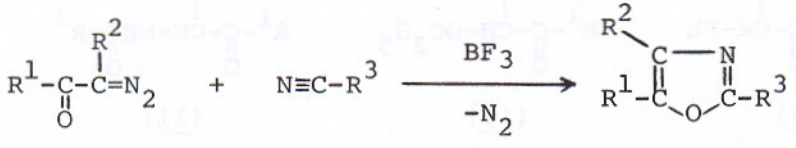
R1575D

GENERAL METHOD OF THE SYNTHESIS OF OXAZOLES BY THE BF_3 CATALYZED DECOMPOSITION OF DIAZOCARBONYL COMPOUNDS IN NITRILES

Toshikazu IBATA and Ryohei SATO

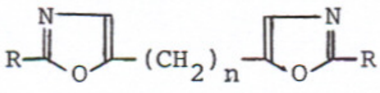
Institute of Chemistry, College of General Education,
Osaka University, Toyonaka, Osaka 560, JAPAN

The authors have preliminary reported the synthesis of oxazoles by the title reaction.[1) In this paper we wish to report the application of this method to the synthesis of various substituted oxazoles. Many aliphatic nitriles (3: R^3=Me, Et, i-Pr, $PhCH_2$, PhCH=CH, $PhCH_2SCH_2$, $ClCH_2$, CH_3OOCCH_2, etc) and substituted benzonitriles gave corresponding oxazoles in high yields in the reaction with substituted α-diazoacetophenones. Although the substituents of the diazoacetophneone did not effect on the yields of oxazoles, electron-attracting groups (p-NO_2, CN) on benzonitrile lower the the yield very much. Other diazocarbonyl compounds gave oxazoles in high yields.

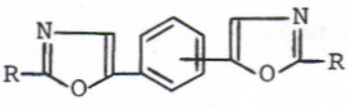


(1) (2) (3)

Bisdiazoketones such as terminal diazoacetylated alkanes and m- and p-bisdiazoacetylbenzene gave corresponding oxazoles (4: n=6,8,10,12; 5).



(4)



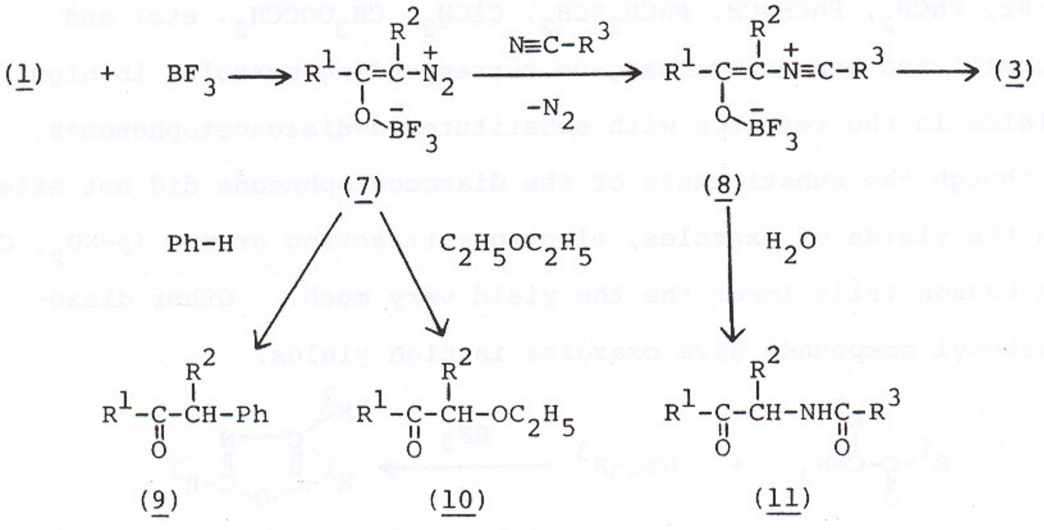
(5)

An attempt to synthesize the oxazolophane by the intramolecular reaction of ω-cyano-1-diazo-2-alkanones (6: n=6,8,10, 12) was unsuccessful.

$$\mathrm{NC(CH_2)_nCOCHN_2} \xrightarrow[\text{in Ph-H}]{\mathrm{BF_3}} \mathrm{NC(CH_2)_nCOCH_2F} \quad + \quad \mathrm{NC(CH_2)_nCOCH_2Ph}$$

(6)

These results are reasonably explained by the mechanism shown below which is initiated by the attack of BF_3 on oxygen atom of diazocarbonyl compound.



Intermediacy of betaines (7) and (8) was supported by the formation of byproducts (9), (10), and (11).

Fluorescence properties. These oxazoles shows strong fluorescence as that of POPOP in UV and visible region (λ_{max} 315-405 nm).

---

1) T. Ibata and R. Sato, *Chem. Lett.*, 1129 (1979).