Cycloaddition Reactions of Thioacylketene Thioacetals and *N*-Thioacyldithioimidocarbonates

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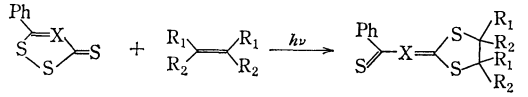
Thioacylketene thioacetals (**7**) and *N*-Thioacyldithioimidocarbonates (**8**) undergo 1,4-cycloaddition reactions with active acetylenes and olefins to give six-membered heterocycles. Tetracyanoethylene behaves in a different way to afford conjugated dienes. In the reactions with diphenylketene and diazo compounds, **7** and **8** undergo different types of reactions; **7** gave products derived from 1,2-cycloaddition to the C=S bond, while **8** afforded 1,4-cycloadducts. Compound **7** was found to be more reactive than **8**. The reactivity difference between **7** and **8** is discussed.

Conjugated dienes and their heteroanalogues (*i.e.*, heterodienes) (**1**) have been thoroughly investigated in organic chemistry.[1-5] However, investigations on heterodienes having a thiocarbonyl group (**1**, W and/or Z=S), are relatively scarce.[6-9]

W=X—Y=Z

1 W, X, Y, Z=C, O, N, S *etc.*

The finding[10] that the photoreactions of 1,2,4-dithiazole-3-thione (**2**) and 1,2-dithiole-3-thione (**3**) with olefins (**4**) provide a facile and efficient route to conjugated thiones such as 2-thioacylimino- (**5**) and 2-thioacylmethylene-1,3-dithiolanes (**6**) has aroused interest in the reactivity of these conjugated heterodienes containing a thiocarbonyl group.



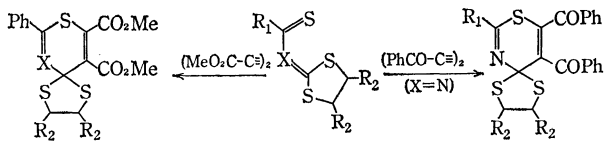
2: X=N
3: X=CH, CPh

4

5: X=N
6: X=CH, CPh

Compounds **5** and **6** undergo 1,2- and 1,4-cycloaddition reactions with some types of reagents.[11,12] This paper gives a detailed account of these cycloaddition reactions.

Reactions with Electron-Deficient Acetylenes. Reactions of **7** and **8** with dibenzoylacetylene or dimethyl acetylenedicarboxylate afforded 1,4-cycloadducts (**9**, **10**, or **11**) in good yields.

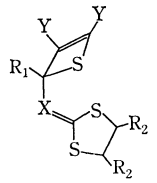


10: X=CH, $R_2R_2=(CH_2)_4$
11: X=N, R_2=H

7: X=CH, R_1=Ph, $R_2R_2=(CH_2)_4$
8a: X=N, R_1=Ph, $R_2R_2=(CH_2)_4$
8b: X=N, R_1=Ph, R_2=H
8c: X=N, R_1=Me, R_2=H

9a—c

The possibility of a 1,2-cycloadducts such as **12** or **13** was excluded for the following reasons: (i) the UV spectra of **9** and **11** show no absorption due to a thiocarbonyl or thioamide group in the visible region, (ii) the NMR signals of four methylene protons in **9b** and **9c** appear as an A_2B_2 multiplet at δ 3.5, while **8b** and **8c**, which have an iminodithiolane ring, show their methylene protons as a singlet at δ 3.5, and (iii) thiete[13] is unstable in contrast to the high thermal stability of **9**—**11** obtained here.



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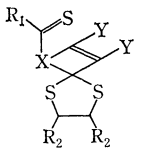

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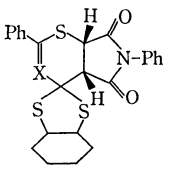
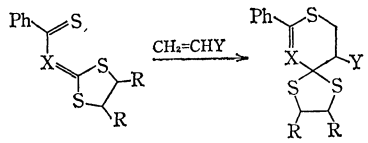


14: X=CH
15: X=N

Reactions with Electron-Deficient Olefins. Reactions of **7** and **8** with *N*-phenylmaleimide in refluxing benzene afforded 1,4-cycloadducts **14** and **15** in 67 and 70% yields, respectively. The NMR signals of the two methine protons at 5- and 6-positions appear as an AB quartet (J=10 Hz for **14** and J=9 Hz for **15**) at about δ 4.4. The value of this coupling constant indicates their *cis* configuration.

Reactions of **7**, **8a**, and **8b** with acrylamide in refluxing xylene afforded 1,4-cycloaddition products **16**, **17a**, and **17b**, respectively. In the case of **8a** and **8b**, the cycloadditions were carried out using acrylonitrile, methyl vinyl ketone, methyl and ethyl acrylates, and acrylaldehyde. The yields of the products and the reaction conditions are summarized in Table 1.



7: X=CH, RR=$(CH_2)_4$
8a: X=N, RR=$(CH_2)_4$
8b: X=N, R=H

16: X=CH, RR=$(CH_2)_4$, Y=$CONH_2$
17: X=N, Y=$CONH_2$
18: X=N, Y=CN
19: X=N, Y=$COCH_3$
20: X=N, Y=CO_2CH_3
21: X=N, Y=CHO
22: X=N, Y=$CO_2C_2H_5$

Compound **17a** consists of two isomers (**17a**α and **17a**β), both of which can be isolated by chromatography. Very similar spectral characteristics of the two isomers (see Experimental) indicate that they are isomeric with respect to the direction of the cyclohexane ring, although no assignment has been made. Hereafter such isomers are denoted by α and β. As regards compound **17b**,

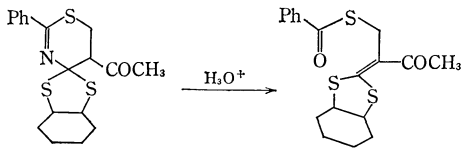
Table 1. Yields and conditions of reactions of **8** with monosubstituted olefins

8	Olefin	Solvent	Temp (°C)	Time (h)	Product (%)
8a	$Y=CONH_2$	Xylene	140	24	**17a** (52)
8b	$Y=CONH_2$	Xylene	140	8	**17b** (22)
8a	Y=CN	Xylene[a]	140	24	**18a** (73)
8a	$Y=COCH_3$	Xylene[a]	140	24	**19a** (80)
8a	$Y=CO_2CH_3$	Xylene[a]	140	24	**20a** (40)
8b	Y=CHO	Benzene[a]	90	9	**21b** (74)
8b	$Y=CO_2C_2H_5$	DMF[a]	154	12	**22b** (44)

a) In a sealed tube.

a single product and no isomer was obtained, in line with the above argument.

