Reactions Of 3-Methoxycarbonylmethylene-2-oxo-1,2,3,4-tetrahydroquinoxaline and Its Derivative Hydrazide with Electrophilic Reagents

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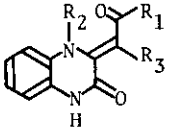
The reactions of 3-methoxycarbonylmethylene-2-oxo-1,2,3,4-tetrahydroquinoxaline (1) and its derivative hydrazide (5) with electrophilic reagents were investigated.

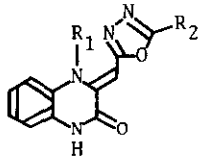
Halogenations of 1 with NBS and NCS afforded N_4-halogeno compounds (2a,b). The systems of H_2O_2/HBr and H_2O_2/HCl were found to convert 1 to N_4- and C-halogeno derivatives (3a,b), and N_4-Br of 3a was eliminated with ZnI_2 to compound (4a).

The reaction of 3-hydrazinocarbonylmethylene-2-oxo-1,2,3,4-tetrahydroquinoxaline (5) with orthoesters provided hydrazones (6a,b), which were cyclized to 1,3,4-oxadiazoles (7a,b). The structures of 7a,b were supported by N_4-bromination with NBS to compounds (8a,b).

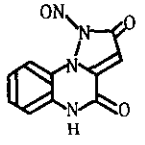
The reactions of 5 with 1.2 eq. of HNO_2 (I) and 5 eq. of HNO_2 (II) gave azide (9) (from I), and pyrazolo[1,5-a]quinoxaline (10) and 3-cyano-2-oxo-1,2-dihydroquinoxaline (11) (from II). Heating of 9 in AcOH or AcOH-H_2O afforded imidazo[1,5-a]-quinoxaline (12).



(1) R_1=OMe, R_2=R_3=H
(2a) R_2=OMe, R_2=Br, R_3=H
(2b) R_1=OMe, R_2=Cl, R_3=H
(3a) R_1=OMe, R_2=R_3=Br
(3b) R_1=OMe, R_2=R_3=Cl
(4a) R_1=OMe, R_2=H, R_3=Br
(5) R_1=$NHNH_2$, R_2=R_3=H
(6) R_1=NHN=C(OEt)R_4
a, R_4=H; b, R_4=Me
(9) R_1=N_3, R_2=R_3=H



(7a) R_1=R_2=H
(7b) R_1=H, R_2=Me
(8a) R_1=Br, R_2=H
(8b) R_1=Br, R_2=Me



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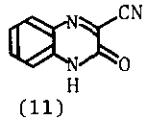

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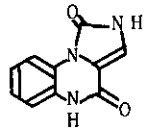

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