The Synthesis and Characterization of Some Eight- and Ten-Membered Sulfur-Containing Heterocycles

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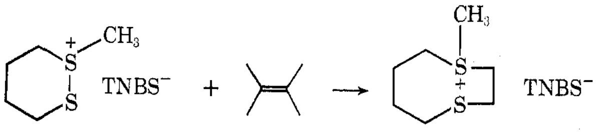
Eight- and ten-membered heterocycles containing two sulfur atoms were prepared by forming olefin and 1,3-diene adducts with 1-methyl-1-thionia-2-thiacyclohexane 2,4,6-trinitrobenzenesulfonate. The nmr spectra of the products suggested the absence of a transannular interaction leading to tetracovalent sulfur.

This research was pursued because of the unique method it provides for the synthesis of certain medium-sized heterocycles. Also, compounds similar to the products have been convenient for the investigation of transannular interactions.[1]

In a previous paper[2] we reported the successful synthesis of ethylene and 2,3-dimethyl-1,3-butadiene adducts of 1-methyl-1-thionia-2-thiacyclohexane 2,4,6-trinitrobenzenesulfonate (**1**). The eight- and ten-membered rings, 1-methyl-1-thionia-4-thiacyclooctane (**2**, eq 1) and 1,3,4-trimethyl-1-thionia-6-thia-3-cyclodecene (**3**, eq 2) cations, were prepared in good yields. (TNBS$^-$ = 2,4,6-trinitrobenzenesulfonate anion.)



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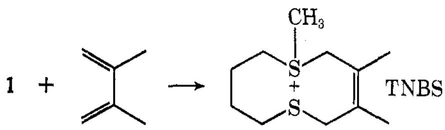

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We would now like to report the successful synthesis of a number of other olefin and diene adducts and interpret their nmr spectra as they relate to transannular interactions.

Results

The reaction of 1-methyl-1-thionia-2-thiacyclohexane cation (**1**) with olefins was investigated. Analytically pure products could be prepared from ethylene, propene, 1-pentene, *cis*- and *trans*-2-butene, and cyclohexene. Olefins which formed an adduct, as indicated by nmr spectra, but did not give products with a good elemental analysis were *cis*-stilbene, 2-methylpropene, and methylene cyclohexane. Olefins which did not react were *trans*-stilbene, *cis*- and *trans*-1,2-dichloroethylene, 2-methyl-2-butene, and tetramethylethylene.

The addition is sensitive to substituents on the olefin. In certain cases the reaction showed evidence of easy reversibility, so that unfavorable substituent interactions in the product and a transannular sulfur–sulfur interaction (at least in the transition state) would disfavor adduct formation. The unreactivity of vinyl chlorides suggests an electron density influence in the olefin, and the unreactivity of highly substituted olefins could be due to unfavorable steric factors in the forward direction of the addition process..

The 1,1-disubstituted olefins gave products of addition as revealed by their nmr spectra, but neither 2-methylpentene nor methylene cyclohexane gave a product with a satisfactory elemental analysis. Like the *cis*-stilbene adduct, the olefin seemed to be regenerated during recrystallization. Olefins which were trisubstituted showed no indication of a reaction. These results again point out the sensitivity of the reaction to steric factors.

The sensitivity of the reaction to electronic effects is revealed by the absence of reactivity of **1** with *cis*- and *trans*-dichloroethylene. The unreactivity was not unexpected because the addition reaction, even with more reactive olefins, was slow.

The scope of the reaction of **1** with 1,3-dienes was also investigated. Among several dienes tested only 2,3-dimethyl-1,3-butadiene, 1,2-dimethylenecyclohexane, and 2,3-diphenyl-1,3-butadiene gave products with good elemental analyses. Others that according to their nmr spectra had reacted but yielded impure products were 1,3-butadiene and 1,3-cyclohexadiene. Those which showed no indication of reaction were hexachlorocyclopentadiene and hexachloro-1,3-butadiene.

The success of the reaction of dienes was related to the nature of substitution at the "internal" sp^2 carbon atoms. Those that were unsubstituted at the 2,3 positions, namely butadiene and 1,3-cyclohexadiene, yielded no satisfactory product even though several different combinations of solvents and reaction times were tried.

