

isomer is further evidence for this mechanism. The low yield of olefinic product from the mercaptans listed in Table II was previously explained. The lack of olefinic products from the *n*-butyl sulfonate and *n*-butyrate ions is probably due to formation of stable  $\alpha$ -carbanions.

### Experimental

**Reagents.**—Lithium, sodium, potassium, rubidium, and cesium *tert*-butoxides were obtained from the Mine Safety Appliance Co. (Callery, Pa.) as the sublimed white powders in wax-sealed containers. All samples were at least 98.5% pure. Dimethyl sulfoxide and *tert*-butyl alcohol were dried and distilled over Linde 13X Molecular Sieves. Gas chromatographic analysis of both solvents indicated the presence of only one compound. Isobutylene, 1-butene, *cis*- and *trans*-2-butene, propylene, and butadiene, which were used for g.c. calibration, were all API samples.

Most reactants were obtained from either Columbia Organic Chemicals or Matheson Coleman and Bell as reagent grade materials and analyzed for purity by g.c. before use. Materials less than 98% pure were distilled under a nitrogen atmosphere through an 18-in. silvered column equipped with a tantalum-wire spiral. In the case of the sulfoxides and sulfones, distillation was carried out in the presence of Linde 13X Molecular Sieves to ensure complete removal of water. All reagents were stored in a nitrogen drybox before use.

**Preparation of Reaction Mixtures.**—All base-solvent systems were prepared in a nitrogen drybox equipped with a moisture conductivity cell attachment. Each solution was prepared to give the desired molarity (0.62 *M*) and stored in sealed containers in the drybox. At the desired time, 7 ml. of the standard solution was withdrawn by a pipet and transferred to a vial containing about 2 mmoles of each reactant. The vial was sealed (under nitrogen) with a self-sealing neoprene diaphragm and immediately transferred to a constant temperature bath ( $55 \pm 0.1^\circ$ ). *n*-Pentane (0.3 ml.) was immediately injected into each reaction mixture by means of a hypodermic syringe thus providing an internal standard for quantitative determination of olefinic products. The total operation required about 2–3 min.

**Analysis of Reaction Mixtures.**—At the desired time, 0.5 ml. of the reaction mixture was withdrawn from the vial by a precooled hypodermic syringe and injected into a neoprene-sealed vial containing a mixture of water and inert hydrocarbon. The sample was then cooled in the presence of Dry Ice. This removed the base and solvent from the hydrocarbon layer. The hydrocarbon layer was then sampled with a syringe and analyzed for the olefin in question on a gas chromatographic unit. This unit was a Perkin-Elmer Model 154 equipped with a 21 ft. DC-200 column (30 wt. % silicone oil, 0.25 in. in diameter). The unit was operated under 12 p.s.i.g. of helium in the temperature range of 40 to 75°. All final yields of olefinic products were based on at least two g.c. determinations. Absolute olefin yields were determined from the g.c. area of the internal standard (*n*-pentane) and the area of the olefin in question; percentage yields were calculated on the basis of one mole of olefin/mole reactant in all cases. In those reactions which were unsuccessful or gave a low yield of olefinic product, analysis for the starting material was desirable. This was carried out on an F & M Flame Ionization Unit (Model 609) equipped with a 2-ft. silicone rubber column (30 wt. %, 0.25 in. in diameter). This unit was temperature programmed at 9°/min. from 75–250°. The latter conditions were also employed in the identification of mercaptans referred to in Tables I and II.

**Miscellaneous Experimental Methods.**—In two cases starting materials were synthesized. *n*-Butyl disulfide was prepared from the reaction of the sodium salt of *n*-butyl mercaptan with iodine according to the method described by Vogel.<sup>21</sup> When isolated, the physical properties of the disulfide were identical to those recorded in Reid.<sup>22</sup> *tert*-Butyl sulfoxide was prepared by the oxidation of *tert*-butyl sulfide with hydrogen peroxide in acetic acid (m.p. 64°, reported<sup>23</sup> m.p. 63.5–65°).

