NH proton)) and 0.26 g (12%) of 4-anilinoquinoline (mp 196–197° (lit.[6] 196–197°); nmr (DMSO-d_6) δ 6.9–8.2 (m, 11, aromatic protons and one NH proton), 9.4 (s, 1, a proton on C-2)).

Preparation of Authentic 4-Anilino-3-ethylquinoline. The reaction was carried out as described above using 3-ethylquinoline 1-oxide (1.70 g, 0.0098 mol), *p*-toluenesulfonyl chloride (1.90 g, 0.01 mol), and aniline (1.80 g, 0.019 mol). After similar treatment, 4-anilino-3-ethyl-qinoline, which was consistent with **7b** obtained above, was isolated in 0.56 g (23%) yield.

Acknowledgment. We wish to thank Dr. K. Matsushita, JEOL Co., for C-13 FT nmr spectrum analysis.

Registry No.—**1a**, 622-16-2; **1b**, 538-75-0; **1c**, 693-64-1; **2a**, 100-52-7; **2b**, 104-88-1; **2c**, 124-13-0; **2d**, 123-72-8; **2e**, 123-38-6; **4a**, 538-51-2; **7a**, 52699-00-0; **7b**, 52699-01-1; **7c**, 52669-02-2; **8a**, 52699-03-3; **8b**, 52699-04-4; **9**, 102-07-8; **11**, 52669-05-5; **12**, 52699-06-6; 2-anilinoquinoline, 5468-85-9; 4-anilinoquinoline, 30696-07-2.

Supplementary Material Available. Table III will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche 105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N. W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JOC-74-3516.

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(13) The site of the anilino group was determined as being at the 4 position since the rather low field signal of **7b** at δ 8.75 was assigned to the 2-position proton, by comparison with the nmr spectra of 4- and 2-anilinoquinolines,[6] in which the signal at δ 9.40 assignable to the proton at the 2 position was observed in the former and no signal below δ 8.00 was present in the latter. Furthermore, in the carbon-13 FT nmr spectrum (Table III[14]), Overhauser enhancement was not observed at C-4 and C-3 carbons, suggesting that **7b** contains substituents at C-4 and C-3.
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Syntheses and Some Properties of 4-Acyl-1-methylthiabenzene 1-Oxides

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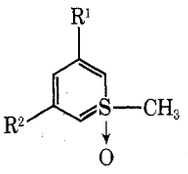
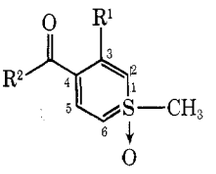
A series of 4-acyl-1-methylthiabenzene 1-oxides are prepared by the reaction of 3-ethoxymethylene-2,4-pentanedione, ethyl 2-(ethoxymethylene)acetoacetate, diethyl ethoxymethylenemalonate, and 2-acetyl-3-methoxy-2-cyclohexen-1-one with dimethyloxosulfonium methylide. Spectral (ir, uv, and nmr) and chemical (deuterium exchange, bromination, and nitration) studies suggest that the 1-oxides are represented by cyclic ylidic structures, in which a negative charge is located on the C-2, C-4, and C-6, and the carbonyl oxygen atom, but both the carbanionic and betaine-like characters are considerably lowered.

1-Methylthiabenzene 1-oxides (**1**), characterized as heterocycles with six π electrons in the ring, were first prepared in 1965 from acetylenic ketones and dimethyloxosulfonium methylide[1] and later by utilization of acetylenic esters.[2] More recently, it has been shown that some β-diketones[3] or β-ethoxyvinyl ketones[4] can also be used in place of acetylenic compounds. Hortmann and Harris[1] have suggested cyclic ylid structures for 3,5-disubstituted thiabenzene 1-oxides (**1**) on the basis of the nmr (^{1}H and ^{13}C) spectral and chemical (deuterium exchange) investigations. Essentially the same conclusion has been reached by Kishida and Ide, who have investigated 6-benzoyl-3-hydroxyl-1-methyl-5-phenylthiabenzene 1-oxide and its derivatives by nmr spectroscopy and deuterium exchange studies[2] as well as X-ray analysis.[5] These results are in fundamental contrast to those of thiabenzenes which have been believed to have aromatic character.[6]

In connection with our interest in the chemistry of the ylides stabilized by α,β-unsaturated carbonyl groups,[7] we have synthesized a series of 4-acyl-1-methylthiabenzene 1-oxides (**2**).[8] These compounds have been found to have interesting spectral and chemical properties which provide further information on the electronic nature of the thiabenzene 1-oxide nucleus.



1



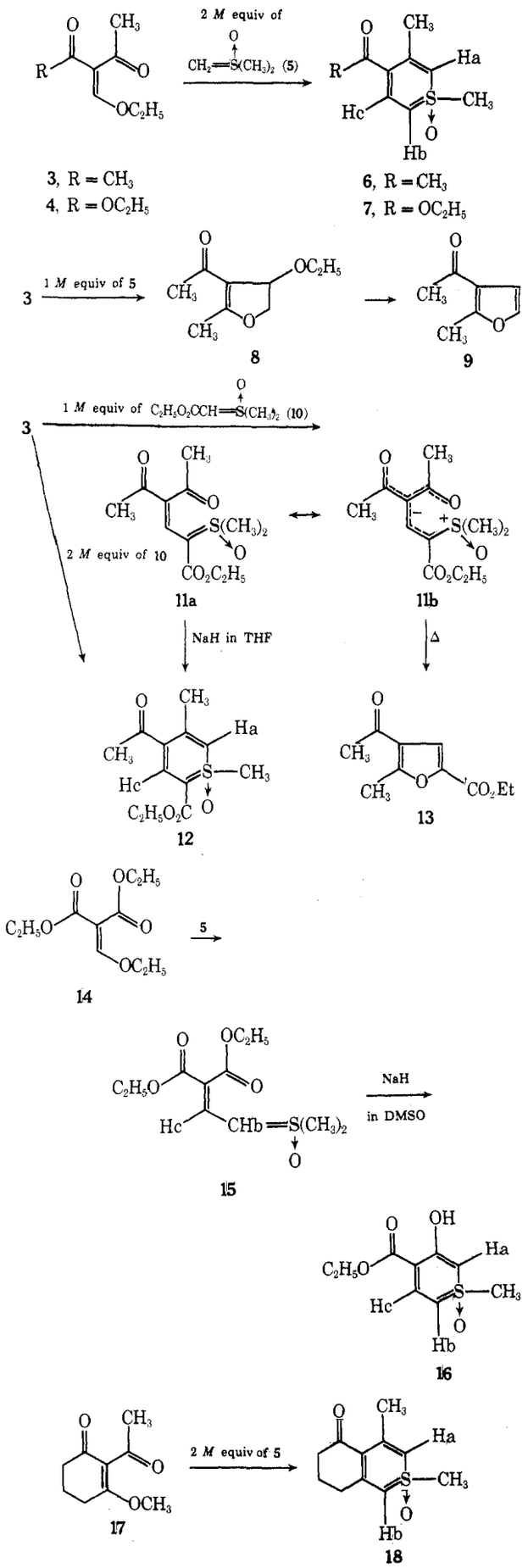
2

Syntheses

4-Acyl-1-methylthiabenzene 1-oxides (**6** and **7**) were synthesized by reaction of 3-ethoxymethylene-2,4-pentanedione (**3**) and ethyl 2-(ethoxymethylene)acetoacetate (**4**) with 2 *M* equiv of dimethyloxosulfonium methylide (**5**) in dimethyl sulfoxide at room temperature in 33 and 12% yields, respectively. This method could be successfully applied to the synthesis of thiabenzene 1-oxide **12** by the use of 2 *M* equiv of dimethyloxosulfonium carbethoxymethylide (**10**) in place of **5**.

