

- in dry *n*-hexane, 1–2% in HOAc, and ~8% in ethanol.
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IpsO Nitration. A Study of the Migratory Aptitude of the Nitro Group in the 1,2-Dimethyl-1-nitrocyclohexadienyl Cation

Sir:

Trapping studies indicate that the ipso ion, 1,2-dimethyl-1-nitrocyclohexadienyl cation (**1**), is formed in >50% yield upon nitration of 1,2-dimethylbenzene.^{1,2} Ion **1** is known to undergo nitro group migration to yield 1,2-dimethyl-3-nitrobenzene (**2**) in acidic, weakly nucleophilic media.^{3,4} We report here results of labeling experiments designed to characterize the nitro group migrations in this cationic system.

This study required the development of a new method of synthesis, one that would yield an unambiguously labeled ipso adduct. 3,4-Dimethyl-4-nitrocyclohexadienone proved to be the key intermediate. As indicated in Scheme I, 3,4-dimethylphenol-2,6-*d*₂ was prepared by repeated exchange in acidified deuterium oxide. Nitration of the acetate derivative in acetic anhydride gave 3,4-dimethyl-4-nitrocyclohexadienone-2,6-*d*₂ in 80% yield.⁵ Reduction of the labeled dienone with sodium borohydride in methanol at 0 °C gave crude 3,4-dimethyl-4-nitrocyclohexadienol-2,6-*d*₂.⁶ The crude dienol was solvolyzed at 0 °C in 85 wt % sulfuric acid, Scheme II. 1,2-Dimethyl-3-nitrobenzene was isolated in 50% overall yield from the dienone.⁷ Careful chromatographic analysis showed that the nitration product was isomerically pure. No 1,2-

dimethyl-4-nitrobenzene could be detected with detection limits of <0.1%. Integration of the ¹H NMR spectrum indicated equal amounts of 1,2-dimethyl-3-nitrobenzene-4,6-*d*₂ (**2-d**₂) and 1,2-dimethyl-3-nitrobenzene-5-*d*₁ (**2-d**₁). Low voltage (11 eV) mass spectrometry indicated a **2-d**₂:**2-d**₁ ratio of 1.021 ± 0.014.⁸

Earlier reports rule out intermolecular transfer of the nitro group during rearrangement in this system.^{1,3,4} The present results confirm the absence of the 4-nitro isomer, and lower detection limits are established. An intramolecular 1,2 shift of the nitro group appears to summarize the data adequately. If this is granted, the distribution of labeled **2-d**₂ and **2-d**₁ provides a measure of the relative rate of migration of a nitro group to an equivalent ipso site vs. migration to an adjacent, open site bearing a hydrogen, Scheme II. With the assumptions that the isotopic isomers of **1** shown are steady-state intermediates and that $k_{\text{ipso}} = k_{\text{ipso}'}$ and $k_o = k_o'$, it may be shown that

$$k_o/k_{\text{ipso}} = [(2-d_2/2-d_1) - 1]$$

This leads directly to the conclusion that the rate of a 1,2 shift of a nitro group to an open position, k_o , is about one-fiftieth of the rate of migration to an equivalent ipso position, k_{ipso} . The nature of the competitive method is such that uncertainties in the ratio are quite large when rates compared are different. It should also be recognized that the scheme has neglected the difference in rates of k_o and k_o' that might be anticipated owing to hybridization changes in the migration transition state. Presumably this secondary isotope effect, k_o/k_o' , is less than unity, and correction of the equation shown above would increase k_o/k_{ipso} estimates.⁹ Despite numerical uncertainties, it seems safe to conclude that migration of a nitro group in **1** to an equivalent ipso site is sufficiently fast so that the isotopic isomers of **1** are nearly equilibrated before migration occurs to an open position.^{10,11}

Are these results consistent with Perrin's suggestion that nitro group migrations occur via an aromatic radical cation-radical pair?¹² Perrin's model does predict a small $k_o:k_{\text{ipso}}$ ratio, since spin density of the *o*-xylene radical cation is large at the ipso positions (C-1 and C-2) and vanishingly small at the adjacent open positions (C-3 and C-6),¹³ but, if this is granted, one must also expect that in the course of repeated dissociations and recombinations a reasonable fraction of the $\cdot\text{NO}_2$ would leak across the ring carbons of very low spin density to C-4 and C-5 where spin density is nearly as large as at C-1 and C-2. However, no trace of this leakage product, 1,2-dimethyl-4-nitrobenzene, has been found. It is most difficult to reconcile this result with Perrin's model without introducing very restrictive and cumbersome conditions involving highly oriented or strongly perturbed radical ion-radical pairs. Such conditions appear to be the operational equivalent of a two-electron three-center 1,2 shift.

