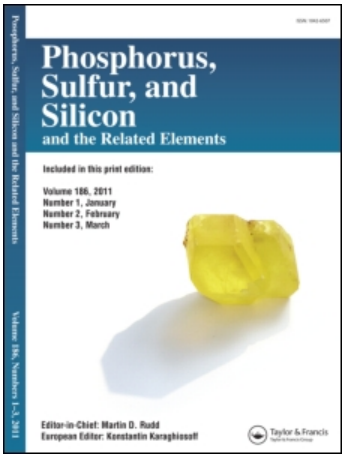

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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

Online publication date: 27 October 2010

To cite this Article Bonaz-Krause, Patricia I. , Kashemirov, Boris A. and Mckenna, Charles E.(2002) 'Oxidative Pathways of α-Diazo Phosphonates', Phosphorus, Sulfur, and Silicon and the Related Elements, 177: 10, 2271
To link to this Article: DOI: 10.1080/10426500214121
URL: http://dx.doi.org/10.1080/10426500214121

Phosphorus, Sulfur and Silicon, 2002, Vol. 177:2271

1042-6507/02 $12.00 + .00
DOI: 10.1080/10426500290106086

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

(Received July 29, 2001; accepted December 25, 2001)

We previously reported that α-diazo phosphonoacetate and methylenebisphosphonate alkyl esters (**1**, **2**) could be oxidized to the corresponding α-ketones (**3**, **4**) by, respectively, Rh(II) acetate [$Rh_2(OAc)_4$]/propylene oxide and *t*-butyl hypochlorite/H_2O. We report here that *t*-butyl hypochlorite similarly oxidizes the *N*,*N*-dimethyl amide of diethyl phosphonoacetic acid (**5**) and triethyl α-diazo (phenylphosphinyl)methylphosphonate (**6**) to the corresponding α-ketones (**7**, **8**). Like **2**, **6** is inert to $Rh_2(OAc)_4$ (refluxing benzene, excess epoxide, >1 day) but both substrates react quickly and quantitatively when the rhodium ligand is changed from acetate to $NHCOC_3F_7$ [$Rh_2(NHCOC_3F7)_4$], thus providing the first anhydrous and easily scaleable route to analytically pure **4**. $Rh_2(NHCOC_3F_7)_4$-mediated epoxide oxidations of **1** (and **5**) also proceed under much milder conditions than with $Rh_2(OAc)_4$. 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 (^{31}P NMR) using H_2O as the nucleophile.

We thank the NIH and Biokeys Pharmaceuticals, Inc. for research support.

This article is a part of the XVth International Conference on Phosphorus Chemistry (ICPC 15) proceedings published in *Phosphorus, Sulfur, and Silicon*, Volume 177, Numbers 6/7 and 8/9.