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Unique Condensation Reactions of Tropones with Bis(benzoylthio)trithiafulvene Leading to 10a*H*-Cyclohepta[*c*]-1,3-dithiolo[*e*][1,2]dithiin-2-thione

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Reactions of tropone derivatives with 4,5-bis(benzoylthio)-1,3-dithiole-2-thione (2,3,6-trithiafulvene derivative) afforded 1,3,5-cycloheptatriene derivatives doubly substituted by trithiafulvene and S–S groups (10a*H*-cyclohepta[*c*]-1,3-dithiolo[*e*][1,2]dithiin-2-thione). The structure of the 1,3,5-cycloheptatriene derivative and its crystal structure were investigated by single crystal X-ray analysis to show the existence of a unique three-dimensional network of the molecules through S···S contacts.

Not only from the viewpoint of pharmacological utilities, but also from chemical and physical interests in their reactivities and electronic natures, the chemistry of sulfur-containing heterocyclic compounds have attracted much attention from chemists.[1] A trithiafulvene derivative, 4,5-bis(benzoylthio)-1,3-dithiole-2-thione (**2**)[2] has been used to prepare donor components of several types of organic superconductors such as bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF).[3] While many studies have been published on the reactivities of sulfur-containing heterocyclic compounds to show facile occurences of cleavages and recombinations of C–S and S–S bonds,[4] only a few have been researched the reaction of trithiafulvene derivatives. The trithiafulvene derivative (**2**) has two benzoylthio groups per molecule, forming a tetrathio-substituted ethylene moiety, which is expected to show characteristic reactivities.

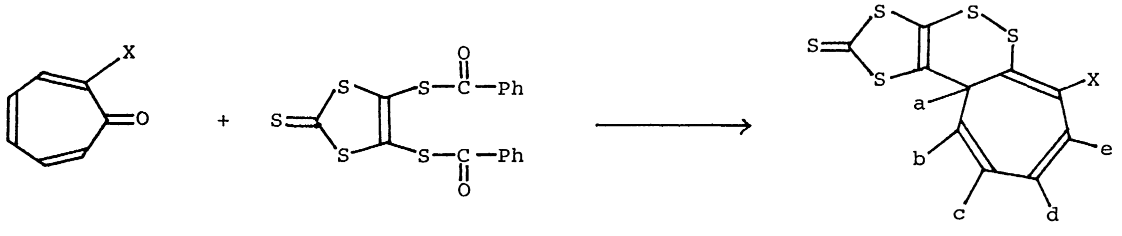
Tropones are known to have dipolar components constructing 6π-electron aromatic structures.[5] Despite their aromaticities, tropones are fairly active in addition reactions. Tropones not only react easily with halogens or hydrogenes,[6] but they also behave as 4π- or 8π-electron units in [4+2]- or [8+2]-type cycloaddition reactions, respectively.[7] Although many types of addition reactions of tropones and olefins or heterocyclic compounds have been researched extensively, studies of reactions with sulfur-containing compounds seem to be relatively few in number. This is curious, considering that tropothione and 2-mercatotropone have been attracting the attention of chemists because of their unique and characteristic reactivities caused by the introduction of sulfur atoms.[8]

As part of our research on the addition reactions of troponoid compounds,[9] we have studied the reactions of **2** with various tropones (**1**) to obtain condensation products leaving benzoic anhydride. We present our results in this report.

Results and Discussion

A solution of **2** and an excess amount of tropone (**1a**) was allowed to react at room temperature for 3 d. Separation and purification of the reaction mixture with silica-gel chromatography gave a crystalline product **3a** in a 39% yield (Scheme 1).[10] The analogous reaction using 2-phenyltropone (**1b**) in benzene resulted in a quantitative recovery of the starting materials. At an elevated temperature of 60 °C for 3 d, however, **3b** was obtained in a 14% yield. The reactions with 2-(*p*-methoxyphenyl)- (**1c**) and 2-methyltropones (**1d**) at 60 °C gave **3c** (26% yield) and **3d** (26% yield), respectively.