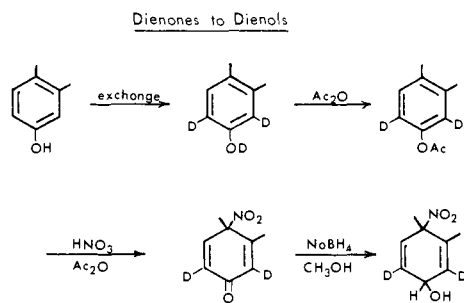
It should be noted that the synthetic method used to prepare 1,2-dimethyl-3-nitrobenzene in this study may represent a generally useful procedure for conversion of *o*- and *p*-alkylphenols to isomerically pure *o*-alkylnitrobenzenes. The synthetic utility of this procedure is under active study.

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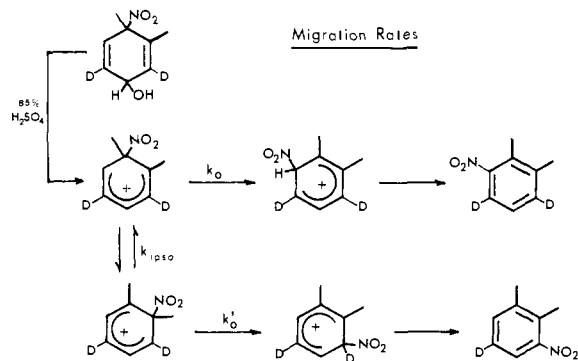
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Scheme I



Scheme II



$M^+_{(m/e)}$	153	152
intensity	1.021	1.000
$k_o/k_{\text{ipso}} = 0.02$		

issue.

- (6) The more general use of 1,2-carbonyl addition reactions to convert nitrocyclohexadienones to nitrocyclohexadienols has not escaped our attention. The method is presently being employed as a useful and often the preferred method of ipso adduct synthesis.
- (7) The major by-products were nitroxylenols formed by thermal rearrangement of the dienone reactant.⁵
- (8) Ratio reported is that obtained after correction for ¹³C and the small amount of residual protium at C-2 and C-6 of the labeled phenol.
- (9) If $k_o \neq k_o'$, the equation shown takes the following form

$$k_o/k_{\text{ipso}} = \{(2-d_2)/(2-d_1) - k_o/k_o'\}$$

- (10) Near equilibration may be taken to imply that $k_o/k_{\text{ipso}} < 0.1$.
- (11) This result might have been predicted on the basis of Hahn's report that strong acid solvolysis of a crude mixture containing 87% 3-isopropyl-4-methyl-4-nitrocyclohexadienyl acetate and 13% 4-isopropyl-3-methyl-4-nitrocyclohexadienyl acetate gave 10% 3-isopropyl-2-methylnitrobenzene and 90% *o*-nitrotoluene (via nitrodeisopropylation): R. C. Hahn, H. Shosenji, and D. L. Strack, *ACS Symp. Ser.*, **No. 22**, 95 (1975).
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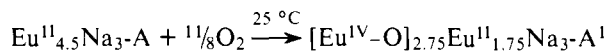
Europium(IV), a New Oxidation State for Europium. Crystal Structure of Dehydrated Europium(II)-Exchanged Sodium Zeolite A, Eu_{4.5}Na₃-A, Partially Oxidized by Oxygen

Sir:

Oxygen gas at a pressure of 1 atm was sorbed into a single crystal of vacuum-dehydrated europium(II)-exchanged zeolite A, Eu_{4.5}Na₃-A,¹ at 25 °C. As a result, ~2.75 previously three-coordinate near-planar Eu(II) ions per unit cell became four coordinate, according to a crystal structure determination, having added one oxide ion each to their coordination spheres. These oxide ions extend into the sodalite cavities² where they participate in no additional coordination interactions. They are therefore one coordinate. The net reaction



has occurred 2.75 times per unit cell to give a product in which the formal oxidation state of 2.75 europium ions is +4. The overall reaction per unit cell is



It was anticipated that the exposure of oxygen to dehydrated Eu(II)-exchanged zeolite A would result either in (1) no reaction, (2) the formation of a dioxygen complex which would be stable within the zeolite, or (3) a reaction to form Eu(III) ions bridged by oxides in the sodalite unit. The oxidation of europium to the tetravalent state, resulting from the coordination of a single nonbridging oxide ion, was unexpected.

Apparently a structure involving Eu(III) and bridging oxide ions has not occurred because of the reluctance of the europium ions to leave their sites of close approach to the zeolite framework. The rigid structure and relatively uniform charge distribution of the oxide ions of the zeolite framework constrains the europium ions to positions which are relatively far apart.

