

the triene in proportionate yield. We have employed this reaction as a highly sensitive method of determining water concentrations in the submillimolar region. In the absence of active quaternary ammonium ions, either wave will serve to quantitatively indicate the presence of protic impurities in the solution. In the presence of TBA⁺, however, the triene wave alone is quantitatively responsive to protons from water donors.

Of fundamental importance to studies of aromaticity is the lack of any observable electrochemical reduction of the radical anion product of reaction 1. There is no evidence that the Hückel aromatic 10 π -electron dianion can be formed in the solvent-electrolyte system studied here. Guidance in interpretation of this result may be found in recent theoretical calculations of the heat of formation of the COT dianion,⁵ which is estimated to require approximately 80 kcal/mol more than formation of either the planar or puckered radical anion. Thus, in the absence of extremely strong preferential interactions between the dianion and components of the condensed phase (*i.e.*, existence of large organizational entropy terms favoring formation of the dianion plus parent over two radical anions), the predicted difference between the reduction potentials of COT and COT \cdot^- would be 3 V. Clearly the aromatic dianion is very difficult to attain by electrochemical reduction.

Lastly, these results call into serious question the generality of a basic assumption made extensively in interpretation of successive electrochemical reductions. The difference in half-wave potentials between the addition of the first and second electron to fused polycyclic aromatics is reported to be approximately -0.4 V.⁶ Most of the data on which these conclusions are based were obtained in 95% dioxane-water solutions, where protonation reactions are known to be extremely rapid. Substitution of aprotic solvents for the dioxane-water has usually been accompanied (for reasons of solubility) by introduction of alkylammonium ions in the background electrolyte, which must themselves be suspected of rapid reaction with radical anion products. The results described here indicate that before valid correlations may be made between observed half-wave potentials and quantum mechanical properties of olefinic and aromatic systems, it is necessary to *unequivocally* establish the mechanism of each reaction under consideration.

The data presented here virtually rule out the possibility that the dianion of COT may be achieved through electrochemical reduction in these media. They do not explain the apparent existence of the dianion as a product of the alkali metal reduction of COT. Indeed, considering the ready reducibility of alkali metal ions at the dropping mercury electrode in the vicinity of -2.5 V *vs.* sce, we are currently pursuing studies of structure and properties of the product of reaction of 2 equiv of alkali metal with COT.

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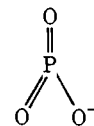
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Oxygen-18 Isotope Effect in the Hydrolysis of 2,4-Dinitrophenyl Phosphate. A Monomeric Metaphosphate Mechanism

Sir:

The role of the monomeric metaphosphate ion intermediate, **1**, in the unimolecular decomposition of phos-



1

phate monoesters has been the subject of much investigation. Numerous studies on such esters as methyl phosphate,¹ acetyl phosphate,² and aryl phosphates^{3,4} have attempted to use pH-rate profile data, entropy of activation comparisons, solvent effects, etc., to confirm the metaphosphate hypothesis. While a substantial body of data now exists⁵ which appears consistent only with the metaphosphate mechanism, as suggested by Jencks,² no one piece of evidence is conclusive in itself, and support for this mechanism must rest upon the accumulation of a sufficient number of reasonable arguments. We now wish to report the ester-oxygen ¹⁸O-isotope effect for the hydrolysis of the dianion of a monoaryl phosphate ester (ArO*PO₃²⁻). We believe this represents the most convincing evidence yet given for this mechanism.

Heavy-atom isotope effects have been shown to be a powerful investigative tool of the mechanistic chemist.⁶ Large (2-4%) ¹³C and ¹⁵N isotope effects have been demonstrated (and theoretically justified⁷) to indicate substantial bond breaking or bond order change in the transition state.^{6,8} Although ¹⁸O-isotope effects have been used only rarely,⁹ they should be just as useful as the other heavy-atom effects in delineating reaction mechanisms.