**Acknowledgment.**—The authors are indebted to the Esso Research and Engineering Co., especially the Process Research Division, for the privilege of publishing this work.

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(22) E. E. Reid, "Organic Chemistry of Bivalent Sulfur," Vol. III, Chemical Publishing Co., New York, N. Y., 1960, p. 396.

(23) L. Bateman, *et al.*, *J. Chem. Soc.*, 5339 (1961).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, BUCKNELL UNIVERSITY, LEWISBURG, PA., AND THE CHEMISCHES INSTITUT DER UNIVERSITÄT KÖLN, KÖLN, GERMANY]

## The Isomerization of Aziridine Derivatives. VII

BY HAROLD W. HEINE

RECEIVED MAY 1, 1963

Four new isomerizations of aziridine derivatives are described. They include the rearrangement of 1-phenylthiocarbonylaziridine into 2-phenylthioethyl isocyanate or methyl *N*-2-phenylthioethylcarbamate and the isomerization of 1-(*o*-chloromethylbenzoyl)-aziridine into either *N*-2-chloroethylphthalimidine or 1-(2-chloroethylimino)-phthalan. The reaction of equimolar quantities of phthaloyl chloride with aziridine to form *N*-2-chloroethylphthalimide is also reported.

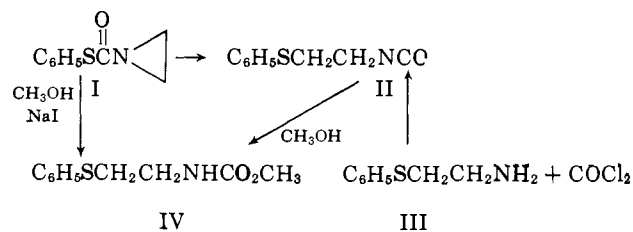
### Introduction

Derivatives of aziridines have been isomerized into oxazolines, imidazolines, imidazolidinones, thiazolines, pyrazolines, triazolines, picramides, *N*- $\beta,\gamma$ -unsaturated amides, and anils.<sup>1</sup> The present communication describes a number of new isomerizations of appropriately substituted aziridines into (1) an isocyanate, (2) an *N*-2-chloroethylphthalimide, (3) a phthalimidine, and (4) a phthalan.

### Results

1-Phenylthiocarbonylaziridine (I, *N,N*-ethylene-*S*-phenylthiocarbamate) is rearranged in refluxing xylene into the isomeric 2-phenylthioethyl isocyanate (II). The structure of II was established by analysis and by comparison of infrared spectra with an authentic sample prepared by reaction of 2-phenylthioethylamine (III) with phosgene.

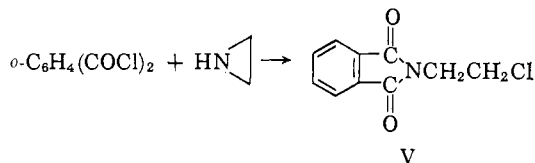
The action of sodium iodide in methanol on 1-phenylthiocarbonylaziridine at room temperature gave methyl



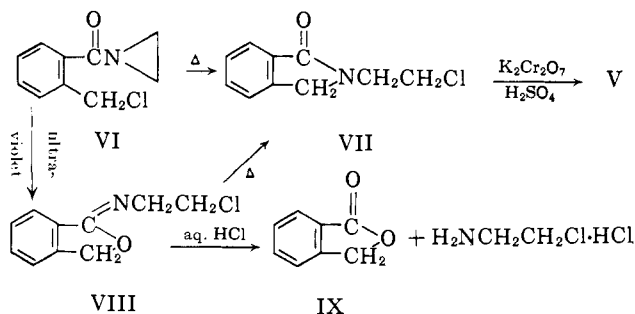
*N*-2-phenylthioethylcarbamate (IV). The structure of IV was confirmed by an independent synthesis involving the reaction of 2-phenylthioethyl isocyanate with methanol. A control run with I in methanol without sodium iodide gave a liquid residue whose infrared spectrum indicated mostly starting material, an isocyanate peak, and some of the peaks characteristic of the carbamate. After compound I was refluxed in methanol for 22 hr. the solvent was evaporated. A white solid whose infrared spectrum was identical with that of IV was obtained. However, this product had an odor characteristic of thiophenol.