The structures of the products were deduced on the basis of their spectral properties. The molecular ion peaks in the high-resolution MS spectra demonstrated



1 **2** **3a—d**

a: X=H, **d**: X=Me,
b: X=Ph, **e**: X=Cl,
c: X=C_4H_6OMe(*p*-), **f**: X=CN

Scheme 1.

that the products were derived from the condensation reactions of **1** and **2** followed by the elimination of benzoic anhydride. ^{1}H NMR spectra and ^{13}C NMR spectra indicated the existence of a 1,3,5-cycloheptatriene moiety with a continued array of ring protons H_a, H_b, H_c, H_d, and H_e in that order, with H_a as a methine proton. The position of the substituents were determined by the use of NOE measurements.[11] The existence of thioxo groups was clearly demonstrated by characteristic absorptions at ca. 1060 cm^{-1} in the IR spectra.[2,3]

Finally, the structure of **3a** was determined unambiguously by X-ray analysis, indicating the existence of a disulfide bond (Fig. 1). The bond lengths and angles obtained were all normal (Table 1). The analysis of molecular planarity indicated that the trithiafulvene moiety had a planar conformation and that the S(5) atom deviated by 0.109 Å from this plane, while the cycloheptatriene moiety had a boat conformation.

In the crystal structure, a noticeable amount of overlapping was observed between two parallel-stacked trithiafulvenes as shown in Fig. 2. The interplanar distance of these rings was 3.57 Å. A three-dimensional network was also formed by intermolecular S····S interactions as shown in Fig. 3. The network was formed by four molecular linkages, which consisted of two types of S····S contacts, S(1)····S(4)=3.43 Å and S(2)····S(5)=3.57 Å, both shorter than the Van der Waals contact of 3.7 Å.

The formation of **3** is hypothesized to proceed as follows. The reaction is thought to be initiated by a nucleophilic attack of the oxygen atom of **1** on the carbonyl carbon of the benzoyl group of **2** to form the

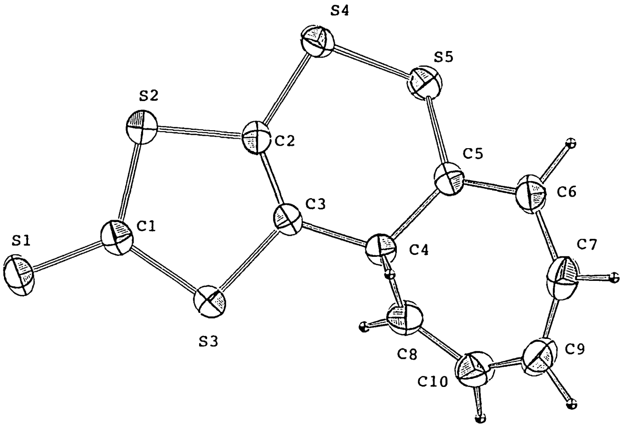


Fig. 1. ORTEP drawing of the crystal structure of **3a**.

Table 1. Fractional Atomic Coordinated (×10^4) and Equivalent Temperature Factors (Å^2). The Form of $B_{eq.}$ is $(4/3)\sum_{ij}\beta_{ij}(\boldsymbol{a}_i\cdot\boldsymbol{a}_j)$

Atom	x	y	z	B_{eq}
S1	5600(1)	−2567(1)	5584(1)	2.8
S2	4919(1)	−1568(1)	3273(1)	2.6
S3	3006(1)	−1288(1)	4568(1)	2.3
S4	3234(1)	−240(1)	1269(1)	2.4
S5	1943(1)	1569(1)	1266(1)	2.5
C1	4562(3)	−1862(4)	4535(2)	2.2
C2	3417(3)	−794(3)	2629(2)	2.0
C3	2511(3)	−671(3)	3225(2)	1.9
C4	1113(3)	−177(3)	2876(2)	1.9
C5	749(3)	616(3)	1788(2)	1.9
C6	−518(3)	693(4)	1267(3)	2.5
C7	−1591(3)	297(4)	1750(3)	2.8
C8	685(3)	917(4)	3661(3)	2.5
C9	−1633(3)	488(5)	2802(3)	3.1
C10	−587(4)	1109(5)	3637(3)	3.0