The exposure of dehydrated Eu(II)-exchanged zeolite A to an even stronger oxidizing agent, chlorine gas, leads to a five-coordinate trigonal-bipyramidal europium(IV) chloride complex containing two chloride ions coordinated axially to each Eu(IV) ion. This structure is reported in the following communication.³

A single crystal of sodium zeolite 4A, Na₁₂-A,¹ 0.085 mm

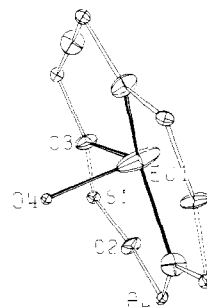


Figure 1. The four-coordinate Eu(IV) complex. The structure shown occurs ~2.75 times per unit cell. Selected bond lengths in angstroms are Eu(1)-O(3) = 2.284 (9) and Eu(1)-O(4) = 2.13 (4); some bond angles are O(3)-Eu(1)-O(3) = 118.4 (7)° and O(3)-Eu(1)-O(4) = 82.7 (3)°. Ellipsoids of 20% probability are shown.

on an edge, was lodged in a fine glass capillary. Lemon yellow Eu(OH)₂ was synthesized by a modification of Bärnighausens' method⁴ under anoxic conditions. Ion exchange proceeded for 4 days in the dark under a nitrogen atmosphere by allowing a saturated aqueous solution of Eu(OH)₂ to flow past the crystal at ~1.0 mm/s. The colorless crystal was then dehydrated for 48 h at 400 °C and 5 × 10⁻⁶ Torr. Microscopic examination showed the crystal to be undamaged; it had developed the bright orange color characteristic of dehydrated Eu(II)-exchanged zeolite A. Finally, the crystal was treated at 25 °C with 760 Torr of zeolitically dried high purity oxygen (99.99%) for 1 h. The capillary containing the crystal was then removed from the vacuum line by torch under 700 Torr of oxygen.

The space group *Pm3m* (no systematic absences) was used throughout this work for reasons discussed previously;^{2a} $a = 12.238$ (2) Å at 23 °C. The structure was solved using the 343 unique observed ($I_o > 3\sigma(I_o)$; $2\theta < 70^\circ$) reflections collected by counter methods using a fully automated Syntex P1 diffractometer with monochromatic Mo K α radiation ($K\alpha_1$, $\lambda = 0.70930$ Å; $K\alpha_2$, $\lambda = 0.71359$ Å) and a pulse-height analyzer. Other experimental details including data reduction are the same as previously presented.⁵ The value of x in the formula of the unit cell, Eu _{x} Na_{12-2 x} Si₁₂Al₁₂O₄₈, exclusive of oxide ions at O(4), was determined to be 4.5 by refinement of the occupancies of europium positions.

Full-matrix least-squares refinement⁶ using anisotropic temperature factors for all positions except O(4) and Na, which were refined isotropically, converged to the error indices, $R_1 = (\sum |F_o - |F_c|| / \sum F_o) = 0.097$ and $R_2 = (\sum w(F_o - |F_c|)^2 / \sum wF_o^2)^{1/2} = 0.095$ at the fixed occupancies shown in Table I. Simultaneous positional, occupancy, and thermal parameter refinement of the Eu(1), Eu(2), Eu(3), O(4), and Na positions led to the occupancy values given in the next to the last column of Table I with nearly no change in the error indices. Decreasing the occupancy of Eu(1) to 2.5 ions per unit cell or increasing it to 3.0, increased R_1 by 0.0005 and 0.004, respectively, as all other parameters varied to convergence. As a result the occupancy of Eu(1) was fixed at 2.75 ions per unit cell. The overdetermination ratio is 9.8 for the 35 parameters varied in least squares.

The Eu(IV) ions are four coordinate, as can be seen in Figure 1. They lie near the planes of 6-rings and coordinate to three O(3) oxide ions of the zeolite framework and to one threefold axis oxide ion, O(4), which extends into the sodalite unit. Each oxide ion at O(4) coordinates only to one Eu(IV) ion at Eu(1). The unusual geometry of the four-coordinate Eu(IV) complex can best be described as a slightly inverted trigonal pyramid.

The Eu(1)-O(3) bond distance, 2.28 Å, is almost 0.1 Å less than the threefold-axis Eu(II)-O(3) bond found in dehydrated Eu_{11.75}-A.⁷ The Eu(1)-O(4) bond at 2.14 Å is very near the sum of the appropriate ionic radii, 2.17 Å, assuming an ionic