The orientation of addition in these reactions was established by acid-catalyzed hydrolysis of **19a**, affording **23**.



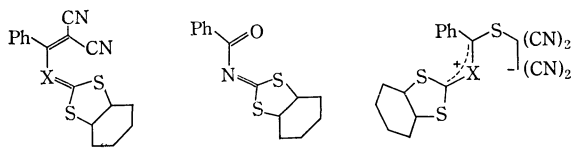
19a **23**

Since the other adducts (**17**—**22**) show similar spectral features to those of **19**, they would have a similar orientation to that in **19**, suggesting that the addition reaction takes place in a regioselective manner.

The reactions of **7** and **8a** with dimethyl fumarate, dimethyl maleate, and crotononitrile were carried out in order to examine the stereospecificity of the 1,4-cycloaddition reactions. However, they did not occur under the same conditions.

Reaction of **7** with tetracyanoethylene (TCNE) in refluxing acetonitrile afforded **24** (57%), while **8a** gave **25** (10%) and **26** (18%).

The formation of **24**—**26** can be explained in terms of the intermediacy of the zwitterion **27**; 1,2-addition followed by the elimination of $(NC)_2C{=}S$[14] would give **24** and **25** and hydrolysis by adventitious water in the solvent would lead to **26**.

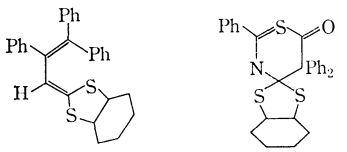


24: X=CH **26** **27**
25: X=N

Reaction with Diphenylketene. Reactions of **7** and **8a** with diphenylketene in *N,N*-dimethylformamide (DMF) at room temperature afforded diene **28** and 1,4-cycloadduct **29** in 88 and 80% yields, respectively. The NMR spectrum of **29** shows two methine protons as multiplets centered at δ 2.60 and 3.25 with equal intensity, suggesting the presence of two isomers (α and β forms). Compound **28** is identical with the compound obtained by desulfurization of episulfide **35** (*vide infra*).

The mass spectrum of **29** shows a weak metastable ion peak corresponding to the loss of COS from the molecular ion, but no molecular ion peak. The IR spectrum shows the presence of a carbonyl group at 1700 cm^{-1}, typical of an ester of alkanethioic *S*-acid.[15]

Formation of vinylketene thioacetal (**28**) is explicable by 1,2-cycloaddition to the thiocarbonyl bond followed by elimination of COS, in contrast to the formation of 1,4-cycloadduct (**29**) from **8a**.

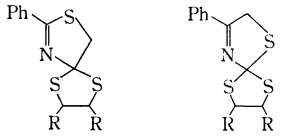


28 **29**

Reactions with Diazo Compounds. Reactions of **8a** and **8b** with diazomethane in ether at room temperature afforded 1,4-adducts **30a** (90%) and **30b** (90%), respectively, while **7** gave no tractable product.

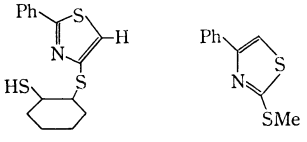
Compound **30a** consists of two stereoisomers (**30a**α and **30a**β), both of which are isolable by chromatography. The fact that the UV spectrum of **30a** has an absorption maximum at 247.5 nm, which is similar to that of the above-mentioned [4+2] adducts with olefins, strongly supports the structure **30** having Ph–C(=N–)S– unit.

A strong peak at *m/e* 121 ($PhCS^+$) in its mass spectrum is compatible with **30**, but not with isomeric structure **31**.



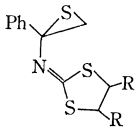
30a: RR=$(CH_2)_4$ **31**
b: R=H

Acid hydrolysis of **30a** yielded **32**. The UV spectrum shows absorption maxima at 254.5 (ε 15700) and 308 nm (7310), which are much higher than those reported[16] for **33** [238 (ε 18000) and 268 nm (12200)], a structure similar to that obtained from **31**.



32 **33**

The possibility of episulfide (**34**) as an alternative structure of **30** is excluded by the fact that **30** was not desulfurized by triphenylphosphine. Episulfide **35** underwent desulfurization by triphenylphosphine to give diene **28**.



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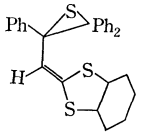
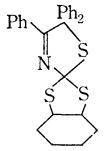


35

Compound **7** reacted with diphenyldiazomethane in ether at room temperature to give episulfide **35** in 47% yield, whereas **8a** (in benzene) afforded **36** (51%), **37** (16%), and **38** (7%).



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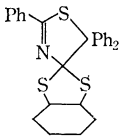

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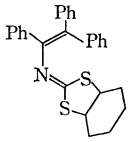
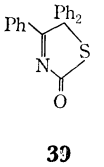


38

Compound **36** also consists of two chromatographically isolable stereoisomers (**36**α and **36**β). The fragmentation pattern of the mass spectrum of **36** is similar to that of **38**, but not to that of **37**. Compound **36** has strong peaks at *m/e* 427 (M^+-S), 287 ($PhCPh_2CS^+$), and 255 ($PhCCPh_2^+$), whereas these peaks are negligible in the case of **37**. Although both **36** and **37** have an absorption maximum near 253 nm, they differ in pattern, that of **37** being very similar to the pattern of [4+2] adducts obtained from olefins. Further support for the structure **36** comes from conversion (treatment with trimethyloxonium tetrafluoroborate and subsequent hydrolysis) of the thioacetal into the carbonyl group to give **39**, which has a different melting point from that reported for **40**.[17]



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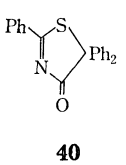

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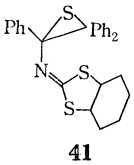
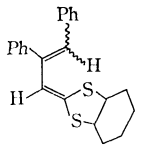


41

The possibility of episulfide **41** as an alternative to **36** or **37** is excluded also in this case; the compounds (**36** and **37**) undergo no desulfurization by triphenylphosphine.

Reaction of **7** with phenyldiazomethane in ether led to diene **42** (61%) instead of the corresponding episulfide like **35**.

Thione **43** also reacted with diphenyl- or phenyldiazomethane to give **44** (93%), or **45** (7%), and **47** (67%), respectively. Episulfide **44** gave **46** by triphenylphosphine.



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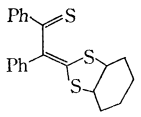

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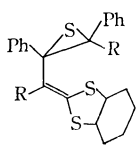
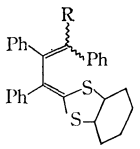
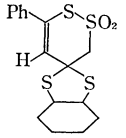


44: R=Ph **45**: R=H



46: R=Ph **47**: R=H

Reaction with Sulfene. Sulfene generated *in situ* from methanesulfonyl chloride and triethylamine at 5 °C in benzene reacted with **7** to afford 1,4-cycloadduct **48** (57%). Under comparable conditions **8a** did not react with sulfene.



