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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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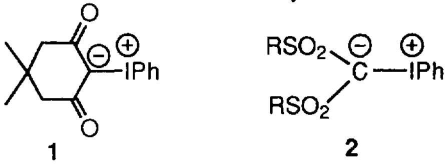
Abstract: Iodonium ylide **4** was prepared in 93% yield from the reaction of β-ketosulfone **3** with phenyl iodosyl bis(trifluoroacetate). Although insoluble in most solvents, ylide **4** was readily soluble in a mixture of CH_2Cl_2 / ethanol (1:1), yielding trimer **5** quantitatively. Upon reaction with various heteroatom nucleophiles the new ylides **7** were isolated, while reaction with CS_2 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 accessible[4] 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 precursors[6] of carbenes (or carbenoids), most early research efforts were directed[7] towards their reactions with several electrophiles at room temperature. Recently, it was shown that 1-phenyliodonium-4,4-dimethyl-2,6-dioxocyclohexylide[8] (**1**) and phenyliodonium bis(phenylsulfonyl)methylide[9] (**2**) undergo a number of thermal (metal-catalyzed) or photochemical intermolecular cycloadditions, such as the reaction with CS_2,[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



1 **2**

Figure 1.

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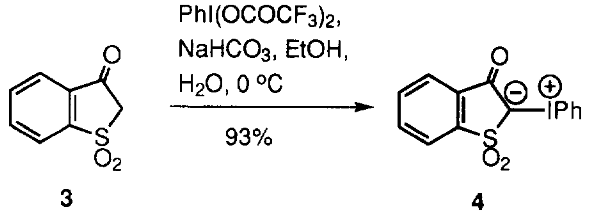
complexes[15] as well as rhodium catalysts,[16] but the structure of the final isolated products depends mainly on the nature of the carbanionic substituents, even if, in most of the reactions, a carbene (or carbenoid) was thought to be the reactive intermediate.

In connection with our interest in extending the synthetic potential of the iodonium ylides, we have recently expanded our focus[17] 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.

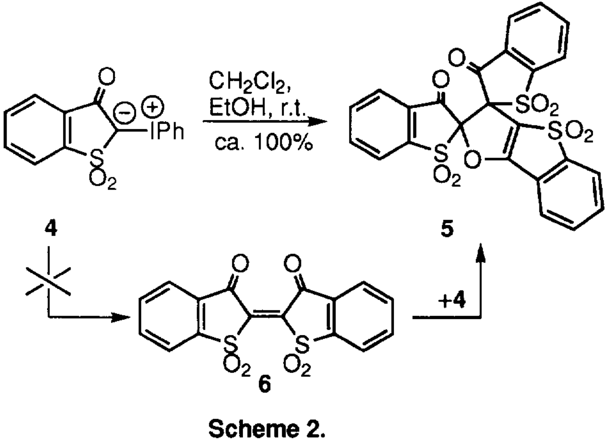
RESULTS AND DISCUSSION

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 $NaHCO_3$ with an ethanolicphenyl iodosyl bis(trifluoroacetate) according to a modified procedure previously described[19] (Scheme 1). This mixture of $PhI(OCOCF_3)_2$/ $NaHCO_3$/ EtOH was necessary to overcome the extensive 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 be used, but with yields of over 90% we did not pursue this possibility.



Scheme 1.

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 CH_2Cl_2 and EtOH (ratio 1:1) at

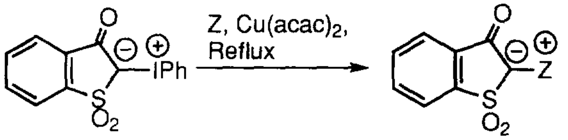


Scheme 2.

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 react[20] 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 ^{13}C NMR carbonyl resonances at 182.9 and 185.2 ppm, while the ^{13}C NMR resonance at 166.6 ppm suggested the presence of an enol ether funtion.

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 always[3] this typical transylidation process constitutes a high-yield procedure for the preparation of ylides with various heteroatoms, i.e. S, P, As etc.

