

tion of the aromatic chromophore, *e.g.*, a σ - π^* or n - π^* transition, or expanding the basis set and invoking, *e.g.*, 3d orbitals. In tyrosine, the oxygen atom of the aromatic chromophore is a ready source of nonbonding orbitals for n - π^* transitions, and the long wave length aromatic Cotton effect is detectable without difficulty.³⁻⁶ In phenylalanine, where the 260 $m\mu$ u_e is itself only very weakly allowed to begin with, this important mechanism for producing a properly directed u_m is absent, and only the less effective mechanisms of mixing with σ - π^* transitions or transitions involving 3d or higher orbitals are available. In view of this situation, the exceptional faintness of the 260 $m\mu$ Cotton effect in I becomes understandable.^{9a}

(9a) NOTE ADDED IN PROOF. Since the time of submission of this communication, Hooker and Tanford (private communication) have corroborated the existence of the 260 $m\mu$ Cotton effect for I.

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Carbon-Carbon Bond Reduction by Complex Metal Hydrides. II. Novel Origin of Cyclopropanes¹

Sir:

We wish to report that reduction of allylic alcohols by lithium aluminum hydride² can be carried beyond the saturated alcohol stage to give cyclopropanes as the ultimate reaction products. We have investigated the behavior of cinnamyl derivatives in greater detail.

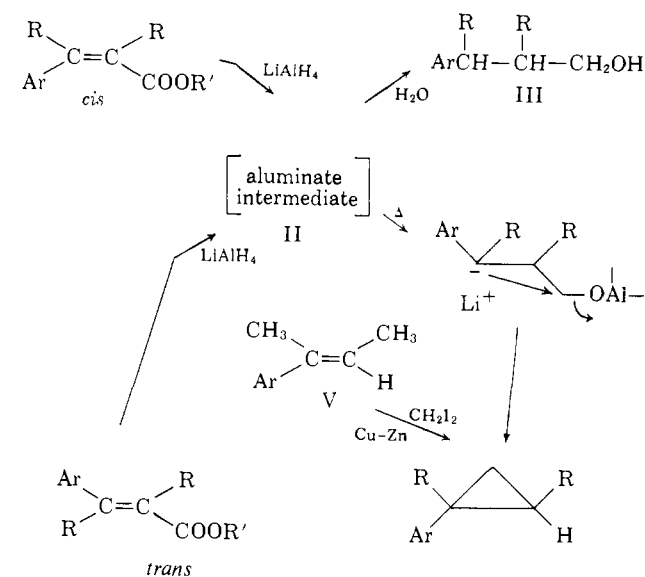
A mixture of *cis* and *trans* ethyl α,β -dimethyl-3,4-dichlorocinnamate (Ia) after reduction in refluxing tetrahydrofuran, under nitrogen, for 1 hr. with a 100% excess of lithium aluminum hydride, followed by neutral or base work-up, gave 45% yield³ of a hydrocarbon, b.p. 78-80° (0.1 mm.). *Anal.* Calcd. for $C_{11}H_{12}Cl_2$: C, 61.42; H, 5.62; Cl, 32.96. Found: C, 61.62; H, 5.81; Cl, 32.68. The n.m.r. spectrum exhibited, in addition to the expected three-proton splitting pattern in the aromatic region, complex absorption corresponding to a total of nine hydrogens at τ 8.7-9.8. This region included a three-proton singlet at τ 8.77 and complex absorption corresponding to one proton at τ 9.4-9.8, peaking strongly at 9.67,⁴ suggesting structure IVa for the hydrocarbon. This assignment of structure and stereochemistry was confirmed by an independent synthesis of IVa in 15% yield *via* the Simmons-Smith reaction,⁵ employing

hydrocarbon V (Ar = 3,4-dichlorophenyl) as starting material.

The double bond reduction of the parent ester Ib took place at a slower rate. In refluxing dimethoxyethane both *cis* and *trans* esters Ib were reduced to the same cyclopropane IVb within 20 hr. At intermediate intervals the conversion to cyclopropane was incomplete; the balance of the product consisted in the case of the *cis* isomer of *threo* alcohol III⁶ (R = CH₃, Ar = phenyl), in the case of the *trans* isomer of small amounts of the same alcohol III and larger amounts of α,β -dimethylcinnamyl alcohol. A mixture of *cis* and *trans* esters Ic, in refluxing tetrahydrofuran, gave cyclopropane IVc in 10 hr.

