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2,3-Dihydro-3-oxo-2-phenyliodonium-benzo[b]thiolenide-1,1-dioxide: Synthesis, Decomposition and Cu-Catalyzed Thermal Reactions.

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Abstract: Iodonium ylide 4 was prepared in 93% yield from the reaction of β -ketosulfone 3 with phenyl iodosyl bis(trifluoroacetate). Although insoluble in most solvents, ylide 4 was readily soluble in a mixture of CH₂Cl₂/ ethanol (1:1), yielding trimer 5 quantitatively. Upon reaction with various heteroatom nucleophiles the new ylides 7 were isolated, while reaction with CS₂ and thiobenzophenones yields thione 10 and alkenes 14 respectively. Furthermore 4 reacts with various alkenes 15 affording cyclopropanes 16 in moderate yields as well as with alkyne 17 affording furan 18. © 1997 Elsevier Science Ltd.

INTRODUCTION

As a rule, ylides and carbenes (or carbenoids) are related species.¹ Ylides are formed when a carbene (or carbenoid) is generated from a diazo precursor in the presence of the appropriate heteroatom nucleophile as trapping agent, and, conversely, carbenes (or carbenoids) are involved in the thermal or photochemical reactions of ylides. Meanwhile, the aryliodonium ylides which might be possible reactive alternatives to the related diazo compounds,² constitute a major class of hypervalent iodine compounds,³ readily accessible⁴ from the reaction of an active methylene compound with a hypervalent iodine precursor. According to the known examples, an iodonium ylide can be practically isolated in a pure form only when the substituents of its carbanionic center are of the same type, and is usually rather labile when these substituents are different.⁵

Although iodonium ylides have been recognized as possible precursors⁶ of carbenes (or carbenoids), most early research efforts were directed⁷ towards their reactions with several electrophiles at room temperature. Recently, it was shown that 1-phenyliodonium-4,4-dimethyl-2,6-dioxocyclohexylide⁸ (1) and phenyliodonium bis(phenylsulfonyl)methylide⁹ (2) undergo a number of thermal (metal-catalyzed) or photochemical intermolecular cycloadditions, such as the reaction with CS₂,¹⁰ thiobenzophenones,¹¹ alkenes,^{12,16} alkynes,^{12,16} and aromatics,¹³ while suitably substituted β -dicarbonyl iodonium ylides undergo intramolecular cyclopropanations.^{14,16} The thermal reactions of iodonium ylides were found to be catalyzed by copper



complexes¹⁵ as well as rhodium catalysts, ¹⁶ but the structure of the final isolated products depends mainly on the nature of the carbanionic substituents, even if, in most of the reactions, a carbene (or carbenoid) was thought to be the reactive intermediate.

In connection with our interest in extending the synthetic potential of the iodonium ylides, we have recently expanded our focus¹⁷ to include the synthetic chemistry of iodonium ylides bearing a mixed substituted carbanionic center, such as the 2,3-dihydro-3-oxo-benzo[b]thiolenide 1,1-dioxide moiety. We thought that such a structure could overcome the leaving ability of the sulfonyl substituent and the elimination of sulfur dioxide, observed for ylide 2. We decided to explore the potential of copper- catalyzed thermal reactions of ylide 4 in heterocyclic synthesis.

RESULTS AND DISCUSSION

2,3-Dihydro-3-oxo-2-phenyliodonium benzo[b]thiolenide 1,1-dioxide (4) was obtained as a yellowish powder in 93% yield from the reaction of 3-oxo-benzo[b]thiophene-1,1-dioxide (3)¹⁸ in aqueous NaHCO3 with an ethanolicphenyl iodosyl bis(trifluoroacetate) according to a modified procedure previously described¹⁹ (Scheme 1). This mixture of PhI(OCOCF3)₂/NaHCO₃/EtOH was necessary to overcome the extensive



Scheme 1.

decomposition of β -ketosulfone 3 by strong bases such as KOH. The ethanolic solution of phenyliodosyl bis(trifluoroacetate) should be immediately used, otherwise the well-known oxidation of ethanol to acetaldehyde occurs. The rate of the addition of this solution should be adjusted, so that the temperature in the reaction vessel does not exceed 5 °C. Probably other solvents readily miscible with water, such as acetonitrile, dimethylformamide could beused, but with yields of over 90% we did not pursue this possibility.

Iodonium ylide 4 is practically insoluble in all common organic solvents, but its reactions could be examined in suspension. Surprisingly, ylide 4 is readily soluble in a mixture of CH₂Cl₂ and EtOH (ratio 1:1) at



Scheme 2.

room temperature, but on evaporation trimer 5 was quantitatively isolated (Scheme 2). The role of ethanol in this experiment is crucial since it clearly demonstrates that the trimer 5 is not formed via alkene 6, a possible reaction intermediate which should be an extremely efficient electron acceptor (i.e. oxidizing agent). If alkene 6 was formed, it should react²⁰ with ethanol (present in large excess) rather than ylide 4. In contrast, the β -ketosulfone 3 was quantitatively isolated when a suspension of iodonium ylide 4 in absolute EtOH was heated to reflux.

The absolute structure of trimer 5 was not rigorously proven. The elemental analysis clearly demonstrates a product with a $(C_8H_4O_3S)_n$ formula. Moreover, the mass spectra (CI) presents a molecular ion fragment at m/ z 540 (3%), suggesting that the product should have a trimeric formula. The proposed structure of compound 5 was based on the two distinct carbonyl absorptions in the IR spectra [1740 and 1715 cm⁻¹] and the two ¹³C NMR carbonyl resonances at 182.9 and 185.2 ppm, while the ¹³C NMR resonance at 166.6 ppm suggested the presence of an enol ether function.

