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Preparation of α,ω-Alkanediylbis-(3-sulfolenes) as Precursors for α,ω-Bis-(1,3-dienyl)alkanes

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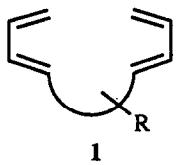
Abstract: The sequential substitution reactions of α,ω-diiodoalkanes with two units of 3-sulfolenyl anions conveniently lead to the formation of α,ω-alkanediylbis-(3-sulfolenes) **7**. These bissulfolenes are stable precursors for the corresponding bis-(1,3-dienyl)alkanes **16** and the transformation can be readily achieved by a simple thermolytic cheletropic reaction.

There has been an increasing interest in the study of the synthetic applications of α,ω-bis-(1,3-dienyl)alkanes **1**.[1] The transition metal or photo-induced [4+4] and the cationic [4+2] intramolecular cycloaddition reactions of them are especially useful for the construction of complex, multicyclic systems. It is therefore essential to explore efficient routes toward their synthesis. Since these diene-containing molecules are not particularly stable under thermal, photo, or acidic conditions, they usually need to be used shortly after having been prepared. It has been well-established that 3-sulfolenes are excellent precursors for conjugated dienes[2] because 3-sulfolenes are relatively stable toward acids, and the thermal removal of SO_2 from substituted 3-sulfolenes is stereospecific.[3] Accordingly, alkanediylbis-(3-sulfolenes) **2** should serve as synthetic equivalents to **1**, and it was our aim to develop a short synthetic method for **2**.



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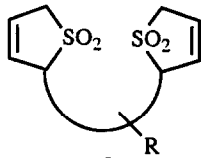

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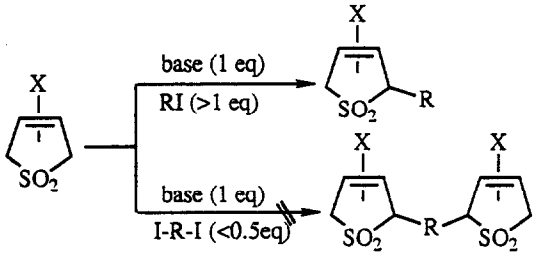
The deprotonation/alkylation reaction sequence is a very well-established method to attach an alkyl group regioselectively to a 3-sulfolene molecule (Scheme I).[4] An attractive extension of this strategy to the synthesis of alkanediylbissulfolenes would be to replace both ends of an α,ω-diiodoalkane with two equivalents of sulfolenyl anion. In principle, this would provide a very efficient route to **2**. However, we were unable to obtain satisfactory results after extensive attempts of modification of reaction conditions. The desired alkanediylbissulfolenes were formed, if at all, in very low yield. Since several possible side reactions such as spirobicyclization,[5] bridged bicyclization, fused-ring bicyclization, double bond isomerization,[6]

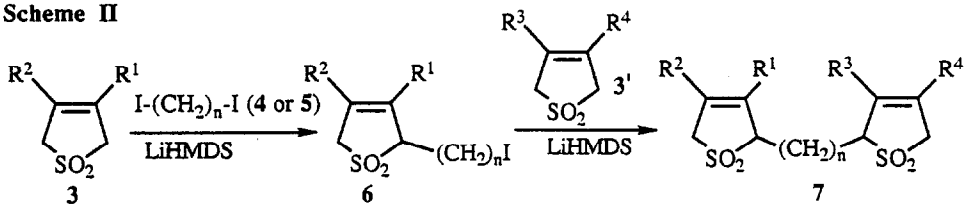
polymerization, and others may occur, and since only symmetric bissulfolenes could be obtained by this approach, this route was not pursued further.

Scheme I



A more versatile approach involves the stepwise connection of two molecules of 3-sulfolenes with one mole of a diiodoalkane. By this route a 3-sulfolenyl anion is first reacted to yield a monoiodoalkylated 3-sulfolene 6. The intermediate 6 can be treated with another 3-sulfolenyl anion to give the desired end product 7 (Scheme II). Therefore, by varying the 3-sulfolenes used at the two stages one would be able to synthesize both symmetric and unsymmetric bissulfolenes.

Scheme II



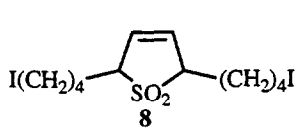
The iodoalkylation reaction of 3-sulfolenes at -78°C using LiHMDS as the base proceeded well with 1,4-diiodobutane **4** and 1,5-diiodopentane **5** and the results are summarized in Table I.

The monoiodoalkylated sulfolenes **6a-i** were formed in acceptable yields (Table I) except for the ones in entries 4 and 5 where undesired side products predominated. Disubstitution appeared to be a general side reaction so that compounds **8** (entry 1), **9** (entry 3), **13** (entry 7), and **14** (entry 9) were produced.[7] These are reasonable side products because a second deprotonation/substitution process could take place on the monosubstituted 3-sulfolenes **6**, and if that occurs, it would preferably take place at the unsubstituted α-position of **6a**, **6c**, **6g** and **6i** for both steric and electronic reasons. The formation of the spirosulfolenes **10** (entry 4) and **12** (entry 5) indicates that **6d** and **6e** prefer to be deprotonated at the α-position which is already substituted. Geminal disubstitution reactions have been observed for **3e** earlier.[8] The electronic effects of a 3-phenylthio substitutent appear to outweigh the steric effects of an alkyl group at the 2-position. The side product **11** (entry 4) should have been formed from **6d** by a double bond migration process which is known to take place for 3-sulfolenes under basic conditions.[6]

Table I. Monoiodoalkylation Reactions of 3-Sulfolenes[a]

entry	3-sulfolene		I-(CH2)n-I	products and yields[b]
1	R^1=R^2=H	**3a**	n=4 **4**	**6a** (47%) + **8** (6%)
2	R^1=Me, R^2=H	**3b**	n=4 **4**	**6b** (53%)
3	R^1=R^2=Me	**3c**	n=4 **4**	**6c** (49%) + **9** (8%)
4	R^1=Cl, R^2=H	**3d**	n=4 **4**	**6d** (27%) + **10** (9%) + **11** (8%)
5	R^1=H, R^2=PhS	**3e**	n=4 **4**	**6e** (5%) + **12** (20%)
6	R^1=H, R^2=TMS	**3f**	n=4 **4**	**6f** (42%)
7	R^1=R^2=H	**3a**	n=5 **5**	**6g** (44%) + **13** (4%)
8	R^1=Me, R^2=H	**3b**	n=5 **5**	**6h** (53%)
9	R^1=R^2=Me	**3c**	n=5 **5**	**6i** (47%) +**14** (8%)

a. The reactions were performed at -78°C by adding a solution of LiHMDS in THF to a mixture of a 3-sulfolene and a diiodide. **b.** The numbers in the parentheses are isolated yields after purification with column chromatography.



