

Vowinckel's phenyl ether preparation [3].

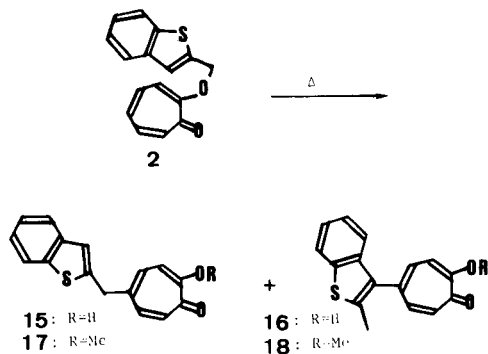
When **1** was heated at 160° in *o*-dichlorobenzene, a neat reaction occurred. The neutral fractions of the thermolysate mixture furnished the recovered **1** and the 5-(2-thienylmethyl) derivative of **1** 2-(2-thienylmethoxy)-5-(2-thienylmethyl)troponone (**5**). The occurrence of **5** and **3** constituted the most direct and firm evidence for the intermolecular reaction mechanism.

In addition, the structure analysis of the acidic thermolysates led to the same conclusion. The acidic thermolysates were methylated with diazomethane, and separated by chromatography as the 2-methoxytroponone derivatives **6-10** and **11** among which **11** was dethienylated 2-methoxytroponone. Two methyl ethers **6** and **7** were hydrolyzed to same 3,5-bis(2-thienylmethyl)troponone (**12**), from which they are 2-methoxy-3,5-bis(2-thienylmethyl)troponone and 2-methoxy-5,7-bis(2-thienylmethyl)troponone, respectively. Another methyl ether, **8**, was hydrolyzed to 5-(2-thienylmethyl)troponone (**13**), and **8** is shown to be 2-methoxy-5-(2-thienylmethyl)troponone.

Two isomeric methyl ethers **9** and **10** obtained from the next fractions were hydrolyzed to another similar 1:1-product **14**.

Unlike **B**, the thermolysis of 2-(2-thienylmethoxy)troponone (**1**) afforded neither 3- nor 5-(2-methyl-3-thienyl)troponone, thus, the thienyl group behaved differently from the furyl group.

Formation of by-products, disubstituted derivative **12** as well as the thienylated (thienylmethoxy)troponone **5** [4], prompted us to carry out the independent thermolysis of **5**; after the thermolysis, the mixture was directly extracted with potassium hydroxide solution, and the whole acidic fraction was chromatographically fractionated to give 3,5-bis(2-thienylmethyl)troponone (**12**) in 37% yield and dethienylation product **13** in 37% yield. The absence of a trisubstituted derivative may be attributed to a steric hindrance in an intermediate **C**.



Scheme 3

Similar treatment of 2-(2-benzo[*b*]thienylmethoxy)troponone (**2**), gave two thermolysates; they were 5-(2-benzo[*b*]

thienylmethyl)troponone (**15**), the major product, and 5-(2-methyl-3-benzo[*b*]thienyl)troponone (**16**) [5], the minor product, according to nmr spectroscopy. Formation of the single methyl ethers **17** and **18**, respectively, from **15** and **16** indicated them to be the 5-substituted troponones. In this case, the absence of a 3-rearrangement product might be attributable to steric hindrance. In the thermolysis of 2-(1-naphthylmethoxy)troponone, the yield of a 5-rearrangement product was also higher than the 3-rearrangement product [1a].

