# 3-Dimethylsulphonioindolide. An Unusually Basic Crystalline Sulphonium Ylide

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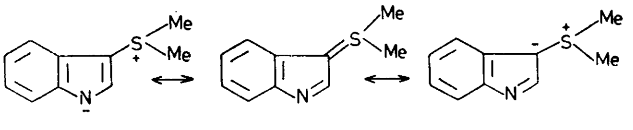
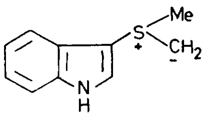
*Summary* 3-Dimethylsulphonioindolide, an unusually basic, crystalline ylide when dissolved in $CDCl_3$ or $CD_3OD$ incorporates deuterium into the methyl groups.

The stable, crystalline ylide (**1**) has been prepared and observed to possess unusual properties; in $CDCl_3$ or $CD_3OD$ solutions at or near room temperature it incorporates deuterium into the methyl groups. This hydrogen exchange requires: (a) the intermediacy of a methylidene ylide, *i.e.* (**2**) or (**3**), which must be present in equilibrium with (**1**) and (b) that ylide (**1**) be sufficiently basic to remove a proton (deuteron) from chloroform or methanol. To our knowledge, no previous example of a stable, crystalline sulphonium ylide which exhibits these properties has been reported.


(1a) (1b) (1c)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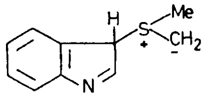
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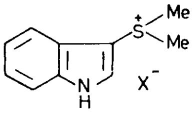
(4)

3-Methylthioindole,[1] prepared by alkylation of indole-3-thiol[2] with $Me_2SO_4$ in aqueous NaOH, was converted into the iodide (**4**; X = I) (97%) m.p. 131—133°, by reaction with MeI in dimethylformamide. Treatment of compound (**4**) with aqueous KOH produced the ylide (**1**) (71%) from $CH_2Cl_2$–$Et_2O$. The ylide (**1**) was characterized by analysis and its spectroscopic properties: *m/e* 177 ($M^+$) and 162 $(M - CH_3)^+$; $\delta[(CD_3)_2SO]$: 3·24 (s, 6H), 7·11 (m, 2H), 7·66 (m, 1H), 7·87 (m, 1H), and 8·10 (s, 1H). When ylide (**1**) was heated rapidly, melting began at 125° with final rapid melting at 147—150°. At temperatures of >100° slow rearrangement into 1-methyl-3-methylthioindole occurred.

The hydrogen exchange reaction was studied for solutions of (**1**) in $CDCl_3$ and $CD_3OD$ at 46°. Kinetic data for the exchange in $CD_3OD$ yield a pseudo-first-order rate constant of $7{\cdot}2 \times 10^{-5}\,s^{-1}$ (no statistical correction). Barbarella *et al.*[3] observed comparable rates for hydroxide-catalysed exchange of the α-methyl hydrogen atoms of trialkylsulphonium salts[4] and noted that sulphonium salt methyl hydrogen atoms undergo base-catalysed hydrogen exchange at about the same specific rate irrespective of the structural environment. The methyl hydrogen atoms of ylide (**1**) undergo similar ready exchange in $CDCl_3$ although, in this case, accurate data are difficult to obtain since (**1**) slowly decomposes, presumably owing to the production of hydrogen (deuterium) chloride by α-elimination from $CCl_3^-$.

During the exchange reaction in $CD_3OD$ no evidence for ylide decomposition was observed indicating that the methylidene ylide formed is (**2**) rather than (**3**) since (**3**) would be expected to undergo rapid Sommelet–Hauser rearrangement[5] to 4-methylthiomethylindole. The data available indicate that the exchange reactions can be formulated as in equation (1) That this exchange occurs

$$(\mathbf{1}) \rightleftharpoons (\mathbf{4})\ X{=}D_3CO^-\ (CCl_3^-) \rightleftharpoons (\mathbf{2}) \qquad (1)$$

in the absence of added base[3,4] is a reflection of the unusually basic nature of this highly stable ylide (**1**). The $pK_a$ value of the conjugate acid of ylide (**1**), the sulphonium salt (**4**), is 11·2,[6] at least three p$K$ units more basic than any carbonyl-stabilized sulphonium ylide for which data are available.[7]

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[2] R. L. N. Harris, *Tetrahedron Letters*, 1969, 4465.
[3] G. Barbarella, A. Garbesi, and A. Fava, *Helv. Chim. Acta*, 1971, **54**, 2297.
[4] See also Y. Yano, T. Okonogi, and W. Tagaki, *J. Org. Chem.*, 1973, **38**, 3912 and references therein.
[5] A. W. Johnson, 'Ylide Chemistry,' Academic Press, New York, 1966, p. 276.
[6] Determined by the method of A. J. Speziale and K. W. Ratts, *J. Amer. Chem. Soc.*, 1973, **85**, 2790.
[7] K. W. Ratts and A. N. Yao, *J. Org. Chem.*, 1966, **31**, 1185; A. W. Johnson and R. T. Amel, *ibid.*, 1969, **34**, 1240; K. W. Ratts, *ibid.*, 1972, **37**, 848; A. W. Johnson and R. B. LaCount, *Tetrahedron*, 1960, **9**, 130.