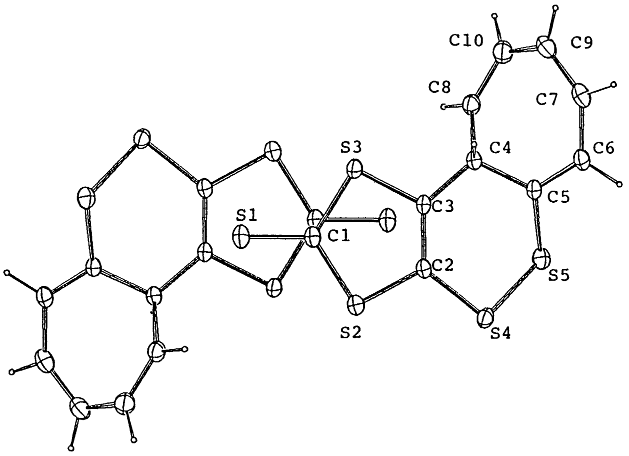


Fig. 2. The molecular overlap between two planar trithiafulvene moieties in molecules related by symmetry operations of x, y, z, and $1-x$, $-y$, $1-z$. The interplanar distance is 3.57 Å.

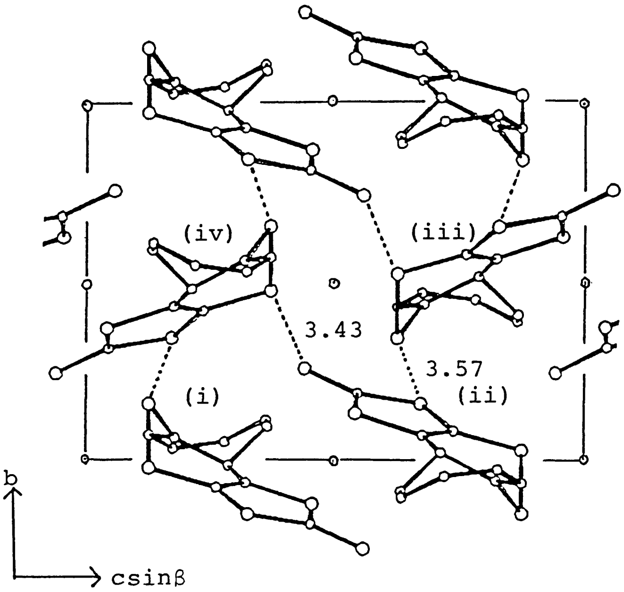
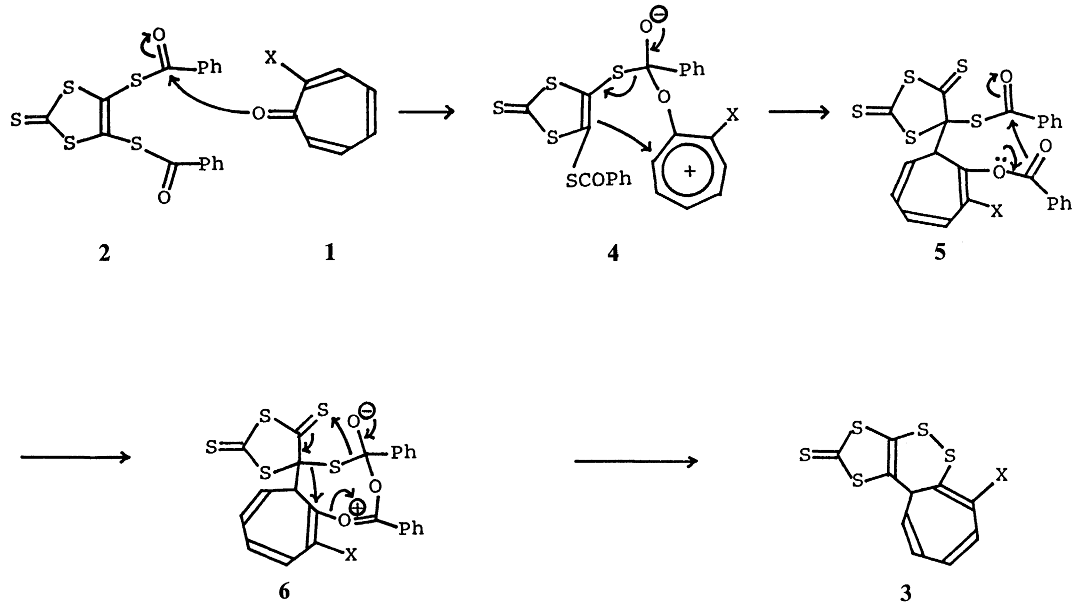


