Synthesis of 1,4-Dithiafulvenes and 1,4-Dithiafulvalenes by Carbonyl Olefination Using 2-Dimethoxyphosphinyl-1,3-benzodithiole

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(Received April 11, 1978)

The reactions of 1,3-dithiolylium salts with tertiary phosphines and trialkyl phosphites in dry acetonitrile gave the corresponding phosphonium salts and the phosphonates respectively in high yields. Both 2-triphenylphosphonio-1,3-benzodithiole tetrafluoroborate and 2-dimethoxyphosphinyl-1,3-benzodithiole were deprotonated with butyllithium in THF at −78 °C and the resulting phosphorane (*A*) and the phosphonate carbanion (*B*) reacted with a variety of carbonyl compounds to give 1,4-benzodithiafulvenes in 74—98% yields. Moreover, *B* reacted with conjugated cyclic ketones (**5**) such as dibenzo[a,d]cyclohepten-5-one, 10*H*-9-thiaanthracen-10-one, 9-alkyl-9,10-dihydro-9-azaanthracen-10-one, 9-fluorenone, and so on to give 1,4-benzodithiafulvalenes (**6**) in 73—96% yields. The UV spectral data of **6** were discussed in comparison with those of **5**.

Heteroaromatic cations such as pyrylium, thiopyrylium, pyridinium, thiazolium, and dithiolylium have been attractive target of research both for physical organic and synthetic chemists. Preparation and use of dithiolylium salts have acquired renewed interest in connection with the synthesis of tetrathiafulvalene derivatives, one component of organic metals. Our interest to develop new utility of heteroaromatic cations in organic synthesis has led us to general preparation of 1,4-dithiafulvenes and fulvalenes, starting from 1,3-dithiolylium salts.

On the other hand, fulvenes and fulvalenes have been investigated from the standpoint of both synthetic and theoretical aspects and dithia analogues have also been investigated as their iso-π-electronic systems. However, there has been no general synthetic method of 1,4-dithiafulvenes (2-alkylidene-1,3-dithioles), although those with electron-withdrawing groups on the exo-methylene can be prepared by condensation of 2-methylthio-1,3-dithiolylium salts with acitve methylene compounds in 34—77% yields.[1] Some of them were obtained among photolysis products of 1,2,3-thiadiazoles in 45—50% yields.[2] It was also reported that 2-benzylidene-4-phenyl-1,3-dithole was prepared by the reaction of 2-methylthio-4-phenyl-1,3-dithiolylium iodide with benzylmagnesium chloride, but this method required long reaction time and the yield was low.[3]

On the other hand, there are a couple of recent reports on the preparation of 2-alkylidene-1,3-dithioles when electron-withdrawing groups are on the ring. 1,3-Dithiol-2-ylidene-tributylphosphoranes were prepared *in situ* by addition of activated acetylenes to a mixture of tributylphosphine and carbon disulfide and used for subsequent Wittig reaction.[4] Intermediate phosphorane can be trapped as a phosphonium salt when the active acetylene has at least one carboxylic acid group.[5] The intermediacy of the same kind of phosphorane during desulfurization of 4,5-dicyano-1,3-dithiole-2-thione with tertiary phosphines was recently reported,[6] however, Scherowsky and Weiland could not detect the same kind of phosphorane in desulfurization of 1,3-benzodithiole-2-thione with triethyl phosphite.[7] To our knowledge, only these three special cases have been reported to date on this type of phosphorane and their Wittig reaction.

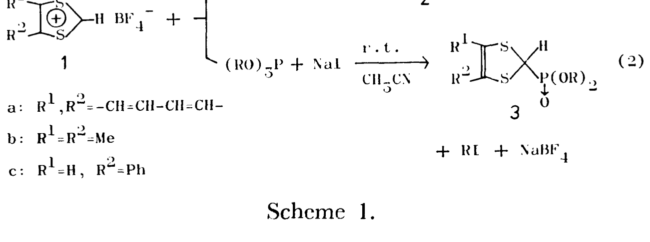
1,4-Dithiafulvalenes have been prepared by condensation of 1,3-dithiolylium salts with cyclopentadienide anions[8] and active methylenes contained in heterocycles,[9] and their properties were compared with sesquifulvalenes which are iso-π-electronic each other.

Now, it is expected that 1,4-dithiafulvenes can generally be prepared by a single method, *i.e.*, Wittig-Horner reaction with acyclic and cyclic carbonyl compounds, if phosphonium salts or phosphonates are prepared from 1,3-dithiolylium salts. This paper offers a new synthetic method for such type of compounds.

Results and Discussion

Synthesis of 2-Phosphonio- and 2-Dialkoxyphosphinyl-1,3-dithioles. Slightly exothermic reaction took place immediately on addition of tertiary phosphine to 1,3-dithiolylium tetrafluoroborate (**1**) in dry acetonitrile solution and stirring was continued for 2 h at room temperature. After evaporation of the solvent under reduced pressure, addition of dry ether to the residue gave the precipitates, 2-phosphonio-1,3-dithiole tetrafluoroborate (**2**) in high yields.

1,3-Dithiolylium salt (**1**) reacted also with trialkyl phosphite in the presence of an equimolar amount of sodium iodide in dry acetonitrile under nitrogen at room temperature. Michaelis-Arbuzov reaction took place very rapidly to give 2-dialkoxyphosphinyl-1,3-dithioles (**3**) in high yields while the reaction did not take place in the absence of sodium iodide under otherwise the same conditions. Yields and mp of **2** and **3** are shown in Table 1.



Scheme 1.

The structures of these products (**2** and **3**) were confirmed by means of elemental analyses, IR, and NMR spectra. The IR spectra of **2** showed very strong absorption bands at about 1100 and 520 cm^{-1}

Table 1. Yields and mp of phosphonium salts (**2**) and phosphonates (**3**)

Compound	R^1	R^2	R	Yield (%)	Mp (°C)
2a	-CH=CH-CH=CH-		Ph	87	211.5—212.5 (dec)
2b	-CH=CH-CH=CH-		*n*-Bu	90	166.5—167.0
2c	Me	Me	Ph	84	175.0—177.0 (dec)
3a	-CH=CH-CH=CH-		Me	93	122.0—123.0
3b	-CH=CH-CH=CH-		Et	90	115.5—116.5
3c	Me	Me	Me	83	—
3d	H	Ph	Me	90	87.0— 88.0

(BF_4^-). The NMR spectrum of each of **2** showed a broad singlet signal assignable to 2-CH (*i.e.*, $J_{PCH} \fallingdotseq 0$). The NMR spectrum of **2c** showed a singlet signal at an extraordinarily high field as a vinylic methyl ($\delta = 1.30$) assignable to two methyl groups at 4 and 5 positions. IR spectra of all the phosphonates (**3**) showed strong absorption bands characteristic of P=O (1250—1260) and P-O-C (1050—1065 and 1030—1040 cm^{-1}), respectively.

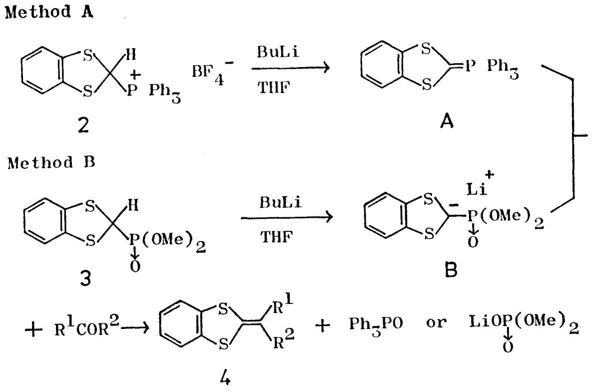
Each NMR spectrum of **3** showed a doublet signal at δ 4.75—5.06 ($J_{PCH}=4.4$—5.8 Hz) assignable to 2-CH and also a doublet signal at δ 3.63—3.85 ($J_{POCH}=$ 10.4—10.8 Hz) assignable to POMe except for **3b**. The compounds (**3a**, **b**, and **d**) showed the parent peak (4—9%) and the base peak assignable to $M^+-P(O)(OR)_2$ in MS.

The ^{31}P-NMR spectrum of **3a** exhibited a signal at δ −19 ppm.

Gross *et al.*[10] reported that the ^{31}P-NMR spectrum of 5,6-dichloro-2-diethoxyphosphinyl-1,3-benzodioxole exhibited a signal at δ −7.3 ppm, and that this value was compared with those of diethyl methylphosphonate and its monochloro-, dichloro-, and trichloromethyl compounds (δ_P −30, −18.1, −9.3, and −6.5 ppm, respectively)[11] in relation to the electronegativity of the substitutent. The effect of the substitution of a catechol ring for two hydrogen atoms of the methyl group nearly corresponded to that of three chlorine atoms for three hydrogen atoms of the methyl group. In the present case, the effect of the substitution of a thiocatechol ring for two hydrogen atoms of the methyl group is smaller than that of a catechol ring and corresponds approximately to that of one chlorine atom for the methyl group.