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Comparison of the Reactivities of Thioacylketene Thioacetal (7) and N-Thioacyldithioimidocarbonate (8). A comparison of the reaction conditions of **7** with those of **8** in some reactions is given in Table 2.

Table 2. Comparison of the reactions of **7** and **8**

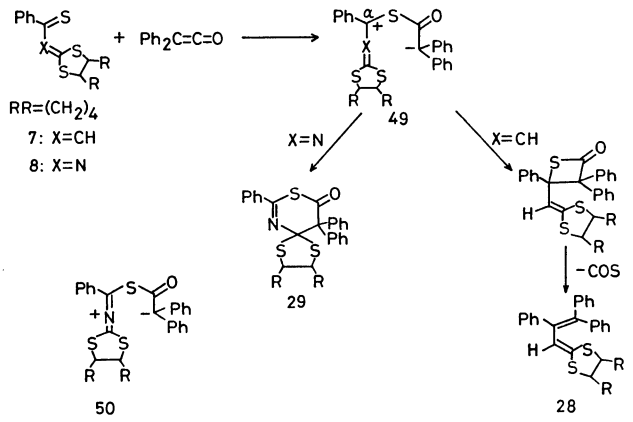
Reagents	**7**	**8**
$MeO_2C-C\equiv C-CO_2Me$	in CH_2Cl_2, r.t. 10 h	in benzene, r.t. 7 days
N-Phenylmaleimide	in benzene, reflux, 4 h	in benzene, reflux, 58 h
Acrylamide	in xylene, reflux, 2 h	in xylene, reflux, 24 h
TCNE	in CH_3CN, reflux, 2 h	in CH_3CN, reflux, 28 h
Ph_2CN_2	in ether, r.t. 15 h	in ether, r.t. 3 days
Sulfene[a]	in benzene, 5 °C, 1 h	no reaction

a) Generated from methanesulfonyl chloride and triethylamine.

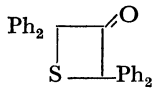
We see that **8** requires severer conditions than **7**, indicating that the reactivity of **8** is lower than that of **7**. This is in line with the known fact[2] that the reactivity of dienes decreases upon replacement of its component carbon by nitrogen, which is due to the lowering of HOMO level of the diene part.

The reactions of **8** with diphenylketene and diazo compounds give rise to 1,4-cycloadducts, while those of **7** afford products *via* 1,2-addition. The preference of 1,4-addition over 1,2-addition in the reactions of **8** presumably reflects an importance of the lone pair electrons of nitrogen in these reactions.

The reaction with diphenylketene most likely proceeds *via* zwitterionic intermediate (**49**). This is strongly supported by the observation that the reaction of **7** with the ketene is greatly accelerated by use of a polar solvent; the reaction requires refluxing for 2 days in benzene whereas in DMF it was complete after 12 h at room temperature.



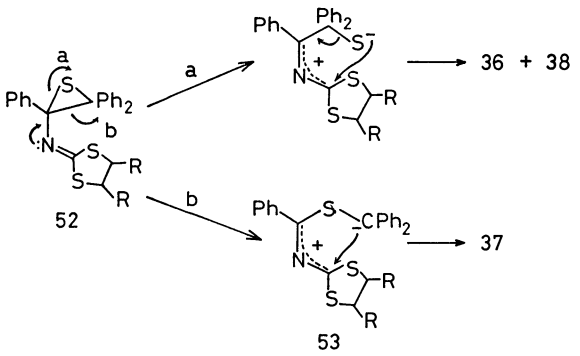
In the case of **8**, the possible contribution of canonical structure (**50**) would reduce reactivity of C_α, thus leading to 1,4-adduct. It is noteworthy that the reaction pattern of **7** and **8** with the ketene differs from that of thiobenzophenone, a typical thioketone, which gives 3-oxothietane (**51**).[18]



51

The fact[19] that the reaction product of a thioketone with diphenyldiazomethane is always an episulfide shows that **35** is the expected product in the reaction of **7** with diphenyldiazomethane.

The instability of **52** as compared with **35** is most probably due to the additional assistance of the heterolytic cleavage by the nitrogen lone pair electrons other than by the N=C double bond as depicted below. The preferable cleavage *via* path *a* over *via* path *b* is presumably due to the higher lability of the C–S bond in heterolytic cleavage and also to the stability of thiolate anion thus formed.



For the formation of **37**, however, the possibility that **53** or its diradical counterpart is formed directly from the two substrates can not be excluded.

Experimental

IR and UV spectra were recorded on Hitachi EPI-G2 and ESP-3 spectrophotometers, respectively. The NMR spectra were obtained in deuteriochloroform solution, unless otherwise noted, at 60 MHz with a Hitachi R-24 spectrometer using tetramethylsilane as an internal standard. The mass spectra were measured with a Hitachi RMU-6 spectrometer (beam energy 70 eV). All the reactions were carried out under nitrogen or argon.

*Preparation of 2-Thiobenzoylimino-1,3-dithiolane (**8b**).* To a solution of 2-benzoylimino-1,3-dithiolane[20] (0.5 g, 2.2 mmol) in benzene (20 ml) was added phosphorus pentasulfide (2 g, 4 mmol) and pyridine (1 ml). The mixture was refluxed for 4.5 h under stirring. The phosphorus pentasulfide was filtered off and the filtrate was washed with water until the aqueous layer became neutral. The benzene layer was dried ($MgSO_4$) and evaporated under reduced pressure. The residue was subjected to dry column chromatography (DCC) (silica gel, ether–hexane (1 : 2)) to give 246 mg (46%) of **8b** as a purple oil. The oil was crystallized from ether at Dry Ice temperature as thin purple crystals, mp 49—50 °C; NMR: δ 3.4 (s, 4H), 7.2—7.6 (m, 3H), and 8.2—8.5 (m, 2H); UV: λ_{max} (CH_2Cl_2) 239 (ε 13400), 327 (25500), 370 sh (10100), and 560 nm (161).

*Preparation of 2-Thioacetylimino-1,3-dithiolane (**8c**).* A mixture of 2-acetylimino-1,3-dithiolane[20] (1 g, 6.2 mmol), phosphorus pentasulfide (3 g, 6 mmol) and pyridine (1 ml) in benzene (40 ml) was heated at 70 °C for 1 h under stirring. After the usual work-up, the residue was subjected to DCC (silica gel, CH_2Cl_2) to give 0.5 g (46%) of **8c** as a red oil, which could not be crystallized. NMR: δ 2.75 (s, 3H) and 3.55 (s, 4H).

