Reactions of 2-Methylenebenzothiazolines with Methylenecyclopropenes

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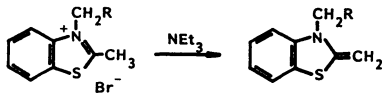
(Received December 4, 1982)

Reactions of 2-methylene-3-phenacylbenzothiazoline and 3-benzyl-2-methylenebenzothiazoline, generated *in situ* from the corresponding 2-methylbenzothiazolium bromide and triethylamine, with methylenecyclopropenes gave a variety of products, cross-conjugated systems, spiro-cyclopentafurans and/or cyclopentabenzothiazines, depending on the nature of substituents of the methylenecyclopropenes. The reaction pathways for the formation of products are also described.

It is known that dehydrohalogenation of 3-phenacylthiazolium halide systems generates the corresponding thiazolium *N*-phenacylides whose synthetic utility as 1,3-dipoles has been established in a few recent reports.[1-6] On the treatment with triethylamine (NEt_3), however, 2-methyl-3-phenacylbenzothiazolium bromide does not yield the *N*-phenacylide but generates 2-methylene-3-phenacylbenzothiazoline which was first confirmed by the formation of Michael adducts to electron-deficient olefins and acetylenes.[7] The methylenebenzothiazoline has an electron-rich exocyclic C=C bond and is classified as a cyclic ketene acetal.

Although the reactions between enamines and methylenecyclopropenes have been extensively investigated[8] and known to give different types of products depending on the nature of substituents at the 4-position of methylenecyclopropenes,[9] few examples for the reaction of a ketene acetal, which is expected to show reaction patterns similar to those of enamines, with methylenecyclopropenes have been reported up to date.[10,11]

This paper describes the reactions of 2-methylene-3-phenacyl- (**3**) and 3-benzyl-2-methylenebenzothiazoline (**4**),[12] generated in situ from 2-methyl-3-phenacyl- (**1**) and 3-benzyl-2-methylbenzothiazolium bromide (**2**), and NEt_3 at 0 °C respectively, with methylenecyclopropenes having electron-withdrawing substituents at the 4-position: Different types of products were found to be formed depending on the nature of the substituents of methylenecyclopropenes.

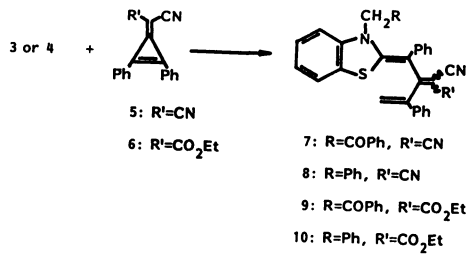


1: R=COPh
2: R=Ph
3: R=COPh
4: R=Ph

Results and Discussion

Reactions with 2-(2,3-Diphenyl-2-cyclopropenylidene)propanedinitrile (5) and Ethyl 2-Cyano-2-(2,3-diphenyl-2-cyclopropenylidene)acetate (6). The reaction of 2-methylenebenzothiazoline **3** with the methylenecyclopropene **5** in dry chloroform at room temperature for 3 h gave a deeply colored 1 : 1 adduct **7** in 95% yield.[13] On the basis of spectral data (Table 1), the 1 : 1 adduct **7** was identified as a cross-conjugated system, 2-(2-dicyanomethylene-1,3-diphenyl-3-butenylidene)-3-phenacylbenzothiazoline. In the ^1H NMR spectrum terminal olefinic protons (2H) are observed, and the ^{13}C NMR spectrum exhibits no sp^3-carbon except for that in the phenacyl group but signals assinable to the olefinic carbons, $=\mathbf{C}(CN)_2$ and $=\mathbf{C}H_2$. The absorption maximum at a long wave region in the electronic spectrum indicates the presence of relatively long conjugation.

Similarly, 2-methylene benzothiazoline **4** reacted with **5** to afford the corresponding cross-conjugated system **8**, whose structure was identified on the basis of spectral data, in an excellent yield. Thus, it can be thought that the behaviour of the methylenebenzothiazolines **3** and **4** toward the methylenecyclopropene **5** is similar to that of enamines.[14]



5: R'=CN
6: R'=CO_2Et
7: R=COPh, R'=CN
8: R=Ph, R'=CN
9: R=COPh, R'=CO_2Et
10: R=Ph, R'=CO_2Et

Scheme 1.

Few examples for the reaction of an enamine with the methylenecyclopropene **6** have been reported.[15] 2-Methylenebenzothiazolines **3** and **4** reacted with **6** in dry THF at room temperature for 1 h to give corresponding cross-conjugated systems **9** and **10** in good yields (Scheme 1). Structural elucidation of **9** and **10** was again accomplished on the basis of spectral data.

