A New and Simple Synthesis of Heterocycle-Fused [*c*]Thiophenes: Reaction of Heteroaromatic Thioketones with Bis(arylsulfonyl)diazomethanes and Phenyliodonium Bis(phenylsulfonyl)methylide

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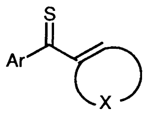
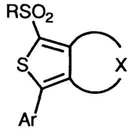
A new method for the synthesis of heterocycle-fused [*c*]thiophenes via reaction of aryl heteroaryl thioketones with the carbene precursors, bis(arylsulfonyl)diazomethanes and phenyliodonium bis(phenylsulfonyl)methylide, is described.

Numerous methods for the synthesis of variously substituted thiophenes have been reported so far.[1,2] One of the most common and useful reactions is probably the Gewald method, which involves the thiophene ring construction via the ring closure of unsaturated nitriles with elemental sulfur.[1,3] Other valuable approaches may be represented by the Paal method and the Hinsberg method, which involves the thiation of 1,4-dicarbonyl compounds and the subsequent ring closure, and condensation of 1,2-dicarbonyl compounds with bis(activated methylene)sulfides.[1,4] A new, useful thiophene synthesis has recently been developed by Nakayama et al. using diketo sulfides (3-thiapentane-1,5-diones).[5] However, even by virtue of these versatile methods in the synthesis of, for example, carbocycle- or heterocycle-fused [*c*]thiophenes, one might occasionally encounter inconvenience in terms of their simplicity, generality or availability of starting materials.[1,6] Therefore, development of a new synthesis of these compounds is always desirable.

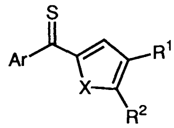
Recently, we have demonstrated that aromatic thioketones reacted with the carbenoids generated from diazodisulfonylmethanes or phenyliodonium disulfonylmethylides, to give the benzo[*c*]thiophenes.[7] The reaction involves the ring closure of the intermediary thiocarbonyl ylides, followed by restorative aromatization via the elimination of a sulfenic acid, thus providing a new entry to the synthesis of benzo[*c*]thiophenes (Scheme 1). These results prompted us to explore the feasibility that this method would be applicable to the synthesis of heterocycle-fused[c]thiophenes **B** when heteroaromatic thioketones **A** are used. Here, we report our successful results using this approach.



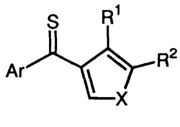
A



B



1, 2, 3, 4



5, 6

$(R^3SO_2)_2CN_2$

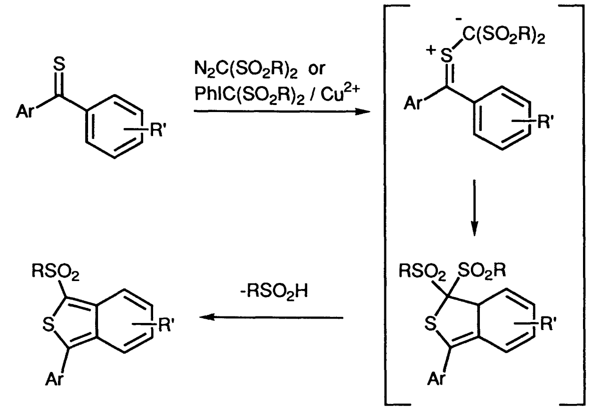
7

$\overset{+\ -}{\text{PhI-C}}(SO_2Ph)_2$

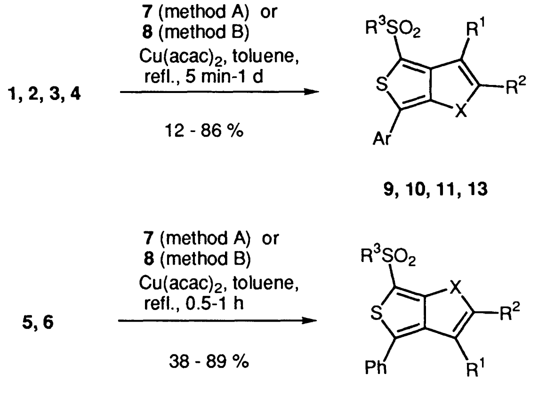
8

	X	Ar	R^1	R^2		R^3
1a	O	Ph	H	H	**7a**	Ph
1b	O	2,4,6-$Me_3C_6H_2$	H	H	**7b**	p-Tol
2	O	Ph	CH=CH-CH=CH			
3	S	Ph	H	H		
4	NMe	Ph	H	H		
5	S	Ph	CH=CH-CH=CH			
6	NMe	Ph	CH=CH-CH=CH			

