Tetrahedron Vol. 26, pp. 1243 to 1247. Pergamon Press 1970. Printed in Great Britain

REACTIONS OF DIPHENYLSULPHONIUM PHENACYLIDE

M. TAKAKU, Y. HAYASI and H. NOZAKI
Department of Industrial Chemistry, Kyôto University, Kyôto, Japan

(*Received in Japan* 8 *September* 1969; *Received in the UK for publication* 24 *October* 1969)

Abstract—Reaction of diphenylsulphonium phenacylide (VII) with acetyl chloride gives O-acetylated sulphonium chloride (IX), and the reaction with tosyl chloride yields a O-tosylated sulphonium salt (XI). These new salts are stable and can be isolated without cleavage of the phenyl–sulphur bond. Heating at 160° results in a novel rearrangement of VII into (Z)-α-phenoxy-β-phenylthiostyrene (XV). The related reactions of iodonium ylides have been investigated.

RECENT investigations on such sulphur ylides as methylphenylsulphonium (Ia, R = Ph)[1] or dimethylsulphonium phenacylides (Ib, R = Me)[2-4] have shown that the reactions are often triggered by the S-methyl group, which is easily heterolytically eliminated or deprotonated. For instance, acetylation of I with carboxylic anhydrides proceeds at the ylide-carbon to afford diketo-ylides II, whereas treatment with acyl chlorides results in O-acylation under elimination of the S-methyl group to give enol-esters III.[5] The reaction of I with sulphonyl chlorides having α-hydrogen produces a keto-sulphone ylide IV, possibly *via* sulphene intermediates, whereas treatment of I with tosyl chloride gives enol tosylates (V) by removal of the S-methyl group.[6] Isomerization of I to VI is effected by heating in such protic solvents as water or ethanol and this is explained by assuming a less stable phenacylsulphonium methylide.[7] In view of the reactivity of the S-methyl group of these ylides, the reactions of an ylide having no S-methyl group was investigated. The present paper is concerned with diphenylsulphonium phenacylide (VII) and in particular, attention has been focused on the chemical behaviour of VII as compared with that of I.

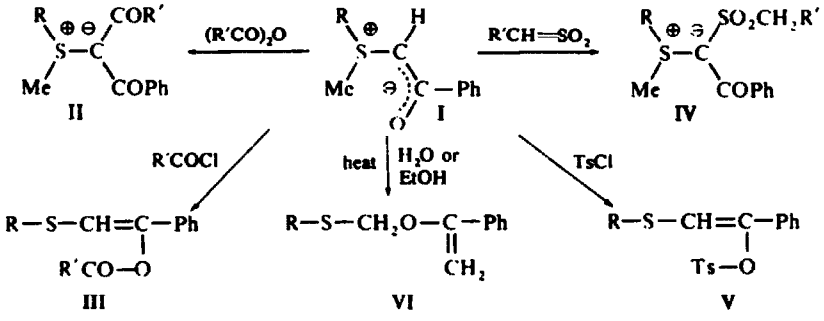


FIG. 1 Reactions of dimethyl- or methylphenylsulphonium phenacylide (I).

* The difference of methyl- and phenylsulphonium ylides in the reaction with Grignard reagents has been reported.[8]

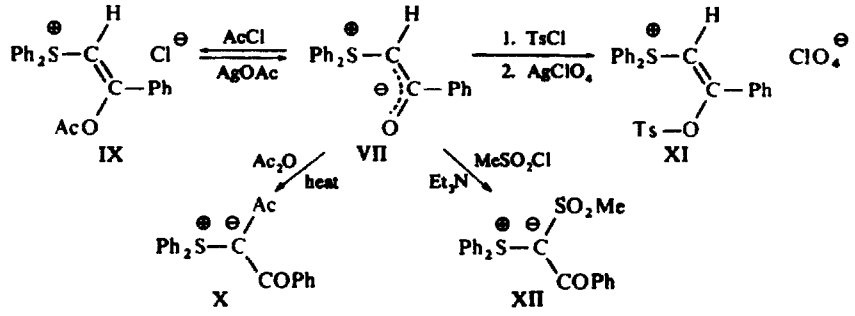


FIG. 2 Reactions of diphenylsulphonium phenacylide (VII).