*Reaction of **7** with Dimethyl Acetylenedicarboxylate.* A solution of **7**[10] (140 mg, 0.48 mmol) and the ester (91 mg, 0.64 mmol) in dichloromethane (3 ml) was left to stand at room temperature for 10 h. After evaporation of the solvent, the residue was recrystallized from methanol to give **10** (173 mg, 83%); mp 128—129 °C; IR (KBr): 1735 cm^{-1}; NMR: δ 1.3—2.2 (m, 8H), 3.85 (s, 6H), 3.9—4.2 (m, 2H), 6.30 (s, 1H), and 7.30—7.65 (m, 5H).

Found: C, 58.32; H, 5.08; S, 21.87%. Calcd for $C_{21}H_{22}O_4S_3$: C, 58.04; H, 5.10; S, 22.13%.

*Reaction of **8a** with Dibenzoylacetylene.* A solution of **8a**[10] (293 mg, 1 mmol) and the acetylene (281 mg, 1.2 mmol) in benzene (30 ml) was refluxed for 9.5 h. The solvent was evaporated *in vacuo* and the residue was subjected to DCC (silica gel, CH_2Cl_2–CCl_4 (1 : 1)) to give **9a** (320 mg, 61%) as colorless crystals; mp 148—149 °C (dec) (from cyclohexane); IR (KBr): 1660 cm^{-1}; NMR: δ 1.1—2.5 (m, 8H), 3.7—4.0 (m, 2H), and 7.1—8.1 (m, 15H); UV: λ_{max} (CH_2Cl_2) 257 nm (ε 35400); MS: *m/e* 104 (30%) and 103 (100).

Found: C, 68.19; H, 4.65; N, 2.48; S, 18.11%. Calcd for $C_{30}H_{25}NO_2S_3$: C, 68.28; H, 4.77; N, 2.65; S, 18.23%.

*Reaction of **8b** with Dibenzoylacetylene.* A solution of **8b** (102 mg, 0.4 mmol) and the acetylene (100 mg, 0.4 mmol) in benzene (20 ml) was stirred at room temperature for 4 days. A similar treatment to that in the reaction of **8a** gave 168 mg (84%) of **9b**; mp 170—170.5 °C (dec) (from CH_2Cl_2–MeOH); IR (KBr): 1660 and 1590 cm^{-1}; NMR: δ 3.5 (m, 4H) and 7.1—8.1 (m, 15H).

Found: C, 66.01; H, 3.90; N, 3.01; S, 20.33%. Calcd for $C_{26}H_{19}NO_2S_3$: C, 65.93; H, 4.04; N, 2.96; S, 20.31%.

*Reaction of **8b** with Dimethyl Acetylenedicarboxylate.* A mixture of **8b** (156 mg, 0.65 mmol) and the ester (*ca.* 0.3 ml) in benzene (20 ml) was stirred at room temperature for 7 days. The benzene was evaporated and the residue was chromatographed (DCC, silica gel) with CH_2Cl_2 to give 196 mg (79%) of **11**; mp 171—172 °C (from CH_2Cl_2–MeOH); IR (KBr): 1730 cm^{-1}; NMR: δ 3.65 (m, 4H), 3.92 (s, 3H), 3.95 (s, 3H), 7.3—7.6 (m, 3H), and 7.7—8.1 (m, 2H); UV: λ_{max}

(CH_2Cl_2) 254.5 nm (ε 22000); MS: *m/e* 381 (M^+, 9%) and 353 (100).

Found: C, 50.32; H, 3.80; N, 3.72; S, 25.04%. Calcd for $C_{16}H_{15}NO_4S_3$: C, 50.37; H, 3.96; N, 3.67; S, 25.21%.

Reaction of ***8c*** *with Dibenzoylacetylene.* A solution of **8c** (231 mg, 1.4 mmol) and the acetylene (332 mg, 1.4 mmol) in chloroform (10 ml) was stirred at room temperature for 4 days. After removal of chloroform, the residue was chromatographed with CH_2Cl_2–CCl_4 (2 : 1) to give 460 mg (80%) of **9c**; mp 62—63 °C (CH_2Cl_2–MeOH); IR (KBr): 1660 cm^{-1}; NMR: δ 2.4 (s, 3H), 3.4 (m, 4H), and 7.1—8.0 (m, 10H); UV: λ_{max} (CH_2Cl_2) 259.5 nm (ε 29800); MS: *m/e* 411 (M^+, trace) and 47 (100%).

Reaction of ***7*** *with* N*-Phenylmaleimide.* A mixture of **7** (144 mg, 0.50 mmol) and the imide (110 mg, 0.63 mmol) in benzene (4 ml) was refluxed for 4 h. The residue obtained after removal of benzene was recrystallized from ethanol to afford **14** (122 mg, 67%); mp 179.5—181.0 °C; IR (KBr): 1720 cm^{-1}; NMR: δ 1.1—2.2 (m, 8H), 3.6—4.2 (m, 2H), 4.35 (ABq, 2H, J=10 Hz, $\Delta\delta$=0.29), 6.97 (s, 1H), and 7.1—7.7 (m, 10H).

Found: C, 59.30; H, 6.48; N, 3.55; S, 26.00%. Calcd for $C_{25}H_{23}NO_2S_3$: C, 59.14; H, 6.34; N, 3.83; S, 26.31%.

Reaction of ***8a*** *with* N*-Phenylmaleimide.* A solution of **8a** (293 mg, 1 mmol) and the imide (208 mg, 1.2 mmol) in benzene (30 ml) was refluxed for 58 h. The solvent was evaporated and the residue was subjected to preparative TLC (silica gel, CH_2Cl_2–hexane (1 : 1)) to give **15** (326 mg, 70%) as colorless crystals; mp 208—209 °C (from EtOH); IR (KBr): 1720 cm^{-1}; NMR: δ 1.0—2.7 (m, 8H), 3.6—4.1 (m, 2H), 4.1 (d, 1H, J=9 Hz), 4.7 (d, 1H, J=9 Hz), and 7.0—8.2 (m, 10H); UV: λ_{max} (EtOH) 249 (ε 19800) and 309 nm (3690); MS: *m/e* 466 (M^+, 19%), and 104 (100).

Found: C, 61.98; H, 4.76; N, 5.96; S, 20.41%. Calcd for $C_{24}H_{22}N_2O_2S_3$: C, 61.77; H, 4.75; N, 6.00; S, 20.61%.