The yields, physical and spectral data of cross-conjugated system **7**—**10** are listed in Table 1.

Reactions with 2-Benzoyl-2-(2,3-diphenyl-2-cyclopropenylidene)-2,4-pentanedione (12). It has been well established that enamines react with methylenecyclopropenes having an acyl group at the 4-position to produce the corresponding 6,6a-dihydro-5*H*-cyclopenta[*b*]furans.[16] In order to compare with the reaction of enamines, the reactions of 2-methylenebenzothiazolines, **3** and **4**, with methylenecyclopropenes, **11** and **12**, having an acyl group at the 4-position were investigated.

The benzoyl-substituted methylenecyclopropene **11** was found to be less reactive than the above methylenecyclopropenes **5** and **6**, being recovered in the reaction with **3** and **4** at room temperature. When the reaction of **3** and **4** with **11** was performed in dry THF under reflux, however, the corresponding 1 : 1 adducts **13** and **14** were obtained in 36 and 46% yields, respectively.

Table 1. Cross-conjugated systems **7**—**10**

Compd	Yield/%	Mp θ_m/°C	IR (KBr) $\tilde{\nu}$/cm^{-1}	^{1}H NMR ($CDCl_3$) δ	^{13}C NMR ($CDCl_3$) δ	UV λ_{max}[a)]/nm(log ε)
7	95	134—135	2200 (C≡N)	5.47 (2H, s, NC**H**$_2$), 5.67,	55.25 (t, N**C**H$_2$), 64.32(s,	241 (4.35)
			1690 (C=O)	5.73 (each 1H, s, =C**H**$_2$),	=**C**(CN)$_2$), 104.77 (s, N,S>=**C**),	511 (3.87)
			1500—1300	6.80—7.75 (19H, m)	117.93 (t, =**C**H$_2$), 146.62 (s), 165.93(s), 169.01 (s), 189.37 (**C**=O)	
8	99	112—113	2200 (C≡N)	5.09 (2H, s, NC**H**$_2$), 5.73	52.75 (t, N**C**H$_2$), 65.24 (s,	236 (4.32)
			1380	(2H, s, =C**H**$_2$), 6.80—7.44	=**C**(CN)$_2$), 105.07 (s, N,S>=C),	299 (3.96)
			1320	(19H, m)	117.93 (t, =**C**H$_2$), 146.74 (s), 166.22 (s), 168.30 (s)	520 (4.31)
9	80	94	2200 (C≡N)	1.12 (3H, t, J=7.5 Hz),		243 (4.31)
			1690, 1650 (C=O)	4.03 (2H, q, J=7.5 Hz),		522 (4.00)
			1400, 1275	5.40 (4H, s, NC**H**$_2$+=C**H**$_2$), 6.75—7.70 (19H, m)		
10	94	97—98	2200 (C≡N)	1.10 (3H, t, J=7.5Hz),	13.95 (q), 52.56 (t, N**C**H$_2$),	243 (4.47)
			1680 (C=O)	4.00 (2H, q, J=7.5 Hz),	60.30 (t), 77.24 (s, =**C**(CN)),	530 (4.09)
			1390	5.10 (2H, s, NC**H**$_2$), 5.46	106.17 (s, N,S>=**C**), 112-.99 (t,	
				(2H, s, =C**H**$_2$), 6.80—7.40 (19H, m)	=**C**H$_2$), 143.31 (s), 148.32 (s), 164.77 (s)	

a) Spectra of **7** and **8** were measured in EtOH, and those of **9** and **10** in $CHCl_3$.

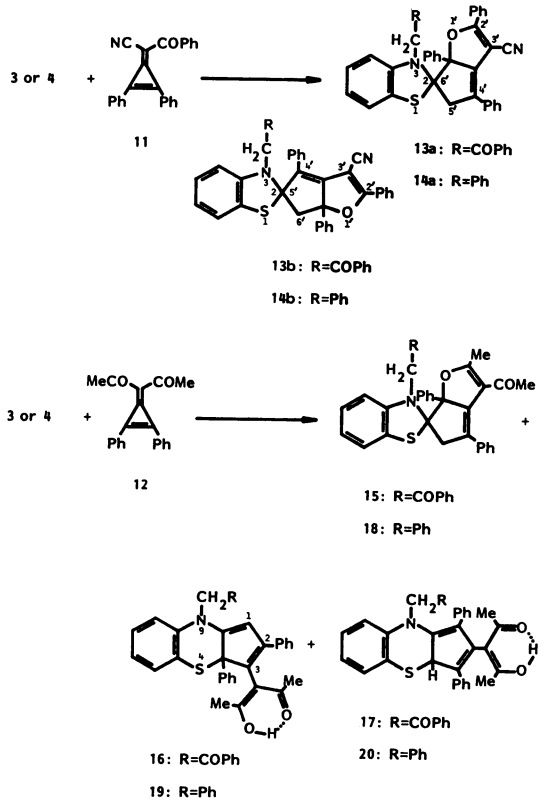
Table 2. Products, **13**—**20**, obtained from the reaction with acyl-substituted methylenecyclopropenes