The ylide VII was prepared by base-treatment of diphenylphenacylsulphonium tetrafluoroborate (VIII).[9] As expected, the reaction of VII with acetyl chloride at room temp gave an O-acetylated sulphonium chloride IX as a hygroscopic oil in which the phenyl-sulphur bond remained intact. NMR spectrum of an equimolar mixture of VII and acetic anhydride (Fig. 3) indicated that ca. 3 : 1 equilibrium with O-acetylated sulphonium acetate was established in 0·2 M $CDCl_3$ solution at room temperature. Heating of the components in boiling THF gave a C-acetylated ylide X.

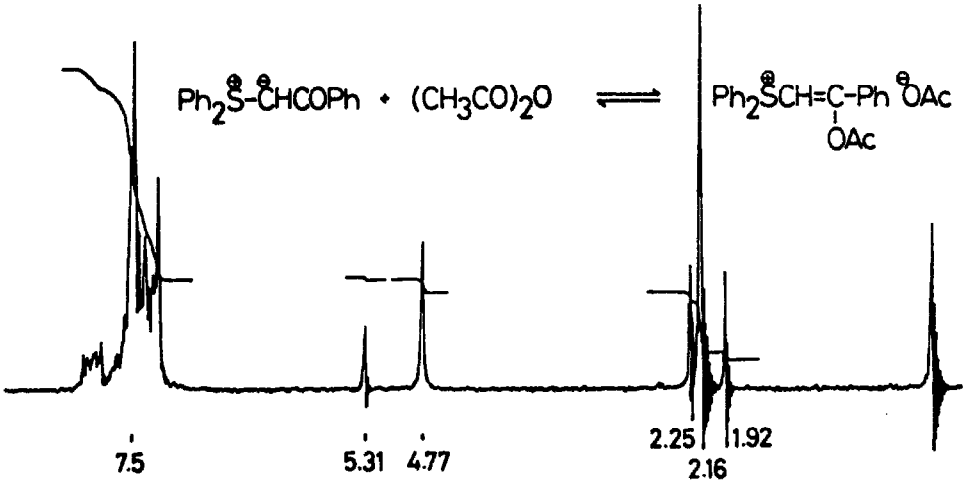
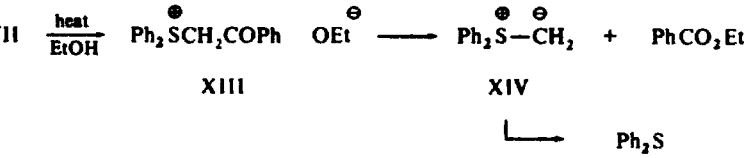


FIG. 3 NMR spectrum of VII and acetic anhydride (1 : 1).

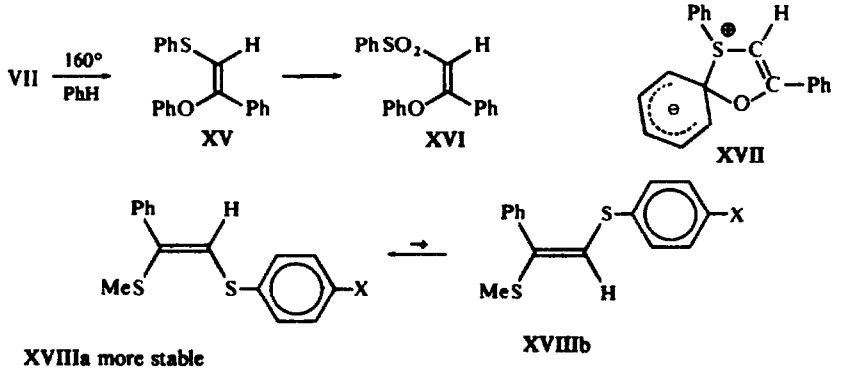
Treatment of VII with tosyl chloride and then with silver perchlorate yielded crystalline O-tosylated sulphonium perchlorate XI. In contrast, reaction of VII with methanesulphonyl chloride in the presence of triethylamine afforded a C-sulphonylated ylide XII in a 68% yield. The isolation of the salts IX and XI is characteristic of the ylide VII.

