

New Stable Sulfonium Ylides. 1-Dimethylsulfuranylidene-1-phenylsulfonyl-2-propanone and Related Compounds*

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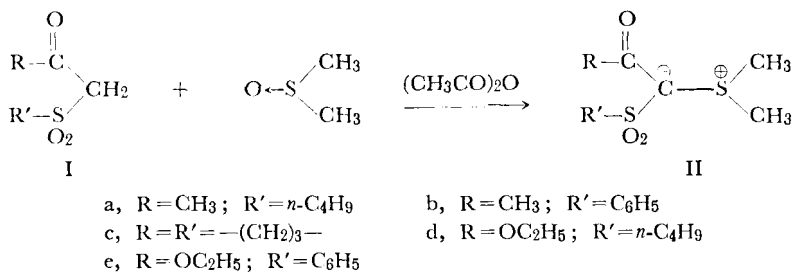
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The preparation of the title compounds as a new type of stable S-ylides has been described. The reaction of 1-dimethylsulfuranylidene-1-phenylsulfonyl-2-propanone (IIb) with lithium aluminium hydride was found to result in the formation of *trans*-phenylpropenylsulfone (IV), phenylsulfonyl-2-propanone (Ib), and an unidentified paraffin as major products.

While it has been well-known^{1,2,3)} that dimethylsulfoxide (DMSO) readily reacts with a variety of active methylene compounds in the presence of dehydrating agents to give stable S-ylides, the reactivity of such compounds as to have a methylene group, which is located between carbonyl and sulfonyl

groups, has not been investigated. We wish to report here the results of our studies on the preparation and the ylide formation of active methylene compounds (I) such as *n*-butylsulfonyl-2-propanone (Ia),⁶⁾ phenylsulfonyl-2-propanone (Ib),⁸⁾ and tetrahydrothiapyran-3-one-1,1-dioxide (Ic)⁹⁾ (see Scheme I).

Scheme I



The condensation was carried out as usual by standing a mixture of DMSO and active methylene compounds in the presence of acetic anhydride for several days, at room temperature. The products (IIa-c) were isolated as stable crystals giving correct analytical values, which correspond to those calculated for the proposed structure (II). Yields, physical and analytical data of these S-ylides are

listed in Table I. The presence of ylide carbonyl group is confirmed by IR absorption bands at 1570 (IIa), 1580 (IIb), and 1550 cm⁻¹ (IIc),^{2,3,11)} as shown in Figure 1.

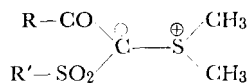
To the contrary, ethyl *n*-butylsulfonylacetate (Id)¹⁰⁾ and ethyl phenylsulfonylacetate (Ie)⁷⁾ did not give the ylides but were recovered unchanged at the reactions carried out as usual. Moreover, when the reaction mixture was kept at reflux temperature, Id gave a small amount of C-acetylated product (III). The failure of the ability to form the stable ylides of these compounds (Id, Ie) is apparently due to the weak activating effect of carbethoxy group as compared to acetyl group.

As a part of the study on the reactivity of S-ylides, the reaction of IIb, which was most

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Table I. S-Ylides^a

	R	R'	Mp, °C	Yield, %	Found, %		Calcd, %	
					C	H	C	H
IIa	CH ₃	<i>n</i> -C ₄ H ₉	67.5–72.0	43.0	45.29	7.43	45.68	7.61
IIb	CH ₃	C ₆ H ₅	122–124	77.5	50.97	5.51	51.13	5.46
IIc	–(CH ₂) ₃ –		209–212 (dec)	63.7	40.82	5.81	40.36	5.81

