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Nitrile imines react with 1-phenylsulphonyl-2-benzoyl (or methoxycarbonyl)alkenes to give 4-phenylsulphonyl-5-benzoyl (or methoxycarbonyl) substituted pyrazolines. The cycloaddition regioselectivity is discussed in terms of Frontier Orbital energies and coefficients.

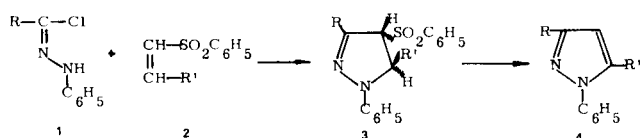
J. Heterocyclic Chem., **16**, 383 (1979).

1,3-Dipoles have been added to a large number of unsaturated systems leading to five membered ring heterocycles (1). Most of such cycloaddition reactions show the characteristics compatible with a four center concerted mechanism (regioselectivity, stereospecificity, small activation enthalpies and large negative activation entropies).

Perturbation theory has been used as method to find an explanation to regioselectivity in 1,3-dipolar cycloadditions and has allowed a qualitative treatment of reactivity of 1,3-dipoles (2). Thus it has been possible to rationalize to some extent the fact that nitrile imines show clean regioselectivity in reaction with electron-rich dipolarophiles to produce 5-substituted pyrazolines exclusively, whereas with electron-deficient dipolarophiles, the mixtures of 5- and 4-substituted adducts are, in some cases, formed (e.g., with α,β -unsaturated esters (3)).

We now have studied the cycloaddition of nitrile imines to unsymmetrically substituted electron-deficient alkenes (2) in order to evaluate the effect of two different electron-withdrawing groups, present on the double bond, on the regioselectivity of the cycloaddition reactions.

The reaction of arylhydrazonyl halides (1) with *trans*-disubstituted alkenes (2) in chloroform solution and in the presence of triethylamine gave only one of the two possible adducts. The main characteristics of the cycloaddition products (3a-d) are summarized in Table I.



The structure of pyrazolines (3a-d) was established on the basis of analytical and spectroscopic data. In fact J₄₋₅ are 2-3 cps accounting for the *trans*-configuration (4). Moreover, pyrazolines (3) can be aromatized by treatment with sodium methoxide in methanol with contemporary elimination of the phenylsulphonyl group to give the corresponding 3,5-disubstituted pyrazoles (4) (5).

The high regioselectivity of our cycloaddition can be explained in a qualitative way by the frontier orbital method. The frontier orbital energies of nitrile imines and monosubstituted electron-deficient alkenes have been

calculated. Comparing the HOMO and LUMO energies for the above species cycloaddition should result to be dipole-HO controlled (Figure 1) (2). This should also be the case of 1,2-disubstituted electron-deficient alkenes where the double substitution should just further decrease the energy values.

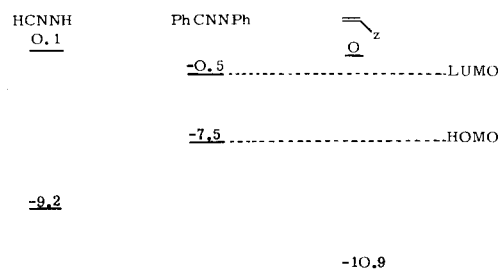


Figure 1 Frontier Orbital Energies of Nitrile Imines and Electrondeficient Dipolarophiles (2)

The coefficients of the relevant orbitals are the second factor affecting the selectivity in the direction of addition. Regioselectivity should follow from large-large/small-small interaction. Since in the HOMO of nitrile imines the phenyl substituted nitrogen has a larger coefficient than the carbon atom (2), in the case of our cycloaddition reaction the exclusive formation of the 4-phenylsulphonyl substituted adducts qualitatively would indicate that in the LUMO of dipolarophile the phenyl sulphonyl substituted carbon has the lower coefficient.

EXPERIMENTAL

Melting points are uncorrected. Nmr spectra were recorded with a Varian A-60 spectrometer (TMS as internal standard).
Dipolarophiles.

Phenyl-2-phenylsulphonylvinylketone (8), methyl 3-phenylsulphonylacrylate (9) and 3-phenylsulphonylacrylonitrile (10) were prepared as reported in the literature.

Nitrile Imines.

α -Chlorobenzaldehyde phenylhydrazone (4) and methyl α -chloroglyoxylate phenylhydrazone (11) were obtained according to the reporting methods.

Table 1

Cycloadduct	R	R'	M.p. °C	Yield %	Molecular Formula	C	H	Calcd.	Analysis			Nmr (Deuteriochloroform) δ		
									N	C	H	N	H ₄	H ₅
3a	C ₆ H ₅	C ₆ H ₅ CO	138-140	84	C ₂₈ H ₂₂ N ₂ O ₃ S	72.09	4.75	6.01	71.95	4.70	6.00	6.5	5.1	2.0
3b	COOCH ₃	C ₆ H ₅ CO	150-152	85	C ₂₄ H ₂₀ N ₂ O ₅ S	64.28	4.50	6.25	64.64	4.53	6.37	6.7	4.9	2.5
3c	C ₆ H ₅	CN	110-112	73	C ₂₂ H ₁₇ N ₃ O ₂ S	68.21	4.42	10.85	68.42	4.31	10.64	6.4	5.2	3.0
3d	C ₆ H ₅	COOCH ₃	156-158	65	C ₂₃ H ₂₀ N ₂ O ₄ S	65.70	4.80	6.66	65.46	4.97	6.37	5.8	5.2	2.0

General Procedure for the Preparation of Cycloadducts (**3a-d**).

Triethylamine (0.01 mole) was added to a solution of unsaturated sulphone (0.01 mole) and of aryl chloride aryl hydrazone (0.01 mole) in chloroform (50 ml.) and the mixture allowed to stand at room temperature for 24 hours. The chloroform was washed with water and dried (sodium sulfate). After evaporation the residue was taken up with diisopropyl ether, filtered and crystallized from methanol.

General Method for Conversion of Pyrazolines into Pyrazoles (**4a-c**).

Phenylsulphonylpyrazoline (0.01 mole) in methanol (50 ml.) was refluxed for 3 hours with sodium methoxide (0.01 mole). The solvent was evaporated and the residue taken up with benzene and water (50:10). The organic layer was washed with water and dried (sodium sulfate). Evaporation of the solvent and crystallization of the residue gave, respectively, **4a-c**.

1,3-Diphenyl-5-benzoylpyrazole (**4a**) (12).

This compound had m.p. 96-98° after recrystallization from diisopropyl ether, yield 85%.

Anal. Calcd. for C₂₂H₁₆N₂O: C, 81.46; H, 4.97; N, 8.64. Found: C, 81.25; H, 4.94; N, 8.62.

1-Phenyl-5-methoxycarbonyl-5-benzoylpyrazole (**4b**) (6).

This compound had m.p. 130-131° after recrystallization from methanol.

1,3-Diphenyl-5-methoxycarbonylpyrazole (**4c**) (3).

This compound had m.p. 108-110° after recrystallization from methanol.

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