If equimolar quantities of **5** and **3** were used, the thiabenzene 1-oxide **6** was not formed, but instead, methyl 2,3-dihydro-3-ethoxy-5-methyl-4-furyl ketone (**8**) and methyl 2-methyl-3-furyl ketone (**9**) were obtained in variable yields. The longer reaction time increased the yield of

Scheme I



9. The structure of 8 was based on its ir and nmr spectra and subsequent transformation. The ir spectrum shows two characteristic bands at 1660 (C=O) and 1590 (C=C) cm^{-1}. Its nmr spectrum reveals signals due to an ethoxyl group, two methyl singlets, a doublet of doublets (1 H) at τ 5.00–5.25 (J = 2 and 6 Hz) (an X portion of an ABX pattern) and a multiplet (2 H) from τ 5.55 to 5.75 (an AB portion of the ABX pattern). Compound 8 spontaneously changed to known compound 9[9] upon standing at room temperature. This result not only confirmed the structure of 8 but also suggests that the reaction product 9 is a secondary product from 8.

When equimolar amounts of 3 and 10 were used, allylide intermediate 11 could be isolated. The structure of 11 was evident from its spectral and chemical data. Its ir spectrum shows carbonyl absorption bands at 1675 and 1620 cm^{-1} and the nmr spectrum shows a singlet due to an olefinic proton at τ 2.52 and two singlets corresponding to two acetyl methyl groups at τ 7.66 and 7.73. Treatment of 11 with sodium hydride in dimethyl sulfoxide gave thiabenzene 1-oxide 12 in 62% yield, while refluxing 11 in xylene without base gave furan derivative 13[10] in 67% yield.

Treatment of diethyl ethoxymethylenemalonate (14) with 1 or 2 M equiv of 5 gave stable allylide 15 in 17–26% yields, whose structure was confirmed by its nmr spectral data. Its nmr spectrum shows an olefinic proton (Hc) at τ 1.96 as a broad doublet and Hb at τ 3.86 as a broad doublet. Addition of one drop of deuterium oxide to a solution of 15 in deuteriochloroform caused a rapid disappearance of the signal at τ 3.86 and converted the doublet at τ 1.96 into a singlet. The allylide 15 was cleanly converted by treatment with sodium hydride in dimethylsulfoxide into thiabenzene 1-oxide 16.

As a further extension of this method, we have applied it to the synthesis of a bicyclic thiabenzene 1-oxide. Thus, treatment of 2-acetyl-3-methoxy-2-cyclohexen-1-one (17) with a 2 M equiv of 5 gave 18 in 29% yield.

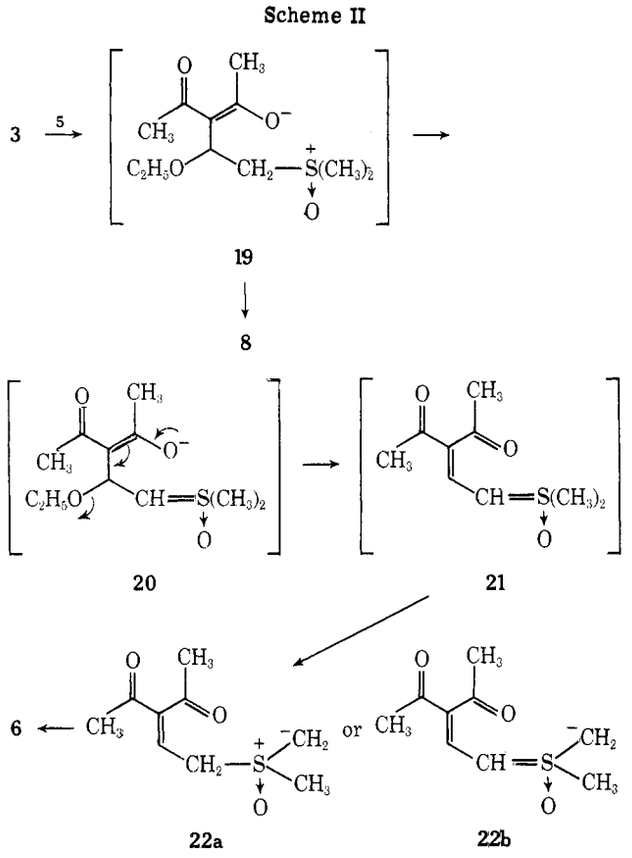
All the thiabenzene 1-oxides described above are stable crystalline compounds and the structures were confirmed by elemental analyses and ir, nmr, and mass spectrometry.

A possible interpretation of the course of the reactions of 3 with 5 is shown in Scheme II. In the absence of the excess methylide 5, the initially formed intermediate 19 undergoes an intramolecular substitution reaction by an oxygen atom to form 8. When 2 M equiv of 5 was used, the excess methylide acts as base and abstracts proton from the methylene group of 19 to form the ylide intermediate 20 which readily loses ethoxyl anion to give the allylide intermediate 21. The intervention of such allylide intermediate was demonstrated by the isolation of 11 and 15. In the case of 11, the presence of the carbethoxyl group enchances the rate of the process (19 → 20), and in the case of 15, the ester carbonyl group is not strong enough to attack the methylene group (*e.g.*, 19 → 8), so that the process (*e.g.*, 19 → 20) becomes the favored reaction pathway.

Whether cyclization of 21 to the thiabenzene 1-oxides 6 occurs *via* ylide 22a or *via* ylidic anion 22b has not been established. However, the fact that a strong base such as dimsyl anion is necessary to effect the cyclization of 11 or 15 suggests that an ylidic anion is involved at least in these cases.

For comparison, we have also examined the reaction of 3 and dimethylsulfonium carbethoxymethylide (23). Thus, treatment of 3 with 1 M equiv of 23 in dimethyl sulfoxide gave yellow crystals of allylide 24 in 41% yield, whose structure was assigned on the basis of the spectral evidence (see Experimental Section). The most striking features of the spectral data of 24 are an nmr signal due to two acetyl methyl groups which appears as a sharp singlet presumably

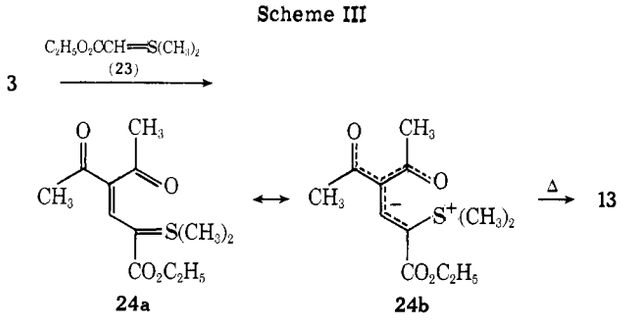
Scheme II



due to rapid rotation around the polarized carbon–carbon double bond[7c] and the longest uv absorption maximum which appears at 376 nm. These are in sharp contrast to those of **11**, in which two acetyl methyl signals show different chemical shifts and the longest absorption maximum is shifted to 339 nm. These observations suggest that the stronger d_{π}–p_{π} bonding is involved in the oxosulfonium ylide (the greater contribution from an ylene form, **11a**) than in the sulfonium ylide (the greater contribution from form **24b**).