The compound (**3c**) has low melting point (−20 °C), and was purified by dry column chromatography over neutral alumina. However, this compound is so hygroscopic and sensitive to air as an oil or in solution that it could not be purified enough for elemental analysis.

*Wittig-Horner Reaction of 2-Triphenylphosphonio-1,3-benzodithiole Tetrafluoroborate (**2a**) and 2-Dimethoxyphosphinyl-1,3-benzodithiole (**3a**): Synthesis of 1,4-Benzodithiafulvenes (**4**).*[12] Both 2-triphenylphosphonio-1,3-benzodithiole tetrafluoroborate (**2a**) and 2-dimethoxyphosphinyl-1,3-benzodithiole (**3a**) were deprotonated with butyllithium in THF at −78 °C and the resulting phosphorane (*A*) and phosphonate carbanion (*B*) were allowed to react with a wide variety of carbonyl compounds to give the expected products, *i.e.*, 1,4-benzodithiafulvene (**4**) at low temperatures in very good yields. The reaction scheme is shown below.



Scheme 2.

Comparison of two methods recommends Method B for synthetic purpose by the following reasons: i) shorter reaction time of Method B than Method A, because the former can be carried out in homogeneous solution but the deprotonation of **2a** is a heterogeneous reaction, ii) no need of chromatographic separation of the product, the resulting phosphoric acid being soluble in water, iii) higher reactivity of *B* than *A*, hence the former can be carried out at lower temperatures than the latter, and *B* reacted smoothly with *p*-dimethylaminobenzaldehyde at low temperature to give **4a** in high yield, but *A* did not react with the same aldehyde even under reflux of THF, iv) higher yield in every case, and v) no by-production of dibenzotetrathiafulvalene, which is the case in method A when the reaction is carried out at higher temperatures (room temperature).

Yields and mp of **4** are shown in Table 2.

All the products (**4a**—**g**) showed correct elemental analysis and reasonable IR, ^1H-NMR, and MS spectra. All **4** showed the parent peak as the base peak in MS, with the exception of **4b** and **4f**. This fact shows large stability of the parent radical cations which are contained in 1,4-benzodithiafulvene ring. The parent peak of **4b** appeared at *m/e* 272 (88%) and the base peak at *m/e* 257 assignable to $M^+ -Me$. The parent peak of **4f** appeared at *m/e* 268 (94%) and the base peak at *m/e* 128 assignable to $M^+-C_6H_4S_2$.

The phosphonate carbanion (*B*) reacted also with 3-buten-2-one (methyl vinyl ketone) to give crude 2-(1-methyl-2-propenylidene)-1,3-benzodithiole (**4r**) in 53% yield. But this compound could not be purified

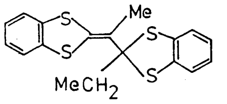
Table 2. Yields and mp of 1,4-benzodithiafulvenes (**4**)

	R^1	R^2	Method	Yield (%)	Mp (°C)
4a	p-$Me_2NC_6H_4$	H	A	No reaction	
			B	95	145—146
b	p-$MeOC_6H_4$	H	A	77 [75][a]	155—156
c	p-MeC_6H_4	H	A	75 [74]	149.5—151
			B	94	
d	Ph	H	A	74 [72]	133—134.5
e	p-ClC_6H_4	H	A	82 [79]	190—190.8
f	PhCH=CH	H	A	78 [80]	148—149
g	MeCH=CH	H	B	95	72— 73
h	$-(CH_2)_4-$		B	96	105.5—107
i	$-(CH_2)_5-$		B	98	96— 97.5
j	$-CH{=}CMeCH_2CMe_2CH_2-$		B	87	99—100
k	PhCH=CH	Me	B	96	170—171
l	p-MeC_6H_4	Me	B	92	80— 81
m	Ph	Me	B	94	oil
n	p-ClC_6H_4	Me	B	91	97— 98
o	p-$MeOC_6H_4$	p-$MeOC_6H_4$	B	96	105—106
p	Ph	Ph	B	80	96— 97
q	p-ClC_6H_4	p-ClC_6H_4	B	95	113—114

a) Numerical values in parentheses show yields of triphenylphosphine oxide.

enough for elemental analysis because of its instability.

The reaction of *B* with acetaldehyde was also carried out under the genreal procedure. Purification of the product by preparative thin-layer chromatography (SiO_2/CCl_4) afforded, however, only a trace amount of a product. The structure of the compound was proposed to be the dimer of the expected one from its ^1H-NMR spectral data; δ (CCl_4) 1.07 (t, 3H), 1.99 (s, 3H), 2.42 (q, 2H), and 6.7—7.6 (m, 8H).



The same type of dimerization accompanied by prototropy is known for active methylene contained in benzothiazoline.[13]

The reaction of *B* with 9(10*H*)-anthracenone resulted in proton abstraction to give an oxidized product, *i.e.*, 9,10-anthracenedione, whereas *B* did not react with 10,10-dibenzyl-10*H*-anthracen-9-one at all, probably because of steric hindrance.[14]

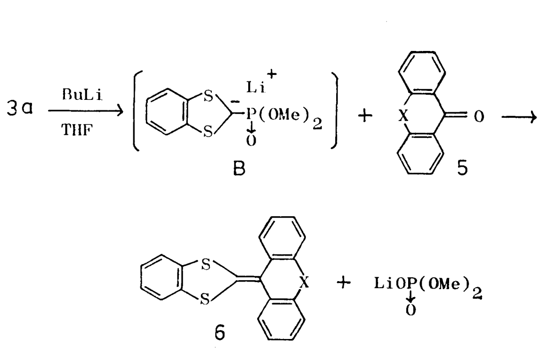
Moreover, the phosphonate carbanion derived from **3d** reacted with 4,4′-dichlorobenzophenone to give 2-[bis(p-chlorophenyl)methylene]-4-phenyl-1,3-dithiole in 83% yield.

It should be noted that extraordinarily rapid Wittig-type reaction was observed in both methods A and B as compared with usual reaction conditions.[15] Furthermore, *B* reacted with cycloalkanones, acetophenones, and even benzophenones at low temperatures in contrast to 1,3-dithiacyclohexylidenetrimethoxyphosphorane which did not react with those ketones mentioned above even by heating at 60 °C for 24 h.[16] It seems that the high reactivity of phosphorane (*A*) and phosphonate carbanion (*B*) can be attributed to the following reasons. These intermediates, especially *B*, can be classified as antiaromatic anions and hence high reactivity is expected toward carbonyl compounds, moreover, it is also probable in our case that some contribution of pseudoaromaticity (dithiolylium) to the product lowered the energy of the transition state, because that of Wittig reaction has been shown to lie at the decomposition of the betaine.[17]

In fact, Mikolajczyk *et al.*[18] and Kruse *et al.*[19] recently reported the preparation of di(thioalkyl)methylphosphonates and their use in Wittig-Horner reaction to give ketone dithioacetals in high yields at low temperatures. However, comparison of reactivity of carbanions of these phosphonates and *B* has not yet been done.

As described above, Wittig-Horner reaction of 2-dimethoxyphosphinyl-1,3-dithioles has been shown to be very useful for the synthesis of 1,4-dithiafulvenes which could not be synthesized by conventional methods or were obtained only in low yields. At the same time, some limitations (steric hindrance, *etc.*) of this new method were revealed.

*Wittig-Horner Reaction of 2-Dimethoxyphosphinyl-1,3-benzodithiole (**3a**) with Conjugated Cyclic Ketones: Synthesis of 1,4-Benzodithiafulvalenes (**6**).*[20] A new synthetic method for the preparation of **4** by Wittig-

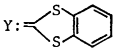
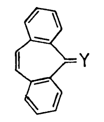
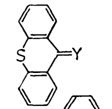
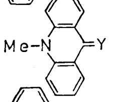
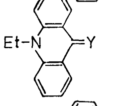
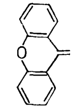
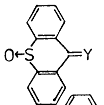
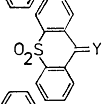
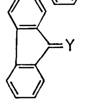
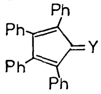
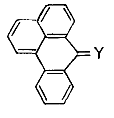
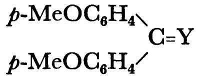
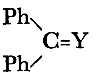
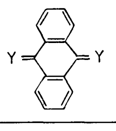


Scheme 3.

Horner reaction of **3a** was extended successfully to the preparation of 1,4-benzodithiafulvalenes (**6**). The phosphonate carbanion (*B*) derived from **3a** reacted with conjugated cyclic ketones (**5**) such as dibenzo-[a,d]cyclohepten-5-one, 9-thiaanthracen-10-one, 9-alkyl-9*H*-9-azaanthracen-10-one, 9-oxaanthracen-10-one (xanthone), 9-fluorenone, tetraphenylcyclopentadienone (tetracyclone), and so on, to afford 1,4-dithia-analogs of heptafulvalene or sesquifulvalene (**6**) in good yields. Yields and mp of **6** and UV spectral data of **6** and **5** are shown in Table 3.

