absence of cyclopropenecarbaldehyde (18) in the direct irradiation of the diene 13. Additionally this experiment shows that cyclopropenecarbaldehyde (18) is not the precursor to furan (19) produced in the photolysis of 13, although this is a well-documented photorearrangement of substituted acylcyclopropenes.[21] As no furan is produced upon irradiation of the diene 13 in the presence of isobenzofuran, either Dewar furan (4) or some intermediate species involved in its thermal rearrangement to cyclopropenecarbaldehyde (18) must be photoreactive and act as the precursor to furan. On the basis of these results we can summarize the photolysis of the diene 13 as shown in Scheme IV, in which Dewar furan (4) plays a key role. Experiments on elucidating the nature of such intermediate(s) are under active investigation and will be reported in due course.

Registry No. 4, 74496-19-8; 6, 3005-27-4; 7, 12078-17-0; 8, 98652-86-9; 9, 98652-87-0; 10, 98652-88-1; 11, 26307-17-5; 12, 98652-89-2; 13, 98652-90-5; 14, 95641-37-5; 15, 270-75-7; 16, 98652-91-6; 17, 98717-52-3; 18, 36998-21-7; 20, 98652-92-7; 21, 98717-53-4; 23, 2957-95-1; 24, 98652-93-8; 25, 98717-54-5; 26, 98717-55-6; 27, 98652-94-9; 28, 98717-56-7; 29, 84636-45-3.

(21) Inter alia: Padwa, A.; Akiba, M.; Chou, C. S.; Cohen, L. J. Org. Chem. 1982, 47, 183–191.
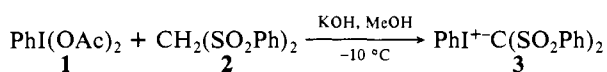
Phenyliodonium Bis(phenylsulfonyl)methylide: A New Hypervalent Iodonium Ylide

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Compounds with a sulfonyl group in general[1] and gem-disulfones in particular[2] are increasingly attracting attention for their potential in organic synthesis. At the same time, iodonium ylides are being established as a class of ylides of synthetic and mechanistic interest.[3] We report the synthesis and chemistry of a new type of iodonium ylide, the carbanion moiety of which is a β-disulfonyl group, i.e., phenyliodonium bis(phenylsulfonyl)-methylide (3). This compound, which could not be formed from the disulfone 2 and iodosylbenzene,[4] has now been prepared from diacetoxyiodobenzene (1) and 2 in 90% yield by the general method of Schank and Lick.[5]

$$PhI(OAc)_2 + CH_2(SO_2Ph)_2 \xrightarrow[-10\ °C]{KOH,\ MeOH} PhI^{+-}C(SO_2Ph)_2$$
$$\quad\ 1 \qquad\qquad 2 \qquad\qquad\qquad\qquad\qquad 3$$

It is mentioned that the synthesis of the related ylides $RC_6H_4I^{+-}C(SO_2F)_2$ has been reported,[6] without any reactions.

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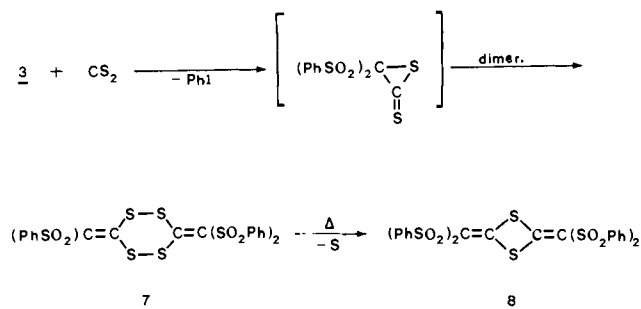(4) Hayasi, Y.; Okada, T.; Kawanisi, M. Bull. Chem. Soc. Jpn. 1970, 43, 2506.
(5) Schank, K.; Lick, C. Synthesis 1983, 392.

