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AIR OXIDATION REACTION OF DIAZOALKENES
EFFICIENT OXYGEN-TRANSFER REACTION TO GIVE EPOXYKETONES

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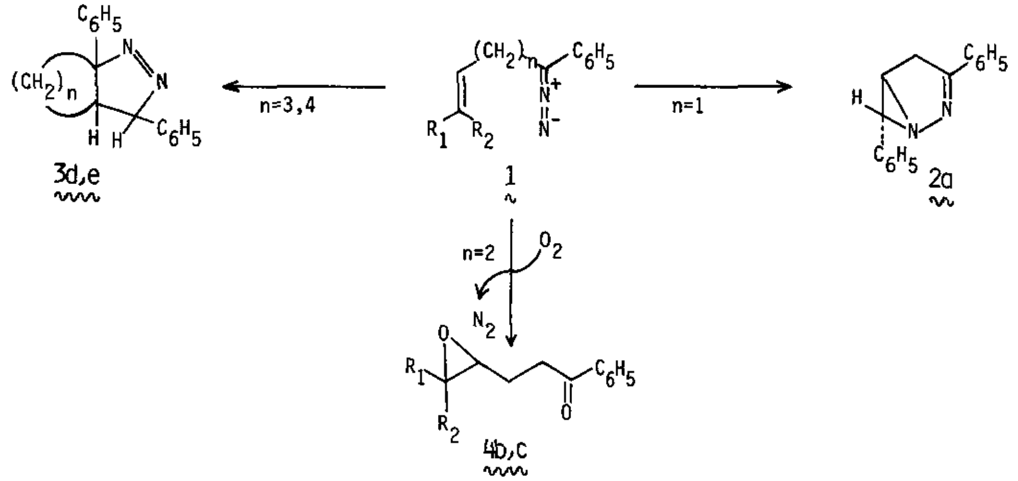
We have reported that allyldiazomethane 1a (n=1, $R_1=C_6H_5$, R_2=H) undergoes a nitrene-type 1,1-cycloaddition[1] to give exo-6-phenyl-1,2-diazabicyclo[3.1.0]hex-2-ene 2a. In order to explore the generality of the 1,1-cycloaddition reaction of diazoalkenes, reactivities of homologous diazoalkenes, 1b (n=2, $R_1=C_6H_5$, R_2=H), 1c (n=2, $R_1=R_2=C_6H_5$), 1d (n=3, $R_1=C_6H_5$, R_2=H) and 1e (n=4, $R_1=C_6H_5$, R_2=H) were tested, generating from the sodium salts of the corresponding tosylhydrazones. It was found that diazoalkenes 1d and 1e did not undergo the 1,1-cycloaddition but the 1,3-dipolar addition to give 3d (n=3) and 3e (n=4) under inert atmosphere, whereas 1b and 1c were unexpectedly stable and remained unchange for more than 2 months when kept under inert atmosphere. In contrast with these reactivities under inert atmosphere, diazoalkenes 1b and 1c were facilely oxidized by molecular oxygen, giving oxygen-transfer products, epoxyketones 4b ($R_1=C_6H_5$, R_2=H) and 4c ($R_1=R_2=C_6H_5$) when 1b and 1c were exposed to air. It is of interest to note that singlet oxygen did not give such epoxyketones at all. A possible mechanism will be discussed.



References: 1) Y. Nishizawa, T. Miyashi, T. Mukai, J. Am. Chem. Soc., 102, 1176 (1980); T. Miyashi, Y. Fujii, Y. Nishizawa, T. Mukai, ibid., 103, 725 (1981); see also Ref.2
2) A. Padwa, H. Ku, Tetrahedron Lett., 1009 (1980); A. Padwa, A. Rodoriguez, ibid., 187 (1981)