Compd	Mp θ_m/°C	IR (KBr) $\tilde{\nu}$/cm^{-1}	^{1}H NMR ($CDCl_3$) δ	^{13}C NMR ($CDCl_3$) δ
13	178—179 (decomp)	2200 (C≡N) 1700 (C=O) 1540	3.06, 3.46 (each 1H, d, C**H**$_2$, J=13.0 Hz), 4.33 (2H, s, NC**H**$_2$), 5.70 (1H, m), 6.42—8.05 (23H, m)	49.70 (t, N**C**H$_2$),58.54 (t, **C**H$_2$), 82.60 (s, 3'-**C**), 92.16, 98.92 (each s, spiro-**C**, 6'a-**C**), 115.18 (s, **C**≡N), 174.39 (s, 2'-**C**), 198.88 (s, **C**=O)
14	195 (decomp)	2200 (CN) 1580 1530 1470 1440	3.26, 3.33 (each 1H, d, C**H**$_2$, J=12.0 Hz), 4.03, 4.30 (each 1H, d, NC**H**$_2$, J=18.0 Hz), 5.76 (1H, m), 6.50—8.03 (23 H, m)	47.82 (t, N**C**H$_2$), 58.05 (t, **C**H$_2$), 82.35 (s, 3'-**C**), 93.13, 98.74 (each s, spiro-**C**, 6'a-**C**), 115.00 (s,**C**≡N), 173.97 (s, 2'**C**)
17	180—181	1700 (C=O) 1610 1570 1550	1.76, 1.92 (each 3H, s), 4.41 (1H, s, >C**H**), 4.83, 5.11 (each 1H, d, NC**H**$_2$, J=19.0 Hz), 6.85—7.65 (19H, m), 16.35 (1H, s, O**H**)	23.63 (q, **C**H$_3$), 43.80 (d, 3a-**C**), 55.13 (t, N**C**H$_2$), 108.30, 117.44,120.06 (each s, 1-**C**, 3-**C**, **C**=C(OH)Me), 190.11, 191.81, 193.95 (each s, **C**=O)
18	184—185 (decomp)	1660 (C=O) 1550 1470	1.80, 2.22 (each 3H, s), 3.20 (2H, s, C**H**$_2$), 3.90. 4.22 (each 1H, d, NC**H**$_2$, J=18.0 Hz), 5.60—5.73 (1H, m), 6.40—7.53(18H, m)	16.32 (q, **C**H$_3$), 30.70 (q, CO**C**H$_3$), 48.00 (t, N**C**H$_2$), 57.50 (t, **C**H$_2$), 83.20 (s, 3'-**C**), 93.86, 98.90 (each s, spiro-**C**, 6'a-**C**), 175.80(s, 2'-**C**), 193.97 (s, **C**=O)
20	207—208	1610 1540 1470	1.70, 1.90 (each 3H, s), 4.26 (1H, s, >C**H**), 4.60, 4.85 (each 1H, d, NC**H**$_2$, J=18.0 Hz), 6.80—7.65 (19H, m), 16.32 (1H, s, O**H**)	23.51, 23.63 (each q, **C**H$_3$), 43.67 (d, 3a-**C**), 52.08 (t, N**C**H$_2$), 108.43, 117.01, 120.85 (each s, 1-**C**, **C**=C(OH)Me), 190.05, 191.75 (each s, **C**=O)

The compounds, **13**, **14**, **17**, **18**, and **20** are all yellow needles. **13**: UV $\lambda_{max}^{CHCl_3}$/nm (log ε) 270 (4.28), 325 (4.21), 360 (4.27). **14**: UV $\lambda_{max}^{CHCl_3}$/nm (log ε) 265 (4.35), 330 (4.29), 360 (4.34). The ^{1}H NMR spectral data of **15**, **16**, and **19** are given as follows: **15**: δ 1.86, 2.15 (each 3H, s), 3.30, 3.43 (each 1H, d, C**H**$_2$, J=13.0 Hz), 4.20 (2H, s, NC**H**$_2$). **16**: δ 0.73, 2.36 (each 3H, s), 5.06, 5.36 (each 1H, d, NC**H**$_2$, J=18.0 Hz), 5.56 (1H, s, =C**H**), 17.10 (1H, s, O**H**). **19**: δ 0.76, 2.28 (each 3H, s), 5.02, 5.20(each 1H, d, NC**H**$_2$, J=18.0 Hz), 5.78 (1H, s, =C**H**), 16.93 (1H, s, O**H**).

