

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

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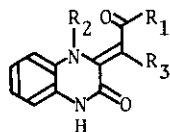
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The reactions of 3-methoxycarbonylmethylene-2-oxo-1,2,3,4-tetrahydroquinoxaline (1) and its derivative hydrazide (5) with electrophilic reagents were investigated.

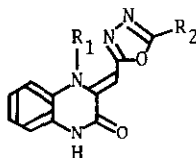
Halogenations of 1 with NBS and NCS afforded  $N_4$ -halogeno compounds (2a,b). The systems of  $H_2O_2/HBr$  and  $H_2O_2/HCl$  were found to convert 1 to  $N_4$ - and C-halogeno derivatives (3a,b), and  $N_4$ -Br of 3a was eliminated with  $ZnI_2$  to compound (4a).

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)  $R_2=OMe, R_3=Br, R_4=H$   
 (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)  $R_1=NHN=$   
     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)  $R_1=Br, R_2=Me$