These experiments indicated that the reaction is a radical chain reaction. It should be emphasized that, although the reactants are structurally eligible to symmetry-allowed electrocyclic reactions [6] such as thermal 3,3- [1a,7] or 5,5-sigmatropy [8], a radical chain reaction actually occurred. This peculiar reactivity can be explained only in terms of a 1,9-sigmatropy. In fact, the 1,9-sigmatropy of troponoids has been already noticed in the "acylotropy," which has been indicated by Masamune and Nozoe *et al.* [9], for the degenerated rearrangement of 2-acyloxytropones such as 2-acetytroponone and 2-benzoyloxytroponone. Namely, in the cases of **1** and **2**, both thermally-allowed electrocyclic processes, Claisen rearrangement (3,3-sigmatropy) and a degenerated rearrangement of the thienylmethyl groups (1,9-sigmatropy) [10] can equally be operative, and if the latter process occurs at a lower temperature than the former, the homolytic bond-breaking from the transition state to the two radical fragments, thienylmethyl- and/or troponyloxy radicals, may occur prior to the former process with only an additional small thermal energy. Therefore, this radical reaction can be interpreted as the intervention of a possible electrocyclic rearrangement by homolysis, whose driving force is the other competitive electrocyclic reaction (1,9-sigmatropy). Liberation of the allyl radicals from the transition state may need only a little excess thermal energy.

From this view point, the extremely mild thermal reaction of 2-(allylsulfinyl)tropones [11] should also be explained by the same principle; *i.e.*, an intervention of a 3,3-sigmatropy by another electrocyclic 2,3-sigmatropy, which was followed by a homolysis to give thermolysates.

Moreover, a formation of 2- and 4-(arylmethyl)tropones from 2-(arylsulfonyl)tropones, *via* homolysis and subsequent loss of sulfur dioxide, must be interpreted in the same way [12].

Although many reactions of troponoids ever studied could have been explained in terms of analogous chemical properties to phenols and played decisive roles to prove the aromatic character of the troponoid, only a few reactions, which have no analogy in benzenoid derivatives and thus specific for the troponoids, are known. The present case, related to the 1,9-sigmatropy, which can not occur in the benzenoid aromatics, is a good example in that sense.

Another thermolysis of troponoids, the 2-alkoxy- and 2-cycloalkoxytropones to alkenes and cycloalkenes *via* an electrocyclic fragmentation [13], could be explained on the same grounds.

EXPERIMENTAL

All the melting points, which were measured by means of a Yanagimoto Micro-mp Apparatus, are uncorrected. Elemental analyses were performed by Miss S. Hirashima of the Research Institute of Industrial Science, Kyushu University. The nmr spectra were recorded with a JEOL FX 100 spectrometer (100 MHz for ^1H and 25 MHz for ^{13}C) in deuteriochloroform solutions; the chemical shifts were expressed in δ units from internal TMS. The mass spectra were run on a JEOL O1SG-2 Spectrometer. The ir spectra were taken on a Jasco IR-A 102 spectrometer either as potassium bromide disks or as inserted liquid films between sodium chloride plates.

Preparation of 2-(2-Thienylmethoxy)troponone (1).

A mixture of 2-thienylmethanol (**4a**, 546 mg), DCC (1.01 g) and cuprous chloride (10 mg), was warmed at 55° for 22 hours, to which, a benzene solution (10 ml) of **3** (585 mg) was added and heated at 95° for 4 hours. After removal of precipitated *N,N'*-dicyclohexylurea from the mixture by filtration, the resultant filtrate was heated *in vacuo* to leave a brown oil, 1.40 g, whose silica-gel column chromatography from hexane-ethyl acetate (8:2) yielded, along with **3** (10 mg), **1** as colorless needles, mp 88-88.5°; 730 mg, 71%; ^1H nmr: δ 5.36 (s, 2H) and 6.6-7.3 (m, 8H); ^{13}C nmr: δ 65.8, 115.8, 126.6, 126.8, 127.5, 128.6, 132.4, 136.3, 137.5 (2C), 163.4, and 180.5; ir: ν 1625, 1580, 1495, 1470, 1270, 1230, 1180, 1065, 975, 945, 780, and 735 cm^{-1} .

Anal. Calcd. for $\text{C}_{12}\text{H}_{10}\text{O}_2\text{S}$: C, 66.05; H, 4.62. Found: C, 65.77; H, 4.61.

Thermolysis of 1. Identification of 5-(2-Thienylmethyl)-2-(2-thienylmethoxy)troponone (5).