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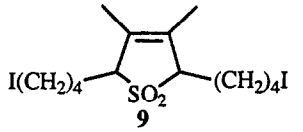

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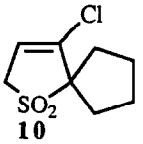

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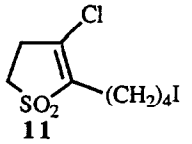

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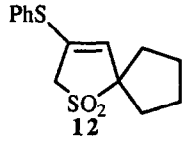

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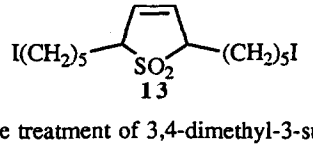

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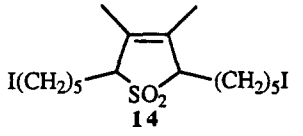

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The treatment of 3,4-dimethyl-3-sulfolene **3c** with diiodomethane or diiodoethane resulted in partial recovery of **3c** (95% and 42%, respectively) without giving the anticipated bissulfolene. The reaction of **3c** with diiodopropane gave a variety of products depending on the reaction conditions but no 2-(iodopropyl)-3-sulfolene was observed. Thus, iodoalkylation reactions appear inapplicable to diiodoalkanes with chains shorter than four atoms.

Table II. Preparation of α,ω-Alkanediylbis-3-sulfolenes

entry	reactants	product and yield[c]	
1	**6a+3a**[a]	R^1=R^2=R^3=R^4=H, n=4	**7a** (19%)
2	**6b+3b**[a]	R^1=R^3=Me, R^2=R^4=H, n=4	**7b** (45%)
3	**6b+3e**[a]	R^1=Me, R^2=R^3=H, R^4=SPh, n=4	**7c** (23%)
4	**6b+15**[b]	R^1=Me, R^2=R^4=H, R^3=CO_2Me, n=4	**7d** (36%)
5	**6c+3b**[a]	R^1=R^2=R^3=Me, R^4=H, n=4	**7e** (56%)
6	**6b+3c**[a]	R^1=R^3=R^4=Me, R^2=H, n=4	**7e** (33%)
7	**6c+3c**[a]	R^1=R^3=R^4=Me, R^2=H, n=4	**7f** (42%)
8	**6c+15**[b]	R^1=R^2=Me, R^3=CO_2Me, R^4=H, n=4	**7g** (41%)
9	**6g+3a**[a]	R^1=R^2=R^3=R^4=H, n=5	**7h** (12%)
10	**6h+3b**[a]	R^1=R^3=Me, R^2=R^4=H, n=5	**7i** (41%)
11	**6h+3e**[a]	R^1=Me, R^2=R^3=H, R^4=SPh, n=5	**7j** (39%)
12	**6h+15**[b]	R^1=Me, R^2=R^4=H, R^3=CO_2Me, n=5	**7k** (36%)
13	**6i+3b**[a]	R^1=R^2=R^3=Me, R^4=H, n=5	**7l** (55%)
14	**6h+3c**[a]	R^1=R^3=R^4=Me, R^2=H, n=5	**7l** (33%)
15	**6i+3c**[a]	R1=R^2=R^3=R^4=Me, n=5	**7m** (34%)
16	**6i+15**[b]	R^1=R^2=Me, R^3=CO_2Me, R^4=H, n=5	**7n** (39%)

a. The reactions were performed under the same conditions as described in Table I. b. The reactions were performed at -78°C by adding the iodoalkylated sulfolene **6** to the dianion of **15** which had been generated by adding two equiv of base to a THF solution of **15**. c. The numbers in the parentheses are isolated yields after purification with column chromatography.

When performing the second-stage alkylation reaction shown in scheme II, it was necessary to consider the problem of competitive deprotonation between the newly-added 3-sulfolene **3** and the iodoalkylated 3-sulfolene **6**. For the reaction to proceed smoothly, the 3-sulfolene **3** should not be less acidic than the monoiodoalkylated 3-sulfolene **6**. Otherwise, the deprotonation would prefer to take place on **6** instead of **3** so as to give undesired results. For example, the reaction of **6e** (more acidic) and **3b** (less acidic) in the presence of LiHMDS gave only the spirocyclic product **12** without giving the desired bissulfolene **7c**.

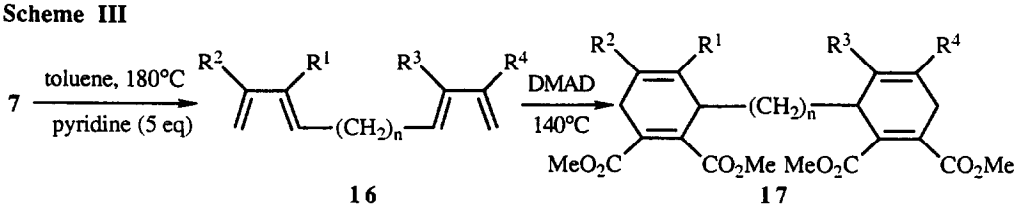
Therefore, only compounds **6a-c** and **6g-i** were chosen to react with another molecule of **3** for the preparation of bissulfolenes. A wide variety of 3-sulfolenes can be used and the competitive deprotonation was not an obvious problem. The results are summarized in TableII. The α,ω-alkanediylbis-(3-sulfolenes) **7** thus produced are expected to exist as mixtures of diastereomers because there does not seem to be any good control factor for stereoselectivity. However, no efforts were made to identify the stereochemistry of each chiral center of these compounds because in the subsequent reaction SO_2 would be removed and the chirality would be lost.

The unsymmetric bissulfolene **7e** were obtained by two routes, *i.e.* the coupling of **6c** with **3b** (entry 5) and the coupling of **6b** with **3c** (entry 6). The yield of the former route (56%) is better than the latter (33%). This may be due to the one more methyl group on the systems bearing 3,4-dimethyl substituents which causes the deprotonation of **3c** and **6c** to be more difficult than **3b** and **6b**. Similar difference in the yields of the synthesis of **7l** (comparing entries 13 and 14) was also observed.