Reaction of ***7*** *with Acrylamide.* A suspension of **7** (146 mg, 0.50 mmol), acrylamide (351 mg, 5.0 mmol) and a trace of hydroquinone in xylene (4 ml) was refluxed for 2 h. After cooling, excess acrylamide was filtered off and the filtrate was washed thoroughly with water to remove acrylamide. After removal of the solvent, the residue was recrystallized from methylcyclohexane to give **16** (127 mg, 70%); mp 190—191 °C; IR (KBr): 3450 and 1670 cm^{-1}; NMR: δ 0.9—2.3 (m, 8H), 3.32 (bs, 3H), 3.7—4.1 (m, 2H), 6.28 (s, 1H), 6.1—6.6 (m, 2H), and 7.1—7.7 (m, 5H).

Found: C, 59.78; H, 5.90; N, 3.75; S, 26.18%. Calcd for $C_{18}H_{21}NOS_3$: C, 59.47; H, 5.82; N, 3.85; S, 26.46%.

Reaction of ***8a*** *with Acrylamide.* A mixture of **8a** (293 mg, 1 mmol), acrylamide (710 mg, 10 mmol) and a small amount of hydroquinone in xylene (10 ml) was refluxed for 24 h. After similar work-up to that in the reaction of **7**, the reaction mixture was subjected to DCC (silica gel, ether). The column was divided into four fractions. The second fraction was recrystallized from methanol to afford 76 mg (21%) of **17a**α; mp 194—194.5 °C; IR (KBr): 3460, 3420, and 1660 cm^{-1}; NMR: δ 1.0—2.5 (m, 8H), 3.35 (m, 1H), 3.4—3.7 (m, 2H), 3.9—4.4 (m, 2H), 5.8—6.9 (bd, 2H), 7.2—7.6 (m, 3H), and 7.7—8.0 (m, 2H); UV: λ_{max} (EtOH) 246 nm (ε 13400); MS: *m/e* 364 (M^+, trace) and 121 (100%).

Found: C, 56.27; H, 5.56; N, 7.39; S, 26.27%. Calcd for $C_{17}H_{20}N_2OS_3$: C, 56.01; H, 5.53; N, 7.68; S, 26.39%.

The third fraction was also recrystallized from methanol to give 112 mg (31%) of **17a**β; mp 192—192.5 °C; IR (KBr): 3450 and 1665 cm^{-1}; NMR: δ 1.2—2.6 (m, 8H), 3.15 (m, 1H), 3.4—3.7 (m, 2H), 3.7—4.1 (m, 2H), 6.2—7.0 (bd, 2H), 7.25—7.65 (m, 3H), and 7.65—8.0 (m, 2H); UV: λ_{max} (EtOH) 246 nm (ε 13400); MS: *m/e* 364 (M^+, trace) and 121 (100%).

Found: C, 55.99; H, 5.55; N, 7.77; S, 26.10%. Calcd for $C_{17}H_{20}N_2OS_3$: C, 56.01; H, 5.53; N, 7.68; S, 26.39%.

Reaction of ***8b*** *with Acrylamide.* A solution of **8b** (359 mg, 1.5 mmol), acrylamide (727 mg, 10 mmol), and a small amount of hydroquinone in xylene (15 ml) was refluxed for 8 h. After the same treatment as described above, the residue was subjected to preparative TLC on silica gel with chloroform–ethyl acetate (1 : 1) to give 69 mg (22%) of **17b**; mp 179—180 °C (from MeOH); IR (KBr): 3460 and 1685 cm^{-1}; NMR: δ 3.2—3.9 (m, 7H), 6.1—6.9 (bd, 2H), 7.2—7.6 (m, 3H), and 7.6—8.0 (m, 2H).

Found: C, 50.10; H, 4.49; N, 8.98; S, 30.70%. Calcd for $C_{13}H_{14}N_2OS_3$: C, 50.29; H, 4.55; N, 9.02; S, 30.98%.

Reaction of ***8b*** *with Ethyl Acrylate.* A solution of **8b** (239 mg, 1 mmol), the ester (1 g, 10 mmol), and a small amount of hydroquinone in DMF (20 ml) was heated at 154 °C for 14 h in a sealed tube. The DMF solution was poured into water and extracted with CH_2Cl_2. The extracts were washed with water, dried ($MgSO_4$) and evaporated. The residue was subjected to preparative TLC (silica gel, CH_2Cl_2) to give 149 mg (44%) of **22b** as a yellow oil; IR (neat): 1730 cm^{-1}; NMR: δ 1.23 (t, 3H, J=7 Hz), 3.2—3.9 (m, 7H), 4.2 (q, 2H, J=7 Hz), 7.2—7.6 (m, 3H), and 7.6—8.0 (m, 2H).

Reaction of ***8a*** *with Acrylonitrile.* A mixture of **8a** (293 mg, 1 mmol), acrylonitrile (530 mg, 10 mmol) and a small amount of hydroquinone in xylene (1 ml) was heated in a sealed tube at 140 °C for 1 day. After removal of the solvent *in vacuo*, the residue was subjected to DCC (silica gel, CH_2Cl_2) to give 252 mg (73%) of **18a** as colorless crystals; mp 134—135 °C (from MeOH); IR (KBr): 2240 cm^{-1}; NMR: δ 1.0—2.1 (m, 8H), 3.45 (bs, 3H), 3.85—4.3 (m, 2H), 7.2—7.65 (m, 3H), and 7.65—7.9 (m, 2H); UV: λ_{max} (EtOH) 248 nm (ε 18100); MS: *m/e* 346 (M^+, 2%) and 121 (100).

Found: C, 59.19; H, 5.30; N, 7.92; S, 27.47%. Calcd for $C_{17}H_{18}N_2S_3$: C, 58.92, H, 5.24; N, 8.08; S, 27.76%.

Reaction of ***8a*** *with Methyl Vinyl Ketone.* The reaction was carried out in the same scale and under the same conditions as those in the reaction with acrylonitrile. The same work-up gave 291 mg (80%) of **19a**; mp 175—176 °C (from MeOH); IR (KBr): 1710 cm^{-1}; NMR: δ 1.0—2.4 (m, 8H), 2.35 (s, 3H), 3.5 (bs, 3H), 3.7—4.0 (m, 1H), 4.0—4.35 (m, 1H), 7.2—7.6 (m, 3H), and 7.6—8.1 (m, 2H); UV: λ_{max} (EtOH) 247 nm (ε 16900); MS: *m/e* 363 (M^+, trace) and 121 (100%).

Found: C, 59.29; H, 5.75; N, 3.81; S, 26.42%. Calcd for $C_{18}H_{21}NOS_3$: C, 59.47; H, 5.82; N, 3.85; S, 26.46%.