It is noteworthy that all **6** were obtained by the same procedure irrespective of the nature of the carbonyl compounds (**5**), *i.e.*, group I (**5a**, **b**, **c**, **d**, and **e**) which

TABLE 3. YIELDS AND mp OF 1,4-BENZODITHIAFULVALENES (**6**) AND FULVENES (**4o**, **4p**) AND UV SPECTRAL DATA OF THEM AND THE CORRESPONDING KETONES (**5**)

		Mp (°C)	**6** Y:= 		**5** Y:=O		
		Yield (%)	$\lambda_{max}^{CH_2Cl_2}$ a) (nm)	log ε	$\lambda_{max}^{CH_2Cl_2}$ a) (nm)	log ε	$\Delta\lambda$ b) (nm)
6a		179.0—180.0 83	340 sh	4.15	361	3.89	−21
6b		219.0—220.0 88	363	4.36	382	3.98	−19
6c		210.0—211.0 62	395	4.28	400	4.13	−5
6d		205.0—206.0 56	399	4.28	401	4.26	−2
6e		202.0—203.0 84	370	4.42	341.5	3.89	+28.5
6f		246.0—247.5 75	370	4.37	340	3.67	+30
6g		315.0—316.0 92	402	4.24	286	3.96	+116
6h		205.0—206.0 96	402 sh	4.66	327.5 sh	3.57	+74.5
6i		383.0—385.0 75	435	4.60	340	3.88	+95
6j		256.0—257.0 80	424	4.49	407 sh	4.06	+17
4o	 $(p\text{-}MeOC_6H_4)_2C{=}Y$	105.0—106.0 96	326	4.35	292	4.48	+34
4p	 $Ph_2C{=}Y$	96.0— 97.0 80	329	4.34	252.5	4.34	+76.5
Cf.		262.0—263.0 73	416	3.97	—	—	—

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a) Only the longest absorption maximum, whose log ε are greater than 3.5 (probably ascribed to π-π* excitation with CT character), is shown. See experimental section for other data. b) The difference of λ_{max} of the product (**6**) and the ketone (**5**) is shown, *i. e.*, $\Delta\lambda=\lambda_{max}(\mathbf{6})-\lambda_{max}(\mathbf{5})$

can be classified as π-excessive carbonyl compounds, group II (**5h**, **i**, and **j**) which can be classified as π-deficient carbonyl compounds, group III (**5o** and **p**) which are benzophenones.

The structures of these 1,4-benzodithiafulvalenes (**6**) were confirmed by means of the elemental analyses, IR, ^{1}H-NMR, UV, and mass spectra. All **6** showed reasonable IR and ^{1}H-NMR spectra without any significant characteristic features. The molecular ion peak in MS was the base peak in all **6** except for **6d** and **6f**. This fact shows large stability of the parent radical cations which are conjugated through the ring system. The parent peak of **6d** appeared at *m*/*e* 359 (72%) and the M^+-Et peak as the base peak. The parent peak of **6f** appeared at *m*/*e* 364 (48%) and the $M^+-C_7H_4OS_2$ ($C_{13}H_8S$) peak as the base peak.

A comparison of absorption maxima of the longest wave length in the UV spectra of compounds **5** and **6** with log $\varepsilon > 3.5$ (probably to be ascribed to π-π* excitation with CT character) reveals the following facts:

—In group I, the longest absorption of **6** is observed at a shorter wavelength than that of **5**, except for the case of **6e**.

—In groups II and III, the longest absorption of **6** and **4** is observed at a longer wavelength than that of **5**.

—In comparison of the data of the sulfides (**5b**/**6b**), the sulfoxides (**5f**/**6f**), and the sulfones (**5g**/**6g**), the distinct change is observed from the blue shift (−19 nm) to the red shifts (+30 and +116 nm) according to the increase of electron-withdrawing ability of the sulfur group.

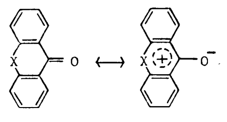
—In the case of xanthone (**5e**/**6e**), the red shift which is almost equal to that of the sulfoxide is observed in spite of the presence of a lone pair of electrons on the oxygen atom.

These facts may be explained as follows, although assignment of each absorption has not been made. The facts obtained in group I may be understood by assuming that the resonance contribution of a polar structure to π* state in **5a**—**d** is significant and thus the excitation energy is reduced, whereas the contribution of a polar structure to π* state in **6a**—**d** is less significant due to the competition between the electron-donating power of the 1,3-benzodithiol-2-ylidene moiety and that of the other part of the molecule, *i.e.*, the π-excessive cyclic system containing vinyl, sulfur, or nitrogen group, and hence the excitation energy is enhanced relatively. This enhancement of the excitation energy due to the electron-donating power of the 1,3-benzodithiol-2-ylidene moiety appears to be stronger than the lowering of the excitation energy by the extenstion of the conjugated system in **6** by the inclusion of the 1,3-benzodithiol-2-ylidene group instead of the carbonyl oxygen atom. The latter effect should be common to groups I, II, and III.

The stretching frequency of a carbonyl group in IR is affected by the contribution of a polar structure to the ground state in a carbonyl compound, *i.e.*, the lower the frequency, the larger the polar character. Indeed, the carbonyl frequencies of group I compounds are lower compared with those of group II compounds due to the π-excessive character of the ring as shown in Table 4.

Table 4. The IR spectral data of some of the carbonyl compounds

Compounds	IR (KBr), $\nu_{C=O}$ (cm^{-1})	Group
5a	1630	I
5b	1630	I
5c	1625	I
5d	1625	I
5e	1670	I
5f	1675	—
5g	1680	—
5h	1700	II
5p	1660	III

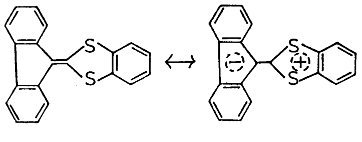


5a—**e**

Carbonyl frequency of **5e** is very close to that of **5f**. This may be the reason for the exception of **5e**/**6e** (+28.5 nm shift) as a member of group I, that is, the contribution of the polar structure in **5e** is smaller than those in **5a**—**d** due to the large electronegativity of the ring oxygen and is almost the same as that by sulfoxide group of **5f** (+30 nm shift). The fact in the case of **5f**,**g**/**6f**,**g** can similarly be understood.

However, it has been shown that even tropone is a highly polyenic compound in the ground state with some contribution of a polar structure.[21] Hence, the degree of the contribution of the polar structure to the ground state in all these carbonyl compounds may not be so significant.

The findings obtained in groups II and III may be understood by assuming that the contribution of a polar structure to π* state in **6h**—**j** is significant due to the electron-donating property of the 1,3-benzodithiolylidene moiety in concurrence with the electron-withdrawing property of the other part of the molecule, whereas the contribution of a polar structure to π* in **5h**—**j** is less significant. The decrease in the excitation energy of **4o**,**p** as compared with **5o**,**p** may chiefly be ascribed to the extension of the conjugated system in **4o**,**p** by the inclusion of the 1,3-benzodithiolylidene group instead of the carbonyl oxygen atom.



The assumption that the contribution of a polar structure to the ground state in **6** is not so significant was supported by the observed ESCA spectral data of **6a**, **b**, **c**, **e**, and **h** ($S_{2p\ 3/2}=163.1\pm0.3$ eV, respectively), which showed almost equal binding energy for all the sulfur atoms contained in a number of molecules.[22]

Neuenschwander *et al.*[23] reported also that the resonance contribution of a dipolar form is not significant in sesquifulvalene, fulvene, and heptafulvene, which were shown to have a largely olefinic character from their ^{13}C-NMR spectral data and relatively small dipole moments.

Experimental

All the melting points are not corrected. IR spectra were measured with a Hitachi EPI-G2 spectrometer, ^{1}H-NMR spectra with Hitachi R-20B and Hitachi R-24 spectrometers (60 MHz, TMS as an internal standard), MS with a Hitachi RMU-6L mass spectrometer at 70 eV, and UV spectra with a Hitachi EPS-3 spectrophotometer. ^{31}P-NMR spectra were measured with a Hitachi R-20B-R-204-PB (24.3 MHz) spectrometer using 85% phosphoric acid as an external standard. ESCA spectra were recorded on a McPherson ESCA 36 electron spectrometer. The Al $K_{\alpha 1,2}$ line (1486.6 eV) provided the activation energy. The instrument was adjusted so that the Au-4f$_{7/2}$ line fell at 84.0 eV. Accuracy: ±0.15 eV.

Materials. 1,3-Benzodithiolylium tetrafluoroborate (**1a**) was prepared according to the literature, mp 149—150 °C (dec) (lit,[24] mp 149—150 °C). 4,5-Dimethyl-1,3-dithiolylium tetrafluoroborate (**1b**), mp 123—125 °C (lit,[25,26] mp is not described), was prepared from 4,5-dimethyl-1,3-dithiole-2-thione[27] and 4-phenyl-1,3-dithiolylium tetrafluoroborate (**1c**), mp 143.5—145.5 °C (dec) (lit,[28] mp 161 °C for ClO_4^- and 180 °C for HSO_4^- salts), was prepared from 4-phenyl-1,3-dithiole-2-thione.[3]

Dibenzo[a,d]cyclohepten-5-one (**5a**) was a commercial material from Sakai Rikagaku Kenkyujyo, mp 88.0—89.0 °C; IR (KBr): 1630 cm^{-1} (C=O); UV (CH_2Cl_2): λ_{max}= 257 (log ε=4.92), 309.5 (4.47), and 361 nm (3.89).

