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NOTE

Reaction of active methylene compounds with 4-dimethylaminobenzalaniline and nematicidal activity of the products

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Abstract : Condensation of active methylene compounds (1-7) with 4-dimethylaminobenzalaniline resulted in the formation of addition-elimination products 1a-7a respectively. The products were characterized on the basis of elemental analysis, m.m.p. determination and spectral studies and were evaluated for their nematicidal activity against *Ditylenchus myceliophagus* and *Caenorhabditis elegans* by aqueous *in vitro* screening technique.

Keywords : Active methylene compounds, 4-dimethylaminobenzalaniline, nematicidal activity.

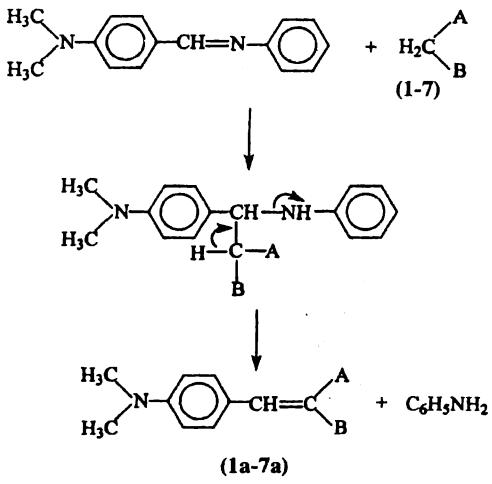
Introduction

In continuation of our work on substitution on benzalaniline[1-3] and biological activity[4,5] of the products, in this communication we have presented our study on the effect of presence of dimethylamino group in the *para* position of C-phenyl ring of benzalaniline on course of the condensation of active methylene compounds and nematicidal activity of the products.

Condensation of 4-dimethylaminobenzalaniline with active methylene compounds (**1-7**) in equimolar ratio in the presence of a base resulted in the formation of crude solids **1a-7a**, respectively, which were recrystallized from benzene. The products were characterized as respective addition-elimination products viz. 4-dimethylaminobenzalcyanoacetic acid (**1a**), ethyl 4-dimethylaminobenzalcyanoacetate (**2a**), 4-dimethylaminobenzalmalononitrile (**3a**), methyl 4-dimethylaminobenzalacetoacetate (**4a**), ethyl 4-dimethylaminobenzalacetoacetate (**5a**), 4-dimethylaminobenzalacetylacetone (**6a**) and 4-dimethylaminobenzalnitromethane (**7a**) on the basis of elemental analysis and spectral studies.

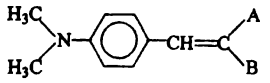
The infrared spectra of the products contained absorption bands at about 1596 and 875 cm^{-1} due to olefinic linkage. In PMR spectra of the compounds in $CDCl_3$, a multiplet between δ 6.8–7.7 accounted for four aromatic protons and one olefinic proton and a six proton singlet at δ 3.0 indicated the protons of the two methyl groups attached to nitrogen. The products alongwith their characteristics and spectral data of functional groups are recorded in Table 1. Further support for the products as addition-elimination compounds came from the m.m.p. determination (no depression) with respective authentic sample. The result of this condensation reaction in case of cyanoacetic acid, ethyl cyanoacetate, ethyl acetoacetate and acetylacetone are at a variance in comparison to such a reaction with benzalaniline[6].

The presence of dimethylamino group in the *para* position of C-phenyl ring of benzalaniline, its seems, facilitates the formation of addition-elimination products rather than addition products. The carbanion formed from the active methylene compound, adds to the carbon-nitrogen double bond of 4-dimethylaminobenzalaniline to give an unstable product which loses aniline molecule to yield a stable addition-elimination product (Scheme 1).