When a suspension of ylide 4 and various heteroatom nucleophiles in chloroform, containing catalytic amounts of Cu(acac)₂, was allowed to reflux, the new ylides 7 were isolated with good yields (Scheme 3). As always³ this typical transplidation process constitutes a high-yield procedure for the preparation of ylides with various heteroatoms, i.e. S, P, As etc.



Scheme 3.

When ylide 4 was allowed to reflux with a large excess of carbon disulfide in the presence of catalytic amounts of Cu(acac)₂, thione 10 was obtained in 38% yield (Scheme 4). The reaction probably proceeds either



Scheme 4.

through the initially formed thiocarbonyl ylide 8, by a transylidation pathway, or the thiolactam 9, by a

cycloaddition pathway. We are unable to differentiate these two reaction mechanisms, since it is well-known that a thermal equilibrium could be established between a thiolactam and a thirane via a thiocarbonyl ylide.²¹

Similarly, when ylide 4 was heated at 100-120 °C with 3 equiv. of thiobenzophenones 11a,b in the presence of catalytic amounts of Cu(acac)₂, alkenes 14a,b were obtained in moderate yields (Scheme 5). We postulated that alkenes 14 were formed via sulfur extrusion from the intermediate thiiranes 13, which presumably were too



Scheme 5.

unstable to be isolated, despite the fact that such thiiranes had been isolated from the thermal Cu-catalyzed reactions of iodonium ylides of β -diketones²² and β -disulfones.⁹ Again, it is not clear whether thiiranes 13 were formed by a stepwise reaction involving formation of the related thiocarbonyl ylide 12 and cyclization or by the direct cycloaddition of a carbene (or carbenoid) to the thiocarbonyl moiety. The elemental analyses of alkenes 12 are consistent with the assigned formulae and the mass spectra show molecular ion fragments. The IR spectra shows a carbonyl absorption at 1695 cm⁻¹, and the ¹³C NMR spectra [178.7 ppm for 14a, 179.8 ppm for 14b] suggested the presence of an α , β -unsaturated ketone function.

Furthermore, when 4 was heated at 80-100 °C with the alkene 15 in the presence of catalytic amounts of Cu(acac)₂, cyclopropanes 16 were isolated in moderate yields (Scheme 6). In contrast to the previously described



Scheme 6.

Alkene	Reaction Conditions Time (min) Temperature (°C)		Product [Yield(%)]
\bigcirc	10	80	16a (46)
\bigcirc	10	80	16b ^a (63)
	20	80	16c ^b (39)
\bigcirc	10	80	16d (65)
	5	80	16e (54)
Ср-сн=сі	H ₂ 15	100	1 6f (80)
С-сн=сн	H₂ 15	100	16g (45)
снзо	H ₂ 10	100	1 6h (69)

unstable thiiranes 13 these cyclopropanes are stable enough to be fully characterized. **Table 1.** Cyclopropanes 16 from the Reaction of Iodonium Ylide 4 with Alkenes 15.

^a exo:endo = 1.4:1. ^b exo:endo = 1:1

The assignment of the absolute configuration of cyclopropanes 16 was not possible, except for cyclopropanes 16b, where the *exo*-16b and *endo*-16b isomers could be separated by column chromatography. Compounds 16 present correct elemental analyses and molecular ion fragments for 1:1 adducts of the 2,3-dihydro-3-oxobenzo[b]thiolenide 1,1-dioxide moiety and the corresponding alkenes. The elucidation of the structure of compounds 16 was based on the strong carbonyl absorption [1700- 1720 cm⁻¹] in the IR spectra, and the related carbonyl peaks [183.6- 192.2 ppm] in the ¹³C NMR spectra, a fact that reveals the formation of cyclopropane ring and not of the related dihydrofurans. The assignment of the structures *exo*-14b and *endo*-14b was based on the expected deshielding of the *endo*-methano bridge due to an electron withdrawal, induced by interaction of the unoccupied Walsh orbital at the bridge carbons with the occupied orbitals of the adjacent carbon atoms,²² as well as shielding²³ of the cyclopropane carbons of an *exo*-isomer towards the *endo*-isomer.

On the other hand, when ylide 4 was heated at 60 °C with phenylacetylene (17) in the presence of catalytic amounts of Cu(acac)₂, the furan derivative 18 was isolated in 34% yield (Scheme 6). Similar reaction products were observed from the reaction of phenylacetylene and various iodonium ylides of β -dicarbonyl

compounds.²⁴ The absence of a carbonyl absorption in the IR spectrum suggests that compound 18 should be a furan derivative. The single peak at δ 6.90 ppm in the ¹H NMR spectrum and the peak at 100.3 ppm in the ¹³C NMR spectrum of compound 18 suggests α -substitution.

All the above mentioned results could be easily explained by the assumption that the metal-thermal catalyzed reaction of iodonium ylide 4 yields initially the carbene (or carbenoid) 21 (Scheme 7), which reacts



Scheme 7.

further with various substrates. However, the recent discovery²⁵ that iodonium ylide 1 slowly catalyzed the isomerization of quadricyclane to norbornadiene, propably via an electron transfer reaction,²⁷ as well as the fact that both Cu^I and Cu^{II} salts could effectively catalyse these cycloadditions¹³, ²⁶ should make us careful concerning the postulation of the existence of carbene (or carbenoid) intermediates.

EXPERIMENTAL

Unless otherwise noted, all starting materials were prepared and purified according to published procedures. All solvents were dried according to established procedures by distillation from an appropriate drying agent under a nitrogen atmosphere. Reactions involving air or moisture sensitive reagents or intermediates were performed under an inert atmosphere of nitrogen. Melting points were determined on a Reichert Thermovar hot stage apparatus and are uncorrected. The IR spectra were recorded on a Perkin-Elmer 1420 instrument as KBr pellets. ¹H and ¹³C NMR spectra were run on a Bruker AM 400 (400 MHz respectively 100 MHz); chemical shifts refer to chloroform-d, or dimethylsulfoxide-d6. Mass spectra were obtained on a Varian MAT CH-7. Elemental analyses were kindly performed by the group of Prof. Dr. M. Regitz at Kaiserlautern.