10*H*-9-thiaanthracen-10-one (thioxanthone) (**5b**) was prepared from *o*-mercaptobenzoic acid and benzene by treatment with concentrated sulfuric acid, mp 214—215 °C (from EtOH) (lit,[29] mp 209 °C); IR (KBr): 1630 cm^{-1} (C=O); UV (CH_2Cl_2): λ_{max}=257.5 (log ε=4.74), 289 sh (3.89), 301 (3.86), 364 (3.90), and 382 nm (3.98).

9-Methyl-9,10-dihydro-9-azaanthracen-10-one (*N*-methylacridone) (**5c**) was prepared by the oxidation of *N*-methylacridinium salt with potassium hexacyanoferrate (III) in aqueous alkaline solution, mp 208—209 °C (lit, 199 °C[30] and 203 °C[31]); IR (KBr): 1625 cm^{-1} (C=O); UV (CH_2Cl_2): λ_{max}=258 (log ε=4.75), 268 sh (4.50), 277 (4.41), 293.7 (3.98), 306 (3.77), 361 sh (3.70), 380 (4.01), and 400 nm (4.13).

9-Ethyl-9,10-dihydro-9-azaanthracen-10-one (*N*-ethylacridone) (**5d**) was also prepared from *N*-ethylacridinium salt, mp 162.5—163.0 °C (lit,[31] 159 °C); IR (KBr): 1625 cm^{-1} (C=O); UV (CH_2Cl_2): 258 (log ε=4.84), 268 sh (4.54), 277 (4.45), 294 (3.87), 306 (3.76), 363 sh (3.81), 381 sh (4.12), and 401 nm (4.26).

10*H*-9-oxaanthracen-10-one (xanthone) (**5e**) was a commercial material, mp 173.0—174.0 °C (from EtOH); IR (KBr): 1670 cm^{-1} (C=O); UV (CH_2Cl_2): λ_{max}=239 (log ε= 4.70), 261.5 (4.15), 277 sh (3.68), 286.5 sh (3.69), 327 sh (3.81), and 341.5 nm (3.89).

10*H*-9-thiaanthracen-10-one 9-oxide (**5f**) was prepared by the oxidation of **5b** with *m*-chloroperbezoic acid (1.33 eq.) in dichloromethane at room temperature and separated from **5b** and its sulfone by dry column chromatography (SiO_2/CH_2Cl_2), yield 50% together with 30% of sulfone, mp 205—206 °C (lit,[32] 199—201 °C); IR (KBr): 1675 (C=O), 1040, and 1095 cm^{-1} (SO); UV(CH_2Cl_2): λ_{max}=284 sh (log ε= 4.17) and 340 nm (3.67).

10*H*-9-thiaanthracen-10-one 9,9-dioxide (**5g**) was prepared by the oxidation of **5b** with *m*-chloroperbenzoic acid (2 eq.) in dichloromethane at room temperature, yield 90%; mp 190.0—191.0 °C (lit,[33] 185.5—186 °C); IR (KBr): 1680, 1310, 1300, 1170, and 1145 cm^{-1} (SO_2); UV (CH_2Cl_2): λ_{max}=286 sh (log ε=3.96); (CH_3CN): λ_{max}=229.5 (log ε= 4.32), 237 sh (4.23), 254 sh (3.88), 263 (3.89), and 283 nm (3.89).

9-Fluorenone (**5h**) was a commercial material, mp 83.0—84.0 °C (from PhH-EtOH); IR (KBr): 1700 cm^{-1} (C=O); UV (CH_2Cl_2): λ_{max}=250.5 (log ε=4.91), 259 (5.15), 284.5 sh (3.84), 296 (3.90), 311.5 sh (3.72), 327.5 sh (3.57), 358 sh (2.43), 378 (2.50), and 398 sh nm (2.46).

Tetraphenylcyclopentadienone (**5i**) was prepared by the reported method, mp 218—220 °C (lit,[34] mp 218—220 °C); UV (CH_2Cl_2): λ_{max}=262 (log ε=4.46), 340 (3.88), and 510 nm (3.03); (CH_3CN): λ_{max}=260 (log ε=4.40) and 338 nm (3.79); (CH_3CN with HBF_4): λ_{max}=258.5 (log ε= 4.40), 337 (3.81), and 502 nm (3.09).

7*H*-benz[d,e]anthracen-7-one (**5j**) was a commercial material, mp 169.0—170.0 °C (from PhH-EtOH); UV (CH_2Cl_2): λ_{max}=231.5 (log ε=4.60), 237 (4.56), 242 (4.51), 254 (4.46), 276 sh (4.06), 285 (4.07), 310 (4.03), 338 sh (3.66), 355 sh (3.86), 389 (4.13), and 407 sh (4.06).

10,10-Dibenzyl-9(10*H*)-anthracenone was prepared by refluxing 9(10*H*)-anthracenone and benzyl chloride with aq. sodium hydroxyde in THF, mp 232.0—233.0 °C. IR (KBr): 1650 cm^{-1} (C=O).

*Preparation of 2-Phosphonio-1,3-dithiole Salts (**2**). General Procedure*: Tertiary phosphine (10 mmol) was added to a stirred solution of 1,3-dithiolylium tetrafluoroborate (**1**: 10 mmol) in dry acetonitrile (50 ml) at room temperature. After stirring for 2 h, the solvent was evaporated to about 10 ml under reduced pressure. Dry ether (50 ml) was added to the residue and the precipitates were collected, washed with ether, and recrystallized from ethanol.

2-Triphenylphosphonio-1,3-benzodithiole tetrafluoroborate (**2a**), yield 87%; mp 211.5—212.5 °C (dec); IR (KBr): 1140—1020 and 520 (BF_4^-), 1430, 770, 760, 750, 740, 730, 720, 700, and 690 cm^{-1}; ^{1}H-NMR (DMSO-d_6): δ 6.7—7.3 (m, 5H, aromatic and 2-CH), and 7.3—8.2 (m, 15H, aromatic).

Found: C, 59.94; H, 4.05%. Calcd for $C_{25}H_{20}BF_4PS_2$: C, 59.78; H, 4.01%.

2-Tributylphosphonio-1,3-benzodithiole tetrafluoroborate (**2b**), yield 90%; mp 166.5—168.0 °C; IR (KBr): 1140—1020 and 520 (BF_4^-), 1440, and 760 cm^{-1}; ^{1}H-NMR (DMSO-d_6): δ 0.5—2.5 (m, 27H, *n*-Bu), 6.42 (bs, 1H, PCH), and 7.0—7.6 (m, 4H, aromatic).

Found: C, 51.30; H, 7.52%. Calcd for $C_{19}H_{32}BF_4PS_2$: C, 51.59; H, 7.29%.

4,5-Dimethyl-2-triphenylphosphonio-1,3-dithiole tetrafluoroborate (**2c**), yield 84%; mp 175.0—177.0 °C (dec); IR (KBr): 1120—1140 and 520 (BF_4^-), 1430, 750, 730, 720, and 690 cm^{-1}; ^{1}H-NMR (DMSO-d_6): δ 1.30 (s, 6H, 4- and 5-Me), 7.35 (bs, 1H, 2-CH), and 7.2—8.4 (m, 15H, aromatic).

Found: C, 57.29; H, 4.65%. Calcd for $C_{23}H_{22}BF_4PS_2$: C, 57.51; H, 4.62%.

*Preparation of 2-Dialkoxyphosphinyl-1,3-dithiole (**3**). General Procedure*: Trialkyl phosphite (10 mmol) and sodium iodide (1.5 g, 10 mmol) were added successively to a stirred solution of 1,3-dithiolylium tetrafluoroborate (10 mmol) in dry acetonitrile (50 ml) under a nitrogen atmosphere at room temperature . The reaction took place rapidly and was slightly exothermic. Stirring was continued for about 30 min, and the solvent was evaporated *in vacuo*. The residue was extracted with dichloromethane (30 ml × 3) after addition of water (50 ml). The combined extracts were dried over anhydrous magnesium sulfate and dichloromethane was removed under reduced pressure. The residue was recrystallized from ethyl acetate or ethanol to give 2-dialkoxyphosphinyl-1,3-dithiole.

2-Dimethoxyphosphinyl-1,3-benzodithiole (**3a**), yield 80%; mp 122.0—123.0 °C (from EtOH); IR (KBr): 1260 (P=O), 1050, and 1035 cm^{-1} (P-O-C): ^{1}H-NMR ($CDCl_3$): δ 3.63 (d, $J_{POCH}=10.4$ Hz, 6H, $POCH_3$), 4.75 (d, $J_{PCH}=5.8$ Hz, 1H, PCH), and 6.7—7.3 (m, 4H, aromatic); ^{31}P-NMR ($CDCl_3$): δ_P −19 ppm; MS: *m/e* 262 (M^+, 8%), 153 ($M^+-P(O)(OMe)_2$, 100), and 77 (Ph^+, 21).

