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Synthesis and Reactions of Sulfonium Diacylmethylide Having Active Hydrogen

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Sulfonium diacylmethylides are easily prepared by acylating sulfonium monoacylmethylides[1] or by condensation of sulfoxides and 1,3-diketones.[2] Nevertheless few of their reactions are known with respect to the remarkable stability and inertness of these ylides.[3] We wish to report the reaction of sulfonium diacylmethylides having active hydrogens with a strong base.

Ylides Ia and Ib were prepared from the corresponding sulfonium phenacylides and phenylacetic anhydride in 71 and 72% yields, respectively, in the usual way. To a stirred solution of Ia in dimethyl sulfoxide (DMSO) under nitrogen was added equimolar sodium hydride in one portion. The reaction mixture was stirred for further 3 hr to produce a deep red solution. To this solution of IIa was added dropwise methyl iodide to give a new ylide IIIa (mp 132—133°C) in a 64% yield. Under the same conditions as above, Ib also yielded a red solution of IIb, which was treated with methyl iodide to give IIIb (mp 149—151°C) in a 70% yield. The

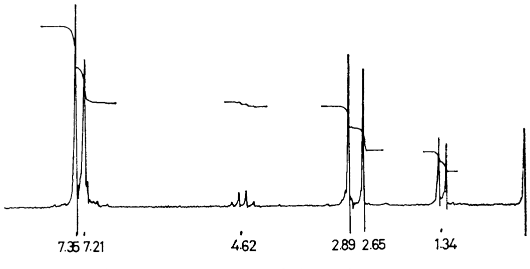

Fig. 1. NMR spectrum of dimethylsulfonium benzoyl(α-phenylpropionyl)methylide (IIIa).

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[1] H. Nozaki, M. Takaku and K. Kondo, *Tetrahedron*, **22**, 2145 (1966).

[2] H. Nozaki, Z. Morita and K. Kondo, *Tetrahedron Lett.*, **1966**, 2913.

[3] a) H. Nozaki, K. Nakamura and M. Takaku, *Tetrahedron*, **25**, 3675 (1969); b) M. Takaku, Y. Hayasi and H. Nozaki, *Tetrahedron Lett.*, **1969**, 2053.

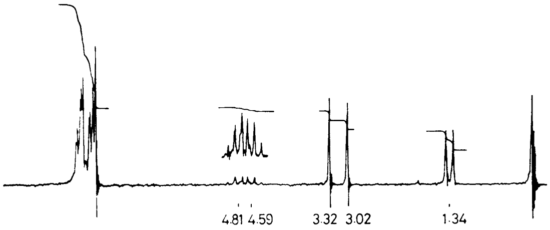
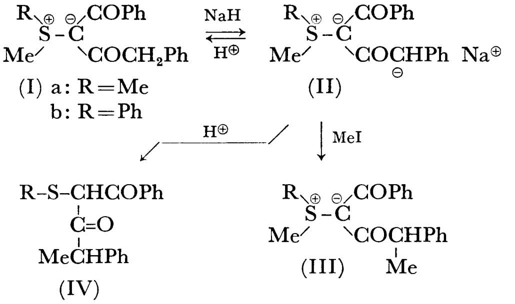


Fig. 2. NMR spectrum of methylphenylsulfonium benzoyl(α-phenylpropionyl)methylide (IIIb).

structures of IIIa and IIIb were determined on the basis of C, H analysis and spectral data. NMR spectrum of IIIa is given in Fig. 1, in which S-methyl signals were observed as two distinct singlets with chemical shift difference of 0.24 ppm. This shows that the S-methyl groups are diastereotopic to each other due to the pyramidal structure of sulfur atom and the presence of asymmetric carbon of α-phenethyl group. NMR spectrum of IIIb is given in Fig. 2. S-Methyl signals were observed as two singlets with chemical shift difference of 0.30 ppm as in IIIa. Methine protons appeared as two quartets (chemical shift difference: 0.22 ppm). The data indicate that IIIb is a *ca.* 1 : 1 mixture of two diastereomers due to two assymetric atoms (sulfur and α-phenethyl carbon), although it has a melting point 149—151°C and proved homogeneous on TLC. These diastereomers, however, have not been separated into components.



Treatment of a solution of IIa with acetic acid gave the starting ylide Ia in a 67% yield. In sharp contrast, however, treatment of IIb with acetic acid gave a rearranged product IVb (64%). The same rearrangement was also observed in DMF solvent. Simple treatment of Ib with acetic acid failed to induce the rearrangement.