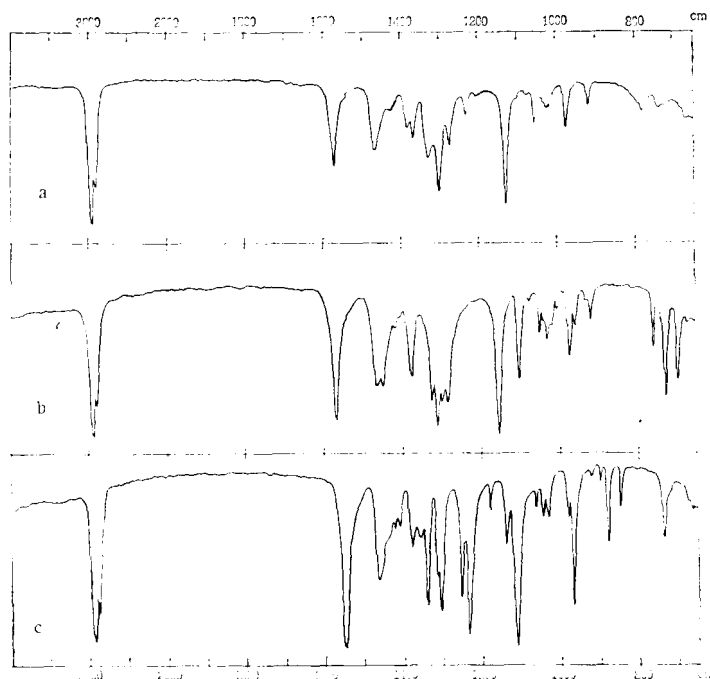
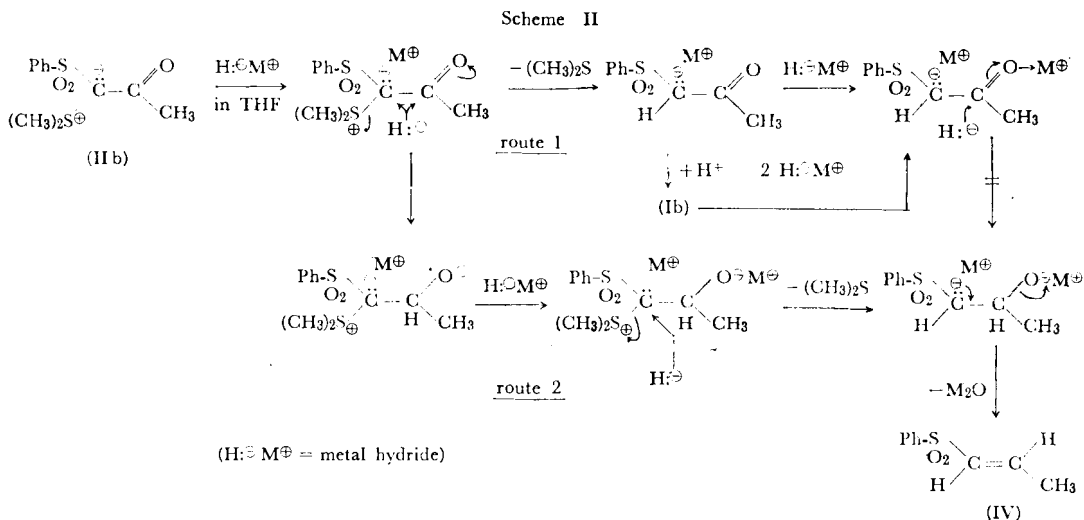


Figure 1. IR spectra of: (a) 1-dimethylsulfuranylidene-1-*n*-butylsulfonyl-2-propanone (IIa), nujol; (b) 1-dimethylsulfuranylidene-1-phenylsulfonyl-2-propanone (IIb), nujol; (c) 2-dimethylsulfuranylidene-tetrahydrothiapyran-3-one-1,1-dioxide (IIc), nujol.

readily accessible, with excess lithium aluminium hydride in tetrahydrofuran was then attempted (see Scheme II). A yellow liquid distilling at 180° (oil bath)/1mm Hg was obtained, when it was discontinued after 0.5 hr of refluxing. IR spectrum of this liquid was quite similar when observed before and after the distillation, and showed a moderate absorption at 1645 cm⁻¹, indicating the presence of olefinic linkage. Thin layer chromatography (tlc) of this fraction revealed the presence of three components (A, B, and C) in roughly equal portions. By means of preparative tlc, Ib (A), unidentified paraffin (C), and as a third component, an oil (B), which readily

