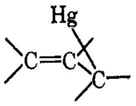

Figure 1.—Suggested structure of the ground state of allylmercuric iodide.

is substantially correct, that a heavy-atom geometry reasonably well suited to the electronic structure I exists in the starting state.

Results

Ultraviolet spectra of allylmercuric iodide were obtained in a number of solvents. In all cases a strong absorption band was observed in the general region of 230 to 250 mμ. These bands are all more or less overlapped by end absorption from still smaller wavelengths, so that their exact shapes are hard to assess, but their widths at half-height seem to range from 30 to 50 mμ.

Peak positions (λ_{max}) and extinction coefficients at the maximum (ϵ_{max}) are given in Table I.

TABLE I

ULTRAVIOLET SPECTRUM OF ALLYLMERCURIC IODIDE IN VARIOUS SOLVENTS

Solvent	λ_{max}[a]	$10^{-4}\ \epsilon_{max}$
H_2O[b]	248	1.59
CH_3OH	246	1.62
$(CH_3)_3COH$	245	1.40
CH_3CN	246	1.7
$(C_2H_5)_2O$	230	1.58
$(CH_3)CCH_2CH(CH_3)_2$[c]	233	1.34

[a] In mμ. [b] Containing 4% methanol. [c] Isooctane.

The uncertainty in λ_{max} values is of the order of ±1-2 mμ and that for ϵ_{max} ±2%, as judged from the reproducibility of known values, except for the values in acetonitrile. Allylmercuric iodide decomposes at a significant rate in acetonitrile, giving mercuric iodide. Mercuric iodide absorbs at longer wavelengths than allylmercuric iodide in acetonitrile, so its concentration could be evaluated, and a correction made, assuming 2 moles of allylmercuric iodide is consumed for each mole of mercuric iodide produced. Nevertheless λ_{max} and ϵ_{max} for acetonitrile must be considered a little more uncertain than those for other solvents.

The ultraviolet spectrum of mercuric iodide in acetonitrile does not seem to have been previously reported. It shows broad bands at 302, 256, and 217 mμ (ϵ_{max} 8.9×10^3, 1.35×10^4, and 2.13×10^4), respectively.

The ultraviolet spectrum of crotylmercuric iodide in water (containing 4% methanol) was also obtained. It showed λ_{max} 256 mμ (ϵ_{max} 1.5×10^4).

Discussion

The longest wavelength ultraviolet maximum usually found in nonconjugated olefins occurs below 200 mμ,[4] and that for saturated alkylmercuric iodides in water occurs at ~230 mμ.[5] Therefore, the occurrence of a strong band at 248 mμ, in water, for the allyl compound, in itself strongly suggests some sort of interaction between the two chromophores. The intensity of the transition implies substantial overlap between the excited state wave function and that of the ground state.[6] The fact that polar solvents lead to a red shift suggests that the transition increases an electronic polarization *already present in the ground state.*[7] In neither state is the direction of this polarization entirely clear, but for purposes of the chemical reaction it is sufficient that the nuclei, in the ground state, are so arranged as to allow a flow of charge between the two chromophores. The arrangement which seems most satisfactory is that shown in Figure 1, which does, indeed, resemble that required by I. It is made even more attractive by the length and deformability of the carbon–metal bond.

Allyltin and other allylmetallic[8] compounds are also cleaved by acid at rates far in excess of the rate of protonation of propene, and it would be of interest to see if they, also showed ultraviolet bands not found in the saturated organometallics or the isolated olefins.

It has been suggested[8] that the occurrence of carbon–metal bond cleavage in the same step as protonation is sufficient explanation for the profoundly increased rate of proton transfer. This explanation requires that the carbon–mercury bond be broken either prior to or simultaneous with the proton transfer. The primary hydrogen isotope effect, 7.3 at 35°,[2] requires that the reaction coordinate be composed almost entirely of proton translation, excluding the second possibility. A study of iodide ion catalytic coefficients reveals very little free HgI^+ character for the iodomercuri fragment in the transition state,[9] excluding the first. The best remaining alternative is that the electron flow from the mercury is unaccompanied by substantial heavy-atom motion, and the present results strongly support this conclusion.