The IR spectra of **13** and **14** showed no carbonyl absorptions came from the benzoyl group in **11**, and two singlets assignable to quaternary carbons appeared in the ^{13}C NMR spectra. Thus, **13** and **14** can be assumed as spiro-cyclopenta[*b*]furans **13a**, **14a** or **13b**, **14b** derived from the participation of the benzoyl group in a cyclization. In the ^{1}H NMR spectra, however, both **13** and **14** showed doublets assignable to allylic methlenes at δ 3.06, 3.46 and 3.26, 3.33, respectively.[17] It is thus reasonable to conclude that 1 : 1 adducts **13** and

14 are spiro[benzothiazole-2(3*H*),6′-cyclopenta[*b*]furan]s **13a**, **14a** rather than isomeric spiro[benzothiazole-2(3*H*),5′-cyclopenta[b]furan]s **13b**, **14b** (Scheme 2).



Scheme 2.

In contrast to the above reaction which exhibited a reaction pattern similar to enamines, the methylenebenzothiazolines **3** and **4** reacted with the diacetyl-substituted methylenecyclopropene **12** to give novel rearranged products.

The reaction of **3** with **12** in dry THF at room temperature for 0.5 h afforded a mixture of three isomeric 1 : 1 adducts **15**, **16**, and **17**, from which only the major product **17** was isolated in 87% yield. The yields of **15** and **16** were so poor that their isolation was unsuccessful, but their formation was shown by inspection of the ^{1}H NMR spectrum of reaction mixture. Under the same conditions, **4** reacted with **12** to give three 1 : 1 adducts **18**, **19**, and **20** in 21, 10 and 57% yields, respectively. In the same reaction for a long time (15 h), a yield of the major product **20** increased up to 84% with decreased yields of **18** (10%) and **19** (trace). Although the products **18** and **20** were isolated in pure forms, **19** was too unstable to be isolated. Actually, **19** gradually changed into **20** even at room temperature in solution.

The spectral data of products **15**—**20** are summarized in Table 2. It is quite certain that the minor products **15** and **18** have the same ring structure to the spiro-cyclopenta[*b*]furans, **13a** and **14a**, by comparison of the spectral data.

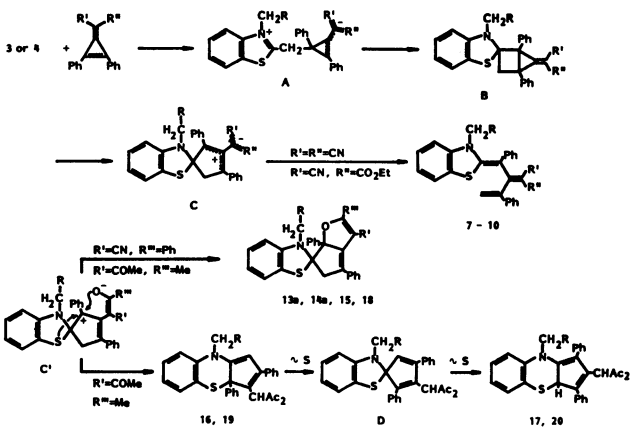
Structural elucidation of the major products, 2-(1-acetylacetonyl)-9-phenacyl-(**17**) and 2-(1-acetylacetonyl)-9-benzyl-1,3-diphenyl-3a,9-dihydrocyclopenta[*b*]-[1,4]benzothiazine (**20**), was accomplished on the basis of the spectral data. The ^{1}H NMR spectrum showed the signals of a methine and an enolic proton at δ 4.41 and 16.35 for **17** or at δ 4.26 and 16.32 for **20**, respectively, and the ^{13}C NMR spectra indicated the presence of a tertiary carbon in both **17** and **20**. In analogy with cross-conjugated systems, **7**—**10**, methylene protons and carbon in the phenacyl group in **17** or in the benzyl group in **20** are observed at considerably lower fields than those of the spiro-cyclopentafuran **13a** or **14a** respectively, meaning that the phenacyl or benzyl group should be located on an enamino nitrogen atom.[18] The above facts strongly support the assigned benzothiazine structures, **17** and **20**, arisen from a rearrangement of benzothiazoline ring.[19]

As mentioned above, the minor product **19**, whose spectral data are similar to those of **16**, changed into the major product **20**. Thus, **16** and **19** can be regarded as the precursors for **17** and **20**, respectively.

