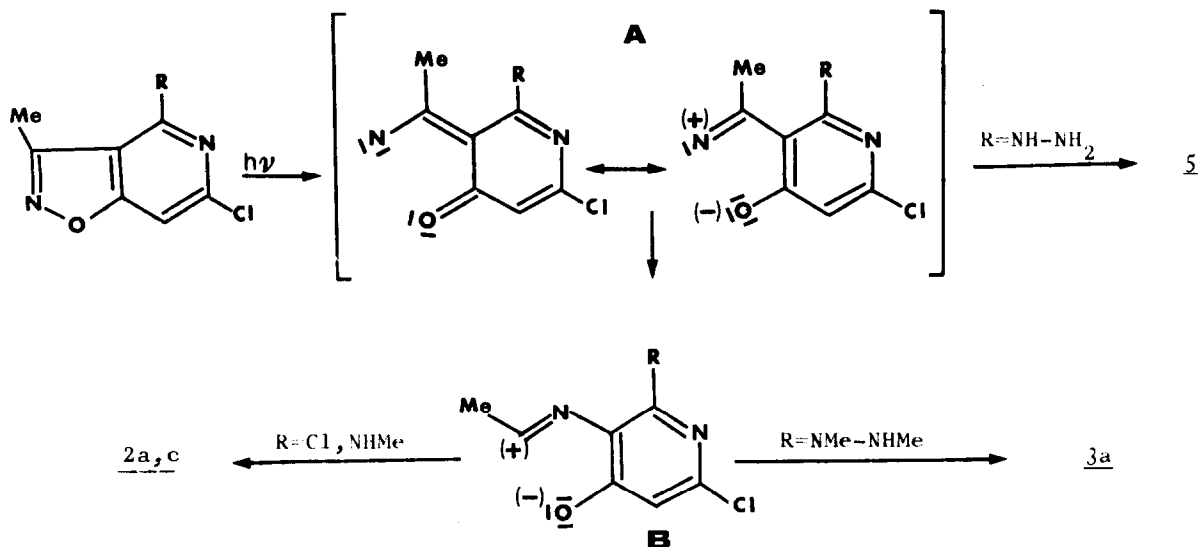


comparison with that of the oxygen of the ylide B.



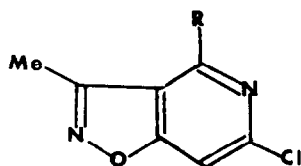
The facile introduction of nucleophiles in the 4 position^{2b} and the possibilities of photorearrangement, render the isoxazolo[4,5-c]pyridine of valuable interest in the synthetic approach to a number of pyridine condensed heterocycles.

Acknowledgment. This work was financially supported by the Consiglio Nazionale delle Ricerche, Roma.

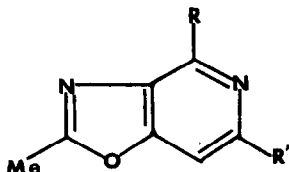
References and Notes

- 1a) G.Adembri, A.Camparini, F.Ponticelli and P.Tedeschi, J.C.S. Perkin I, 1977, 971; b) G.Adembri, A.Camparini, F.Ponticelli and P.Tedeschi, ibid., in press; c) G.Adembri, A.Camparini, D.Donati, F.Ponticelli and P.Tedeschi, Tetrahedron Lett., 1978, 4439.
- 2a) G.Adembri, A.Camparini, F.Ponticelli and P.Tedeschi, J.C.S. Perkin I, 1975, 2190; b) G.Adembri, A.Camparini, F.Ponticelli and P.Tedeschi, J.Heterocycl. Chem., 1979, 16, 49.
- 3) Anhydrous ether (1a,c) or ethanol (1b,d) solutions were irradiated with an unfiltered low pressure mercury lamp (1a,c) or a medium pressure mercury lamp, filtered with a CuSO_4 solution (1b,d). N_2 was bubbled through the solutions. In the case of 1c, solution was continuously circulated through a silica gel column to stop the photoproduct 3a in the column.
- 4) J.Fraser and E.Tittensor, J.C.S., 1956, 1781.

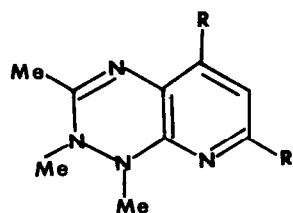
between 4a and 4b added further support.