All the reactions in Table II, except for those involving the use of 3-methoxycarbonyl-3-sulfolene **15**, were run by standard procedure where the reacting sulfolene and iodide were mixed at -78°C followed by the addition of LiHMDS. The alkylation reaction of the monoanion of **15** is known to undertake substitution at the carbon bearing the ester functionality giving a 4,4-disubstituted 2-sulfolene.[9] In order to maintain a 3-sulfolene structure after alkylation reactions, the dianion of **15** had to be used. Therefore, compound **15** was first treated with two equivalents of LiHMDS to give its dianion and was then reacted with a proper iodoalkylated 3-sulfolene to form the corresponding bissulfolene **7** (entries 4, 8, 12, and 16).

The alkanediylbis-3-sulfolenes **7** listed in Table II are potential precursors to the corresponding bis-1,3-dienes. To illustrate that the transformation can be conveniently achieved, **7b**, **7l**, **7m**, and **7n** were thermolyzed in the presence of pyridine (5 equiv) at 180°C to extrude SO_2 giving the corresponding bisdienes **16a-d** (Scheme III and Table III). The geometry of the dienes are presumably in the *E*-form as they are produced from cheletropic reactions.[3] Pyridine was used to complex with SO_2 generated from thermolysis to avoid the polymerization of **16** induced by SO_2. Indeed, the bisdienes were formed in much lower yields when the reactions were performed without the added pyridine. Although $LiAlH_4$ is known to cause SO_2 extrusion from many 3-sulfolenes,[10] its reaction with **7b**, **7l**, **7m** or **7n** gave the corresponding bisdiene only in less than 50% yield. Compounds **16a-d** are sensitive to acid, as expected, and they polymerized gradually in the NMR solvent $CDCl_3$ which contains trace amount of HCl. Whereas **16a-d** reacted as active dienes and underwent Diels-Alder reactions readily with dimethyl acetylenedicaboxylate (DMAD) at 140°C giving the bis-cycloadducts **17a-d** (Table III), the attempted one-pot reactions of bissulfolenes **7** with DMAD at 180°C gave the cycloadducts **17a-d** in lower yields. Since there are no apparent factors which can control the stereochemistry in the Diels-Alder reactions, compounds **17a-d** should be produced as mixtures of diastereomers. However, these stereoisomers could not be separated by chromatographic methods.

Scheme III



16 **17**

Table III. Extrusion of SO_2 from Alkanediylbis-(3-sulfolenes) and the Subsequent Diels-Alder Reactions with DMAD

entry	reactant 7		bisdiene 16[a]	cycloadduct 17[a]
1	R^1=R^3=Me, R^2=R^4=H, n=4	**7b**	**16a** (98%)	**17a** (46%)
2	R^1=R^2=R^3=Me, R^4=H, n=5	**7l**	**16b** (95%)	**17b** (58%)
3	R^1=R^2=R^3=R^4=Me, n=5	**7m**	**16c** (87%)	**17c** (35%)
4	R^1=R^2=Me, R^3=CO_2Me, R^4=H, n=5	**7n**	**16d** (72%)	**17d** (53%)

a. The numbers in the parentheses are isolated yields after column chromatography.

Although **7a-n** were obtained only in fair yields, the two-stage substitution approach described herein is synthetically useful because of its conciseness and versatility. By varing the sulfolenyl anions and the α,ω-diiodoalkanes and by properly arranging the sequence of substitution reactions, a large variety of precursors for α,ω-bis-1,3-dienes can be prepared conveniently.

EXPERIMENTAL SECTION

General Methods. ^{1}H NMR spectra were determined on a Bruker ACF-200 NMR spectrometer as solutions in $CDCl_3$. IR spectra were determined on a Perkin-Elmer 882 IR spectrophotometer. Mass spectra were determined on a VG 70-250S mass spectrometer. Elemental analyses were performed on a Perkin-Elmer 240C analyzer. THF and toluene were freshly distilled from potassium before use.

General Procedure for the Alkylation Reactions of 3-Sulfolenes with Iodoalkanes.

Method A : To a solution of a 3-sulfolene **3** (14.5 mmol), a diiodoalkane **4** or **5** (14.5 mmol), and hexamethyl phosphoramide (HMPA, 29.0 mmol) in THF (80 ml) at -78°C was slowly added a solution of lithium hexamethyldisilazide (LiHMDS, 7.2 mmol) and the stirring was continued at -78°C for 30 min. Saturated NH_4Cl (15 ml) was added and the layers separated. The aqueous layer was extracted with EtOAc (3 × 50 ml) and the combined organic layers were dried ($MgSO_4$), concentrated, and purified on a silica gel column (hexane/EtOAc, 2:1). The same procedure was used to prepare compounds **6a-i** and **7a-c**, **7e-f**, **7h-j**, and **7l-m**. The products and yields are summarized in Table I and II.

Method B : To a solution of a 3-methoxycarbonyl-3-sulfolene **15** (0.29 mmol) in THF (4 ml) at -105°C was gradually added n-BuLi in hexane (2.4 M, 0.24 ml, 0.58 mmol) and the stirring was continued for 10 min. A solution of an iodoalkylated 3-sulfolene **6** (1.16 mmol) in THF (1 ml) was added at once and the reaction mixture was then stirred at -78°C for 30 min. Saturated NH_4Cl (2 ml) was added and the layers

separated. The aqueous layer was extracted with EtOAc (3 × 50 ml) and the combined organic layers were dried ($MgSO_4$), concentrated, and purified on a silica gel column (hexane/EtOAc, 1:1). The same procedure was used to prepare compounds **7d**, **7g**, **7k**, and **7n**. The yields are listed in Table II.

2-(4-Iodobutyl)-3-sulfolene 6a. light yellow oil: IR (neat) 2940, 2861, 1450, 1303, 1250, 1127 cm^{-1}; ^1H NMR δ 1.54-2.08 (m, 6H), 3.21 (t, 2H, J = 6.8 Hz), 3.62-3.81 (m, 3H), 6.05 (s, 2H); MS 300 (M^+), 236, 173, 107, 79, 67 , 55. $C_8H_{13}I$ (M^+ - SO_2)requires: 236.0062; found: 236.0069.

