thiophene ring is substantially larger than for the simple substituents on the benzene ring.

Experimental Section[18]

Preparation of Materials.—2-Acetylthiophene was reduced with sodium borohydride to afford 1-(2-thienyl)ethanol, which was converted into **1-(2-thienyl)ethyl *p*-nitrobenzoate,** mp 64.5–65.8° from 20:1 hexane–ethyl acetate, using *p*-nitrobenzoyl chloride and pyridine.

Anal. Calcd for $C_{13}H_{11}NO_4S$: C, 56.31; H, 4.00; N, 5.05; S, 11.56. Found: C, 56.33; H, 4.24; N, 5.06; S, 11.50.

1-(3-Thienyl)ethanol.—The procedure of Gronowitz[19] for the preparation of 3-thienyllithium was followed. To this reagent at −70°, a solution of acetaldehyde in ether was added. The mixture was allowed to warm to room temperature and was worked up in the usual manner. There was obtained 65% 1-(3-thienyl)ethanol, bp 102–105° (15 mm). The ir spectrum and nmr spectrum were consistent. Conversion into the ester was accomplished in the usual manner to give **1-(3-thienyl)ethyl *p*-nitrobenzoate,** colorless needles from hexane–ethyl acetate (20:1), mp 54.0–54.5°.

Anal. Found: C, 56.49; H, 3.99.

***cis*-2-Styrylthiophene.**—Condensation of thiophene-2-carboxaldehyde with phenylacetic acid afforded α-phenyl-β-(2-thienyl)-acrylic acid, mp 190–191.5° (lit.[20] mp 188.5–190°). Decarboxylation with copper and quinoline[21] afforded a mixture from which a small amount of the *trans* isomer crystallized. The remaining oil was separated by glpc over 20% SE-30 on 60–80 mesh Chromosorb, at 180°. The early fraction was *cis*-2-styrylthiophene. The spectral characteristics showed the absence of *trans* olefinic absorption in the ir and an uv spectrum distinct from that of authentic *trans*-2-styrylthiophene.

Anal. Calcd for $C_{12}H_{10}S$: C, 77.38; H, 5.41; S, 17.21. Found: C, 77.06; H, 5.42; S, 17.21.

Kinetic Methods.—The procedures for the solvolysis rate measurements have been described.[3] The rate of the acid-catalyzed isomerization was followed by uv spectrometry, using procedures like those described previously.[22]

Registry No.—1-(2-Thienyl)ethyl *p*-nitrobenzoate, 23516-71-4; 1-(3-thienyl)ethyl *p*-nitrobenzoate, 23516-72-5; *cis*-2-styrylthiophene, 23516-73-6.

(18) Melting points and boiling points are uncorrected. Analyses were performed by the Microanalytical Laboratory of The Department of Chemistry, University of California.

(19) S. Gronowitz, *Ark. Kemi*, **8**, 441 (1955).

(20) G. M. Badger, J. A. Elix, and G. E. Lewis, *Aust. J. Chem.*, **19**, 1243 (1966).

(21) R. E. Buckles and N. G. Wheeler, *Org. Syn.*, **38**, 88 (1953).

(22) D. S. Noyce, D. R. Hartter, and F. B. Miles, *J. Amer. Chem. Soc.*, **90**, 4633 (1968).

The Reaction of 4-Methylmercaptocyclohexene with Hydrogen Iodide

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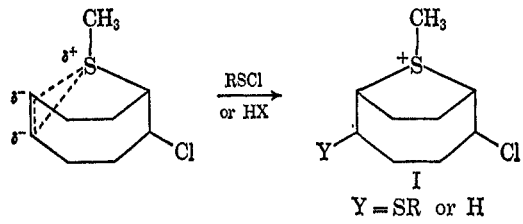
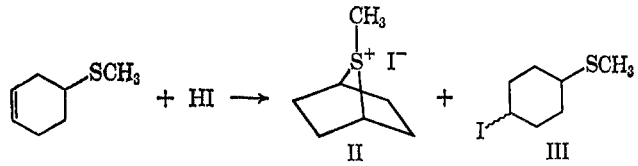
It has recently been shown that activation of the double bond of the monoadduct of 1,5-cyclooctadiene and methanesulfenyl chloride toward a second molecule of the sulfenyl chloride practically precludes isolation of the monoadduct even when the diolefin is initially present in tenfold excess.[1] To account for this effect, transannular activation of the double bond by the methylmercapto group forming a 9-methyl-9-thiabicyclo[4.2.1]nonanesulfonium ion (I) was invoked and subsequently verified by its isolation.