Acid-catalyzed Hydrolysis of ***19a.*** A mixture of **19a** (530 mg, 1.46 mmol) and 1 M sulfuric acid (3 ml) in ethanol (10 ml) was refluxed for about 10 h. After removal of ethanol 100 ml of water was added and the solution was extracted with CH_2Cl_2. The dried extract was evaporated and the residue was subjected to DCC (silica gel, CH_2Cl_2) gave 177 mg (33%) of **23**; mp 127—128 °C (from MeOH); IR (KBr): 1650 and 1630 cm^{-1}; NMR: δ 1.05—2.30 (m, 8H), 2.30 (s, 3H), 3.47—3.96 (m, 2H), 4.25 (s, 2H), 7.0—7.46 (m, 3H), and 7.5—8.17 (m, 2H); UV: λ_{max} (EtOH) 238 (ε 12600), 273 (11100), and 330 nm (14700); MS: *m/e* 364 (M^+, 5%) and 227 (100).

Found: C, 59.22; H, 5.42; S, 26.36%. Calcd for $C_{18}H_{20}O_2S_3$: C, 59.31; H, 5.53; S, 26.39%.

Reaction of ***8a*** *with Methyl Acrylate.* The reaction was also carried out in the same way as that in the reaction with acrylonitrile to give **20a** (154 mg, 40%); mp 132.5—133 °C

(from MeOH); IR (KBr): 1740 cm^{-1}; NMR: δ 1.0—2.6 (m, 8H), 3.4—3.75 (m, 3H), 3.72 (s, 3H), 3.75—4.1 (m, 2H), 7.15—7.5 (m, 3H), and 7.6—7.9 (m, 2H); UV: λ_{max} (EtOH) 247 nm (ε 14000); MS: *m/e* 379 (M^+, trace) and 121 (100%).

Found: C, 57.16; H, 5.54; N, 3.65; S, 25.11%. Calcd for $C_{18}H_{21}NO_2S_3$: C, 56.96; H, 5.58; N, 3.69; S, 25.34%.

Reaction of ***8b*** *with Acrylaldehyde.* A solution of **8b** (239 mg, 1 mmol), acrylaldehyde (168 mg, 3 mmol), and a small amount of hydroquinone in benzene (3 ml), was heated at 90 °C for 9 h in a sealed tube. After evaporation of the solvent, the residue was chromatographed with ether-hexane (4 : 1) to give 219 mg (74%) of **21b** as a yellow oil; IR (KBr): 1720 cm^{-1}; NMR: δ 2.8—4.0 (m, 7H), 7.2—7.6 (m, 3H), 7.6—7.9 (m, 2H), and 9.9 (s, 1H).

Reaction of ***7*** *with TCNE.* A solution of TCNE (144 mg, 1.12 mmol) and **7** (290 mg, 1.0 mmol) in acetonitrile (5 ml) was refluxed for 2 h. After the usual work-up, the reaction mixture was subjected to DCC (silica gel, $CHCl_3$) to give yellow crystals **24** (212 mg, 57%); mp 146.5—148 °C (from MeOH); IR (KBr): 2200 (C≡N) and 1495 cm^{-1} (conj. C=C); NMR: δ 1.1—2.0 (m, 8H), 3.6—4.0 (m, 2H), 6.98 (s, 1H), and 7.1—7.6 (m, 5H); MS: *m/e* 324 (M^+, 33%) and 81 (100).

Found: C, 66.75; H, 5.02; N, 8.77; S, 19.55%. Calcd for $C_{18}H_{16}N_2S_2$: C, 66.63; H, 4.97; N, 8.63; S, 19.76%.

Reaction of ***8a*** *with TCNE.* A solution of **8a** (293 mg, 1 mmol) and TCNE (153 mg, 1.2 mmol) in acetonitrile (50 ml) was refluxed for 28 h. Purification by DCC (silica gel, CH_2Cl_2-CCl_4 (2 : 1)) and preparative TLC (silica gel, CH_2Cl_2-hexane (2 : 1)) gave 32 mg (10%) of **25** (a yellow oil); IR (neat): 2220 cm^{-1}; NMR: δ 1.2—2.4 (m, 8H), 3.9—4.4 (m, 2H), and 7.2—7.9 (m, 5H); UV: λ_{max} (CH_2Cl_2) 230 (ε 13500), 277 (17200), 314 (19600), and 324 nm (18400); MS: *m/e* 325 (M^+, 2%) and 81 (100); and 51 mg (18%) of **26** (colorless crystals); mp 110.5—111 °C (from EtOH); IR (KBr): 1625 cm^{-1}; NMR: δ 1.2—2.4 (m, 8H), 3.7—4.2 (m, 2H), 7.25—7.65 (m, 3H), and 8.15—8.45 (m, 2H); MS: *m/e* 277 (M^+, 3%) and 105 (100).

Found: C, 60.85; H, 5.40; N, 4.85; S, 23.09%. Calcd for $C_{14}H_{15}NOS_2$: C, 60.62; H, 5.45; N, 5.05; S, 23.12%. Compound **25** was not purified so as to give an analytically pure specimen.

Reaction of ***7*** *with Diphenylketene.* A DMF solution (10 ml) of **7** (292 mg, 1 mmol) and the ketene[21] (1.0 g, 5.2 mmol) was stirred at room temperature for 10 h. Addition of water, extraction with ether and then DCC (hexane-ether (9 : 1)) afforded **28** (376 mg, 88%) as yellow crystals. A similar reaction in refluxing benzene for 47 h also gave **28** (85%), which was identical with the desulfurization product of **35** by triphenylphosphine (*vide infra*).

Reaction of ***8a*** *with Diphenylketene.* A solution of **8a** (293 mg, 1 mmol) and the ketene (1.07 g, 5.5 mmol) in DMF (10 ml) was stirred at room temperature for 2 days. After similar work-up to that described above, DCC (silica gel, CH_2Cl_2-hexane (2 : 1)) of the residue afforded 389 mg (80%) of **29**. It was thermally unstable, undergoing fragmentation to **8a** upon refluxing in ethanol. Mp 122—125 °C (dec) (from CH_2Cl_2-MeOH). IR (KBr): 1700 cm^{-1}; NMR: δ 0.7—2.5 (m, 8H), 2.4—2.8 (m, 1H), 3.05—3.45 (m, 1H), and 6.9—7.85 (m, 15H); UV: λ_{max} (CH_2Cl_2)229 (ε 17400) and 251 nm (18200); MS: *m/e* 427 (0.3%) and 165 (100).

Found: C, 68.68; H, 5.11; N, 2.86; S, 19.49%. Calcd for $C_{28}H_{25}NOS_3$: C, 68.96; H, 5.17; N, 2.87; S, 19.72%.

