CHELATE SYNTHESIS OF DERIVATIVES OF 7-DIAMINOMETHYLENE-4,5,6,7-TETRAHYDRO-2H-INDAZOL-6-ONE

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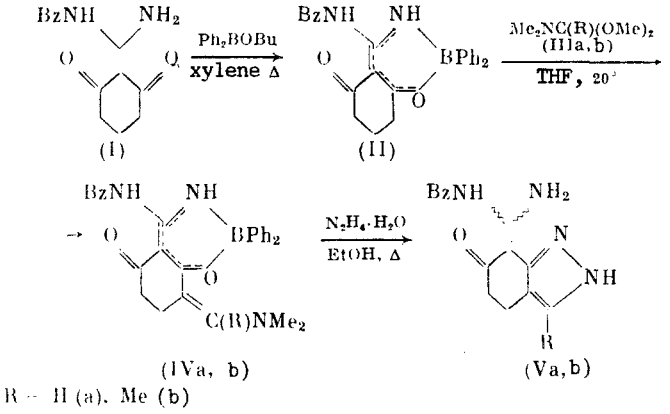
Diacylketone aminals (DKA) are promising reagents for organic synthesis [1]. The use of DKA as boryl chelate complexes opens new pathways for the preparation of functionally substituted heterocyclic systems [2]. Using this approach, we found a simple method for constructing the 4,5,6,7-tetrahydroindazole system from DKA (I), which is readily obtained from 1,3-cyclohexanedione and benzoylcyanamide [3]. Diphenylboryl chelate (II), which is smoothly obtained from (I), reacts with DMF (IIIa) or dimethylacetamide (IIIb) under mild conditions to give condensation products (IVa) and (IVb), which are converted by the action of hydrazine hydrate into 7-(N-benzoyldiaminomethylene)-4,5,6,7-tetrahydro-2H-indazol-6-one (Va) or 3-methyl-7-(N-benzoyldiaminomethylene)-4,5,6,7-tetrahydro-2H-indazol-6-one (Vb):



Chelate (II) was obtained in 98% yield by heating (I) and Ph_2BOBu in xylene at reflux, mp 162-163°C (from 1:1 benzene–hexane). Mass spectrum, m/z: 345 $[M - Ph]^+$. A solution of 3 mmoles (II) and 6 mmoles (IIIa) or (IIIb) was stirred at 20°C under argon for 48 h. The solvent was distilled off and the residue was heated at reflux with 12 mmoles hydrazine hydrate in 50 ml ethanol for 3 h. The crystalline precipitate was filtered off and an additional amount of (Va) or (Vb) was obtained by chromatography on a silica gel column with chloroform as the eluent. Product (Va) was obtained in 80% yield, mp 229-230°C (toluene). Mass spectrum, m/z: 282 $[M]^+$. PMR spectrum in $CDCl_3$ at 250 MHz (δ, ppm): 15.19 s, 9.68 s, 9.40 s, 9.23 s (4NH), 8.13 d (2H, Ph), 7.64 t (1H, Ph), 7.57 t (2H, Ph), 7.33 s (CH=), 2.82 t and 2.69 t ($2CH_2$, J = 7 Hz). Product (Vb) was obtained in 63% yield, mp 276-278°C (from benzene). Mass spectrum, m/z: 296 $[M]^+$.

The elemental analysis data for (II), (IV), and (V) correspond to the calculated data.

LITERATURE CITED

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