magnetic resonance spectra were determined on a Varian Model A-60 nmr spectrometer using tetramethylsilane as a standard.

Preparation of 5-Methyl-2,3-dihydro-1,4-dithiin (1a).—A 250-ml single neck flask fitted with a Dean–Stark trap and a magnetic stirrer was charged with 120 ml of benzene (sodium dried), 26.6 g (0.196 mol) of α-bromoacetone,[14] 18.3 g (0.195 mol) of 1,2-ethanedithiol and 0.044 g of purified *p*-toluenesulfonic acid. The resulting solution was stirred and refluxed for 3 hr, and 4.22 ml of water was collected in the trap. The reaction mixture was cooled and washed twice with 100 ml of 2 *N* sodium hydroxide and twice with 100 ml of water. The organic layer was concentrated and distilled, giving 13.7 g, bp 44–52° (0.5–0.7 mm), and 2.6 g, bp 70–94° (0.7–0.9 mm). The purity of these fractions was checked by glpc using a 6 ft Carbowax column; the first fraction was 98% **1a** and the second fraction 72% **1a**. A total yield of 60% **1a** was obtained in this reaction (by glpc assay); this product showed the correct microanalysis, nmr, and infrared spectra for **1a** as previously reported.[10]

Preparation of 4,5-Diphenyl-2,3-dihydro-1,4-dithiin (1b).—The above described apparatus was charged with 5.31 g (0.0194 mol) of 2-bromo-2-phenylacetophenone (Eastman), 2.48 g (0.0265 mol) of 1,2-ethanedithiol, 0.02 g of *p*-toluenesulfonic acid, and 120 ml of benzene (sodium dried). The resulting solution was refluxed for 54 hr, and 0.4 ml of water was collected. The reaction mixture was washed and concentrated as above, leaving a solid residue. This was recrystallized three times from methanol, giving a white solid: 2.66 g (50.6%), mp 101.9–102.2°. Examination of the nmr spectrum (CCl_4) showed a singlet at δ 7.05 (aromatic) and a singlet at δ 3.31 (aliphatic); the ratio of aliphatic to aromatic protons was 2:5.

Anal. Calcd for $C_{16}H_{14}S_2$: C, 71.1; H, 5.18; S, 23.7. Found: C, 71.30; H, 5.22; S, 23.73.

Registry No.—1a, 5769-49-3; 1b, 20273-71-6.

[14] P. A. Levene in "Organic Syntheses," Coll. Vol. II, A. H. Blatt, Ed., John Wiley & Sons, New York, N. Y., 1963, p 88.

Synthesis of 2,5-Dihydrothiophenonium 2,4,6-Trinitrobenzenesulfonates from Butadienes and Methanesulfenyl 2,4,6-Trinitrobenzenesulfonates[1]

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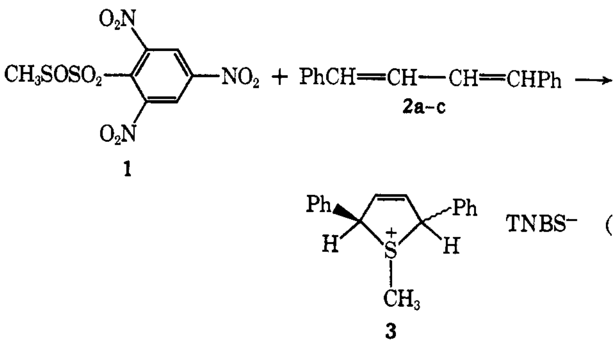
The reaction of a very limited variety of sulfenyl compounds with conjugated dienes has received recent attention, but the process has the potential of providing interesting results related to the problem of concerted cycloaddition. Mueller and Butler[4,5] studied the reaction of methanesulfenyl or benzenesulfenyl chloride with a number of conjugated dienes. Their findings showed that the additions occurred predominantly in a 1,2 manner. This was in contrast to the report of earlier workers[6] in which 1,4 addition was tentatively proposed to occur in the reaction of sulfenyl chlorides with cyclopentadiene or cyclooctatetraene.