In the ^{1}H NMR spectrum of **16** or **19**, an enolic proton is also observed, but an olefinic proton appears instead of the methine one in **17** or **20**.[19] The phenacyl or benzyl group is under circumstance similar to that in **17** or **20**. Thus, it was deduced that the precursors are 3-(1-acetylacetonyl)-9-phenacyl-(**16**) and 3-(1-acetylacetonyl)-9-benzyl-2,3a-diphenyl-3a,9-dihydrocyclopenta[*b*][1,4]benzothiazine (**19**). In these cases, both the methyl groups are magnetically quite different (δ 0.73, 2.36 for **16** and δ 0.76, 2.28 for **19**) since one of them is forced to face the plane of the phenyl group at the 3a-position. The thermal isomerization of **16** into **17** or **19** into **20** might be driven by release from the steric hindrance around 3a-position.

Reaction Pathways. Although the mechanistic aspects concerning the reactions of enamines with methylenecyclopropenes have not been fully established,[8] the reaction of a cyclic enamine with methylenecyclopropenes leading to pentalene derivatives[20] and cross-conjugated systems[21] has been interpreted as *via* an intermediary [2+2] cycloadduct. The reaction pathways in this paper can be again explained as *via* an intermediary [2+2] cycloadduct (Scheme 3).

The electron-deficient endocyclic C=C bond of methylenecyclopropenes, **5**, **6**, **11**, and **12**, interacts



Scheme 3.

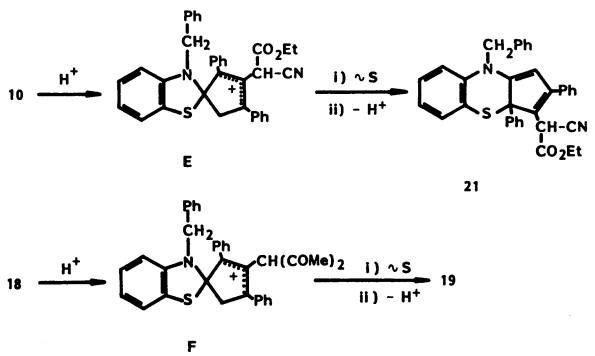
with the electron-rich exocyclic one of methylenebenzothiazolines, **3** and **4**, forming an intermediary [2+2] cycloadduct **B**, probably *via* a zwitterion **A**. The intermediate **B** undergoes a ring opening of the fused cyclopropane moiety to yield a new zwitterion **C** that is stabilized by the electron-withdrawing substituents (R′ and R″).

The five-membered ring of cyclopentadienyl cation in **C** opens in a conrotatory manner[21] to give the cross-conjugated systems, **7**—**10**, when the substituents have a relatively weak stabilization effect on the zwitterion **C** (R′ is cyano and R″ is cyano or ethoxycarbonyl).[22] On the other hand, when the substituents strongly stabilize **C** (R′=CN, R″=COPh; R′=R″=COMe)[22] and have at least one acyl moiety, the zwitterion **C** (=**C**′, R″=Ph, Me) takes an opportunity for the cyclization of the acyl group to give the spiro-cyclopentafurans, **13a**, **14a**, **15**, and **18**.

Another novel rearrangement also occurs in the case of **C** having two acetyl groups. The rearrangement of sulfur atom in **C**′ onto the cationic center followed by concurrent proton transfer gives the unstable cyclopenta[*b*][1,4]benzothiazines, **16** and **19**. Their lability might be due to steric hindrance between the phenyl group at the 3a-position and the 1-acetylacetonyl group. Release from the steric hindrance may cause the 1,5-sigmatropic rearrangement of sulfur atom to give a spiro intermediate **D**. A further rearrangement gives rise to the less hindered cyclopenta[*b*][1,4]benzothiazines, **17** and **20**. The reason why only the sulfur atom migrates in the rearrangements would be that the nitrogen migration does not reduce the steric hindrance around the position to which the nitrogen atom migrates.