The same electronic limitations that applied to the olefins applied to the dienes. The dienes substituted with strongly electron-withdrawing chlorine were completely unreactive toward **1**.

Discussion of Possible Mechanisms.—The addition of dialkyl (alkylthio)sulfonium salts (**4**) (compounds analogous to **1**) to olefins has been thoroughly investigated and the stereochemistry of the products (**6**) has been demonstrated.[3] The mechanism proposed for this addition (eq 3) involved the initial formation of an

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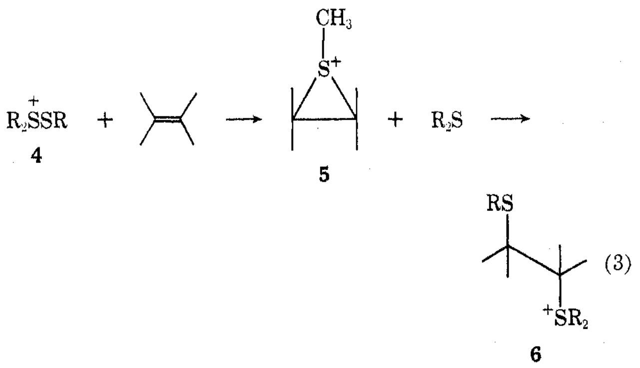
[1] S. M. Johnson, C. A. Maier, and I. C. Paul, *J. Chem. Soc. B*, 1603 (1970).

[2] N. E. Hester, G. K. Helmkamp, and G. L. Alford, *Int. J. Sulfur Chem., Part A*, **1**, 65 (1971).

[3] G. K. Helmkamp, B. A. Olsen, and J. R. Koskinen, *J. Org. Chem.*, **30**, 1623 (1965).



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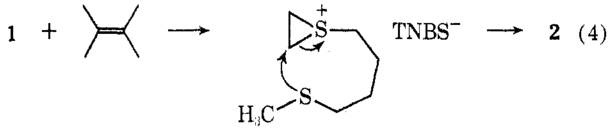
episulfonium ion intermediate (**5**) (where the anion in each case is 2,4,6-trinitrobenzenesulfonate) followed by back-side attack to give trans addition.

If this mechanism is operative for the addition of **1** to olefins, then a seven-membered transition state (**7**, eq 4) is required for the backside displacement,



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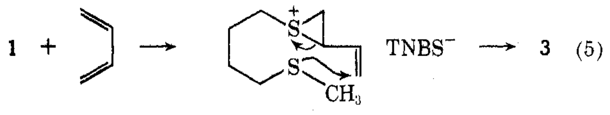
which is highly unlikely to develop. Also, if an episulfonium ion intermediate (**8**) is formed when **1** reacts with a diene and if the ring closes by an S_N2' type mechanism, then a nine-membered transition state (**8**, eq 5) is required. This possibility would be even less favorable than in the olefin addition.



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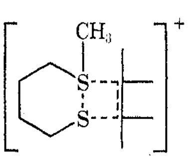
A mechanism which avoids the problems of the seven- and nine-membered transition states would be a concerted or nearly concerted addition. This manner of addition would give a four-membered transition state for the olefin addition (**9**) and a six-membered transition state for the addition of dienes (**10**). Although a 2 + 2 addition normally is symmetry forbidden, the present system involves an unsymmetrical, highly polarized bond between atoms which can utilize d orbitals in the transition state. Given these arguments and the facts that the reactions proceed fairly rapidly without high-dilution techniques, a concerted or nearly concerted mechanism is highly probable.



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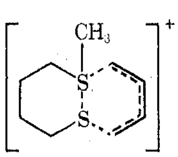

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One consequence of a concerted *vs.* episulfonium ion mechanism is that the stereochemistry of the products of the olefin adducts would be different. It was anticipated that the nmr spectra of some of the products would shed light on the stereochemistry, but the spectra were extremely complicated in the area of interest. An X-ray crystal structure determination of one of the 2-butene or cyclohexene adducts will shed the necessary light on the reaction mechanism.