Attempts to cyclize **24** to a thiabenzene were unsuccessful, but **24** was smoothly transformed into furan **13** by simply heating in refluxing mesitylene. This reaction is analogous to the formation of furan derivatives from β-ethoxyvinyl ketones and dimethylsulfonium methylide.[4]

Scheme III



Physical Properties of Thiabenzene 1-Oxides

Since the detailed ir, uv, and nmr spectral data are recorded in the Experimental Section, several aspects of the spectral characteristics which define the electronic structures of the 4-acyl-1-methylthiabenzene 1-oxides (**2**) will be discussed here.

In the nmr spectra (60 MHz) of **6**, **7**, and **16**, Ha and Hb appear as an AB part of an ABX pattern in a range of τ 4.22–4.81 with J_{ab} = 4.6–4.8 Hz, J_{bc} = 8.8–10.0 Hz, and J_{ac} = 0, while Hc (an X part of the ABX pattern) is shifted to low field and appears at τ 2.00–2.26. The multiplicity of the latter depends upon the difference in the chemical shifts of Ha and Hb; thus, the Hc of **16** appears as an expected sharp doublet, whereas the Hc's of **6** and **7** occur as a six-line multiplet. These unexpected splitting patterns observed for **6** and **7** may be attributed to virtual coupling[11,12] arising from the fact that the chemical shifts of Ha and Hb are very close to each other. In fact, measurement of the nmr spectrum of **7** at 90 MHz removed the complexity of the Hc signal to give an expected doublet with J_{bc} = 8.8 Hz. In the nmr spectrum of **18**, Ha and Hb appear as an AB quartet centered at τ 4.55 with J_{ab} = 4.5 Hz. The coupling constants (J_{ab} = 4.5–4.8 Hz) observed for **6**, **7**, **16**, and **18** are in good agreement with the reported values[1] for the thiabenzene 1-oxides **1**.

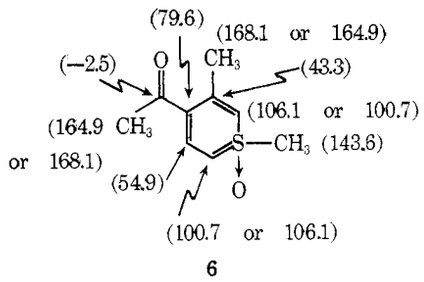


Figure 1. Carbon-13 chemical shifts (ppm from CS_2) of **6** in $CDCl_3$ ($\delta_{CS_2} = \delta_{Me_4Si} + 192.8$ ppm)

The chemical shifts of Ha and Hb are well outside of the aromatic region in accord with Hortmann's observation on **1**[1] suggesting that there is no significant diamagnetic ring current. It should be noted, however, that the values are considerably lower than those of Ha of noncyclic ylides **25** (τ 6.15)[7d] and **26** (τ 6.29).[13,14] The low-field shift of Hc may be a result of the combined anisotropic, mesomeric, and inductive effects[15] of the carbonyl groups.

The ir spectra of thiabenzene 1-oxides **6**, **7**, and **18** show the carbonyl absorption bands at 1641, 1686, and 1632 cm^{-1}, respectively. These carbonyl absorption bands are lower when compared with those of α,β-unsaturated ketones[16] (around 1680 cm^{-1}) or esters[16] (around 1700 cm^{-1}) but higher than those of noncyclic ylides **25**[7d] (1589 cm^{-1}) or **26**[13] (1667 cm^{-1}), in which a negative charge is well delocalized over the α,β-unsaturated carbonyl groups. The carbonyl absorption band of **16** appears at 1640 cm^{-1} and this marked displacement to lower frequency compared with that of **7** is ascribed to the formation of a hydrogen bond between the carbonyl and hydroxyl groups.

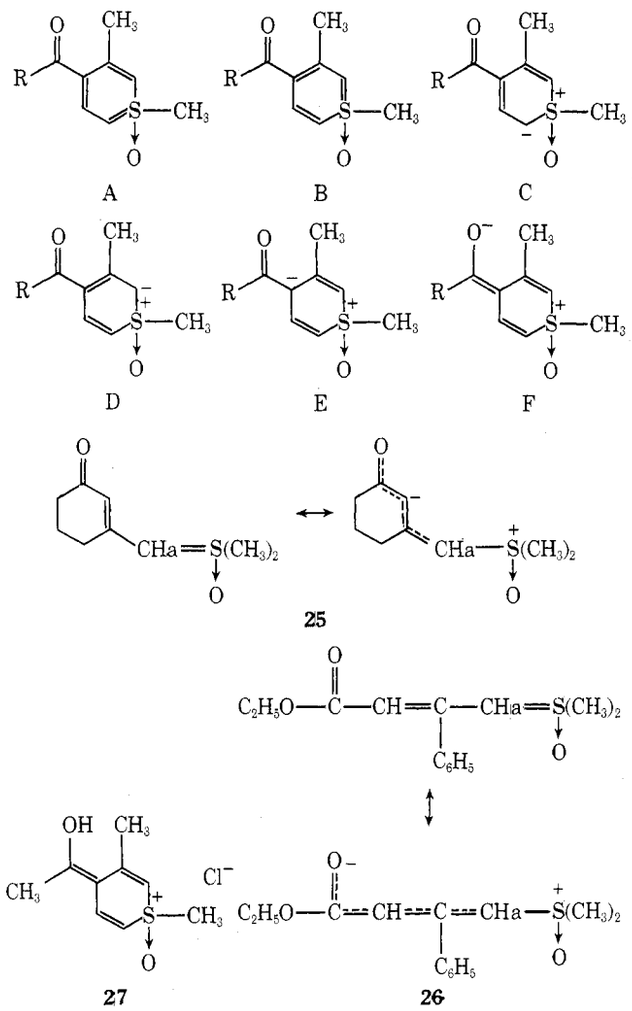
The uv spectra of thiabenzene 1-oxides **6**, **7**, and **18** show two main absorption maxima at 274–299 and 211–229 nm, the former of which are considerably hypsochromic compared to those reported for 3,5-dialkyl-1-methylthiabenzene 1-oxides (**1**) which have the longest absorption maxima at 333–335 nm.[1] In sharp contrast to the noncyclic ylide **25**,[7d] the position of the absorption maxima is affected neither by the solvent used nor by addition of a small amount of 10% hydrochloric acid. Only in strongly acidic media (*e.g.*, an ethanolic 6 *N* hydrochloric acid solution), the absorption of **6** and **18** is shifted to 320–330 nm presumably as a result of protonation on the carbonyl oxygen atom (*i.e.*, **27**).