The ylide VII was found to remain unchanged upon melting at 146–148°. The absence of a S-methyl group naturally excludes the possibility of such a rearrangement as I→VI. Refluxing of VII in EtOH for 2 days gave diphenyl sulphide and ethyl benzoate besides starting material and some unidentified products. A possible scheme for these products is as follows. A sulphonium salt XIII from VII and EtOH is primarily formed and then decomposed to ethyl benzoate and diphenylsulphonium

methylide (XIV), which is further stabilized by elimination of methylene to give diphenyl sulphide.



A solution of VII in benzene was unchanged at refluxing temp for 24 hr at atmospheric press but gave a rearranged product XV by heating in a sealed glass tube at 160° for 24 hr. Oxidation of XV with H_2O_2aq gave a sulphone XVI. The tentatively assumed (Z)-configuration of XV is based on the following points. (a) It is presumed that a phenyl group migrates *via* the intermediate XVII. (b) Treatment of XV with HCl/CCl_4 did not give the isomerized product. As Oki *et al.*[10] reported that XVIIIa (X=H) is thermodynamically more stable than XVIIIb (ΔH −2·2 kcal/mol), therefore XV should be the more stable isomer. (c) Oki *et al.* also reported that the methine proton of XVIIIa shows a peak at δ 6·47–6·60 and that of XVIIIb at δ 6·20–6·30, respectively. The methine proton of XV appeared at δ 6.54.

