtained as a yellow oil (242 mg, 64%), which was subjected to preparative g.l.c. (SE-30; 1 m; 130°) to give a pure sample (Found: C, 75·65; H, 7·95; N, 7·3. Calc. for $C_{12}H_{15}NO$: C, 76·15; H, 8·0; N, 7·4%).

Methyl 2-(5,5-*Dimethyl*-3-*oxocyclohex*-1-*enyl*)*cyclopropane*-1-*carboxylate* (VII).—A suspension of the methanide (Ia) (214 mg) and methyl acrylate (860 mg) in dry tetrahydrofuran (10 ml) was refluxed for 3 h. Work-up as described for (VI) gave a yellow oil (92 mg, 41%), along with another unidentified oil (46 mg) [$\nu_{max.}$ ($CHCl_3$) 1725 and 1655 cm^{-1}; $\lambda_{max.}$ (EtOH) 240 nm, no vinyl proton in its n.m.r. spectrum]. The *cyclopropane* (VII) was purified by preparative g.l.c. (SE-30; 1 m; 110°) (Found: C, 70·05; H, 8·1. $C_{12}H_{18}O_3$ requires C, 70·25; H, 8·15%).

trans-1-(5,5-*Dimethyl*-3-*oxocyclohex*-1-*enyl*)-1a,7a-*dihydro*-1H-*cyclopropa*[b]*naphthalene*-2,7-*dione* (VIII).—A suspension of the methanide (Ia) (214 mg) and α-naphthoquinone (158 mg) in dry tetrahydrofuran (10 ml) was refluxed for 1 h. Evaporation *in vacuo* followed by preparative t.l.c. [alumina; benzene–ether (2 : 1)] gave the *cyclopropane* (VIII) (77 mg, 26%) as purple crystals. Recrystallisation from ethanol gave colourless crystals, m.p. 164—167° (Found: C, 77·55; H, 6·15. $C_{19}H_{18}O_3$ requires C, 77·55; H, 6·15%).

trans-1-(3-*Oxocyclohex*-1-*enyl*)-1a,7a-*dihydro*-1H-*cyclopropa*[b]*naphthalene*-2,7-*dione* (IX).—A suspension of the methanide (Ib) (186 mg) and α-naphthoquinone (158 mg) in dry tetrahydrofuran (10 ml) was refluxed for 30 min. Work-up as for (VIII) gave purple *crystals* (IX) (98 mg, 36%). Recrystallisation from ethanol gave colourless crystals, m.p. 174—174·5° (Found: C, 76·8; H, 5·35. $C_{17}H_{14}O_3$ requires C, 76·65; H, 5·3%). The cyclopropane (IX) (38 mg, 47%) was also obtained from the methanide (Ib) (56 mg) and α-naphthoquinone (95 mg) by refluxing in ethanol (3 ml) for 2 h.

trans-6-(5,5-*Dimethyl*-3-*oxocyclohex*-1-*enyl*)-3-*phenyl*-3-*azabicyclo*[3.1.0]*hexane*-2,4-*dione* (X).—A suspension of the methanide (Ia) (214 mg) and *N*-phenylmaleimide (173 mg) in dry tetrahydrofuran (10 ml) was refluxed for 30 min. Concentration *in vacuo* followed by trituration of the residue with ethanol gave purple *crystals* (X) (94 mg, 30%). Recrystallisation from ethanol gave colourless crystals, m.p. 164—164·5° (Found: C, 73·6; H, 6·2; N, 4·45. $C_{19}H_{19}NO_3$ requires C, 73·75; H, 6·2; N, 4·55%).

trans-6-(3-*Oxocyclohex*-1-*enyl*)-3-*phenyl*-3-*azabicyclo*-[3.1.0]*hexane*-2,4-*dione* (XI).—A suspension of the methanide (Ib) (186 mg) and *N*-phenylmaleimide (173 mg) in dry tetrahydrofuran (10 ml) was refluxed for 1 h. Work-up as described for (X) gave (XI) (105 mg, 37%) as slightly purple *crystals*. Recrystallisation from ethanol gave colourless crystals, m.p. 212·5—213·5° (Found: C, 72·55; H, 5·1; N, 4·95. $C_{17}H_{15}NO_3$ requires C, 72·6; H, 5·35; N, 5·0%).

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