Ethyl cinnamate is reduced to hydrocinnamyl alcohol within 30 min. at room temperature in ether.² Under these conditions no cyclopropane formation was observed. We have found that more vigorous conditions lead to the formation of phenylcyclopropane (IVd), a 70-hr. reflux in dimethoxyethane yielding 28%⁷ IVd.

The following interpretation is offered for the mechanistic origin of cyclopropanes. It is evident that cyclopropanes result from a reaction taking place subsequent to the formation of an aluminate intermediate.^{2b} This reaction may proceed *via* an internal displacement sequence, in a lithium salt formed from reorganization of the aluminate intermediate, or it may take place *via* a concerted loss of an aluminate species. Steric and electronic factors exert strong control over the reaction; a quantitative correlation of these effects with reaction rate is in progress.



(1) For part I, see M. J. Jorgenson, *Tetrahedron Letters*, **13**, 559 (1962).

(2) (a) N. G. Gaylord, "Reduction with Complex Metal Hydrides," Interscience Publishers, Inc., New York, N. Y., 1956, Chapter 15; (b) F. A. Hochstein and W. G. Brown, *J. Am. Chem. Soc.*, **70**, 3484 (1948); R. F. Nystrom and W. G. Brown, *ibid.*, **69**, 1197 (1947).

(3) The balance consisted of 3- and 4-chloro- α,β -dimethylcinnamyl and hydrocinnamyl alcohols, formed from the reduction of one of the chlorines in the benzene ring. Loss of one chlorine reduces the rate of subsequent cyclopropane formation substantially; less than 5% of monochlorocyclopropane products were formed.

(4) The complex spectrum is caused by virtual coupling of the ring protons with one methyl group *via* the tertiary hydrogen (*cf.* the spectrum of deuterated VII).

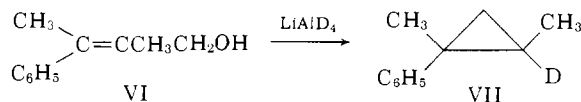
(5) The procedure of R. S. Shank and H. Shechter, *J. Org. Chem.*, **24**, 1825 (1959), was employed.

Ia, R = CH₃; R' = CH₂CH₃; Ar = 3,4-dichlorophenyl
 b, R = R' = CH₃; Ar = phenyl
 c, R = CH₃; R' = CH₂CH₃; Ar = 4-chlorophenyl
 d, R = H; R' = CH₂CH₃; Ar = phenyl
 IVa, R = CH₃; Ar = 3,4-dichlorophenyl
 b, R = CH₃; Ar = phenyl
 c, R = CH₃; Ar = 4-chlorophenyl
 d, R = H; Ar = phenyl

(6) The implications of this stereochemistry with regard to the structure of the intermediate and the mechanism of the reduction will be elaborated in a subsequent publication.

(7) Since the second step appears to be pyrolytic in nature, the experimental procedure should be adaptable to give higher yields in shorter time.

Consistent with the proposed scheme is the observed course of reduction with lithium aluminum deuteride. An isomeric mixture of alcohol VI yields deuterated cyclopropane VII both on water or deuterium oxide work-up. The n.m.r. spectrum of VII, in contrast to that of IVb, is normal, exhibiting the following absorption: a sharp three-proton singlet at τ 8.65, a broad three-proton singlet at τ 8.80, and two broad one-proton doublets centered at τ 8.98 and 9.72 ($J = 4.5$ c.p.s.).



We are investigating in detail the mechanistic course of these reactions and are elucidating the structural features favorable for cyclopropane formation.