An *o*-dichlorobenzene solution (15 ml) of **1** (1.153 g) was refluxed for 1.5 hours under a nitrogen atmosphere. The mixture was then dissolved in ether, and extracted with aqueous potassium hydroxide to collect free tropolone fractions, from which, after acidification with hydrochloric acid yielded a yellow oil (940 mg). Silica-gel column chromatography of the neutral fractions with hexane-ethyl acetate (9:1) gave recovered **1** (35 mg, 3%) and **5** as a colorless oil, 100 mg, 6%; ^1H nmr: δ 3.93 (s, 2H), 5.29 (s, 2H), and 6.6-7.3 (m, 10H); ^{13}C nmr: δ 38.9, 65.6, 116.1, 124.6, 125.7, 126.4, 126.6, 126.8, 127.3, 130.8, 137.2, 137.5, 138.2, 140.8, 141.6, 162.5, and 179.9; ir: ν 1630, 1560, 1505, 1460, 1385, 1280, 1240, 1185, 1125, 1105, 960, 855, and 700 cm^{-1} .

Anal. Calcd. for $\text{C}_{17}\text{H}_{14}\text{O}_2\text{S}_2$: C, 64.96; H, 4.49. Found: C, 65.05; H, 4.43.

Isolation of the Thermolysates as Methyl Ethers.

The above mixture of acidic compounds was then dissolved in ether, and treated with diazomethane to give the methyl ethers (1.03 g). Subsequent chromatography of the mixture on a silica-gel column with benzene-ethyl acetate (9:1) and hplc [Micropolasil, hexane-ethyl acetate (90:10)] gave the following compounds together with **11** (170 mg, 24%):

2-Methoxy-3,5-bis(2-thienylmethyl)troponone (6).

This compound was obtained as a yellow oil, 108 mg, 6%; ^1H nmr: δ 3.87 (s, 3H), 3.95 (s, 2H), 4.14 (d, $J = 1$ Hz, 2H), and 6.7-7.2 (m, 9H); ^{13}C nmr: δ 34.8, 39.7, 58.9, 124.2, 124.8, 125.5, 125.9, 126.7, 127.0, 135.2, 137.5, 138.3, 141.5, 141.7, 141.9, 162.3, and 181.2; ir: ν 2930, 1630, 1580, 1500, 1460, 1435, 1230, 1110, 1035, 985, 845, 785, and 700 cm^{-1} .

Anal. Calcd. for $\text{C}_{18}\text{H}_{16}\text{O}_2\text{S}_2$: C, 65.85; H, 4.91. Found: C, 65.88; H, 4.83.

7-Methoxy-2,4-bis(2-thienylmethyl)troponone (7).

This compound was obtained as a yellow oil, 105 mg, 6%. ^1H nmr: δ 3.83 (s, 3H), 3.96 (s, 2H), 4.18 (s, 2H), and 6.5-7.4 (m, 9H); ^{13}C nmr: δ 35.6,

39.5, 56.0, 112.2, 124.1, 124.6, 125.6, 126.2, 126.6, 126.9, 130.1, 138.3, 138.9, 141.6, 142.1, 147.3, 163.0, and 178.3; ir: ν 1595, 1560, 1460, 1425, 1385, 1250, 1200, 1170, 1055, 1035, and 850 cm^{-1} .

Anal. Calcd. for $\text{C}_{18}\text{H}_{16}\text{O}_2\text{S}_2$: C, 65.85; H, 4.91. Found: C, 66.10; H, 4.96.

2-Methoxy-5-(2-thienylmethyl)troponone (8).

This compound was obtained as yellow needles, mp 127-128°, 310 mg, 26%; ^1H nmr: δ 3.90 (s, 3H), 4.02 (d, $J = 1$ Hz, 2H), 6.67 (d, $J = 10$ Hz, 1H), 6.79 (ddt, $J = 3.5, 1.5, 1$ Hz, 1H), 6.92 (dd, $J = 5, 3.5$ Hz, 1H), 6.94 (dt*, $J = 10, 1$ Hz, 1H), 7.14 (d*, $J = 1$ Hz, 2H), and 7.16 (dd, $J = 5, 1.5$ Hz, 1H); ^{13}C nmr: δ 39.2, 56.1, 112.4, 124.8, 125.8, 127.0, 131.2, 136.9, 138.7, 140.1, 142.0, 164.3, and 180.0; ir: ν 1625, 1590, 1565, 1500, 1455, 1280, 1200, 1175, 1155, 1125, 1105, 975, 865, 845, and 705 cm^{-1} .