Experimental

Preparation of Dimethylsulfonium Benzoyl(phenylacety)methylide (Ia). A solution of dimethylsulfonium phenacylide (3.6 g, 0.02 mol) and phenylacetic anhydride (5.1 g, 0.02 mol) in THF (100 m*l*) was stirred for 10 hr at room temperature. The reaction mixture was concentrated *in vacuo* and treated with chloroform. The chloroform solution was washed with aq. $NaHCO_3$, dried ($MgSO_4$) and concentrated. The residual solid was recrystallized from benzene to afford Ia (4.2 g, 70.5%), mp 108—110°C, IR (Nujol): 1591, 1565 and 1145 cm^{-1}, NMR: δ ($CDCl_3$) 2.86 (6H, s), 4.01 (2H, s), 7.2—7.5 (10H, m). (Found: C, 72.9; H, 6.1%. Calcd for $C_{18}H_{18}O_2S$: C, 72.5; H, 6.1%.)

Preparation of Methylphenylsulfonium Benzoyl(phenylacetyl)methylide (Ib). Treatment of methylphenylsulfonium phenacylide (4.8 g, 0.02 mol) with phenylacetic anhydride (5.1 g, 0.02 mol) in THF (100 m*l*) gave Ib (5.2 g, 72%), mp 130—132°C (from benzene), IR (KBr): 1596, 1570, 1350, 1118, 960, 735 and 710 cm^{-1}, NMR: δ ($CDCl_3$) 3.30 (3H, s), 4.09 (2H, s), 7.3—7.7 (15H, m). (Found: C, 76.8; H, 5.3%. Calcd for $C_{23}H_{20}O_2S$: C, 76.7; H, 5.6%.)

Reaction of Ia with Sodium Hydride Followed by Addition of Methyl Iodide. To a solution of Ia (3.0 g, 0.01 mol) in DMSO (50 m*l*) under nitrogen was added sodium hydride (1.0 g, 50% dispersion in mineral oil, 0.01 mol) in one portion at room temp. The reaction mixture was stirred for 3 hr to afford a red solution of IIa. To this solution of IIa was added dropwise a solution of methyl iodide (5.6 g, 0.04 mol) in DMSO (10 m*l*). After being stirred for an additional 1 hr, the reaction mixture was diluted with water and extracted with chloroform. The chloroform solution was dried ($MgSO_4$) and evaporated to afford a solid, which was recrystallized from benzene to yield IIIa (2.0 g, 64%), mp 132—133°C, IR (Nujol): 1590, 1580, 1565—1550 (broad), 1195, 1178, 1140, 1021 and 985 cm^{-1}. (Found: C, 72.8; H, 6.4%. Calcd for $C_{19}H_{20}O_2S$: C, 73.0; H, 6.5%.)

Reaction of Ib with Sodium Hydride Followed by Addition of Methyl Iodide. According to the same procedure as Ia, Ib (3.6 g, 0.01 mol) was treated with sodium hydride (1.0 g, 50% dispersion in mineral oil, 0.01 mol) followed by addition of methyl iodide (5.6 g, 0.04 mol) and gave IIIb (2.6 g, 70%), mp 149—151°C (from benzene-hexane), IR (KBr): 1580, 1570, 1295 and 1225 cm^{-1}. (Found: C, 76.6; H, 6.3%. Calcd for $C_{24}H_{22}O_2S$: C, 77.0; H, 5.9%.)

Treatment of IIa with Acetic Acid. To a solution of IIa (0.01 mol) in DMSO (50 m*l*) was added dropwise acetic acid (0.9 g, 0.015 mol) in DMSO (10 m*l*). The reaction mixture was diluted with aq. $NaHCO_3$ and extracted with chloroform. The chloroform solution was concentrated to afford Ia (2.0 g, 67%).

Treatment of IIb with Acetic Acid. A solution of IIb (0.01 mol) in DMSO (50 m*l*) was treated with acetic acid (0.9 g, 0.015 mol), diluted with water and extracted with chloroform. The chloroform solution was concentrated and ether was added to the residual oil to give a solid, which was recrystallized from ethanol to afford IVb (2.3 g, 64%), mp 90—93°C, IR (KBr): 1605, 1582, 1540 (broad), 1480 and 1380 cm^{-1}, NMR: δ ($CDCl_3$) 1.47 (3H, d, J=7.2 Hz), 4.11 (1H, s), 4.78 (1H, q, J=7.2 Hz), 7.0—7.8 (15H, m). (Found: C, 76.4; H, 5.5%. Calcd for $C_{23}H_{20}O_2S$: C, 76.7; H, 5.6%.)