(1) For a review of isomerizations of aziridines see H. W. Heine, *Angew. Chem.*, **74**, 772 (1962); *Angew. Chem. Internat. Edit. Engl.*, **1**, 528 (1962).

Another rearrangement, involving an aziridine as an unstable intermediate, was observed when equimolar quantities of phthaloyl chloride and aziridine were allowed to react in ether containing triethylamine. Filtration of the triethylamine hydrochloride formed followed by ebullition of the filtrate for several hours gave *N*-2-chloroethylphthalimide (V) in 85% yield. The latter compound was identified by comparison of spectra and a mixture melting point with a genuine sample.



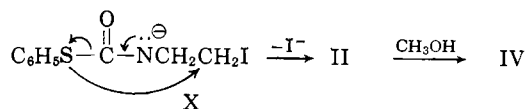
In a related reaction of aziridine with *o*-chloromethylbenzoyl chloride the intermediate 1-(*o*-chloromethylbenzoyl)-aziridine (VI) can be isolated and isomerized in refluxing toluene into the corresponding *N*-2-chloroethylphthalimidine (VII). The product was characterized by analysis and by oxidation in excellent yield to the known *N*-2-chloroethylphthalimide (V).



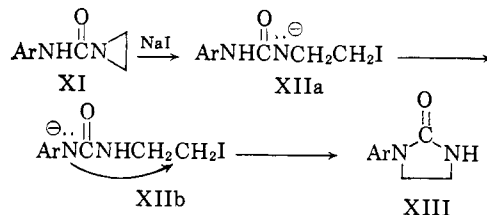
Irradiation of VI slowly transformed it into an oil which could be distilled and which was isomeric with VI. The oil was assigned the structure 1-(2-chloroethylimino)-phthalan (VIII) on the basis of analysis, chemical reactions, and infrared spectrum. The oil readily dissolved in dilute hydrochloric acid and formed a picrate which analyzed satisfactorily as a picrate of a substance isomeric with VI. Acid hydrolysis of the oil gave phthalide IX in 73% yield and 2-chloroethylamine hydrochloride. 1-Iminophthalans have been observed to hydrolyze to phthalides.<sup>2,3</sup> Furthermore, the oil could be transformed into VII by prolonged heating in refluxing toluene. The conversion of imido esters into amides by heating is well documented.<sup>4,5</sup> All these results are compatible with the structure VIII for the oil. In addition, the infrared spectrum of VIII is quite similar to phthalide and has two absorption peaks at 5.62 and 5.80  $\mu$  (Nujol). An oxazoline structure for VIII is precluded by the fact that 2-*o*-tolyl-2-oxazoline absorbs at significantly longer wave lengths, namely, 5.90 and 6.05  $\mu$ .

### Discussion

The conversion of 1-phenylthiocarbonylaziridine by iodide ion in methanol to the carbamate IV can be envisaged as a nucleophilic attack on an aziridinyl carbon by the iodide ion to give the ion X. Displacement of the iodine of X by sulfur leads to the isocyanate II which subsequently reacts with the solvent to form the carbamate. The rearrangement is quite similar



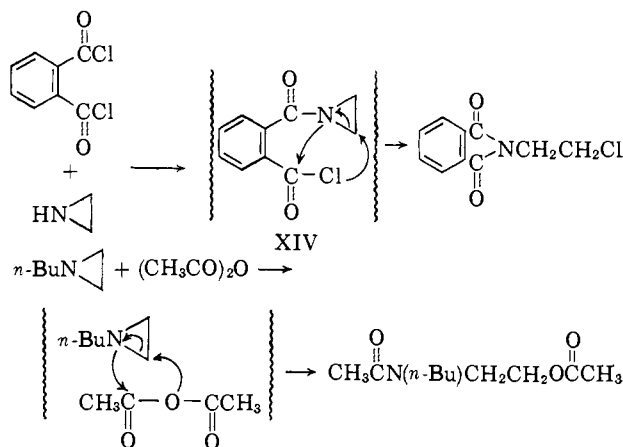
to the isomerization of 1-aziridinecarboxanilides (XI) into 1-aryl-2-imidazolidinones (XIII) by iodide ion in acetone solution.<sup>6,7</sup> In this case a tautomerization of the intermediate ion XIIa to the ion XIIb may occur prior to the internal alkylation step. The facile trans-