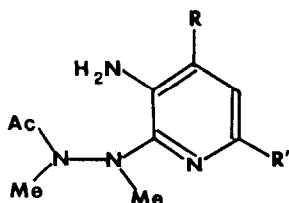
1a R=Cl
1b R=NHMe
1c R=NMeNHMe
1d R=NHNH₂



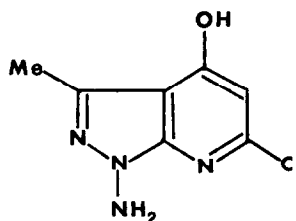
2a R=R'=Cl
2b R=R'=H
2c R=NHMe, R'=Cl
2d R=NHMe, R'=H



3a R=OH, R'=Cl
3b R=OMe, R'=Cl
3c R=R'=H



4a R=OMe, R'=H
4b R=R'=H



5

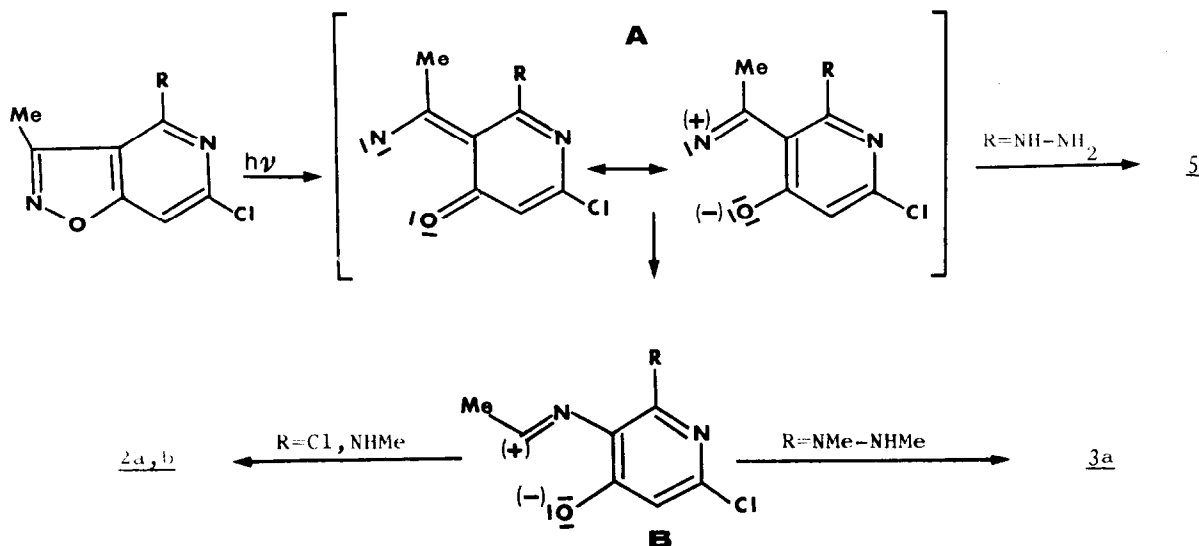
1-Aminopyrazolo[3,4-b]pyridine 5 was recovered as main product of irradiation of 1d. The structure of compound 5 was proved by transformation into 3-methylpyrazolo[3,4-b]pyridine, prepared in an unambiguous way⁷.

Some differences in respect to the photobehaviour of isoxazol-5-ylhydrazines^{1c} are to be pointed out, mainly: i) isoxazol-5-ylhydrazines rearrange to 1-aminopyrazoles only by thermal^{1a}, but not by photochemical activation^{1c}; ii) no product deriving from 3-methyl shift through ketenimine intermediate was found after irradiation of isoxazolopyridine 1a-d.

Even if additional work is necessary in order to evidentiate the relative importance of different parameters, the results obtained can be rationalized in the scheme reported.

Initial N-O bond opening leads to the intermediate A, which is trapped to 1-aminopyrazolo[3,4-b]pyridine 5 by unsubstituted α -hydrazinic nitrogen present at the 4 position of the isoxazolopyridine 1d. Otherwise rearrangement of intermediate A to the ylide B takes place. Pyrido-1,2,4-triazine 3a or oxazolopyridines 2a,c are formed depending on the nucleophilic strength of 2-substituent in

comparison with that of the oxygen of the ylide B.



The facile introduction of nucleophiles in the 4 position^{2b} and the possibilities of photorearrangement, render the isoxazolo[4,5-c]pyridine of valuable interest in the synthetic approach to a number of pyridine condensed heterocycles.