Anal. Calcd. for $\text{C}_{13}\text{H}_{12}\text{O}_2\text{S}$: C, 67.23; H, 5.21. Found: C, 66.93; H, 5.23.

2-Methoxy-3-(2-thienylmethyl)troponone (9).

This compound was obtained as a yellow oil, 128 mg, 11%; ^1H nmr: δ 3.92 (s, 3H), 4.16 (d, $J = 0.7$ Hz, 2H), 6.7-7.0 (m, 4H), and 7.0-7.2 (m, 3H); ^{13}C nmr: δ 34.4, 58.8, 124.2, 125.5, 126.7, 129.6, 135.3, 136.5, 137.4, 138.3, 141.5, 163.3, and 181.6; ir: ν 2950, 1625, 1580, 1570, 1435, 1335, 1275, 1245, 1210, 1125, 1005, 950, 845, 805, and 700 cm^{-1} .

Anal. Calcd. for $\text{C}_{13}\text{H}_{12}\text{O}_2\text{S}$: C, 67.23; H, 5.21. Found: C, 67.44; H, 5.33.

2-Methoxy-7-(2-thienylmethyl)troponone (10).

This compound was obtained as a yellow oil, 255 mg, 21%; ^1H nmr: δ 3.90 (s, 3H), 4.25 (s, 2H), 6.6-7.2 (m, 6H), and 7.32 (dd, $J = 8, 1$ Hz, 1H); ^{13}C nmr: δ 35.4, 56.2, 112.2, 124.1, 126.2, 126.6, 126.8, 131.5, 136.1, 141.7, 164.1, and 178.7; ir: ν 2950, 2840, 1615, 1590, 1575, 1500, 1470, 1375, 1270, 1220, 1170, 1050, 940, 845, 795, and 750 cm^{-1} .

Anal. Calcd. for $\text{C}_{13}\text{H}_{12}\text{O}_2\text{S}$: C, 67.23; H, 5.21. Found: C, 67.21; H, 5.59.

From the most polar fractions eluted with benzene-ethyl acetate (7:3), **11** (170 mg, 24%) was obtained.

Hydrolysis of 6 to 3,5-bis(2-Thienylmethyl)tropolone (12).

An aqueous 48% hydrobromic acid solution (2 ml) of **6** (29 mg) was refluxed for 2 hours, and the mixture was subsequently fractionated by ptlc to give **12** as a yellow oil, 15 mg, 54%; ^1H nmr: δ 4.06 (s, 2H), 4.25 (s, 2H), 6.6-7.0 (m, 4H), 7.0-7.5 (m, 5H), and 7.7 (br s, 1H); ^{13}C nmr: δ 34.9, 40.1, 120.7, 124.4, 124.8, 125.8, 126.1, 126.8, 127.0, 136.3, 139.6, 139.9, 140.4, 141.1, 142.2, 166.9, and 171.8.

Anal. Calcd. for $\text{C}_{17}\text{H}_{14}\text{O}_2\text{S}_2$: C, 64.96; H, 4.49. Found: C, 64.91; H, 4.44.

Hydrolysis of 7 to 12.

An aqueous 48% hydrobromic acid solution (2 ml) of **7** (23 mg) was refluxed for 4 hours. a similar ptlc work up afforded **12** (13 mg, 59%).

Hydrolysis of 8 to 5-(2-Thienylmethyl)tropolone (13).

