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-

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TABLE I

Amine N-oxide	Yield, %
Trimethylamine N-oxide	96
Tribenzylamine N-oxide	96
Dimethylaniline N-oxide	94
Nicotine N′-oxide	98
Nicotine N,N′-dioxide	98[a]
Codeine N-oxide	98
Morphine N-oxide	86[b]

[a] Using 2.0 molar equiv of *m*-chloroperbenzoic acid. [b] The solvent in this experiment was tetrahydrofuran. Methylation with diazomethane gave codeine N-oxide, identical by melting point, mixture melting point, and tlc.

cooled, stirred solution of 1.0 mol of the amine in chloroform. Stirring was continued for a total of 3 hr, during which the mixture was allowed to come to room temperature. The solution was passed through a column of alkaline alumina (100–200 mesh, *ca.* 20 times the weight of the combined starting materials), and traces of unreacted amine were removed by washing with chloroform. Elution with methanol–chloroform (1:3) then gave the amine N-oxide in the yield stated in Table I, after crystallization from alcohol–ether or acetone–hexane. All compounds had the melting points reported in the literature, and gave single spots on tlc.

Registry No.—*m*-Chloroperbenzoic acid, 937-14-4; trimethylamine N-oxide, 1184-78-7; tribenzylamine N-oxide, 6852-46-6; dimethylaniline N-oxide, 874-52-2; nicotine N,N′-dioxide, 2055-29-0; codeine N-oxide, 3688-65-1; morphine N-oxide, 639-46-3.

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Bridged Polycyclic Compounds. LX. *syn*-Bromine Activation in Free-Radical Bromination of Janusenes[1]

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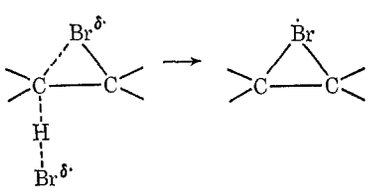
Recently, several workers have postulated neighboring-group participation by bromine in the radical bromination of a variety of alkyl bromides.[2-5] They suggest that the bromo substituents assist in the abstraction of a β hydrogen by bridging in the transition state. An *anti* orientation between the β hydrogen and the bromo substituent is presumably required



in the transition state for this mechanism to obtain. We wish now to report an example in which the β hydrogen of an alkyl bromide is activated in a compound where that hydrogen is *cis* to and eclipsed by the bromo substituent.

When janusene (5,5a,6,11,11a,12-hexahydro-5,12:6,11-di-*o*-benzenonaphthacene, **1**)[6] was treated with bromine in carbon tetrachloride, it was observed that replacement of the second hydrogen atom occurred more rapidly than that of the first. From the data in Table I, we calculate[7] that k_2/k_1 in eq 1 is 1.4 at 72°. As

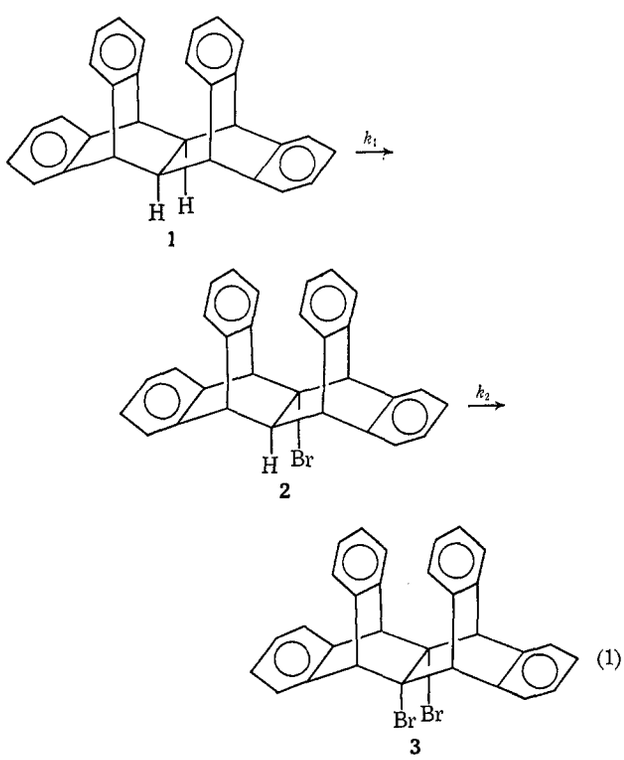
TABLE I

PRODUCT DISTRIBUTIONS FROM PHOTOBROMINATION OF JANUSENE (1) IN CARBON TETRACHLORIDE AT 72°

% 1	% 2	% 3
76	19	5
66	25	9
51	28	20
50	30	20
36	31	33
32	26	42
31	28	41[a]
8	14	78

[a] These data were from a reaction that was run until only 40% of the initial bromine added had been consumed.

there are two reactive hydrogen atoms in **1** and only one in **2**, this means that, compared with hydrogen, bromine activates the β hydrogen by a factor of 2.8 Similar data at 12° gave a factor of 5.2.



Unlike bromine, chlorine decreased reactivity. A competitive photobromination experiment between 5a-chlorojanusene (**4**) and janusene (**1**) at 72° revealed

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