Experimental Section

The materials have been previously described.[2] The solvents were all of Spectro Grade, and were used, as supplied, without further purification. The spectra were obtained by conventional techniques, using a Beckman DK-2 spectrophotometer.

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(4) H. H. Jaffe and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962, p 177.

(5) M. M. Kreevoy and R. L. Hansen, *J. Am. Chem. Soc.*, **83**, 626 (1961).

(6) Reference 4, p 117.

(7) Reference 4, p 191.

(8) H. G. Kuivila and J. A. Verdone, *Tetrahedron Letters*, 119 (1964). This work was carried out in a solvent containing 94% methanol and 4% water, but it is unlikely that the results would be dramatically different in a more aqueous solvent.

(9) M. M. Kreevoy, D. J. W. Goon, and R. A. Kayser, *J. Am. Chem. Soc.*, **88** (1966).

Sodium Selenide Vicinal Dihalide Elimination

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The reaction of sodium selenide with alkyl halides in anhydrous liquid ammonia results in the formation of dialkyl selenides.[1] Alkyl halides or dialkyl

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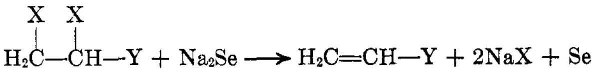
(1) L. Brandsma and H. Wijes, *Rec. Trav. Chim.*, **82**, 68 (1963).

sulfates also react with sodium selenide to give symmetrical selenides. The procedure has been used for the preparation of spiro derivatives.[2] Cyclic selenides are made from polymethylene dibromides and alcoholic sodium selenide.[3] No cases of elimination of halogen from vicinal dihalides by sodium selenide have been reported.

We wish to report the convenient preparation of alkenes from vicinal dihalides by treatment with sodium selenide in dimethylformamide or dimethyl sulfoxide solution. Terminal alkenes are prepared in good to excellent yields from either vicinal dichloro- or dibromoalkanes. The following reaction illustrates our findings.



$$H_2\overset{X}{C}-\overset{X}{C}H-Y + Na_2Se \longrightarrow H_2C{=}CH-Y + 2NaX + Se \quad (1)$$

Table I summarizes the data obtained for a series of 1,2-dihalogen-substituted alkanes. The ease of removal of halogen is I > Br > Cl. The effect of added substituents on the elimination is to reduce the apparent yield of the alkene. Yields were based upon the amount of gas evolved. All gases were analyzed by gas chromatography[4] and found to be only the expected alkene in each case.

TABLE I

EFFECT OF SUBSTITUENTS ON DIHALIDE ELIMINATION REACTION

Dihalide		Alkene yield, %	
X	Y	Dimethylformamide	Dimethyl sulfoxide
I	H	85.2	88.0
Br	H	77.7	72.7
Br	CH_3	52.6	64.6
Br	C_2H_5	46.6	54.2
Cl	H	75.0	70.6
Cl	CH_3	50.5	57.4
Cl	C_2H_5	28.1	33.3

As the above reaction is exceedingly simple to perform, it can be suggested as a convenient new alternative to either prepare or purify alkenes.[5] Further work is in progress to determine the stereochemistry of this reaction and elucidation of its mechanism.

Experimental Section

The dihalides were obtained in high purity from the following sources: 1,2-dibromoethane, 1,2-dichloroethane (Fisher Scientific Co.); 1,2-diiodoethane, 1,2-dibromobutane, 1,2-dichlorobutane (City Chemical Co.); 1,2-dibromopropane, 1,2-dichloropropane (Matheson Coleman and Bell).

A representative experimental procedure is as follows. The dihalide in dimethylformamide (or dimethyl sulfoxide) is added to a rapidly stirred suspension of sodium selenide (ground to <100 mesh) in dimethylformamide (or dimethyl sulfoxide) at 70–75°. The reaction commences almost immediately and is evidenced by rapid gas evolution and a gradual darkening of the reaction mixture. Evolved gases are collected over water and analyzed by gas chromatography. Reaction is essentially complete after 1 hr. Each reaction was repeated several times and the results were reproducible. The yields of olefin are given in Table I.

