SYNTHESIS OF A NOVEL CLASS OF CONDENSED 1,2-THIAZINE-S-OXIDES. CYCLOADDITION REACTION OF N-ARYL-4H-5,7a-EPOXYISOINDOLINES WITH N-SULPHINYLANILINE

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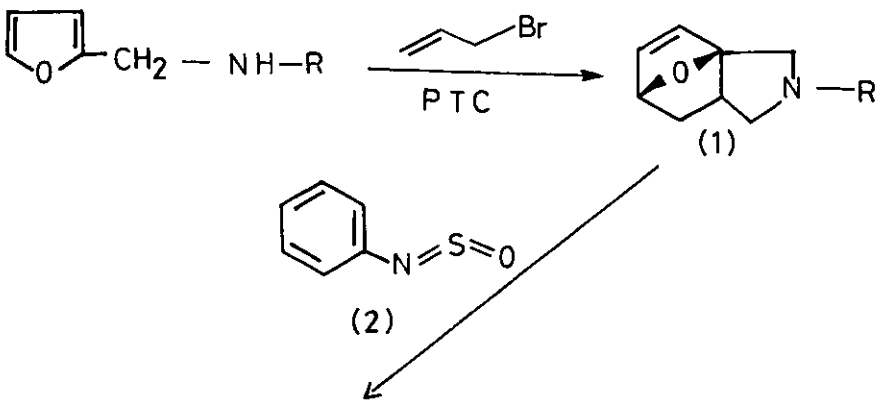
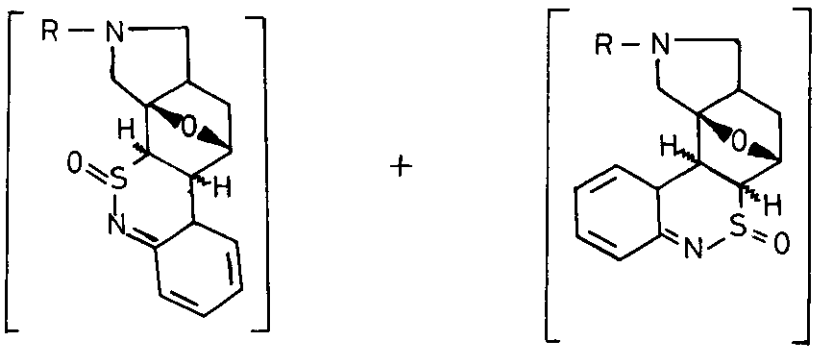
Abstract - N-Sulphinylaniline (2) reacts readily with N-aryl-4H-5,7a-epoxyisoindolines (1) to give a novel class of condensed 1,2-thiazine-S-oxides (3) in good yields.

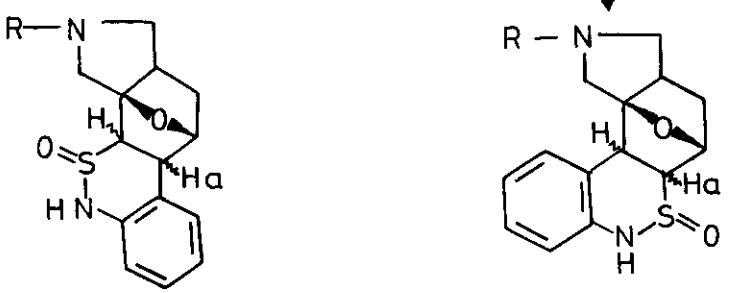
Diels-Alder reaction constitutes a powerful synthetic tool for the synthesis of a variety of polycyclic organic compounds. In the recent years the inverse electron demand Diels-Alder reaction has attracted much attention and is of continuing interest in the synthesis of complex heterocycles as well as natural products[1]. In this context N-sulphinylanilines are typical heterodienophiles and in few cases are reported to react with azadienes[2] as well as alkenes[3]. In case of alkenes only bridged alkenes like norbornenes[4] are found to be reactive. Here we wish to describe an interesting example of inverse electron demand Diels-Alder reaction employing N-sulphinylaniline and N-aryl-4H-5,7a-epoxyisoindolines (1) as dienophilic partners affording us a novel class of condensed 1,2-thiazine-S-oxides (3) in good yields.