An aqueous 48% hydrobromic acid solution (2 ml) of **8** (92 mg) was refluxed for 50 minutes. Silica-gel column chromatography of the mixture with benzene-ethyl acetate (8:2) yielded **13** as yellow needles, mp 101-102°, 71 mg, 82%; ^1H nmr: δ 4.07 (d, $J = 1$ Hz, 2H), 6.77 (ddd, $J = 3, 1.2, 1$ Hz, 1H), 6.90 (dd, $J = 5, 3$ Hz, 1H), 7.14 (dd, $J = 5, 1$ Hz, 1H), 7.24 (s, 4H), and 8.2-8.5 (br s, 1H); ^{13}C nmr: δ 39.6, 123.9 (2C), 124.8, 125.8, 127.0, 138.0 (2C), 140.7, 142.1, and 170.8 (2C); ir: ν 3200, 1615, 1550, 1460, 1260, 1215, 1085, and 690 cm^{-1} .

Anal. Calcd. for $\text{C}_{12}\text{H}_{10}\text{O}_2\text{S}$: C, 66.05; H, 4.62. Found: C, 66.32; H, 4.57.

Hydrolysis of 9 to 3-(2-Thienylmethyl)tropolone (14).

An aqueous 48% hydrobromic acid solution (3 ml) of **9** (75 mg) was refluxed for 2 hours, after which, the mixture was diluted with water and extracted with chloroform.

The acidic material was extracted from the chloroform to an aqueous layer by potassium hydride, and dissolved back into chloroform solution by adding dilute hydrochloric acid to give **14** as pale yellow prisms, mp 58-60°, 60 mg, 85%. ^1H nmr: δ 4.33 (s, 2H), 6.90 (m, 2H), 7.1-7.4 (m, 4H), 7.48 (d, $J = 9$ Hz, 1H), and 8.1-9.2 (br s, 1H); ^{13}C nmr: δ 34.6, 120.5,

124.4, 126.1, 126.9, 127.4, 136.2, 139.1, 140.0, 141.1, 167.8, and 172.6; ir: ν 3170, 1610, 1600, 1550, 1475, 1415, 1375, 1295, 1230, 990, 890, 850, 830, 745, 735, and 705 cm^{-1} .

Anal. Calcd. for $\text{C}_{12}\text{H}_{10}\text{O}_2\text{S}$: C, 66.05; H, 4.62. Found: C, 66.19; H, 4.62.

Hydrolysis of **10** to **14**.

Similarly, **10** (96 mg) was converted to **14** (79 mg, 87%).

Thermolysis of **5** to 3,5-bis(2-Thienylmethoxy)tropolone (**12**) and 5-(2-Thienylmethoxy)tropolone (**13**).

An *o*-dichlorobenzene solution (4 ml) of **5** (217 mg) was refluxed for 1.5 hours. After dilution of the mixture with ether, the mixture was extracted with aqueous potassium hydroxide from the acidic fractions, **12** (68 mg, 31%), and **13** (67 mg, 44%), were isolated.

Preparation of 2-Benzo[*b*]thienylmethanol (**4b**).

An anhydrous THF solution of benzothiophene (3.40 g) was treated with butyllithium (15% ether solution, 19 ml) at 0° to form lithiated compound, to which anhydrous *N,N*-dimethylformamide (4 ml) was added dropwise, and refluxed for 1 hour. The mixture was diluted with water, and extracted with ether. The ether extract (3.75 g) was then, without purification, treated with sodium borohydride in methanol to give **4b** as colorless plates, mp 102-103° (lit [14] 55-56°), 3.75 g, 90%; ¹H nmr: δ 4.84 (s, 2H), 7.13 (s, 1H), 7.2-7.4 (m, 2H), and 7.6-7.8 (m, 2H). ¹³C nmr: δ 60.8, 121.4, 122.4, 123.5, 124.3 (2C), 139.5, 139.9, and 144.7.

Preparation of 2-(2-Benzo[*b*]thienylmethoxy)tropolone (**2**).