The reaction pathways depicted in Scheme 3 are supported by the following facts. The cross-conjugated compound **10** canged into the cyclopenta[*b*][1,4]-benzothiazine **21**, whose structure was identified on the basis of the spectral data, when treated with a catalytic amount of hydrochloric acid at room temperature. Contrary to thermal instability of the previous cyclopenta[*b*][1,4]benzothiazines, **16** and **19**, the compound **21** is much more stable on heating. This stability may be due to the less steric hindrance of the cyano(ethoxycarbonyl)methyl substituent. On the treatment with hydrochloric acid, the spiro-cyclopenta[*b*]furan **18** quantitatively isomerized into **19** which further thermally changed into **20** (Scheme 4).

The above isomerizations seem to be explained as follows: Protonation onto the carbon possessing two electron-withdrawing substituents of **10** and a conrotatory cyclization of the resulting pentadienyl cation lead to an intermediate **E** that corresponds to a protonated **C** in Scheme 3. The similar rearrangement of sulfur atom with concurrent deprotonation gives **21**. Similarly, the oxygen atom of furan ring in **18** is protonated and the furan ring opens to form the similar intermediate **F** that gives **19** in the same manner.



Scheme 4.

As shown in Scheme 3, it is reasonable to say that the degree of stabilization of **C** by the electron-withdrawing substituents (R′ and R″)[22] primarily controls the reaction pathways.

Experimental

All melting points were determined on a Yanagimoto micro melting point apparatus and were uncorrected. The IR spectra were taken with a JASCO IRA-1 or a JASCO A-102 spectrometer. The ^{1}H NMR spectra were recorded on a Hitachi R-40 or a JEOL FX-100 instrument and ^{13}C NMR spectra were obtained on a JEOL FX-100 spectrometer at 25.05 MHz. Chemical shifts are expressed in parts per million downfield from tetramethylsilane. The UV spectra were recorded on a Shimadzu UV-240 spectrometer, and mass spectra were measured with a JEOL JMS-01SG-2 spectrometer at 75 eV of ionization energy. Elemental analyses were performed on a Hitachi 026 CHN analyzer. Thin-layer chromatography was accomplished on 0.2-mm precoated plates of silica gel 60 F-254 (Merck) or on 0.2-mm precoated plates of aluminum oxide 60 F-254 type E (Merck). Visualization was with ultraviolet light (254 and 365 nm) and iodine. Preparatory column chromatography was performed on silica gel Wako C-300 (Wako) or on neutral aluminum oxide Woelm type N (Woelm).

The reactions were performed under nitrogen atmosphere, and solvents were evaporated with a Tokyo Rikakikai rotary vacuum evaporator type V at 50 °C.

Materials. 2-Methyl-3-phenacylbenzothiazolium bromide (**1**)[23] was prepared according to the reported method. 3-Benzyl-2-methylbenzothiazolium bromide (**2**), mp 255—256 °C, was similarly prepared by refluxing equimolar amounts of 2-methylbenzothiazole and benzyl bromide in dry acetone for 7 h: Yield 31%; colorless prisms; IR 1570, 1450, 1430 cm^{-1}. 2-(2,3-Diphenyl-2-cyclopropenylidene)propanedinitrile (**5**),[24] ethyl 2-cyano-2-(2,3-diphenyl-2-cyclopropenylidene)acetate (**6**),[25] 2-benzoyl-2-(2,3-diphenyl-2-cyclopropenylidene)acetonitrile (**11**),[16] and 3-(2,3-diphenyl-2-cyclopropenylidene)-2,4-pentanedione (**12**)[26] were synthesized by the reaction of 1-ethoxy-2,3-diphenylcyclopropenium tetrafluoroborate with the corresponding active methylene compounds, respectively.

Reactions with 2-(2,3-Diphenyl-2-cyclopropenylidene)propanedinitrile (5). A solution of NEt_3 (0.12 g, 1.2 mmol) in dry chloroform (5 mL) was added dropwise, at 0 °C, to a stirred suspension of the benzothiazolium bromide **1** (0.41 g, 1.2 mmol) and **5** (0.3 g, 1.2 mmol) in dry chloroform (40 mL). After 3 h at room temperature, the reaction mixture was poured into water (200 mL) and extracted with chloroform (130 mL). The extract was dried over $MgSO_4$, and evaporated to give a red residue. The residue was chromatographed on silica gel using chloroform as an eluent to give 583 mg (95%) of the cross-conjugated system **7** which was recrystallized from benzene afforded reddish violet prisms. Found: C, 80.01; H, 4.93; N, 6.87%. Calcd for $C_{34}H_{23}N_3OS \cdot C_6H_6$: C, 80.07; H, 4.87; N, 7.00%. MS *m/e* 521 (M^+).

