REACTION OF 5-ARYLIDENERHODAMINE DERIVATIVES WITH 1-PIPERIDINOCYCLOHEXENE AND DIETHYLAMINOHEPTENE ENAMINES

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1,2-Cycloaddition and Michael type reaction of enamines with α,β-unsaturated systems are known to lead to cyclobutanes[1 - 6] and Michael adducts[7 - 9]. The mode of cycloaddition is dependent upon the nature of the enamine[10,11] as well as the position, type and number of electron-withdrawing substituents[12,13] on the heterodiene.

The present paper deals with the reaction of arylidenerhodamine derivatives *Ia – Id* with enamines 1-piperidinocyclohexene *IIa* and diethylaminoheptene *IIb*, stronger nucleophiles[10,11] than 1-morpholinocyclohexane described earlier[14].

EXPERIMENTAL

All melting points are uncorrected. IR spectra (cm^{-1}) were recorded in KBr pellets on a Perkin–Elmer 137 spectrophotometer in KBr. ^1H NMR spectra were recorded in $CDCl_3$ at 60 MHz on a Varian A-60 Spectrometer. The chemical shifts are expressed in δ (ppm) values relative to TMS. Elemental analyses were done by Micro Analytical Laboratory, University of Cairo, Giza, Egypt.

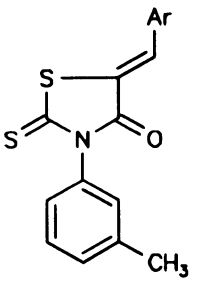
Reaction of Arylidenerhodamine Derivatives *Ia – Id* with Enamines *IIa*, *IIb* (General Procedure)

A mixture of 1.0 equivalent of the arylidenerhodamine, 1.5 equivalent of enamine and few crystals of hydroquinone in dry acetonitrile under dry condition was refluxed for 2 – 5 days. The reaction was followed by ^1H NMR or IR spectra. The solvent was removed under reduced pressure and the residue was triturated with petroleum ether. The crude products, *IIIa – IIId* and *IVa – IVd* were recrystallized from chloroform–petroleum ether. Yields and conditions for the isolated adducts are summarized in Table I and spectral data in Tables II and III.

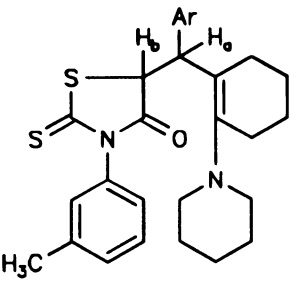
Reaction of Arylidenerhodamine Derivative *Ia* with Enamine *IIa* in the Presence of Tetracyanoethylene

To a mixture of arylidenerhodamine derivative *Ia* (3.0 mmol) and enamine *IIa* (4.0 mmol) in dry acetonitrile (10 ml) was added tetracyanoethylene (3.0 mmol). The reaction mixture was refluxed for 48 h followed by IR spectra. The spectra showed a new band in the region of cyano group. The solvent was evaporated under reduced pressure. The residue was triturated with petroleum ether and

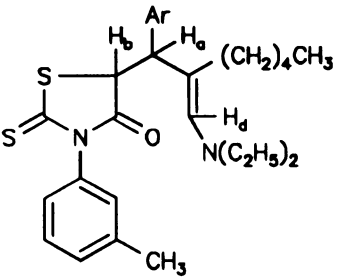
solidified. The product *V* was recrystallized from chloroform–petroleum ether and its experimental data are given in Tables I – III.



I

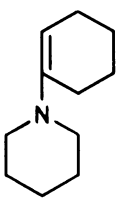


III

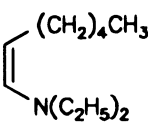


IV

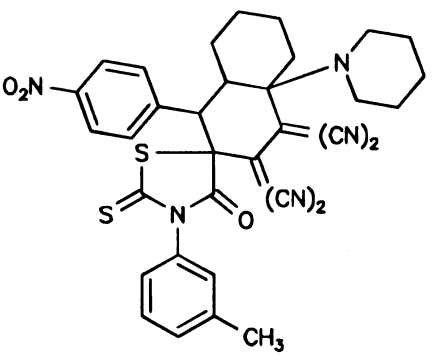
In formulae *I*, *III*, *IV* : *a*, Ar = *p*-NO_2Ph
b, Ar = *p*-ClPh
c, Ar = *p*-CH_3OPh
d, Ar = piperidyl



