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# REACTIONS OF 2,3-DIHYDRO-2-PHENYLIODONIUM-3-OXO-BENZO[b] THIOLENIDE-1,1-DIOXIDE

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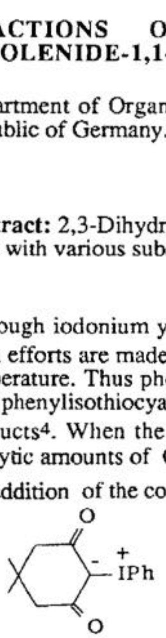
**Abstract:** 2,3-Dihydro-2-phenyliodonium-3-oxo-benzo[b]thiolenide-1,1-dioxide was found to react with various substrates like alkenes, alkynes, thiobenzophenones etc.

Although iodonium ylides have been recognized as precursors of carbenes (or carbenoids)[2], main efforts are made to study their reactions with several electrophilic compounds[3] at room temperature. Thus phenyliodonium dimedonate **1**, a remarkably stable iodonium ylide, reacts with phenylisothiocyanate affording 2-(2-benzothiazoyl) dimedone **2** (36% yield) among other products[4]. When the same reaction is repeated at elevated temperature[5] in the presence of catalytic amounts of $Cu(acac)_2$ 1,3-benzoxathiole **3** is isolated (74% yield), probably through 1,3-addition of the corresponding α-keto carbene (or carbenoid).



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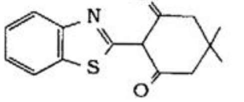

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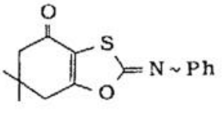

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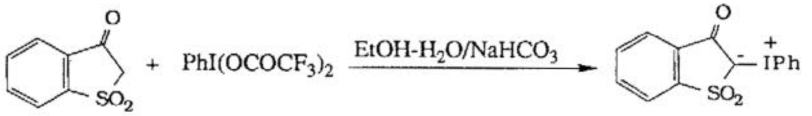
We are presenting our results with 2,3-dihydro-2-phenyliodonium-3-oxo-benzo[b]thiolenide-1,1-dioxide **5** an iodonium ylide[6] with a carbanionic center substituted by a carbonyl- and a sulphonyl-group under thermolytic conditions.



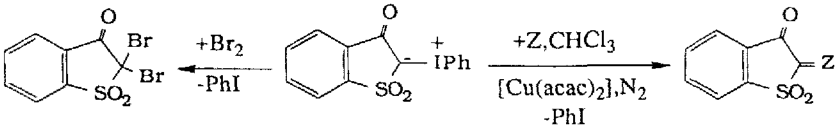
(eq. 1)

4

5

3-Oxo-benzo[b]thiophene-1,1-dioxide[7] **4** reacts with phenyl iodosyl bis (trifluoroacetate) and $NaHCO_3$ / $EtOH$-$H_2O$ to give 2,3-dihydro-2-phenyliodonium-3-oxo-benzo[b]thiolenide-1,1-dioxide[8] **5** in 93% yield as a yellowish solid (eq. 1) : mp: 193-194 °C; IR (KBr) : 1600,1280,1125,990 $cm^{-1}$; $^1H$ NMR(400MHz , $[D_6]$ DMSO) :$\delta = 7.41$-$7.45$ (2H,m), 7.50-7.51(1H,m),7.67-7.73 (3H,m),7.82-7.84 (1H,m),7.93-7.95 (2H,m); $^{13}C$ NMR ( 100MHz, $[D_6]$ DMSO): $\delta = 67.3$, 118.3,119.6,122.0,130.7,131.0,132.1,132.7, 133.3,143.2,172.3.

Although iodonium ylide **5** was insoluble in most aprotic solvents, including $CHCl_3$ and $CH_3CN$, its reactions could be examined in suspension. Thus, it reacts with excess bromine forming 2,2-dibromo-3-oxo-benzo[b]thiophene-1,1-dioxide **6** in 72% yield as well as with various nucleophiles leading to the new ylides **7** and iodobenzene (eq. 2).

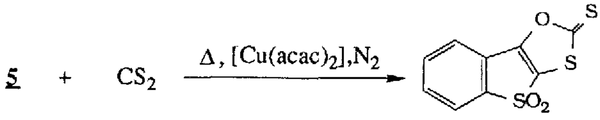


(eq. 2)

6 5 7

7a, Z=pyridine (89%)
7b, Z=$Ph_3P$(82%)
7c, Z=$Ph_3As$(86%)

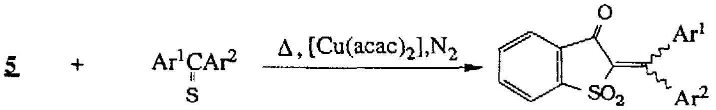
Thione **8** was isolated in 36% yield after refluxing iodonium ylide **5** in carbon disulfide in the presence of $Cu(acac)_2$ under nitrogen atmosphere (eq. 3).



(eq. 3)

8

Substituted thiobenzophenones reacted thermally (in the presence of catalytic amounts of $Cu(acac)_2$ under nitrogen atmosphere) with iodonium ylide **5** forming alkenes **9** (eq. 4), probably via the corresponding thiiranes. These results are in agreement with the already published results[9] of the thermal reactions of thiobenzophenones with phenyliodonium bis(alkyl- or aryl-sulphonyl)methylides.