Found: C, 41.01; H, 4.14; S, 24.40%. Calcd for $C_9H_{11}O_3PS_2$: C, 41.21; H, 4.23; S, 24.45%.

2-Diethoxyphosphinyl-1,3-benzodithiole (**3b**), yield 95%; mp 115.5—116.5 °C (from EtOH); IR (KBr): 1250 (P=O), 1050, and 1030 cm^{-1} (P-O-C); ^{1}H-NMR ($CDCl_3$): δ 1.22 (t, $J_{HCCH}=6.8$ Hz, 6H, $POCCH_3$), 4.15 (dq, $J_{POCH}=7.7$, $J_{HCCH}=6.8$ Hz, 4H, $POCH_2$), 4.89 (d, $J_{PCH}=5.2$ Hz, 1H, PCH), and 6.9—7.3 (m, 4H, aromatic). The triplet signal at δ 1.22 of $POCCH_3$ was irradiated to give a doublet signal at δ 4.15 for $POCH_2$ with a coupling constant of 7.7 Hz. MS: *m/e* 290 (M^+, 4.4%), 153 ($M^+-P(O)(OEt)_2$, 100), and 77 (Ph^+, 23).

Found: C, 45.43; H, 5.25; S, 22.21%. Calcd for $C_{11}H_{15}O_3PS_2$: C, 45.51; H, 5.21; S, 22.09%.

4,5-Dimethyl-2-dimethoxyphosphinyl-1,3-dithiole (**3c**); After usual work-up, the product was submitted to dry column chromatography over neutral alumina (activity III) with dichloromethane. The fraction (R_f 0.2—0.4) was eluted with ethyl acetate to give 83% yield of **3c**. This compound has low melting point (<20 °C), and is so hygroscopic and sensitive to air in an oily state or in solution that it could not be purified enough for elemental analysis. IR (neat): 1255 (P=O), 1180, 1055, and 1030 cm^{-1}; ^{1}H-NMR (CCl_4): δ 1.83 (s, 6H, 4,5-dimethyl), 3.80 (d, $J_{POCH}=10.4$ Hz, 6H, $POCH_3$), and 4.73 (d, $J_{PCH}=4.5$ Hz, 1H, PCH).

Found: C, 33.52; H, 5.23%. Calcd for $C_7H_{13}O_3PS_2$: C, 34.99, H, 5.45%.

2-Dimethoxyphoshinyl-4-phenyl-1,3-dithiole (**3d**), yield 90%; mp 87.0—88.0 °C (from AcOEt); IR (KBr): 1255 (P=O), 1180, 1065, and 1040 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 3.89 (d, $J_{POCH}=10.5$ Hz, 6H, $POCH_3$), 5.06 (d, $J_{PCH}=4.5$ Hz, 1H, PCH), 6.24 (s, 1H, 5-CH), and 7.2—7.5 (m, 5H, aromatic); MS: *m/e* 288 (M^+, 9.4%), 179 ($M^+-P(O)(OMe)_2$, 100); metastable ion, found: 111.3, calcd for 288→179: 111.25.

Found: C, 45.82; H, 4.55; S, 21.91%. Calcd for $C_{11}H_{13}O_3PS_2$: C, 45.82; H, 4.54; S, 22.24%.

Wittig Reaction of (1,3-Benzodithiol-2-ylidene)triphenylphosphorane (Method A). *General Procedure*: To a suspension of 2-triphenylphosphonio-1,3-benzodithiole tetrafluoroborate (**2a**) (1.005 g, 2.0 mmol) in THF (50 ml) was added butyllithium in hexane (1.5 ml, 2.3 mmol) at −78 °C under a nitrogen atmosphere with stirring. Stirring was continued for 2.0—2.5 h to give a dark red solution of (1,3-benzodithiol-2-ylidene)triphenylphosphorane (*A*). A carbonyl compound (2.0 mmol) was added at −78 °C. Immediately the dark red color of the solution turned yellow. The mixture was allowed to get warm to room temperature and the solvent was evaporated under reduced pressure. The residue was extracted with dichloromethane (30 ml×3) after addition of water (50 ml). The combined extracts were dried over anhydrous magnesium sulfate, dichloromethane was removed under reduced pressure, and the residue was submitted to dry column chromatography over silica gel (activity III) with carbon tetrachloride as a developing solvent. The fraction of R_f value 0.7—0.9 was eluted with dichloromethane or ether to give 2-alkylidene-1,3-benzodithiole (**4**) and the fraction of R_f value 0.1—0.2 was eluted with ethyl acetate to give triphenylphosphine oxide.

Reaction of **2a** with *p*-anisaldehyde gave triphenylphosphine oxide, yield 75%, mp 155.0—156.0 °C (from AcOEt), and 2-(*p*-methoxyphenylmethylene)-1,3-benzodithiole (**4b**), yield 77%; mp 144.5—145.5 °C (from ErOH-Et_2O); IR (KBr): 1250, 1180, and 1040 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 3.83 (s, 3H, OCH_3), 6.51 (s, 1H, olefinic), and 6.8—7.6 (m, 8H, aromatic); MS: *m/e* 272 (M^+, 88%), 257 (M^+-Me, 100), and 229 (257−CO, 26).

Found: C, 66.17; H, 4.38; S, 23.36%. Calcd for $C_{15}H_{12}OS_2$: C, 66.14; H, 4.44; S, 23.54%.

Reaction of **2a** with *p*-tolualdehyde gave triphenylphosphine oxide (74%) and 2-(*p*-tolylmethylene)-1,3-benzodithiole (**4c**), yield 75%; mp 149.5—151.0 °C (from EtOH); IR (KBr): 1580, 1550, 1445, 1430, 1130 and 930 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 2.33 (s, 3H, Me), 6.51 (s, 1H, olefinic), and 6.9—7.5 (m, 8H, aromatic); MS: *m/e* 256 (M^+, 100%), 140 ($C_6H_4S_2^{+\cdot}$, 14), 128 (M^{2+}, 14), and 115 ($M^+-C_6H_5S_2$, 20).

Found: C, 70.52; H, 4.58; S, 24.88%. Calcd for $C_{15}H_{12}S_2$: C, 70.27; H, 4.72; S, 25.01%.

Reaction of **2a** with benzaldehyde gave triphenylphosphine oxide (72%) and 2-benzylidene-1,3-benzodithiole (**4d**), yield 74%; mp 133.0—134.5 °C (from EtOH); IR (KBr): 1580, 1470, and 1430 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 6.60 (s, 1H, olefinic) and 7.0—7.6 (m, 9H, aromatic); MS: *m/e* 242 (M^+, 100%), 165 (M^+-Ph, 18), 140 ($C_6H_4S_2^{+\cdot}$, 39), 121 (M^{2+}, 37), and 108 (140−S, 18).

Found: C, 69.25; H, 4.10; S, 26.33%. Calcd for $C_{14}H_{10}S_2$: C, 69.38; H, 4.16; S, 26.46%.

Reaction of **2a** with *p*-chlorobenzaldehyde gave triphenylphosphine oxide (79%) and 2-(*p*-chlorophenylmethylene)-1,3-benzodithiole (**4e**), yield 82%; mp 190.0—190.8 °C (from EtOH); IR (KBr): 1580, 1540, and 1100 cm^{-1}; ^{1}H-NMR ($CDCl_3$ with CF_3CO_2H[35]): δ 5.05 (s, 2H, benzyl proton), 7.1—7.7 (m, 4H, aromatic), and 7.8—8.7 (m, 4H, aromatic); MS: *m/e* 278 (M^+ for ^{37}Cl, 47%), 277 (M^+-1, 24), 276 (M^+, for ^{35}Cl, 100), 240 (M^+-HCl, 24), and 140 ($C_6H_4S_2^{+\cdot}$, 47).

Found: C, 60.52; H, 3.21; S, 22.89; Cl, 12.99%. Calcd for $C_{14}H_9S_2Cl$: C, 60.75; H, 3.28; S, 23.17; Cl, 12.81%.

Reaction of **2a** with cinnamaldehyde gave triphenylphosphine oxide (80%) and 2-(3-phenyl-2-propenylidene)-1,3-benzodithiole (**4f**), yield 78%; mp 148.0—149.0 °C (from EtOH-Et_2O); IR (KBr): 1570, 1540, 960, and 950 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 5.9—6.8 (m, 3H, olefinic) and 6.8—7.5 (m, 9H, aromatic); MS: *m/e* 268 (M^+, 94%), 140 ($C_6H_4S_2^{+\cdot}$, 23), 134 (M^{2+}, 20), and 128 ($M^+-C_6H_4S_2^{+\cdot}$, 100).

Found: C, 71.60; H, 4.39; S, 24.02%. Calcd for $C_{16}H_{12}S_2$: C, 71.60; H, 4.51; S, 23.89%.