Interpretation of Nmr Spectra as They Relate to Transannular Interactions between Sulfur Atoms.—In order to determine if a transannular interaction between the "thia" and "thionia" sulfurs was present, the chemical shift of the *S*-methyl protons was monitored. It was assumed that an upfield shift, similar to that observed by Owsley,[4,5] would be detected.

Owsley treated cyclooctene-*S*-methylepisulfonium 2,4,6-trinitrobenzenesulfonate with chloride ion, and the *S*-methyl peak shifted 36 cycles upfield.[3,4] It was expected that this 36-cycle shift would approximate that which would result from a transannular interaction.

The ethylene and 2,3-dimethyl-1,3-butadiene adducts were investigated in detail, since they provided the simplest spectra for the respective olefin and diene adducts. The *S*-methyl peaks were clean singlets.

In order to determine if an interaction was occurring, model compounds were prepared in which no sulfide ("thia") sulfur was available to interact with the sulfonium ("thionia") sulfur.

An approximate model for the ethylene adduct might be simply trimethylsulfonium 2,4,6-trinitrobenzenesulfonate. However, since the size of the alkyl chain would influence the chemical shift of an *S*-methyl peak, dimethylethylsulfonium 2,4,6-trinitrobenzenesulfonate also were prepared. The chemical shifts of all four compounds are summarized in Table I.

TABLE I

CHEMICAL SHIFTS OF THE *S*-METHYL PROTONS OF 1-METHYL-1-THIONIA-4-THIACYCLOOCTANE 2,4,6-TRINITROBENZENESULFONATE (2) AND MODEL SULFONIUM SALTS

Compd	Chemical shift, δ (cycles)
2	2.98 (179)
$(CH_3)_3S^+TNBS^{-\,a}$	2.93 (176)
$CH_3CH_2\overset{+}{S}(CH_3)_2TNBS^-$	2.92 (175)
$(CH_3CH_2)_2\overset{+}{S}CH_3TNBS^-$	2.84 (170)

[a] TNBS = 2,4,6-Trinitrobenzenesulfonate anion.

Similarly, a model for the 2,3-dimethyl-1,3-butadiene adduct might be a trialkylsulfonium salt such as trimethylsulfonium 2,4,6-trinitrobenzenesulfonate. The possibility that the allylic double bond could influence the chemical shift of the *S*-methyl group also was considered; so dimethylallylsulfonium 2,4,6-trinitrobenzenesulfonate and diallymethylsulfonium 2,4,6-trinitrobenzenesulfonate were prepared. The chemical shifts of these compounds are summarized in Table II.

Table I reveals that the *S*-methyl protons of 1-methyl-1-thionia-4-thiacyclooctane 2,4,6-trinitrobenzenesulfonate (**2**) fall at 179 cycles, whereas the *S*-methyl protons of diethylmethylsulfonium 2,4,6-trinitrobenzenesulfonate, probably the best model, appear at 170 cycles. This would represent a downfield shift for **2** of 9 cycles. The shift is nowhere near the magnitude of the shift of 36 cycles observed by Owsley

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(4) D. C. Owsley, G. K. Helmkamp, and M. F. Rettig, *J. Amer. Chem. Soc.*, **91**, 5239 (1969).

(5) D. C. Owsley, Ph.D. Dissertation, University of California, Riverside, Calif.

TABLE II

CHEMICAL SHIFTS OF THE *S*-METHYL PROTONS OF 1,3,4-TRIMETHYL-1-THIONIA-6-THIA-3-CYCLODECENE 2,4,6-TRINITROBENZENESULFONATE (**3**) AND MODEL SULFONIUM SALTS

Compd	Chemical shift, δ (cycles)
3	2.92 (175)
$(CH_3)_3S^+TNBS^-$[a]	2.93 (176)
$(CH_3)_2\overset{+}{S}CH_2CH{=}CH_2\ TNBS^-$	2.85 (171)
$CH_3\overset{+}{S}(CH_2CH{=}CH_2)_2\ TNBS^-$	2.82 (169)

[a] TNBS = 2,4,6-Trinitrobenzenesulfonate anion.

and is in the opposite direction. The 9-cycle difference probably is due to the presence of the other sulfur in the ring, so that the shift most likely represents a "through space" interaction of the lone pair electrons on the sulfide sulfur rather than a bonding interaction.