Fig. 3. The crystal structure viewed along the a axis. The network is formed by four molecular linkages of two types of S···S contacts. Symmetry operations of the molecules are (i)=x, y, z; (ii)=$1-x$, $-y$, $1-z$; (iii)=x, $1/2-y$, $1/2+z$; (iv)=$1+x$, $1/2+y$, $1/2-z$.



Scheme 2.

Table 2. Net Atomic Charges of Tropones (**1a**—**1f**)

X	Oxygen atom	Carbon atom of carbonyl group
H (**1a**)	−0.3302	+0.2731
Ph (**1b**)	−0.3234	+0.2833
C_6H_4OMe(-*p*) (**1c**)	−0.3386	+0.2948
Me (**1d**)	−0.3325	+0.2896
Cl (**1e**)	−0.2981	+0.2744
CN (**1f**)	−0.3093	+0.2811

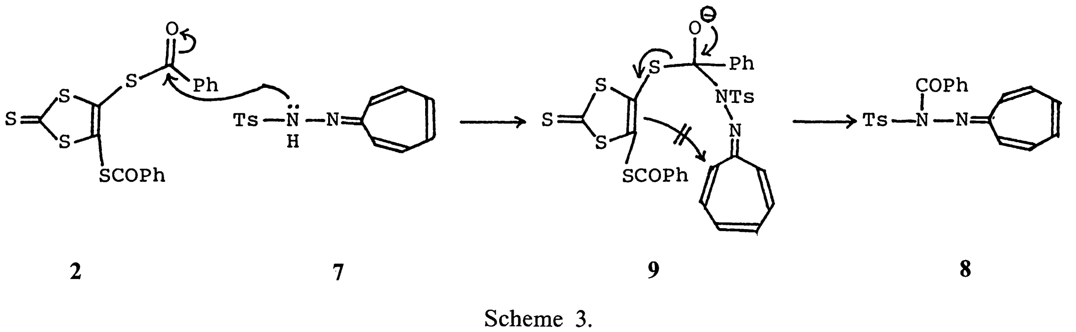
tropylium cation intermediate **4** (Scheme 2). The following observation seems to support this hypothesis.[7] Analogous reactions using tropones bearing electron-withdrawing groups such as a chloro (**1e**) or cyano (**1f**) group failed to give products of type **3**, but resulted in quantitative recoveries of the starting materials.

The MO calculations obtained by the MNDO method showed the existence of a relatively large charge separation between the carbon and the oxygen atoms of the carbonyl groups of **1a**—**1d**, supporting an initial nucleophilic attack by the carbonyl oxygen in the reaction as described above. The failure of the reactions of tropones bearing electron-attracting substituents such as chloro (**1e**) or cyano (**1f**) groups is thought to be attributable to the small degree of negative charge at the carbonyl oxygen atoms of these tropones (Table 2).[12]

The subsequent cleavage of a C–S bond and a nucleophilic attack of a C=C double bond of the trithiafulvene part on the tropylium cation moiety gives intermediate **5**. The substitution of four sulfur atoms is thought to contribute to the promotion of the nucleophilicity of the C=C bond. An attack by the carbonyl oxygen on the carbon atom of another carbonyl group yields intermediate **6**. A C–S bond cleavage and the elimination of benzoic anhydride produces the final product **3**.

