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A NOVEL SYNTHETIC METHOD FOR ANGULARLY FUNCTIONALIZED POLYCYCLIC SYSTEMS BY VINYLOGOUS WOLFF REARRANGEMENT OF β,γ-UNSATURATED DIAZOKETONES

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Summary : Decompositions of the rigid polycylic β,γ-unsaturated diazomethyl ketones (1a and b) and (2a and b) promoted by $Cu(acac)_2$, $Cu(OTf)_2$, $Ni(acac)_2$ or silver benzoate-triethylamine in the presence of methanol are shown to give the respective rearranged γ,δ-unsaturated angularly substituted esters (3a and b) and (6a and b) along with other products.

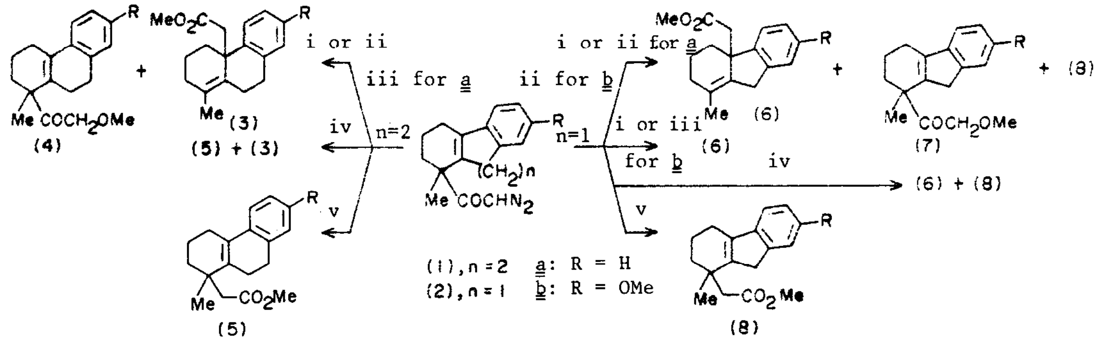
The copper salt-catalyzed decomposition of a number of monocyclic[1,2] and acyclic[2] β,γ-unsaturated diazoketones in the presence of a nucleophile, e.g. methanol, has been shown to lead to the respective γ,δ-unsaturated esters via skeletal rearrangement, termed as the "vinylogous Wolff rearrangement"[2]. Surprisingly, the scope of this transformation, a synthetic alternative to Claisen rearrangement[3] and a potentially attractive method for a functionalized angular alkylation[4] in polycyclic systems has remained unexplored so far. In conjunction with our interests in the intramolecular alkylation and rearrangement of β,γ-unsaturated diazoketones[5], we wish to report here that the easily accessible hexahydrophenanthrene and the tetrahydrofluorene diazoacetyl derivatives (1a,b)[6] and (2a,b)[6] (Scheme) undergo facile vinylogous Wolff rearrangement under certain conditions, providing a simple one-step method for the introduction of an angular acetic ester residue, thereby considerably increasing the flexibility of this reaction.

The comparative effectiveness of two established copper catalysts, copper (II) acetylacetonate /¯$Cu(acac)_2$_7[1,2] and copper (II) triflate /¯$Cu(OTf)_2$_7[2d], and the homogeneous nickel catalysts, $Ni(acac)_2$, recently introduced by us[7] for the intramolecular oxocarbenoid insertion reactions in C-H and C=C bonds, have been examined with methanol as the nucleophile with reference to the formations of various products from the diazoketones (1a,b) and (2a,b). In addition, we have also investigated the reactions of these substrates under normal Wolff rearrangement and photolysis.

As a typical example (Scheme), treatment of the diazoketone (1a) (0.75m mol) with dry $Cu(acac)_2$ or $Cu(OTf)_2$ (0.1m mol) in boiling cyclohexane (80ml) containing 1% MeOH for 3h in each case, gave mixtures of the rearranged ester (3a)[8] and the MeOH insertion product[9] (4a) in the ratios of 1 : 1 (69%) and 3 : 1 (93%) respectively /¯GLC and 200 MHz ^1H NMR_7. While the methoxy analogue (1b) on similar reactions with $Cu(acac)_2$ produced a 7 : 3 (79%) mixture of (3b) and (4b), the $Cu(OTf)_2$ induced reaction gave (3b) and (4b) in a ratio of 5 : 3 (75%) besides ca 18% of an unidentified compound. In each case the mixtures were cleanly separated by chromatography on neutral alumina. The decomposition of (1a) in the presence of $Ni(acac)_2$ (1 mol eq) in cyclohexane containing 1% of MeOH under reflux and irradiation with tungsten lamps (250W X 2) required 26h and gave a 9 : 1 (71%) mixture of (3a) and (4a). Under similar condition, however, the methoxy analogue (1b) led to a complex mixture. Treatment of a methanolic solutions of (1a) and (1b) with silver benzoate-TEA under traditional Arndt-Eistert synthesis[10] gave in each case, 80-82% yield of the mixtures of the respective homologated esters and the rearranged esters (5a) and (3a), and (5b) and (3b) in ca 1 : 1 ratio. While photolysis[1,2a] of the desmethoxy-diazoketone (1a) in methanol smoothly produced (5a) in 93% yield, the corresponding methoxy-analogue (1b) afforded the normal homologated ester (5b) (69%) along with an unidentified component.

The reaction of the methoxytetrahydrofluorene diazoketone (2b) (Scheme) in the presence of $Cu(acac)_2$ (3h) or $Ni(acac)_2$ under irradiation (26h), afforded in each case, a mixture of the rearranged ester (6b) and an unidentified product in a ratio of 85 : 15 (ca 67%) from which (6b) could be isolated (ca 50%) by chromatography. In contrast, the desmethoxy analogue (2a)

SCHEME



Reagents : i, Cu(acac)$_2$, C_6H_{12}, MeOH(1%), heat; ii, Cu(OTf)$_2$, C_6H_{12}, MeOH(1%), heat; iii, Ni(acac)$_2$, C_6H_{12}, MeOH(1%), heat, hυ(W); iv, C_6H_5COOAg, NEt_3, MeOH; v, MeOH, hυ.

under identical condition with Cu(acac)$_2$ or Cu(OTf)$_2$ produced a mixture of the rearranged ester (6a), the normal homologated ester (8a) and the MeOH insertion product (7a) in a ratio of 3:2:5 (66%). The Ni(acac)$_2$ promoted reaction of (2a), however, gave a complex mixture. The Cu(OTf)$_2$-catalysed reaction of (2b) again gave a mixture of (6b), (8b) and (7b) in the ratio of 60:13:27 (93%). Treatment of (2a) and (2b) in MeOH with silver benzoate-TEA gave in each case, mixture of the respective homologoated esters and the rearranged esters (83-93%) in the ratio of ca 62:38 and 45:55 respectively along with some unidentified products. On photolysis in MeOH (2a) and (2b) gave the respective homologous esters (8a) (94%) and (8b) (61%).

The present results demonstrate clearly that depending upon the reaction conditions it is possible to control the nature of the rearrangement products in rigid β,γ-unsaturated diazoketones. The copper and nickel salts catalysed reaction provides a simple synthetic entry to the angular acetic ester substituted hydrophenanthrene or hydrofluorene systems. The details mechanistic interpretations of the various courses of metal promoted reactions of β,γ-unsaturated diazoketones and synthetic usefulness of the vinylogous Wolff rearrangement in polycyclic systems will be reported in due course.[11]

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