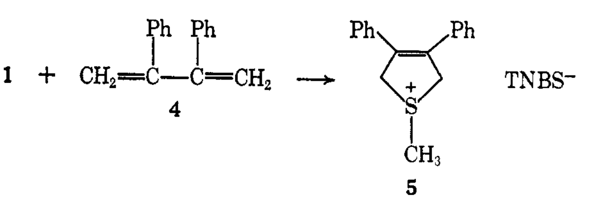
An alkanesulfenium ion (RS^+, or its alkanesulfenyl 2,4,6-trinitrobenzenesulfonate progenitor) can be compared to nitrenes and carbenes with regard to formation of three-membered rings from alkenes. With one exception, all of the reported examples of the reaction of conjugated dienes with carbenes[7] and nitrenes[8] proceed by formation of 1,2 adducts as primary reaction products. In that exceptional case[9] a concerted 1,4 cycloaddition of cyanonitrene to cyclooctatetraene was proposed on the basis of a time- and temperature-dependency study of the stability of the 1,2 adduct in the system.

As part of our continuing studies on the synthetic utility of methanesulfenyl 2,4,6-trinitrobenzenesulfonate[10,11] (**1**), some of the isomeric diphenylbutadienes have been used as substrates for this reagent. It was of interest to determine whether the products isolated from these reactions arose from a 1,4 cycloaddition in a concerted manner, a 1,2 addition, or a 1,2 addition followed by rearrangement to the 1,4 product.

The reaction of **1** with *trans,trans*- (**2a**), *cis,trans*- (**2b**), or *cis,cis*-1,4-diphenylbutadiene (**2c**) was found to yield the same product, namely 2,5-dihydro-2,5-diphenyl-S-methylthiophenonium 2,4,6-trinitrobenzenesulfonate (**3**) as shown in eq 1. The structure of **3** was assigned on the basis of its nmr spectrum and molecular weight (data are provided in the Experimental Section). The structural equivalence of **3** originating from the three different dienes was based on comparison of infrared and nmr spectra, on mixture melting points, and on constancy of these physical characteristics on repeated purification procedures.



(1)



(2)

TNBS⁻ = 2,4,6-trinitrobenzenesulfonate anion

The reaction of the same reagent (**1**) with 2,3-diphenylbutadiene (**4**, eq 2) yielded 2,5-dihydro-3,4-diphenyl-S-methylthiophenonium 2,4,6-trinitrobenzenesulfonate (**5**).

The stereochemistry of **3** has not been established unequivocally, although nmr data suggest that the

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[3] NSF-URP Summer Fellow, 1968 (Grant No. GY-3041).

[4] W. H. Mueller and P. E. Butler, *Chem. Commun.*, 646 (1966).

[5] W. H. Mueller and P. E. Butler, *J. Org. Chem.*, **33**, 2642 (1968).

[6] H. Brintzinger and H. Eilwanger, *Chem. Ber.*, **87**, 300 (1954).

[7] See, for example, W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y., 1964.

[8] For example of isolable, stable 1,2-adducts see: S. Masamune and N. T. Castellucci, *Angew. Chem.*, **76**, 569 (1964); K. Hafner, W. Kaiser, and R. Puttner, *Tetrahedron Lett.*, 3953 (1964).

[9] A. G. Anastassiou, *J. Amer. Chem. Soc.*, **90**, 1527 (1968).

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

[11] G. K. Helmkamp, D. C. Owsley, W. M. Barnes, and H. N. Cassey, *J. Amer. Chem. Soc.*, **90**, 1635 (1968).

phenyl groups are *cis*, and the observation of constancy of product suggests thermodynamic control. If compound **3** contained *trans*-phenyl groups, the nmr spectrum might be expected to show nonequivalence of the hydrogen atoms at the 2 and 5 positions. Since the methynyl hydrogens appear as only one singlet[12] (at δ 6.07), it seems most likely that they are *cis*, for the S-methyl group would provide a different chemical environment for a *trans* pair. An unfavorable interaction between the S-methyl group and an adjacent phenyl group also leads to the tentative conclusion that a *cis*-diphenyl array is thermodynamically favored over the opposite configuration.