IIa



IIb



V

TABLE I
Physico-chemical data for synthesized compounds

Compound	Formula M.w.	Reaction time, h	M.p., °C Yield, %	Calculated/Found			
				% C	% H	% N	% S
IIIa	$C_{28}H_{31}N_3O_3S_2$	48	185 – 187	64.46	5.99	8.05	12.29
	521.7		70	64.09	5.45	7.96	12.58
IVa	$C_{28}H_{36}N_3O_3S_2$	60	103 – 105	63.85	6.89	7.98	12.17
	526.7		65	64.89	6.05	8.36	12.58
IIIb	$C_{28}H_{31}ClN_2OS_2$	120	150 – 152	65.80	6.11	5.48	12.52
	511.1		45	66.05	6.38	5.79	12.25
IVb	$C_{28}H_{36}ClN_2OS_2$	130	159 – 160	65.03	7.02	5.42	12.40
	517.2		35	65.38	6.38	5.29	12.75
IIIc	$C_{29}H_{34}N_2O_2S_2$	160	139 – 140	68.74	6.76	5.53	12.63
	506.7		25	68.87	6.92	5.58	13.05
IVc	$C_{29}H_{40}N_2O_2S_2$	170	148 – 150	67.93	7.86	5.46	12.50
	512.8		20	68.97	6.42	5.23	12.35
IIId	$C_{33}H_{41}N_3OS_2$	96	169 – 171	70.80	7.38	7.51	11.45
	559.8		50	66.72	6.45	5.08	12.01
IVd	$C_{33}H_{47}N_3OS_2$	100	171 – 173	70.05	8.37	7.43	11.33
	565.8		48	66.42	6.35	5.18	12.51
V	$C_{34}H_{31}N_7O_3S_2$	48	150 – 152	62.85	4.81	15.09	9.87
	649.8		71	62.56	4.72	15.30	10.00

[a] Reaction followed by TLC or ^{1}H NMR spectra (show no vinyl protons signal) or IR spectra (the carbonyl bands are shifted to the higher frequencies).

TABLE II
IR Spectroscopic data for compounds *I*, *III* – *V*

Compound	ν(C=C, exocyclic)	ν(enamine)	ν(C=O, lactam)
Ia	1 590	–	1 710
IIIa	–	1 660	1 720
IVa	–	1 665	1 715
Ib	1 580	–	1 700
IIIb	–	1 670	1 710
IVb	–	1 680	1 710
Ic	1 580	–	1 705
IIIc	–	1 680	1 715
IVc	–	1 660	1 720
Id	1 580	–	1 690
IIId	–	1 650 sh	1 710
IVd		1 670 sh	1 705
V	–	–	1 725[a]

[a] 2 240 for ν(C=N).

TABLE III
^{1}H NMR Spectra for compounds *III* – *V*

Compound	CH_2–N	CH_3(tolyl)	$H_{a,b}$	H_d	Arom. proton
IIIa	2.6 m (4 H)	2.4 s (3 H)	4.85 d (2 H)	–	7.0 – 8.3 m
IIIb	2.7 m (4 H)	2.3 s (3 H)	5.4 d (2 H)	–	7.0 – 7.9 m
IIIc	2.9 m (4 H)	2.3 s (3 H)	4.9 d (2 H)	–	6.9 – 7.9 m
IIId	2.8 m (4 H)	2.2 s (2 H)	5.3 d (2 H)	–	6.6 – 7.8 m
IVa	3.6 m (4 H)	2.4 s (3 H)	4.5 d (2 H)	5.2 t (1 H)	7.9 – 8.2 m
IVb	3.1 m (4 H)	2.3 s (3 H)	4.9 d (2 H)	5.1 t (1 H)	7.0 – 7.9 m
IVc	3.0 m (4 H)	2.3 s (3 H)	4.8 d (2 H)	5.0 t (1 H)	6.9 – 7.9 m
IVd	3.2 m (4 H)	2.25 s (3 H)	4.8 d (2 H)	5.2 t (1 H)	6.6 – 7.8 m
V	2.8 m (4 H)	2.3 s (3 H)	5.4 d (2 H)	–	7.8 – 8.4 m

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