2,5-Bis-(4-iodobutyl)-3-sulfolene 8. light yellow oil: IR (neat) 2930, 2860, 1728, 1445, 1423, 1296, 1204, 1118 cm^{-1}; ^1H NMR δ 1.53-2.08 (m, 12H), 3.21 (t, 4H,J = 6.8 Hz), 3.58-3.71 (m, 2H), 6.02 (s, 2H); MS *m/z* 418 (M^+ - SO_2), 290, 197, 153, 122, 93, 79, 67 (100%); $C_{12}H_{20}I_2O_2S$ requires: 481.9275; found: 481.9273.

2-(4-Iodobutyl)-3-methyl-3-sulfolene 6b. light yellow oil: IR (neat) 2938, 2865, 1437, 1301, 1244, 1118 cm^{-1}; ^1H NMR δ 1.51-1.98 (m, 6H), 1.81-1.90 (m, 3H), 3.21 (t, 2H, J = 6.8 Hz), 3.45-3.58 (m, 1H), 3.59-3.82 (m, 2H), 5.68-5.76 (m, 1H); MS *m/z* 314 (M^+), 250, 187, 121, 93, 81 (100%), 67, 55. $C_9H_{15}I$(M^+ - SO_2) requires: 250.0219; found: 250.0223.

3,4-Dimethyl-2-(4-iodobutyl)-3-sulfolene 6c. light yellow oil: IR (neat) 2944, 2919, 2861, 1442, 1298, 1277, 1169, 1103 cm^{-1}; ^1H NMR δ 1.42-1.91 (m, 6H), 1.71 (s, 6H), 3.14 (t, 2H, J = 7 Hz), 3.41-3.51 (m, 1H), 3.58 (s, 2H); MS *m/z* 328 (M^+), 264, 201 (100%), 135, 109, 95, 81, 67. Anal. Calcd. for $C_{10}H_{17}IO_2S$: C, 36.60; H, 5.22. Found: C, 37.08; H, 5.27.

3,4-Dimethyl-2,5-bis-(4-iodobutyl)-3-sulfolene 9. light yellow oil: IR (neat) 2934, 2862, 1447, 1293, 1168, 1110 cm^{-1}; ^1H NMR δ 1.51-1.98 (m, 12H), 1.74 (s, 6H), 3.20 (t, 4H, J = 6.7 Hz), 3.40-3.52 (m, 2H); MS *m/z* 446 (M^+ - SO_2), 383 (100%), 319, 263, 183, 95, 55. $C_{14}H_{24}I_2$ (M^+ - SO_2) requires: 447.0063; found: 447.0046.

3-Chloro-2-(4-iodobutyl)-3-sulfolene 6d. light yellow oil: IR (neat) 2933, 2863, 1621, 1449, 1318, 1237, 1188, 1130 cm^{-1}; ^1H NMR δ 1.54-2.07 (m, 6H), 3.20 (t, 2H, J = 6.8 Hz), 3.63-3.78 (m, 1H), 3.80-3.94 (m, 2H), 6.03-6.12 (m, 1H); MS *m/z* 334 (M^+), 270, 207, 142, 107, 101, 79, 65 (100%); $C_8H_{12}ClI$(M^+ - SO_2) requires: 269.9672; found: 269.9679.

9-Chloro-6-thiaspiro[4.4]-8-nonene 6,6-Dioxide 10. colorless oil: IR (neat) 2947, 2931, 2869, 1614, 1434, 1406, 1303, 1239, 1126, 1092 cm^{-1}; ^1H NMR δ 1.77-1.98 (m, 6H), 2.38-2.56 (m, 2H), 3.81 (d, 2H, J = 3.2 Hz), 5.91-6.02 (m, 1H); MS *m/z* 206 (M^+), 142, 107 (100%), 91, 79, 65. Anal. Calcd. for $C_8H_{11}ClO_2S$: C, 46.49; H, 5.36. Found: C, 46.27; H, 5.23.

3-Chloro-2-(4-iodobutyl)-2-sulfolene 11. colorless oil: IR (neat) 2956, 2860, 1652, 1457, 1425, 1288, 1170, 1120, 1076 cm^{-1}; ^1H NMR δ 1.74-1.96 (m, 4H), 2.54 (t, 2H, J = 7.1 Hz), 3.06 (t, 2H, J = 6 Hz), 3.20 (t, 2H, J = 7.1 Hz), 3.42 (t, 2H, J = 6 Hz); MS *m/z* 334 (M^+), 207 (100%), 145, 109, 83, 65. Anal. Calcd. for $C_8H_{12}ClIO_2S$: C, 28.72; H,3.61. Found: C, 29.05; H, 3.46.

4-(Benzenethio)-2-(4-iodobutyl)-3-sulfolene 6e. light yellow oil: IR (neat) 3057, 2934, 2860, 1580, 1474, 1437, 1308, 1219, 1128 cm^{-1}; ^1H NMR δ 1.48-2.09 (m, 6H), 3.19 (t, 2H, J = 6.8 Hz), 3.69-3.76 (m, 2H), 3.76-3.88 (m, 1H), 5.67-5.75 (m, 1H), 7.37-7.51(m, 5H); MS *m/z* 344 (M^+ - SO_2), 252, 237, 218 (100%), 125, 109, 97, 83. $C_{14}H_{17}IS$ (M^+ - SO_2) requires: 344.0096; found: 344.0104.

8-(Benzenethio)-6-thiaspiro[4.4]-8-nonene 6,6-Dioxide 12. light yellow oil: IR (neat) 2961, 2874, 1581, 1473, 1438, 1297, 1220, 1128, 1021 cm^{-1}; ^1H NMR δ 1.57-1.88 (m, 6H), 2.51-2.59 (m, 2H),

3.69 (m, 2H), 5.74-5.79 (m, 1H), 7.34-7.42 (m, 5H); MS *m/z* 280 (M^+), 216 (100%), 207, 183, 155, 139, 125, 106, 83, 67. $C_{14}H_{16}O_2S_2$ requires: 280.0592; found: 280.0586.

4-(Trimethylsilyl)-2-(4-iodobutyl)-3-sulfolene 6f. light yellow oil: IR (neat) 2952, 2864, 1734, 1584, 1398, 1302, 1249, 1122,1035 cm^{-1}; ^1H NMR δ 0.09 (s, 9H), 1.46-1.98 (m, 6H), 3.15 (t, 2H, J = 6.8 Hz), 3.23-3.54 (m, 3H), 6.02-6.09 (m, 1H); MS *m/z* 308 ($M^+ - SO_2$), 245, 185, 107, 93, 73 (100%); $C_{11}H_{21}ISi(M^+ - SO_2)$ requires: 308.0457; found: 308.0461.