Scheme 1

Table 1. Characteristics and spectral data of 4-dimethylaminobenzal derivatives



Compd.	A	B	m.p. (°C)	Yield (%)	Infrared spectrum (cm^{-1})	PMR spectrum (δ)
1a	CN	COOH	55	80	2240 (nitrile)	-
					1710 (carboxylic)	
2a	CN	$COOC_2H_5$	42	82	2235 (nitrile)	4.4 (2H, q, $-OCH_2$, CH_3)
					1725 (ester)	1.5 (3H, t, $-OCH_2$, CH_3)
3a	CN	CN	48	75	2240 (nitrile)	-
4a	$COCH_3$	$COOCH_3$	82	72	1735 (acetyl)	2.4 (3H, s, $COCH_3$)
					1725 (ester)	4.0 (3H, s, $COOCH_3$)
5a	$COCH_3$	$COOC_2H_5$	90	80	1740 (acetyl)	2.4 (3H, s, $COCH_3$)
					1727 (ester)	4.5 (2H, q, $-OCH_2CH_3$)
						1.4 (3H, t, $-OCH_2CH_3$)
6a	$COCH_3$	$COCH_3$	75	76	1740 (acetyl)	2.5 (6H, s, 2 × $COCH_3$)
7a	H	NO_2	120	79	1540 (nitro)	-
					1360 (nitro)	

The melting points are uncorrected. The compounds gave satisfactory elemental analysis.

Table 2. Nematicidal activity of 4-dimethylaminobenzal derivatives

Compd.	Per cent mortality at concentration (ppm) after 96 h exposure against							
	D. mycleiophagus				*C. elegans*			
	1000	500	250	100	1000	500	250	100
1a	65	50	24	*	74	63	41	*
2a	97	89	70	61	63	42	*	*
3a	47	*	*	*	32	*	*	*
4a	76	48	*	*	28	*	*	*
5a	66	40	*	*	20	*	*	*
6a	36	*	*	*	75	69	44	*
7a	69	52	*	*	85	74	60	22

*Not tested at lower concentration.

4-Dimethylaminobenzal derivatives **1a-7a** were evaluated for nematicidal activity against *Ditylenchus mycleiophagus* and *Caenorhabditis elegans* by aqueous *in vitro* screening technique[7] (Table 2). Five of the test compounds induced more than 50 per cent mortality of *D. myceliophagus* at 1000 ppm and two compounds at 500 ppm. The most effective compound of the present study against *D. mycleiophagus* was found to be ethyl 4-dimethylaminobenzalcyanoacetate (**2a**) which inflicted 61 per cent mortality at 100 ppm. Four of the test compounds showed more than 50 per cent mortality against *C. elegans* at 1000 ppm and three compounds at 500 ppm. The best among the test compounds against *C. elegans* was found to be 4-dimethylaminobenzalnitromethane (**7a**) which induced 60 per cent mortality at 250 ppm.

Experimental

Reaction of active methylene compounds with 4-dimethylaminobenzalaniline : 4-Dimethylaminobenzalaniline (0.01 mol) was dissolved in benzene (20 ml) in a conical flask (100 ml). Active methylene compound (**1-7**) (0.01 mol) was then added to above solution. Then a few drops of pyridine were added. The contents were warmed with stirring, cooled, stoppered and kept at room temperature overnight when a crude solid separated out which

was filtered and recrystallized from benzene to get respective 4-dimethylaminobenzal derivative (**1a-7a**).

In vitro screening for nematicidal activity : The stock solution of each compound was prepared by dissolving the chemical (20 mg) in absolute alcohol (0.5 ml) and the volume was made to 10 ml by adding sterilized distilled water. The stock solution of 2000 ppm of each compound, thus, prepared on active ingredient basis was serially diluted as and when required. The test solution (2 ml) was taken in a glass vial (5 ml) and about 20 nematodes concentrated in a drop of water were added to it and incubated at 25 ± 1 °C. The number of dead or living nematodes was recorded after 96 h by pouring the suspension of the vial in a counting dish and viewing under stereobinocular microscope. The immobile nematode with a definite shape were recorded as dead and per cent mortality was calculated.

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