Further evidence for the electronic structures of the thiabenzene 1-oxides was provided by the ^{13}C nmr spectrum of **6** (Figure 1) in which high shielding of the C-2, C-4, and C-6 is indicated.[17]

These spectral data imply that 4-acyl-1-methylthiaben-

zene 1-oxides (2) are represented by the cyclic ylidic structures C–F. However, it should be emphasized that both the carbanionic and betaine-like characters in 2 are considerably lowered and the thiabenzene 1-oxide ring system is much more stabilized, when compared with the noncyclic ylides. The delocalization of the negative charge within the ring and the contribution of p_π–d_π bonding in the C_2–S–C_6 moiety[18] (ylene forms A and B) may be responsible for this.

Scheme IV

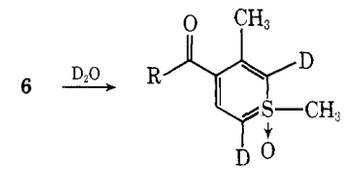


Chemical Properties of Thiabenzene 1-Oxides

All of the aforementioned physical properties revealed that 4-acyl-1-methylthiabenzene 1-oxides (2) can be best represented by cyclic ylidic structures whose negative charge is located on the C-2, C-4, and C-6 positions and the carbonyl oxygen atom. It appeared to be of interest to see how the structural characteristics are reflected by the chemical properties of the thiabenzene 1-oxides. Consequently, we have examined the reactivity of 6 and 7 toward various electrophiles and found that they did not react with methyl iodide or acyl halides (*e.g.*, acetyl chloride or benzoyl chloride) under various conditions but displayed electrophilic substitution reactions such as H–D exchange, bromination, and nitration at the expected positions, thus supporting the cyclic ylidic structures suggested by the physical data.

Deuterium Exchange

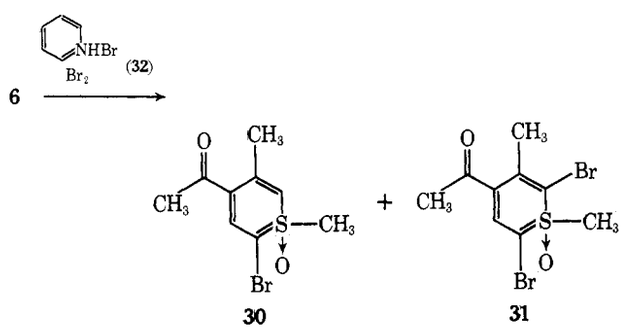
H–D exchange in 6 and 7 with deuterium oxide in deuteriochloroform was followed by nmr spectroscopy. At 35° exchange took place at C-2 and C-6 within 8 hr. No other protons were exchanged under these conditions. This result is in contrast to the cases of noncyclic ylides 25[7d] and 26,[12] in which, under similar conditions, both Ha and S–CH_3 group were readily exchanged by deuterium.



28, R = CH_3
29, R = OC_2H_5

Bromination

A solution of 6 in acetic acid was treated with 1 *M* equiv of pyridinium hydrobromide perbromide (32) at room temperature to give monobromo derivative 30 in 46% yield. The structure is supported by a satisfactory elementary analysis and by nmr spectrum; Hb signal disappeared and Ha and Hc signals appeared as singlets at τ 4.42 and 2.07, respectively. When 6 was brominated with 2 *M* equiv of 32, 30 and dibromo derivative 31 were obtained in 21 and 25% yields, respectively. The structure of the latter is evident from the nmr spectrum, in which a two-proton multiplet due to Ha and Hb disappeared. These bromo compounds are relatively unstable and turn to a black tar after standing at room temperature for a few months. The formation of 30 may be explained in terms of the steric effect of the methyl group at the 3 position.



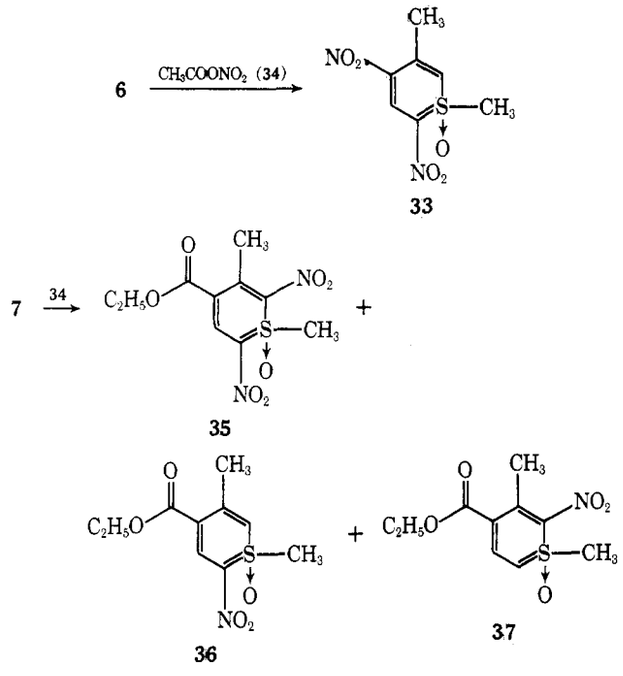
Similar treatment of 7 gave very unstable crystals which turned to a black tar at the isolation procedure.

Nitration

Nitration of 6 was carried out by treating with excess acetyl nitrate (34) in acetic acid at –5–0°. The crude product consisted of two yellow components on tlc analysis. The major product 33 (20%) was readily separated by crystallization from chloroform. The minor product was resolved only with difficulty by tlc but amounts obtained were insufficient to permit complete characterization. The structural assignment of 33 is based on the following evidence. Its elemental analysis and mass spectrum confirmed the molecular formula $C_7H_8N_2O_5S$. The ir spectrum showed no carbonyl absorption band but two strong bands at 1585 and 1280 cm^{-1} assignable to nitro groups. In the nmr spectrum (in dimethyl sulfoxide-d_6), there is no signal due to an acetyl methyl group and Ha and Hc signals appeared at τ 1.18 and 2.93 as singlets, respectively.

Nitration of 7 under the same conditions gave three products, from which only one product was isolated in a pure state by preparative tlc (in 5% yield). This compound was readily identified as dinitro derivative 35 by elemental analysis and by the examination of its ir and nmr spectra

(see Experimental Section). The most striking spectral feature is the shift of the ester carbonyl group (1715 cm^{-1}) to a region generally expected for α,β-unsaturated ester carbonyl groups. The other two compounds (9% yield as a mixture) could not be separated by tlc but the nmr spectrum of the mixture suggested that it consists of two mononitro derivatives **36** and **37** in an about 1:1 ratio.