When furyl phenyl thioketone (**1a**) was heated with diazobis(phenylsulfonyl)methane (**7a**) (Method A) in the presence of a catalytic amount of copper acetylacetonate in toluene, the reaction proceeded smoothly to produce the furo[2,3-*c*]thiophene **9a** in a yield of 62% (Scheme 2). The reaction of **1a** with phenyliodonium bis(phenylsulfonyl)methane (**8**) (Method B) also afforded **9a** albeit in a lower yield (30%).[8] In a similar manner the furo- (**9b–d**), benzofuro- (**10**), thieno- (**11**), benzothieno- (**12**), pyrrolo- (**13**) and indolo- (**14**) fused [*c*]thiophenes were obtained. The results are summarized in Tables 1–3.



Scheme 1



Scheme 2

12, 14

Table 1. Reaction of Thioketones **1–6** with Diazomethanes **7** or Iodonium Methylide **8** to Give Heterocycle-fused [*c*]Thiophenes **9–14**

Thio-ketone	X	Ar	R^1	R^2	R^3	Method	Reaction Time (h)	Prod-uct	Yield (%)
1a	O	Ph	H	H	Ph	A	0.3	**9a**	62
1a	O	Ph	H	H	Ph	B	0.3	**9a**	30
1a	O	Ph	H	H	*p*-Tol	A	1	**9b**	50
1b	O	2,4,6-$Me_3C_6H_2$	H	H	Ph	A	0.3	**9c**	39
1b	O	2,4,6-$Me_3C_6H_2$	H	H	*p*-Tol	A	0.3	**9d**	45
2	O	Ph	CH=CH–CH=CH		Ph	A	2	**10a**	76
2	O	Ph	CH=CH–CH=CH		*p*-Tol	A	0.7	**10b**	86
3	S	Ph	H	H	Ph	A	5	**11a**	71
3	S	Ph	H	H	Ph	B	5 min	**11a**	49
3	S	Ph	H	H	*p*-Tol	A	1	**11b**	75
5	S	Ph	CH=CH–CH=CH		Ph	A	1	**12a**	89
5	S	Ph	CH=CH–CH=CH		*p*-Tol	A	1	**12b**	81
4	NMe	Ph	H	H	Ph	A	1 d	**13a**	12
4	NMe	Ph	H	H	Ph	B[a]	2.5	**13a**	27
4	NMe	Ph	H	H	*p*-Tol	A	1 d	**13d**	18
4	NMe	Ph	H	H	*p*-Tol	B[a]	2.5	**13b**	24
6	NMe	Ph	CH=CH–CH=CH		Ph	A	0.5	**14a**	38
6	NMe	Ph	CH=CH–CH=CH		*p*-Tol	A	0.5	**14b**	51

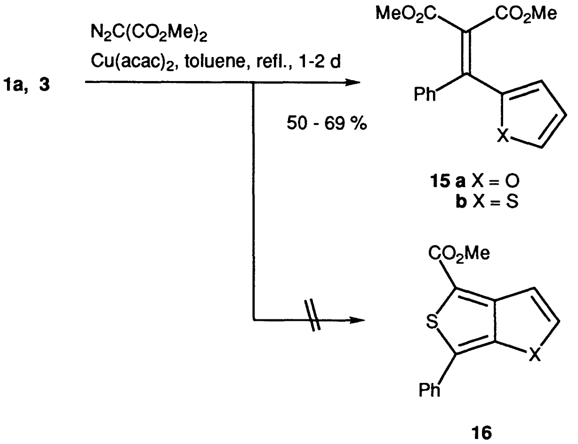
[a] In refluxing CH_2Cl_2.

