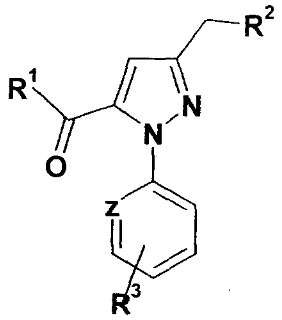
Process for preparing aryl-substituted pyrazoles

Abstract

The present invention relates to a process for preparing 1-aryl-substituted pyrazoles, comprising the reaction of alkoxy enones and enamino ketones with arylhydrazine derivatives to give 1-aryl-substituted dihydro-1H-pyrazoles, the further reaction thereof with elimination of water to give 1-aryl-substituted trihalomethylpyrazoles, and the further processing thereof.

Claims

1. Process for preparing aryl-substituted pyrazole derivatives of the general formula (I)



(I)

in which

R^1 is hydroxyl, alkoxy, aryloxy, halogen,

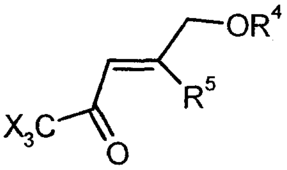
R^2 is hydroxyl, alkoxy, arylalkoxy, alkylthio, halogen, O-(C=O)alkyl, O-(C=O)O-alkyl, (C=O)haloalkyl, OSO_2alkyl, OSO_2-haloalkyl, OSO_2-aryl,

R^3 is halogen, CN, NO_2, alkyl, cycloalkyl, haloalkyl, halocycloalkyl, alkoxy, haloalkoxy, alkylamino, dialkylamino, cycloalkylamino,

Z is CH, N,

characterized in that

(A) alkoxy enones and enamino ketones of the formula (II)



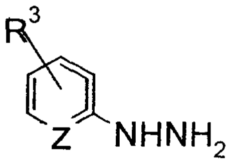
(II)

in which

R^4 is H, alkyl, arylalkyl, -(C=O)alkyl, (C=O)haloalkyl, -(C=O)O-alkyl, SO_2alkyl, SO_2-haloalkyl, SO_2-aryl,

X is fluorine, chlorine, bromine, iodine,

R^5 is alkoxy, dialkylamino, cycloalkylamino, thioalkyl, or is cycloalkyl which may optionally contain 1-3 heteroatoms from the group of O, N, S, are reacted with arylhydrazines of the formula (III)

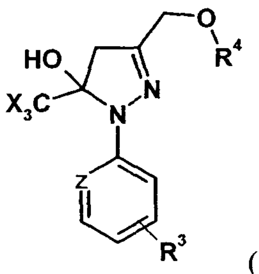

(III)

in which

R^3 is halogen, CN, NO_2, alkyl, cycloalkyl, haloalkyl, halocycloalkyl, alkoxy, haloalkoxy, alkylamino, dialkylamino, cycloalkylamino,

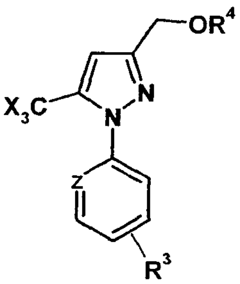
Z is CH, N,

to give 1-aryl-substituted dihydro-1H-pyrazoles of the formula (IV)


(IV)

in which X, R^3, R^4, Z are each as defined above,

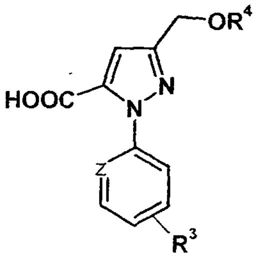
(B) the latter are optionally converted further, without preceding isolation, with elimination of water, to 1-aryl-substituted trihalomethylpyrazoles of the formula (V)


(V)

in which X, R^3, R^4, Z are each as defined above,

(C) these compounds of the general formula (V)

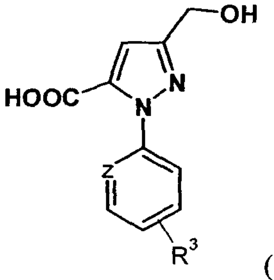
are converted with addition of HCl, H_2SO_4 or a base, for example, to pyrazolecarboxylic acids of the formula (VI)



(VI)

in which R^3, R^4, Z are each as defined above,

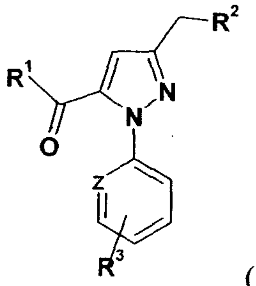
(D) the latter are converted, after detaching the R^4 group, to hydroxymethylpyrazole acids of the formula (VII)



(VII)

in which R^3, Z are as defined above, and

(E) the latter are converted to compounds of the formula (I)



(I).

2. Process according to Claim 1, characterized in that

R^1 is hydroxyl, $(C_1\text{-}C_6)$-alkoxy, halogen,

R^2 is hydroxyl, halogen, $O\text{-}(C{=}O)(C_1\text{-}C_6)$alkyl,

R^3 is halogen, CN, NO_2, $(C_1\text{-}C_6)$-alkyl, halo$(C_1\text{-}C_6)$-alkyl, $(C_1\text{-}C_6)$-alkoxy, halo$(C_1\text{-}C_6)$alkoxy,

X is fluorine, chlorine, bromine,

Z is N,

R^4 is aryl(C_1-C_6)-alkyl, (C=O)(C_1-C_6)-alkyl, (C=O)halo(C_1-C_6)-alkyl, -(C=O)O-(C_1-C_6)-alkyl, SO_2(C_1-C_6)-alkyl, SO_2phenyl, SO_2 ¯halo(C_1-C_6)-alkyl,

R^5 is (C_1-C_6)-alkoxy, di(C_1-C_6)-alkylamino, morpholino, thioalkyl.

3. Process according to either of Claims 1 and 2, characterized in that

R^1 is (C_1-C_6)alkoxy, hydroxyl,

R^2 is hydroxyl, C(=O)CH_3,

R^3 is chlorine,

R^4 is (C=O)CH_3,

R^5 is methoxy,

X is chlorine,

Z is N.

4. Compound of the general formula (IV) according to Claim 1, characterized in that

X, R^3, Z are each as defined above,

R^4 is (C=O)(C_1-C_6)-alkyl, (C=O)halo(C_1-C_6)-alkyl.

5. Compound of the general formula (V) according to Claim 1, characterized in that

X, R^3, Z are each as defined above,

R^4 is (C=O)(C_1-C_6)-alkyl, (C=O)halo(C_1-C_6)-alkyl.

6. Compound of the general formula (IV) according to Claim 4, characterized in that

R^4 is (C=O)CH_3 and X is chlorine.

7. Compound of the general formula (V) according to Claim 5, characterized in that

R^4 is (C=O)CH_3 and X is chlorine.

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(HRISHIKESH RAY CHAUDHURY)
OF REMFRY & SAGAR
ATTORNEY FOR THE APPLICANT[S]