Experimental Section

Melting points are uncorrected. Nmr spectra were determined with a Hitachi R-20A spectrometer (tetramethylsilane as internal standard). Ir spectra were recorded with a Hitachi EPI-G3 spectrophotometer and uv spectra with a Hitachi 124 spectrophotometer. Mass spectra were obtained with a Hitachi RMU-6D with a direct inlet system operating at 70 eV. Preparative tlc was carried out on Merck Alumina PF_{254} or Merck Kieselgel GF_{254}.

4-Acetyl-1,3-dimethylthiabenzene 1-Oxide (6). A solution of 3.6 g (0.023 mol) of **3**[19] in 10 ml of dimethyl sulfoxide (DMSO) was added to a stirred solution of 0.046 mol of dimethyloxosulfonium methylide (**5**) in 30 ml of DMSO (prepared by the method of Corey and Chaykovsky[20]) at room temperature under nitrogen. After stirring for 3 hr at room temperature, the reaction mixture was poured into ice–water. The resulting mixture was thoroughly extracted with $CHCl_3$. The extract was washed with H_2O and a saturated NaCl solution and dried over Na_2SO_4. Evaporation of the solvent *in vacuo* at 40° and trituration with Et_2O gave a solid, which was recrystallized from EtOH–petroleum ether (bp 30–60°) to give 1.4 g (33%) of **6** as white crystals: mp 126.5–127°; ir ($CHCl_3$) 1641 (s), 1550 (s), 1260 (s), 1155 (s) cm^{-1}; uv_{max} (EtOH) 213 (log ϵ 4.20), 297 nm (4.32); uv_{max} [concentrated HCl–EtOH (1:1)] 210 (log ϵ 3.99), 327 (4.47), 333 nm (4.46); nmr ($CDCl_3$) τ 2.24 (m, 1 H, Hc), 4.28–4.55 (m, 2 H, Ha and Hb), 6.56 (s, 3 H, SCH_3), 7.49 (s, 3 H, ring CH_3), 7.69 (s, 3 H, $COCH_3$); mass spectrum *m/e* (rel intensity) 184 (M^+, 99), 169 (100), 125 (29).

Anal. Calcd for $C_9H_{12}O_2S$: C, 58.66; H, 6.57. Found C, 58.74; H, 6.53.

4-Carbethoxy-1,3-dimethylthiabenzene 1-Oxide (7). Using a similar procedure to that described above for **6**, this compound was obtained from 0.04 mol of **5** (in 30 ml of DMSO) and 3.7 g (0.02 mol) of **4**[19] in 12% yield as white crystals: mp 92–92.5° [from AcOEt–petroleum ether (bp 30–60°)]; ir ($CHCl_3$) 1686 (s), 1563 (s), 1265 (s), 1125 (s) cm^{-1}; uv_{max} (EtOH) 211 (log ϵ 4.25), 278 (4.30), 316 nm (3.68); uv_{max} [concentrated HCl–EtOH (1:1)] 213 (log ϵ 3.98), 281 nm (4.21); nmr ($CDCl_3$) τ 2.00 (m, 1 H, Hc), 4.22–4.58 (m, 2 H, Ha and Hb), 5.80 (q, 2 H, J = 7 Hz, OCH_2CH_3), 6.54 (s, 3 H, SCH_3), 7.47 (s, 3 H, ring CH_3), 8.68 (t, 3 H, J = 7 Hz, OCH_2CH_3); irradiation of the Hc converted the multiplet at τ 4.22–4.58 into an AB quartet with J_{ab} = 4.5 Hz; mass spectrum *m/e* (rel intensity) 214 (M^+, 39), 199 (55), 169 (50), 125 (51) (the base peak is *m/e* 45).

Anal. Calcd for $C_{10}H_{14}O_3S$: C, 56.05; H, 6.59. Found: C, 56.14; H, 6.55.

Methyl 2,3-Dihydro-3-ethoxy-5-methyl-4-furyl Ketone (8) and Methyl 2-Methyl-3-furyl Ketone (9). A solution of 1.56 g (0.01 mol) of **3** in 5 ml of DMSO was added to a stirred solution of 0.01 mol of **5** in 15 ml of DMSO at room temperature under nitrogen. After stirring for 3 hr at room temperature, work-up as described for **6** gave 0.78 g of **8** as a yellow oil, which contained a trace of **9** by tlc and nmr analyses: ir ($CHCl_3$) 1660 (s), 1590 (s) cm^{-1}; nmr ($CDCl_3$) τ 5.00–5.25 (dd, 1 H, J = 6 and 2 Hz, H_3), 5.55–5.75 (m, 2 H, H_2), 6.50 (q, 2 H, J = 7.5 Hz, OCH_2CH_3), 7.75 (s, 3 H, CH_3), 7.80 (s, 3 H, $COCH_3$), 8.80 (t, 3 H, J = 7.5 Hz, OCH_2CH_3).

After 3 days at room temperature, a part of **8** was changed to **9** which was isolated as an oil by column chromatography on silica gel using $CHCl_3$ as solvent: ir ($CHCl_3$) 1670 (s), 1580 (s) cm^{-1}; nmr ($CDCl_3$) τ 2.80 (d, 1 H, J = 2 Hz, H_2), 3.40 (d, 1 H, J = 2 Hz, H_3), 7.48 (s, 3 H, CH_3), 7.66 (s, 3 H, $COCH_3$); 2,4-dinitrophenylhydrazone was prepared by a usual procedure:[20] mp 204–206° (lit.[9] 205–206°).

Dimethyloxosulfonium 1-Carbethoxy-3,3-diacetylallylide (11). A solution of 1.27 g (0.012 mol) of ethyl chloroformate in 10 ml of tetrahydrofuran was added to a stirred solution of **5** which was prepared by stirring a solution of 5.2 g (0.024 mol) of trimethyloxosulfonium iodide and 566 mg (0.024 mol) of sodium hydride in 50 ml of tetrahydrofuran–DMSO (4:1) for 4 hr at room temperature under nitrogen and the mixture was stirred for 10 min at room temperature. A solution of 1.84 g (0.012 mol) of **3** in 10 ml of tetrahydrofuran was added to the mixture at 5°. After the mixture was stirred for 1 hr at 5°, it was poured into 100 ml of ice–water and extracted with $CHCl_3$. The extract was washed with a saturated NaCl solution, dried (Na_2SO_4), and concentrated *in vacuo* below 25°. The residual oil was chromatographed on alumina with AcOEt as solvent to give 0.87 g of **11** as a yellow solid which was recrystallized from $CHCl_3$–petroleum ether (bp 30–60°): mp 140°; ir ($CHCl_3$) 1675 (w), 1620 (s), 1560 (s), 1170 (s), 1070 (s) cm^{-1}; uv_{max} (EtOH) 231 (log ϵ 3.85), 273 (3.69), 339 nm (4.25); nmr ($CDCl_3$) τ 2.52 (s, 1 H, olefinic proton), 5.80 (q, 2 H, J = 7 Hz, OCH_2CH_3), 6.44 (s, 6 H, $S(CH_3)_2$), 7.66 (s, 3 H, $COCH_3$), 7.73 (s, 3 H, $COCH_3$), 8.68 (t, 3 H, J = 7 Hz, OCH_2CH_3).