Table 2. Mp and IR and Mass Spectral Data of Compounds **9–14**, **15**, **17** and **18**

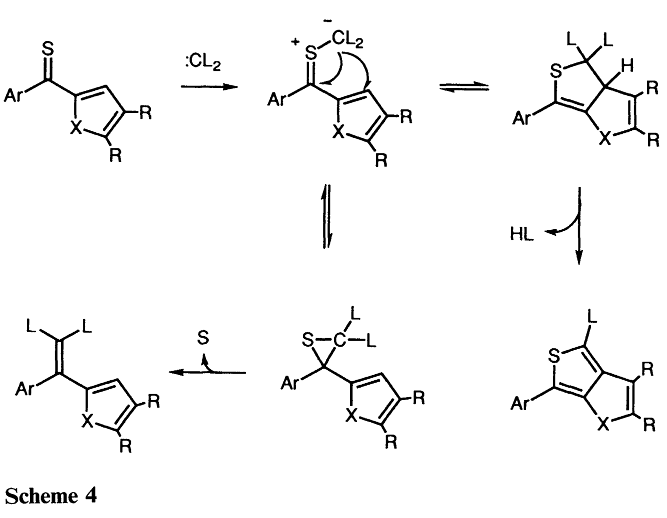
Compound[a]	mp (°C)	IR (KBr) (cm^{-1}) ν (SO_2) or ν (CO, others)	MS (70 eV) M^+	(rel. int, %) M^+-SO_2 (others)
9a	123–124	1320, 1156	340 (100)	276 (10)
9b	109–112	1324, 1156	354 (100)	290 (12)
9c	178–180	1314, 1154	382 (100)	241 (25)
9d	148.5–149	1318, 1154	396 (100)	241 (30)
10a	189.5–190	1322, 1148	390 (100)	326 (20)
10b	171–172	1326, 1146	404 (100)	340 (13)
11a	151–152	1316, 1152	356 (100)	292 (10)
11b	98–98.5	1342, 1152	370 (100)	306 (18)
12a	161–162.5	1324, 1152	406 (100)	342 (5)
12b	196–197	1318, 1144	420 (100)	356 (15)
13a	184–185	1310, 1154	353 (100)	289 (10)
13b	164–164.5	1318, 1152	367 (100)	303 (10)
14a	188–189	1304, 1140	403 (100)	278 (8)
14b	155–157	1302, 1140	417 (100)	353 (2)
15a	77–78	1728	286 (100)	255 (40)
15b	66–67	1730	302 (100)	271 (85)
17	126–127	1614	318 (100)	227 (60)
18	111–113	1318, 1150, 1644, 3448	386 (45)	121 (100)

[a] Satisfactory microanalyses obtained: C, H ±0.3.

On the other hand, the treatment of thioketones **1a** and **3** with dimethyl diazomalonate afforded the methylenemalonates **15** exclusively, no expected [*c*]thiophenes **16** being formed (Scheme 3). A mechanism shown in Scheme 4 can rationalize these results.



Scheme 3



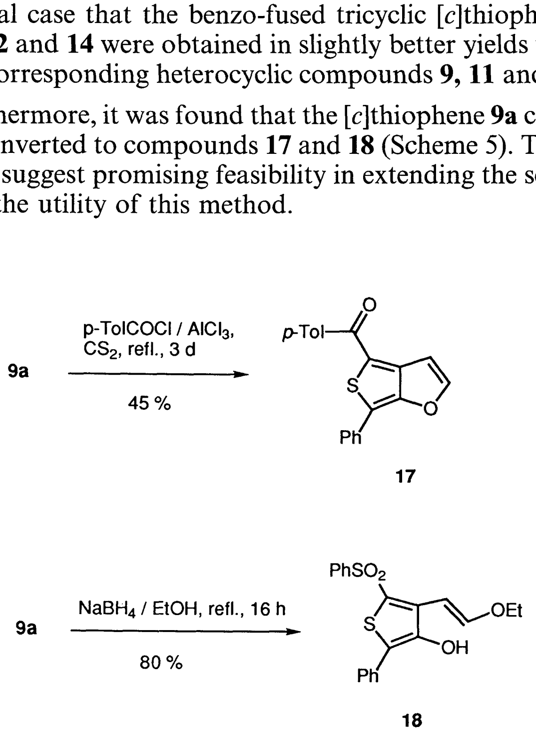
Scheme 4

Table 3. ^1H and ^{13}C NMR Spectral Data of Compounds **9–15**, **17** and **18**