I
Y = SR or H

To test the limits of such transannular interactions, the behavior of 1,4-cyclohexadiene under similar conditions was studied. The difference between the two cases was signaled by the observation that, unlike 1,5-cyclooctadiene, the six-membered-ring analog readily affords a monoadduct with methanesulfenyl chloride. A diadduct can subsequently be prepared which is identical with the product of 1,4-cyclohexadiene and 2 mol of the sulfenyl chloride in one step. Contrary to the finding with the eight-membered-ring diene, it could be demonstrated that the remaining double bond of the monoadduct (sans the chlorine atom) is somewhat *deactivated* toward attack of a second methanesulfenyl chloride in competition with cyclohexene.[2] This deactivation may arise from adverse steric effects of the methylmercapto group which may effectively limit the corridors of approach of an incoming group and thereby hinder addition. These ostensibly contradicting observations may result from subtle differences in geometry between the two monoadducts (evident in their molecular models).[3] Also, in contrast with the results of 1,5-cyclooctadiene, the presently formed diadduct is covalent, and, as expected, indications are that it is a mixture of isomeric dimethylmercaptodichlorocyclohexanes.

Participation of the 4-methylmercapto group was, however, clearly evident in the reaction of 4-methylmercaptocyclohexene with hydrogen iodide. In methylene chloride, a white precipitate which proved to be 7-methyl-7-thiabicyclo[2.2.1]heptanesulfonium iodide (II) was isolated. This substance was identical in all respects with the compound reported by Corey and Block which results from addition of methyl iodide to 7-thiabicyclo[2.2.1]heptane.[4]



II III

An oil containing predominantly *cis*- and *trans*-4-methylmercaptoiodocyclohexane (III) could be isolated from the mother liquors.[5] The structural assignment

(1) W. H. Mueller, *J. Amer. Chem. Soc.*, **91**, 1223 (1969).

(2) The disappearance under competitive conditions of 4-methylmercaptocyclohexene and cyclohexene in the presence of methanesulfenyl chloride was followed by gc. It was found that the latter is consumed 1.17 times as fast as the former.

(3) One alternative rationale for this deactivation involves a fast and reversible attack of electrophiles upon the sulfur atom. The adverse effect can then be both steric and electronic in origin.

(4) E. J. Corey and E. Block, *J. Org. Chem.*, **31**, 1663 (1966).

(5) Although this mixture showed but a single sharp $-SCH_3$ signal in the nmr (in several solvents), gc indicated three products of composition 42:7.5:50.5. The minor isomer is believed to be 3-methylmercaptoiodocyclohexane, the major isomers III.

of III is primarily based on the fact that silver ion induced elimination of hydrogen iodide from the isomeric mixture yields only 4-methylmercaptocyclohexene.

Addition of hydrogen iodide to a solution of 4-methylmercaptocyclohexene in trifluoroacetic acid in an nmr tube followed by spectral examination of the solution clearly indicated *ca.* 15% formation of II, the only other product being III. The formation of compounds II and III is believed to be kinetically controlled since their noninterconvertibility under the conditions employed was demonstrated.

The structure of both products (and the near absence of 3-methylmercaptoiodocyclohexane among them) clearly implies some degree of participation of the sulfur group across the ring in the mechanism of their formation.[6] However, the seemingly inconsistent nature of the results thus far garnered precludes any confident mechanistic interpretation of such interactions.

Experimental Section

General.—Chemicals and solvents used were not specially purified unless specifically stated. Melting and boiling points are uncorrected. Infrared spectra were run on a Beckman IR-20 and nmr spectra were obtained on a Varian A-60. All reactions described were carried out under nitrogen. All gc was done on an Aerograph 1520 instrument with 5% SE-30 on Chromosorb W 5 ft × 0.25 in. columns.

4-Methylmercapto-5-chlorocyclohexene.—To a methylene chloride solution of 1,4-cyclohexadiene (0.10 mol in 50 ml) maintained at −20° a solution of 8.25 g (0.10 mol) of methanesulfenyl chloride in the same solvent was slowly added. After 15 min, the reaction was warmed to room temperature and the solvent was evaporated to yield 15.2 g of clear oil, a single component as assayed by gc. The nmr spectrum ($CDCl_3$) of the oil contained a narrow multiplet at δ 5.60 (2 H), a broad quartet at 4.28 (1 H, $>C<^{H}_{Cl}$), and a multiplet with a strong singlet at 2.2–3.1 (8 H). Further evidence that a double bond was maintained was the presence of weak absorptions at 3050 and 1665 cm^{-1} in the thin-film infrared spectrum. This material was used without further purification.

Diadduct of 1,4-Cyclohexadiene with Methanesulfenyl Chloride.—It was found that the identical product, a faintly yellowish oil, was obtained by either subjecting 1,4-cyclohexadiene under the contitions described above to 2 mol of the sulfenyl halide or by treating 4-methylmercapto-5-chlorocyclohexene with 1 mol of the sulfenyl chloride under those conditions. The identity was ascertained by a comparison of nmr and infrared spectra as well as gc. The oil does not crystallize when standing at room temperature indefinitely and is freely soluble in ether, although insoluble in water.