Table II reveals that the *S*-methyl peak of 1,3,4-trimethyl-1-thionia-6-thia-3-cyclodecene 2,4,6-trinitrobenzenesulfonate (**3**) appears at 175 cycles and the *S*-methyl peak of dimethylallylsulfonium 2,4,6-trinitrobenzenesulfonate, probably the best model, apears at 171 cycles. Again the magnitude of the shift is small and in the wrong direction. This difference of only 4 cycles could be due to experimental error. However, since it is in the same direction as the 9-cycle difference mentioned above, it may also represent a through space effect of the lone pair electrons on the sulfide sulfur. In both of these systems then, the nmr evidence points very strongly toward the absence of any bonding interaction across the rings.

Experimental Section[6]

1,2-Dithiane.—The 1,2-dithiane[7] was used as the crude product isolated by evaporation of the CH_2Cl_2 extraction solvent. Alternatively the following combination of thiol preparation[8] and conversion to the 1,2-dithiane,[7] followed by direct alkylation as in procedure A, was effective. A mixture of 41 g (0.19 mol) of 1,4-dibromobutane, 29 g (0.38 mol) of thiourea, and 25 ml of water was refluxed with stirring for 3 hr. Then 30 g of NaOH in 300 ml of water was added and the solution was refluxed for an additional 3 hr. After the mixture was cooled (0°), 36.5 g (0.19 mol) of *p*-toluenesulfonyl chloride was added and the contents of the reaction flask were stirred for 1 hr. The resulting solution was extracted with four 50-ml portions of CH_2Cl_2. The combined organic extract was washed twice with water, dried over $MgSO_4$, and evaporated on a rotary evaporator to give crude 1,2-dithiane.

1-Methyl-1-thionia-2-thiacyclohexane 2,4,6-Trinitrobenzenesulfonate (1). Procedure A. Alkylation of 1,2-Dithiane with an Oxonium Salt.—Trimethyloxonium 2,4,6-trinitrobenzenesulfonate[9] (1.77 g, 0.0050 mol) was dissolved in a minimum amount of nitromethane, and 1.20 g (0.010 mol) of crude 1,2-dithiane in 10 ml of CH_2Cl_2 was added. The bright yellow solution was allowed to stand for 0.5 hr. Crystalline product was isolated by slowly adding dry Et_2O until all product precipitated, yield 87%. Three precipitations from CH_3NO_2–Et_2O gave mp 179–180° dec, nmr δ 8.48 (s, 3), 3.75–3.05 and 3.33 (m and s, respectively, 7), 2.43–1.92 (m, 4).

Anal. Calcd for $C_{11}H_{13}N_3O_9S_3$: C, 30.91; H, 3.07; N, 9.83. Found:[10] C, 31.07; H, 2.93; N, 10.11.

Procedure B. Alkylation of 1,2-Dithiane with Methyl Iodide in the Presence of Silver 2,4,6-Trinitrobenzenesulfonate.—The following mixture was refluxed overnight: 1.41 g (0.010 mol) of CH_3I in 5 ml of CH_2Cl_2; 5.2 g (0.010 mol) of the acetonitrile complex of silver 2,4,6-trinitrobenzenesulfonate[9] in 20 ml of CH_3NO_2; and 1.2 g (0.010 mol) of crude 1,2-dithiane[7] in 15 ml of CH_2Cl_2. After AgI was removed by filtration (Celite) the product was precipitated by adding the filtrate to 500 ml of dry Et_2O. The solid was redissolved in CH_3NO_2, warmed with decolorizing charcoal, filtered (Celite), and reprecipitated, yield 58%. Drying (15 hr, 0.1 mm, 40°) led to a melting point and nmr spectrum that were the same as those given above.

Reactions of 1-Methyl-1-thionia-2-thiacyclohexane 2,4,6-Trinitrobenzenesulfonate (1) with Alkenes. A. With Ethene.—A solution of 1 (0.43 g, 0.0010 mol) in 35 ml of CH_3NO_2–CH_2Cl_2 (2.5:1.0) was saturated with gaseous ethene twice a day for 4 days. The product was isolated by pouring the solution into 1 l. of vigorously stirred anhydrous Et_2O and collecting the precipitated: yield 78% after one reprecipitation from the same solvents; after three precipitations, mp 115–121° with effervescence; nmr δ 8.56 (s, 2), 2.98 (s, 3), 3.92–1.42 (a singlet at δ 2.98 superimposed on a series of multiplets, 15).