Compound	^1H NMR ($CDCl_3$/TMS) δ, *J* (Hz)	^{13}C NMR ($CDCl_3$/TMS) δ, (DEPT)
9a	6.79 (d, 1H, *J*= 2.31), 7.30–7.42 (m, 3H), 7.44–7.59 (m, 3H), 7.75 (dd, 2H, *J*= 7.26, 1.65), 7.80 (d, 1H, *J*= 2.31), 8.02 (dd, 2H, *J*= 8.58, 1.98)	103.77 (CH), 124.83 (C), 126.49 (2CH), 126.86 (2CH), 128.88 (CH), 129.16 (2CH), 129.32 (2CH), 130.10 (C), 133.12 (CH), 139.39 (C), 142.53 (C), 151.43 (C), 156.24 (CH)
9b	2.38 (s, 3H), 6.77 (d, 1H, *J*= 2.31), 7.29 (d, *J*= 8.58), 7.32–7.43 (m, 3H), 7.73 (dd, 2H, *J*= 6.93, 1.98), 7.78 (d, 1H, *J*= 2.31), 7.89 (d, 2H, *J*= 8.58)	21.56 (CH_3), 103.77 (CH), 118.58 (C), 124.40 (C), 126.45 (2CH), 126.93 (2CH), 128.79 (CH), 129.14 (2CH), 129.95 (2CH), 130.15 (C), 139.08 (C), 139.64 (C), 144.13 (C), 151.41 (C), 156.12 (CH)
9c	2.10 (s, 6H), 2.31 (s, 3H), 6.76 (d, 1H, *J*= 2.31), 6.95 (s, 2H), 7.49–7.61 (m, 3H), 7.69 (d, 1H, *J*= 2.31), 8.03 (dd, 2H, *J*= 8.25, 1.98)	20.70 (2CH_3), 21.13 (Me), 103.79 (CH), 119.76 (C), 122.55 (C), 124.06 (C), 126.92 (2CH), 128.61 (2CH), 129.31 (2CH), 133.06 (CH), 138.15 (C), 138.58 (2C), 139.58 (C), 142.62 (C), 152.27 (C), 156.30 (CH)
9d	2.16 (s, 6H), 2.31 (s, 3H), 2.40 (s, 3H), 6.75 (d, 1H, *J*= 2.31), 6.95 (s, 2H), 7.31 (d, 2H, *J*= 8.58), 7.68 (d, 1H, *J*= 2.31), 7.92 (d, *J*= 8.58)	20.70 (2CH_3), 21.13 (CH_3), 21.58 (CH_3), 103.77 (CH), 120.32 (C), 122.06 (C), 124.15 (C), 126.99 (2CH), 128.59 (2CH), 129.94 (2CH), 137.82 (C), 138.58 (2C), 139.51 (C), 139.71 (C), 144.02 (C), 152.23 (C), 156.15 (CH)
10a	7.30–7.57 (m, 9H), 7.82 (dd, 2H, *J*= 7.92, 1.65), 8.08 (dd, 2H, *J*= 8.25, 1.65), 8.45 (d, 1H, *J*= 7.58)	112.42 (CH), 119.94 (C), 122.30 (C), 123.93 (CH), 124.20 (C), 124.49 (CH), 126.61 (2CH), 126.90 (2CH), 128.86 (CH), 129.16 (2CH), 129.40 (2CH), 129.95 (CH), 130.17 (C), 133.35 (CH), 135.16 (C), 142.42 (C), 151.84 (C), 164.15 (C)
10b	2.35 (s, 3H), 7.27 (d, 2H, *J*= 8.25), 7.31–7.52 (m, 6H), 7.81 (dd, 2H, *J*= 7.26, 1.32), 7.96 (d, 2H, *J*= 8.25), 8.44 (d, 1H, *J*= 7.58)	21.56 (CH_3), 112.36 (CH), 119.96 (C), 122.87 (C), 123.77 (C), 123.86 (CH), 124.47 (CH), 126.56 (2CH), 126.95 (2CH), 128.75 (CH), 129.13 (2CH), 129.85 (CH), 130.01 (2CH), 130.20 (C), 134.84 (C), 139.48 (C), 144.40 (C), 151.80 (C), 164.09 (C)