Acknowledgment.—The authors gratefully acknowledge the support of the Selenium-Tellurium Development Association, Inc.

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[2] H. J. Backer and H. J. Winter, *Rec. Trav. Chim.*, **56**, 492 (1937).

[3] G. T. Morgan and F. H. Burstall, *J. Chem. Soc.*, 1096, 1497, 2197 (1929); 1497 (1930).

[4] A 50-ft di-*n*-butylmaleate column was used.

[5] This elimination reaction may also be carried out in acetone with similar results. For example, 1,2-dibromoethane results in a 78.6% yield of ethylene.

The Synthesis and Resolution of 1- and 2-Methylcholanthrene[1]

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The idea of testing optical isomers of cancer-producing hydrocarbons is not new,[3] but prior to this work such optically active isomers had not been prepared.[4] In this paper we report on the synthesis of 1-methylcholanthrene (I) and 2-methylcholanthrene (II) and the resolution of each into optical antipodes.[5]

The synthesis of I was modeled after, but not the same as, the method described.[6] Modifications were needed in several steps because of the increased size of runs, our inability to reproduce reported[6] results, and the desire for higher yields.

The preparation of β-(3-phenanthroyl)propionic acid (III, Scheme I) was essentially that described[7] except for the purification procedure (see Experimental Section). The reduction to γ-(3-phenanthryl)butyric acid (IV) was effected[8] in markedly improved (94%) yield. Ring closure to V in hydrogen fluoride went in 94% yield.

As implied by Bachmann[9] the Reformatsky reaction of V was erratic. In our hands many attempts to duplicate Bachmann's result failed completely; yet, after many runs had failed, a few succeeded, although the yields was never so high as Bachmann reported for a 2-g run. On a larger scale (30 g of V), success was attained when the reactions were carried out in pure dry benzene, but occasionally, the reaction could not be started despite careful attention to details. The hydroxy ester was dehydrated without purification, the crude unsaturated ester was dehydrogenated by heating with sulfur, and the crude ester was hydrolyzed to the acid (VIa) in an over-all yield of 80% from V. Cyclization of VIa to VIIa proceeded well (83%) in hydrogen fluoride.

The conversion of VIIa to I was not so easy as anticipated. The best route involved condensation

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[1] Part of the work herein presented was taken from the Ph.D. thesis of R. W. Wotring, Jr., The Ohio State University, 1965.

[2] Postdoctoral Fellow on funds supplied by a grant from the National Institutes of Health, Bethesda, Md.

[3] L. F. Fieser and A. M. Seligman [*J. Am. Chem. Soc.*, **57**, 1377 (1935)] mention the interest and they synthesized, 2,3-dimethylcholanthrene but made no attempt at securing the optical isomers.

[4] The above 2,3-dimethylcholanthrene was reported to be carcinogenic by M. J. Shear, *Am. J. Cancer*, **28**, 334 (1936). One attempt to prepare it in optically active form failed; see M. S. Newman and J. Linsk, *J. Org. Chem.*, **14**, 480 (1949).

[5] The testing of these isomers for carcinogenic activity is being carried out by Dr. Charles Huggins, Ben May Laboratory for Cancer Research, Chicago, Ill., Dr. James Miller, McArdle Laboratory for Cancer Research, Madison, Wis., and Professor E. Von Haam, The Ohio State University. These workers will report their results independently.

[6] W. E. Bachmann and S. R. Safir, *J. Am. Chem. Soc.*, **63**, 2601 (1941).

[7] R. D. Haworth and C. R. Mavin, *J. Chem. Soc.*, 1012 (1933).

[8] Huang-Minlon, *J. Am. Chem. Soc.*, **68**, 2487 (1946).

[9] W. E. Bachmann, *J. Org. Chem.*, **3**, 434 (1938).