2-(5-Iodopentyl)-3-sulfolene 6g. light yellow oil: IR (neat) 2931, 2860, 1424, 1303, 1246, 1195, 1122 cm^{-1}; ^1H NMR δ 1.39-2.09 (m, 8H), 3.20 (t, 2H, J = 6.8 Hz), 3.62-3.81 (m, 3H), 5.94-6.07 (m, 2H); MS *m/z* 314 (M^+), 250, 196, 187, 121, 93, 81 (100%), 69; $C_9H_{15}IO_2S$ requires: 313.9837; found: 313.9836.

2,5-Bis-(5-iodopentyl)-3-sulfolene 13. light yellow oil: IR (neat) 2935, 2858, 1454, 1298, 1198, 1121 cm^{-1}; ^1H NMR δ 1.49-2.08 (m, 16H), 3.20 (t, 4H, J = 6.8 Hz), 3.50-3.68 (m, 2H), 5.99 (s, 2H); MS *m/z* 510 (M^+), 446, 383, 319, 263, 183, 123, 109, 95, 81 (100%).

3-Methyl-2-(5-iodopentyl)-3-sulfolene 6h. light yellow oil: IR (neat) 2933, 2858, 1734, 1439, 1295, 1197, 1246, 1124 cm^{-1}; ^1H NMR δ 1.41-1.98 (m, 8H), 1.84 (s, 3H), 3.20 (t, 2H, J = 6.8 Hz), 3.45-3.57 (m, 1H), 3.59-3.78 (m, 2H), 5.68 (s, 1H); MS *m/z* 264 ($M^+ - SO_2$), 201, 136, 107, 95, 81 (100%), 68, 55, 41. $C_{10}H_{17}I(M^+ - SO_2)$ requires: 264.0375; found: 264.0361.

3,4-Dimethyl-2-(5-iodopentyl)-3-sulfolene 6i. light yellow oil: IR (neat) 2932, 2860, 1734, 1440, 1306, 1171, 1108 cm^{-1}; ^1H NMR δ 1.37-1.91 (m, 8H), 1.71-1.90 (m, 6H), 3.20(t, 2H, J = 6.9 Hz), 3.49-3.51 (m, 1H), 3.64 (s, 2H); MS *m/z* 342 (M^+), 278, 215, 149, 109, 95 (100%). $C_{11}H_{19}I(M^+ - SO_2)$ requires: 278.0532; found: 278.0546.

3,4-Dimethyl-2,5-bis-(5-iodopentyl)-3-sulfolene 14. light yellow oil: IR(neat) 2928, 2857, 1731, 1429, 1295, 1195, 1107 cm^{-1}; ^1H NMR δ 1.45-1.95 (m, 16H), 1.76 (s, 6H), 3.19 (t, 4H, J = 6.9 Hz), 3.37-3.52 (m, 2H); MS *m/z* 474 ($M^+ - SO_2$), 411, 347, 291, 277, 198, 167, 149, 70, 61 (100%); $C_{16}H_{28}I_2O_2S$ requires: 537.9901; found: 537.9925.

2,2'-(1,4-Butanediyl)-2,2',5,5'-tetrahydrobisthiophene 1,1,1',1'-Tetraoxide 7a. white solid: mp 96-98°C; IR(KBr) 3072, 2929, 2854, 1288, 1232, 1112 cm^{-1}; ^1H NMR δ 1.47-2.22 (m, 8H), 3.60-3.85 (m, 6H), 5.90-6.18 (m, 4H); MS *m/z* 226 ($M^+ - SO_2$), 161, 133, 119, 105, 93, 79, 67(100%), 64, 48. Anal. Calcd. for $C_{12}H_{18}O_4S_2$: C, 49.63; H, 6.25. Found: C, 49.58; H, 6.12.

3,3'-Dimethyl-2,2'-(1,4-butanediyl)-2,2',5,5'-tetrahydrobisthiophene 1,1,1',1'-Tetraoxide 7b. white solid: mp 144-146°C; IR (KBr) 2935, 2858, 1443, 1292, 1248, 1118 cm^{-1}; ^1H NMR δ 1.44-2.01 (m, 8H), 1.84 (s, 6H), 3.43-3.59 (m, 2H), 3.59-3.81 (m, 4H), 5.67 (s, 2H); MS *m/z* 318 (M^+), 254, 189, 175, 161, 147, 133, 121, 109 (100%), 93, 81, 67. Anal. Calcd. for $C_{14}H_{22}O_4S_2$: C, 52.80; H, 6.96. Found: C, 52.70; H, 7.27.

3-Methyl-4'-(benzenethio)-2,2'-(1,4-butanediyl)-2,2',5,5'-tetrahydrobisthiophene 1,1,1',1'-Tetraoxide 7c. light yellow oil: IR (neat) 2938, 2862, 1708, 1581, 1473, 1438, 1300, 1217, 1121, 1022 cm^{-1}; ^1H NMR δ 1.41-2.00 (m, 11H), 3.41-3.56 (m, 1H), 3.59-3.76 (m, 4H), 3.76-3.89 (m, 1H), 5.62-5.75 (m, 2H), 7.32-7.50 (m, 5H); MS *m/z* 348 ($M^+ - SO_2$), 284, 218 (100%), 185, 154, 109, 77, 65; $C_{19}H_{24}O_2S_2$ ($M^+ - SO_2$) requires: 348.1218; found: 348.1205.

3-Methyl-3'-methoxycarbonyl-2,2'-(1,4-butanediyl)-2,2',5,5'-tetrahydrobisthiophene 1,1,1',1'-Tetraoxide 7d. colorless oil ; IR (neat) 2947, 1714, 1622, 1433, 1302, 1122, 1081 cm^{-1}; ^1H

NMR δ 1.41-2.06 (m, 8H), 1.84 (s, 3H), 3.41-3.57 (m, 1H), 3.60-3.76 (m, 2H), 3.83 (s, 3H), 3.91-4.01(m, 3H), 5.69 (s, 1H), 7.04 (s, 1H); MS *m/z* 362 (M^+), 298, 282, 266, 201, 187, 173, 121, 109 (100%), 95, 81, 64.