To a benzene solution of benzothiophenylmethanol, **4b** (2.02 g), DCC (2.83 g) and cuprous chloride (30 mg), a benzene solution of **3** (1.50 g) was added and heated at 95° for 16 hours. The mixture was worked up by an ordinary method to give **2** as yellow crystals, mp 171-172°, 2.88 g, 87%; ¹H nmr: δ 5.48 (2H, d, J = 1 Hz), 6.8-7.0 (2H, m), 7.1-7.4 (2H, m), and 7.6-7.8 (m, 2H); ¹³C nmr: δ 60.8, 121.4, 122.4, 123.5, 124.3 (2C), 139.5, and 144.7; ir: ν 2940, 1620, 1560, 1180, 1075, and 745 cm^{-1} .

Anal. Calcd. for $\text{C}_{16}\text{H}_{12}\text{O}_2\text{S}$: C, 71.63; H, 4.51. Found: C, 71.59; H, 4.53.

Thermolysis of **2**. Isolation of **15**.

An *o*-dichlorobenzene solution (5 ml) of **2** (400 mg) was refluxed for 2 hours. The mixture was then diluted with ethyl acetate and fractionated with aqueous potassium hydroxide. From the aqueous extract, **15** was obtained as yellow crystals, mp 137-138°, 9 mg, 2%; ¹H nmr: δ 4.17 (s, 2H), 7.02 (t, J = 1 Hz, 1H), and 7.2-7.4 (m, 6H); ¹³C nmr: δ 40.5, 122.2, 122.5, 123.1, 123.8, 124.1, 124.1, 124.4, 138.1 (3C), 139.8 (2C), 143.2, and 170.9 (2C); ir: ν 3210, 1615, 1550, 1460, 1270, 1210, and 870 cm^{-1} .

Anal. Calcd. for $\text{C}_{16}\text{H}_{12}\text{O}_2\text{S}$: C, 71.63; H, 4.51. Found: C, 71.66; H, 4.63.

Isolation of the Methylated Thermolysates, **17** and **18**.

The above mother liquor (310 mg) was treated with ethereal diazomethane and chromatographed on a silica-gel column with benzene-ethyl acetate (9:1) to give, together with **11** (37 mg, 18%), **17** below.

5-(2-Benzo[*b*]thienylmethyl)-2-methoxytropolone (**17**).

This compound was obtained as a pale yellow oil, 278 mg, 59%; ¹H nmr: δ 3.82 (s, 2H), 3.99 (s, 2H), 6.59 (d, J = 11 Hz, 1H), 6.92 (dm, J = 11 Hz, 1H), 6.95 (s, 1H), 7.0-7.5 (m, 4H), and 7.5-7.7 (m, 2H); ¹³C nmr: δ 39.9, 56.1, 112.4, 122.1, 122.4, 123.0, 124.0, 124.3, 131.6, 133.6, 138.5 (2C), 139.1, 139.7, 143.1, 164.3, and 179.8; ir: ν 3050, 1620, 1560, 1490, 1455, 1280, 1245, 1115, 980, and heated at 95° for 16 hours. The mixture was worked up by an ordinary method to give **2** as yellow crystals, mp 171-172°, 2.88 g, 87%; ¹H nmr: δ 5.48 (2H, d, J = 1 Hz), 6.8-7.0 (2H, m), 7.1-7.4 (2H, m), and 7.6-7.8 (m, 2H); ¹³C nmr: δ 60.8, 121.4, 122.4, 123.5, 124.3 (2C), 139.5, and 144.7; ir: ν 2940, 1620, 1560, 1180, 1075, and 745 cm^{-1} .

Anal. Calcd. for $\text{C}_{16}\text{H}_{12}\text{O}_2\text{S}$: C, 71.63; H, 4.51. Found: C, 71.59; H, 4.53.

Thermolysis of **2**. Isolation of **15**.

An *o*-dichlorobenzene solution (5 ml) of **2** (400 mg) was refluxed for 2 hours. The mixture was then diluted with ethyl acetate and fractionated with aqueous potassium hydroxide. From the aqueous extract, **15** as

yellow crystals was obtained, mp 137-138°C, 9 mg, 2%; ¹H nmr: δ 4.17 (s, 2H), 7.02 (t, J = 1 Hz, 1H), and 7.2-7.4 (m, 6H); ¹³C nmr: δ 40.5, 122.2, 122.5, 123.1, 123.8, 124.1, 124.4, 138.1 (3C), 139.8 (2C), 143.2, and 170.9 (2C); ir: ν 3210, 1615, 1550, 1460, 1270, 1210, and 870 cm^{-1} .