11a	7.33–7.57 (m, 8H), 7.65 (dd, 2H, *J*= 6.60, 1.32), 8.04 (dd, 2H, *J*= 8.25, 1.98)	117.12 (CH), 123.63 (C), 126.45 (2CH), 126.86 (2CH), 129.14 (CH), 129.34 (2CH), 129.38 (2CH), 131.79 (C), 133.12 (CH), 136.03 (C), 137.91 (CH), 138.27 (C), 142.55 (C), 149.93 (C)
11b	2.36 (s, 3H), 7.28 (d, 2H, *J*= 8.25), 7.34–7.47 (m, 4H), 7.62 (d, 1H, *J*= 5.61), 7.65 (dd, 2H, *J*= 7.92, 1.65), 7.91 (d, 2H, *J*= 8.25)	21.55 (CH_3), 117.16 (CH), 124.29 (C), 126.45 (2CH), 126.95 (2CH), 129.05 (CH), 129.36 (2CH), 129.95 (2CH), 131.88 (C), 135.97 (C), 137.68 (CH), 137.86 (C), 139.71 (C), 144.13 (C), 149.68 (C)
12a	7.15 (ddd, 1H, *J*= 7.92, 7.92, 0.99), 7.32 (ddd, 1H, *J*= 7.92, 7.92, 0.99), 7.48–7.68 (m, 10H), 8.11 (dd, 2H, *J*= 7.92, 1.98)	122.39 (CH), 123.66 (CH), 124.33 (C), 124.94 (CH), 126.95 (2CH), 127.53 (CH), 129.11 (2CH), 129.23 (2CH), 129.32 (2CH), 129.59 (C), 129.81 (CH), 131.57 (C), 133.48 (CH), 139.03 (C), 141.79 (C), 142.35 (C), 144.85 (C), 144.98 (C)
12b	2.39 (s, 3H), 7.16 (ddd, 1H, *J*= 8.58, 8.58, 1.32), 7.32 (d, 2H, *J*= 8.24), 7.33 (ddd, 1H, *J*= 8.58, 7.26, 1.32), 7.48–7.53 (m, 3H), 7.59–7.69 (m, 4H), 7.99 (d, 2H, *J*= 8.24)	21.62 (CH_3), 122.39 (CH), 123.68 (CH), 124.90 (CH), 127.04 (2CH), 127.49 (CH), 129.09 (2CH), 129.27 (2CH), 129.65 (C), 129.76 (CH), 129.95 (2CH), 131.66 (C), 138.90 (C), 138.97 (C), 142.01 (C), 144.45 (C), 144.53 (C), 145.05 (C)
13a	3.39 (s, 3H), 6.37 (d, 1H, *J*= 3.30), 7.18 (d, 1H, *J*= 3.30), 7.39–7.50 (m, 8H), 8.03 (dd, 2H, *J*= 8.25, 2.31)	35.13 (Me), 96.24 (CH), 115.92 (C), 123.83 (C), 126.59 (2CH), 128.59 (2CH), 128.70 (CH), 129.05 (2CH), 130.20 (2CH), 130.85 (C), 132.50 (CH), 138.81 (C), 141.53 (C), 142.93 (CH), 143.29 (C)
13b	2.35 (s, 3H), 3.38 (s, 3H), 6.35 (d, 1H, *J*= 3.30), 7.16 (d, 1H, *J*= 3.30), 7.25 (d, 2H, *J*= 8.25), 7.38–7.45 (m, 5H), 7.91 (d, 2H, *J*= 8.25)	21.46 (CH_3), 35.04 (CH_3), 96.14 (CH), 116.42 (C), 123.31 (C), 126.60 (2CH), 128.50 (2CH), 128.55 (CH), 129.61 (2CH), 130.14 (2CH), 130.85 (C), 138.74 (C), 140.34 (C), 141.22 (C), 142.75 (CH), 143.25 (C)