Anal. Calcd for $C_{13}H_{15}N_3O_9S_3$: C, 34.28; H, 3.76; N, 9.23. Found:[10] C, 34.31; H, 3.68; N, 9.27.

B. With Propene.—A 2-week reaction similar to that described above was carried out with propene, yield 85%. Three precipitations yielded the final product: mp 62–66° with effervescence; nmr δ 8.55 (s, 2), 3.83–1.67 (overlapping multiplets, 17).

Anal. Calcd for $C_{14}H_{19}N_3O_9S_3$: C, 35.81; H, 4.08; N, 8.95. Found:[10] C, 35.72; H, 4.03; N, 9.17.

C. With 1-Pentene.—A solution of about 0.03 mol of 1-pentene and 0.86 g (0.0020 mol) of 1 in 20 ml of CH_3NO_2 was allowed to stand for 5 days. An oily product was obtained by adding the solution to 1 l. of ether–petroleum ether (bp 30–60°) (9:1). Reprecipitation from the same solvent system yielded a pale yellow solid, yield 90%. Two additional precipitations yielded final product: mp 62–67° with effervescence; nmr δ 8.50 (s, 2), 2.42–0.58 (overlapping multiplets, 21).

Anal. Calcd for $C_{16}H_{23}N_3O_9S_3$: C, 38.62; H, 4.66; N, 8.45. Found:[10] C, 38.42; H, 4.62; N, 8.64.

D. With *cis*-2-Butene.—An excess of *cis*-2-butene was maintained as a separate layer in a reaction flask containing 0.86 g (0.0020 mol) of 1 in 15 ml of CH_3NO_2. After 5 days the precipitated product was collected and washed with a few milliliters of cold CH_3NO_2, yield 67%. The product was dried at reduced pressure: mp 161–163° dec; nmr δ 8.52 (s, 2), 3.90–0.97 (a singlet *S*-methyl peak at 2.86 superimposed on a series of multiplets, total area 19).

Anal. Calcd for $C_{15}H_{21}N_3O_9S_3$: C, 37.26; H, 4.38; N, 8.69. Found:[10] C, 37.15; H, 4.36; N, 8.46.

E. With *trans*-2-Butene.—The process described above was used with *trans*-2-butene: yield after 6 days 51%; mp 161–163° dec; nmr δ 8.52 (s, 2), 3.90–0.97 (a single *S*-methyl peak at 2.88 superimposed on a series of multiplets, total area 19).

Anal. Calcd for $C_{15}H_{21}N_3O_9S_3$: C, 37.26; H, 4.38; N, 8.69. Found:[10] C, 37.15; H, 4.36; N, 8.69.

F. With Cyclohexene.—The process described above was used with about 0.02 mol of cyclohexene: yield after 5 days 54%; slow decomposition above 93°; nmr δ 8.55 (s, 2), 3.78–0.95 (singlet *S*-methyl peak superimposed on a series of multiplets, total area 22 ± 1).

Anal. Calcd for $C_{17}H_{23}N_3O_9S_3$: C, 40.07; H, 4.55; N, 8.24. Found:[10] C, 40.10; H, 4.84; N, 8.60.

G. With *cis*-Stilbene, 2-Methylpropene, and Methylenecyclohexane.—Reactions run according to the method described for *cis*-2-butene, but with reaction times of up to 19 days, yielded products whose nmr spectra were consistent with those expected of the usual adducts. However, elemental analyses were never adequate, and often the attempted purification procedures resulted in partial reversal of the addition process.

H. With *trans*-Stilbene, *cis*-1,2-Dichloroethene, *trans*-1,2-Dichloroethene, 2-Methyl-2-butene, and Tetramethylethylene.—Reactions carried out under any of the conditions described above failed to yield any products. Starting materials were recovered.