2,3-Dihydro-3-oxo-2-phenyliodoniobenzo[b]thiolenide-1,1-dioxide (4) :

A freshly prepared solution of phenyl iodosyl bis(trifluoroacetate) (11.8 g, 27.44 mmol) in ethanol (40 mL) was slowly added to a cooled (0 °C), well-stirred suspension of the β -ketosulfone 3^{18} (5.00g, 27.47 mmol) in 10% aqueous NaHCO3 (100 mL). The reaction temperature was not allowed to exceed 5 °C during the addition and the stirring (0-5 °C) was continued for 1 h. Cold water (200 ml) was added, the precipitate was filtered out, washed with dry ether (3x100 ml), and dried over P2O5 in a desiccator at -10 °C until constant weight (~ 24-36 h) to yield ylide 4 (9.80 g, 93%) as a yellow solid: ¹⁸ m.p. 193-194 °C - IR (KBr) : v = 3100 cm⁻¹, 3080, 1610, 1600, 1580, 1550, 1475, 1445, 1340, 1300, 1280, 1260, 1150, 1125, 1055, 990, 750, 730, 670.- ¹H NMR (400 MHz, DMSO [D6]): δ = 7.41-7.45 (m, 2H), 7.50-7.51 (m, 1H), 7.67-7.73 (m, 3H), 7.82-7.84 (m, 1H), 7.93-7.95 (m, 2H).- ¹³C NMR (100 MHz, DMSO [d6]): δ = 67.3, 118.3, 119.7, 122.0, 130.7, 131.0, 132.7, 133.3, 143.2, 172.3 **Decomposition of Iodonium Ylide 4.**

A suspension of 4 (3.84 g, 10 mmol) in a mixture of abs. CH₂Cl₂ (100 mL) and abs. EtOH (100 mL) was stirred at r.t. (1-2 min), until dissolved. The solvent was evaporated under reduced pressure (ca. 20 °C at 15 Torr) and the reaction residue was triturated with abs. ether (200 ml). The precipitate was filtered off to yield 5 (3.80 g, ca. 100%) as colorless needles: m.p. 241-242 °C (acetone).- IR(KBr) : $v = 3100 \text{ cm}^{-1}$, 3030, 1740, 1715, 1640, 1590, 1575, 1455, 1390, 1340, 1330, 1285, 1230, 1170, 1130, 1070, 1050, 960, 910, 870, 770, 720, 710 .- ¹H NMR (400 MHz, CDCl₃) : $\delta = 7.83$ -7.90 (m, 3H), 8.07-8.09 (m, 1H), 8.15-8.18 (m, 2H), 8.27-8.32 (m, 3H), 8.35-8.42 (m, ...)

3H).- 13 C NMR (400 MHz, CDCl₃) : δ = 77.9, 99.5, 112.9, 120.6, 122. 8, 125.4, 126.3, 128.7, 129.2, 134.4, 134.6, 136.3, 136.4, 139.9, 140.3, 142.7, 143.4, 144.9, 166.6, 182.9, 185.2 - MS (CI) : m/z (%) = 540 (M⁺, 3), 355 (100), 344 (45), 328 (38), 295 (87), 208 (14), 152 (23).- Anal. Calcd for C₂₄H₁₂O9S₃ (540.5) : C 53.33; H 2.24.- Found C 53.10; H 2.08.

Reaction of Ylide 4 with Heteroatom Nucleophile. General Procedure:

A mixture of ylide 4 (3.84 g, 10 mmol), an excess of the heteroatom nucleophile, and Cu(acac)₂ (20 mg) was allowed to reflux for 20 min under N₂ atmosphere. The solvent was removed under reduced pressure (ca. 20 °C at 15 Torr) and the residue was triturated with abs. ether (100 ml). The precipitate was filtered off and recrystallization (from chlorobenzene) afforded pure ylide 7 as a colorless powder.

2,3-dihydro-3-oxo-2-pyridoniobenzo[b]thiolenide-1,1-dioxide (7a) (2.31g, 89%) was isolated as a colorless powder, m.p. 267-268 °C, by following the above mentioned procedure, in which a mixture of iodonium ylide **4** (3.84 g, 10 mmol), dry pyridine(25 mL), and Cu(acac)₂ (20 mg) was allowed to reflux for 20 min.- IR (KBr) v = 3130, 3080, 2940, 2870, 1610, 1575, 1480, 1465, 1370, 1355, 1270, 1140, 1120, 1060, 760, 745, 670 cm⁻¹.- ¹H NMR (400 MHz, [d₆]DMSO) : δ = 7.74-7.84 (m, 4H), 8.11-8.31 (m, 3H), 9.36-9.38 (m, 2H).- ¹³C NMR (100 MHz, [d₆]DMSO) : δ = 106.4, 119.3, 122.1, 128.2, 132.1, 132.6, 133.5, 137.7, 138.1, 139.7, 163.0.- Anal. Calcd for C₁₃H₉NO₃S (259.3): C, 60.22 ; H, 3.50 ; N, 5.40.- Found : C, 60.20 ; H, 3.60 ; N, 5.50