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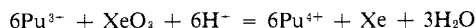
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Oxidation of Plutonium(III) by Xenon Trioxide¹

Sir:

The oxidizing properties of aqueous solutions of xenon trioxide have been described by Williamson and Koch,² and by Appelman and Malm,³ who estimated the xenon-xenon(VI) potential to be -1.8 v. in acid solution. Xenon trioxide is, therefore, one of the most powerful oxidizing agents in acidic aqueous solution, and it has the advantage that its reduced form, xenon, is a relatively insoluble gas and does not contaminate the solution. Despite these advantages, the reactions of xenon trioxide have received little study; the kinetics of only two reactions—the oxidation of bromide and iodide—have been reported.⁴

The xenon-xenon(VI) potential suggests that xenon trioxide should be capable of oxidizing plutonium(III) to plutonium(IV)



We have found this reaction to proceed at a measurable rate, and this communication reports the preliminary results of a study of its kinetics.

The oxidation reaction was studied at $30.0 \pm 0.2^\circ$ in perchlorate solutions with a constant ionic strength ($I = 2.0 M$); the extent of reaction was followed by measurement of the intensity of the plutonium(III) absorption peak at 6000 \AA . with a Cary Model 14 recording spectrophotometer. Runs were made at different plutonium(III), xenon trioxide, and hydrogen

(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission.

(2) S. M. Williamson and C. W. Koch, "Noble Gas Compounds," H. H. Hyman, Ed., University of Chicago Press, Chicago, Ill., 1963, pp. 158-166.

(3) E. H. Appelman and J. G. Malm, *J. Am. Chem. Soc.*, **86**, 2141 (1964).

(4) C. W. Koch and S. M. Williamson, ref. 2, pp. 181-184.

ion initial concentrations, and the data were analyzed using the integrated second-order rate expression. The second-order constants did not vary appreciably as the initial concentrations of the reactants were changed, and second-order plots of the individual runs were straight lines with very little scatter. (Generally the reaction was followed to 50% completion.) The results, shown in Table I, further indicate that the rate

Table I. Second-Order Rate Constants for the Oxidation of Pu^{3+} by XeO_3 (30° , $I = 2.0 M$)

$[\text{Pu(III)}]_0$, M	$[\text{XeO}_3]_0$, M	$[\text{H}^+]$, M	$k \times 10^2$, $\text{l. mole}^{-1} \text{ sec.}^{-1}$
0.0117	0.00097	2.0	1.6
0.0230	0.00097	2.0	1.9
0.0225	0.00194	2.0	1.5
0.0459	0.00194	2.0	1.6
0.0452	0.00388	2.0	1.5
0.0433	0.00388	0.5	1.6

is apparently independent of acidity in the 0.5-2.0 M perchloric acid range. The reaction is therefore second order, and is described by the rate expression

$$-\frac{d[\text{Pu}^{3+}]}{dt} = k[\text{Pu}^{3+}][\text{XeO}_3]$$

with k having an average value of $1.6 \times 10^{-2} \text{ l. mole}^{-1} \text{ sec.}^{-1}$ at 30° . It may therefore be concluded that the rate-controlling step is the reaction of xenon trioxide with plutonium(III) to form an unstable species of xenon in an intermediate oxidation state. Subsequent steps, involving oxidation by transitory lower-valent species of xenon, are all rapid compared to the initial step.

Xenon trioxide also oxidizes plutonium(IV) to plutonyl(VI), but significant competition from this reaction was avoided in the present study by selecting conditions such that the concentration of plutonium(IV) was always much less than that of plutonium(III). Nevertheless, there was a slight drift in values of k toward the end of the reaction in 0.5 M perchloric acid, apparently due to plutonium(IV)-plutonyl(VI) oxidation. Investigation of the oxidation of plutonium(III) and plutonium(IV) by xenon trioxide is continuing and will be described in greater detail later.

Acknowledgments. The xenon trioxide solution used in this study was very kindly supplied by Mr. J. G. Malm of the Chemistry Division, Argonne National Laboratory. The author expresses his appreciation to Mr. P. G. Hagan for experimental assistance and to Mr. G. J. Werkema for aid in the computer analysis of the data. The helpful suggestions of Professor Edward L. King of the University of Colorado Chemistry Department are also acknowledged.

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4-Methyl-4-trichloromethyl-2,5-cyclohexadienylidene

Sir:

We wish to report a new thermal reaction of tosyl-hydrazone¹ salts. Pyrolysis of the sodium salt of 4-