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Oxidative Pathways of α -Diazo Phosphonates

Patricia I. Bonaz-Krause^a; Boris A. Kashemirov^a; Charles E. Mckenna^a

^a Department of Chemistry, University of Southern California, Los Angeles, CA, USA

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OXIDATIVE PATHWAYS OF α -DIAZO PHOSPHONATES

*Patricia I. Bonaz-Krause, Boris A. Kashemirov,
and Charles E. Mckenna**

*Department of Chemistry, University of Southern California,
Los Angeles, CA 90089-0744, USA*

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We previously reported that α -diazophosphonoacetate and methylenebisphosphonate alkyl esters (**1**, **2**) could be oxidized to the corresponding α -ketones (**3**, **4**) by, respectively, Rh(II) acetate [Rh₂(OAc)₄]/propylene oxide and *t*-butyl hypochlorite/H₂O. We report here that *t*-butyl hypochlorite similarly oxidizes the *N,N*-dimethyl amide of diethyl phosphonoacetic acid (**5**) and triethyl α -diazophosphonylmethylphosphonate (**6**) to the corresponding α -ketones (**7**, **8**). Like **2**, **6** is inert to Rh₂(OAc)₄ (refluxing benzene, excess epoxide, >1 day) but both substrates react quickly and quantitatively when the rhodium ligand is changed from acetate to NHCOC₃F₇ [Rh₂(NHCOC₃F₇)₄], thus providing the first anhydrous and easily scaleable route to analytically pure **4**. Rh₂(NHCOC₃F₇)₄-mediated epoxide oxidations of **1** (and **5**) also proceed under much milder conditions than with Rh₂(OAc)₄. These more facile oxidations were further accelerated when styrene oxide was used in place of a 1,2-epoxyalkane as the [O] donor, suggesting a change in the rate-determining step.

The relative ketone reactivity of **3**, **4**, and **7** to nucleophiles was estimated by calculation (*ab initio*, 3-21G*) as **3** > **4** > **7**. This predicted order of reactivity was found experimentally in a competition experiment (³¹P NMR) using H₂O as the nucleophile.

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