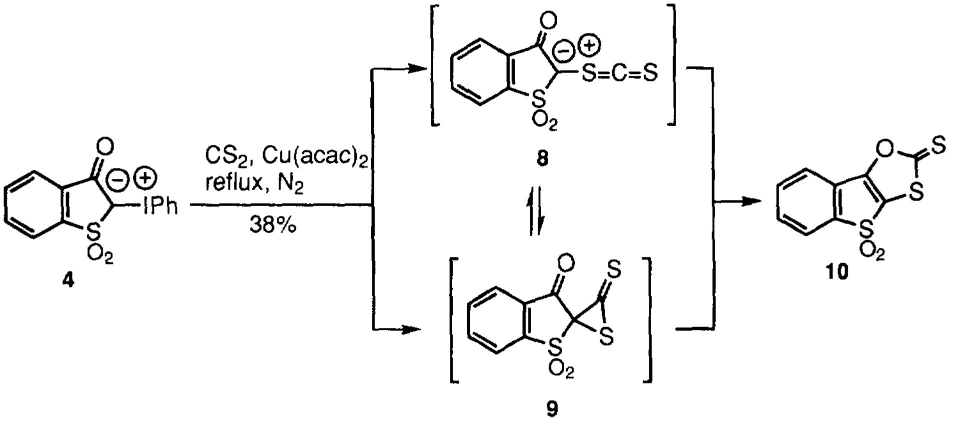


4 **7**

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

Scheme 3.

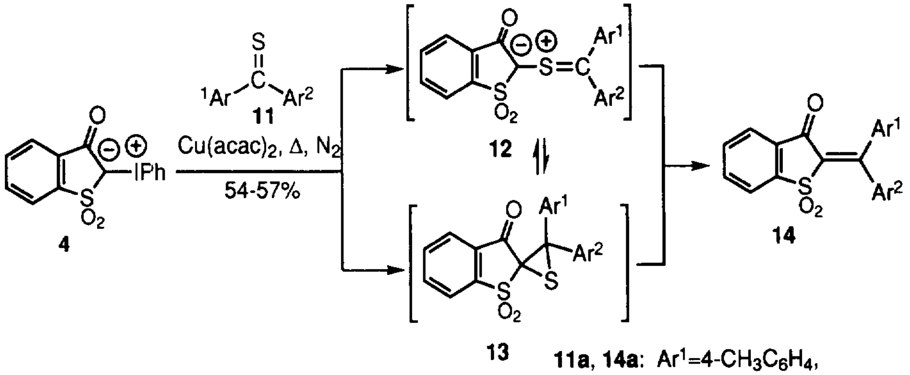
When ylide **4** was allowed to reflux with a large excess of carbon disulfide in the presence of catalytic amounts of Cu(acac)$_2$, thione **10** was obtained in 38% yield (Scheme 4). The reaction probably proceeds either



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

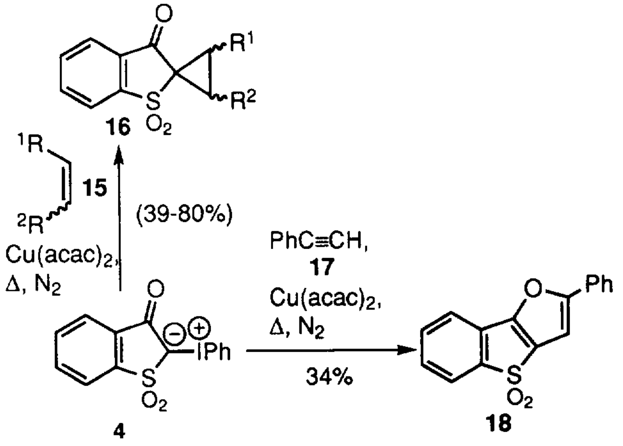


11a, 14a: Ar^1=4-$CH_3C_6H_4$, Ar^2=4-$CH_3OC_6H_4$ (57%)
11b, 14b: Ar^1=Ar^2=4-$CH_3OC_6H_4$(54%)

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-diketones[22] 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 ^{13}C NMR spectra [178.7 ppm for **14a**, 179.8 ppm for **14b**] suggested the presence of an α,β-unsaturated ketone function.

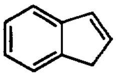
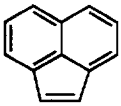
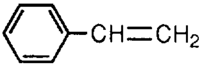
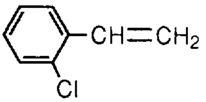
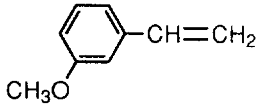
Furthermore, when **4** was heated at 80-100 °C with the alkene **15** in the presence of catalytic amounts of Cu(acac)$_2$, cyclopropanes **16** were isolated in moderate yields (Scheme 6). In contrast to the previously described



Scheme 6.

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**.

