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A Trans Cyclohexene

Sir:

We wish to report experimental evidence for a twisted form of 1-phenylcyclohexene presenting a double bond past orthogonality and commonly called *trans*-1-phenylcyclohexene.

Laser photolysis[1] of 1-phenylcyclohexene (I) in methanol solution at room temperature forms a transient species which absorbs in the range 300-430 nm with a maximum near 380 nm. The lifetime of this transient, $\tau = 1/k_1$, is 9 μs and it is unaffected by the presence of dissolved oxygen. A transient species with absorption characteristics similar to those obtained in methanol solution is also observed in the laser photolysis of I in acetonitrile and cyclohexane solution (lifetimes: 14 and 9 μs, respectively).

In methanol solution, the 1-phenylcyclohexene transient is quenched by hydrogen ion with a rate constant $k_Q = 7.6 \times 10^6$ $M^{-1}\ s^{-1}$, as found by plotting the reciprocal of the decay-time of the transient as a function of added acid concentration. This sensitivity of the transient species to proton concentration is an indication that it may be identical with the intermediate postulated by Kropp[2] on purely photochemical grounds. We now proceed to demonstrate this identity.

Let us consider the classical mechanism of acid-catalyzed photodddition of methanol, where X is the reactive intermediate and II the methyl 1-phenylcyclohexyl ether:

$$\begin{array}{ll}
\mathrm{I} \xrightarrow{h\nu} \mathrm{X} & \varphi \text{ (quantum yield)} \\
\mathrm{X} \rightarrow \mathrm{I} & k_0 \\
\mathrm{X} + \mathrm{H}^+ \rightarrow \text{carbocation} & k_Q|\mathrm{H}^+| \\
\text{carbocation} \xrightarrow{\mathrm{MeOH}} \mathrm{II} & \alpha \text{ (chemical yield)}
\end{array}$$

completed by reactions accounting for photochemical disappearance of I in neat methanol.

$$\begin{array}{ll}
\mathrm{X} + \mathrm{MeOH} \rightarrow \text{carbocation} + \mathrm{MeO}^- & k'|\mathrm{MeOH}| = k'_r \\
\mathrm{X} \xrightarrow{\mathrm{MeOH,I}} \text{products} & k_r''
\end{array}$$ [3]

If ϕ and ϕ' are respectively the quantum yields of disappearance of I and of formation of II, then:

$$\phi = \varphi \frac{k_r + k_Q|\mathrm{H}^+|}{k_1 + k_Q|\mathrm{H}^+|} \tag{1}$$

and

$$\phi' = \varphi' \frac{k_r' + k_Q|\mathrm{H}^+|}{k_1 + k_Q|\mathrm{H}^+|} \tag{1'}$$

with $k_1 = k_0 + k_r' + k_r''$, $k_r = k_r' + k_r''$ and $\varphi' = \alpha\varphi$. The value of ϕ for any H^+ concentration is given by the relation:

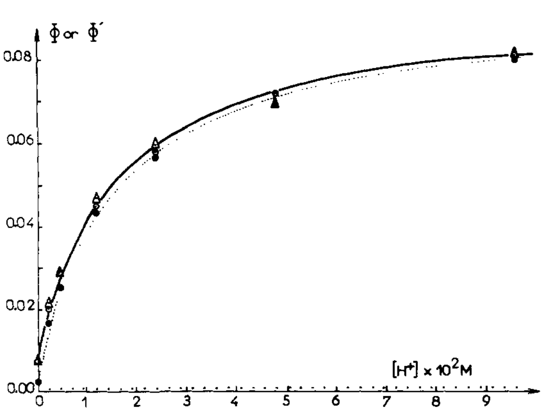

Figure 1. Dependence of the quantum yields ϕ and ϕ' on the hydrogen ion concentration, $|\mathrm{H}^+|$. The curves are the theoretical variations of ϕ (solid line) and ϕ' (dotted line) calculated using the expression (eq 2) given in the text. Plots are experimental values of ϕ measured by uv spectroscopy (⊙) and GC (△) and of ϕ' measured by gc (●).

