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STUDIES IN CYCLOADDITION REACTIONS : REGIOSPECIFIC CYCLOADDITION REACTION OF NITRILE IMINES WITH 2H-1-BENZOPYRAN-2-THIONE

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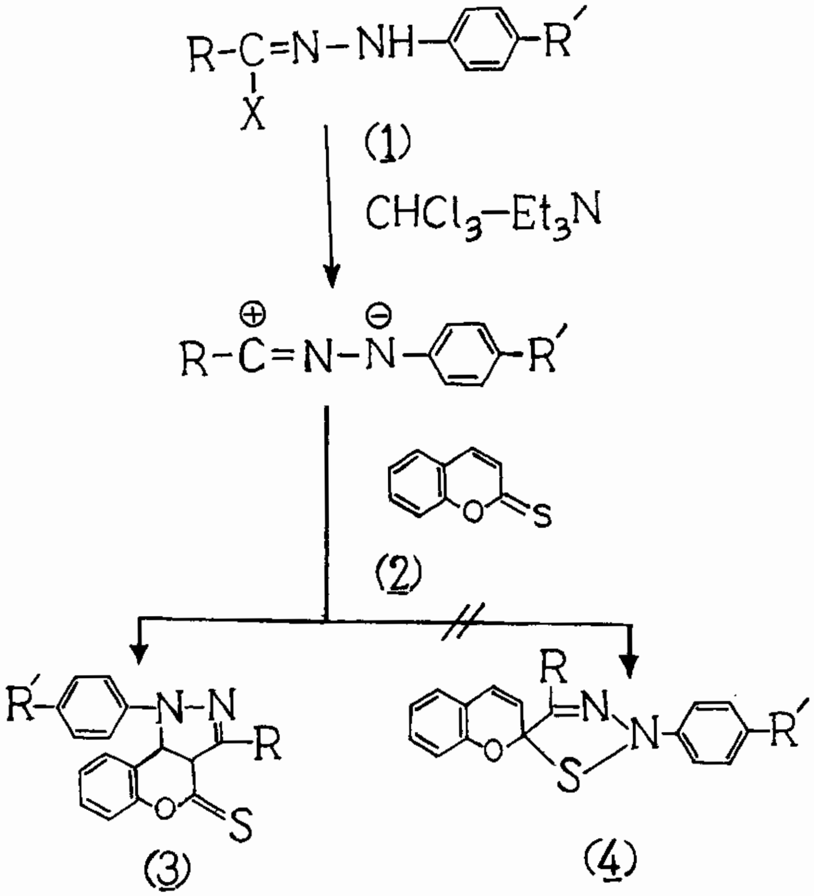
Abstract - Nitrile imines (1) reacted with 2H-1-benzopyran-2-thione to afford cycloadducts (3) in good yields. There was no evidence for the formation of any other regioisomer or the reaction occurring at the thione site.

Cycloaddition chemistry have made considerable impact in organic synthesis[1] and in recent years there has been several reports describing synthesis of complex natural products using this chemistry[2]. The initial recognition of various dipoles[3] and dipolarophiles aroused tremendous interest in this area of research and rationalization of mechanistic aspects[4]. During the past several years we have been studying the behaviour of various dipoles towards substrates having more than one dipolarophilic site. In these investigations when 1-aza-1,3-butadienes were reacted with dipoles like benzonitrile oxides[5] nitrilimines[6] and aziridines[7] only more polar carbon-nitrogen double bond reacted and carbon-carbon double bond remained intact. In the present investigation we report our preliminary results on another bifunctional substrate, 2H-1-benzopyran-2-thione which reacted preferentially with nitrilimines at carbon-carbon double bond leaving the thione site intact[8].

The thione (2) and hydrazinoyl halide (1a) were reacted in equimolar proportions in dry chloroform in the presence of dry triethyl amine at 0 - 5°C and the reaction mixture was stirred for 30 min. The removal of solvent gave a residue which was dissolved in dry benzene and triethylamine hydrobromide thus precipitated was filtered and solvent was removed under vacuum. The residue thus obtained was further purified by column chromatography, and the compound obtained was essentially a single product (3a) (vide tlc) which was readily crystalizable from light petroleum (bp 60-80°C) in 70% yield as yellow crystals mp 135-136°C. H^1 NMR (60 MHz, $CDCl_3$) δ : 2.40 (s, 3H), 5.5 (d, 1H, J=11Hz), 6.8-7.1 (complex multiplet, 9H) ; ν_{max} (KBr), 1250 (lactone, C - O - C), 1505 (C = S), 1695 (C = O). The mass spectrum showed a strong molecular ion at m/z 401. Similarly were obtained compounds (<u>3b-e</u>) in 70 - 75% yield and their characteristics are recorded in the Table.



	R	R'	X
a	CH_3CO	Br	Br
b	CH_3CO	CH_3	Br
c	C_2H_5COO	Br	Br
d	C_2H_5COO	CH_3	Br
e	C_6H_5	H	Cl.

It was remarkable to note that the cycloadducts (3a-e) could also be obtained in excellent yields by reacting (1) with (2) under two phase system using TEBA (Tetrabutylammonium bromide) as a phase transfer catalyst and 25% sodium bicarbonate as a base and following rest of the procedure similar to the one as described above. Apparently this procedure involves the slow production of the dipole and eliminates any formation of dimeric products of dipoles.

Table : Characteristic data of cycloadducts (3a - e)*

Compd	Yield (%)	Yield in TPS (%)	Mp °C	IR (KBr) cm^{-1}	^{1}H NMR (60MHz, CDCl$_3$) δ ppm.	MS (M$^+$) m/z
3a	70	90	135-136	1250, 1505, 1605, 1695.	2.4(s, 3H), 5.5(d, 1H, J=11Hz), 6.8 - 7.1(m, 9H).	401, 369, 358, 245.
3b	75	92	110-112	1250, 1510, 1605, 1690.	2.2(s, 3H), 2.4 (s, 3H), 5.5(d, 1H, J=11Hz), 6.1-7.05(m, 9H).	336, 304, 293, 245.
3c	72	91	103-104	1250, 1490, 1610, 1720.	1.1(t, 3H), 3.9 (q, 2H), 5.6(d, 1H, J=11Hz), 6.3-7.0(m, 9H).	431, 399, 358, 275.
3d	75	90	92-94	1245, 1490, 1610, 1720.	1.2(t, 3H), 4.0 (q, 2H), 5.5(d, 1H, J=11Hz), 6.2-7.0(m, 9H).	366, 334, 293, 275.
3e	70	88	113-114	1225, 1500, 1605.	5.5(d, 1H, J=11Hz), 6.15-7.30(m, 15H).	356, 324, 279, 265.

*All the compounds reported here gave satisfactory elemental analyses.

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