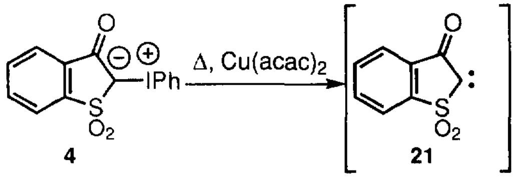
Alkene	Reaction Conditions		Product [Yield(%)]
	Time (min)	Temperature (°C)	
	10	80	**16a** (46)
	10	80	**16b**^{a} (63)
	20	80	**16c**^{b} (39)
	10	80	**16d** (65)
	5	80	**16e** (54)
	15	100	**16f** (80)
	15	100	**16g** (45)
	10	100	**16h** (69)

^{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-oxo-benzo[*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 ^{13}C 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 shielding[23] 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 ^{13}C 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 discovery[25] 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 cycloadditions[13, 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 ^{13}C NMR spectra were run on a Bruker AM 400 (400 MHz respectively 100 MHz); chemical shifts refer to chloroform-d, or dimethylsulfoxide-d_6. 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 $NaHCO_3$ (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 P_2O_5 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) : ν = 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).- ^{13}C NMR (100 MHz, DMSO [d_6]): 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. CH_2Cl_2 (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) : ν = 3100 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, $CDCl_3$) : δ = 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, $CDCl_3$) : 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 $C_{24}H_{12}O_9S_3$ (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 N_2 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) ν = 3130, 3080, 2940, 2870, 1610, 1575, 1480, 1465, 1370, 1355, 1270, 1140, 1120, 1060, 760, 745, 670 cm^{-1}.- ^{1}H NMR (400 MHz, [d_6]DMSO) : δ = 7.74-7.84 (m, 4H), 8.11-8.31 (m, 3H), 9.36-9.38 (m, 2H).- ^{13}C NMR (100 MHz, [d_6]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 $C_{13}H_9NO_3S$ (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) : ν = 3080, 1620, 1575, 1485, 1440, 1305, 1280, 1260, 1165, 1150, 1110, 1050, 1000, 750, 720, 690 cm^{-1}.- ^{1}H NMR (400 MHz, [d_6]DMSO) : δ = 7.60-7.80 (m, 19H).- Anal. Calcd for $C_{26}H_{19}PO_3S$ (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) : ν = 3060, 1610, 1570, 1485, 1445, 1320, 1305, 1275, 1260, 1150, 1120, 1090, 1060, 1040, 1000, 800, 740 cm^{-1}.- ^{1}H NMR (400 MHz, [d_6]DMSO) : δ = 7.60-7.80 (m, 19H).- ^{13}C NMR (100 MHz, [d_6]DMSO) : δ = 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 $C_{26}H_{19}AsO_3S$ (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 N_2. 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 ($CHCl_3$ / petroleum ether).- IR (KBr) : ν = 1555 , 1325, 1205, 1190, 1170, 1160, 1135, 990, 760 cm^{-1}.- ^{1}H NMR (400 MHz, $CDCl_3$) : 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 $C_9H_4O_3S_3$ (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 °C for 5-10 min under N_2. The reaction mixture was purified by column chromatography on silica gel (CH_2Cl_2) 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) : ν = 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, $CDCl_3$) : δ = 2.42-2.43 (m, 3H), 3.85-3.87 (m, 3H), 6.89-7.98 (m, 12H).- ^{13}C NMR (100 MHz, $CDCl_3$) : δ = 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 $C_{23}H_{18}O_4S$ (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 ($CHCl_3$ / 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) : ν = 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, $CDCl_3$) : 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).- ^{13}C NMR (100 MHz, $CDCl_3$) : 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 $C_{23}H_{18}O_3S$ (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 N_2. The reaction mixture was column chromatographed on silica gel (CH_2Cl_2 /petroleum ether) to afford cyclopropane **16**.