formation of I into IV represents still another example of a rearrangement of an aziridine system that is catalyzed by a nucleophile.<sup>8-10</sup>

The thermal isomerization of I into II in refluxing xylene is analogous to the pyrolytic isomerization of 1-benzoylaziridine whereby 2-phenyl-2-oxazoline is obtained as the product.<sup>11,12</sup>

It seems likely that the reaction between equimolar quantities of aziridine and phthaloyl chloride proceeds through an aziridine intermediate such as XIV. A reaction for which a similar mechanistic pathway can be postulated is the interaction of 1-alkyl substituted aziridines with low molecular weight aliphatic acid anhydrides to yield ester amides. For example, 1-*n*-butylaziridine reacts with acetic anhydride to produce *N*-2-acetoxyethyl-*N*-*n*-butylacetamide.<sup>13</sup> The in-



intermediate XIV seems even more reasonable on the basis of the analogous isomerization of 1-(*o*-chloromethylbenzoyl)-aziridine (VI) into *N*-2-chloroethylphthalimidine (VII).

Although internal *N*-alkylation of the intermediate XIV or of the compound VI would yield the observed products directly, one cannot discount a prior isomerization of XIV or VI to an oxazoline. The nitrogen atom of the oxazoline ring could in turn react with an

(6) H. W. Heine, W. G. Kenyon, and E. M. Johnson, *ibid.*, **83**, 2570 (1961).

(7) H. Najer, R. Giudicelli, J. Menin, and C. Morel, *Compt. rend.*, **253**, 2369 (1961).

(8) H. W. Heine, M. E. Fetter, and E. M. Nicholson, *J. Am. Chem. Soc.*, **81**, 2202 (1959).

(9) H. W. Heine and H. S. Bender, *J. Org. Chem.*, **25**, 461 (1960).

(10) H. W. Heine and D. A. Tomalia, *J. Am. Chem. Soc.*, **84**, 993 (1962).

(11) S. Gabriel and R. Stelzner, *Ber.*, **28**, 2929 (1895).

(12) A. A. Goldberg and W. Kelley, *J. Chem. Soc.*, 1919 (1948).

(13) Badische-Anilin- und Soda-Fabrik Akt. Ges., British Patent 784,058, Oct. 2, 1957; *Chem. Abstr.*, **52**, 5034h (1958).

(2) S. Gabriel, *Ber.*, **20**, 2235 (1887).

(3) S. Gabriel and W. Landsberger, *ibid.*, **31**, 2732 (1898).

(4) A. W. Chapman, *J. Chem. Soc.*, 1992 (1925); 2296 (1926); 1749 (1927).

(5) K. B. Wiberg and B. 1. Rowland, *J. Am. Chem. Soc.*, **77**, 2205 (1955).

adjacent *o*-carbonyl chloride group or an *o*-chloromethyl group to form the reaction products. The reaction of 2-(*p*-nitrophenyl)-2-oxazoline with benzoyl chloride<sup>14</sup> on a steam bath for 3 min. to yield *N*-( $\beta$ -chloroethyl)-*N*-benzoyl-*p*-nitrobenzamide lends support to this idea.