Scheme I[a]
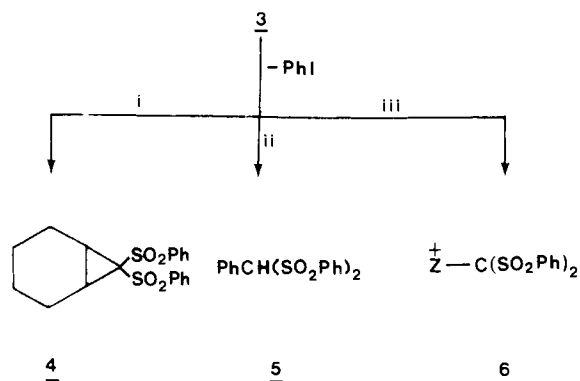
[a] Reactants, conditions, and products (with % yields). (i) cyclohexene, MeCN–hν, 4 h, 4 (31%); (ii) PhH, hν, 6 h, 5 (65%); (iii) Z = pyridine, reflux, Cu(acac)₂, 4 h, 6a (75%); Z = Ph₃P, CHCl₃, reflux, Cu(acac)₂, 3 h, 6b (92%); Z = (Me₂N)₂CS, CHCl₃, reflux, Cu(acac)₂, 7 h, 6c (78%); Z = Me₂S, hν, 2.5 h, 6d (84%); Z = PhSMe, reflux, Cu(acac)₂, 1 h, 6e (29%).

Scheme II

The stability of 3 is limited, and it decomposes on attempted recrystallization. However, it can be stored for at least 2 weeks at −10 °C without change. Its spectral characteristics are in agreement with the proposed structure.[7] Ylide 3 enters into several types of reactions, three of which are shown in Scheme I and involve transfer of the bis(phenylsulfonyl)methylene moiety to several nucleophiles to give gem-disulfones which are otherwise not easily accessible. Thus, cycloaddition occurs with cyclohexene to yield the bicyclic disulfone 4; C–H bond insertion is observed with benzene to give the phenylated disulfone 5, and transylidation occurs with various S, N, and P nucleophiles which are converted into their ylides 6. With few exceptions yields are good. These reactions have been carried out under two sets of conditions, either photolytically[8] or thermally in the presence of catalytic amounts of Cu(acac)₂, and optimal conditions are shown in Scheme I. It is noted that ylides 6b,[9] 6c,[10] and 6d[11] have been prepared previously in low yields.

When 3 was heated in carbon disulfide under reflux precipitation of the tetrathianic tetrasulfone 7 occurred in 30% yield. The formation of 7 probably proceeds as suggested for an analogous reaction of diphenyldiazomethane with CS₂.[12] Heating 7 in diglyme with Cu powder leads to partial desulfurization yielding the dithietanic tetrasulfone 8 (Scheme II).

The dihalobis(phenylsulfonyl)methanes 9a–c have been obtained from 3 and N-halosuccinimides without any added catalyst. The

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(7) All new compounds have elemental analysis and spectral data (IR, ¹H NMR, MS) consistent with the assigned structures.
(8) A Philips 400-W low-pressure mercury lamp has been used. Irradiation was performed in Pyrex tubes under N₂ (λmax (3) 277 nm, in MeOH).
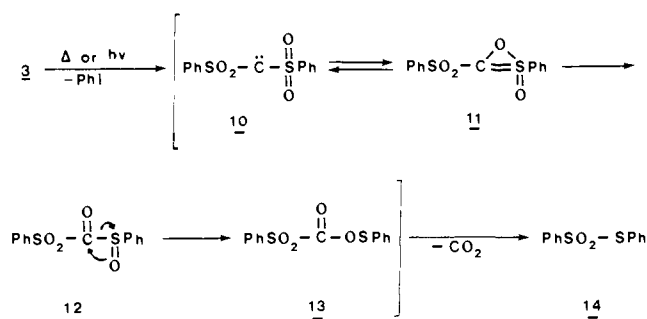(9) Horner, L.; Oedinger, H. Chem. Ber. 1958, 91, 437.
(10) Lloyd, D.; Millar, R. W. Tetrahedron 1980, 36, 2675.
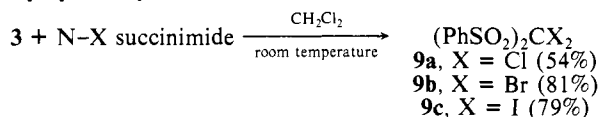(11) Dieckman, J. J. Org. Chem. 1965, 30, 2272.
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Scheme III

