tographic fractionation gave ether with physical characteristics described elsewhere in this publication.

Preparation of (+)-2-Methoxyoctane.—(+)-2-Octanol was converted to (+)-2-methoxyoctane by the procedure of Kenyon and McNicol.[14] Distillation of the product under reduced pressure gave ether, b.p. 59–60° at 11 mm. (lit.[14] b.p. 76–77° at 44 mm.), n^{20}_D 1.4072, n^{25}_D 1.4065 (literature values are given in Table III).

Reactions in Dimethylformamide.—These were similar to those in dimethyl sulfoxide except that the solvent was dried overnight over a mixture of potassium hydroxide and barium oxide, filtered, and fractionally distilled before use.

The Addition of Dialkylalkylthiosulfonium Salts to Alkenes[1]

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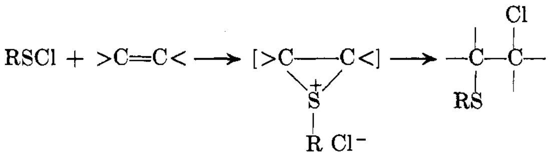
Alkylated disulfides in the form of dialkylalkylthiosulfonium trinitrobenzenesulfonates, RR'S$^+$SR TNBS$^-$, add to substituted ethylenes or acetylenes to yield 1-alkylthio-2-dialkylsulfonio derivatives. Acetylene itself is fairly unreactive, and the presence of electron-withdrawing substituents in alkenes leads to decreased reactivity. The addition is probably *trans*, for dimethylmethylthiosulfonium trinitrobenzenesulfonate adds to *cis*-cyclooctene to yield a product identical with that from the reaction of *cis*-cyclooctene S-methylepisulfonium trinitrobenzenesulfonate with dimethyl sulfide.

In the reaction of sulfenyl halides with alkenes, the proposed mechanism involves electrophilic addition initiated by transfer of a sulfenium group, RS$^+$, to the substrate. The episulfonium intermediate, **1** (eq. 1), reacts with halide with net *trans* addition.[3-5]



1 (1)

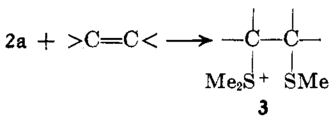
Other nucleophiles could be intercepted by the intermediate, and, indeed, other types of compounds could act as sulfenium transfer agents if an appropriate leaving group were present.

Recently we reported the formation of alkylated disulfides **2** from alkyl disulfides and oxonium salts of trinitrobenzenesulfonic acid[6] (eq. 2). These salts

$$\mathrm{RSSR} + \mathrm{R'_3O^+} \longrightarrow \mathrm{R'_2O} + \mathrm{RR'S^+SR} \qquad (2)$$

2a, R = R' = Me
b, R = Et; R' = Me
c, R = R' = Et

had structural features that led to the prediction that they would transfer the sulfenium group to an alkene, for dimethyl sulfide seemed to represent a good leaving group. It was found that such a reaction was feasible, for a 1-alkylthio-2-dialkylsulfonioalkane (**3**) formed very readily with many alkenes (eq. 3).

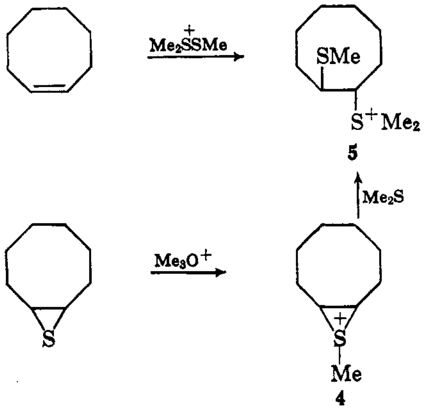


$$\mathbf{2a} + {>}\mathrm{C{=}C}{<} \longrightarrow -\underset{\mathrm{Me_2S^+}}{\overset{|}{\underset{|}{\mathrm{C}}}}-\underset{\mathrm{SMe}}{\overset{|}{\underset{|}{\mathrm{C}}}}- \qquad (3)$$

3

If cyclooctene were used as the alkene, the adduct **3** could be prepared by an alternate route. The stable cyclooctene S-methylepisulfonium 2,4,6-trinitrobenzenesulfonate[7] (**4**) reacted readily with methyl sulfide to yield the same product, **5**, as that formed in the addition of dimethylmethylthiosulfonium 2,4,6-trinitrobenzenesulfonate to cyclooctene (eq. 4).