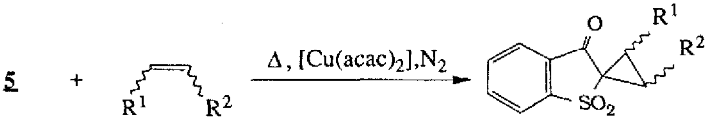


(eq. 4)

9

9a, $Ar^1=Ar^2=p\text{-}CH_3OC_6H_4$ (54%)
9b, $Ar^1=p\text{-}CH_3OC_6H_4$; $Ar^2=p\text{-}CH_3C_6H_4$ (57%)

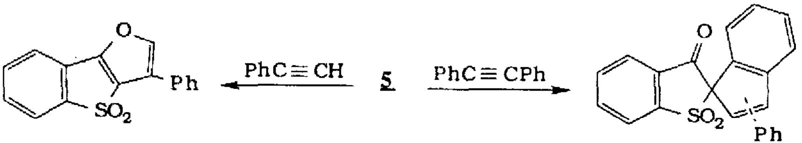
Iodonium ylide **5** reacts thermally (in the presence of $Cu(acac)_2$ under nitrogen atmosphere, cf. Table I) with various alkenes forming the corresponding cyclopropanes **10** (eq.5) (stereochemistry not elucidated).



(eq. 5)

10

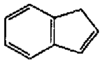
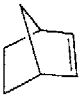
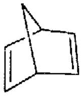
Correspondingly , alkynes react thermally with iodonium ylide **5** . Phenylacetylene yields furan **11** in 34% yield, and diphenyl acetylene yields indene **12** in 14% yield(eq. 6).



(eq. 6)

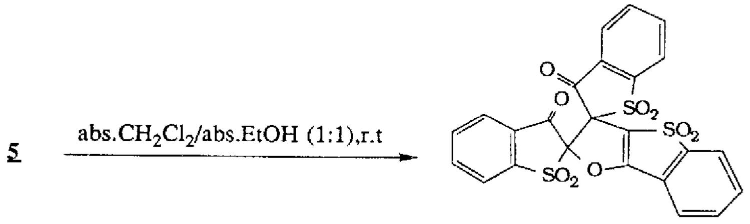
11 12

Table I. Cyclopropanes 10 by reaction of iodonium ylide 5 with alkenes

| Entry | Alkene | Time[min] | Temperature[°C] | Yield[a][%] of 10 |
|---|---|---|---|---|
| 1 | $C_6H_5CH{=}CH_2$ | 15 | 100 | 80 |
| 2 | o-$ClC_6H_4CH{=}CH_2$ | 15 | 100 | 45 |
| 3 | m-$CH_3OC_6H_4CH{=}CH_2$ | 10 | 100 | 69 |
| 4 |  | 10 | 80 | 65 |
| 5 |  | 10 | 80 | 46 |
| 6 |  | 10 | 80 | 63 |
| 7 |  | 20 | 80 | 39 |

[a] All yields are corresponding to isolated products. All products have been fully characterized by spectral means and elemental composition established by combustion analysis.

We suppose that in most of the above cases, the iodonium ylide should dissociate thermally, in the presence of catalytic amounts of $Cu(acac)_2$, to a carbene (α-substituted by a carbonyl as well as a sulphonyl group) and iodobenzene. This carbene( or carbenoid) should be responsible for the observed products. In contrast, when the iodonium ylide **5** is dissolved in a mixture of abs. $CH_2Cl_2$- abs. EtOH, the trimer **13** is isolated quantitively. By use of pure abs. EtOH, β-ketosulphone **4** is isolated instead.



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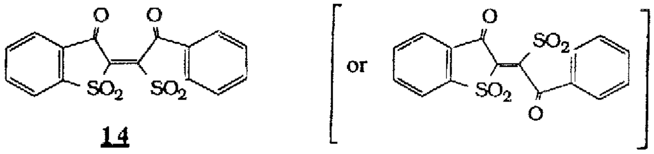
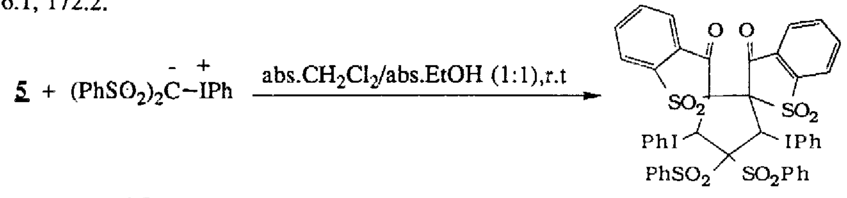
   A slight modification of the described procedure had been used. This consists of washing the precipitate (iodonium ylide) with abs. ether and drying over $P_2O_5$ at -20 °C until constant weight.
9. a. Hadjiarapoglou, L. P. *Ph.D Thesis*, Aristotelian University, Thessaloniki 1987.
   b. Hadjiarapoglou, L.; Varvoglis, A. *J. Chem. Soc., Perkin I* 1989,379.
10. Although it seems that the trimer **13** is the addition product of iodonium ylide **5** to an alkene[11] **14**, the use of large excess of abs. EtOH (compared to the quantity of **5**) proves that such an alkene is never formed, because it had to react[12] with EtOH instead of the ylide **5**.



14

A mixture of iodonium ylide **5** and phenyliodonium bis(phenylsulphonyl) methylide **15** (ratio 2:1) is readily dissolved in a mixture of abs. $CH_2Cl_2$- abs. EtOH forming quantitively iodinane **16**. $^{13}C$ NMR (100 MHz, [$D_6$] DMSO):$\delta$= 59.2, 67.7, 118.2, 118.5, 119.5, 121.9, 126.3, 128.2, 130.3, 130.4, 130.6, 130.9, 131.0, 132.0, 132.6, 133.3, 143.2, 146.1, 172.2.



15

16

11. Such an alkene had been proposed[8] as the product of the self-decomposition after the dissolution of iodonium ylide **5** in $CH_2Cl_2$.
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