2,3-dihydro-3-oxo-2-triphenylphosphoniobenzo[b]thiolenide-1,1-dioxide (7b) (2.36 g, 82%) was isolated as a colorless powder, m.p. > 260 °C, by following the above mentioned procedure in which a mixture of iodonium ylide **4** (2.59 g, 6.51 mmol), triphenylphosphine (3.41 g, 13.02 mmol), and Cu(acac)₂ (20 mg) was allowed to reflux for 45 min.- IR (KBr) : $v = 3080, 1620, 1575, 1485, 1440, 1305, 1280, 1260, 1165, 1150, 1110, 1050, 1000, 750, 720, 690 cm⁻¹.- ¹H NMR (400 MHz, [d₆]DMSO) : <math>\delta = 7.60$ -7.80 (m, 19H).- Anal. Calcd for C₂₆H₁₉PO₃S (442.5) : C, 70.58 ; H, 4.33.-Found : C, 70.70 ; H, 4.39

2,3-dihydro-3-oxo-2-triphenlarsoniobenzo[b]thiolenide-1,1-dioxide (7c) (3.27 g, 86%) was isolated as a colorless powder, m.p > 260 °C, by following the above mentioned procedure, in which a mixture of iodonium ylide **4** (3.00 g, 7.81 mmol), triphenylarsine (5.00 g, 16.34 mmol), and Cu(acac)₂ (20 mg) was allowed to reflux for 20 min. IR (KBr) : $v = 3060, 1610, 1570, 1485, 1445, 1320, 1305, 1275, 1260, 1150, 1120, 1090, 1060, 1040, 1000, 800, 740 cm⁻¹.- ¹H NMR (400 MHz, [d₆]DMSO) : <math>\delta = 7.60-7.80$ (m, 19H).- ¹³C NMR (100 MHz, [d₆]DMSO) : $\delta = 76.1, 119.0, 121.5, 123.9, 130.2, 132.2, 132.5, 133.1, 133.2, 145.0, 175.8.- Anal. Calcd for C₂₆H₁₉AsO₃S (486.4) : C, 64.20 ; H, 3.94.- Found : C, 64.30 ; H, 4.03$ **Reaction of 4 with Carbon Disulfide.**

A mixture of ylide 4 (1.0 g, 2.60 mmol), carbon disulfide (150 mL) and Cu(acac)₂ (20 mg) was allowed to reflux for 1 h under N₂. The insoluble materials were filtered off and the filtrate was evaporated under reduced pressure (20 °C at 15 Torr). The residue was triturated with abs. ether (100 ml). The precipitate was filtereed off and recrystallization afforded compound **10** (0.25g, 38%) as white crystalls.- m.p. = 209-210 °C (CHCl₃ / petroleum ether).- IR (KBr) : v = 1555, 1325, 1205, 1190, 1170, 1160, 1135, 990, 760 cm⁻¹.- ¹H NMR (400 MHz, CDCl₃) : δ = 7.60-7.66 (m, 3H), 7.78-7.80 (m, 1H).- MS (70 eV) : m/z (%) = 256 (7, M⁺), 211 (4), 169 (18), 155 (59), 141 (100), 88 (15).- Anal. Calcd for C₉H₄O₃S₃ (256. 3): C, 42.17; H, 1.57.-Found : C, 42.40; H, 1.72. **Reaction of Ylide 4 with thiobenzophenones.**

A mixture of ylide 4 (0.70 g, 1.82 mmol), thiobenzophenone 11 (1.00 g, 3.88 mmol), and Cu(acac)₂ (20 mg) was heated at 100 $^{\circ}$ C for 5-10 min under N₂. The reaction mixture was purified by column chromatography on silica gel (CH₂Cl₂) to yield alkenes 14 as yellow crystals.

2,3-dihydro-3-oxo-2-[(p-methoxyphenyl)-(p'-methylphenyl)methyleno]-benzo[b]thiophene-1,1-dioxide (**14a**) (0.462g, 57%) was isolated as yellow crystals, m.p. 121-122 °C (EtOH), by following the above mentioned procedure, in which a mixture of iodonium ylide 4 (0.80g, 2.08 mmol), p-methoxy-p'-methylthiobenzophenone (1.50 g, 6.20 mmol), and Cu(acac)₂(20 mg) was heated at 120 °C for 10min.- IR (KBr) : v = 1695, 1610, 1510, 1460, 1315, 1300, 1265, 1225, 1190, 1170, 1160, 1120, 1050, 1030, 970, 840, 820, 750, 700 cm⁻¹.- ¹H NMR (400 MHz, CDCl₃) : $\delta = 2.42$ -2.43 (m, 3H), 3.85-3.87 (m, 3H), 6.89-7.98 (m, 12H).- ¹³C NMR (100 MHz, CDCl₃) : $\delta = 20.7$, 54.4, 112.5, 112.8, 119.9, 123.4, 127.9, 129.2, 130.3, 132.0, 132.6, 134.0, 134.6, 135.0, 140.4, 141.5, 142.4, 162.0, 163.8, 178.7.- MS (70 eV) : m/z (%) = 390 (100, M⁺), 375 (39), 359 (10), 311 (10), 295 (5), 252 (6), 240 (11), 222 (11), 105 (13), 77 (15).- Anal. Calcd. for C₂₃H₁₈O₄S (390.5) : C, 70.75; H, 4.65.- Found : C, 70.80; H, 4.76.