4-Methylmercaptocyclohexene.—A solution of the monoadduct of methanesulfenyl chloride with 1,4-cyclohexadiene (22.3 g, 0.135 mol) in 25 ml of dry ether was added carefully to a slurry of 3.38 g (0.089 mol) of lithium aluminum hydride (Alfa Inorganics) in 150 ml of dry ether. The reaction was allowed to proceed for 3 days at room temperature; then it was worked up according to the method described in Fieser and Fieser ("Reagents for Organic Synthesis," p 584). From the ether 16.4 g of clear oil was obtained. After a distillation [33° (4 Torr)] 11.0 g of oil, $n^{20}D$ 1.5145, was obtained. The 4-methylmercaptocyclohexene thus afforded had in its nmr spectrum ($CDCl_3$) two narrow multiplets at δ 5.66 (2 H) and 2.10 (10 H). The infrared spectrum (thin film) showed the presence of a double bond ($\nu_{C=C}$ 1655 cm^{-1}).

Anal. Calcd for $C_7H_{12}S$: C, 65.59; H, 9.44; S, 24.97. Found: C, 65.70; H, 9.75; S, 24.99.

Treatment of 4-Methylmercaptocyclohexene with Hydrogen Iodide.—Dry hydrogen iodide (Matheson) was bubbled into a solution of 2.0 g of 4-methylmercaptocyclohexene in 25 ml of methylene chloride. After about 1 hr, the solution became cloudy and a white precipitate fell out. The gas flow was continued for 0.5 hr and the flask was then stoppered and allowed to stand overnight. From this reaction 0.180 g of white solid, II, mp 140–142°, was collected by filtration and ether washing (lit.[4] mp 135.5–136°). The nmr matched that described previously[4] as well.

(6) As implied in footnote 3, the "sulfur group" spoken of may or may not be a sulfonium species reversibly formed by hydrogen iodide addition.

Registry No.—4-Methylmercaptocyclohexene, 23600-52-4; hydrogen iodide, 10034-85-2.

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An Improved Preparation of Tertiary Amine N-Oxides

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Preparation of tertiary amine N-oxides by the use of hydrogen peroxide[1] in water, acetic acid, or acetic anhydride is slow and frequently leads to low yields of products containing varying amounts of hydrogen peroxide[2] and requiring further purification.[3] Organic peracids[4] such as peracetic, perbenzoic, and monoperphthalic acids may be used, but give salts which require further processing. In some cases when the carbon skeleton is highly branched, Cope eliminations have been reported to occur during oxidation of the amine.[5]

We wish to report an improved preparation of amine N-oxides which proceeds rapidly to completion at or below room temperature, requires no basification or extraction procedures, and affords the pure N-oxides in excellent yields, employing entirely nonaqueous solvents.

Using equimolar quantities of pure[6] *m*-chloroperbenzoic acid and the amine, reaction in chloroform at 0–25° gave a solution of the amine N-oxide *m*-chlorobenzoate, from which the pure N-oxide was readily obtained by passage through a column of alumina. The amine N-oxides shown in Table I were obtained in the yields stated. With this procedure it was not necessary to protect the hydroxyl group of morphine as the methoxymethyl ether[7] before carrying out the reaction.

Experimental Section

General Procedure.—A solution of 1.0 mol of *m*-chloroperbenzoic acid in chloroform was added gradually at 0–5° to an ice-

(1) J. Meisenheimer and K. Bratring, *Justus Liebigs Ann. Chem.*, **397**, 286 (1913); D. Jerchel and G. Jung, *Chem. Ber.*, **85**, 1130 (1952); M. Izumi, *Pharm.* Bull. (Tokyo), **2**, 279 (1954).

(2) K. Bodendorf and B. Binder, *Arch. Pharm.* (Weinheim), **287**, 326 (1954); C. C. Sweeley and E. C. Horning, *J. Amer. Chem. Soc.*, **79**, 2620 (1957).

(3) A. C. Cope and P. H. Towle, *ibid.*, **71**, 3426 (1949); E. C. Taylor and N. E. Boyer, *J. Org. Chem.*, **24**, 275 (1959).

(4) M. A. Stahmann and M. Bergmann, *ibid.*, **11**, 586 (1946); D. Swern, *Chem. Rev.*, **45**, 1 (1949).

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(6) N. N. Schwartz and J. H. Blumbergs, *J. Org. Chem.*, **29**, 1976 (1964).

(7) F. N. H. Chang, J. F. Oneto, P. P. T. Sah, B. M. Tolbert, and H. Rapoport, *ibid.*, **15**, 634 (1950).