$$\phi = \frac{\phi_0 + \varphi|\mathrm{H}^+|k_Q/k_1}{1 + |\mathrm{H}^+|k_Q/k_1} \tag{2}$$

From two particular values of ϕ, measured in neat methanol and in an acid solution ($\mathrm{H}^+ = 0.096$ N) and respectively denoted ϕ_0 and ϕ_1, combined with the values of k_1 and k_Q measured in the laser-photolysis experiments reported above, we calculate: first, the value of $\varphi = 0.082$ obtained from

$$\varphi = \phi_1 + \frac{k_1(\phi_1 - \phi_0)}{0.096 k_Q}$$

derived from relation 2 then the function

$$\frac{\phi_0 + \varphi|\mathrm{H}^+|k_Q/k_1}{1 + |\mathrm{H}^+|k_Q/k_1} = f(\mathrm{H}^+)$$

represented in Figure 1 (solid line).

Relations 1 and 1′ having identical functional dependence, the same treatment applies to quantum yields ϕ', ϕ_0', ϕ_1', and φ'. Measurements of ϕ and ϕ' [4] for other H^+ concentrations give the experimental values also plotted in Figure 1. The good agreement of the experimental plots with the calculated curves indicates that relation 2 is verified within experimental errors. Therefore the ratio k_Q/k_1 is the same for the reactive intermediate involved in the above mechanism and for the transient observed in laser-photolysis experiments. Such a coincidence would be highly improbable if there were two different species; this leads us to conclude that the transient observed in laser photolysis is the reactive intermediate involved in Markovnikov addition reactions.

The observed intermediate can be potentially identified with (a) orthogonal triplet phenylcyclohexene A, (b) an orthogonal zwitterionic phenylcyclohexene B, or (c) the trans phenylcyclohexene C (with partial singlet diradical character if the twist is not fully completed to 180°).

Rosenberg and Serve[5] identified the reactive intermediate with the triplet state. In fact their experiments, as well as many other works[6] on sensitization of the photosolvatation of cycloalkenes by triplet donors, demonstrate only that the triplet state is either the reactive intermediate or a precursor of this intermediate. The intermediate is not quenched by dissolved oxygen and its lifetime would be surprisingly long for an orthogonal alkene triplet;[7] hence intermediate A is highly improbable but our work is consistent with the possibility that the triplet, like the singlet, is a precursor of the intermediate, without being the intermediate itself.

The chemistry of the intermediate is consistent with both B and C. Although our initial purpose was to trap a zwitterionic intermediate such as B, the relative insensitivity of lifetime to the polar nature of the solvent appears to rule out the sol-

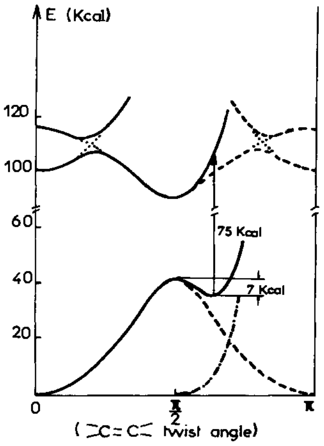

Figure 2. Estimated potential surfaces of 1-phenylcyclohexene (—) constructed as the sum of 1-phenylpropene surfaces (- - -) and of a ring constraint energy curve (-·-·-·).