N-Aryl-4H-5,7a-epoxyisoindolines (1) were prepared according to our earlier reported[5] procedure and were reacted with N-sulphinylaniline[6] (2) in equimolar quantities in dry benzene. The reaction mixture was stirred for 1 h and then kept at ambient temperature for 48 h, the removal of solvent and usual workup gave a white crystalline solid (3a) mp 248-250°C (dec.) in 70% yield[7].

The molecular formula $C_{22}H_{24}N_2O_3S$ of (3a) was determined by high resolution mass spectrometry in which molecular ion showed at m/z 396.1524 (100%) (calculated value 396.1508) and other major fragments at 380(28%), 367(24%),







(3) (4)

	R	Mp (°C)
3a	C_6H_4- OC_2H_5(p)	248 - 250 (dec.)
3b	C_6H_4- OCH_3(p)	235 - 237 (dec.)
3c	C_6H_4- CH_3(p)	> 275
3d	C_6H_4- Cl(p)	258 - 260 (dec.)
3e	C_6H_4- Br(p)	268 - 270 (dec.)

201(20%), 150(16%) and 118(28%). The IR (KBr) spectrum showed a band at 1075 cm^{-1} indicating the presence of -S=O and other typical absorption at 3190 cm^{-1} corresponds to -NH group. The ^1H NMR (100 MHz, TFA) δ : 1.45 (3H, t), 2.20-2.80 (2H, m), 3.40-5.00 (10H, m) and 6.80-7.70 (8H, m, aromatic) consistent with the structure (3a). Similarly were prepared compounds (3b-e) in 61-70% yield and their characteristics are recorded in the Table.

Table : Physical Data of 1,2-Thiazine-S-oxides (3a-e)

Compd.	Rectn. time	Yield %	*Molecular formula	MS (M^+) m/z	ν max (KBr) cm^{-1}	^1H (100 MHz, CF_3COOH)
3a	48 h	70	$C_{22}H_{24}N_2O_3S$	396	3190,1075	1.45(3H, t), 2.20-2.80 (2H, m), 3.40-5.00(10H, m), 6.80-7.70(8H, m, aromatic).
3b	50 h	65	$C_{21}H_{22}N_2O_3S$	382	3200,1075	2.15-2.75(2H, m), 3.45-5.05(11H, m), 6.85-7.80(8H, m, aromatic).
3c	48 h	66	$C_{21}H_{22}N_2O_2S$	366	3210,1065	1.60(3H, s), 2.40-2.90 (2H, m), 3.30-4.75(8H, m), 6.90-7.80(8H, m, aromatic).
3d	65 h	61	$C_{20}H_{19}N_2O_2SCl$	386	3200,1070	2.30-2.85(2H, m), 3.50-5.10(8H, m), 6.85-7.65 (8H, m, aromatic).
3e	68 h	68	$C_{20}H_{19}N_2O_2SBr$	431	3250,1075	2.35-2.91(2H, m), 3.53-5.05(8H, m), 6.90-7.70 (8H, m, aromatic).

*The microanalyses of these compounds were in satisfactory agreement with the expected results (C $\pm$ 0.43, H $\pm$ 0.30, N $\pm$ 0.26).

ACKNOWLEDGEMENT

The authors are thankful to Dr. Toshio Honda of Hoshi University, Japan for the mass and PMR spectra of one of our samples. One of us (DRB) thanks the Council of Scientific and Industrial Research, New Delhi for the award of a Junior Research Fellowship.

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7. The formation of regioisomer (4) was observed 5 - 10% vide tlc and in one case i.e. (3e) the regioisomer separation was effected to isolate (4e) in 10% yield mp 225 - 227°C (dec.). The ^{1}H NMR (400 MHz, $CDCl_3$) of (3e) and (4e) was clearly distinctive and supporting the regioisomers. In (3e) the bridge head proton showed a doublet at δ 4.5 while in (4e) this proton shifted downfield and showed at δ 4.7. In both the cases it was a clean doublet showing no coupling with ring junction proton Ha which proved the endo configuration of the later.

Received, 23rd May, 1986