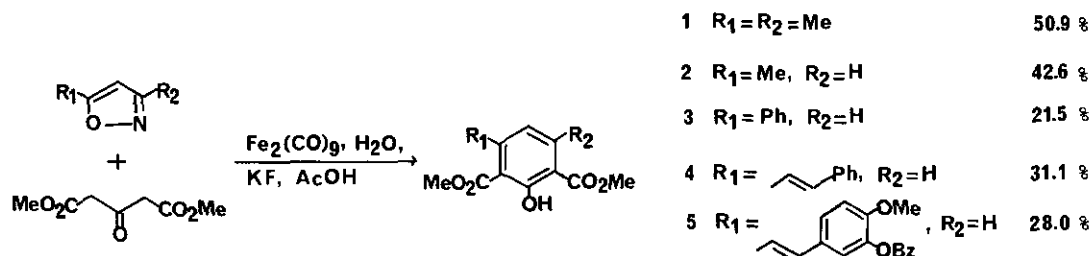


A NEW AROMATIC ANNEALATION REACTION UTILIZING REACTION OF
ISOXAZOLE WITH DIIRONNONACARBONYL

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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 -enaminones by catalytic hydrogenation is widely applicable reaction for organic synthesis. Interest has centred, recently, reactions of isoxazoles with transition-metal carbonyls such as $\text{Mo}(\text{CO})_6$, $\text{Fe}(\text{CO})_5$ with $h\nu$, and $\text{Fe}_2(\text{CO})_9$ 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 $\text{KF}\text{-AcOH}$.

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