The important role of the tropylium cation moiety in the reaction pathway was shown by the following experiment. Reaction of tropone tosylhydrazone (**7**)[13] with **2** in benzene at room temperature for 3 d gave no product corresponding to **3**, but yielded tropone *N*-benzoyltosylhydrazone (**8**) in a 74% yield (Scheme 3).

The reaction is thought to proceed through a pathway analogous to that of **1** initiated by an attack of the amino group of **7** on the carbonyl group of **2** to form an intermediate (**9**), which then undergoes a C–S bond cleavage.[14]



Scheme 3.

Experimental

Melting points were recorded on a Yanagimoto Micro Melting Point Apparatus and were uncorrected. The NMR spectra were measured with Hitachi R20B or Varian XL-200 spectrometers. IR, UV, and MS spectra were measured with JASCO FT/IR-5300, Hitachi 220A, and Hitachi M-2000S spectrometers, respectively. Wakogel C-200 and Wakogel B5-F were used for column and thin-layer chromatography, respectively.

Reaction of Tropone (1a) and 2. A mixture of **1a** (2.00 g, 20 mmol) and **2** (410 mg, 1 mmol) was stirred at room temperature for 3 d. Separation of the reaction mixture by column chromatography on silica gel gave crystals of **3a** (110 mg, 39% yield, with hexane), recovery of **2** (80 mg, with hexane–ethyl acetate 9:1), benzoic acid (78 mg, 32% yield, with hexane–ethyl acetate 4:1), and recovery of **1a** (1.67 g, with hexane–ethyl acetate 3:1). Recrystallization from benzene gave yellow plates of **3a**: Mp 147—149 °C. Found: C, 41.78; H, 2.00; S, 56.06%. Calcd for $C_{10}H_6S_5$: C, 41.93; H, 2.11; S, 55.96%. MS m/z (rel intensity) 286 (M^+, 46), 253 (41), 210 (46), 177 (82), and 146 (100). IR (KBr) 3030, 1360, 1050, 1030, 790, and 710 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=2.72 (dd, H_a), 5.43 (dd, H_b), 6.45 (m, H_c), and 6.62—6.84 (m, 3H, $H_{d,e,f}$). Coupling constants in Hz: J_{ab}=6.0, J_{ac}=1.0, J_{bc}=9.2, and J_{cd}=4.8. ^{13}C NMR ($CDCl_3$) δ=42.4, 122.7, 123.8, 126.7, 127.1, 130.2, and 131.7.

Reaction of 2-Phenyltropone (1b) and 2. A solution of **1b** (960 mg, 6 mmol) and **2** (410 mg, 1 mmol) in benzene (5 ml) was heated at 60 °C for 4 d. The reaction mixture was separated by column chromatography on silica gel to give crystals of **3b** (34 mg, 14% yield, with hexane–ethyl acetate 49:1), recovery of **2** (130 mg, with hexane–ethyl acetate 11:1), benzoic acid (60 mg, 25% yield, with hexane–ethyl acetate 11:1), and recovery of **1b** (830 mg, by hexane–ethyl acetate 9:1). Recrystallization from benzene gave yellow plates of **3b**: Mp 144—145 °C. High-resolution MS Found: m/z 361.9382. Calcd for $C_{16}H_{10}S_5$: m/z 361.9385. MS m/z (rel intensity) 362 (M^+, 14), 197 (50), and 165 (100). IR (KBr) 3030, 1480, 1070, 760, and 700 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=3.38 (d, H_a), 5.47 (dd, H_b), 6.38 (dd, H_c), 6.81 (d, H_e), 6.90 (dd, H_d), and 7.26—7.52 (m, 5H, Ph). Coupling constants in Hz: J_{ab}=6.0, J_{bc}=8.0, J_{cd}=4.8, and J_{de}=10.4. ^{13}C NMR ($CDCl_3$) δ=48.0, 123.4, 123.9, 125.7, 128.6, 129.7, 132.2, 134.0, 135.3, and 137.7.