Reaction of ***8a*** *with Diazomethane.* A solution of **8a** (293 mg, 1 mmol) and a large excess of diazomethane[22] in ether (150 ml) was stirred for 1 h. The ether was evaporated and the residue was subjected to preparative TLC (silica gel, benzene) to give 129 mg (41%) of **30a**α and 154 mg (50%) of **30a**β. **30a**α: mp 90—91 °C (from EtOH); NMR: δ 1.1—2.7 (m, 8H), 4.07 (s, 2H), 3.8—4.3 (m, 2H), 7.3–7.7 (m, 3H), and 7.8—8.2 (m, 2H); UV: λ_{max} (EtOH) 247.5 (ε 17800) and 285 sh nm (6340); MS: *m/e* 307 (M^+, 12%), 274 (10), 225 (100), and 121 (22).

Found: C, 58.69; H, 5.61; N, 4.63; S, 31.01%. Calcd for $C_{15}H_{17}NS_3$: C, 58.59; H, 5.56; N, 4.56; S, 31.28%.

30aβ: mp 92—93 °C (from EtOH); NMR: δ 1.1—2.7 (m, 8H), 4.07 (s, 2H), 3.9—4.4 (m, 2H), 7.3—7.7 (m, 3H), and 7.8—8.2 (m, 2H); UV: λ_{max} (EtOH) 247.5 (ε 17800) and 285 sh nm (6340); MS: *m/e* 307 (M^+, 5%), 274 (4), 225 (27), 193 (100), and 121 (10).

Found: C, 58.83; H, 5.55; N, 4.80; S, 30.96%. Calcd for $C_{15}H_{17}NS_3$: C, 58.59; H, 5.56; N, 4.56; S, 31.28%.

Acid-Catalyzed Hydrolysis of ***30a***α. An ethanol solution (25 ml) of **30a**α (192 mg, 0.63 mmol) and 3/2M sulfuric acid (2 ml) was refluxed for 15 h. After removal of ethanol, 50 ml of water was added and the solution was extracted with CH_2Cl_2, the extract being dried over $MgSO_4$, and the solvent evaporated. The residue subjected to preparative TLC (silica gel, hexane-ether (4 : 1)) gave 108 mg (56%) of **32** as a colorless oil; IR (neat): 2550 cm^{-1}; NMR: δ 0.8—2.1 (m, 8H), 2.04 (d, 1H, J=6.5 Hz), 3.5 (m, 1H), 3.86 (m, 1H), 7.18 (s, 1H), 7.25—7.6 (m, 3H), and 7.7—8.15 (m, 2H); MS: *m/e* 307 (M^+, 4%) and 193 (100); and 21 mg (11%) of **30a**β.

Reaction of ***8b*** *with Diazomethane.* A solution of **8b** (239 mg, 1 mmol) and a large excess of diazomethane in ether (200 ml) was stirred at room temperature for 1 h. The solvent was evaporated and the residue was chromatographed (DCC, silica gel) with CH_2Cl_2-CCl_4 (1 : 1) to give 228 mg (90%) of **30b**; mp 104—105 °C (from EtOH); NMR: δ 3.52 (m, 4H), 3.95 (s, 2H), 7.2—7.6 (m, 3H), and 7.6—8.0 (m, 2H); MS: *m/e* 253 (M^+, 28%), 193 (100), and 121 (29).

Found: C, 52.26; H, 4.21; N, 5.43; S, 37.86%. Calcd for $C_{11}H_{11}NS_3$: C, 52.14; H, 4.34; N, 5.53; S, 37.96%.

Reaction of ***7*** *with Diphenyldiazomethane.* A mixture of **7** (876 mg, 3.0 mmol) and the diazomethane[23] (873 mg, 4.5 mmol) in ether (70 ml) was stirred at room temperature for 17 h. Colorless precipitates **35** (651 mg, 47%) were collected and recrystallized from benzene-ether; mp 147—148 °C; NMR: δ 0.9—2.0 (m, 8H), 3.5—3.75 (m, 2H), 5.85 (s, 1H), and 6.8—7.7 (m, 15H); MS: *m/e* 458 (M^+, trace), 426 (70%), and 344 (100).

Found: C, 73.41; H, 5.86; S, 20.67%. Calcd for $C_{28}H_{26}S_3$: C, 73.31; H, 5.72; S, 20.97%.

Reaction of ***8a*** *with Diphenyldiazomethane.* A solution of **8a** (879 mg, 3 mmol) and the diazomethane (679 mg, 3.5 mmol) in benzene (30 ml) was stirred for 5 days. The solvent was evaporated *in vacuo* and the residue was subjected to preparative TLC (silica gel, benzene-CCl_4 (1 : 1)) to give 592 mg (43%) of **36**α, 109 mg (8%) of **36**β, 219 mg (16%) of **37**α, and 93 mg (7%) of **38** as pale yellow crystals. **36**α: mp 158.5—159 °C (from CH_2Cl_2-MeOH); NMR: δ 1.0—2.5 (m, 8H), 3.8—4.15 (m, 2H), and 6.9—7.9 (m, 15H); UV: λ_{max} (EtOH) 253 (ε 12900) and 281 nm (9180); MS: *m/e* 459 (M^+, 2%), 427 (100), 345 (56), 313 (42), 287 (39), and 255 (42).

Found: C, 70.32; H, 5.37; N, 3.22; S, 20.93%. Calcd for $C_{27}H_{25}NS_3$: C, 70.55; H, 5.48; N, 3.05; S, 20.92%.

36β: mp 171—172 °C (from CH_2Cl_2-MeOH); NMR: δ 1.0—2.5 (m, 8H), 3.9—4.3 (m, 2H), and 6.8—7.8 (m, 15H); UV: λ_{max} (EtOH) 253 (ε 12900) and 281 nm (9180); MS: *m/e* 459 (M^+, 8%), 427 (87), 345 (35), 313 (45), 287 (26), 255 (38), and 81 (100).

Found: C, 70.49; H, 5.38; N, 3.17; S, 20.99%. Calcd for $C_{27}H_{25}NS_3$: C, 70.55; H, 5.48; N, 3.05; S, 20.92%.

37α: mp 185—186 °C (from CH_2Cl_2–MeOH); NMR: δ 1.0—2.5 (m, 8H), 3.1—3.5 (m, 2H), and 6.9—8.0 (m, 15H); UV: λ_{max} (EtOH) 253 (ε 16100) and 310 nm (3350); MS: *m/e* 459 (M^+, 11%), 427 (3), 345 (8), 313 (54), 261 (41), and 121 (100).

Found: C, 70.82; H, 5.47; N, 3.23; S, 20.84%. Calcd for $C_{27}H_{25}NS_3$: C, 70.55; H, 5.48; N, 3.05; S, 20.92%.

38: mp 92—93 °C (from hexane); NMR: δ 1.0—2.0 (m, 8H), 3.6—4.1 (m, 2H), and 7.0—7.6 (m, 15H); UV: λ_{max} (EtOH) 236 (ε 14200) and 305 nm (8110); MS: *m/e* 427 (M^+, 100%), 345 (38), 313 (13), 287 (30), and 255 (33).

