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AN UNPRECEDENTED FAVORSKI-LIKE RING CONTRACTION OF THE 1,3,4-OXADIAZINONE RING TO A BIMANE

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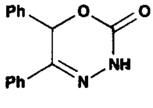
Abstract: The reaction of oxadiazinone **5** with sodium hydride in THF leads to an unprecedented Favorski-like ring contraction to the diazacyclopentadienone **1** which then dimerizes with loss of one molecule of nitrogen to give the observed bimane **3**. Copyright © 1996 Elsevier Science Ltd

As part of our investigation of the chemistry of 1,3,4-oxadiazin-2-ones,[1] we needed 3,6-dihydro-5,6-diphenyl-3-(carbo-*t*-butoxy)-1,3,4-oxadiazin-2-one (**5**). Our initial attempt to acylate 3,6-dihydro-5,6-diphenyl-1,3,4-oxadiazin-2-one (**4**)[2] with di-*tert*-butyl dicarbonate [$(Boc)_2O$, Boc anhydride] in the presence of 4-dimethylaminopyridine (DMAP) gave only a 28% yield of the desired product;[3] a bright yellow fluorescent color pervaded the reaction mixture.[4] In an effort to improve the yield and selectivity of the reaction, it was decided to attempt the acylation of the sodium salt of **4** according to the procedure used to prepare 3,6-dihydro-5,6-diphenyl-3-tosyl-1,3,4-oxadiazin-2-one.[1] Thus addition of Boc anhydride to the sodium salt generated by treatment of **4** with excess sodium hydride in THF resulted in the development of a bright yellow fluorescent color. Trituration of the bright yellow oil obtained after work-up, with benzene-pet ether led to the isolation of bright yellow crystals (19%), mp. 309-311°.[5] Combustion analysis data coupled with the presence of a parent peak at 440 in the mass spectrum established its molecular formula as $C_{30}H_{20}N_2O_2$.



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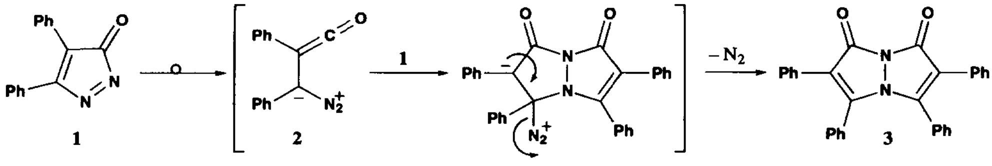
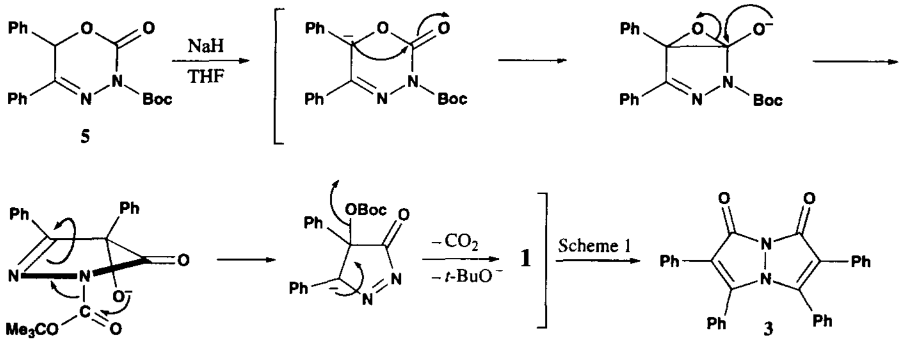
In 1978, Kosower and his group[5] had described the formation of highly fluorescent compounds -given the short name *bimanes*- from the alkaline treatment of 4-chloropyrazolin-5-ones. Although the reported mp. (312°)[5] and tlc match with an authentic sample[6] strongly suggested that our compound was *syn*-(Ph,Ph)bimane (**3**), there was insufficient quantity of the authentic sample to carry out further comparisons. This fact coupled with unusual nature of the reaction led us to to obtain an X-*ray* crystal structure[7] which indeed confirmed our product to be 3,4,6,7-tetraphenyl-1,5-diazabicyclo[3.3.0]octa-3,6-diene-2,8-dione (**3**). Kosower had rationalized the formation of the bimanes *via* the dimerization of the transient 1,2-diazacyclopentadienone (e. g. **1**) as depicted in *Scheme 1.* Since we established that the anion of the *parent* oxadiazinone (**4**) failed to produce **3** upon treatment with sodium hydride, it thus became apparent that, *in contrast* to the corresponding 3-tosyl derivative of **4**,[1] the absence of a leaving group at the 3-position of the anion



Scheme 1

of **5** results in an unprecedented Favorski-like ring contraction suggested in *Scheme 2* to produce the diazacyclopentadienone **1** which then follows the path proposed by Kosower in *Scheme 1*.[8] It was also established that authentic **5** produced **3** upon treatment with sodium hydride in THF. We are currently exploring further extensions of this novel reaction.



Scheme 2

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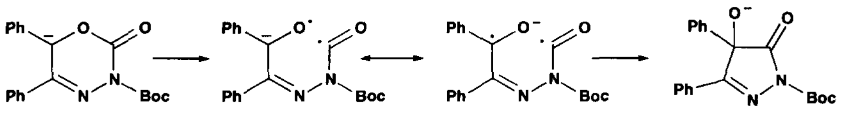
† Taken in part from the M. Sc. Thesis of Aberdeen Allen, University of Massachusetts at Boston, June 1996.

1. Allen, A.; Anselme, J.-P., *Bull. Soc. Chim. Belges* **1995**, *104*, 577-578.
2. Rosenblum, M.; Fuchs, B., *J. Am. Chem. Soc.*, **1968**, *90*, 1061-1062 and earlier papers.
3. Colorless solid, mp. 138-140°. *Anal.* Calcd for $C_{20}H_{20}N_2O_4$: C, 68.17; H, 5.72; N, 7.95. Found: C, 68.15; H, 5.76; N, 7.83.
4. The major product (32%) was the diacylated compound, 3,6-*bis*-(carbo-*t*-butoxy)-3,6-dihydro-5,6-diphenyl-1,3,4-oxadiazin-2-one, off-white solid, mp. 154-156°. *Anal.* Calcd for $C_{25}H_{29}N_2O_6$: C, 66.36; H, 6.24; N, 6.19. Found: C, 66.45; H, 6.29; N, 6.06.
5. Kosower, E. M. *et al.*, *J. Am Chem. Soc.* **1978**, *100*, 6516-6518; **1980**, *102*, 4983-4993. See also Rees and Yelland [*J. Chem. Soc. Perkin 1* **1973**, 221-225 for the isolation of the *anti* isomer of **3**.
6. We are grateful to Prof. Kosower for providing a sample of **3**.
7. We thank Dr. Byron H. Arison (*Merck & Co, Rahway, NJ*) for his help in obtaining this datum.
8. A referee has suggested that the ring contraction could also proceed *via* a 1,2-Wittig rearrangement.



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