TABLE I

REACTIONS OF BUTADIENE WITH ETHYLENE[a]

Run no.	Iron halide, mmoles	Phosphine, mmoles	Organoaluminum compound,[b] mmoles	Butadiene, g	Reaction conditions			Products, g			Conversion,[d] %	Selectivity,[e] %
					Pressure, kg/cm^2	Temperature, °C	Time, hr	1,4-HD[c]	2,4-HD[c]	Residue		
1	2	DPE, 1	TEA, 7.3	67	70	50	5	35.7	...	7.2	42.9	82.7
2	2	DPE, 1	TEA, 7.3	67	60	80	3	69.5	1.5	10.4	86.6	80.6
3	2	DPE, 0.1	TEA, 7.3	100	60	80	18	51.3	1	41.4	76	45
4	1	DPE, 0.5	TEA, 7.3	100	60	80	18	35.4	1	13.3	37.5	62.8
5	1	DPE, 1	TEA, 7.3	100	60	80	18	95.5	2.3	13.1	78.2	81.1
6	5	DPE, 1	TEA, 7.3	100	60	80	18	92.8	2.5	10.4	74	83.7
7	0.1	DPE, 1	TEA, 7.3	67	60	80	3	3.2	...	2.8	7.4	...
8	2	DPE, 1	TEA, 7.3	20	68	80	2	24.6	0.2	2	86.6	95
9	2	DPE, 1	TIBA, 4	67	65	80	2	78.6	1.2	7.2	90.6	86.8
10	2	DPE, 1	DIBAH, 5.6	67	65	80	2	61.5	...	8.1	73.4	83.5
11	2	DPE, 1	DEAC, 8	67	65	80	2	18.9	...	2.7	24.4	82.4
12	0.5	DPM, 1	TEA, 7.3	67	60	85	2	2.5	...	26.7	42.3	...
13	0.5	DPP, 1	TEA, 7.3	67	60	85	3	96	...	2.6	100	96.2
14	0.5	PDP, 1	TEA, 7.3	67	60	85	3	29.3	...	22.3	62.5	...
15	2	*cis*-DPET, 1	TEA, 7.3	67	50	85	3	64.3	2	26	97.3	66
16	2	*trans*-DPET, 1	TEA, 7.3	67	50	85	3	40	...	10.4	55.3	72
17	0.5	DPE, 0.5	TOA, 7.3	67	40	80	17	79.3	...	7.6	90.5	87.2
18	0.7	DPE, 0.5	TEA, 16	40	40	80	3	11.2	...	2.5	24.6	76.6

[a] Twenty milliliters of monochlorobenzene was used through all runs. Runs 1–16 ferric chloride; 17, ferric bromide; and 18, ferrous iodide. [b] TEA = triethylaluminum, TIBA = triisobutylaluminum, DIBAH = diisobutylaluminum hydride, DEAC = diethylaluminum chloride. [c] HD = hexadiene. [d] Moles of butadiene reacted/moles of butadiene charged × 100. [e] Moles of 1,4-hexadiene formed/moles of butadiene reacted × 100.

runs. In case monodentate triphenylphosphine was added to the catalytic system instead of ditertiary phosphine, 1,4-hexadiene, 3-methyl-1,4-pentadiene, and 1,3-hexadiene were prepared.[1] Therefore, it is considered that a coordination of the ditertiary phosphine governs the reaction of π-butenyl group with the coordinated ethylene to form exclusively 1,4-hexadiene. The exclusive formation of *cis* isomer may be a clue to make clear the reaction mechanism, however, further study will be required to elucidate the detail.

Experimental Section

Materials.—Anhydrous ferric chloride was purified by sublimation before use. Ferric bromide and ferrous iodide of extra pure grade were used without further purification. Organoaluminum compounds were obtained commercially. Monochlorobenzene was dried with phosphorus pentoxide and subsequently distilled. Ditertiary phosphines were prepared according to the method of Hewertson and Watson.[11]

Reaction of Butadiene with Ethylene.—In a typical example, 2 mmoles of ferric chloride, 1 mmole of DPE, 20 g of liquefied butadiene, and 7.3 mmoles of triethylaluminum were added in that order into 80 ml of monochlorobenzene in a stainless steel autoclave (200 ml) equipped with a magnetic stirrer. After the autoclave was tightly closed, ethylene was introduced directly from a cylinder up to 68 kg/cm^2 at 80°. The reaction was carried out for 2 hr under a constant pressure and temperature. By adding a small amount of dilute hydrochloric acid in a separatory funnel. The upper layer was washed thoroughly with water and dried with anhydrous sodium sulfate. Then the atmospheric distillation was carried out and the distillate was analyzed by gas chromatography (Apiezon grease L packing column 3 m, carrier gas helium, 100°). The yield was calculated from the relative peak area in comparison with the peak area of toluene added as an internal standard. The validity was confirmed by the analysis of known mixtures. In the example, the yield of 1,4-hexadiene was 24.6 g, and 0.2 g of 2,4 isomer and 2 g of nondistillable material were also obtained. 1,4-Hexadiene and 2,4-hexadiene were purified by preparative gas chromatography, and were identified by elementary analysis, infrared absorption spectroscopy, mass spectroscopy, and gas chromatography.

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[11] W. Hewertson and H. R. Watson, *J. Chem. Soc.*, 1490 (1962).

The Ultraviolet Spectrum of Allylmercuric Iodide and Its Acid Cleavage Mechanism[1a]

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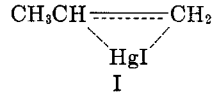
Allylmercuric iodide is cleaved by acid some six powers of 10 faster than propene is hydrated, in spite of the fact that both of them involve the attack of the proton on the methylene group of the carbon–carbon double bond.[2,3] This requires that considerable electron density be transferred, in the transition state, from the mercury to the carbon acquiring the formal positive charge. An attractive way to accomplish this would be to have a transition state resembling the olefin–mercuric iodide π complex (I) in its elec-



$\underset{\text{HgI}}{CH_3CH\text{=====}CH_2^+}$

I

tronic structure. Kinetic isotope effects, however, require that the reaction coordinate *not* contain large components of heavy atom motions.[2] Therefore, a structure similar to I in its heavy-atom geometry would either have to be formed in the activation process or would have to be already present in the starting state. It is the purpose of the present note to suggest, on the basis of ultraviolet spectra, that the latter

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[1] (a) Supported, in part, by the National Science Foundation through GP-5088; (b) National Science Foundation Cooperative Graduate Fellow, 1963–1965.

[2] M. M. Kreevoy, P. J. Steinwand, and W. V. Kayser, *J. Am. Chem. Soc.*, **88**, 124 (1966).

[3] B. T. Baliga and E. Whalley, *Can. J. Chem.*, **42**, 1019 (1964).

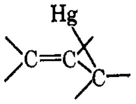

Figure 1.—Suggested structure of the ground state of allylmercuric iodide.

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).