Reaction of 2-(*p*-Methoxyphenyl)tropone (1c) with 2. A solution of **1c** (760 mg, 4 mmol) and **2** (410 mg, 1 mmol) in benzene (5 ml) was reacted at 60 °C for 5 d. The reaction mixture was separated by column chromatography on silica gel to give recovery of **2** (200 mg, with hexane–ethyl acetate 1:9), recovery of **1c** (680 mg, with hexane–ethyl acetate 1:4), and **3c** as an oil (50 mg, 26% yield, with hexane–ethyl acetate 1:9).

3c: High-resolution MS Found: m/z 391.9501. Calcd for $C_{17}H_{12}OS_5$: m/z 391.9492. MS m/z (rel intensity) 392 (M^+, 40), 290 (14), and 239 (100). IR (oil) 3030, 1600, 1500, 1240, 1060, 760, and 700 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=3.34 (d, H_a), 3.88 (s, 3H, Me), 5.48 (dd, H_b), 6.38 (dd, H_c), 6.82 (d, H_e), 6.91 (dd, H_d), and 6.96—7.40 (AA′BB′, 4H, benzene ring protons). Coupling constants in Hz: J_{ab}=4.5, J_{bc}=6.6, J_{cd}=3.9, and J_{de}=8.4. ^{13}C NMR ($CDCl_3$) δ=47.7, 55.2, 113.8, 114.1, 123.0, 123.3, 125.5, 129.9, 130.0, 131.0, 132.1, and 134.1.

Reaction of 2-Methyltropone (1d) with 2. A solution of **1d** (390 mg, 3 mmol) and **2** (410 mg, 1 mmol) in benzene (5 ml) was heated at 60 °C for 6 d. The reaction mixture was separated by column chromatography on silica gel to give **3d** as an oil (41 mg, 26% yield, with hexane), recovery of **2** (190 mg, with hexane–ethyl acetate 4:1), and recovery of **1d** (290 mg, with hexane–ethyl acetate 7:3).

3d: High-resolution MS Found: m/z 299.9217. Calcd for $C_{11}H_8S_5$: m/z 299.9229. MS m/z (rel intensity) 300 (M^+, 17), 205 (39), and 110 (100). IR (oil) 3020, 2950, 1050, 760, and 700 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=2.08 (s, 3H, Me), 3.30 (d, H_a), 5.41 (dd, H_b), 6.26 (dd, H_c), 6.73 (dd, H_d), and 6.87 (d, H_e). Coupling constants in Hz: J_{ab}=4.2, J_{bc}=6.8, J_{cd}=3.1, and J_{de}=8.3. ^{13}C NMR ($CDCl_3$) δ=29.7, 30.3, 123.2, 123.6, 125.4, 125.5, 130.9, and 135.5.

Reaction of Tropone Tosylhydrazone (7) with 2. A solution of **7** (280 mg, 1 mmol) and **2** (200 mg, 0.5 mmol) in benzene (5 ml) was stirred at room temperature for 4 d. The reaction mixture was separated by column chromatography on silica gel to give recovery of **2** (110 mg, with hexane–ethyl acetate 4:1) and an oil of a mixture of **7** and **8** (330 mg, with hexane–ethyl acetate 7:3). The mixture was subjected to preparative thin-layer chromatography on silica gel using chloroform–hexane 2:1 as a developing solvent to give **8** as an oil (63 mg, 74% yield, R_f=0.16).

8: High resolution MS Found: m/z 378.1045. Calcd for $C_{21}H_{18}N_2O_3S$: m/z 378.1039. MS m/z (rel intensity) 378 (M^+, 100), 278 (41), and 245 (38). IR (oil) 3030, 2980, 1670, 1530, 1350, 1250, and 1160 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=2.44 (s, 3H, Me), 6.60—7.00 (m, 6H, seven-membered ring protons), and 7.28—8.00 (m, 9H, benzene-ring protons). ^{13}C NMR ($CDCl_3$) δ=21.6, 127.7, 128.5, 128.9, 129.2, 129.6, 131.8, 133.0, 134.1, 134.9, 135.0, 135.1, 135.6, 136.6, 144.7, and 173.8.