We have chosen to measure the isotope effect by a direct kinetic approach,¹⁰ comparing the rate of hydrolysis of the aryl ¹⁸O-2,4-dinitrophenyl phosphate to that of the ¹⁶O ester. The mono-2,6-lutidinium salts of the phosphate esters were prepared from the appropriate phenol oxygen labeled, 2,4-dinitrophenol by the method of Kirby and Varvoglis.⁴ The ¹⁸O-labeled phenol was prepared by the reaction of redistilled 2,4-

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Table I. Selected Rate Constants for the Hydrolysis of Aryl ^{18}O - and ^{16}O -2,4-Dinitrophenyl Phosphate

pH	Conditions ^a		$k_{^{16}\text{O}},^b \text{ sec}^{-1} (\times 10^3)$		$k_{^{18}\text{O}},^b \text{ sec}^{-1} (\times 10^3)$		$k_{^{18}\text{O}}/k_{^{16}\text{O}}$
	Phosphate buffer concn, M	Temp, °C ^c					
7.72	0.025	51.1	0.4733	0.4695	0.4663	0.4620	1.0157
7.72	0.025	51.1	0.4737	0.4652	0.4588	0.4577	1.0244
7.70	0.010	51.0	0.4473	0.4500	0.4416	0.4400	0.0193
7.70	0.010	51.0	0.4464	0.4445	0.4374	0.4360	1.0249
7.70	0.010	51.0	0.4333	0.4301	0.4255	0.4185	1.0200
7.62	0.005	51.1	0.4799	0.4849	0.4716	0.4716	1.0230
7.70	0.010	39.0	0.08101	0.07931	0.07815	0.07830	1.0184
7.70	0.010	38.9	0.07736	0.07803	0.07658	0.07635	1.0161
8.0	0.05	55.0	0.8268		0.8160	0.8235	1.0225
4.4	0.05	51.0	0.07019		0.06869		1.0226

^a Ionic strength maintained at 0.05 M with KCl. ^b ^{16}O and ^{18}O samples were run concurrently in sets of three or four. ^c Temperature precision during a given run is $\pm 0.05^\circ$. Accuracy of the temperature from one run to another is $\pm 0.20^\circ$.

dinitrofluorobenzene with excess 98% H_2^{18}O (Bio-Rad) in the presence of anhydrous, redistilled 2,6-lutidine. After 3 days at 80° the mixture was bulb-to-bulb distilled to recover the unreacted H_2^{18}O and lutidine. The remaining solid was extracted with sodium bicarbonate solution, and the aqueous solution acidi-

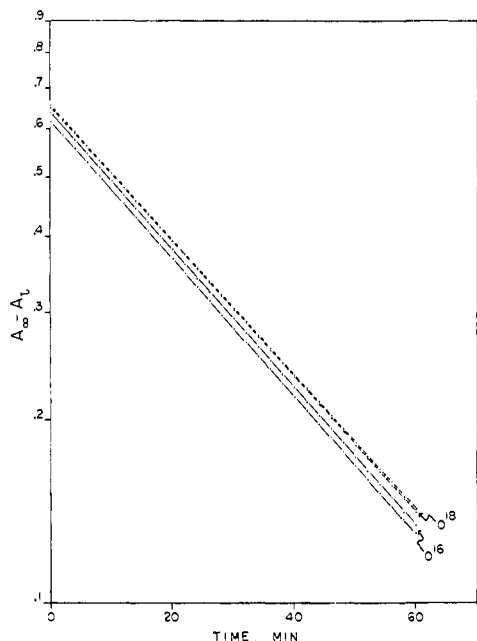


Figure 1. Plot of first-order rates of hydrolysis of aryl ^{16}O - (—) and aryl ^{18}O - (---) 2,4-dinitrophenyl phosphate at 51.0° and pH 7.7 phosphate buffer.

fied and extracted with benzene. The benzene solution was evaporated and the ^{18}O -2,4-dinitrophenol was recrystallized from ethanol, yielding 100 mg, mp 112 – 113° (lit.¹¹ mp 111.6°), of the yellow crystals. Comparison of the m/e 186–184 peaks on a Perkin-Elmer Model 270 mass spectrometer shows that less than 6% ^{16}O -phenol is present. Synthesis of the phosphate ester from the labeled phenol yielded, after recrystallization, 45 mg of white crystals, mp 143 – 144° (lit.⁴ mp of 142° for the ^{16}O ester).