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(6) Reaction solvents were reagent grade and were dried over Molecular Sieve (Linde 4A) before use. Melting points are uncorrected. All nmr spectra were run using deuterionitromethane as solvent, and the residual absorbance due to undeuterated material was used as a standard (δ 4.28); spectra were recorded on a Varian A-60D spectrometer.

(7) L. Field and R. B. Barbee, *J. Org. Chem.*, **34**, 36 (1969).

(8) A. I. Vogel, "Practical Organic Chemistry," 3rd ed, Wiley, New York, N. Y., 1966.

(9) D. J. Pettitt and G. K. Helmkamp, *J. Org. Chem.*, **29**, 2702 (1964).

(10) Analysis by Galbraith Laboratories, Inc., Knoxville, Tenn.

Reactions of 1-Methyl-1-thionia-2-thiacyclohexane 2,4,6-Trinitrobenzenesulfonate (1) with 1,3-Dienes. A. With 2,3-Dimethyl-1,3-butadiene.—A mixture of 10 ml (about 0.09 mol) of 2,3-dimethyl-1,3-butadiene, 2.14 g (0.0050 mol) of **1**, and 75 ml of acetone was brought to boiling and then was allowed to stand for 1.5 days. The precipitated product was recrystallized from acetone: yield 72%; mp 143–144° dec; nmr δ 8.50 (s, 2), 2.93 (s, 3), 1.88 (s, 6), 4.12–1.33 (series of multiplets including the listed superimposed singlets, total area 21).

Anal. Calcd for $C_{17}H_{23}N_3O_9S_3$: C, 40.07; H, 4.52; N, 8.25. Found:[10] C, 40.17; H, 4.66; N, 8.14.

B. With 1,2-Dimethylenecyclohexane.—A reaction similar to that described above was carried out with 0.86 g (0.0020 mol) of **1**, about 0.02 mol of 1,2-dimethylenecyclohexane,[11] and 20 ml of acetone: yield 70%; mp 140–142° dec; nmr δ 8.52 (s, 2), 4.13–3.07 (m, 4), 2.93 (s, 3), 2.77–1.33 (a series of overlapping multiplets, 16).

Anal. Calcd for $C_{19}H_{25}N_3O_9S_3$: C, 42.60; H, 4.70; N, 7.84. Found:[10] C, 42.72; H, 4.72; N, 7.65.

C. With 2,3-Diphenyl-1,3-butadiene.—A mixture of 1.6 g (0.0080 mol) of 2,3-diphenyl-1,3-butadiene[12] and 0.86 g (0.0020 mol) of **1** was warmed until the diene started to melt, and then 15 ml of CH_3NO_2 was added. After 15 days the product was precipitated by addition of the solution to 500 ml of anhydrous Et_2O: yield 79%; mp >94° dec; nmr δ 8.55 (s, 2), 7.70–6.93 (m, 10), 3.68–1.10 (series of multiplets superimposed on singlets at 2.80 and 1.77, total area 12).

Anal. Calcd for $C_{27}N_{27}N_3O_9S_3$: C, 51.17; H, 4.30; N, 6.63. Found:[13] C, 50.70; H, 4.46; N, 6.76.

D. With 1,3-Butadiene and 1,3-Cyclohexadiene.—Reactions carried out by the above procedure yielded products with an appropriate nmr spectra, but purification procedures were inadequate for the production of analytically pure materials.

E. With Hexachlorocyclopentadiene and Hexachloro-1,3-butadiene.—These substractes failed to react with **1** under the conditions described above.

Dimethylethylsulfonium 2,4,6-Trinitrobenzenesulfonate.—An excess (0.76 g, 0.010 mol) of methyl ethyl sulfide in 20 ml of CH_3NO_2 was alkylated with 1.41 g (0.0040 mol) of trimethyloxonium 2,4,6-trinitrobenzenesulfonate.[9] The product was precipitated by the addition of anhydrous Et_2O (yield 90%) and recrystallized from CH_3NO_2: mp 196.5–197.5°; nmr δ 8.52 (s, 2), 3.33 (q, 2), 2.92 (s, 6), 1.45 (t, 3).