The photochemically induced rearrangement of 1-(*o*-chloromethylbenzoyl)-aziridine appears to be due to an energized oxygen atom which displaces the halogen from the *o*-chloromethyl carbon with formation of the phthalan VIII as the product. 1-Iminophthalans have also been isolated as products of pyrolysis of *o*-chloromethylbenzamide and 2-chloromethyl-4-nitrobenzamide.<sup>2,3</sup>

### Experimental

**Phenylthiocarbonyl chloride** was prepared by a modification of a published procedure.<sup>15</sup> Into a solution of 47.7 g. of thio-phenol in 500 ml. of benzene cooled in an ice bath was bubbled 53.5 g. of phosgene which had been previously passed through concentrated sulfuric acid. To this mixture was added portionwise and with stirring 46.0 g. of triethylamine. The mixture was stirred 1 hr. without the ice bath and the triethylamine hydrochloride filtered. The benzene was distilled at atmospheric pressure under a hood. From the residue was obtained 49.6 g. of phenylthiocarbonyl chloride, b.p. 100–104° (12 mm.). Redistillation gave a sharp boiling fraction at 104° (12 mm.) (lit.<sup>15</sup> value 104° (13 mm.)).

**1-Phenylthiocarbonylaziridine (I)**.—A solution of 21.2 g. of phenylthiocarbonyl chloride in 150 ml. of dry ether was cooled in an acetone–Dry Ice bath. To this solution was added with vigorous shaking over a 10-min. interval a solution (previously cooled in an acetone–Dry Ice bath) of 5.3 g. of aziridine and 12.3 g. of triethylamine in 100 ml. of dry ether. A precipitate of triethylamine hydrochloride formed immediately. After the reaction mixture stood at room temperature for 0.5 hr. the precipitate was filtered and the ether evaporated in a flask immersed in a water bath kept at room temperature or below. A crude yield of 18.3 g. of I was obtained and recrystallized, usually immediately after isolation, from petroleum ether (b.p. 40–70°), care being taken not to keep the recrystallization flask on the hot plate too long. After filtration the solution was cooled in an acetone–Dry Ice bath. The recrystallized material melted at 39–41°.

*Anal.* Calcd. for C<sub>9</sub>H<sub>9</sub>NOS: C, 60.32; H, 5.06; N, 7.81. Found: C, 60.76; H, 5.08; N, 7.73.

**2-Phenylthioethyl Isocyanate (II)**.—Phosgene (24.2 g.) was passed through concentrated sulfuric acid into a flask immersed in an ice bath and containing 120 ml. of anhydrous toluene. The resulting solution was added quickly to a well stirred solution of 11.0 g. of 2-phenylthioethylamine<sup>19</sup> in 120 ml. of toluene. A white precipitate formed immediately. The reaction mixture was stirred for an additional 30 min. and then refluxed gently for about 35 min. During this time the reaction mixture became clear. The toluene was distilled *in vacuo* and the residue vacuum distilled. A crude yield of 8.7 g. of II, b.p. 106–108° (0.5 mm.), was obtained. Redistillation gave material boiling at 101° (0.25 mm.).

*Anal.* Calcd. for C<sub>9</sub>H<sub>9</sub>NOS: C, 60.32; H, 5.06; N, 7.81. Found: C, 60.50; H, 5.07; N, 7.73.

**Isomerization of I into II**.—A mixture of 8.2 g. of I and 200 ml. of anhydrous mixed xylenes was refluxed in a dry atmosphere for 3 days in an oil bath held at 200°. All but about 10–15 ml. of the solvent was removed by vacuum distillation. The residue was placed in an addition tube and the remaining solvent flashed off under vacuum by dropwise addition into a distillation flask immersed in an oil bath held at about 80°. The residue in the distillation flask was distilled to yield 5.1 g. of II, b.p. 83–87° (0.1 mm.). The infrared spectrum was identical with the material prepared by reaction of phosgene with 2-phenylthioethylamine. If the reaction mixture was refluxed for less than 3 days the distillate contained some unreacted I as was evident by examination of the infrared spectrum.

**Methyl *N*-2-Phenylthioethylcarbamate (IV)**. **Method A**.—A mixture of 0.5 g. of 2-phenylthioethyl isocyanate and 0.5 g. of anhydrous methanol was kept at room temperature for 1 hr. The methanol was evaporated and the solid remaining was slurried with petroleum ether (b.p. 40–70°) and filtered. The crude IV weighed 0.4 g. and melted at 60–62°. Recrystallization from petroleum ether gave material melting at 66–67°.

