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REGIOSELECTIVITY IN THE REACTIONS OF DIPHENYLNITRILIMINE WITH COUMARIN AND CHROMONE

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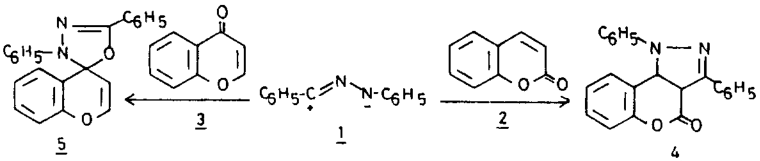
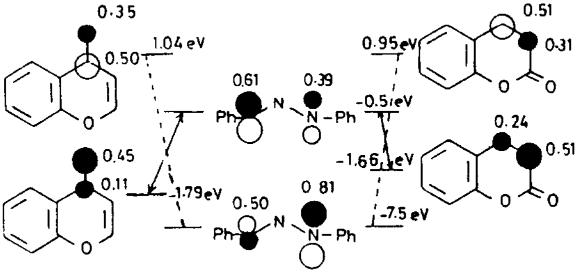
Summary : The cycloaddition of diphenylnitrilimine with coumarin and chromone gave the cycloadducts 4 and 5 respectively. The structures of these products were based on elemental and spectral analyses and alternate synthesis. The orientations of the cycloaddition are interpreted in terms of FMO theory.

In an attempt to evaluate the effect of the presence of electron - donating and electron-withdrawing groups in direct conjugation with the double bond of the dipolarophile on the regioselectivity in the cycloaddition reactions, we have studied the reactions of diphenylnitrilimine 1 with coumarin 2 and chromone 3. The reaction between 2 and 1, prepared in situ from N-phenylbenzohydrazidoyl chloride in benzene in the presence of triethylamine, was carried out at 80°C for 2 h. The sole reaction product was found to be the coumarino (4,3-*d*)pyrazoline derivative 4 (Scheme 1). The other regioisomer was not identified (as evidenced by TLC) in the reaction mixture. The structure of 4 was established by elemental analysis, PMR and IR spectra1) and by comparison with an authentic sample prepared by refluxing 3-benzoylcoumarin phenylhydrazone in acetic acid for 5 h. The regioselectivity of 4 can be explained in terms of the FMO interactions. In scheme 2, the frontier orbital energies and coefficients of 12,3) and 2 (calculated in this work by the extended Huckel Molecular orbital method)4) are given. As shown from this scheme that the favourable LUMO(1)-HOMO(2) interaction would yield 4.

The reaction between chromone and 1 was found to be very slow, it requires 15 h reflux in benzene and gives one isolable product separated by preparative TLC on silica gel. Spectral and elemental analyses indicated the structural formula 5 for the product isolated.5) In contrast, the cycloaddition of 1 to benzoylethylene gives 1,3-diphenyl-5-benzoylpyrazoline



Scheme 1



Scheme 2

(100%).6) The different orientation in case of chromone is undoubtedly due to the strong resonance interaction between the etheric oxygen and the carbonyl group as evidenced by the basicity, pK_b = -2.05 and dipole moment, μ = 5.05 D of chromone.7,8) Such interaction would rather increase the electron density on the carbonyl oxygen of the pyrone ring moiety, thus facilitating the cycloaddition to the C=O bond. This conclusion seems to be substantiated by the results of the molecular orbital calculations summarized in Scheme 2.

References

1) Mp 176-177°C (ethanol), Yield 35%, IR (KBr, cm^{-1}) 1735 (C=O), 1220 (C-O-CO); PMR ($CDCl_3$, ppm) : 4.7 (d, 1H, J = 12 Hz), 4.5 (d, 1H, J = 12 Hz), 7.0-8.0 (m, 14H); Anal. Found : C, 77.68; H, 4.71; N, 8.41%. Calcd. for $C_{22}H_{16}N_2O_2$: C, 77.63; H, 4.74; N, 8.23%.

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5) Mp 172°C ($CHCl_3$-CH_3)H), yield 12%, IR (KBr, cm^{-1}) 1620 (C=N), 1200 (C-O-O), 1150 (C-O-C); PMR ($CDCl_3$, ppm) 7.04 (d, 1H, J = 6 Hz), 6.64 (d, 1H, J = 6 Hz) 7.3-8.3 (m, 14H); Anal. Found : C, 77.39; H, 4.51; N, 7.92%. Calcd. for $C_{22}H_{16}N_2O_2$: C, 77.63; H, 4.74; N, 8.23%.

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