Anal. Calcd. for $\text{C}_{16}\text{H}_{12}\text{O}_2\text{S}$: C, 71.63; H, 4.51. Found: C, 71.66; H, 4.63.

Isolation of the Methylated Thermolysates, **17** and **18**.

The above mother liquor (310 mg) was treated with ethereal diazomethane and chromatographed on a silica-gel column with benzene-ethyl acetate (9:1) to give, together with **11** (37 mg, 18%):

5-(2-Benzo[*b*]thienylmethyl)-2-methoxytropolone (**17**).

This compound was obtained as a pale yellow oil, 278 mg, 59%; ¹H nmr: δ 3.82 (s, 2H), 3.99 (s, 2H), 6.59 (d, J = 11 Hz, 1H), 6.92 (dm, J = 11 Hz, 1H), 6.95 (s, 1H), 7.0-7.5 (m, 4H), and 7.5-7.7 (m, 2H); ¹³C nmr: δ 39.9, 56.1, 112.4, 122.1, 122.4, 123.0, 124.0, 124.3, 131.6, 133.6, 138.5 (2C), 139.1, 139.7, 143.1, 164.3, and 179.8; ir: ν 3050, 1620, 1560, 1490, 1455, 1280, 1245, 1115, 980, and 745 cm^{-1} .

Anal. Calcd. for $\text{C}_{17}\text{H}_{14}\text{O}_2\text{S}$: C, 72.33; H, 5.00. Found: C, 72.25; H, 5.06.

2-Methoxy-5-(2-methylbenzo[*b*]thienyl)tropolone (**18**).

This compound was obtained as a colorless oil, 24 mg, 5%; ¹H nmr: δ 2.38 (s, 3H), 3.95 (s, 2H), and 6.7-7.9 (m, 8H); ¹³C nmr: δ 14.9, 56.5, 112.0, 121.8, 121.9, 123.9, 126.5, 132.6, 132.8, 137.6, 138.1, 139.3, 139.8, 141.8, 165.4, and 178.4.

Anal. Calcd. for $\text{C}_{17}\text{H}_{14}\text{O}_2\text{S}$: C, 72.33; H, 5.00; M⁺, 282.0715. Found: C, 72.05; H, 5.19; M⁺, 282.0715.

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- [4] Occasionally **5** was isolated in up to 10% yields as the by-product in the preparation of **1**. However, the sample of **1** used in this study was free from **5**.
- [5] The nmr spectrometry of the whole mixture showed a ratio of **15:16** is 13:1.
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- [10] Previously, we have noticed the identical product distribution of the thermolysis of 2-(4-furylmethoxy) derivatives of 4- and 6-isopropyltropolones [1b]. This must indicate an operation of the 1,9-sigmatropy.
- [11] H. Takeshita, H. Motomura, K. Uchida, and H. Mametsuka, *Heterocycles*, **22**, 467 (1984).
- [12] H. Takeshita, N. Matsuo, and H. Mametsuka, *Bull. Chem. Soc. Japan.*, **57**, 2321 (1984).
- [13] Recently published review article unfortunately made an incorrect citation with our electrocyclic fragmentation reaction. The reviewer suggested the reaction might simply be the *trans*-elimination of tropolonyl ethers by DMSO as a base. *cf.*, R. S. Atkinson, Annual Reports B, Vol **80**, 1983, Royal Soc. Chem., London, 1984, p 66. However, we have already shown in the paper that the reaction proceeded will in dioxane and in decalin.
- [14] F. F. Blicke and D. G. Sheets, *J. Am. Chem. Soc.*, **71**, 2856 (1949). We have no explanation for this discrepancy of the mp. Our material has fully characterized and its structure is certain in every respect.