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# INTRAMOLECULAR CYCLOADDITIONS OF NITRILIMINES ON OLEFINS AND ACETYLENES

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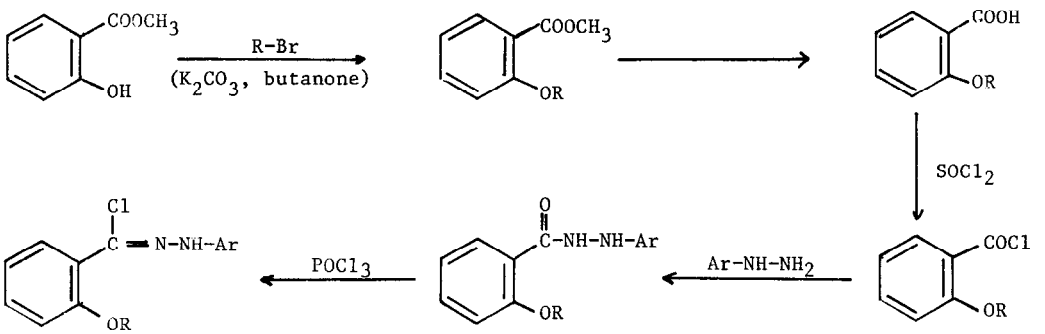
Intramolecular 1,3-dipolar cycloadditions have been extensively studied, but in the particular case of the nitrilimines, the only publications are those by GARANTI et al. (1-3) and those by MEIER et al. (4,5).

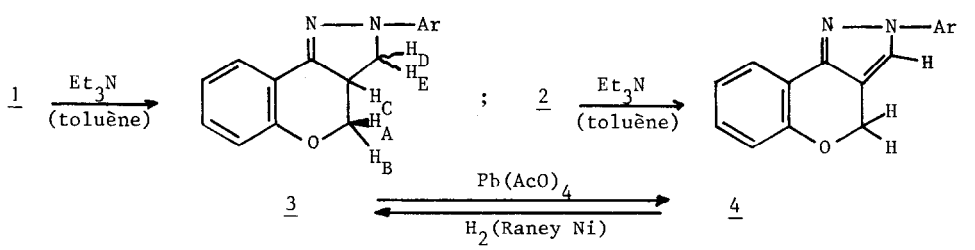
We have studied the nitrilimines derived from α-chlorohydrazones 1 and 2 in which the dipole and the dipolarophile are oriented in the opposite way as in the cases studied by GARANTI et al.

The α-chlorohydrazones 1 and 2 are prepared as follows :




1 : Ar = 2,4-dinitrophenyl, R = $CH_2 - CH = CH_2$ (m.p. 140 °C)

2 : Ar = 2,4-dinitrophenyl, R = $CH_2 - C \equiv CH$ (m.p. 207 °C)



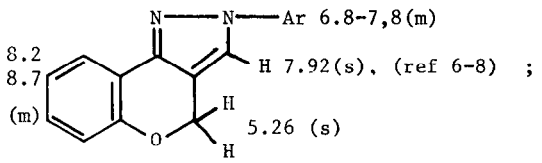

Treatment of 1 in toluene at room temperature with triethylamine (five fold excess) leads to the 2-(2,4-dinitrophenyl) 3,3a-dihydrochromano[4,3-c]pyrazole 3 (m.p. 252 °C ; 85 % yield). In the same conditions, but starting the reaction by warming up to 50 °C, substance 2 leads to the 2-(2,4-dinitrophenyl)chromano[4,3-c]pyrazole 4 (m.p. 165 °C ; 45 % yield).

Treatment of 3 by $Pb(AcO)_4$ in dichloromethane at room temperature leads to 4 and catalytic hydrogenation (Raney Ni) of 4 gave a complex mixture from which 3 was obtained by chromatography.

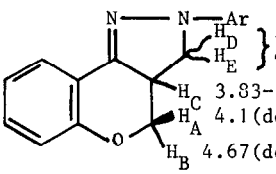
The structures proposed for 3 and 4 are based on the properties mentioned above and on $^1H$ NMR spectra :

Substance 4 ($CDCl_3$, 60 MHz):($O-CH_2$) = 5.26 ppm (s) ; between 6.8 and 7.8 ppm : multiplet (4 aromatic protons) and between 8.2 and 8.7 ppm : multiplet (3 aromatic protons) ; 7.92 ppm (s). This last value agrees with the chemical shifts indicated in the litterature (6-8) for a proton in 5 position of a pyrazole ring.

Substance 3 : 5 spin aliphatic system which could be analysed on a 250 MHz spectra ($D_8$ dioxane)(9) : of the two diastereotopic protons H-C(4) one appears at $H_B$ = 4.67 ppm (dd), $J_{gem\ AB}$ = 10 Hz, $J_{cis\ BC}$ = 5.7 Hz and the other at $H_A$ = 4.1 ppm (dd), $J_{gem\ AB}$ = 10 Hz, $J_{trans\ AC}$ = 11 Hz ; of the two other diastereotopic protons H-C(3) one appears at $H_D$ = 4.12 ppm (dd), $J_{gem\ DE}$ = 10.5 Hz, $J_{DC}$ = 11.5 Hz and the other $H_E$ about 3.2 ppm is partly hidden by dioxan signals.




4




3

$J_{AB}$ = 10Hz(gem)
$J_{BC}$ = 5.7Hz(cis)
$J_{AC}$ = 11Hz(trans)
$J_{DE}$ = 10.5Hz(gem)
$J_{DC}$ = 11.5Hz

Finally, the methynic proton H-C(3a) appears as a multiplet between 3.83 and 3.93 ppm. Each aromatic proton gives a signal which is easily analysed between 6.9 and 8.5 ppm.

The previous results show how easy it is to run these intramolecular cycloaddition reactions : there are done quickly, with little heating and in fairly good yields, even though the dipolarophilic groups in 1 and 2 are generally not very reactive. Moreover, while the usual intermocular cycloaddition orientation of the nitrilimines on a monosubstitued acetylene leads to 5-substituted pyrazoles (10-12) we obtain here, from 2, a 4-substituted pyrazole.

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