A similar reaction of the benzothiazolium bromide **2** (0.38 g, 1.2 mmol) with **5** (0.3 g, 1.2 mmol) in the presence of NEt_3 (0.12 g, 1.2 mmol) gave 545 mg (99%) of the cross-conjugated system **8** which was purified by recrystallization from benzene to give reddish violet prisms. Found: C, 81.87; H, 5.12; N, 7.50%. Calcd for $C_{33}H_{23}N_3S \cdot C_6H_6$: C, 81.90; H, 5.07; N, 7.35%. MS *m/e* 493 (M^+).

The spectral data of **7** and **8** are shown in Table 1.

*Reactions with Ethyl 2-Cyano-2-(2,3-diphenyl-2-cyclopropenylidene)acetate (**6**).* A solution of NEt_3 (0.1 g, 1 mmol) in dry THF (5 mL) was added dropwise, at 0 °C, to a stirred suspension of the benzothiazolium bromide **1** (0.35 g, 1 mmol) and **6** (0.3 g, 1 mmol) in dry THF (40 mL). After 1 h at room temperature, the precipitated triethylammonium bromide was filtered off and the filtrate was evaporated. The residue was chromatographed over neutral alumina using chloroform as an eluent affording 550 mg (80%) of the cross-conjugated system **9** which was purified by recrystallization from benzene to give violet prisms. Found: C, 76.22; H, 5.12; N, 4.95%. Calcd for $C_{36}H_{28}N_2O_3S$: C, 76.06; H, 4.93; N, 4.93%. MS *m/e* 568 (M^+).

A similar reaction of the benzothiazolium bromide **2** (0.32 g. 1 mmol) with **6** (0.3 g, 1 mmol) in the presence of NEt_3 (0.1 g, 1 mmol) yielded 510 mg (94%) of the cross-conjugated system **10** as reddish violet prisms. Found: C, 77.65; H, 5.19; N, 5.20%. Calcd for $C_{35}H_{28}N_2O_2S$: C, 77.76; H, 5.22; N, 5.18%. MS *m/e* 540 (M^+).

The spectral data of **9** and **10** are shown in Table 1.

*Reactions with 2-Benzoyl-2-(2,3-diphenyl-2-cyclopropenylidene)-acetonitrile (**11**).* A mixture of the benzothiazolium bromide **1** (0.35 g, 1 mmol), **11** (0.34 g, 1.1 mmol), and NEt_3 (0.1 g, 1 mmol) in dry THF (40 mL) was refluxed for 1 h. The precipitated triethylammonium bromide was filtered off and the filtrate was evaporated to give a colored residue. The residue was chromatographed over silica gel using benzene as an eluent to afford 215 mg (36%) of the spiro-cyclopenta[*b*]-furan **13a** which was purified by recrystallization from benzene–hexane. Found: C, 79.82; H, 4.95; N, 4.36%. Calcd for $C_{40}H_{28}N_2O_2S$: C, 79.98; H, 4.70; N, 4.66%. MS *m/e* 600 (M^+), 105.

Similarly, the benzothiazolium bromide **2** (0.32 g, 1 mmol) reacted with **11** (0.34 g, 1.1 mmol) in the presence of NEt_3 (0.1 g, 1 mmol) to give 264 mg (46%) of the spiro-cyclopenta-[*b*]furan **14a**. Found: C, 81.74; H, 4.90; N, 4.70%. Calcd for $C_{39}H_{28}N_2OS$: C, 81.80; H, 4.93; N, 4.89%. MS *m/e* 572 (M^+), 481, 105.

*Reactions with 3-(2,3-Diphenyl-2-cyclopropenylidene)-2,4-pentanedione (**12**).* A solution of NEt_3 (0.3 g, 3 mmol) in dry THF (5 mL) was added dropwise, at 0 °C, to a suspension of the benzothiazolium bromide **1** (1.04 g, 3 mmol) and **12** (0.86 g, 3 mmol) in dry THF (60 mL). After 0.5 h at room temperature, the precipitated triethylammonium bromide was filtered off and the filtrate was evaporated. The residue was dissolved in benzene and the benzene solution was passed through a short column packed with neutral alumina to afford a mixture of **15**, **16**, and **17** (1.48 g, 90%). The formation of the spiro-cyclopentafuran **15** and benzothiazine **16** was indicated by inspection of the ^1H NMR spectrum of the above mixture. Evaporation of the benzene gave yellow pasty material that solidified on trituration with hexane to give 1.45 g (87%) of the benzothiazine **17** which was purified by recrystallization from benzene–hexane.