^a All the compounds listed here are new.

solidified to yellow crystal melting at 57–59°, were separated. From IR data and mixed mp, the substance B was identified as *trans*-phenylpropenylsulfone (IV).⁴ As a whole, the reactions like route 1 (nucleophilic substitution at C-1) and route 2 (nucleophilic addition to C-2) are expected to compete, for the hydride anion can attack either C-2 or C-1 of IIb. Evidenced by the fact that IV was not produced by the action of lithium aluminium hydride on Ib, route 2 rather than route 1 has now been postulated as a reasonable reaction mechanism of the formation of IV. It is also assumed that by the formation of the metal salt of Ib in route 1, the electron density at C-2 would increase, hence the nucleophilic addition of the



second hydride anion to C-2 becomes suppressed.

Experimental Section

All melting and boiling points are uncorrected. Thin layer chromatography (tlc) and preparative tlc were effected using silica gel G (E. Merck) as a support and chloroform as a developer, and the spots were visualized with a potassium permanganate-sulfuric acid solution.

***n*-Butylsulfonyl-2-propanone (Ia).**—This compound was prepared by the reaction of sodium *n*-butanesulfinate⁵⁾ with chloroacetone in a 18.7% yield, bp 137–140° (4 mm) [lit.⁶⁾ bp 136–137° (4 mm)]; IR, 1320 (ν SO₂), and 1720 cm⁻¹ (ν C=O).

Phenylsulfonyl-2-propanone (Ib).—This compound was prepared in a 20.5% yield by the reaction of sodium benzenesulfinate⁷⁾ with chloroacetone, in the same manner as above, mp 53–55° (lit.⁸⁾ mp 57°); IR, 1310, 1160 (ν SO₂), and 1725 cm⁻¹ (ν C=O). It gave correct analyses.

Tetrahydrothiapyran-3-one-1,1-dioxide (Ic).—This compound was prepared by the oxidation of tetrahydrothiapyran-3-one⁹⁾ in a 42.9% yield, mp 138.5–140° (lit.⁹⁾ mp 140–140.5°); IR, 1315, 1125 (ν SO₂), and 1725 cm⁻¹ (ν C=O).

1-Dimethylsulfuranylidene-1-*n*-butylsulfonyl-2-propanone (IIa).—A mixture of *n*-butylsulfonyl-2-propanone (4.0 g, 0.023 mole), dimethylsulfoxide (17.6 g, 0.23 mole), and acetic anhydride (23.0 g, 0.23 mole) was kept for three days at room temperature, using a cal-

cium chloride tube to avoid moisture. After removing the solvent *in vacuo*, the residual gummy material was recrystallized from carbon tetrachloride to afford 2.3 g (43.0%) of IIa, mp 67.5–72.0°; IR, 1330, 1130 (ν SO₂), and 1570 cm⁻¹ (ylide ν C=O). *Anal.* Calcd for C₁₈H₁₈O₅S₂: C, 45.68; H, 7.61. Found: C, 45.29; H, 7.43.

1-Dimethylsulfuranylidene-1-phenylsulfonyl-2-propanone (IIb).—In a similar manner as described in the above paragraph, from a mixture of phenylsulfonyl-2-propanone (26.9 g, 0.136 mole), dimethylsulfoxide (106 g, 1.36 mole), and acetic anhydride (109 g, 1.36 mole), a brownish oil was obtained, which crystallized upon scratching. Recrystallization from ethanol gave 27.2 g (77.5%) of IIb, mp 122°; IR, 1310, 1150 (ν SO₂), and 1580 cm⁻¹ (ylide ν C=O). *Anal.* Calcd for C₁₁H₁₄O₅S₂: C, 51.14; H, 5.46. Found: C, 50.97; H, 5.51.