Reaction of **2a** with *p*-dimethylaminobenzaldehyde did not proceed and a red color of the phosphorane did not disappear up to room temperature. Therefore, the solution was refluxed for 30 min, when the solution slightly darkend. Many products were observed by TLC, however, the expected product (**4a**) could not be isolated.

Wittig-Horner Reaction of 2-Dimethoxyphosphinyl-1,3-benzodithiole (3a) (Method B). *General Procedure*: Butyllithium in hexane (1.5 ml, 2.3 mmol) was added to a stirred solution of 2-dimethoxyphosphinyl-1,3-benzodithiole (**3a**) (524.6 mg, 2.0 mmol) in THF (20 ml) at −78 °C under a nitrogen atmosphere. After 10 min, a carbonyl compound (2.0 mmol) was added to the yellow solution of the resulting phosphonate carbanion (*B*). The mixture was stirred for 10 min at −78 °C, allowed to get warm to room temperature, and THF was evaporated under reduced pressure. The residue was extracted with dichloromethane (30 ml × 3) after addition of water (50 ml). The combined extracts were dried over anhydrous magnesium sulfate, dichloromethane removed under reduced pressure, and the residue was recrystallized from an appropriate solvent to give the corresponding 2-alkylidene-1,3-benzodithiole (1,4-benzodithiafulvene) (**4**).

Reaction of **3a** with *p*-dimethylaminobenzaldehyde gave 2-(*p*-dimethylaminophenylmethylene)-1,3-benzodithiole (**4a**), yield 95%; mp 145.0—146.0 °C (from EtOH); IR (KBr): 1600, 1510, 1440, and 1360 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 2.97 (s, 6H, N-CH_3), 6.47 (s, 1H, olefinic), and 6.6—7.4 (m, 8H, aromatic); MS: *m/e* 285 (M^+, 100%), 270 (M^+-Me, 28), 240 (M^+-Me_2NH, 10), and 142.5 (M^{2+}, 26): metastable ion, found: 255.5, calcd for 285→270: 255.7.

Found: C, 66.81; H, 5.21; N, 4.82: S, 22.60%. Calcd for $C_{16}H_{15}NS_2$: C, 67.33; H, 5.30; N, 4.91; S, 22.47%.

Reaction of **3a** with *p*-tolualdehyde gave 2-(*p*-tolylmethylene)-1,3-benzodithiole (**4c**), yield 94%; mp 150.0—151.0 °C (from EtOH).

Reaction of **3a** with *trans*-2-butenal gave 2-(2-butenylidene)-1,3-benzodithiole (**4g**), yield 95%; mp 72.0—73.0 °C (from ethanol–hexane); IR (KBr): 1540, 1440, 1430, and 960 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 1.79 (d, J_{HCCH}=6.0 Hz, 3H, CH_3), 5.2—6.3 (m, 3H, olefinic), and 6.9—7.4 (m, 4H, aromatic); MS: *m/e* 206 (M^+, 100%), 205 (M^+-H, 31), 179 (205$-C_2H_2$, 39), and 140 ($C_6H_4S_2^{+\cdot}$, 39).

Found: C, 63.53; H, 4.83; S, 31.00%. Calcd for $C_{11}H_{10}S_2$: C, 64.03; H, 4.89; S, 31.08%.

Reaction of **3a** with cyclopentanone gave 2-cyclopentylidene-1,3-benzodithiole (**4h**), yield 96%; mp 105.5—107.0 °C (from EtOH); IR (KBr): 1440, 1420, and 1120 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 1.4—2.6 (m, 8H, aliphatic)and 6.7—7.4 (m, 4H, aromatic); MS: *m/e* 220 (M^+, 100%), 219 (M^+-H, 31), 192 ($M^+-C_2H_4$, 97), 179 ($M^+-C_3H_5$, 14), 166 ($M^+-C_4H_6$, 23), and 153 ($M^+-C_5H_7$, 29).

Found: C, 65.43; H, 5.44; S, 29.04%. Calcd for $C_{12}H_{12}S_2$: C, 65.41; H, 5.49; S, 29.10%.

Reaction of **3a** with cyclohexanone gave 2-cyclohexylidene-1,3-benzodithiole (**4i**), yield 98%; mp 96.0—97.5 °C (from EtOH); IR (KBr): 1420, 1120, and 740 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 1.2—1.8 (m, 6H, 3'-CH_2, 4'-CH_2 and 5'-CH_2), 1.8—2.2 (m, 4H, 2'-CH_2 and 6'-CH_2), and 6.7—7.3 (m, 4H, aromatic); MS: *m/e* 234 (M^+, 100%), 233 (M^+-H, 21), 205 (233$-C_2H_4$, 39), 179 ($M^+-C_4H_7$, 31), 166 ($M^+-C_5H_8$, 31), and 153 ($M^+-C_6H_9$, 53).

Found: C, 66.37; H, 6.28; S, 27.24%. Calcd for $C_{13}H_{14}S_2$: C, 66.62; H, 6.02; S, 27.36%.

Reaction of **3a** with 3,5,5-trimethyl-2-cyclohexen-1-one gave 2-(3,5,5-trimethyl-2-cyclohexenylidene)-1,3-benzodithiole (**4j**), yield 87%; mp 99.0—100.0 °C (from EtOH); IR (KBr): 1560, 1540, 1440, 1420, and 1120 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 0.95 (s, 6H, 5',5'-dimethyl), 1.7—1.95 (m, 5H, 3'-CH_3 and 4'-CH_2), 1.97 (s, 2H, 6'-CH_2), 5.85—5.95 (m, 1H, 2'-CH), and 6.9—7.4 (m, 4H, aromatic). The multiplet signal at δ 1.7—1.95 was irradiated to give a singlet signal at δ 5.9 for 2'-CH. Protonation occurred at 3'-position, giving a conjugated cation; ^{1}H-NMR ($CDCl_3$ with CF_3CO_2H): δ 1.02 (s, 3H, 5'-CH_3), 1.20 (s, 3H, 5'-CH_3), 1.29 (d, J_{HCCH}=6.8 Hz, 3H, 3'-CH_3), 1.5—1.75 (m, 2H, 4'-CH_2), 2.47 (br s, 2H, 6'-CH_2), 2.6—2.9 (m, 1H, 3'-CH), 7.58 (br s, 1H, 2'-H), and 7.8—8.5 (m, 4H, aromatic). MS: *m/e* 274 (M^+, 100%), 259 (M^+-Me, 36), 231 (259$-C_2H_4$, 13), 153 ($M^+-C_9H_{13}$, 44), and 121 (C_9H_{13}, 23); metastable ion, found, 244.9, calcd for 274→259: 244.8.

Found: C, 69.95; H, 6.61; S, 23.05%. Calcd for $C_{16}H_{18}S_2$: C, 70.02; H, 6.61; S, 23.37%.

Reaction of **3a** with benzylideneacetone gave 2-(1-methyl-3-phenyl-2-propenylidene)-1,3-benzodithiole (**4k**), yield 96%; mp 170.0—171.0 °C (from EtOH); IR (KBr): 955, 750, and 695 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 1.99 (s, 3H, 1'-CH_3), 6.44 (d, J_{HCCH}=16 Hz, 1H, olefinic), 7.03 (d, J_{HCCH}=16 Hz, 1H olefinic), and 7.0—7.7 (m, 9H, aromatic); MS: *m/e* 282 (M^+, 100%), 153 ($M^+-PhC_4H_4$, 30), 142 ($M^+-C_6H_4S_2$, 71), and 141 (142$-$H, 44); metastable ion, found: 71.6, calcd for 282→142: 71.5.

Found: C, 72.14; H, 4.89; S, 22.39%. Calcd for $C_{17}H_{14}S_2$: C, 72.30; H, 5.00; S, 22.71%.

Reaction of **3a** with *p*-methylacetophenone gave 2-(1-*p*-tolylethylidene)-1,3-benzodithiole (**4l**), yield 92%; mp 80.0—81.0 °C (from EtOH); ^{1}H-NMR ($CDCl_3$): δ 2.15 (s, 3H, 2'-CH_3), 2.38 (s, 3H, ArMe), and 6.8—7.5 (m, 8H, aromatic); MS: *m/e* 270 (M^+, 100%), 269 (M^+-H, 31), 255 (M^+-Me, 8), 179 (M^+-tolyl, 17), and 153 ($M^+-C_9H_9$, 33); metastable ion, found: 240.9, calcd for 270→255: 240.8.

Found: C, 70.96; H, 5.18; S, 23.86%. Calcd for $C_{16}H_{14}S_2$: C, 71.07; H, 5.22; S, 23.71%.

Reaction of **3a** with acetophenone gave the crude product which was submitted to dry column chromatography over silica gel with carbon tetrachloride as an eluent to afford oily 2-(1-phenylethylidene)-1,3-benzodithiole (**4m**), yield 94%; IR (neat): 3050, 1590, 1435, 1130, and 1035 cm^{-1}; ^{1}H-NMR (CCl_4): δ 2.09 (s, 3H, CH_3) and 6.7—7.5 (m, 9H, aromatic); MS: *m/e* 256 (M^+, 100%), 255 (M^+-H, 17), 179 (M^+-Ph, 12), and 153 ($M^+-C_8H_7$, 11); metastable ion, found: 125.1, calcd for 256→179: 125.16.