Single Crystal X-Ray Analysis of 3a. The colorless crystals of $C_{10}H_6S_5$ belonged to the monoclinic space group $P2_1/c$. The cell constants were a=10.536(2), b=8.603(1), c=12.624(5) Å, β=102.62(2)°, and V=1116.6(6) Å^3. The unit cell contained four molecules giving a calculated density of 1.70 g cm^{-3}. A total of 4799 reflections within 2θ=65° were collected on a Rigaku-AFC-5PR defractometer with a rotating anode (200 mA, 45 kV) using graphite monochromated Mo-$K\alpha$ radiation (λ=0.71069 Å) with 2θ–ω mode. The structure was solved by the direct method and refined by the block-diagonal least-squares method anisotropically for non-hydrogen atoms and isotropically for hydrogen atoms which were located by a D-Fourier map. The final R-factor was 0.069 (R_w=0.054) for 4177 unique reflections with $F_o<3\sigma(F_o)$. All calculations were carried out on an ACOS2000 computer at Tohoku University using the applied library program UNICSIII.[15] A listing of positional and thermal parameters, bond lengths and angles, and structure factors are deposited as Document No. 8948 at the Office of the Editor of Bull. Chem. Soc. Jpn.

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10) All the yields were calculated on the basis of the actually consumed starting materials.

11) Irradiations of the phenyl groups of **3b** and **3c** resulted in 10 and 6% enhancements of the signals of proton H_e, respectively, but the signals of H_a showed no change. This fact showed that the phenyl groups are located close to H_e but not to H_a, suggesting the product structures to be **3**, but not **10** (Fig. 4).

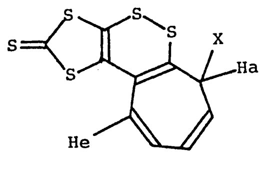

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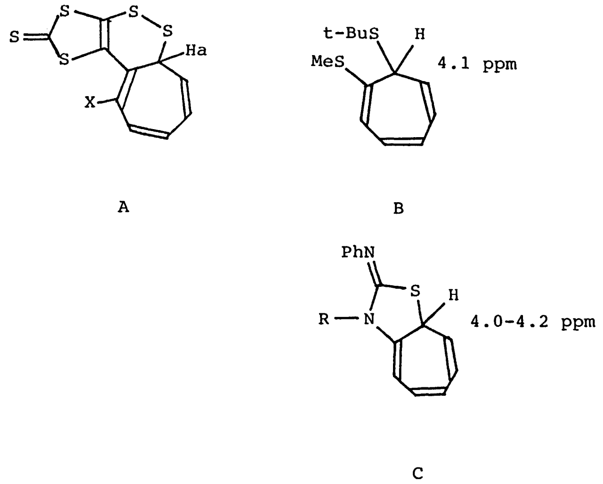
Fig. 4.



A B

C

Fig. 5.

Other possible structures such as A (Fig. 5) can be rejected by the fact that the chemical shifts of H_a of A should be expected to be about δ=4.0—4.2 refering to the analogous compounds B or C in the literatures. The observed chemical shifts of H_a of **3** (δ=2.72—3.38) are obviously different from these values, supporting the structures of **3** shown in Scheme 1. Y. Yamamoto, S. Kajigaeshi, and S. Kanemasa, *Chem. Lett.,* **1977**, 85; M. Cawazza, G. Morganti, and F. Pietra, *J. Chem. Soc., Chem. Commun.,* **1978**, 945.

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14) The subsequent nucleophilic attack by the double bond on the seven-membered ring, which was observed in intermediate **4**, did not occur. This discrepancy in the results can be explained by the difference between the reactivities of the tropilium cation moiety in **4** and the iminotropone moiety in **9** toward nucleophiles.

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