3,3',4-Trimethyl-2,2'-(1,4-butanediyl)-2,2',5,5'-tetrahydrobisthiophene 1,1,1',1'-Tetraoxide 7e. white solid: mp 118-120°C ; IR (KBr) 2925, 1167, 1455, 1289, 1246, 1109 cm^{-1}; ^1H NMR δ 1.49-1.98 (m, 8H), 1.84 (s, 9H), 3.45-3.58 (m, 2H), 3.60-3.79 (m, 4H), 5.67 (s, 1H); MS *m/z* 268 ($M^+ - SO_2$), 204, 185, 175, 161, 136, 121, 107, 93, 79 (100%), 67. Anal. Calcd. for $C_{15}H_{24}O_4S_2$: C, 54.19; H, 7.27. Found: C, 53.93; H, 6.86.

3,3',4,4'-Tetramethyl-2,2'-(1,4-butanediyl)-2,2',5,5'-tetrahydrobisthiophene 1,1,1',1'-Tetraoxide 7f. white solid: mp 120-122°C; IR (KBr) 2945, 2865, 1729, 1433, 1303, 1168, 1108 cm^{-1}; ^1H NMR δ 1.42-1.85 (m, 8H), 1.74 (s, 6H), 1.76 (s, 6H), 3.47-3.60 (m, 2H), 3.64 (s, 4H); MS *m/z* 346 (M^+), 282 (100%), 217, 175, 147, 123, 109, 71. Anal. Calcd. for $C_{16}H_{26}O_4S_2$: C, 55.46; H, 7.56. Found: C, 54.95; H, 7.36.

3,4-Dimethyl-3'-methoxycarbonyl-2,2'-(1,4-butanediyl)-2,2',5,5'-tetrahydrobis-thiophene 1,1,1',1'-Tetraoxide 7g. colorless oil; IR (neat) 2935, 2859, 1716, 1623, 1433, 1292, 1104 cm^{-1}; ^1H NMR δ 1.39-2.08 (m, 8H), 1.71 (s, 3H), 1.74 (s, 3H), 3.44-3.57 (m, 1H), 3.61 (s, 2H), 3.80 (s, 3H), 3.85-3.96 (m, 3H), 6.99-7.03 (m, 1H); MS *m/z* 312 ($M^+ - SO_2$), 233, 216, 188, 117, 83 (100%). $C_{16}H_{24}O_4S(M^+ - SO_2)$ requires: 312.1395; found: 312.1403.

2,2'-(1,5-Pentanediyl)-2,2',5,5'-tetrahydrobisthiophene 1,1,1',1'-Tetraoxide 7h. colorless oil; IR (neat) 2933, 2852, 1722, 1299, 1244, 1127 cm^{-1}; ^1H NMR δ 1.36-2.08 (m, 10H), 3.60-3.71 (m, 2H), 3.71-3.83 (m, 4H), 6.03 (s, 4H); MS *m/z* 240 ($M^+ - SO_2$), 175, 147, 133, 122, 107, 93, 80 (100%), 67.

3,3'-Dimethyl-2,2'-(1,5-pentanediyl)-2,2',5,5'-tetrahydrobisthiophene 1,1,1',1'-Tetraoxide 7i. colorless oil: IR (neat) 2939, 2857, 1634, 1435, 1293, 1245, 1115 cm^{-1}; ^1H NMR δ 1.48-1.91 (m, 10H), 1.85 (s, 6H), 3.41-3.56 (m, 2H), 3.59-3.78 (m, 4H), 5.64-5.71 (m, 2H); MS *m/z* 268 ($M^+ - SO_2$), (100%),204, 189, 175, 161, 147, 133, 121, 109, 94, 81. Anal. Calcd. for $C_{15}H_{24}O_4S_2$: C, 54.19; H, 7.27. Found: C, 53.94; H, 7.19.

3-Methyl-4'-(benzenethio)-2,2'-(1,5-pentanediyl)-2,2',5,5'-tetrahydrobisthiophene 1,1,1',1'-Tetraoxide 7j. light yellow oil; IR(neat) 2933, 2860, 1710, 1581, 1438, 1306, 1217, 1121, 1035, 910 cm^{-1}; ^1H NMR δ 1.31-2.08 (m, 10H), 1.80 (s, 3H), 3.42-3.52 (m, 1H), 3.52-3.73 (m, 4H), 3.73-3.87 (m, 1H), 5.61-5.76 (m, 2H), 7.36-7.49 (m, 5H); MS *m/z* 362 ($M^+ - SO_2$), 298, 218, 189, 176, 161, 148, 107, 93 (100%), 79, 67; $C_{20}H_{26}O_2S_2$ ($M^+ - SO_2$) requires: 362.1374; found: 362.1361.

3-Methyl-3'-methoxycarbonyl-2,2'-(1,5-pentanediyl)-2,2',5,5'-tetrahydrobisthiophene 1,1,1',1'-Tetraoxide 7k. colorless oil; IR (neat) 2949, 2857, 1711, 1622, 1433, 1289, 1118, 1078 cm^{-1}; ^1H NMR δ 1.33-2.01 (m, 10H), 1.80-1.87 (m, 3H), 3.42-3.54 (m, 1H), 3.63-3.72 (m, 2H), 3.84 (s, 3H), 3.91 (d, 2H, J = 3.2 Hz), 3.89-3.99 (m, 1H), 5.62-5.71 (m, 1H), 7.00-7.05 (m, 1H); MS *m/z* 376 (M^+), 312 (100%), 296, 280, 216, 191, 159, 135, 119, 107, 95, 81, 68. Anal. Calcd. for $C_{16}H_{24}O_6S_2$: C, 51.04; H, 6.43. Found: C, 50.54; H, 6.24.

3,3',4-Trimethyl-2,2'-(1,5-pentanediyl)-2,2',5,5'-tetrahydrobisthiophene 1,1,1',1'-Tetraoxide 7l. colorless oil; IR (neat) 2942, 2859, 1437, 1287, 1243, 1106 cm^{-1}; ^1H NMR δ 1.44-1.98 (m, 10H), .174 (s, 3H), 1.77 (s, 3H), 1.84 (s, 3H), 3.44-3.59 (m, 2H), 3.63 (s, 2H), 3.68 (s, 2H), 5.62-

5.71 (m, 1H); MS *m/z* 346 (M^+), 282 (100%), 217, 203, 175, 161, 147, 124, 109, 95, 83, 64. $C_{16}H_{26}O_2S(M^+ - SO_2)$ requires: 282.1654; found: 282.1668.