Anal. Calcd for $C_{10}H_{13}N_3O_9S_3$: C, 31.33; H, 3.42; N, 10.96. Found:[13] C, 31.66; H, 3.42; N, 10.50.

Diethylmethylsulfonium 2,4,6-Trinitrobenzenesulfonate.—An excess of diethyl sulfide (0.9 g, 0.01 mol) in 5 ml of CH_2Cl_2 was alkylated with 0.71 g (0.0050 mol) of methyl iodide. After a few minutes a solution of 2.60 g (0.0050 mol) of silver 2,4,6-trinitrobenzenesulfonate–acetonitrile complex in 15 ml of CH_3NO_2 was added. After 24 hr AgI was removed by filtration and the product was precipitated by adding anhydrous Et_2O to the filtrate, yield 78%. The product was recrystallized from CH_3NO_2: mp 173–174°; nmr δ 8.52 (s, 2), 3.33 (q, 4), 2.84 (s, 3), 1.44 (t, 6).

Anal. Calcd for $C_{11}H_{15}N_3O_9S_2$: C, 33.25; H, 3.42; N, 10.96. Found:[13] C, 33.67; H, 3.78; N, 11.16.

Diallylmethylsulfonium 2,4,6-Trinitrobenzenesulfonate.—The compound was prepared by the methyl iodide alkylation and anion metathesis described above, using 0.71 g (0.0050 mol) of diallyl sulfide: yield 81%; mp 120–121°; nmr δ 8.53 (s, 2), 6.52–5.02 (m, 6), 4.02 (d, 4), 2.80 (s, 3).

Anal.[14] Calcd for $C_{13}H_{15}N_3O_9S_2$: C, 37.05; H, 3.59; N, 9.97. Found: C, 36.91; H, 3.77; N, 9.73.

Dimethylallylsulfonium 2,4,6-Trinitrobenzenesulfonate.—The procedure described above was applied to methyl allyl sulfide: yield 91%; mp 173–174°; nmr δ 8.50 (s, 2), 5.93–5.36 (m, 3), 4.00 (d, 2), 2.85 (s, 6).

Anal.[14] Calcd for $C_{11}H_{13}N_3O_9S_2$: C, 33.42; H, 3.31; N, 10.63, Found: C, 33.14; H, 3.49; N, 10.31.

Registry No.—**1**, 33909-82-9; **2**, 33909-83-0; **3**, 33909-84-1; $C_{13}H_{15}N_3O_9S_3$, mp 115–121°, 37447-66-8; $C_{14}H_{19}N_3O_9S_3$, mp 62–66°, 37447-67-9; $C_{16}H_{23}N_3O_9S_3$, mp 62–67°, 37447-68-0; $C_{15}H_{21}N_3O_9S_3$, mp 161–163°, 37447-69-1; $C_{17}H_{23}N_3O_9S_3$, mp >93°, 37447-70-4; $C_{19}H_{25}N_3O_9S_3$, mp 140–42°, 37447-71-5; $C_{27}H_{27}N_3O_9S_3$, mp >94°, 37447-72-6; trimethyloxonium 2,4,6-trinitrobenzenesulfonate, 13700-00-0; 1,2-dithiane, 505-20-4; silver 2,4,6-trinitrobenzenesulfonate, 37447-76-0; ethene, 74-85-1; propene, 115-07-1; 1-pentene, 109-67-1; *cis*-2-butene, 590-18-1; *trans*-2-butene, 624-64-6; cyclohexene, 110-83-8; 2,3-dimethyl-1,3-butadiene, 513-81-5; 1,2-dimethylenecyclohexane, 2819-48-9; 2,3-diphenyl-1,3-butadiene, 2548-47-2; dimethylethylsulfonium 2,4,6-trinitrobenzenesulfonate, 37508-14-8; diethylmethylsulfonium 2,4,6-trinitrobenzenesulfonate, 37447-75-9; diallylmethylsulfonium 2,4,6-trinitrobenzenesulfonate, 37447-77-1; dimethylallylsulfonium 2,4,6-trinitrobenzenesulfonate, 37567-15-0.

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(13) Analysis by Geiger Laboratory, Ontario, Calif.

(14) Analysis by Elek Microanalytical Laboratories, Harbor City, Calif.