2,3-dihydro-3-oxo-2-[bis(p-methoxyphenyl)methyleno]-benzo[b]thiophene-1,1-dioxide(14b) (0.399g, 54%) was isolated as yellow crystals, m.p. 134-135 °C (CHCl₃ / petroleum ether), by following the above mentioned procedure, in which a mixture of iodonium ylide 4 (0.70 g, 1.82 mmol), p.p'-dimethoxythiobenzophenone (1.00g, 3.88 mmol), and Cu(acac)₂ (20 mg) was heated at 100 °C for 5 min.- IR (KBr) : v = 3080, 2970, 2930, 1695, 1610, 1580, 1510, 1470, 1320, 1290, 1270, 1230, 1180, 1125, 1070, 1050, 1030, 970, 840, 755 cm⁻¹.- ¹H NMR (400 MHz, CDCl₃) : δ = 3.86 (s, 3H), 3.87 (s, 3H), 6.90 (d, J= 8.8 Hz, 2H), 6.98 (d, J= 8.8 Hz, 2H), 7.17 (d, J= 8.8 Hz, 2H), 7.55 (d, J= 8.8 Hz, 2H), 7.74-7.76 (m, 1H), 7.83-7.84 (m, 1H), 7.91-7.93 (m, 1H), 7.96-7.98 (m, 1H).- ¹³C NMR (100 MHz, CDCl₃) : δ = 55.5, 113. 7, 113.8, 120.9, 124.4, 129.9, 130.3, 130.4, 133.1, 133.6, 133.8, 135.9, 143.4, 162.5, 164.9, 179.8.- MS (70 eV) : m/z (%) = 406 (100, M⁺), 375 (10), 341 (8), 327 (9), 299 (5), 238 (12), 223 (17), 135 (12), 119 (21), 76 (12).- Anal. Calcd. for C₂₃H₁₈O₃S (406.45) : C, 67.97; H, 4.46.- Found : C, 67.90; H, 4.46.

Reaction of 4 with alkenes. General Procedure.-

A mixture of iodonium ylide 4 (1.95-2.08 mmol), an excess of alkene 15, and $Cu(acac)_2$ (20 mg) was heated at 80-100 °C for 10-20 min under N₂. The reaction mixture was column chromatographed on silica gel (CH₂Cl₂ /petroleum ether) to afford cyclopropane 16.

Cyclopropane 16a (0.251 g, 46% yield) was obtained as colorless crystals, m.p. 143-144 $^{\text{O}}$ C (CHCl₃/n-hexane), by following the above procedure, in which a total of iodonium ylide 4 (0.80 g, 2.08 mmol), cyclohexene (20 mL), and Cu(acac)₂ (20 mg) was heated at 80 $^{\text{O}}$ C for 10 min. IR (KBr) : v = 3100, 3000, 2970, 2880, 1710, 1585, 1455, 1390, 1295, 1210, 1190, 1165, 1150, 1120, 1065, 1055, 1025, 1010, 900, 830, 765, 735, 690 cm⁻¹.- ¹H NMR (400 MHz, CDCl₃) : δ = 1.39 -1.43 (m, 2H), 1.74 -1.86 (m, 4H), 1.99 - 2.05 (m, 2H), 2.65 -2.71 (m, 2H), 7.77 - 7.81 (m, 1H), 7.86 - 7.91 (m, 1H), 7.99 - 8.01 (m, 2H).- ¹³C NMR (100 MHz, CDCl₃) : δ = 17.6, 20.5, 32.0, 53.6, 121.3, 123.5, 133.7, 134.0, 135.6, 144.3, 188.4.- MS (70 eV) : m/z (%) = 262 (53, M⁺), 208 (55), 197 (100), 183 (61), 170 (87), 153 (55), 77 (95).-Anal. Calcd for C₁₄H₁₄O₃S (262.3) : C, 64.10; H, 5.38.- Found : C, 63.80; H, 5.32

Cyclopropane 16b (0.359 g, 63% yield; exo: endo = 1.4 : 1) was obtained, by following the above procedure, in which a mixture of iodonium ylide (0.80g, 2.08 mmol) **4**, norbornylene (1.50 g, 15.95 mmol), and Cu(acac)₂ (20 mg) was heated at 80 °C for 10 min.

exo-Cyclopropane **16b** (0.211 g, 37% yield) was obtained as colorless crystals, m.p. 111-112 °C (CHCl₃ / n-hexane).- IR (KBr) : v = 3070, 3000, 2970, 2940, 1700, 1580, 1480, 1460, 1450, 1350, 1310, 1250, 1200, 1170, 1160, 1120, 1035, 1025, 990, 970, 950, 90, 820, 780, 750, 690 cm⁻¹.- ¹H NMR (400 MHz, CDCl₃) : $\delta = 0.86 - 0.93$ (m, 1H), 1.30 - 1.44 (m, 2H), 1.60 - 1.70 (m, 2H), 2.49 (s, 2H), 2.70 - 2.81 (m, 1H), 2.92 (s, 2H), 7.73 - 7.80

(m, 1H), 7.84 - 7.88 (m, 1H), 7.95 - 8.10 (m, 2H).- 13 C NMR (100 MHz, CDCl₃) : δ = 27.4, 30.0, 36.8, 39.5, 51.8, 120.0, 123.2, 132.8, 133.4, 134.5, 142.1, 189.5.- Anal. Calcd for C₁₅H₁₄O₃S (274.3) : Calcd. C, 65.67; H, 5.14.- Found : C, 65.60; H, 5.21

endo-Cyclopropane **16b** (0.148 g, 26% yield) was obtained as colorless crystals, m.p. 205 -206 °C (CHCl₃ / n-hexane).- IR (KBr) : v = 3030, 2990, 2970, 2900, 1720, 1590, 1460, 1340, 1315, 1295, 1250, 1220, 1180, 1160, 1135, 1085, 1070, 1020, 1005, 975, 880, 810, 780, 750, 690, 640 cm⁻¹. ⁻¹H NMR (400 MHz, CDCl₃) : $\delta = 1.23$ (d, J = 12.6 Hz, 1H), 1.42 - 1.49 (m, 2H), 1.71 (d, J = 7.6 Hz, 2H), 1.87 (d, J = 12.6 Hz, 1H), 2.14 (s, 2H), 2.94 (s, 2H), 7.74 - 7.78 (m, 1H), 7.88 - 8.01 (m, 3H).- ¹³C NMR (100 MHz, CDCl₃) : $\delta = 28.0$, 32.4, 37.0, 42.6, 53.2, 121.3, 123.8, 131.2, 133.5, 136.2, 147.2, 189.5.- MS (70 eV) : m/z (%) = 274 (56, M⁺), 246 (37), 210 (36), 196 (68), 182 (87), 169 (59), 153 (100), 77 (80).- Anal. Calcd for C₁₅H₁₄O₃S (274.3) : C, 65.67; H, 5.14.- Found : C, 65.60; H, 5.21