(14) E. M. Fry, *J. Org. Chem.*, **15**, 802 (1950).

(15) H. Rivier, *Bull. soc. chim.*, [4] **1**, 733 (1907).

(16) A. E. Senear, M. M. Rapport, and J. B. Koepfli, *J. Biol. Chem.*, **167**, 229 (1947).

*Anal.* Calcd. for C<sub>10</sub>H<sub>13</sub>NO<sub>2</sub>S: C, 56.88; H, 6.19; N, 6.63. Found: C, 56.86; H, 6.24; N, 6.50.

**Method B**.—Four grams of sodium iodide was added to a solution of 1.00 g. of I and 20 ml. of methanol. The reaction mixture became warm. After standing overnight at room temperature the solvent was evaporated and the residue washed with cold water and filtered. The crude IV weighed 1.05 g. and melted at 58–64°. Recrystallization gave crystals identical with that prepared by method A.

**Reaction of Phthaloyl Chloride with Aziridine**.—A solution of 4.1 g. of phthaloyl chloride in 50 ml. of benzene was added dropwise to a solution of 0.86 g. of aziridine and 2.02 g. of triethylamine in 50 ml. of benzene. The precipitate of triethylamine hydrochloride was filtered and washed with 50 ml. of benzene. The combined filtrates were refluxed for 1.5 hr. and the solvent evaporated. The yield of crude *N*-2-chloroethylphthalimide was 4.3 g. and melted at 74–77°. A sample recrystallized from ethanol melted at 79–81° and had an infrared spectrum identical with that of an authentic sample.

**1-(*o*-Chloromethylbenzoyl)-aziridine (VI)**.—A cooled solution of 2.15 g. of aziridine and 5.06 g. of triethylamine in 60 ml. of dry ether was added portionwise over 10 min. to a cold solution of 9.45 g. of *o*-chloromethylbenzoyl chloride<sup>17</sup> in 60 ml. of dry ether. The reaction mixture was filtered and the filtrate evaporated. The 8.4 g. of crude VI was immediately slurried with 10 ml. of cold 95% ethanol and filtered. The compound was twice recrystallized from a small quantity of 95% ethanol at 30–35°. The recrystallized VI melted at 52–53.5°. It is important to purify the crude VI at once and to store it in a refrigerator.

*Anal.* Calcd. for C<sub>10</sub>H<sub>10</sub>ClNO; N, 7.16. Found: N, 6.80.

**Isomerization of VI to *N*-2-Chloroethylphthalimidine (VII)**.—A mixture of 2.5 g. of VI and 40 ml. of dry toluene was refluxed 15 hr. The solvent was evaporated and the residue of light yellow crystals weighed 2.5 g. Recrystallization from petroleum ether gave material melting at 81–83°.

*Anal.* Calcd. for C<sub>10</sub>H<sub>10</sub>ClNO; N, 7.16. Found: N, 6.95.

**Oxidation of VII to *N*-2-Chloroethylphthalimide**.—A solution of 2.0 g. of sodium dichromate in 5 ml. of water was added carefully to a solution of 0.7 g. of VII in 2 ml. of cold concentrated sulfuric acid. Much heat was evolved. The reaction mixture was refluxed for 30 min., then cooled, diluted with 3 ml. of water, and filtered. The residue weighed 0.65 g. and had an infrared spectrum that was identical with that of an authentic sample of *N*-2-chloroethylphthalimide. The crude product was recrystallized from 95% ethanol and melted at 80–83°.