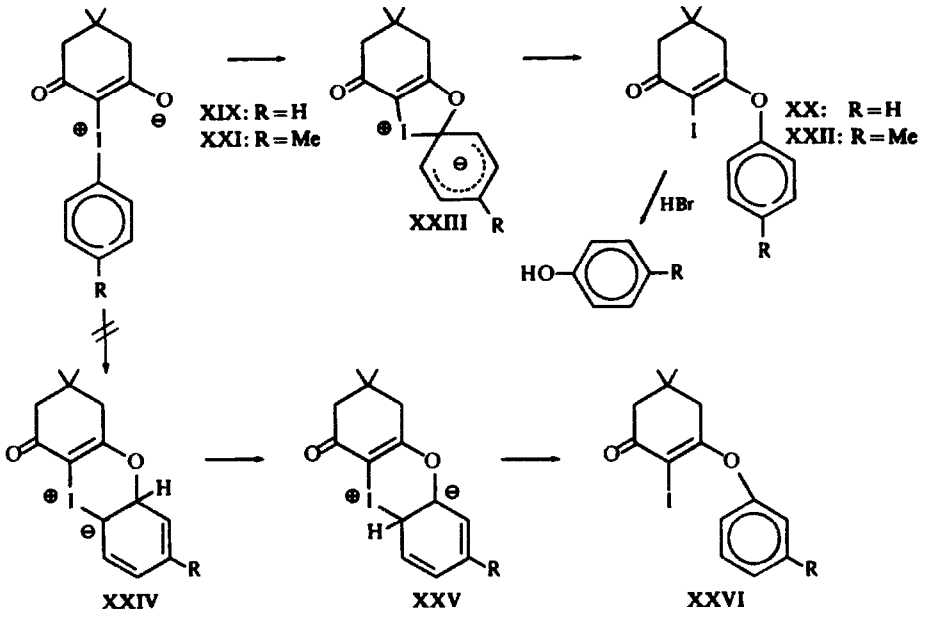


Although this rearrangement is the first example observed with sulphur ylides, analogous reactions of phosphorus ylides[11] and iodonium ylides [12] have been reported. Neilands *et al.* recorded the rearrangement of XIX to XX upon heating without establishing the mechanism. In order to examine this rearrangement in detail, we prepared a novel ylide XXI from *p*-iodosotoluene diacetate and dimedone. Heating of a solution of XXI in pyridine for 30 min under reflux gave an ether XXII and not XXVI. Both IR and NMR spectra of XXII are characteristic of the 1,4-disubstituted benzene ring. Furthermore, treatment of XXII with HBr aq afforded *p*-cresol. These results show that the benzene carbon attached to oxygen in XXII is the same one attached to iodine in XXI. That is, the rearrangement must proceed *via* a 5-membered intermediate XXIII, which is analogous to XVII, rather than a 6-membered intermediate such as XXIV and XXV.

EXPERIMENTAL

All m.ps and b.ps are uncorrected. Microanalyses were performed at the Elemental Analyses Centre of Kyôto University. The NMR spectra were obtained on JEOL C-60-H spectrometer.

Preparation of diphenylphenacylsulphonium tetrafluoroborate (VIII). A mixture of Ph_2S (5·0 g, 27



mmoles), $PhCOCH_2Br$ (5·4 g, 27 mmoles) and $AgBF_4$ (5·3 g, 27 mmoles) in CH_2Cl_2 (100 ml) was stirred for 2 days at room temp. After filtration, the extract was concentrated to afford solids, which were recrystallized from a small amount of CH_2Cl_2 to yield VIII (6·1 g, 58%), m.p. 158–160° (lit.[9] 161–162°), IR (Nujol): 1685, 1100–1000 (broad) cm^{-1}. (Found: C, 61·4; H, 4·5. Calc. for $C_{20}H_{17}BF_4OS$: C, 61·2; H, 4·4%).

Preparation of diphenylsulphonium phenacylide (VII). To a stirred suspension of VIII (3·9 g, 10 mmoles) in THF (30 ml) cooled with ice–water bath was added NaH (0·5 g, 50% dispersion in mineral oil, 10 mmoles) in one portion. The reaction mixture was stirred until the evolution of H_2 stopped (ca. 2 hr). The mixture was filtered to remove $NaBF_4$ and the filtrate was evaporated to give a red oil, which was solidified upon addition of ether. These solids were recrystallized from PhH to afford VII (2·6 g, 86%), m.p. 146–148° (lit.[9] 142–143°), IR (KBr): 1580, 1510 (very strong), 1448, 1384, 865, 750 and 714 cm^{-1}, NMR: δ ($CDCl_3$) 4·72 (1H, s), 7·2–8·0 (15H, m). (Found: C, 78·7; H, 5·2. Calc. for $C_{20}H_{16}OS$: C, 78·9; H, 5·3%).

Reaction of VII *with* MeCOCl. To a soln of VII (3·0 g, 10 mmoles) in THF (50 ml) was added dropwise a soln of MeCOCl (0·8 g, 10 mmoles) in THF (10 ml) over 10 min at room temp. The mixture was stirred for 2 hr at the same temp and an oil was separated. Most of the solvent was removed by decantation and the residual solvent was evaporated to afford a hygroscopic oil of IX (3·6 g, 95%), IR (neat): 1780, 1605, 1450, 1160, 1050, 760 and 690 cm^{-1}, which was unable to be pure form to allow a rigorous structure proof.

Reaction of IX *with* AgOAc. A mixture of IX (1·0 g, 2·6 mmoles) in THF at room temp was treated with AgOAc (0·43 g, 2·6 mmoles). After filtration, the filtrate was concentrated to afford VII (0·63 g, 80%) and Ac_2O (0·15 g, 57%).

Reaction of VII *with* Ac_2O. A soln of VII (1·5 g, 5 mmoles) and Ac_2O (0·5 g, 5 mmoles) in THF (30 ml) was refluxed for 12 hr. After evaporation of the solvent, the residue solidified upon addition of ether. These solids were recrystallized from PhH–hexane to afford X (0·8 g, 46%), m.p. 154–155°, IR (KBr): 1588, 1568, 1320, 788, 745, 713 and 686 cm^{-1}, NMR: δ ($CDCl_3$) 2·23 (3H, s), 7·1–7·7 (15H, m). (Found: C, 76·5; H, 5·5. $C_{22}H_{18}O_2S$ requires: C, 76·3; H, 5·2%).