The production of the same product from each of the isomeric compounds **2a**, **2b**, and **2c** is inconsistent with a concerted 1,4 addition[13] of the methanesulfenyl group, CH_3S^+, to the diene. In such a reaction, **2b** should yield a product that is stereoisomeric with that obtained from either **2a** or **2c**. A concerted, stereospecific addition has been observed, for example, in the reaction of sulfur dioxide with 1,3-dienes.[14,15] Thus, the reaction of **1** with **2a**, **2b**, or **2c** probably proceeds *via* 1,2 addition followed by rearrangement, even though it has been impossible to detect any primary product under a variety of reaction conditions and with different isolation techniques. Our results show direct agreement with the conclusions of Mueller and Butler[4,5] that addition of sulfenyl compounds to conjugated dienes occurs in a 1,2 manner.

Experimental Section

Micoanalyses on the dihydrothiophene products were carried out by Elek Microanalytical Laboratories, Torrance, Calif., and Galbraith Laboratories, Knoxville, Tenn. All solvents were reagent grade and were dried over Linde 4A Molecular Sieves before use. **2a** was prepared by the method described by Fieser;[16] **2b** was prepared from the Wittig reaction of triphenylcinnamylphosphonium bromide with benzaldehyde;[17] and **2c** was prepared by catalytic hydrogenation of 1,4-diphenylbutadiyne as described by Lindlar.[18] The 2,3-diphenylbutadiene was prepared from acetophenone pinacol by the prodedure of Alder and Hayden.[19] All melting points are uncorrected.

2,5-Dihydro-2,5-diphenyl-S-methylthiophenonium 2,4,6-Trinitrobenzenesulfonate.—On the fritted disk of a modified Schlenk tube apparatus as previously described[11] was placed a solution of 5.23 g (0.01 mol) of silver 2,4,6-trinitrobenzenesulfonate (acetonitrile complex)[10] in 20 ml of dry nitromethane. Dry nitrogen was passed upward through the fritted disk to keep the reaction mixture blanketed with an inert atmosphere. A solution of 0.01 mol of methanesulfenyl bromide in 35 ml of dichloromethane (solution prepared *in situ* from bromine and dimethyl disulfide) was added to the silver salt solution, with immediate formation of a silver bromide precipitate. The solution was stirred for 30 min, then filtered free of silver bromide by forcing the mixture through the fritted disk with positive nitrogen pressure above and a partial vacuum below. The solution of methanesulfenyl 2,4,6-trinitrobenzenesulfonate was mixed with 2.06 g (0.01 mol) of one of the isomeric 1,4-diphenylbutadienes in 35 ml of dichloromethane. The color of the reaction mixture immediately turned a deep purple. The product was isolated by the addition of about 650 ml of anhydrous ether to the stirred solution. The precipitate was dissolved in acetone and crystallized from warm acetone–ether to yield crystals of the thio phenonium salt, mp 132–135.5° dec. The yields from the three isomers of 1,4-diphenylbutadiene were as follows: *trans,trans*, 49%; *cis,trans*, 15%; *cis,cis*, 29%.

Anal. Calcd for $C_{23}H_{19}N_3O_9S_2$: C, 50.64; H, 3.51; N, 7.70; S, 11.75; mol wt, 546. Found: C, 50.90; H, 3.72; N, 7.08; S, 11.37; mol wt, 565 (by vapor pressure osmometry).

The nmr spectrum of the product in perdeuterionitromethane showed peaks at δ 3.40 (singlet, three protons assigned to S-methyl); 6.07 (singlet, two methynyl protons); 6.59 (singlet, two vinyl protons); 7.45 (broad singlet, ten phenyl protons); and 8.50 (singlet, two protons from the anion).