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References and Notes

- 1a) G.Adembri, A.Camparini, F.Ponticelli and P.Tedeschi, J.C.S. Perkin I, 1977, 971; b) G.Adembri, A.Camparini, F.Ponticelli and P.Tedeschi, ibid., in press; c) G.Adembri, A.Camparini, D.Donati, F.Ponticelli and P.Tedeschi, Tetrahedron Lett., 1978, 4439.
- 2a) G.Adembri, A.Camparini, F.Ponticelli and P.Tedeschi, J.C.S. Perkin I, 1975, 2190; b) G.Adembri, A.Camparini, F.Ponticelli and P.Tedeschi, J.Heterocycl. Chem., 1979, 16, 49.
- 3) Anhydrous ether (1a,c) or ethanol (1b,d) solutions were irradiated with an unfiltered low pressure mercury lamp (1a,c) or a medium pressure mercury lamp, filtered with a CuSO_4 solution (1b,d). N_2 was bubbled through the solutions. In the case of 1c, solution was continuously circulated through a silica gel column to stop the photoproduct 3a in the column.
- 4) J.Fraser and E.Tittensor, J.C.S., 1956, 1781.

- 5a) W.Heinzelmann and M.Märky, Helv.Chim.Acta, 1974, 57, 376; b) J.P.Ferris and F.R.Antonucci, J.Amer.Chem.Soc., 1974, 96, 2014; c) C.Skötsch and E.Breitmaier, Chem.Ber., 1979, 112, 3282.
- 6) Preparation of compounds 1b,c was performed according to the procedure described in the ref. 2a for compound 1d.
- 7) Compound 2a: m.p. 136-138° (sublimation in vacuo), δ (CDCl₃) 2.70(s,3,Me), 7.44 (s,1,H₇); compound 2c: m.p. 127-128° (ether/light petroleum), ν (KBr) 3280 cm⁻¹; δ (CDCl₃) 2.55(s,3,Me), 3.11(d, J=5.5, s with D₂O, 3, NMe), 5.27(exch. br. s,1,NH), 6.73(s,1,H₇); compound 2d: m.p. 80-81° (sublimation in vacuo), ν (KBr) 3240 cm⁻¹, δ (CDCl₃) 2.52(s,3,Me), 3.10(d, J=5.5, s with D₂O, 3, NMe), 5.33 (exch. br. s,1,NH), 6.70(d, J=6.0, 1, H₇), 7.98(d, J=6.0, 1, H₆); compound 3a: m.p. 185-188° (sublimation in vacuo), ν (KBr) 3100-2200 cm⁻¹, δ (CDCl₃) 2.27(s,3,Me), 2.87(s,3,NMe), 3.27(s,3,NMe), 6.46(s,1,H₆), 8.75(exch. br. s,1,NH/OH); compound 3b: δ (CDCl₃) 2.16(s,3,Me), 2.85(s,3,NMe), 3.20(s,3,NMe), 3.91(s,3,OMe), 6.58(s,1,H₆); compound 3c: m.p. 65-66° (sublimation in vacuo), δ (CDCl₃) 2.10 (s,3,Me), 2.86(s,3,NMe), 3.20(s,3,NMe), 6.92(dd, J=8.0 and 5.0, 1, H₆), 7.23(dd, J=8.0 and 1.8, 1, H₅), 7.98(dd, J=5.0 and 1.8, 1, H₇); compound 4a: ν (KBr) 3490, 3400 and 1660 cm⁻¹, δ (CDCl₃) 2.12 and 2.33(s,3,MeCO), 2.92(s,3,NMe), 3.02 and 3.08(s,3,NMe), 3.60(exch. br. s,2,NH₂), 3.89(s,3,OMe), 6.58(s,1,H₅); compound 4b: m.p. 118-120°, ν (KBr) 3460, 3340, 1640 cm⁻¹, δ (CDCl₃) 2.12 and 2.34(s,3, MeCO), 2.89(s,3,NMe), 3.03 and 3.09(s,3,NMe), 3.70(exch. br. s,2,NH₂), 6.80-7.08(m,2,H₄ and H₅), 7.73-7.91(m,1,H₆); compound 5: m.p. >350° (ethanol/water), ν (KBr) 3320, 3195 and 3160-2200 cm⁻¹, δ (DMS-d₆) 2.46(s,3,Me), 6.10(exch. br. s,2,NH₂), 6.42(s,1,H₅), 11.77(exch. br. s,1,NH/OH).
- Satisfactory elemental analysis were obtained for all new compounds. Synthetic details will be given in our full manuscript.
- 8) A.Lewis and R.G.Shepherd, J.Heterocycl.Chem., 1971, 8, 41.

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