Cyclopropane 16a (0.251 g, 46% yield) was obtained as colorless crystals, m.p. 143-144 °C ($CHCl_3$/ 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 °C for 10 min. IR (KBr) : ν = 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, $CDCl_3$) : 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).- ^{13}C NMR (100 MHz, $CDCl_3$) : 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 $C_{14}H_{14}O_3S$ (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 ($CHCl_3$ / n-hexane).- IR (KBr) : ν = 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, $CDCl_3$) : δ = 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, $CDCl_3$) : 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 $C_{15}H_{14}O_3S$ (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 ($CHCl_3$ / n-hexane).- IR (KBr) : ν = 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}.- ^{1}H NMR (400 MHz, $CDCl_3$) : δ = 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).- ^{13}C NMR (100 MHz, $CDCl_3$) : δ = 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 $C_{15}H_{14}O_3S$ (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 ($CHCl_3$/ 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) : ν = 2940, 1710, 1580, 1450, 1305, 1275, 1220, 1150, 1060, 910, 870, 710 cm^{-1}.- ^{1}H NMR (400 MHz, $CDCl_3$) : δ = 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).- ^{13}C NMR (100 MHz, $CDCl_3$) : δ = 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 $C_{15}H_{12}O_3S$ (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 ($CHCl_3$/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) : ν = 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}.- ^{1}H NMR (400 MHz, $CDCl_3$) : 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).- ^{13}C NMR (100 MHz, $CDCl_3$) : 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 $C_{17}H_{12}O_3S$ (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 ($CHCl_3$/ n-hexane), by following the above mentioned procedure, in which a total of iodonium ylide **4** (0.80 g, 2.08 mmol), acenaphtylene (1.0 g, 5.62 mmol), and $Cu(acac)_2$ (20 mg)was heated at 80 °C for 5 min.- IR (KBr) : ν = 1710, 1580, 1310, 1290, 1245, 1195, 1170, 1160, 1125, 1060, 970, 820, 780, 750 cm^{-1}.- ^{1}H NMR (400 MHz, $CDCl_3$) : δ = 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).- ^{13}C NMR (100 MHz, $CDCl_3$) : δ = 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 $C_{20}H_{12}O_3S$ (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 ($CHCl_3$/ 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) : ν = 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}.- ^{1}H NMR (400 MHz, $CDCl_3$) : δ = 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) .- ^{13}C NMR (100 MHz, $CDCl_3$) : δ = 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 $C_{16}H_{12}O_3S$ (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 ($CHCl_3$/ n-hexane), by following the above mentioned procedure, in which a mixture of iodonium ylide of **4** (0.80 g, 2.08 mmol), o-chlorostyrene(1.5 g,10.83 mmol), and Cu(acac)$_2$ (20 mg)was heated at 100 °C for 15 min.- IR (KBr) : ν = 3030, 1715, 1590, 1480, 1440, 1375, 1310, 1215, 1180, 1145, 1135, 1060, 1030, 1010, 860, 790, 780, 755 cm^{-1}.- ^{1}H NMR (400 MHz, $CDCl_3$) : δ = 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).- ^{13}C NMR (100 MHz, $CDCl_3$) : δ = 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 $C_{16}H_{11}O_3S$ (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 °C ($CHCl_3$/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 °C for 10 min.- IR (KBr) : ν = 2920, 2840, 1720, 1610, 1590, 1510, 1450, 1360, 1305, 1250, 1220, 1170, 1140, 1120, 1080, 1060, 1030, 990, 840, 770, 740, 690 cm^{-1}.- ^{1}H NMR (400 MHz, $CDCl_3$) : 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).- ^{13}C NMR (100 MHz, $CDCl_3$) : 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 $C_{17}H_{14}O_3S$ (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 N_2. 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 ($CHCl_3$ / petroleum ether) to yield furan **18** (0.199 mg, 34% yield) as colorless crystals, m.p. = 215 - 216 °C ($CHCl_3$ / hexane).- IR (KBr) : ν = 1610, 1520, 1470, 1440, 1395, 1305, 1160, 1120, 1045, 910, 790, 765, 735, 680 cm^{-1}.- ^{1}H NMR (400 MHz, $CDCl_3$) : δ = 6.90 (s, 1H), 7.26 - 7.46 (m, 5H), 7.55 - 7.56 (m, 2H), 7.69 - 7.73 (m, 3H).- ^{13}C NMR (100 MHz, $CDCl_3$) : δ = 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 $C_{16}H_{10}O_3S$ (282.3) : C, 68.07; H, 3.57.- Found : C, 67.80; H, 3.64.

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REFERENCES

1. Trost, B.M.; Melvin, L.S. *Sulfur Ylides Emerging Synthetic Intermediates*; Academic Press: New York 1975.
2. 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.
3. 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.
5. There are a few examples of iodonium ylides with different carbanionic substitunts 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.
7. 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.
11. Hadjiarapoglou, L.; Varvoglis, A. *J. Chem. Soc. Perkin Trans. I* **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 I* **1991**, 1405.
12. 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.
14. 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.
20. 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.

22. 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.

24. 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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