A similar experiment was carried out in ether using 293 mg (1 mmol) of **8a** and 241 mg (1.2 mmol) of diphenyldiazomethane, 144 mg (31%) of **36α**, 62 mg (13%) of **36β**, 57 mg (12%) of **37α**, 73 mg (16%) of **37β** and 101 mg (24%) of **38** being obtained. **37β**: mp 231—232 °C (from CH_2Cl_2–MeOH); NMR: δ 1.0—2.0 (m, 8H), 3.8—4.2 (m, 2H), and 6.9—7.9 (m, 15H); UV: λ_{max} (EtOH) 253 (ε 16100) and 305 nm (3350); MS: *m/e* 459 (M^+, 8%), 427 (4), 345 (24), 313 (49), 261 (36), and 121 (100).

Found: C, 70.54; H, 5.44; N, 3.42; S, 20.40%. Calcd for $C_{27}H_{25}NS_3$: C, 70.55; H, 5.48; N, 3.05; S, 20.92%.

*Conversion of **36α** into **39**.* A solution of **36α** (100 mg, 0.22 mmol) and trimethyloxonium tetrafluoroborate (66 mg, 0.46 mmol) in CH_2Cl_2 (20 ml) was refluxed for 10 h. The reaction mixture was subjected to preparative TLC (silica gel, benzene) to give 27 mg (27%) of unchanged **36α**, 48 mg (48%) of **36β**, and 15 mg (27%) of **39**, mp 166—167 °C; IR (KBr): 1705 cm^{-1}; NMR: δ 7.3—7.8 (m, 13H) and 7.8—8.15 (m, 2H); MS: *m/e* 329 (M^+, 21%) and 198 (100).

*Reaction of **7** with Phenyldiazomethane.* An ethereal solution (40 ml) of **7** (205 mg, 0.7 mmol) and excess phenyldiazomethane[24] was stirred at room temperature for 2 h. TLC purification afforded **42** (176 mg, 61%) as a yellow oil. NMR: δ 1.0—2.1 (m, 8H), 3.5—3.85 (m, 2H), 6.50 (s, 1H), 7.10 (s, 1H), and 6.9—7.5 (m, 10H); MS: *m/e* 350 (M^+, 14%) and 278 (100).

Found: C, 75.16; H, 6.07%. Calcd for $C_{22}H_{22}S_2$: C, 75.37; H, 6.34%.

*Reaction of **43** with Diphenyldiazomethane.* A benzene solution (35 ml) of **43**[10] (368 mg, 1 mmol) and diphenyldiazomethane (388 mg, 2 mmol) was stirred at room temperature for 15 h. After the usual work-up, **44** (447 mg, 93%) was obtained as colorless crystals. No analytically pure sample could be obtained. Mp 157—158.5 °C (dec) (from hexane-ether); NMR: δ 0.8—2.1 (m, 8H), 3.2—3.6 (m, 2H), and 6.8—7.6 (m, 20H); MS: *m/e* 534 (M^+, trace), 502 (trace), and 78 (100%).

*Reaction of **43** with Phenyldiazomethane.* A benzene solution (25 ml) of **43** (204 mg, 0.55 mmol) and excess phenyldiazomethane was stirred at room temperature for 2 h. DCC (SiO_2, hexane-benzene(1 : 1)) gave yellow crystals (201 mg), recrystallization of which from ether gave **45** (18 mg, 7.1%) as colorless crystals, the filtrate affording **47** (157 mg, 67%) as pale yellow crystals. **45**: mp 159—160.2 °C (dec); NMR: δ 0.9—1.55 (m, 8H), 3.2—3.75 (m, 2H), 4.45 (s, 1H), and 6.9—7.6 (m, 15H); MS: *m/e* 458 (M^+, trace), 426 (8%), and 344 (100). **47**: mp 64—65 °C; NMR: δ 0.8—1.9 (m, 8H), 3.3—3.85 (m, 2H), and 6.9—7.6 (m, 16H); MS: *m/e* 426 (M^+, 13%) and 344 (100). No analytically pure sample could be obtained.

*Desulfurization of Episulfides **35** and **44**.* a) A benzene solution (10 ml) of **35** (46 mg, 0.1 mmol) and triphenylphosphine (29 mg, 0.11 mmol) was left to stand at room temperature for 5 days. The usual work-up afforded **28** (43 mg) quantitatively as yellow crystals. Mp 144—145.5 °C (from EtOH); NMR: δ 0.9—1.9 (m, 8H), 3.4—3.7 (m, 2H), 6.25 (s, 1H), and 6.7—7.35 (m, 15H); MS: *m/e* 426 (M^+, 71%) and 344 (100).

Found: C, 78.55; H, 5.88; S, 14.90%. Calcd for $C_{28}H_{26}S_2$: C, 78.82; H, 6.15; S, 15.03%.

Desulfurization was also effected by refluxing benzene solution (24 h) of **35** without triphenylphosphine.

b) A benzene solution (10 ml) of **44** (54 mg, 0.1 mmol) and triphenylphosphine (29 mg, 0.11 mmol) was refluxed for 4 h. TLC purification gave 46 mg (91%) of **46** as yellow crystals; mp 164.5—165.5 °C (from EtOH); NMR: δ 1.0—2.0 (m, 8H), 3.5—3.8 (m, 2H), and 6.9—7.8 (m, 20H); MS: *m/e* 502 (M^+, 52%), 420 (76), and 344 (100).

Found: C, 81.43; H, 6.01; S, 17.55%. Calcd for $C_{34}H_{30}S_2$: C, 81.24; H, 6.02; S, 17.75%.

*Reaction of **7** with Sulfene.* To a benzene solution (5 ml) of **7** (292 mg, 1.0 mmol) and methanesulfonyl chloride (296 mg, 2.58 mmol) was added dropwise triethylamine (290 mg, 2.87 mmol) in benzene at 5 °C. After 1 h, insoluble material was filtered off, the filtrate being washed with water and dried over anhydrous magnesium sulfate. The solvent was evaporated to give brown solid (0.356 g), which was purified by TLC (silica gel, $CHCl_3 : CCl_4 = 1 : 2$) to afford **48** (211 mg, 57%); mp 149—150 °C (from MeOH); IR (KBr): 1450 and 1320 cm^{-1} (SO_2); NMR: δ 1.2—2.3 (m, 8H), 4.0—4.4 (m, 2H), 4.51 (s, 2H), 6.02 (s, 1H), and 7.2—7.6 (m, 5H); MS: *m/e* 306 (M^+–SO_2, 16%) and 64 (100).

Found: C, 51.57; H, 4.95; S, 34.28%. Calcd for $C_{16}H_{18}O_2S_4$: C, 51.86; H, 4.90; S, 34.61%.

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