Anal. Calcd for $C_{12}H_{18}O_5S$: C, 52.54, H, 6.61. Found: C, 52.62; H, 6.68.

4-Acetyl-6-carbethoxy-1,3-dimethylthiabenzene 1-Oxide (12). A. From Dimethyloxosulfonium 1-Carbethoxy-3,3-diacetylallylide (11). A solution of 110 mg of **11** and 9.6 mg of sodium hydride in 4 ml of tetrahydrofuran was stirred for 40 min at room temperature under nitrogen. After evaporation of the solvent, the residue was extracted with hot AcOEt. The dried extract was concentrated and the residual solid was recrystallized from EtOH to give 64 mg (62%) of **12** as white crystals: mp 165.5–166°; ir ($CHCl_3$) 1685 (s), 1660 (s), 1575 (s), 1170 (s), 1080 (s) cm^{-1}; uv_{max} (EtOH) 229 (log ϵ 4.19), 286 (4.25), 345 nm (4.00); (log ϵ 4.19), 286 (4.25), 345 nm (4.00); nmr ($CDCl_3$) τ 1.63 (s, 1 H, Hc), 4.18 (bs, 1 H, Ha), 5.60 (q, 2 H, J = 7 Hz, OCH_2CH_3), 6.19 (s, 3 H, SCH_3), 7.48 (s, 3 H, ring CH_3), 7.61 (s, 3 H, $COCH_3$), 8.61 (t, 3 H, J = 7 Hz, OCH_2CH_3); mass spectrum *m/e* (rel intensity) 256 (M^+, 35), 241 (29), 213 (17), 193 (24), 169 (24), 167 (21). (The base peak is *m/e* 51.)

Anal. Calcd for $C_{12}H_{16}O_4S$: C, 56.23; H, 6.29. Found: C, 56.18; H, 6.21.

B. From 3-Ethoxymethylene-2,4-pentanedione (3) and Dimethyloxosulfonium Carbethoxymethylide (10). A solution of 2.16 g (0.02 mol) of ethyl chloroformate in 10 ml of tetrahydrofuran was added to a stirred solution of 0.04 mol of **10** in 30 ml of tetrahydrofuran at room temperature under nitrogen.[20] After the reaction mixture was stirred for 1 hr at room temperature, a solution of 1.56 g (0.01 mol) of **3** in 10 ml of tetrahydrofuran was added. The resulting red reaction mixture was stirred overnight at room temperature. Work-up as described above gave 0.33 g (13%) of white crystals, identical with A (see above) in all respects.

Dimethyloxosulfonium 3,3-Dicarbethoxyallylide (15). A solution of 4.4 g (0.02 mol) of **14** in 10 ml of DMSO was added to a stirred solution of 0.02 mol of **5** in 20 ml of DMSO at room temperature under nitrogen. After stirring for 3 hr, the reaction mixture was poured into ice–water and extracted with $CHCl_3$. The extract was washed with H_2O and a saturated NaCl solution and dried over Na_2SO_4. Evaporation of the solvent *in vacuo* at 40° and trituration with Et_2O gave a solid which was recrystallized from

AcOEt–petroleum ether (bp 30–60°) to give 0.42 g (17%) of **15**: mp 121.5–122.5; ir ($CHCl_3$) 1673 (s), 1642 (s), 1515 (s), 1175 (s), 1065 (s) cm^{-1}; uv_{max} (EtOH) 244 (log ϵ 4.09), 320 nm (4.57); nmr ($CDCl_3$) τ 1.96 (bd, 1 H, J = 13.5 Hz, Hc), 3.86 (bd, 1 H, J = 13.5 Hz, Hb), 5.81 and 5.84 (2 × q, 2 × 2 H, J = 7 Hz, 2 × OCH_2CH_3), 6.60 (s, 6 H, $S(CH_3)_2$), 8.71 and 8.74 (2 × t, 2 × 3 H, J = 7 Hz, 2 × OCH_2CH_3), the signal at τ 3.86 disappeared by treatment with deuterium oxide.

Anal. Calcd for $C_{11}H_{18}O_5S$: C, 50.36; H, 6.92. Found: C, 50.58; H, 6.81.

Using a similar procedure to that described above except the use of 2.2 g (0.01 mol) of **14**, **15** was obtained in 26% yield.

4-Carbethoxy-3-hydroxy-1-methylthiabenzene 1-Oxide (16). A solution of 0.15 g (0.6 mmol) of **15** in 10 ml of DMSO was added dropwise to a solution of dimsyl anion in DMSO prepared from 0.014 g (0.6 mmol) of sodium hydride and 10 ml of DMSO under nitrogen. After stirring for 3 hr at room temperature, the reaction mixture was poured into ice–water. The resulting mixture was extracted with $CHCl_3$ and the extract was washed with H_2O and a saturated NaCl solution and dried over Na_2SO_4. Evaporation of the solvent *in vacuo* at 40° gave a brown oil which was passed through a short silica gel column with $CHCl_3$. The evaporation of the solvent gave a crystalline compound which was recrystallized from AcOEt–petroleum ether (bp 30–60°) to give 0.07 g (52%) of **16**: mp 111–112°; ir ($CDCl_3$) 1640 (s), 1590 (m), 1378 (s), 1282 (s), 1138 (s) cm^{-1}; uv_{max} (EtOH) 213 (log ϵ 4.26), 230 (3.89), 274 (4.32), 304 nm (3.88); nmr ($CDCl_3$) τ −2.24 (s, 1 H, OH), 2.26 (d, 1 H, J = 9.8 Hz, Hc), 4.57 (dd, 1 H, J = 9.8 and 4.6 Hz, Hb), 4.81 (d, 1 H, J = 4.6 Hz, Ha), 5.75 (q, 2 H, J = 7.5 Hz, OCH_2CH_3), 6.59 (s, 3 H, SCH_3), 8.71 (t, 3 H, J = 7.5 Hz, OCH_2CH_3); mass spectrum *m/e* (rel intensity) 216 (M^+, 50), 201 (84), 171 (36), 155 (71), 127 (41), 107 (100). This compound gave a reddish brown color with ferric chloride solution.

Anal. Calcd for $C_9H_{12}O_4S$: C, 49.98; H, 5.60. Found: C, 50.20; H, 5.61.

2,4-Dimethyl-5-oxo-5,6,7,8-tetrahydro-2-thianaphthalene 2-Oxide (18). A solution of 0.42 g (2.5 mmol) of 2-acetyl-3-methoxy-2-cyclohexen-1-one[21] (**17**) in 10 ml of dry tetrahydrofuran was added to a cooled and stirring solution of 5 mmol of **5** in 20 ml of dry tetrahydrofuran at room temperature under nitrogen. After stirring overnight at room temperature, the resulting yellow reaction mixture was filtered to remove the precipitates. The filtrate was concentrated *in vacuo* and triturated with Et_2O to give a yellow solid, which was passed through a short alumina column with $CHCl_3$. Evaporation of the solvent gave a solid, which was recrystallized from AcOEt to give 0.153 g (29%) of **18** as colorless crystals: melted at 155–160°, solidified and remelted at 170–174°; ir ($CHCl_3$) 1632 (s), 1538 (s), 1143 (s) cm^{-1}; uv_{max} (EtOH) 218 (log ϵ 4.20), 299 nm (4.32); uv_{max} (concentrated HCl–EtOH (1:13)] 262, 321 nm; nmr ($CDCl_3$) τ 4.50 (d, 1 H, J = 4.5 Hz, Ha or Hb), 4.64 (d, 1 H, J = 4.5 Hz, Hb or Ha), 6.63 (s, 3 H, SCH_3), 7.47 (bs, 3 H, ring CH_3), 7.20–8.30 (m, 6 H, $-(CH_2)_3-$); mass spectrum *m/e* (rel intensity) 210 (M^+, 99), 195 (58), 147 (100).