2,5-Dihydro-3,4-diphenyl-S-methylthiophenonium 2,4,6-Trinitrobenzenesulfonate.—In a manner exactly analogous to that described above, 0.01 mol of methanesulfenyl 2,4,6-trinitrobenzenesulfonate and 0.01 mol of 2,3-diphenylbutadiene yielded 3.40 g of an amorphous solid that melted with decomposition at about 110°. The desired product could be isolated only with great difficulty from this mixture. After many recrystallizations from acetone–ether, 30 mg of an analytically consistent sample of 2,5-dihydro-3,4-diphenyl-S-methylthiophenonium 2,4,6-trinitrobenzenesulfonate was isolated: mp 230.5–231.5°.

Anal. Calcd for $C_{23}H_{19}N_3O_9S_2$: C, 50.64; H, 3.51; N, 7.70; S, 11.75. Found: C, 50.75; H, 3.48; N, 7.75; S, 11.81.

Registry No.—**3**, 20178-09-0; **5**, 20178-10-3.

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[12] The absence of splitting between the methynyl protons and the adjacent vinyl protons can be accounted for by a dihedral angle that may be as large as 80° owing to ring distortion from phenyl-phenyl interaction.

[13] R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968).

[14] W. L. Mock, *J. Amer. Chem. Soc.*, **88**, 2857 (1966).

[15] S. D. McGregor and D. M. Lemal, *ibid.*, **88**, 2858 (1966).

[16] L. F. Fieser, "Organic Experiments," 2nd ed, Raytheon Education Co., Lexington, Mass., 1968, pp 121–123.

[17] H. Misumi and M. Nakagawa, *Bull. Chem. Soc. Jap.*, **36**, 399 (1963).

[18] H. Lindlar, *Helv. Chim. Acta*, **35**, 446 (1952).

[19] K. Alder and J. Hayden, *Ann.*, **570**, 201 (1950).

Concerning the Postulated Rearrangement of 4-Acyloxy- and 4-Aroyloxycoumarins to 5-Acyl- and 5-Aroyl-4-hydroxycoumarins

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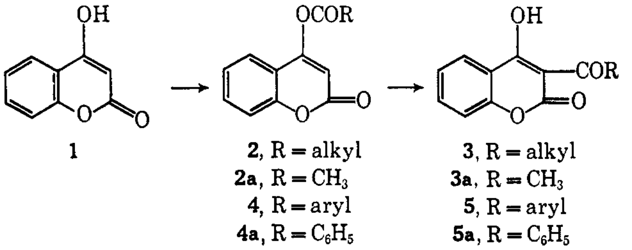
There have been a number of reports on the acylation of 4-hydroxycoumarin (**1**) with aliphatic and aromatic acid chlorides.[1-3] Eisenhauer and Link[2] studied the mechanism of the reaction of **1** with aliphatic acid chlorides in pyridine leading to 3-acyl-4-hydroxycoumarins (**3**), using acetyl chloride as representative of this class, and found that the initial product formed was 4-acetoxycoumarin (**2a**), which then rearranged to 3-acetyl-4-hydroxycoumarin (**3a**). These authors also investigated the reaction of **1** with various aromatic acid chlorides in pyridine and observed that the initially formed esters **4** did not rearrange to the corresponding 3-aroyl-4-hydroxycoumarins (**5**) as in the aliphatic series.[3] The ester **4a**, however, can be rearranged to 3-benzoyl-4-hydroxycoumarin (**5a**) with aluminum chloride.[4]



1

2, R = alkyl
2a, R = CH_3
4, R = aryl
4a, R = C_6H_5

3, R = alkyl
3a, R = CH_3
5, R = aryl
5a, R = C_6H_5

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[1] T. Ukita, S. Nojima, and M. Matsumoto, *J. Amer. Chem. Soc.*, **72**, 5143 (1950).

[2] H. R. Eisenhauer and K. P. Link, *ibid.*, **75**, 2044 (1953).

[3] H. R. Eisenhauer and K. P. Link, *ibid.*, **75**, 2046 (1953).

[4] K. Veres and V. Horak, *Coll. Czech. Chem. Commun.*, **20**, 371 (1955).