vent-stabilized zwitterion B.[8] Hence, in all likelihood, the observed intermediate must be the trans phenylcyclohexene C. It is appreciated that, in the classical sense, the molecule cannot be fully trans. It must be highly twisted and slightly past orthogonality. This hypothesis is substantiated by the increase in transition energy when going from *trans*-phenylcyclohexene to the corresponding *trans*-phenylcycloheptene intermediate, the absorption of which peaks at 305 nm.[9] Approximate potential surfaces of 1-phenylcyclohexene can be obtained as the sum of the ordinary dumbbell curves for cis–trans isomerization and of a steeply rising curve due to ring-strain for twist angles of the double bond above 90°.[10,11] In Figure 2, the dumbbell curves are drawn with the 42 kcal energy barrier in the ground state and 25 kcal energy well in the excited state reported[12] for the 1-phenylpropene. The strain energy curve is empirically adjusted to obtain, on the ground state surface, an energy barrier equal to the energy of activation for return from *trans*- to *cis*-phenylcyclohexene (~7 kcal as calculated from temperature dependence of the lifetime of the transient) and, between the ground state and the excited state surfaces, a 75 kcal energy gap corresponding to the optical absorption of the transient. Of course the equilibrium angle for the trans species depends on the shape of the two dumbbell curves; therefore the value of 115° found in the figure must be considered as tentative.[13]

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References and Notes

(1) We used a frequency doubled neodymium glass laser which provides a pulse of 265-nm light with a duration of about 3×10^{-8} s. The concentration of 1-phenylcyclohexene (K and K) in methanol (Prolabo, U.V. spectroscopic grade) was about 10^{-4} M.

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(3) The first-order rate constant k_r'' is equivalent to the sum of the rates of all processes leading to products such as phenylcyclohexane, dimer of I, 1-hydroxymethyl-1-phenylcyclohexane, etc . . . .

(4) ϕ and ϕ' were measured under continuous illumination by the 2537 Å line of a low pressure mercury lamp, isolated by an interferential filter. The absorbed light flux was measured by actinometry. The rate of disappearance of I was measured by both uv spectroscopy and gas-phase chromatography. The rate of formation of II was measured by gas-phase chromatography after identification by comparison with an authentic specimen prepared by J. P. Desvergnes. Tridecane was used as internal reference in the GC experiments.

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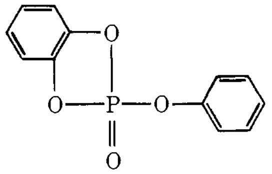
Experimental Evidence in Support of Oxyphosphorane Intermediates in Reactions of Cyclic Phosphate Esters

Sir:

The existence of stable *oxyphosphoranes*[1] is well established. The hypothesis that oxyphosphoranes are formed as transient intermediates in nucleophilic displacements of compounds with tetracoordinate phosphorus has been a fruitful concept in the interpretation of the chemical and stereochemical behavior of phosphonium salts and phosphate esters,[2] and has also led to useful synthetic reactions.[3] However, the direct observation or trapping of such intermediates has remained an elusive goal.[4]

We have carried out reactions of phosphate esters which can be interpreted as proceeding via oxyphosphorane intermediates, and have slightly modified the same phosphate esters in order to trap the postulated intermediates. The results are summarized in this communication.

Phenyl *o*-phenylene phosphate[4a] (**1**) reacts with *O*-trimethylsilylphenol[5] (**2**) in aprotic solvents, under amine catalysis, to form diphenyl (2-trimethylsilyloxy)phenyl phosphate[6] (**3**).



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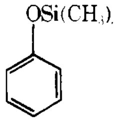
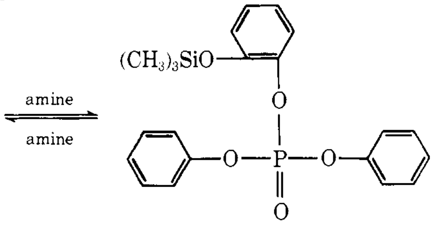


2

1, δ^{31}P −6.2 ppm



3, δ^{31}P +16.8 ppm

This novel reaction is reversible, and reaches a state of equilibrium between the two reagents and the product. The ratio of cyclic **1** to acyclic **3** phosphates is about 2/1 at 35° in