3,3',4,4'-Tetramethyl-2,2'-(1,5-pentanediyl)-2,2',5,5'-tetrahydrobisthiophene 1,1,1',1'-Tetraoxide 7m. colorless oil; IR (neat) 2941, 2876, 1432, 1293, 1229, 1168, 1101 cm^{-1}; ^1H NMR δ 1.44-1.83 (m, 10H), 1.73-1.78 (m, 12H), 3.47-3.60 (m, 2H), 3.60-3.69 (m, 4H); MS *m/z* 360 (M^+), 296 (100%), 253, 231, 189, 161, 147, 123, 107, 95, 64. $C_{17}H_{28}O_2S(M^+ - SO_2)$ requires: 296.1810; found: 296.1800.

3,4-Dimethyl-3'-methoxycarbonyl-2,2'-(1,5-pentanediyl)-2,2',5,5'-tetrahydrobis-thiophene 1,1,1',1'-Tetraoxide 7n. white solid: mp 110-112°C; IR (KBr) 2949, 2862, 1707, 1619, 1433, 1305, 1253, 1122, 1102, 1091 cm^{-1}; ^1H NMR δ 1.34-2.09 (m, 10H), 1.74 (s, 3H), 1.77 (s, 3H), 3.47-3.58 (m, 1H), 3.64 (s, 2H), 3.83 (s, 3H), 3.88-3.98 (m, 3H), 6.99-7.07 (m, 1H); MS *m/z* 231 ($M^+ -2SO_2$ - OMe), 213 (100%), 164, 148, 133, 112, 107, 93, 82. $C_{16}H_{23}O(M^+ - 2SO_2$ - OMe) requires: 231.1749; found: 231.1753.

Thermolysis of Alkanediylbis-(3-sulfolenes) 7. A solution of **7** (0.20 mmol), pyridine (1.0 mmol) in toluene (3 ml) in a sealed tube was heated at 180°C for 1 hr. The crude mixture was concentrated under reduced pressure and purified on an aluminum oxide column (hexane). The yields are listed in Table III.

3,10-Dimethyl-1,3,9,11-dodecatetraene 16a. colorless oil: IR (neat) 2927, 2855, 1633, 1602, 1435, 1076, 985, 889 cm^{-1}; ^1H NMR δ 1.38-1.46 (m, 4H), 1.74 (s, 6H), 2.13-2.17 (m,4H), 4.94 (d, 2H, J = 10.6 Hz), 5.09 (d, 2H, J = 17.2 Hz), 5.50 (t, 2H, J = 7.4 Hz), 6.38 (dd, 2H, J = 10.6, 17.2 Hz); MS *m/z* 190 (M^+), 175, 161, 147, 133, 107, 93, 79 (100%), 67. Anal. Calcd. for $C_{14}H_{22}$: C, 88.35; H, 11.65. Found: C, 88.50; H, 11.62.

2,3,11,-Trimethyl-1,3,10,12-tridecatetraene 16b. colorless oil: IR (neat) 3089, 2926, 2856, 1638, 1603, 1439, 1369, 1305, 1108, 1080, 986, 884 cm^{-1}; ^1H NMR δ 1.36-1.44 (m, 6H), 1.73(s, 3H), 1.79 (s, 3H), 1.90 (s, 3H), 2.08-2.15 (m, 4H), 4.87 (s, 1H), 4.97 (s, 1H), 4.92 (d, 1H, J = 10.6 Hz), 5.07 (d, 1H, J = 17.4 Hz), 5.49 (t, 1H, J = 7.5 Hz), 5.59 (t, 1H, J = 7.3 Hz), 6.38 (dd, 1H, J = 10.6, 17.4 Hz); MS *m/z* 218 (M^+), 203, 189, 175, 161, 147, 133, 121, 107 (100%), 93, 81, 67.

2,3,11,12-Tetramethyl-1,3,10,12-tridecatetraene 16c. colorless oil: IR (neat) 2924, 2854, 1760, 1601, 1435, 1367, 1303, 1083, 1037, 985, 879 cm^{-1}; ^1H NMR δ 1.36-1.44 (m, 6H), 1.79 (s, 6H), 1.90 (s, 6H), 2.09-2.15 (m, 4H), 4.87 (s, 2H), 4.97 (s, 2H), 5.60 (t, 2H, J = 6.2 Hz); MS *m/z* 232 (M^+), 217, 189, 161, 147, 133, 121, 107 (100%), 93, 81, 67.

2,3-Dimethyl-11-methoxycarbonyl-1,3,10,12-tridecatetraene 16d. colorless oil: IR (neat) 2868, 1718, 1617, 1428, 1369, 1245, 1216, 1192, 1159, 877 cm^{-1}; ^1H NMR δ 1.37-1.49 (m, 6H), 1.79 (s, 3H), 1.90 (s, 3H), 2.08-2.35 (m, 4H), 3.80 (s, 3H), 4.87 (s, 1H), 4.97 (s, 1H), 5.09 (d, 1H, J = 10.9 Hz), 5.24 (d, 1H, J = 17.5 Hz), 5.59 (t, 1H, J = 6.7 Hz), 5.95 (t, 1H, J = 7.7 Hz), 6.34 (dd, 1H, J_1 = 17.5 Hz, J_2 = 10.9 Hz); MS *m/z* 262 (M^+), 230, 215, 202, 191, 147, 135, 121, 107 (100%), 95, 79, 67. Anal. Calcd. for $C_{17}H_{26}O_2$: C, 77.82; H, 9.99. Found: C, 77.55; H, 9.84.

Cycloaddition Reactions of Bis-(1,3-dienyl)alkanes with Dimethyl Acetylenedicarboxylate (DMAD). A solution of **16** (0.18 mmol) and DMAD (1.8 mmol) in toluene was heated at 140°C in a sealed tube for 1 hr. The solvent was evaporated under reduced pressure and the crude product was purified by HPLC (LiChrosorb column, hexane/EtOAc, 2:1). The yields are listed in Table III.

1,4-Bis-[2-methyl-4,5-bis(methoxycarbonyl)-1,4-cyclohexadien-3-yl]butane 17a. white solid: mp 80-82°C; IR (KBr) 2925, 1696, 1645, 1429, 1253, 1130, 1052, 945, 744 cm^{-1}; ^1H NMR δ 1.06-1.10 (m, 4H), 1.69 (s, 6H), 1.36-1.82 (m, 4H), 2.89-2.91 (m, 4H), 3.08-3.21 (m, 2H), 3.75 (s, 6H), 3.78 (s, 6H), 5.48 (s, 2H); MS *m/z* 443 (M^+ - OMe), 324, 291, 234, 177 (100%), 119, 91.

