Tetrahedron Letters No.4, pp. 251-254, 1965. Pergamon Press Ltd.
Printed in Great Britain.

A STABLE SULPHONIUM YLIDE

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(Received 5 December 1964)

Stable sulphoxonium ylides have recently been recorded by two research groups (1,2) independently. The present communication concerns isolation and characterization of an unexpectedly stable sulphonium ylide (II).

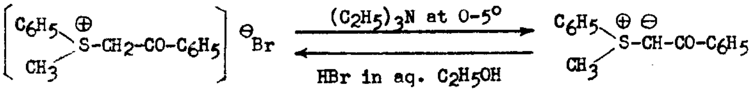
Methylphenacylphenylsulphonium bromide (I) (3) was treated with two equivalents of triethylamine in 98% ethanol solution at 0-5°. The mixture was treated with water, extracted with chloroform and the organic layer was concentrated _in vacuo_ to afford methylphenylsulphonium phenacylide (II), m.p. 113-114° (recrystallized from benzene), in 70% yield (Found: C, 74.69; H, 6.05. $C_{15}H_{14}OS$ requires: C, 74.34; H, 5.82%). Mol. wt. (chryoscopic in benzene) 254 (Calc. 242). UV max. (100% ethanol): 310 mμ (log ϵ 4.16).

A broad IR absorption (Nujol mull) at 1505-1470 cm.$^{-1}$ was ascribed to the carbonyl group of II which is in conjugation with the sulphonium ylide S-C bond. The UV and IR data are analogous to those recorded by Corey and Chaykovsky (2) for their dimethylsulphoxonium phenacylide.

The molecular peak of II appeared at m/e 242 and the intensities of M + 1 and M + 2 peaks also supported the molecular formula given. Fragment peaks were observed at m/e 124 (the base peak, assigned to $[C_6H_5SCH_3]^+$), 109, 105 ($C_6H_5CO^+$), 91, 78, 77, 69, 65, 51, 50, 45 and at 39. With exceptions of the peaks at 105, 77 and 51, the intensities of fragment peaks were in accord with those of the mass spectrum of thioanisole.

NMR spectrum ($CDCl_3$ solution with $Si(CH_3)_4$ internal ref. on Varian A-60) consisted of a methyl singlet at 3.16 p.p.m. (wt. 3), a methine singlet at 4.56 p.p.m. (wt. 1) and an aromatic multiplet at 7.2-8.0 p.p.m. (wt. 10).

The spectroscopically assigned structure II was chemically supported by the reconversion of II to I. This was accomplished by the addition of aqueous hydrobromic acid to an ethanolic solution of the ylide II. The sulphonium bromide (I) isolated in 86% yield was identified by IR and mixed m.p.



$$\left[\begin{matrix} C_6H_5 \searrow \oplus \\ \quad S\text{-}CH_2\text{-}CO\text{-}C_6H_5 \\ CH_3 \nearrow \end{matrix} \right] \overset{\ominus}{Br} \underset{HBr \text{ in aq. } C_2H_5OH}{\overset{(C_2H_5)_3N \text{ at } 0\text{-}5^{\circ}}{\rightleftarrows}} \begin{matrix} C_6H_5 \searrow \oplus \ominus \\ \quad S\text{-}CH\text{-}CO\text{-}C_6H_5 \\ CH_3 \nearrow \end{matrix}$$

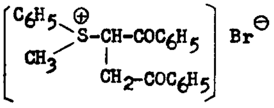
I II

The action of other bases on I also afforded the ylide II. For example, treatment with 1% sodium ethoxide solution in ethanol at 0-5° gave II in 63% yield and with 8% aqueous sodium hydroxide solution at 0-5° in 75% yield, respectively. No change occurred upon treatment of I with triethylamine in benzene solution even at room temperature. Heating of this mixture at 40-50° resulted in the formation of phenacyl bromide and thioanisole. When I was treated with triethylamine in 98% ethanol at 20-30°, the yield of II decreased to 33% and 1,2,3-tribenzoylcyclopropane (IV) (4) was produced in 10% yield. Only IV was obtained in 25% yield upon treatment of I with triethylamine in boiling ethanol.

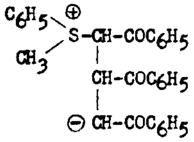
The formation of IV from I upon caustic alkali treatment (5) has been ascribed to the trimerisation of benzoylcarbene supposedly produced by the pyrolysis of an "imaginary" ylide II. Decomposition of dimethylsulphonium fluorenylide, the only stable sulphonium ylide ever known (6), is considered to afford biphenylenemethylene first, which is then transformed into its dimer and the oxidation product, fluorenone (7). Other examples of carbene formation have been recorded in the decomposition of unstable sulphonium ylides (8). Remarkably, however, the ylide II above-isolated was found to be quite inert to the thermal decomposition.

Thus, no change was observed upon refluxing II with two equivalents of aqueous sodium hydroxide solution in the presence or absence of one equivalent of sodium bromide. Refluxing of the tetrahydrofuran solution of II for 2 hrs. resulted in the total recovery of unchanged II. Even a trace of IV could not be isolated in these experiments. The notable inertness of this particular sulphonium ylide (II) clearly disproves the benzoylcarbene hypothesis.

Refluxing of a benzene solution of I and II in 1:4 mole ratio for 2 hrs. afforded the cyclopropane (IV) in 45% yield. Since I easily decomposes into phenacyl bromide and thioanisole, the formation of IV in the basic treatment of I at higher temperature should proceed *via* the adduct (V) of phenacyl bromide to the ylide II. The adduct V reacts with II to afford 1,2-dibenzoylethylene (III), the sulphonium bromide I and thioanisole. The ethylene III is further transformed into the other adduct (VI), which is then finally converted into the cyclopropane IV and thioanisole. The proposed mechanism is analogous to the one of the reaction of triphenylphosphonium phenacylide with phenacyl bromide (9). In contrast to the phosphorus ylide reaction, however, no 1,2-dibenzoylethylene (III) could be isolated in the present reactions of I and/or II.



V



VI

In view of the recent reports (10,11) on the condensation of sulphonium ylides with carbonyl compounds giving epoxides, an equimolar mixture of II and benzaldehyde or *p*-nitrobenzaldehyde dissolved in tetrahydrofuran was refluxed for several hours. Any appreciable sign of the expected reaction could not be observed, but the starting materials were recovered unchanged.

Acknowledgment - The authors are indebted to Dr. S. Yuguti, Central Research Institute of Toyo Rayon Co., for NMR and Mass spectra.

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