Scheme IV

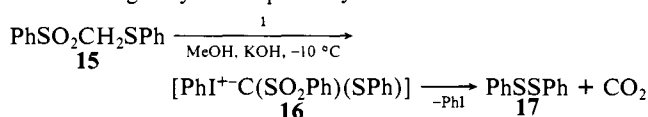
formation of **9c** is noteworthy since, unlike **9a** and **9b**, **9c** cannot be prepared by direct iodination of **2**.[13]

$$3 + \text{N-X succinimide} \xrightarrow[\text{room temperature}]{CH_2Cl_2} (PhSO_2)_2CX_2$$

9a, X = Cl (54%)
9b, X = Br (81%)
9c, X = I (79%)

Compounds **9b** and **9c** were also formed from **3** and the corresponding elemental halogen, while **9a** was obtained from **3** with SO_2Cl_2. The ylide **3** has oxidizing properties: thus **3** reacts with aniline to give *trans*-azobenzene, with anthracene to give 9,10-anthraquinone, and with diphenylacetylene to give benzil, all in low yields. Furthermore, phenylalkenes such as styrene, *trans*-stilbene, and ethyl cinnamate undergo cleavage of the double bond with **3** at room temperature to afford benzaldehyde as the main product. Acrylonitrile was polymerized by **3** exothermically.

When **3** was heated in such diverse H-containing solvents as AcOH, CH_2Cl_2, MeCN, etc., the formation of iodobenzene and the disulfone **2** was observed. However, when **3** was heated under reflux in *t*-BuOH in the presence of $Cu(acac)_2$ and under N_2, CO_2 was evolved, and the unexpected product phenyl benzenethiosulfonate (**14**) was obtained, in 80% yield. The same ester was formed in varying amounts in most of the reactions of **3**. We propose the mechanism shown in Scheme III for the formation of **14**. Apparently the solvent plays a passive role since CO_2 evolution has been detected during the thermolysis of solid **3**. Support for this mechanism is provided by an attempted synthesis of ylide **16** from (phenylsulfonyl)(phenylthio)methane (**15**) and **1**, where the decomposition product of the expected ylide diphenyl disulfide (**17**) was obtained. The formation of **17** probably proceeds analogously to the pathway in Scheme III.

$$\text{PhSO}_2\text{CH}_2\text{SPh} \xrightarrow[\text{MeOH, KOH, }-10\,°C]{1}$$
15

$$[\text{PhI}^+\text{-C}(SO_2Ph)(SPh)] \xrightarrow[-\text{PhI}]{} \text{PhSSPh} + CO_2$$
16   **17**

The reactions of **3** with nucleophiles as well as its thermolysis probably involve dissociation of the ylide into iodobenzene and bis(phenylsulfonyl)carbene (**10**).[14] Carbene formation from iodonium ylides has previously been suggested in two cases.[4,15] The carbene **10** is apparently in equilibrium with **11**, as oxirenes are with ketocarbenes.[16] Rearrangement of **11** into **12** followed by intramolecular nucleophilic collapse of **12** to **13** and decarboxylation of **13** would give **14**. This stage (**13** → **14**) is possibly responsible for the production of free radicals and the polymerization of acrylonitrile.