14a	3.91 (s, 3H), 7.04 (dd, 1H, *J*= 8.25, 7.92), 7.13 (d, 1H, *J*= 8.25), 7.36 (dd, 1H, *J*= 8.25, 7.92), 7.45–7.54 (m, 6H), 7.75 (dd, 2H, *J*= 7.59, 1.98), 7.82 (d, 1H, *J*= 7.92), 8.01 (dd, 2H, *J*= 7.92, 1.65)	31.97 (CH_3), 106.18 (C), 109.22 (CH), 118.83 (C), 120.21 (CH), 120.86 (CH), 126.81 (2CH), 127.22 (CH), 128.44 (2CH), 129.14 (2CH), 129.25 (2CH), 129.40 (CH), 130.19 (C), 132.54 (C), 132.59 (CH), 140.02 (C), 144.26 (C), 145.10 (C), 148.69 (C)
14b	2.36 (s, 3H), 3.92 (s, 3H), 7.04 (dd, 1H, *J*= 8.25, 7.92), 7.14 (d, 2H, *J*= 8.25), 7.27 (d, 2H, *J*= 8.25), 7.36 (dd, 1H, *J*= 8.25, 7.92), 7.45–7.54 (m, 3H), 7.75 (dd, 2H, *J*= 8.25, 1.65), 7.82 (d, 1H, *J*= 7.92), 7.90 (d, 2H, *J*= 8.25)	21.49 (CH_3), 31.97 (CH_3), 106.79 (C), 109.20 (CH), 118.87 (C), 120.14 (CH), 120.86 (CH), 126.92 (2CH), 127.20 (CH), 128.46 (2CH), 129.13 (2CH), 129.34 (CH), 129.85 (2CH), 130.17 (C), 132.63 (C), 139.64 (C), 141.35 (C), 143.52 (C), 144.90 (C), 148.73 (C)
15a	3.35 (s, 3H), 3.90 (s, 3H), 6.17 (dd, 1H, *J*= 3.30, 0.66), 6.41 (dd, 1H, *J*= 3.30, 1.98), 7.26–7.30 (m, 2H), 7.38–7.41 (m, 3H), 7.52 (dd, 1H, *J*= 1.98, 0.66)	52.06 (CH_3), 52.47 (CH_3), 112.33 (CH), 118.65 (CH), 120.22 (C), 127.96 (2CH), 128.75 (2CH), 128.82 (CH), 136.59 (C), 141.82 (C), 145.66 (CH), 151.88 (C), 164.46 (C), 167.28 (C)
15b	3.55 (s, 3H), 3.78 (s, 3H), 7.01 (dd, 1H, *J*= 4.95, 3.96), 7.06 (dd, 1H, *J*= 3.96, 1.32), 7.26 (dd, 2H, *J*= 7.92, 1.98), 7.33–7.41 (m, 3H), 7.47 (dd, 1H, *J*= 4.95, 1.32)	52.15 (CH_3), 52.67 (CH_3), 123.16 (C), 127.42 (CH), 128.05 (2CH), 128.91 (2CH), 129.31 (CH), 130.38 (CH), 131.25 (CH), 139.73 (C), 141.67 (C), 148.25 (C), 165.14 (C), 167.01 (C)
17	2.43 (s, 3H), 6.45 (d, 1H, *J*= 2.31), 7.28 (d, 2H, *J*= 7.92), 7.33 (dd, 1H, *J*= 7.26, 1.65), 7.41 (dd, 2H, *J*= 7.26, 7.26), 7.73 (d, 1H, *J*= 2.31), 7.78 (d, 2H, *J*= 7.92), 7.85 (dd, 2H, *J*= 7.26, 1.65)	21.64 (CH_3), 105.78 (CH), 121.18 (C), 125.44 (C), 126.65 (CH), 128.68 (CH), 128.91 (2CH), 129.05 (4CH), 130.80 (C), 136.15 (C), 139.58 (C), 142.68 (C), 152.43 (CH), 155.31, 186.66 (C)
18	1.32 (t, 3H, *J*= 6.93), 3.90 (q, 2H, *J*= 6.93), 5.68 (s, 1H), 6.21 (d, 1H, *J*= 12.87), 7.30–7.55 (m, 8H), 7.49 d, 1H, *J*= 12.87), 7.90–7.94 (m, 2H)	14.66 (CH_3), 65.70 (CH_2), 96.42 (CH), 125.69 (C), 127.19 (2CH), 127.98 (2CH), 128.68 (CH), 129.09 (2CH), 129.45 (2CH), 131.01 (C), 133.08 (CH), 141.87 (C), 146.48 (C), 153.78 (CH)