Variations in the structure of the alkene had little influence on the reaction, as in the case of Kharasch's extensive survey of the addition of 2,4-dinitrobenzenesulfenyl chloride.[8] However, the presence of electron-withdrawing groups in the vinyl positions slows down or inhibits the addition. Neither isomer of 1,2-dichloroethylene was found to react under time and temperature conditions in which alkyl-substituted ethylenes reacted readily, but chalcone seemed to form a product slowly. Substituted acetylenes also reacted *via* monoaddition, but no catalytic process related to the sulfenyl chloride addition[9] to acetylene was investigated. The compounds included in the present work are described in Table I.



5 **4** (4)

Abrupt limitations were encountered in the preparation of homologs of methylated methyl disulfide,[6] but it was possible to carry out additions with diethylethylthiosulfonium trinitrobenzenesulfonate (**6**), methylethylethylthiosulfonium trinitrobenzenesulfonate (**7**), and methylethylmethylthiosulfonium trinitrobenzenesulfonate (**8**) (Table II).

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[1] Supported in part by Grant GM 8185 from the National Institutes of Health, U. S. Public Health Service.

[2] Abstracted in part from the Ph.D. Thesis of D. J. Pettitt.

[3] N. Kharasch and A. J. Havlik, *J. Am. Chem. Soc.*, **75**, 3734 (1953).

[4] N. R. Slobodkin and N. Kharasch, *ibid.*, **82**, 5837 (1960).

[5] D. J. Cram, *ibid.*, **71**, 3883 (1949).

[6] G. K. Helmkamp, H. N. Cassey, B. A. Olsen, and D. J. Pettitt, *J. Org. Chem.*, **30**, 933 (1965).

[7] D. J. Pettitt and G. K. Helmkamp, *ibid.*, **28**, 2932 (1963).

[8] See, for example, N. Kharasch and C. M. Buess, *J. Am. Chem. Soc.*, **71**, 2725 (1949); N. Kharasch, C. M. Buess, and S. I. Strashun, *ibid.*, **74**, 3422 (1952).

[9] N. Kharasch and S. J. Assony, *ibid.*, **75**, 1081 (1953).

TABLE I

ADDITION PRODUCTS FROM ALKENES AND ALKYNES WITH DIMETHYLMETHYLTHIOSULFONIUM TRINITROBENZENESULFONATE

Substrate	Decompn. point, °C.	Yield, %	Calcd. % C	Calcd. % H	Calcd. % N	Found[a] % C	Found[a] % H	Found[a] % N
cis-2-Butene	134–136	94	34.14	4.19	9.18	34.51	4.42	9.56
trans-2-Butene	136–138	95	34.14	4.19	9.18	33.87	4.53	9.46
1-Pentene	141–142	93	35.66	4.49	8.91	35.68	4.59	9.13
Cyclopentene	139.5–140	89	35.81	4.08	8.95	36.11	4.05	9.26
Cyclohexene	141–143	99	37.26	4.38	8.69	37.01	4.32	8.45
Cyclooctene	122–123	74	39.91	4.93	8.21	39.42	5.06	7.95
3-Hexyne	134.5–135	89	37.26	4.38	8.69	36.87	4.39	8.51
Phenylacetylene	147–147.5	77	40.55	3.40	8.35	40.77	3.49	8.58
Diphenylacetylene	200–200.5	. .	47.66	3.66	7.25	47.49	4.03	7.40

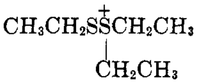
[a] Analyses were by C. F. Geiger, Ontario, Calif., and A. Elek, Torrance, Calif.

