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THE OXIDATION OF CYCLOPROPANES BY CERIC AMMONIUM NITRATE

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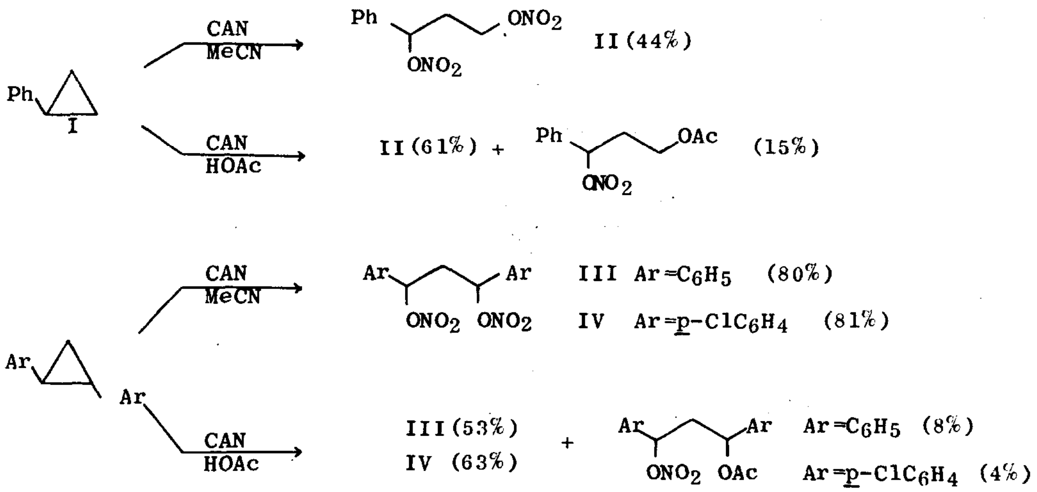
Although electrophilic attack on the cyclopropane ring is well established (1-6), it has not previously been established that certain cyclopropanes are readily susceptable to reaction with one-electron oxidizing agents. I wish to report that ceric ammonium nitrate (CAN), $(NH_4)_2Ce(NO_3)_6$, cleaves arylcyclopropanes readily at room temperature with the formation of dinitrates and nitrate acetates formally derived from the most stable dication. The results are summarized in Chart I.

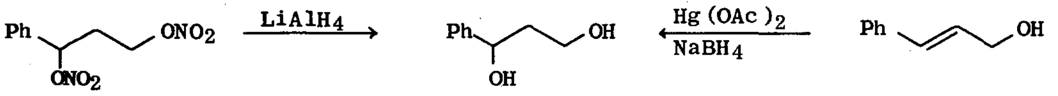
Chart I

Summary of the Reactions of Ceric Ammonium Nitrate with Cyclopropanes



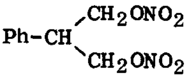
In a typical experiment, 0.50g (4.24 mmoles) of phenylcyclopropane (I) was dissolved in 18.6 ml of anhydrous acetonitrile and 5.11g (9.3 mmoles) of primary standard grade CAN was added. The reaction mixture was stirred at room temperature. The orange cerium(IV) salt dissolved and as the reaction proceeded, a yellow-white solid (Ce(III) salts) precipitated. After 23 hours, the yellow reaction mixture was poured into water and extracted with ether. To the crude isolated product was added a weighed amount of methylene iodide as standard, and the yields of products were obtained by integration of the nuclear magnetic resonance (nmr) spectrum. Oxidation occurred more rapidly in acetonitrile than in acetic acid, and diarylcyclopropanes reacted more rapidly than phenylcyclopropane.