The same reaction in dry acetonitrile (30 mL) gave **17** in 73% yield. The benzothiazine **17**. Found: C, 78.08; H, 5.49; N, 2.70%. Calcd for $C_{36}H_{29}NO_3S$: C, 77.84; H, 5.23; N, 2.52%. MS *m/e* 555 (M^+), 450, 435, 105.

A similar reaction of the benzothiazolium bromide **2** (0.96 g, 3 mmol) with **12** (0.86 g, 3 mmol) in THF (60 mL) in the presence of NEt_3 (0.3 g, 3 mmol) yielded a mixture of **18**, **19**, and **20** (1.39 g, 88%) whose relative yields were determined on the basis of the ^1H NMR spectrum (**18**: 21%; **19**: 10%; **20**: 57%). The mixture was carefully chromatographed over neutral alumina. The first benzene–hexane eluent afforded almost pure **20** and the next benzene eluent gave **18** which was contaminated with **20**. Both the spiro-cyclopentafuran **18** and benzothiazine **20** were purified by recrystallization from benzene–hexane.

The spirocyclopentafuran **18**. Found: C, 79.96; H, 5.61; N, 2.89%. Calcd for $C_{35}H_{29}NO_2S$: C, 79.67; H, 5.54; N, 2.66%. MS *m/e* 527 (M^+), 436, 91. The benzothiazine **20**. Found: C, 79.97; H, 5.59; N, 2.52%. Calcd for $C_{35}H_{29}NO_2S$: C, 79.67; H, 5.54; N, 2.66%. MS *m/e* 527 (M^+), 436, 394, 350, 91.

The spectral data of **15**—**20** are listed in Table 2.

*Acid-catalyzed Isomerization of the Cross-conjugated System **10**.* An ethanol solution (15 mL) of **10** (0.27 g, 0.5 mmol) containing a catalytic amount of hydrochloric acid was stirred at room temperature for 24 h and evaporated to give a residue. The residue was treated with 10% aqueous potassium carbonate and extracted with chloroform. The chloroform extract was dried over $MgSO_4$ and evaporated. Column chromatography of the residue over neutral alumina using benzene as an eluent afforded the benzothiazine **21** (0.057 g, 31%) which on recrystallization from benzene gave yellow prisms, mp 154—155 °C. IR (KBr) 2230 (C≡N), 1730 (C=O), 1590, 1540, 1440 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.03 (3H, t), 3.60 (2H, q), 4.56 (1H, s, –CH), 4.90, 5.10 (each 1H, d, NCH_2, J=18.0 Hz), 5.55 (1H, s, =CH), 6.60—7.60 (19H, m); ^{13}C NMR ($CDCl_3$) δ=13.55 (q, CH_3), 35.38 (d, CH), 53.36 (t, NCH_2), 59.01 (s, 3a-C), 62.67 (t, CH_2Me), 103.02 (d, 1-C), 164.17 (s, C–O); MS *m/e* 540 (M^+), 449, 403, 375, 91. Found: C, 77.70; H, 5.33; N, 5.10%. Calcd for $C_{35}H_{28}N_2O_2S$: C, 77.76; H, 5.22; N, 5.18%.

*Acid-catalyzed Isomerization of the Spiro-cyclopenta[b]furan **18**.* A drop of hydrochloric acid was added to a solution of **18** in deuteriochloroform and the ^1H NMR spectrum was started to measure at room temperature. The signals for **18** gradually disappeared with the appearance of those for the dihydrocyclopenta[*b*][1,4]benzothiazine **19**. In 0.5 h the change was completed and then **19** was observed to isomerize into **20**. After 15 h, the solvent was evaporated to give **20** in a quantitative yield.

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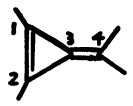
9) The numbering of methylenepropene system is as follows.[8)]



10) Some reactions of a ketene acetal with methylenecyclopropenes have been described as unpublished results in Ref. 8.

11) Part of this work has been reported as a preliminary communication: O. Tsuge, M. Tanaka, H. Shimoharada, and S. Kanemasa, *Chem. Lett.*, **1982**, 1353.

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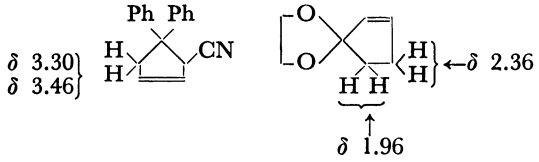

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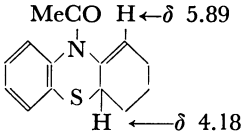

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