TABLE II

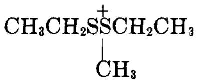
ADDITION PRODUCTS FROM 1-PENTENE AND ALKYLATED DISULFIDES

Addend	Yield, %	Product m.p., °C.	Calcd. % C	Calcd. % H	Calcd. % N	Found[a] % C	Found[a] % H	Found[a] % N
6	66	114.5–115.5	39.75	5.30	8.18	39.73	5.59	8.47
7	94	105.5–106.5	38.46	5.04	8.41	38.83	5.25	8.44
8	68	130.5–131	37.10	4.77	8.65	36.74	4.69	8.66

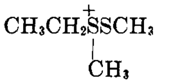
[a] Analyses were by C. F. Geiger, Ontario, Calif.


$CH_3CH_2S\underset{CH_2CH_3}{\overset{+}{S}}CH_2CH_3$

6


$CH_3CH_2S\underset{CH_3}{\overset{+}{S}}CH_2CH_3$

7


$CH_3CH_2\underset{CH_3}{\overset{+}{S}}SCH_3$

8

(the anion in each case is 2,4,6-trinitrobenzenesulfonate)

The stereochemical course of the addition reaction involving alkenes is most likely *trans*. The evidence arises from the identity of the cyclooctene addition product **5** as described by eq. 4 with that arising from the cyclooctene episulfide. The principal assumption involved is simply that nucleophilic opening of the episulfonium ring is *trans*, for alkylation of the episulfide should not involve bonds between sulfur and the carbocyclic ring.[10]

Experimental

1-Dimethylsulfonio-2-methylthiocyclooctane 2,4,6-Trinitrobenzenesulfonate.—As a typical example of the addition of an alkylated disulfide to an alkene, 2.50 g. (0.00625 mole) of dimethylmethylthiosulfonium trinitrobenzenesulfonate was suspended in 7 ml. of nitromethane and 1.10 g. (0.00100 mole) of cyclooctene was added in one portion. When the mixture was swirled, the undissolved solid quickly disappeared. After 20 min., 50 ml. of absolute ether was added. A light yellow oil separated which quickly crystallized. The solid was isolated by filtration, washed with 20 ml. of ether and 20 ml. of pentane, and air dried for a few minutes. After drying the product at reduced pressure, 2.80 g., m.p. 119–121°, was obtained. One crystallization from nitromethane–ether gave 2.35 g. (74%) of white crystals, m.p. 122–123°.

Identical reaction, isolation, and purification conditions were used for the addition of the sulfonium compound to alkynes.

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[10] It should be noted at this point that the reaction of episulfonium salts with nucleophiles does not invariably result in ring opening and the formation of β-substituted sulfonium salts.[4] As examples of other situations, iodide ion yields the original alkene, iodine, and a disulfide, and mercaptide ion yields the original alkene and a disulfide.[11]

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

Synthesis of Ethyl *p*-Nitrophenyl α-Methoxyalkylphosphonates

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Synthesis of a new class of organophosphorus compounds, ethyl *p*-nitrophenyl α-methoxyalkylphosphonates, is reported. The compounds were prepared *via* the Michaelis–Arbuzov reaction of diethyl *p*-nitrophenyl phosphite and α-chloroalkyl methyl ethers. Confirmation of structure of the compounds was ascertained by hydrolysis to the known crystalline α-hydroxybenzylphosphonic acid, isolated as the aniline salt.

We are reporting the chemistry of some new ethyl *p*-nitrophenyl α-methoxyalkylphosphonates (IV), which were synthesized as part of a program for the preparation of novel organophosphonates that should have enhanced antienzymatic activity and decreased mammalian toxicity, and be applicable for possible therapeutic use.[1]

The initial preparation of these compounds *via* the Michaelis–Arbuzov reaction of triethyl phosphite and α-chloroamyl methyl ether was as follows. Although II was easily prepared using the above routine, III was synthesized with difficulty. For example, the treatment with phosphorus pentachloride, at times, proceeded too far, and, in addition to III, the dichloridate resulted which was not easily separable from III. Occasionally, for unknown reasons, reaction of II with phosphorus pentachloride did not yield III, or the dichloridate, but rather an unworkable sirupy residue.

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[1] E. L. Becker, T. R. Fukuto, B. Boone, D. C. Canham, and E. Boger, *Biochemistry*, **2**, 72 (1963); B. H. Alexander, L. S. Hafner, M. V. Garrison, and J. E. Brown, *J. Org. Chem.*, **28**, 3499 (1963).