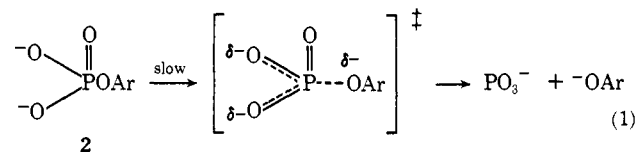
Kinetics were determined on a Zeiss PMQ-II or a Cary 16K uv-vis spectrophotometer. Reactions were followed by the appearance of 2,4-dinitrophenoxide for

(11) Beilstein, 6, 251.

at least 2 half-lives and the infinity absorbance values taken after 10 or more half-lives. Excellent first-order rate constants (errors less than $\pm 0.5\%$) were determined both by hand plotting of the absorbance data and by computer calculation with an infinity varying, least-squares program. All errors are standard deviations.

Typical plots are shown in Figure 1 and representative rate constants are presented in Table I. Since no discernible trend in the isotope effect in the temperature range 39 – 55° and the pH range 4.4 – 8.0 in any buffer solution was observed, all values were statistically analyzed together to give an isotope effect of 1.0204 ± 0.0044 . Since this value is more than four standard deviations from unity (*i.e.*, no isotope effect) we can state with greater than 99%¹² confidence that at least some isotope effect is experimentally verifiable. It should be noted that an isotope effect less than 1.000 was *never* observed in any of the more than 30 kinetic runs made.

Kirby and Varvoglis⁴ and Bunton, *et al.*,¹³ have previously shown that the hydrolysis of the dianion of 2,4-dinitrophenyl phosphate (2) occurs *via* P–O cleavage and that the reaction probably proceeds through a monomeric metaphosphate ion mechanism. Our observation of a large ^{18}O -isotope effect in this reaction strongly indicates that substantial P–O bond breaking is occurring in the transition state, as shown in eq 1.



While our result may definitely rule out only those mechanisms which do not involve a rate-determining P–O bond cleavage (such as rate-determining hydration or rate-determining pseudorotation of a pentacovalent intermediate^{14,15}), alternative schemes involving either rate-limiting breakdown of a pentacovalent intermediate or direct $\text{S}_{\text{N}}2$ -type displacement unfortunately are not completely eliminated. However, in a preliminary study we have found *no* isotope effect in the hydrolysis of dibenzyl 2,4-dinitrophenyl phosphate to yield 2,4-

(12) A simple t-test calculation: F. Rohlf and R. Sokal, "Statistical Tables," W. H. Freeman, San Francisco, Calif., 1969, pp 159–161.

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dinitrophenol. Hydrolysis of the triester must necessarily proceed *via* either an addition-elimination or a direct $S_N2(P)$ mechanism.⁵ This would indicate (but again certainly not prove) that only in a unimolecular metaphosphate mechanism will an isotope effect be observed.

Details of these results as well as those of a diester hydrolysis and enzymatic systems will be presented later.

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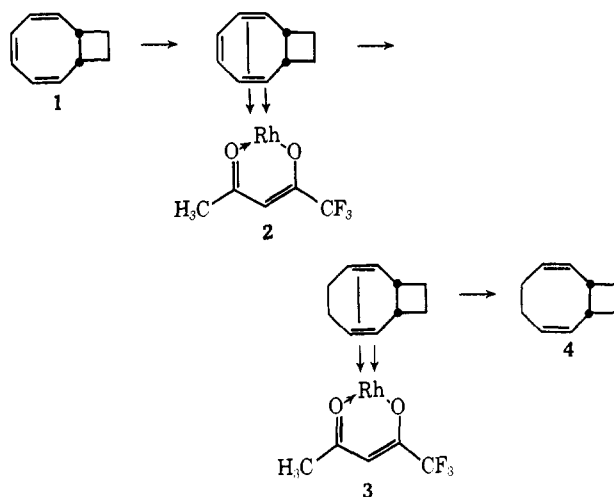
cis-Bicyclo[6.2.0]deca-2,6-diene¹

Sir:

The visualization of a degenerate Cope rearrangement has been very fruitful, leading to the celebrated homotropilidene² and bullvalene³ with fluxional structures. On the same concept was based the synthesis of *trans*-bicyclo[8.4.0]tetradeca-*trans*-2,8-diene,⁴ whose degenerate Cope rearrangement is not fast enough to give a dynamic nmr spectrum, but reveals itself by the racemization of the optically active compound.⁵ In fact, the whole series of bicyclo[(*n* + 4).*n*.0]di-(*n* + 4)-enes may be expected to undergo this kind of rearrangement. We describe here the synthesis of *cis*-bicyclo[6.2.0]deca-2,6-diene (**4**), the next higher homolog of homotropilidene in this series.

Treating *cis*-bicyclo[6.2.0]deca-2,4,6-triene (**1**)⁶ with dicarbonyltrifluoroacetylacetonatorhodium(I)⁷ in hexane solution yielded complex **2** (87% after sublimation at 90° (0.005 mm); mp 91°)⁸ in which both outer double bonds of the starting triene are attached to the metal, due to the preferred square-planar geometry of tetracoordinated Rh(I). The complex **2** smoothly absorbed 1 mol equiv of hydrogen in hexane solution over 5% Pd/C. The resulting complex **3** (93%; mp 108°),⁸ exhibiting in the vinyl region of the nmr spectrum only a singlet at τ (CCl₄) 4.25 due to the enolic proton of the trifluoroacetylacetonate ligand, was decomposed by shaking a pentane solution with 10% aqueous KCN. After filtration through alumina and evaporation of the solvent, *cis*-bicyclo[6.2.0]deca-2,6-diene (**4**) was obtained in 90% yield.

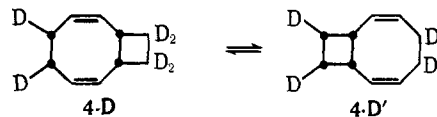
The structural assignment is based on the nmr spectrum, shown in Figure 1A [τ 4.62 (four olefinic protons), 6.65 (two bridgehead protons), 7.4–8.4 (eight



methylene protons]), and on the ozonolysis followed by work-up with peracetic acid and diazomethane which gave *cis*-1,2-dicarbomethoxycyclobutane and dimethyl succinate.

The nmr spectrum of **4** does not show averaged shifts or temperature-dependent line shapes, characteristic for a rapidly reversible process. Thus, the degenerate Cope rearrangement had to be detected by isotopic labeling. 9,9,10,10-Tetradeuterio-*cis*-bicyclo[6.2.0]deca-2,4,6-triene, obtained by Staley's synthesis with tetradeuterio-1,2-dibromoethane, was selectively deuterated at the central double bond as above *via* the rhodium complex. The resulting 4,5,9,9,10,10-hexadeuterio-*cis*-bicyclo[6.2.0]deca-2,6-diene (**4-D**) shows in its nmr spectrum (Figure 1B), with H,D decoupling, three sharp signals at τ 4.66, 6.70, and 7.66 for the olefinic protons, the bridgehead protons, and the two remaining methylene protons, respectively. As indicated by their narrow peak, these latter protons are of only one type. Accordingly, the addition of D₂ was regio- as well as stereoselective and the Cope rearrangement had not occurred during the preparation, including glpc at 120°. Since the two remaining methylene protons absorb at lowest field of all the methylene protons in **4**, we assign to them the *trans* configuration (with respect to the attached cyclobutane ring) which, in the open conformation, locates them in the deshielding zone⁹ of the flanking double bonds.

Heating to 135° for 3 hr had no effect on **4-D**; indeed, 30 min at 180° was needed to bring about a change in the spectrum of the structurally unaffected compound.



After heating for 3 hr at 185° in the gas phase, **4-D** gives the spectrum shown in Figure 1C, which is interpreted as arising from the equilibrium mixture of **4-D** with its Cope rearrangement product **4-D'**. The methylene protons in the cyclobutane ring of **4-D'** couple with the bridgehead protons in an A₂X₂ manner ($J_{A,X} = J_{A,X'} = 5$ Hz) giving rise to two triplets at τ 6.70 and 7.90, the former being superimposed by the

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