

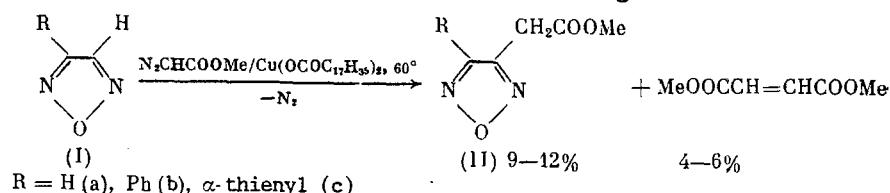
# CATALYTIC REACTION OF MONOSUBSTITUTED FURAZANES WITH METHYL DIAZOACETATE

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UDC 542.97:547.793.2:547.467.2

There is no information in the literature on the direct introduction of substituents into the furazane ring.

We have discovered that the thermocatalytic reaction of monosubstituted furazanes (I) with methyl diazoacetate (MDA) in the presence of cupric stearate leads to the formation of the corresponding 4-methoxycarbonylmethylfurazanes (II) obtained by the formal insertion of methoxycarbonylcarbene into a C-H bond of the furazane ring



The product of the formal insertion of methoxycarbonylcarbene into the  $\alpha$ -C-H bond of the thiophene ring, namely, 3-(5-methoxycarbonylmethylthienyl-2)-furazane is also formed in the case of (Ic) in addition to (IIc).

The decomposition of MDA is not observed when  $\text{Rh(OAc)}_2$  is used as the catalyst, apparently as a consequence of the formation of the catalytically inactive complex of  $\text{Rh(OAc)}_2$  with starting (I), as indicated by a change in the color of the benzene solution from emerald green to reddish purple upon the addition of (Ia) or (Ib). Carrying out the reaction of (I) with MDA under conditions for the thermal decomposition of the diazo compound does not lead to the formation of (II).

A solution of 0.8 g MDA in 1.0 g (Ib) was added with stirring over 40 min to 2.5 g (Ib) and 0.1 g  $\text{Cu(OCOC}_{17}\text{H}_{35})_2$  at  $60^\circ\text{C}$ . Stirring was continued until no further nitrogen was released (about 20 min). The reaction mixture was separated on a  $90 \times 2$ -cm chromatographic column packed with silica gel 40/100  $\mu\text{m}$  using 3:1 hexane-ether as the eluent to give 0.182 g (12%) (IIb), mp  $92-94^\circ\text{C}$ . PMR spectrum ( $\delta$ , ppm): 3.81 s (3H), 4.88 s (2H), 7.46 m (2H), 7.58 m (1H), 8.10 m (2H). Mass spectrum,  $m/z$ : 218 ( $\text{M}^+$ ), 187 ( $\text{M}^+ - \text{OMe}$ ), 159 ( $\text{M}^+ - \text{CO}_2\text{Me}$ ), 129 ( $\text{PhC=N-O}^+$ ).

The other products (II) were obtained by analogy.