Anal. Calcd for $C_{11}H_{14}O_2S$: C, 62.82; H, 6.71. Found: C, 62.75; H, 6.48.

Dimethylsulfonium 1-Carbethoxy-3,3-diacetylallylide (24). A solution of 156 mg (1 mmol) of **3** in 2 ml of DMSO was added to a stirred solution of 229 mg (1 mmol) of carbethoxymethyldimethylsulfonium bromide[22] and 24 mg (1 mmol) of sodium hydride in 2 ml of DMSO at room temperature under nitrogen. After stirring at room temperature for 30 min, the reaction mixture was poured into 10 ml of cold water and extracted with $CHCl_3$. The extract was washed with water, dried over Na_2SO_4, and concentrated to give a yellow solid. Recrystallization from benzene–petroleum ether gave 105 mg (41%) of **24** as yellow needles: mp 97–99°; ir ($CHCl_3$) 1660 (w), 1600 (s), 1490 (s), 1380 (s), 1300 (s), 1075 (s) cm^{-1}; uv_{max} (EtOH) 290 (log ϵ 3.11), 376 nm (4.57); nmr ($CDCl_3$) τ 1.77 (s, 1 H, olefinic proton), 5.77 (q, 2 H, J = 7 Hz, OCH_2CH_3), 7.01 (s, 6 H, $S(CH_3)_2$), 7.65 (s, 6 H, 2 × $COCH_3$), 8.66 (t, 3 H, J = 7 Hz, OCH_2CH_3).

Anal. Calcd for $C_{12}H_{18}O_4S$: C, 55.79; H, 7.02. Found: C, 55.81; H, 7.06.

Ethyl 4-Acetyl-5-methylfuran-2-carboxylate (13). A. From Dimethyloxosulfonium 2-Carbethoxy-3,3-diacetylallylide (11). A solution of 50 mg of **11** in 10 ml of xylene was refluxed until the starting material disappeared on tlc (1 hr). The solvent was removed *in vacuo* and the residual oil was chromatographed on alumina with $CHCl_3$ as solvent to give 24 mg (67%) of **13** as white needles: mp 107–109° (from petroleum ether) (lit.[10] 75–77°); the ir, uv, and nmr spectral data are in good agreement with the reported data;[10] mass spectrum *m/e* (rel intensity) 196 (M^+, 45), 181 (69), 167 (56), 153 (65), 43 (100).

Anal. Calcd for $C_{10}H_{12}O_4$: C, 61.21; H, 6.17. Found: C, 60.83; H, 6.05.

B. From Dimethylsulfonium 1-Carbethoxy-3,3-diacetylallylide (24). A solution of 250 mg of **24** in 10 ml of mesitylene was refluxed until the starting material disappeared on tlc (3 hr). Work-up as described above gave 136 mg (69%) of white crystals which are identical with **13** in all respects.

Deuterium Exchange of 6 and 7. Deuterium oxide (one drop) was added to a solution of 0.1 mmol of **6** or **7** in 0.4 ml of $CDCl_3$ in an nmr tube and the mixture was shaken for a few minutes. The exchange was allowed to proceed at 35° and followed by nmr spectroscopy. Complete exchange of Ha and Hb in both **6** and **7** occurred within 8 hr.

Bromination of 6. A. To a solution of 0.13 g (0.7 mmol) of **6** in 5 ml of acetic acid was added 0.22 g (0.7 mmol) of pyridinium hydrobromide perbromide (**32**).[23] The reaction mixture was heated to 40–50° for a few minutes and then allowed to stand for 1 hr at room temperature and poured into ice–water. The resulting mixture was extracted with $CHCl_3$ and the extract was washed with a saturated $NaHCO_3$ solution, H_2O, and a saturated NaCl solution and dried over Na_2SO_4. Evaporation of the solvent *in vacuo* at 40° and trituration with Et_2O gave 0.08 g (46%) of **30**, which was recrystallized from EtOH–petroleum ether (bp 30–60°); when the temperature was rapidly raised, it melted at 159–160°, but when the temperature was slowly raised, it decomposed; ir ($CDCl_3$) 1620 (s), 1545 (s), 1260 (s), 1165 (s) cm^{-1}; uv_{max} (EtOH) 218 (log ϵ 4.18), 301 nm (4.24); nmr ($CDCl_3$) τ 2.07 (s, 1 H, Hc), 4.42 (s, 1 H, Ha), 6.42 (s, 3 H, SCH_3), 7.49 (s, 3 H, ring CH_3), 7.66 (s, 3 H, $COCH_3$); mass spectrum *m/e* (rel intensity) 263 (17), 261 (M^+, 18), 248 (13), 246 (9), 200 (10), 198 (10) (the base peak is *m/e* 124).

Anal. Calcd for $C_9H_{11}BrO_2S$: C, 41.07; H, 4.21. Found: C, 41.11; H, 4.20.

B. To a solution of 0.46 g (2.5 mmol) of **6** in 20 ml of acetic acid was added 1.6 g (5 mmol) of **32**. The reaction mixture was warmed at 40–50° for a few minutes and allowed to stand for 1 hr at room temperature. Work-up as described above in method A gave a mixture of two products, which was separated by preparative tlc using $CHCl_3$ as solvent to give 0.14 g (21%) of **30** and 0.22 g (25%) of **31**. Compound **31** was recrystallized from EtOH–petroleum ether (bp 30–60°): mp 134–135°; ir ($CHCl_3$) 1640 (s), 1540 (s), 1240 (s) cm^{-1}; uv_{max} (EtOH) 227 (log ϵ 4.15), 302 nm (4.15); nmr ($CDCl_3$) τ 2.17 (s, 1 H, Hc), 6.20 (s, 3 H, SCH_3), 7.39 (s, 3 H, ring CH_3), 7.65 (s, 3 H, $COCH_3$); mass spectrum *m/e* (rel intensity) 344 (56), 342 (100), 340 (M^+, 52), 205 (52), 203 (48).

Anal. Calcd for $C_9H_{10}Br_2O_2S$: C, 31.60; H, 2.95. Found C, 31.45; H, 2.92.