Cyclopropane 16c (0.221 g, 39% yield) was obtained as colorless crystals, m.p. 162-163 °C (CHCl₃/ n-hexane), by following the above mentioned procedure, in which a mixture of iodonium ylide 4 (0.80 g, 2.08 mmol), norbornadiene (2.0 mL), and Cu(acac)₂(20 mg) was heated at 80 °C for 20 min.- IR (KBr) : v = 2940, 1710, 1580, 1450, 1305, 1275, 1220, 1150, 1060, 910, 870, 710 cm⁻¹.- ¹H NMR (400 MHz, CDCl₃) : $\delta = 1.58 - 1.66$ (m, 1H), 1.99 (d, J=11.4 Hz, 1H), 2.21 (m, 1H), 2.40 (s, 2H), 2.83 (d, J=10.3 Hz, 1H), 2.94 - 2.97 (m, 1H), 3.33 - 3.36 (m, 1H), 3.52 (d, J=1.9 Hz, 1H), 5.17 - 5.19 (m, 1H0, 6.27 - 6.29 (m, 1H), 6.64-6.75 (m, 2H), 7.78-7.83 (m, 1H), 7.92-8.01 (m, 3H).- ¹³C NMR (100 MHz, CDCl₃) : $\delta = 38.9$, 42.1, 42.9, 43.9, 45.5, 48.3, 69.2, 71.1, 118.4, 121.4, 122.0, 124.2, 125.2, 139.5, 131.2, 131.6, 133.8, 134.2, 136.5, 136.9, 142.1, 142.5, 145.1, 145.3, 146.6, 187.5, 192.2.- MS (70 eV) : m/z (%) = 272 (42, M⁺), 255 (5), 226 (9), 207 (32), 179 (44), 165 (37), 153 (44), 152 (100), 120 (24), 104 (28), 92 (29), 77 (59) .-Anal. Calcd for C₁₅H₁₂O₃S (272.2) : C, 66.16; H, 4.44.- Found : C, 66.10; H, 4.42

Cyclopropane 16d (0.400 g, 65% yield) was obtained as colorless crystals, m.p. 206 -207 °C (CHCl₃/n-hexane), by following the above mentioned procedure, in which a total of iodonium ylide **4** (0.80 g, 2.08 mmol), indene (2.0 g, 17. 24 mmol), and Cu(acac)₂ (20 mg) was heated at 80 °C for 10 min.- IR (KBr) : v = 3080, 2920, 1705, 1585, 1480, 1460, 1420, 1350, 1325, 1300, 1250, 1215, 1200, 1175, 1150, 1125, 1060, 1020, 990, 820, 755, 720, 695, 660 cm⁻¹.- ¹H NMR (400 MHz, CDCl₃) : δ = 3.43 - 3.49 (m, 1H), 3.53 (d, J = 3.4 Hz, 2H), 4.15 (d, J = 6.7 Hz, 1H), 7.21 - 7.34 (m, 4H), 7.67 - 7.73 (m, 1H), 7.76 - 7.78 (m, 1H), 7.84 - 7.88 (m, 1H), 8.00 - 8.02 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) : δ = 33.2, 35.9, 46.0, 51.1, 121.4, 123.6, 123.7, 125.4, 126.6, 128.3, 133.8, 134.9, 135.7, 144.2, 146.3, 185.8.- MS (70 eV) : m/z (%) = 296 (25, M⁺), 232 (86), 231 (100), 204 (31), 203 (67), 202 (70), 128 (56), 127 (46), 115 (49), 77 (37), 76 (47).- Anal. Calcd for C₁₇H₁₂O₃S (296.3) : C, 68.90; H, 4.08.-Found : C, 68.30; H, 4.17.

Cyclopropane 16e (0.373 g, 54% yield) was obtained as colorless crystals, m.p. 204 -205 °C (CHCl₃/n-hexane), by following the above mentioned procedure, in which a total of iodonium ylide 4 (0.80 g, 2.08 mmol), accnaphtylene (1.0 g, 5.62 mmol), and Cu(acac)₂ (20 mg)was heated at 80 °C for 5 min.- IR (KBr) : v = 1710, 1580, 1310, 1290, 1245, 1195, 1170, 1160, 1125, 1060, 970, 820, 780, 750 cm⁻¹.- ¹H NMR (400 MHz, CDCl₃) : $\delta = 4.54$ (s, 2H), 7.49 - 7.53 (m, 4H), 7.54 - 7.64 (m, 2H), 7.79 - 7.82 (m, 3H), 7.99 - 8.01 (m, 1H).- ¹³C NMR (100 MHz, CDCl₃) : $\delta = 41.3$, 56.0, 121.3, 123.6, 123.7, 125.8, 127.8, 130.1, 133.5, 133.9, 135.2, 135.8, 140.1, 143.8, 183.6.- MS (70 eV) : m/z (%) = 332 (14, M⁺), 300 (17), 270 (24), 268 (60), 267 (43), 240 (26), 239 (100), 237 (24), 164 (35), 163 (37), 85 (28), 83 (46) .- Anal. Calcd for C₂₀H₁₂O₃S (332.38) : C, 72.29; H, 3.73.-Found : C, 71.90; H, 3.76