1-[1,2-Dimethyl-4,5-bis(methoxycarbonyl)-1,4-cyclohexadien-3-yl]-5-[2-methyl-4,5-bis(methoxycarbonyl)-1,4-cyclohexadien-3-yl]pentane 17b. colorless oil: IR (neat) 2931, 2859, 1725, 1683, 1649, 1431, 1380, 1249, 1191, 1129, 1051, 947, 754 cm^{-1}; ^1H NMR δ 0.87-1.18 (m, 6H), 1.39-1.72 (m, 4H), 1.64-1.69 (m, 9H), 2.69-3.15 (m, 6H), 3.75-3.78 (m, 12H), 5.49 (s, 1H).

1-[1,2-Dimethyl-4,5-bis(methoxycarbonyl)-1,4-cyclohexadien-3-yl]-5-[1,2-dimethyl-4,5-bis(methoxycarbonyl)-1,4-cyclohexadien-3-yl]pentane 17c. colorless oil: IR (neat) 2949, 2860, 1716, 1650, 1429, 1250, 1196, 1125, 1056, 1019, 780, 751 cm^{-1}; ^1H NMR δ 0.95-1.18 (m, 6H), 1.37-1.72 (m, 4H), 1.64 (s, 6H), 1.69 (s, 6H), 2.80-3.11 (m, 6H), 3.76 (s, 6H), 3.78 (s, 6H).

1-[1,2-Dimethyl-4,5-bis(methoxycarbonyl)-1,4-cyclohexadien-3-yl]-5-[2,4,5-tris(methoxycarbonyl)-1,4-cyclohexadien-3-yl]pentane 17d. colorless oil: IR(neat) 2997, 2948, 2877, 1726, 1639, 1426, 1371, 1289, 1229, 1127, 1053, 952, 915, 749 cm^{-1}; ^1H NMR δ 0.90-1.18 (m, 6H), 1.47-1.74 (m, 4H), 1.68 (s, 3H), 1.75 (s, 3H), 2.80-3.17 (m, 6H), 3.75-3.80 (m, 15H), 7.03 (s, 1H). MS *m/z* 515 (M^+ - OMe), 467, 455, 423, 395, 277, 223, 191 (100%), 179, 133, 105. $C_{28}H_{35}O_9$ (M^+ - OMe) requires: 515.2281; found: 515.2273.

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REFERENCES

1. (a) Gassman, P. G.; Singleton, D. A. *J. Am. Chem. Soc.* **1984**, *106*, 6085. (b) Gassman, P. G. Singleton, D. A. *J. Org. Chem.* **1986**, *51*, 3075. (c) Gassman, P. G.; Singleton, D. A. *J. Am. Chem. Soc.* **1990**, *112*, 8623. (d) Wender, P. A.; Ihle, N. C. *J. Am. Chem. Soc.* **1986**, *108*, 4678. (e) Wender, P. A.; Correia, C. R. D. *J. Am. Chem. Soc.* **1987**, *109*, 2523. (f) Wender, P. A.; Snapper, M. L. *Tetrahedron Lett.* **1987**, *28*, 2221. (g) Wender, P. A.; Ihle, N. C. *Tetrahedron Lett.* **1987**, *28*, 2451. (h) Wender, P. A.; Tebbe, M. J. *Synthesis*, **1991**, 1089. (i) Williams, D. R.; Gaston, R. D.; Horton, III, I. B. *Tetrahedron Lett.* **1985**, *26*, 1391. (j) Hertel, R.; Mattay, J.; Runsink, J. *J. Am. Chem. Soc.* **1991**, *113*, 657. (k) Takacs, J. M.; Zhu, J.; Chandramouli, S. *J. Am. Chem. Soc.* **1992**, *114*, 773.
2. Chou, T. S.; Tso, H. H. *Org. Prep. Proc. Int.* **1989**, *21*, 257.
3. (a) Mock, W. L. *J. Am. Chem. Soc.* **1966**, *88*, 2857. (b) McGregor, S. D.; Lemal, D. M. *J. Am. Chem. Soc.* **1966**, *88*, 2858. (c) Mock, W. L. *J. Am. Chem. Soc.* **1975**, *97*, 3666.
4. (a) Chou, T. S.; Tso, H. H.; Chang, L. J. *J. Chem. Soc., Chem. Commun.* **1984**, 1323. (b) Chou, T. S.; Tso, H. H.; Chang, L. J. *J. Chem. Soc., Perkin Trans. 1.* **1985**, 515. (c) Tao, Y. T.; Liu, C. L.; Lee, S. J.; Chou, S. S. P. *J. Org. Chem.* **1986**, *51*, 4718. (d) Yamada, S.; Ohsawa, H.; Suzuki, T.; Takayama, H. *Chem. Lett.* **1983**, 1003. (e) Desai, S. R.; Gore, V. K.; Mayelvaganan, T.; Padmakumar, R.; Bhat, S. V. *Tetrahedron*, **1992**, *48*, 481.
5. (a) Chou, T. S.; Lee, S. J.; Tso, H. H.; Yu, C. F. *J. Org. Chem.* **1987**, *52*, 5082. (b) Chou, T. S.; Chang, C. Y. *J. Org. Chem.* **1991**, *56*, 4560.

6. (a) Broaddus, C. D. *J. Am. Chem. Soc.* **1966**, *88*, 3863. (b) Zimmermannova, H.; Prochazka, M. *Collect. Czech. Chem. Commun.* **1965**, *30*, 286. (c) Chou, T. S.; You, M. L. *Bull. Inst. Chem., Acad. Sin.* **1986**, *33*, 13.
7. Chou, T. S.; Chang, L. J.; Tso, H. H. *J. Chem. Soc., Perkin Trans. 1.* **1986**, 1039.
8. (a) Chou, S. S. P.; Liou, S. Y.; Tsai, C. Y.; Wang, A. J. *J. Org. Chem.* **1987**, *52*, 4468. (b) Chou, S. S. P.; Lee, W. H. *Synthesis*, **1990**, 219.
9. Chou, T. S.; Tsai, C. Y.; Huang. L. J. *J. Org. Chem.* **1990**, *55*, 5410.
10. Gaoni, Y. *Tetrahedron Lett.* **1977**, 947.