Nitration of 6. A solution of 0.46 g (2.5 mmol) of **6** in 10 ml of acetic anhydride and 4 ml of acetic acid was added dropwise to a cooled solution of acetyl nitrate (**34**)[24] prepared by adding 1.8 ml of 70% HNO_3 to 12 ml of acetic anhydride at −5°. The reaction mixture was allowed to stand for 1 hr at room temperature and poured into ice–water. The resulting mixture was extracted with $CHCl_3$ and the extract was washed with a saturated $NaHCO_3$ solution, H_2O, and a saturated NaCl solution and dried over $CaSO_4$. Evaporation of the solvent *in vacuo* at 40° and trituration with Et_2O–$CHCl_3$ gave a yellow crystalline solid which was collected and recrystallized from EtOH–petroleum ether (bp 30–60°) to give 0.11 g (20%) of **33**: mp 185–186.5°; ir (KCl) 1585 (s), 1520 (s), 1275 (s), cm^{-1}; uv_{max} (EtOH) 220 (log ϵ 3.97), 255 (3.94), 315 (3.98), 398 nm (4.06); nmr (DMSO-d_6) τ 1.18 (s, 1 H, Hc), 2.93 (bs, 1 H, Ha), 5.77 (s, 3 H, SCH_3), 7.51 (s, 3 H, ring CH_3); mass spectrum *m/e* (rel intensity) 232 (M^+, 95), 169 (47), 153 (68), 109 (100).

Anal. Calcd for $C_7H_8N_2O_5S$: C, 36.20; H, 3.47; N, 12.06. Found: C, 36.35; H, 3.50; N, 11.95.

Tlc examination showed that the mother liquor contained a minor yellow product which was resolved only with difficulty by tlc from **33** (the amounts obtained were insufficient to permit complete characterization).

Nitration of 7. Using a procedure similar to that described for nitration of **6**, 0.54 g (2.5 mmol) of **7** was nitrated by **34** to give a mixture of three products, from which 0.04 g (5%) of **35** was obtained in a pure state by preparative tlc on silica gel using $CHCl_3$ as solvent and recrystallization from EtOH: mp 142–143°; ir ($CHCl_3$) 1715 (s), 1575 (s), 1510 (s), 1290 (s) cm^{-1}; uv_{max} (EtOH) 245 (log ϵ 4.30), 312 (3.46), 444 nm (4.06); nmr τ 1.04 (s, 1 H, Hc), 5.64 (s, 3 H, SCH_3), 5.71 (q, 2 H, J = 7 Hz, OCH_2CH_3), 7.22 (s, 3 H, ring CH_3), 8.66 (t, 3 H, J = 7 Hz, OCH_2CH_3); mass spectrum *m/e* 304 (M^+).

Anal. Calcd for $C_{10}H_{12}O_7N_2S$: C, 39.47; H, 3.98; N, 9.21. Found: C, 39.76; H, 4.10; N, 8.96.

The other two products were obtained as a yellow crystalline mixture (0.06 g) of **36** and **37** in a ratio 1:1. The ir spectrum ($CHCl_3$) showed the presence of an ester group (1705 cm^{-1}) and a nitro group (1580 and 1295 cm^{-1}). The nmr spectrum ($CDCl_3$) showed two series of signals due to **33** and except for the common signals of the ethoxyl group which appear at τ 5.74 (q, 2 H, J = 6 Hz) and 8.68 (t, 3 H, J = 6 Hz): the signals for **33**, τ 1.24 (s, 0.5 H, Hc), 3.93 (s, 0.5 H, Ha), 6.02 or 6.07 (s, 1.5 H, SCH_3), 7.47 (s, 1.5 H, ring CH_3); the signals for **34**, τ 2.15 (d, 0.5 H, J = 10 Hz, Hc), 3.70 (d, 0.5 H, J = 10 Hz, Hb), 6.07 or 6.02 (s, 1.5 H, SCH_3), 7.22 (s, 1.5 H, ring CH_3).

Registry No.—**3**, 33884-41-2; **4**, 3788-94-1; **5**, 5367-24-8; **6**, 49836-26-2; **7**, 49836-27-3; **8**, 52873-52-6; **9**, 16806-88-5; **10**, 19956-89-9; **11**, 52873-53-7; **12**, 52873-54-8; **13**, 29172-08-5; **14**, 87-13-8; **15**, 49836-33-1; **16**, 49836-32-0; **17**, 21014-78-8; **18**, 49836-34-2; **23**, 7380-81-6; **24**, 52873-55-9; **30**, 52873-56-0; **31**, 52873-59-3; **32**, 34842-62-1; **33**, 52873-57-1; **34**, 591-09-3; **35**, 52873-60-6; **36**, 52873-58-2; **37**, 52873-61-7.

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Simple Deaminations. V.[1–3] Preparation and Some Properties of *N*-Alkyl-*N*,*N*-disulfonimides[4]

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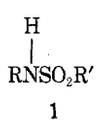
A simple two-step derivatization procedure for the preparation of a variety of *N*-alkyl-*NN*-disulfonimides (**2**) from the parent amines and sulfonyl chlorides is presented. Yields of up to 99% have been obtained. The diarylsulfonimides **2** are in general stable, crystalline solids. The synthetic procedure was developed since these compounds have been observed to undergo facile and synthetically useful deamination. Some ir and pmr properties of these novel compounds are presented and discussed here. In various respects, the disulfonimides **2** behave analogously to the alkyl halides and alkyl pseudohalides.

Whereas numerous references to the preparations and properties of a large variety of *N*-alkyl- and *N*-aryl-monosubstituted sulfonamides (**1**) exist in the literature,[6b,37–46] references to the preparations or properties of *N*-aryl- or *N*-alkyl-*N*,*N*-disulfonimides (**2**)[4] are by comparison



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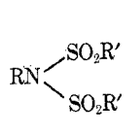
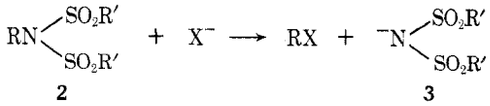


2

rare.[47,48] Thus sulfonamide derivatives (**1**) have long been used in the analysis of amines,[38,39] as protecting groups for amines,[42,43] and in pharmacology.[44] Some of the properties of sulfonamides have been reviewed[41] and good procedures for the preparation of sulfonamides (**1**) are known.[6,37–41] But, until our investigations, only a few scattered reports[15,49–50,57] of the intentional synthesis of *N*-alkyl- or *N*-aryldisulfonimides (**2**) had appeared; several others[51–53] considered disulfonimides as bothersome side products in the characterization or separation of primary and secondary amines by the Hinsberg method.[54] To date, apparently the most "useful" property of disulfonimides **2** is the property first predicted[56] and generally observed[1–3] in our laboratories, that the disulfonimides **2** undergo carbon–nitrogen bond cleavage in the presence of nucleophiles (eq 1).



(1)

2 **3**

That the disulfonimide anions **3**[57] are good leaving groups is predicted from consideration of the pK_a values of the conjugate acids. Thus, for example, the pK_a of *N*,*N*-di(*p*-nitrobenzene)sulfonimide is 0.30.[27] The pK_a values of the parent amines, on the other hand, are in the range of *ca.* 35.[56,59] Our initial successful demonstrations of this new nucleophilic substitution deamination (eq 1) supplied mo-