Cyclopropane 16f (0.443 g, 80% yield) was obtained as colorless crystals, m.p. 138 -139 °C (CHCl₃/ n-hexane), by following the above mentioned procedure, in which a mixture of iodonium ylide 4 (0.75g, 1.95 mmol), styrene(1.5 g, 14.42 mmol), and Cu(acac)₂ (20 mg) was heated at 100 °C for 15 min.- IR (KBr) : $v = 3100, 3070, 3050, 1710, 1570, 1500, 1460, 1310, 1220, 1180, 1150, 1130, 1030, 1020, 1010, 1000, 950, 840, 785, 770, 760, 740, 690 cm⁻¹.- ¹H NMR (400 MHz, CDCl₃) : <math>\delta = 2.16 - 2.51$ (m, 1H), 2.57 - 2.73 (m, 1H), 3.64 - 3.78 (m, 1H), 7.25 - 7.32 (m, 5H), 7.72 - 7.76 (m, 1H), 7.84 - 7.85 (m, 2H), 8.05 - 8.07 (m, 1H) .- ¹³C NMR (100 MHz, CDCl₃) : $\delta = 21.2, 38.9, 52.5, 121.6, 124.0, 128.2, 128.3, 129.2, 133.8, 136.0, 185.9.$ - MS (70 eV) : m/z (%) = 284 (67, M⁺), 219 (54), 191 (100), 189 (52), 136 (77), 116 (75), 115 (73), 76 (56).- Anal. Calcd for C₁₆H₁₂O₃S (284.3) : C, 67.59; H, 4.25.- Found : C, 67.10; H, 4.36.

Cyclopropane 16g (0.298 g, 45% yield) was obtained as colorless crystals, m.p. 206 -207 °C (CHCl₃/n-hexane), by following the above mentioned procedure, in which a mixture of iodonium ylide of 4 (0.80 g, 2.08 mmol), ochlorostyrene(1.5 g, 10.83 mmol), and Cu(acac)₂ (20 mg)was heated at 100 °C for 15 min.- IR (KBr) : v = 3030, 1715, 1590, 1480, 1440, 1375, 1310, 1215, 1180, 1145, 1135, 1060, 1030, 1010, 860, 790, 780, 755 cm⁻¹.- ¹H NMR (400 MHz, CDCl₃) : $\delta = 2.24 - 2.69$ (m, 2H), 3.61 - 3.74 (m, 1H), 7.26 - 7.32 (m, 4H), 7.76 - 7.78 (m, 1H), 7.86 - 7.93 (m, 2H), 8.06 - 8.08 (m, 1H).- ¹³C NMR (100 MHz, CDCl₃) : $\delta = 20.6$, 36.5, 51.4, 121.5, 123.8, 126.7, 129.2, 130.9, 132.9, 133.7, 135.6, 136.0, 145.7, 185.7.- Anal. Calcd for C₁₆H₁₁O₃S (318.8) : C, 60.29; H, 3.48.- Found : C, 60.80; H, 3.67

Cyclopropane 16h (0.451, 69% yield) was obtained as colorless crystals, m.p. 154 -155 $^{\circ}$ C (CHCl₃/n-hexane), by following the above mentioned procedure, in which a mixture of iodonium ylide 4 (0.80 g, 2.08 mmol), m-methoxystyrene (1.5 g, 11.19 mmol), Cu(acac)₂ (20 mg)was heated at 100 $^{\circ}$ C for 10 min.- IR (KBr) : v = 2920, 2840, 1720, 1610, 1590, 1510, 1450, 1360, 1305, 1250, 1220, 1170, 1140, 1120, 1080, 1060, 1030, 990, 840, 770, 740, 690 cm⁻¹.- ¹H NMR (400 MHz, CDCl₃) : δ = 2.12 - 2.68 (m, 2H), 3.63 - 3.80 (m, 4H), 6.62 - 6.90 (m, 2H), 7.21 - 7.30 (m, 2H), 7.71 - 7.75 (m, 1H), 7.84 - 7.90 (m, 2H), 8.03 - 8.06 (m, 1H).- ¹³C NMR (100 MHz, CDCl₃) : δ = 21.2, 38.8, 52.6, 55.1, 113.6, 113.9, 121.5, 123.4, 123.7, 129.8, 130.3, 133.7, 135.9, 145.7, 159.4, 185.9.- Anal. Calcd for C₁₇H₁₄O₃S (314.4) : C, 64.95; H, 4.49.- Found : C, 64.40; H, 4.60

Reaction of 4 with Phenyacetylene.

A solution of ylide 4 (0.80 g, 2.08 mmol), phenylacetylene (17) (1.50g, 14.71 mmol), and Cu(acac)₂ (20 mg) in chloroform (20 mL) was allowed to reflux for 10 min under N₂. The solvent was evaporated under reduced pressure (ca. 20 °C at 15 Torr) and the reaction residue was purified by column chromatography on silica gel (CHCl₃ / petroleum ether) to yield furan 18 (0.199 mg, 34% yield) as colorless crystals, m.p. = 215 - 216 °C (CHCl₃ / hexane).- IR (KBr) : $v = 1610, 1520, 1470, 1440, 1395, 1305, 1160, 1120, 1045, 910, 790, 765, 735, 680 cm⁻¹.- ¹H NMR (400 MHz, CDCl₃) : <math>\delta = 6.90$ (s, 1H), 7.26 - 7.46 (m, 5H), 7.55 - 7.56 (m, 2H), 7.69 - 7.73 (m, 3H).- ¹³C NMR (100 MHz, CDCl₃) : $\delta = 100.3, 118.9, 122.2, 124.3, 125.1, 126.4, 129.0, 129.3, 129.5, 133.2, 144.5, 155.6, 160.3.- MS (70 eV) : m/z (%) = 282 (100, M⁺), 189 (34), 105 (17), 85 (23), 83 (35), 77 (11).-Anal. Calcd for C₁₆H₁₀O₃S (282.3) : C, 68.07; H, 3.57.- Found : C, 67.80; H, 3.64.$