Reaction of VII *with tosyl chloride.* A soln of VII (1·5 g, 5 mmoles) and TsCl (0·95 g, 5 mmoles) in $MeNO_2$ (30 ml) was stirred at room temp for ca. 3 hr, and then $AgClO_4$ (1·0 g, 5 mmoles) was added to the mixture followed by stirring for 1 day at the same temp. After filtration, the solvent was removed at reduced press, and a residual oil solidified upon addition of EtOH to give XI (2·2 g, 79%), m.p. 174–175°

(from EtOH—$CHCl_3$), IR (KBr): 1600, 1375, 1172 and 1120–1060 (broad) cm^{-1}, NMR: δ ($CDCl_3$) 2·35 (3H, s), 7·0–8·1 (20H, m). (Found: C, 58·0; H, 4·2. $C_{27}H_{23}ClO_3S_2$ requires: C, 58·0; H, 4·2%).

Reaction of VII *with methanesulphonyl chloride.* To a mixture of VII (1·5 g, 5 mmoles) and Et_3N (2·0 g, 20 mmoles) in THF (40 ml) at −60° under N_2 a soln of $MeSO_2Cl$ (1·2 g, 10 mmoles) in THF (10 ml) was added dropwise over 30 min. After the reaction mixture was stirred for 2 hr at the same temp, it was allowed to warm slowly to room temp with continuous stirring. The resulting crystals were filtered off, washed with a small amount of water and extracted to afford XII (1·3 g, 68%), m.p. 208–209·5°, IR (KBr): 1572, 1317, 1282, 1136 and 1122 cm^{-1}, NMR: δ ($CDCl_3$) 2·95 (3H, s), 7·2–7·8 (15H, m). (Found: C, 66·1; H, 5·0. $C_{21}H_{18}O_3S_2$ requires: C, 66·0; H, 4·8%).

Thermolysis of VII *in* EtOH. A soln of VII (2·5 g, 8·2 mmoles) in EtOH (100 ml) was refluxed for 48 hr. After evaporation of the solvent, the residual oil was chromatographed on a column of Florizil with benzene as an eluant to give Ph_2S (1·0 g, 66%) and PhCOOEt (0·4 g, 33%).

Thermolysis of VII *in* PhH. A soln of VII (0·5 g, 1·6 mmoles) in PhH (30 ml) was heated in a sealed glass tube at 160° for 24 hr. After the solvent was removed, the residue was purified on a column chromatograph (silicagel, hexane) to yield XV as an oil (0·31 g, 62%). This oil solidified on standing at room temp for 1 day, m.p. 78–79°, IR (KBr): 1590, 1488, 1203, 1016, 736 and 682 cm^{-1}, NMR: δ (CCl_4) 6·54 (1H, s), 6·8–7·6 (15H, m). (Found: C, 79·1; H, 5·3. $C_{20}H_{16}OS$ requires: C, 78·9; H, 5·3%).

Oxidation of XV. A soln of XV (0·3 g, 1·0 mmole) and H_2O_2aq (30%, 3 ml) in AcOH (5 ml) was stirred at room temp for 1 day. The reaction mixture was diluted with water, neutralized with $NaHCO_3$aq and extracted with $CHCl_3$. After drying, the solvent was removed to afford crystals of XVI (0·31 g, 92%), m.p. 135–135·5° (from PhH–hexane), IR (KBr): 1613, 1595, 1488, 1292, 1134, 1080, 740 and 682 cm^{-1}, NMR: δ ($CDCl_3$) 6·65 (1H, s), 6·9–8·1 (15H, m). (Found: C, 71·6; H, 4·9. $C_{20}H_{16}O_3S$ requires: C, 71·4; H, 4·8%).

