

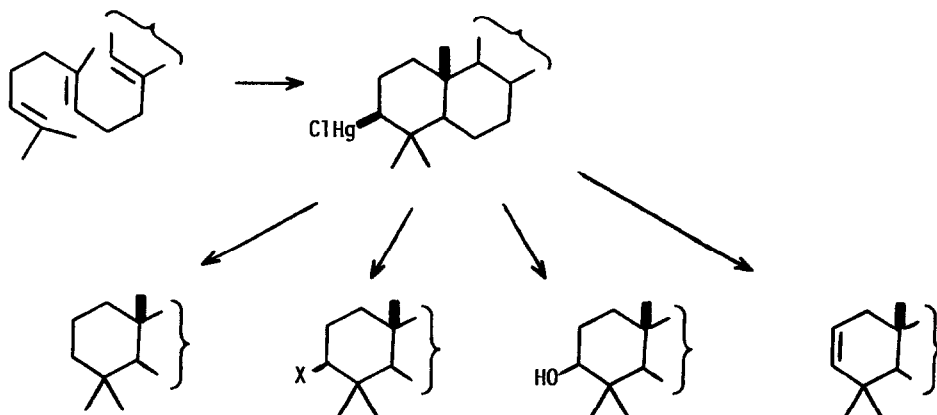
## AN EFFICIENT METHOD FOR THE CONVERSION OF ALKYL MERCURIC HALIDES INTO OLEFINS

by

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**Abstract:** Photolysis of an alkylmercuric halide in the presence of diphenyldiselenide yields the corresponding alkylphenylselenium intermediate, which can be converted into an olefin on treatment with sodium periodate.

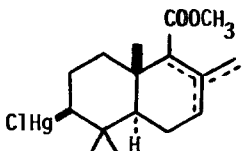
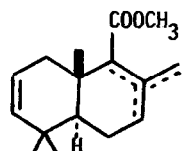
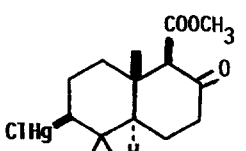
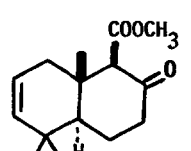
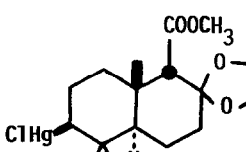
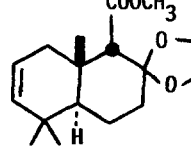
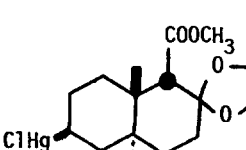
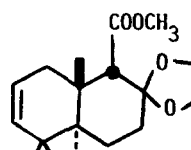
Easily prepared by electrophilic addition of mercuric ion to alkene double bonds, alkylmercuric halides are valuable synthetic intermediates for transformation into many other classes of compounds.<sup>1</sup> For example, alkylmercurials have been prepared by mercuric-ion induced cyclizations of dienes<sup>2</sup> and then converted into alkanes by treatment with sodium borohydride,<sup>3</sup> into alkyl iodides by treatment with potassium triiodide,<sup>4</sup> into alkyl bromides by treatment with bromine,<sup>5</sup> and into alcohols by treatment with molecular oxygen and sodium borohydride.<sup>6</sup> Conversion of an alkylmercuric halide into an olefin is also possible, but is usually effected<sup>7</sup> by a two-step procedure involving either bromination/dehydrobromination or hydroxylation/dehydration. In our hands, however, these procedures have proven to be low-yielding, and we were therefore driven to develop a more reliable method.



The major problem with the dehydrobromination and dehydration methods in cyclic systems is that both rely on prior conversion of the alkylmercuric halide to an axial bromide or alcohol so that the subsequent elimination step can take place with favorable antiperiplanar geometry. In practice one usually obtains a mixture of axial and equatorial diastereomers, making elimination difficult. We reasoned that these stereochemical difficulties could be overcome if the organomercurial were converted into the corresponding organoselenium species, whose axial and equatorial diastereomers could both undergo syn elimination on treatment with sodium periodate.

We have found that the selenenylation/elimination reaction takes place exactly as desired. Exposure of an alkylmercuric halide in benzene solution to 2 equiv. diphenyldiselenide under irradiation with a sunlamp for 5 minutes at room temperature effects rapid conversion into the corresponding phenylselenide.<sup>8</sup> Oxidation with sodium periodate, followed by spontaneous elimination of the intermediate phenylselenoxide, then gives the olefin. Some of our results are shown in the Table.<sup>9</sup>

TABLE. Conversion of Alkylmercuric Halides into Olefins

Entry	Alkylmercuric Halide	Product	Yield <sup>10</sup> (%)
1			83
2			89
3			90
4			91

As illustrated in the Table, high yields were obtained in all cases studied. The superiority of this method over the standard bromination/dehydrobromination sequence is illustrated particularly well in the case of the substrate shown in entry 4. On treatment of **7** with either bromine or iodine, opening of the cyclopropane ring occurred to the exclusion of halogenation. Thus, olefin product **8** could not be obtained. On phenylselenenylation of **7**, however, no ring opening was observed, and olefin **8** was obtained smoothly in high yield after elimination.

In a representative experiment, organomercuric chloride **3** (17 mg, 0.034 mmol) and diphenyldiselenide (21 mg, 0.068 mmol) were slurried in benzene (0.5 mL) and the yellow mixture was deoxygenated by several freeze/thaw cycles. The reaction vessel was then filled with argon and stirred next to a sunlamp for 3 min. After stirring in the absence of light for an additional 10 min, the white precipitate that formed during the course of the reaction was removed by dilution with hexane and filtration through a pad of celite. The filtrate was then concentrated and rapidly passed through a short silica-gel column to give the product (16 mg, 100%) as a pale yellow foam. Spectroscopic analysis indicated that a mixture of  $\alpha$  and  $\beta$  diastereomers was present. This material was dissolved in tetrahydrofuran (0.7 mL), cooled to 0°C, and treated with a solution of sodium periodate (26 mg, 0.12 mmol) in water (0.3 mL). After standing for 12 h at room temperature, the reaction mixture was diluted with ether, washed with water and brine, dried ( $\text{MgSO}_4$ ) and concentrated. Column chromatography on silica gel (elution with 15% ethyl acetate/hexane) gave pure olefin **4** (7.7 mg, 89%) as a colorless oil that crystallized on standing: IR ( $\text{CDCl}_3$ ), 1715, 1745  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  5.45 (m, 2H), 3.69 (s, 3H), 3.29 (s, 1H), 2.55-2.30 (m, 2H), 2.10-1.55 (m, 5H), 1.16 (s, 3H), 1.04 (s, 3H), 0.93 (s, 3H).

We believe that the simplicity and high yields obtained make this selenenylation/oxidation sequence the method of choice for converting alkylmercuric halides into olefins.

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**Notes and References**

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8. This reaction has also been noted recently by Russell: Russell, G. A.; Tashtoush, H. **J. Amer. Chem. Soc.** **1983**, 105, 1398.
9. Complete experimental details for the preparation of all substances shown in the table are available: Erion, M. D.; Ph.D. Thesis submitted to Cornell University, 1984. Copies are may be obtained from University Microfilms, Ann Arbor, Michigan.
10. The figures given represent isolated yields. All products were fully characterized by IR, MS, and 300 MHz <sup>1</sup>H NMR.

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