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REFERENCES

- Trost, B.M.; Melvin, L.S. Sulfur Ylides Emerging Synthetic Intermediates; Academic Press: New York 1975.
- Ye, T.; McKervey, M.A. Chem. Rev. 1994, 94, 1091.
 Padwa, A.; Krumpe, K.E. Tetrahedron 1992, 48, 5385.
 Padwa, A.; Hornbuckle, S. F. Chem. Rev. 1991, 91, 263.
 Adams, J.; Spero, D.M. Tetrahedron 1991, 47, 1765.
 Padwa, A. Acc. Chem. Res. 1991, 24, 22.
- Koser, G.F. in *The Chemistry of Functional Groups*; Patai, S. (ed.); Wiley: New York 1983, Supplement D, Chapter 18, pp. 771-811. Moriarty, R.M.; Vaid, R.K. Synthesis 1990, 431. Varvoglis, A. *The Organic Chemistry of the Polycoordinated Iodine*; VCH: New York 1992.
- 4. Schank, K.; Lick, C. Synthesis 1983, 392.
- There are a few examples of iodonium ylides with different carbanionic substitutts which have postulated as reactive intermediates or were isolated but were too labile to be purified, c.f. Abramovitch, R.A.; Grins, G.; Rogers, R.B.; Shinkai, I. J. Am. Chem. Soc. 1976,98, 5671. Kang, J.; Lee, J.H.; Noh, S.B.; Oh, C.S; Kim, H.Y.; Chung, B.Y. Synlett 1990, 153.
- 6. Hayasi, H.; Okada, T.; Kawanisi, M. Bull. Chem. Soc. Jpn 1970, 43, 2506.
- Koser, G.F.; Yu, S.-M. J. Org. Chem. 1975, 40, 1166.
 Koser, G.F.; Yu, S.-M. J. Org. Chem. 1976, 41, 125.
 Koser, G.F.; (Yu)Linden, S.-M.; Shih, Y.-J. J. Org. Chem. 1978, 43, 2676.
- 8. Hadjiarapoglou, L.P. Tetrahedron Lett. 1987, 28, 4449.
- 9. Hadjiarapoglou, L.P. Ph.D Thesis, Aristotelian University, Thessaloniki 1987.
- 10. Hadjiarapoglou, L.; Spyroudis, S.; Varvoglis, A. J. Am. Chem. Soc. 1985, 107, 7178.
- Hadjiarapoglou, L.; Varvoglis, A. J. Chem. Soc. Perkin Trans. 1 1989, 379.
 Saito, T.; Kikuchi, H.; Kondo, A. Synthesis 1995, 87.
 Saito, T.; Ayukawa, H.; Sumizawa, N.; Shizuta, T.; Motoki, S.; Kobayashi, K. J. Chem. Soc. Perkin Transactions 1 1991, 1405.
- Hadjiarapoglou, L.; Varvoglis, A.; Alcock, N.W.; Pike, G.A. J. Chem. Soc. Perkin Transactions I 1988, 2839.
- 13. Hadjiarapoglou, L.; Varvoglis, A, J. Heterocyclic Chem. 1988, 25, 1599.
- Moriarty, R.M.; Prakash, O.; Raid, R.K.; Zhao, L. J. Am. Chem. Soc. 1989, 111, 6443.
 Gallos, J.K.; Koftis, T.V.; Koumbis, A.E. J. Chem. Soc. Perkin Transactions I 1994, 611.
- 15. Hood, J.N.C.; Lloyd, D.; MacDonald, W.A.; Shepherd, T.M. Tetrahedron 1982, 38, 3355.
- 16. Müller, P.; Fernandez, D. Helv. Chim. Acta 1995, 78, 947.
- 17. Hadjiarapoglou, L.; Schank, K. Tetrahedron Lett. 1989, 30, 6673.
- 18. Schank, K. in Houben-Weyl, 4th Ed., Vol. E11; Klammann, D. ed.; Thieme : Stuttgart 1985; p. 1137.
- 19. Lick, C. Ph.D Dissertation, Saarlandes Universität, Saabrücken 1983.
- Martin, E. J. Am. Chem. Soc. 1981, 103, 2757.
 Schank, K.; Fünfrocken, M. Chem. Ber. 1992, 125, 675.
- 21. Oka, K.; Dodachi, A.; Hara, S. J. Am. Chem. Soc. 1981, 103, 2757.

- Christl, M. Chem. Ber. 1975, 108, 2781.
 Christl, M.; Herbert, R. Chem. Ber. 1979, 112, 2022.
- 23. Breitmaier, E.; Voelter, W. Carbon-13 NMR Spectroscopy; VCH : Weinheim 1987; pp. 189.
- Kalogiannis, S.; Spyroudis, S. J. Org. Chem. 1990, 55, 5041.
 Hatzigrigoriou, E.; Spyroudis, S.; Varvoglis, A. Liebigs Ann. Chem. 1989, 167.
 Spyroudis, S.; Tarantili, P. J. Org. Chem. 1993, 58, 4885.
 Spyroudis, S.; Tarantili, P. Tetrahedron 1994, 50, 11541.
- 25. Hadjiarapoglou, L.P. unpublished results.
- 26. In general, the intramolecular cycloaddition proceeds even without any added catalyst, i.e. Cu salt, but the catalyst effects in a much more cleaner reaction with a better yield of the desired product.
- 27. McDonald, R.N. Tetrahedron 1989, 45, 3393.

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