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A NEW AROMATIC ANNELATION REACTION UTILIZING REACTION OF ISOXAZOLE WITH DIIRONNONACARBONYL

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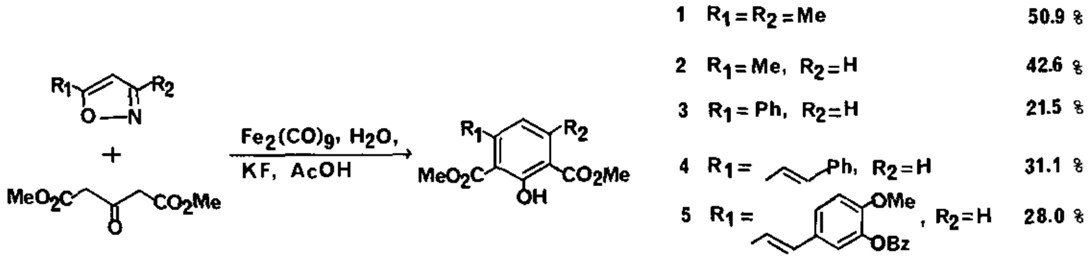
Isoxazoles can be considered as an equivalent synthon of β-enaminones in protected form and the reductive cleavage of isoxazoles into β-eneminones by catalytic hydrogenation is widely applicable reaction for organic synthesis. Interest has centred, recently, reactions of isoxazoles with transition-metal carbonyls such as $Mo(CO)_6$, $Fe(CO)_5$ with hν, and $Fe_2(CO)_9$ to undergo β-enaminones by reductive cleavage through aziridine intermediates. This instance is of considerable interest, for it generation of enaminones *in situ* in connection with a aromatic annelation reaction of the enaminones with 3-oxoglutarate.$^{1)}$ We report a new simple method for aromatic annelation reaction utilizing reaction of isoxazoles with diironnonacarbonyl and water followed by reaction with 3-oxoglutarate in presence of KF-AcOH.

A typical annelation reaction was carried out as follows. Diironnonacarbonyl 7.5 g (20.6 mmol) was added to a solution of 2,5-dimethylisoxazole 1 g (10.3 mmol) in benzene 50 ml with water 180 mg (10 mmol) under a nitrogen atomosphere and stirred at 45°C for 30 min. And then, a solution of dimethyl 3-oxoglutarate 3.59 g (10.6 mmol), KF 1.19 g (20.6 mmol), and AcOH 2.47 g (41.2 mmol) in dry benzene 50 ml was added and refluxed for 12 h removing water with water separator. Resulted mixture gave dimethyl 2-hydroxy-4,6-dimethyl-1,3-benzene dicarboxylate 1, mp 105-107°C, 1.25 g (50.9% yield). Some experimental results are shown as follows.



1	$R_1=R_2=Me$	50.9 %
2	$R_1=Me$, $R_2=H$	42.6 %
3	$R_1=Ph$, $R_2=H$	21.5 %
4	$R_1=$ Ph, $R_2=H$	31.1 %
5	$R_1=$, $R_2=H$	28.0 %

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(1) N. Takeuchi, K. Ochi, M. Murase, and S. Tobinaga, J. Chem. Soc., Chem. Commun., 1980, 593.