There is precedent[17] for *O*-sulfonyl attack at highly electrophilic C. The enhanced nucleophilic character of the sulfonyl oxygen

of **3** or **10** must be responsible for the oxidations effected by **3** under mild conditions. Both **3** and **10** are probably stabilized by resonance so that considerable negative charge may be acquired by the sulfonyl oxygens. However, carbene formation here and in reactions of **3** with electrophiles seems unlikely. The formation of transient iodonium salts is more justifiable. We note, for example, that phenyliodonium dinitromethylide gives isolable iodonium salts[18] with FSO_3H.

Iodobenzene is a byproduct in all the above reactions of **3**. A different type of reactivity was observed when **3** was allowed to react with dimedone (**18**) in non-hydroxylic solvents. In this case, "reversed" transylidation occurred, and the phenyliodonio dimedonate (**19**) was obtained in 50% yield (Scheme IV). This reaction may involve proton transfer from **18** ($pK_a = 5$) to **3** (estimated[19] pK_a of protonated **3** is ~4) and subsequent attack of the dimedonate ion on protonated **3**.

Registry No. 1, 3240-34-4; **2**, 3406-02-8; **3**, 98858-34-5; **4**, 98858-35-6; **5**, 38564-68-0; **6** (Z = pyridine), 98858-36-7; **6** (Z = Ph_3P) (P(V) entry), 96415-47-3; **6** (Z = Ph_3P) (ylide entry), 25809-68-1; **6** (Z = $(Me_2N)_2CS$), 77134-48-6; **6** (Z = Me_2S), 2292-72-0; **6** (Z = PhSMe), 53799-65-8; **7**, 98858-37-8; **8**, 98858-38-9; **9a**, 603-35-0; **9b**, 2782-91-4; **9c**, 75-18-3; **14**, 1212-08-4; **15**, 15296-86-3; **17**, 882-33-7; CS_2, 75-15-0; *N*-chlorosuccinimide, 128-09-6; *N*-bromosuccinimide, 128-08-5; *N*-iodosuccinimide, 516-12-1; aniline, 62-53-3; azobenzene, 103-33-3; 9,10-anthraquinone, 84-65-1; diphenylacetylene, 501-65-5; benzyl, 2154-56-5; styrene, 100-42-5; *trans*-stilbene, 103-30-0; ethyl cinnamate, 103-36-6; benzaldehyde, 100-52-7; acrylonitrile, 107-13-1; polyacrylonitrile, 25014-41-9; anthracene, 120-12-7.

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Oxidative Nucleophilic Addition of Organovanadium Reagents to Aldehydes with Formation of Ketones

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A variety of organometallic reagents have been developed for selective molecular elaboration.[1,2] In particular, alcohol formation via carbonyl addition reactions constitutes one of the important C–C bond construction methods. Herein we describe a new methodology for carbonyl alkylation which involves an organovanadium compound as a key reagent for oxidative nucleophilic addition.

The organovanadium reagents employed here were generated in situ in dichloromethane from equimolar amounts of vanadium trichloride and organolithium or magnesium compounds. The reactions of the reagents thus obtained with aldehydes resulted in oxidative C–C bond formation leading to the corresponding ketones (Scheme I). For example, vanadium trichloride was

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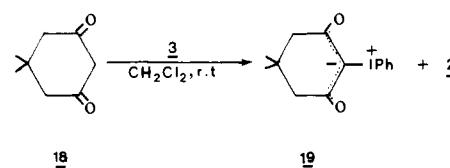(13) Jarvis, B.; Fried, H. E. *J. Org. Chem.* **1975**, *40*, 1278.

(14) The formation of **10** has been proposed in reactions of the unusually stable bis(phenylsulfonyl)diazomethane,[11] but no reaction occurred with benzene and alkenes, whereas triphenylphosphine did react to give the phosphazene. Therefore formation of **10** from this precursor is unlikely.

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