**Isomerization of VI to 1-(2-Chloroethylimino)-phthalan (VIII)**.—Four grams of VI was placed in a test tube and exposed to ultraviolet irradiation supplied by a Hanovia mercury arc type 16106 and equipped with a Corning filter 7–37 for 5 days. The transformation also takes place with sunlight but with a reaction time of about 2 weeks. The solid VI gradually changed to a dark yellowish green oil. An infrared spectrum of this crude VIII indicated complete conversion of the starting material. Distillation of the crude oil was difficult but could be accomplished by a rapid distillation at high vacuum. The boiling point of VIII was 115–116° (0.25 mm.). If the distillation was attempted at a higher temperature the iminophthalan converts into VII. The spectra of the crude and the redistilled VIII were identical.

*Anal.* Calcd. for C<sub>10</sub>H<sub>10</sub>ClNO; N, 7.16. Found: N, 6.70.

The picrate of VIII decomposed at 175–182° after recrystallization from ethanol.

*Anal.* Calcd. for C<sub>16</sub>H<sub>13</sub>ClN<sub>4</sub>O<sub>8</sub>; N, 13.19. Found: N, 13.00.

**Hydrolysis of VIII**.—One gram of VIII was refluxed 10 hr. with 20 ml. of 10% hydrochloric acid. The reaction mixture was extracted three times with ether and the ether extracts were evaporated to yield 0.50 g. (73%) of phthalide which was identified by comparing with a genuine sample. Evaporation of the aqueous layer gave deliquescent crystals which were placed in a vacuum desiccator for several days. An infrared spectrum of this material was identical with that of a commercial sample of 2-chloroethylamine hydrochloride. No yield was recorded.

**Isomerization of VIII to VII**.—In one instance an attempted distillation of VII at 8 mm. converted all of it to a solid in the distillation flask. The solid was shown to be VII by melting point, mixture melting point, and infrared spectrum. In another experiment 0.93 g. of VIII in 30 ml. of toluene was refluxed for 3 days. Evaporation of the solvent and seeding of the residual oil with VII caused solidification. Recrystallization of the crude VII gave 0.43 g. of material melting at 77–81°.

**Acknowledgment**.—The author wishes to express his appreciation to the National Science Foundation for a Senior Faculty Fellowship and to Professor Emanuel

(17) I. G. Hinton, F. G. Mann, and A. Vanterpool, *J. Chem. Soc.*, 610 (1959).

Vogel for a delightful year at the University of Köln, where a part of this work was accomplished. The author thanks Mr. Donald Tomalia for the initial syn-

thesis of 1-phenylthiocarbonylaziridine and for an experiment of this material in moist acetone containing sodium iodide.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF CALIFORNIA, SAN DIEGO, LA JOLLA, CALIF., AND THE DOW CHEMICAL CO., PITTSBURG, CALIF.]

## The Oxymercuration of Olefins. I. A General Method for Determination of the Stereochemistry of Oxymercuration

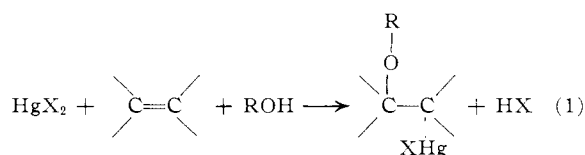
BY T. G. TRAYLOR AND A. W. BAKER

RECEIVED MARCH 30, 1963

The addition of mercuric salts to olefins in water produces hydroxymercurials,  $\text{HO}(\text{CR}_2\text{CR}_2\text{HgX})$ , whose OH stretching frequency differs from that of the parent alcohol,  $\text{HO}(\text{CR}_2\text{CR}_2\text{H})$ , by an amount which depends on the mercury-oxygen distance. The frequency difference,  $\Delta\nu$ , amounts to 6–10  $\text{cm}^{-1}$  for either open chain or *trans*-hydroxymercurials; *cis*-hydroxymercurials show a  $\Delta\nu$  of 18–22  $\text{cm}^{-1}$ . Consequently, it is possible to deduce the stereochemistry of oxymercuration from the OH stretching frequency of the product. Using this technique, and other methods for corroboration, we have confirmed our previous conclusion that, although cyclopentene and cyclohexene form *trans*-oxymercuration products, norbornene is oxymercured exclusively *cis-exo*. Because the latter result is anomalous on two counts, we have extended this finding to dicyclopentadiene and benz-norbornene, concluding that such strained olefins generally add mercuric salts without rearrangement to afford exclusively *exo-cis* products. These findings are incorporated into previously proposed mechanisms of electrophilic addition. Structural effects responsible for changes in stereochemistry of addition are discussed.