Found: C, 70.12; H, 4.67; S, 24.88%. Calcd for $C_{15}H_{12}S_2$: C, 70.27; H, 4.72; S, 25.01%.

Reaction of **3a** with *p*-chloroacetophenone gave 2-(1-*p*-chlorophenylethylidene)-1,3-benzodithiole (**4n**), 91%; mp 97.0—98.0 °C (from hexane); IR (KBr): 1580, 1480, 1425, 1095, and 1015 cm^{-1}; ^{1}H-NMR (CCl_4): δ 2.10 (s, 3H, CH_3) and 6.7—7.4 (m, 8H, aromatic); MS: *m/e* 292 (M^+, for ^{37}Cl, 39%), 291 (M^+-H, 30), 290 (M^+, for ^{35}Cl, 100), 289 (M^+-H, 30), 255 (M^+-Cl, 12), and 153 ($M^+-C_8H_6Cl$, 31); metastable ion, found 224.2, calcd for 290→255: 224.2.

Found: C, 62.25; H, 3.72; S, 22.07%. Calcd for $C_{15}H_{11}S_2Cl$: C, 61.95; H, 3.81; S, 22.05%.

Reaction of **3a** with 4,4'-dimethoxybenzophenone gave 2-[bis(*p*-methoxyphenyl)methylene]-1,3-benzodithiole (**4o**), yield 96%; mp 105.0—106.0 °C (from ethyl acetate and hexane); IR (KBr): 1600, 1495, 1240, 1170, 1030 cm^{-1}; UV (CH_2Cl_2): λ_{max}=247 (logε=4.55), 256 sh (4.49), 326 nm (4.35); ^{1}H-NMR (CCl_4): δ 3.78 (s, 6H, OCH_3), 6.78 (d, J=8.6 Hz, 4H, aromatic), 7.00 (br s, 4H, aromatic), and 7.20 (d, J=8.6 Hz, 4H, aromatic); MS: *m/e* 378 (M^+, 100%) and 363 (M^+-Me, 43); metastable ion, found: 349.0, calcd for 378→363: 348.6.

Found: C, 69.76; H, 4.60; S, 17.21%. Calcd for $C_{22}H_{18}O_2S_2$: C, 69.81; H, 4.79; S, 16.94%.

Reaction of **3a** with benzophenone gave 2-(diphenylmethylene)-1,3-benzodithiole (**4p**), yield 80%; mp 96.0—97.0 °C (from ethyl acetate and hexane); IR (KBr): 1570, 1535, 1435, and 1130 cm^{-1}; UV (CH_2Cl_2): λ_{max}=244 (log ε= 4.51), 252 sh (4.43), and 329 nm (4.34); MS: *m/e* 318 (M^+, 100%) and 178 ($M^+-C_6H_4S_2$, 36).

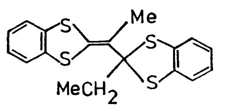
Found: C, 75.15; H, 4.29; S, 20.09%. Calcd for $C_{20}H_{14}S_2$: C, 75.43; H, 4.43; S, 20.14%.

Reaction of **3a** with 4,4'-dichlorobenzophenone gave 2-[bis(*p*-chlorophenyl)methylene]-1,3-benzodithiole (**4p**), yield 95%; mp 113.0—114.0 °C (from EtOH); IR (KBr): 1480, 1100, and 1020 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 7.1 (br s, 4H, aromatic) and 7.3 (br s, 8H, aromatic); MS: *m/e* 390 (M^+, for two ^{37}Cl, 18%), 389 (17), 388 (M$^+$, for one ^{37}Cl and one ^{35}Cl, 68), 387 (23), and 386 (M$^+$ for two ^{35}Cl, 100); ESCA: $S_{2p\ 3/2}$=163.1±0.15 eV.

Found: C, 61.98; H, 3.42; S, 16.70; Cl, 18.50%. Calcd for $C_{20}H_{12}S_2Cl_2$: C, 62.02; H, 3.12; S, 16.56; Cl, 18.31%.

Reaction of **3a** with 3-buten-2-one gave crude 2-(1-methyl-2-propenylidene-1,3-benzodithiole (**4r**), yield 53%; mp 87.0—89.0 °C (from ethanol and hexane); IR (KBr): 1595, 1440, and 1425 cm^{-1}; ^{1}H-NMR (CDCl$_3$): δ 1.86 (s, 3H, CH$_3$), 4.8—5.3 (m, 2H, olefinic CH), 6.2—6.8 (m, 1H, olefinic CH), and 6.8—7.4 (m, 4H, aromatic); MS: *m/e* 206 (M$^+$, 100%), 205 (M$^+$−H, 31), 179 (M$^+$−C_2H_3, 26), 166 (M$^+$−C_3H_4, 91), and 153 (M$^+$−C_4H_5, 21); metastable ion, found: 133.9, calcd for 206→166: 133.8. This compound was not so stable as to give an analytically pure sample.

Reaction of **3a** with acetaldehyde in 1.0 mmol scale gave a crude product (170 mg). However, purification by preparative thin-layer chromatography (SiO$_2$/CCl$_4$) afforded only a trace amount of a dimeric compound. The structure of the compound was proposed to be shown below from its ^{1}H-NMR spectral data. ^{1}H-NMR (CCl$_4$): δ 1.07 (t, J=7 Hz, 3H, -C-CH$_3$), 1.99 (s, 3H, CH$_3$), 2.42 (q, J=7 Hz, 2H, CH$_2$-C), and 6.7—7.6 (m, 8H, aromatic).



Reaction of **3a** with 9(10*H*)-anthracenone gave a reaction mixture which was submitted to dry column chromatography over neutral alumina with dichloromethane to give 9,10-anthracenedione (73%, mp 285 °C) together with recovered **3a** (41%).

Reaction of **3a** with 10,10-dibenzyl-9(10*H*)-anthracenone did not take place even under reflux for 30 min. A large amount of the ketone was recovered (70—80%).

Reaction of 2-dimethoxyphosphinyl-4-phenyl-1,3-dithiole (**3d**) with 4,4′-dichlorobenzophenone in 1.0 mmol scale gave 4-phenyl-2-[bis(*p*-chlorophenyl)methylene]-1,3-dithiole, yield 83%; mp 183.5—185.0 °C (from methanol and hexane); IR (KBr): 1480, 1100, 1090, and 1020 cm^{-1}; ^{1}H-NMR (CDCl$_3$): δ 6.40 (s, 1H, olefinic) and 7.2—7.5 (m, 13H, aromatic); MS: *m/e* 416 (M$^+$ for two ^{37}Cl, 15%), 415 (16), 414 (M$^+$, for one ^{37}Cl and one ^{35}Cl, 74), 413 (22), and 412 (M$^+$ for two ^{35}Cl, 100).

Found: C, 64.07; H, 3.20; Cl, 16.65%. Calcd for $C_{22}H_{14}S_2Cl_2$: C, 63.92; H, 3.41; Cl, 17.15%.

Reaction of **3a** with dibenzo[a,d]cyclohepten-5-one (**5a**) gave 2-(dibenzo[a,d]cyclohepten-5-ylidene)-1,3-benzodithiole (**6a**), yield 83%; mp 179.0—180.0 °C (from EtOH); IR (KBr): 1570, 1440, 1425, and 1125 cm^{-1}; UV (CH$_2$Cl$_2$): λ_{max}=232 (log ε=4.73), 273 (4.39), 299 (4.37), and 340 sh nm (4.15); ^{1}H-NMR (CDCl$_3$): δ 6.83 (s, 2H, olefinic), 7.00 (s, 4H, aromatic), 7.2—7.7 (m, 8H, aromatic); MS: *m/e* 342 (M$^+$, 100%), 308 (M$^+$−H$_2$S, 16), 234 (M$^+$−C_6H_4S, 13), 202 (M$^+$−$C_6H_4S_2$, 35), and 189 (M$^+$−$C_7H_5S_2$, 35); ESCA: $S_{2p\ 3/2}$=163.3±0.15 eV.

Found: C, 77.38; H, 3.93; S, 18.54%. Calcd for $C_{22}H_{14}S_2$: C, 77.16; H, 4.12; S, 18.72%.

Reaction of **3a** with 10*H*-9-thiaanthracen-10-one (**5b**) gave 10-(1,3-benzodithiol-2-ylidene)-10*H*-9-thiaanthracene (**6b**), yield 88%; mp 219.0—220.0 °C (from EtOH); IR (KBr): 1525, 1445, 1425, and 1125 cm^{-1}; UV (CH$_2$Cl$_2$): λ_{max}=243.5 (logε=4.69), 270.5 sh (4.16), 312 sh (4.05), and 363 nm (4.36); MS: *m/e* (M$^+$, 100%); ESCA: $S_{2p\ 3/2}$=162.9±0.15 eV.