The reactive thiocarbonyl ylide species,[9] initally formed from the carbenoid and the thioketone, is in equilibrium with both the 1,3- and 1,5-dipolar cyclization intermediates during the reaction. The former one (thiirane) affords the ethylene compound with the extrusion of a sulfur atom and the latter species gives the [*c*]thiophene with the elimination of HL. Based on the experimental results, the formation of the final products via the competitive reaction paths seems to be affected by mainly both the capability of the leaving group L and the aromaticity of the product: The facile leaving group L such as a sulfonyl group preferentially leads to the [*c*]thiophene formation whereas the group L such as a methoxycarbonyl group which is reluctant to leave, consequently directs the reaction toward the alternative path. The increasing aromaticity[10] of the heterocycle-fused [*c*]thiophenes in the order of benzo-[7] > thieno- > furo- ≅ pyrrolo-, tends to increase the yields (Table 1). It is the typical case that the benzo-fused tricyclic [*c*]thiophenes **10, 12** and **14** were obtained in slightly better yields than the corresponding heterocyclic compounds **9, 11** and **13**.

Furthermore, it was found that the [*c*]thiophene **9a** could be converted to compounds **17** and **18** (Scheme 5). These facts suggest promising feasibility in extending the scope and the utility of this method.



Scheme 5

In conclusion, the present method provides simple and facile access to the heterocycle-fused [*c*]thiophenes starting from the easily available thioketones and the carbene precursors.

Melting points were measured on a Yanaco MP-S2 melting point apparatus and are uncorrected. The following instruments were used for recording the spectra. IR: Hitachi 270-30, MS: Hitachi RMU 7M or M-80; ^{1}H (270 MHz) and ^{13}C NMR (67.5 MHz): JEOL JNM-EX 270.

Thieno[3,4-*b*]furans (9), -benzofurans (10), -thiophenes (11), -benzothiophenes (12), -pyrroles (13) and -indoles (14); General Procedure:
A mixture of thioketone **1–6** (2.0 mmol), Cu(acac)$_2$ (0.04 mmol) and bis(arylsulfonyl)diazomethane **7** (2.0–2.5 mmol) (Method A) or phenyliodonium bis(phenylsulfonyl)methylide (**8**, 2.0–2.6 mmol) (Method B) was heated in toluene (25 mL) under reflux under an Ar atmosphere. The mixture was cooled, concentrated, and subjected to column chromatography [silica gel, EtOAc/hexane (1 : 20–90) or CH$_2$Cl$_2$/hexane (1 : 1–50)] to give colorless or yellowish [*c*]thiophenes **9–14** as crystals (recrystallized from CH$_2$Cl$_2$/hexane).

4-(4-Toluoyl)-6-phenylthieno[3,4-*b*]furan (17):
A mixture of compound **9a** (204 mg, 0.6 mmol), *p*-toluoyl chloride (280 mg, 1.8 mmol) and AlCl$_3$ (480 mg, 3.6 mmol) was heated in CS$_2$ (30 mL) under reflux for 95 h. After being cooled, the mixture was treated with H$_2$O, extracted with Et$_2$O and dried (MgSO$_4$). The extract was evaporated and the residue was column chromatographed (*vide supra*) to give compound **17** as red plates (recrystallized from CH$_2$Cl$_2$/hexane); yield: 84 mg (44 %).

4-(2-Ethoxyvinyl)-3-hydroxy-2-phenyl-5-(phenylsulfonyl)thiophene (18):
A mixture of compound **9a** (68 mg, 0.2 mmol) and NaBH$_4$ (76 mg, 2 mmol) in EtOH (30 mL) was heated under reflux for 16.5 h. The mixture was then treated with aq NH$_4$Cl solution, extracted with Et$_2$O and dried (MgSO$_4$). Evaporation of the extract and column chromatography (*vide supra*) of the residue afforded compound **18** as pale yellow crystals (from CH$_2$Cl$_2$ hexane); yield: 62 mg (80 %).

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