Preparation of XXI. A soln of *p*-MeC_6H_4IO (0·7 g, 3 mmoles) and dimedone (0·42 g, 3 mmoles) in Ac_2O (10 ml) was allowed to stand for 10 hr at room temp. The reaction mixture was made basic (pH ca. 10) with 20% NaOH aq and extracted with $CHCl_3$. After the solvent was evaporated, the residual oil solidified upon addition of ether. These solids were recrystallized from PhH to yield XXI (0·78 g, 73%), m.p. 129–130°, λ_{max}^{EtOH} 259 nm (log ε 4·30), IR (Nujol): 1530 cm^{-1}. (Found: C, 50·3; H, 4·7. $C_{15}H_{17}IO_2$ requires: C, 50·6; H, 4·9%).

Thermolysis of XXI *in pyridine.* A soln of XXI (10 g, 28 mmoles) in pyridine (50 ml) was refluxed for 30 min. The reaction mixture was neutralized with dil HCl and extracted with $CHCl_3$. After the solvent was removed, the residue was solidified upon addition of hexane to yield XXII (3·3 g, 33%), m.p.158–160° (from EtOH), IR (Nujol): 1660, 1582, 1505 and 1238 cm^{-1}, NMR: δ ($CDCl_3$) 1·03 (6H, s), 2·29 (2H, s), 2·36 (3H, s), 2·47 (2H, s), 6·94 (2H, d, *J* 9 Hz), 7·21 (2H, d, *J* 9 Hz). (Found: C, 50·7; H, 4·8. $C_{15}H_{17}IO_2$ requires: C, 50·6; H, 4·9%).

Treatment of XXII *with* HBr. A mixture of XXII (0·6 g, 1·7 mmoles) and 48% HBr (0·5 g) in H_2O (10 ml) was refluxed for 2 hr. The reaction mixture was made basic with NaOH aq and extracted with ether. The aqueous layer was made acidic with HCl aq and extracted with ether. Concentration of the combined ether soln gave *p*-cresol (0·04 g, 22%).

Acknowledgements—The authors are indebted to Professor K. Sisido for help and encouragement. Work on iodonium ylides was carried out in collaboration with Zyun-iti Morita and Tadasige Yamaguti. Their valuable contribution is acknowledged with pleasure. This work was partially supported by the Scientific Research Fund of Ministry of Education, Japanese Government.

REFERENCES

[1] H. Nazaki, M. Takaku, D. Tunemoto, Y. Yamamoto and K. Kondo, *Nippon Kagaku Zasshi*, **88**, 1 (1967).
[2] K. W. Ratts and A. N. Yao, *J. Org. Chem.* **31**, 1185 (1966).
[3] B. M. Trost, *J. Am. Chem. Soc.* **89**, 138 (1967).
[4] A. W. Johnson and R. T. Amel, *Tetrahedron Letters* 819 (1966).
[5] H. Nozaki, M. Takaku and K. Kondo, *Tetrahedron* **22**, 2145 (1966).
[6] H. Nozaki, M. Takaku, Y. Hayasi and K. Kondo, *Ibid.* **24**, 6563 (1968).
[7] K. W. Ratts and A. N. Yao, *J. Org. Chem.* **33**, 70 (1968).
[8] H. Nozaki, K. Nakamura and M. Takaku, *Tetrahedron* **25**, 3675 (1969).
[9] T. Hashimoto, H. Yano, H. Kitano and K. Fukui, *Nippon Kagaku Zasshi* **89**, 703 (1968)

[10] M. Oki and K. Kobayashi, *Abstracts of Papers* presented at the 22nd Annual Meeting of the Chemical Society of Japan, No. 15321 (1969).
[11] H. J. Bestmann and G. Hofmann, *Liebigs Ann.* **716**, 98 (1968).
[12] B. Karele and O. Neilands, *Zh. Org. Khim.* **2**, 1680 (1966); *Chemical Abstr.* **66**, 64882j (1967).