Found: C, 68.73; H, 3.54%. Calcd for $C_{20}H_{12}S_3$: C, 68.93; H, 3.47%.

Reaction of **3a** with 9-methyl-9,10-dihydro-9-azaanthracen-10-one (**5c**) in 1.0 mmol scale gave 9-methyl-10-(1,3-benzodithiol-2-ylidene)-9,10-dihydro-9-azaanthracene (**6c**) yield 62%; mp 210.0—211.0 °C (from EtOH). Refluxing of the mixture (30 min) was necessary to effect the reaction. IR (KBr): 1455, 750, and 740 cm^{-1}; UV (CH$_2$Cl$_2$): λ_{max}=238 (logε=4.77), 262.5 sh (4.26), 314 (4.18), 395 nm (4.30); ^{1}H-NMR (CDCl$_3$): δ 3.39 (s, 3H, N-CH$_3$) and 6.8—7.7 (m, 12H, aromatic); MS: *m/e* 345 (M$^+$, 100%), 330 (M$^+$−Me, 77), 222 (330−C_6H_4S, 10), and 172.5 (M^{2+}, 12); ESCA: $S_{2p\ 3/2}$=162.9±0.15 eV.

Found: C, 72.90; H, 4.38; N, 4.31; S, 18.68%. Calcd for $C_{21}H_{15}NS_2$: C, 73.01; H, 4.38; N, 4.05; S, 18.56%.

Reaction of **3a** with 9-ethyl-9,10-dihydro-9-azaanthracen-10-one (**5d**) in 1.0 mmol scale gave 9-ethyl-10-(1,3-benzodithiol-2-ylidene)-9,10-dihydro-9-azaanthracene (**6d**), yield 56%; mp 205.0—206.0 °C (from EtOH). Refluxing of the mixture was necessary to effect the reaction. IR (KBr): 1455, 1445, and 1260 cm^{-1}; UV (CH$_2$Cl$_2$): λ_{max}=238 (logε=4.73), 263 sh (4.26), 314 (4.18), and 399 nm (4.28); ^{1}H-NMR (CDCl$_3$): δ 1.43 (t, J=6.8 Hz, 3H, N-C-CH$_3$), 4.03 (q, J=6.8 Hz, 2H, N-CH$_2$-C), and 6.9—7.7 (m, 12H, aromatic); MS: *m/e* 359 (M$^+$, 72%), 330 (M$^+$−Et, 100), and 296 (330−H$_2$S, 9); metastable ion, found: 303.3, calcd for 359→330: 303.3.

Found: C, 73.60; H, 4.78; N, 3.84; S, 17.50%. Calcd for $C_{22}H_{17}NS_2$: C, 73.50; H, 4.77; N, 3.90; S, 17.84%.

Reaction of **3a** with 10*H*-9-oxaanthracen-10-one (**5e**) gave 10-(1,3-benzodithiol-2-ylidene)-10*H*-9-oxaanthracene (**6e**), yield 84%; mp 202.0—203.0 °C (from EtOH); IR (KBr): 1440, and 1265 cm^{-1}; UV (CH$_2$Cl$_2$): λ_{max}=255 sh (log ε=4.44), 300 (4.01), and 370 nm (4.42); MS: *m/e* 332 (M$^+$, 100%) and 166 (M^{2+}, 29); ESCA: $S_{2p\ 3/2}$=163.2±0.15 eV.

Found: C, 72.50; H, 3.48; S, 19.36%. Calcd for $C_{20}H_{12}OS_2$: C, 72.26; H, 3.64; S, 19.29%.

Reaction of **3a** with 10*H*-9-thiaanthracen-10-one 9-oxide (**5f**) in 1.0 mmol scale gave 10-(1,3-benzodithiol-2-ylidene)-10*H*-9-thiaanthracene 9-oxide (**6f**), yield 75%; mp 246.0—247.5 °C (from EtOH); IR (KBr): 1090 and 1040 (S=O) cm^{-1}; MS: *m/e* 364 (M$^+$, 48%), 348 (M$^+$−O, 76), 316 (M$^+$−SO, 39), 212 (M$^+$−$C_7H_4S_2$, 85), and 196 (M$^+$−$C_7H_4OS_2$, 100).

Found: C, 65.05; H, 3.05%. Calcd for $C_{20}H_{12}OS_3$: C, 65.90; H, 3.32%.

Reaction of **3a** with 10*H*-9-thiaanthracen-10-one 9,9-dioxide (**5g**) in 1.0 mmol scale gave 10-(1,3-benzodithiol-2-ylidene)-10*H*-9-thiaanthracene 9,9-dioxide (**6g**), yield 92%; mp 315.0—316.0 °C (from EtOH); IR (KBr): 1570, 1520, 1300 (SO$_2$, asym.), 1170, and 1165 (SO$_2$, sym) cm^{-1}; UV (CH$_2$Cl$_2$): λ_{max}=402 nm (logε=4.24); (MeCN): λ_{max}=265 (logε=4.06), 295.5 (3.72), 318.5 (3.76), and 396 nm (4.32); MS: *m/e* 380 (M$^+$, 100%) and 316 (M$^+$−SO$_2$, 7).

Found: C, 62.57; H, 2.99%. Calcd for $C_{20}H_{12}O_2S_3$: C, 63.13; H, 3.18%.

Reaction of **3a** with 9-fluorenone (**5h**) gave 2-(9-fluorenylidene)-1,3-benzodithiole (**6h**), yield 96%; mp 205.0—206.0 °C (from EtOH and CHCl$_3$). This compound was only slightly soluble in usual solvents such as benzene, chloroform, ethanol, and dimethyl sulfoxide. IR (KBr): 1540, 1440, and 775 cm^{-1}; UV (CH$_2$Cl$_2$): λ_{max}=251 (logε=4.98), 298 (4.00), 309 (4.02), 329 sh (4.07), 388 (4.68), 402 sh nm (4.66); (MeCN): λ_{max}=248.5 (log ε=4.83), 273 sh (3.88), 296.5 sh (3.66), 307.5 sh (3.71), 326 sh (3.79), 385 (4.52), and 400 sh nm (4.49); ESCA: $S_{2p\ 3/2}$=163.4±0.15 eV; MS: *m/e* 316 (M$^+$, 100%) and 158 (M^{2+}, 29).

Found: C, 75.76; H, 4.12; S, 20.30%. Calcd for $C_{20}H_{12}S_2$: C, 75.91; H, 3.82; S, 20.27%.

Reaction of **3a** with tetraphenylcyclopentadienone (**5i**) gave 2-(tetraphenylcyclopentadienylidene)-1,3-benzodithiole (**6i**), yield 75%; mp 383—385 °C (from $CHCl_3$ and EtOH). This compound was only slightly soluble in usual solvents. IR (KBr): 1475, 1460, and 885 cm^{-1}; UV (CH_2Cl_2): λ_{max}=247 sh (logε=4.45), 255.5 (4.50), 274 sh (4.39), and 435 nm (4.60); (MeCN): λ_{max}=244.5 sh (logε=4.33), 253 (4.38), 272 sh (4.24), and 430 nm (4.45); (MeCN with HBF_4): λ_{max}=232 sh (logε=4.43), 314 sh (3.75), and 532 nm (4.44); MS: *m/e* 520 (M^+, 100%).

Found: C, 82.70; H, 4.86; S, 11.71%. Calcd for $C_{36}H_{24}S_2$: C, 83.04; H, 4.65; S, 12.32%.

Reaction of **3a** with 7*H*-benz[d,e]anthracen-7-one (**5j**) gave 2-(7*H*-benz[d,e]anthracen-7-ylidene)-1,3-benzodithiole (**6j**), yield 80%; mp 256.0—257.0 °C (from $CHCl_3$ and EtOH); IR (KBr): 830, 770, and 735 cm^{-1}; UV (CH_2Cl_2): λ_{max}=247.5 sh (logε=4.66), 272 sh (4.38), 318 (4.40), and 424 nm (4.49); MS: *m/e* 366 (M^+, 100%), 332 (M^+-H_2S, 14), and 183 (M^{2+}, 47).

Found: 78.37; H, 3.58; S, 17.36%. Calcd for $C_{24}H_{14}S_2$: C, 78.65; H, 3.85; S, 17.50%.

Reaction of **3a** with 9,10-anthracenedione in 1.0 mmol scale gave yellow crystals of 9,10-bis(1,3-benzodithiol-2-ylidene)-9,10-dihydroanthracene, yield 73%; mp 262.0—263.0 °C (from EtOH); UV (CH_2Cl_2): λ_{max}=237 (log ε=4.34), 273 sh (3.77), 352 sh (3.78), 395 sh (3.89), and 416 nm (3.97); ESCA: $S_{2p\,3/2}$=162.9±0.15 eV; MS: *m/e* 480 (M^+, 100%) and 240 (M^{2+}, 51).

Found: C, 69.70; H, 3.16; S, 26.28%. Calcd for $C_{28}H_{16}S_4$: C, 69.96; H, 3.36; S, 26.68%.

Authars are grateful to Itoh Science Foundation for partial support of this work.

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