### Introduction

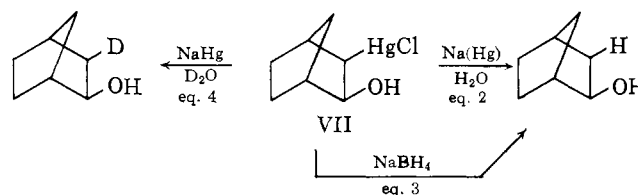
The similarity of oxymercuration to other electrophilic olefin addition reactions is well established.<sup>1</sup>



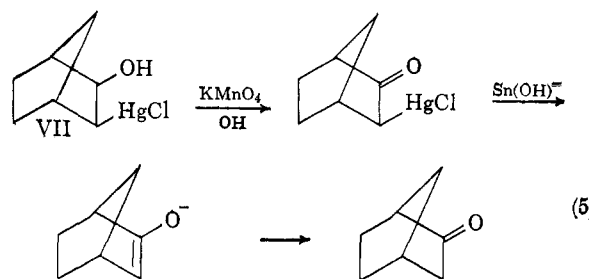
The addition is first order in mercuric salt, first order in olefin, and is stereospecific.<sup>1</sup> The products of this addition to cyclopentene and cyclohexene have been demonstrated to have *trans* configurations by their elimination rates,<sup>2,3</sup> dipole moments,<sup>4</sup> and nuclear magnetic resonance spectra.<sup>5</sup> Therefore, the recent observation that norbornene adds mercuric salts to give the *exo-cis* configuration<sup>6</sup> seems to warrant further investigation of olefin oxymercuration, especially the oxymercuration of strained and bicyclic olefins. We have consequently undertaken the tasks of establishing the generality of the *cis* addition in 2.2.1-bicyclic olefins and of determining whether this change from complete *trans*-oxymercuration to complete *cis*-oxymercuration with change in olefin structure is due to olefin angle strain or some more specific property of bicyclic systems. This paper reports our progress on the former along with some conclusions concerning the mechanisms of ionic additions to olefins.

In order to pursue efficiently the stereochemistry of the addition reaction with a variety of olefins it was necessary to develop a simple, general method of structure proof. This proof must establish the skeletal structure, the -OR configuration, and the position and configuration of the mercury atom. The first of these can usually be accomplished by reducing the mercurial with sodium amalgam<sup>7</sup> or sodium borohydride<sup>8,9</sup> to re-

place mercury by hydrogen. Typical reductions are illustrated in eq. 2 and 3 for the norbornene adduct.



We have occasionally employed sodium borodeuteride or sodium amalgam in  $\text{D}_2\text{O}$  to afford additional stereochemical evidence (eq. 4). Identification of the resulting alcohol with a known alcohol establishes the skeletal structure and configuration of the OH (or OR) group. The position of the mercury atom can be ascertained by the deuterium replacement shown in eq. 4, by the n.m.r. spectrum of the mercurial,<sup>5</sup> or by a less equivocal process of oxidizing the alcohol with permanganate to a ketone<sup>10</sup> in which the mercury is enolizable only if it is  $\alpha$  to the ketone group<sup>11</sup> (eq. 5).



We have employed all three methods.

The configuration of the mercury atom relative to the OH group can be inferred from rates of elimination in acid<sup>2</sup> or from dipole moment measurement.<sup>4a,b</sup> This configuration can be established in some cases (*e.g.*, in VII) from the n.m.r. coupling constant between protons attached to the carbon atoms in question.<sup>5</sup> But the most general and convenient method for demonstrating the stereochemical relationship of these two groups is the infrared method presented here.

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- (2) M. M. Kreevoy and F. R. Kowitz, *J. Am. Chem. Soc.*, **82**, 739 (1960).
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