That the reaction product was an alkyl nitrate was verified by its characteristic infrared (ir) spectrum (7) which showed strong absorptions at 1640, 1280, 850, 755, and 700 cm^{-1}. The nmr spectrum was consistent with structure II (chemical shifts are in p.p.m. downfield from TMS): δ7.37, 5H, singlet; δ5.93, 1H, structured triplet; δ4.48, 2H, structured triplet; _ca_. δ2.3, 2H, multiplet. These chemical shifts can be compared with those for the α protons in _n_-butyl nitrate, δ4.48, and in benzyl nitrate, δ5.30. The mass spectrum of the reaction product shows a weak parent ion at m/e = 242. Further evidence for structure II was furnished by the lithium aluminum hydride reduction of II to a diol (8), the nmr spectrum of which was identical to that of the diol prepared by the oxymercuration-reduction of cinnamyl alcohol (eq 1) (9).



II (1)

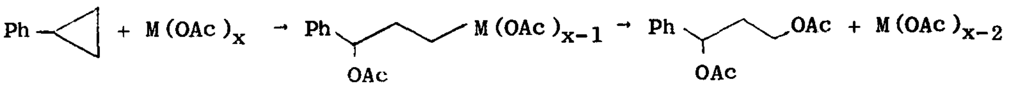
The absence of the symmetrical cleavage product, V, is apparent from the nmr spectrum of the product which shows no doublet at δ4.7-4.8 for the hydrogens α to the nitrates. Dinitrates III and IV were identified by their characteristic ir and nmr spectra. The absence of cleavage products other than those shown in Chart I was verified by nmr.



$$Ph\text{-}CH\begin{matrix} \nearrow CH_2ONO_2 \\ \searrow CH_2ONO_2 \end{matrix}$$

V

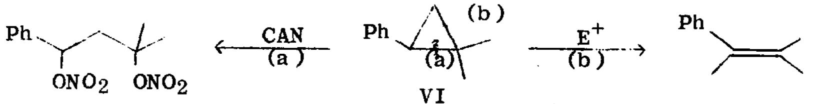
Ouellette has found that the lead tetraacetate oxidation of phenylcyclopropane produces 1-phenyl-1,3-propanediacetate (63%), cinnamyl acetate (32%), and 2-phenyl-1,3-propanediacetate (5%) (1), and the thallium triacetate oxidation produces 1-phenyl-1,3-propanediacetate (92%) and cinnamyl acetate (8%) (2). He has suggested that the lead(IV), thallium(III), and mercury(II) acetate oxidations of cyclopropanes occur _via_ electrophilic attack by a metal acetate species to produce an organo-metal compound which is then acetolyzed (eq 2)



(2)

(1-3,5). Indeed, in the case of thallium triacetate, the organothallium intermediate has apparently been observed by gas-liquid phase chromatography (2). In the mercuric acetate cleavage of arylcyclopropane, Ouellette has found a Hammett ρ of -3.2, indicating a considerable amount of positive charge development on the benzylic carbon atom in the transition state of the cleavage reaction (5).

Like the lead, thallium, and mercury oxidations, the CAN oxidation of cyclopropanes is facilitated by the substitution of aryl groups on the ring (norcarane requires more than 5 days at 50^0 for complete reaction while phenylcyclopropane (I) reacts in one day at room temperature), possibly indicating a similarity in mechanism between the CAN and lead, thallium, and mercury oxidations. However, the CAN oxidation of 1,1-dimethyl-2-phenylcyclopropane (VI) results in exclusive cleavage between the phenyl- and gem-dimethyl-substituted carbons while electrophilic cleavage by acid and presumably also by the metal acetates occurs between the methylene group and the gem-dimethyl-substituted carbon (eq 3). Thus CAN cleaves cyclopropanes to give the most stable "dication" while electrophilic cleavage by metal acetate occurs between the most and least substituted positions.



VI

(3)

(E$^+$ = electrophile)

Since the electronic nature of cerium(IV) is not amenable to metal-carbon bond formation (due to the lack of effective bonding orbitals on the metal), and it is unlikely that cerium(IV) converts the substrate to a dication in one two-electron-oxidation step (cerium(II) is unknown in solution), the reaction path for cerium(IV) oxidation of cyclopropanes must be quite different than in the lead, thallium, and mercury acetate oxidations. Further investigation is underway concerning the stereochemistry of the reaction and the effect of substituents on the rate and direction of cleavage.

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