2-Dimethylsulfuranylidene-tetrahydrothiapyran-3-one-1,1-dioxide (IIc).—A mixture of tetrahydrothiapyran-3-one-1,1-dioxide (1.0 g, 0.0068 mole), dimethylsulfoxide (5.3 g, 0.068 mole), and acetic anhydride (7.0 g, 0.068 mole) was kept for two days. The resulting precipitate was filtered and recrystallized from ethanol to yield 0.9 g (63.7%) of IIc, mp 209–212° (dec); IR, 1340, 1110 (ν SO₂), and 1550 cm⁻¹ (ylide ν C=O). *Anal.* Calcd for C₇H₁₂O₃S₂: C, 40.36; H, 5.81. Found: C, 40.82; H, 5.81.

Reaction of Ethyl *n*-Butylsulfonylacetate with Dimethylsulfoxide.—A mixture of ethyl *n*-butylsulfonylacetate¹⁰⁾ (2.1 g, 0.01

mole), dimethylsulfoxide (7.8g, 0.1 mole) and acetic anhydride (5.0g, 0.05 mole) was refluxed for 1.5 hr at 165°. The reaction was continued for additional 0.5hr after 5.0g of acetic anhydride was added. Slightly yellow oil (0.2g, bp 131.5° (0.06 mm)), was obtained after the removal of solvent *in vacuo*. Identification as ethyl 2-*n*-butylsulfonylacetoacetate (III): IR, 1735 (ester ν C=O), 1725 (ketone ν C=O), 1325, and 1115 cm^{-1} (ν SO₂). *Anal.* Calcd for C₁₀H₁₈O₅S: C, 47.99; H, 7.63. Found: C, 47.61; H, 7.57.

Reaction of 1-Dimethylsulfuranylidene-1-phenylsulfonyl-2-propanone (IIb) with Excess Lithium Aluminium Hydride. — A mixture of IIb (2.0g, 0.0077 mole) and lithium aluminium hydride (0.46g, 0.012 mole) suspended in 20 ml of THF was refluxed for 0.5 hr. After the removal of the solvent under reduced pressure, 1.2g of a crude product was obtained. On vacuum distillation, it gave a yellow liquid (ca. 0.5g) boiling at 180° (oil bath)/1 mmHg. The infrared spectrum of this liquid was identical with that of the crude product.

The constituents of the distillate were separated by preparative tlc. R_f: A, 0.30; B, 0.45; hydrocarbon, 0.99. By the comparison of the weight of each components collected from the spots on tlc plates, the following ratio was roughly estimated: A/B/hydrocarbon-1/1/1. The substance A, mp 49–52°, mixed mp 52–54°, IR bands at 1725, 1310, and 1160 cm^{-1} . Authentic sample of phenylsulfonyl-2-propanone⁸⁾: IR, 1725, 1310, and 1160 cm^{-1} . The substance B, mp 57–59°, mixed mp 61–63°, IR bands at 1645 (double bond), 1310, 1155 (ν SO₂), and 965 cm^{-1} (*trans* disubstituted olefin). Authentic sample of *trans*-phenylpropenylsulfone⁴⁾: IR, 1645, 1310, 1155, and 965 cm^{-1} . Characterization of the hydrocarbon was by IR data.

Reaction of Phenylsulfonyl-2-propanone (Ib) with Lithium Aluminium Hydride. —

In the same manner as described in the above experiment, a mixture of Ib (1.5g, 0.0077 mole) and lithium aluminium hydride (0.46g, 0.012 mole) suspended in 20 ml of THF was refluxed for 0.5 hr. The constituents of the yellow oil (ca. 0.5g), which was obtained by the distillation [180° (oil bath)/1 mmHg] of the crude product, was treated by preparative tlc as usual. R_f: A', 0.27; B', 0.40; hydrocarbon, 0.99. The following ratio was roughly estimated for the constituents: A'/B'/hydrocarbon-1/6/3. The substance A' was identified as the starting material. The oily substance B' had strong bands at 1310 and 1165, and weak bands at 1725 and 1590, no absorption at 1645 cm^{-1} . Characterization of the hydrocarbon was by IR data.

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