Synthesis of some Schiff's bases derivatives from aminoazo compounds

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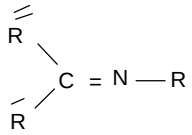
Abstract:

Reaction of,2- [(4- amio phenyl) diazenyl] 1,3,4- thiadiazole -5- thiol (S_1) with p- chlorobenzeldehyde,3,4 – dimethoxy benzaldehyde and pyrrol-2- carbonxaldehyde gave -5- [{4-(4-chlorobenzylidene amino) phenyl} diezenyl]-1,3,4- thiadiazole-2- thiol (S_2),5-[{ 4-[(3,4- dimethoxybenzyldene)amino phenyl] diazenyl)-1,3,4- thiadiazole-2- thiol,(S_3) and -5- [4-(1,H – pyrrol -2- yl- methylene)amino phenyl] diazenyl)-1,3,4- thiadiazole-2- thiol (S_4) respectively as schiff's bases compounds. On the same route-2- [(4-amino-1- naphthyl) diazenyl] -1,3,4- thiadiazole -5- thiol (S_5) reacts with –p- chloro benzaldehyde and –m- nitrobenzaldehyde to give the follwing schiff's bases -5-[{ 4-(4-chloro benzylidene) amino -1- naphthyl} diazenyl] -1,3,4- thiadiazole -2- thiol (S_6) and -5- ({ 4- [3- nitrobenzylidene) amino] -1- naphthyl({ diazenyl) -1,3,4 – thiadiazole-2- thiol (S_7). S_n2 reaction was carried out by the reaction of compound (S_6,S_7) with bromo ethyl acetate to get ethyl[5{4-(4- chlorobenzylidene amino)-1- naphthyl} diazenyl] -1- 1,3,4- thiadiazole-2- yl- thio] acetate (S_8) and ethyl [5-{4- (2- nitrobenzylidene amino)-1- naphthyl diazenyl] -1,3,4- thiadiazole -2-yl-acetate (S_9).(Fig.1).

Introduction:

Schiff's bases, are compounds characterized by the presence of isomethine group ($\rangle C = N -$) and have a general formula



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R, R` , R`` = alkyl or aryl group

Aliphatic Schiff's bases are relatively unstable in aqueous solution while aromatic counterparts are stable due to the resonance[2]. In general, Schiff's bases are prepared by the reaction of equimlor quantities of aromatic or aliphatic aldehydes or ketones with primary aliphatic or aromatic amines in proper solvents[3]. Hammet [4] suggested the presence of acid catalyst to form oxonium ion which accelerates the attack of amine. Schiff's bases are capable to synthesis a hetrocyclic compounds and their metallic complexes [5].Different polymers as antioxidants, heat resistance can be prepared from schiff's bases[6]. Reactions of 2-amino-5-alkythio -1,3,4- thiadiazole with different aromatic aldehydes gave schiff's bases in a god yield

Results and discussion :

Amino group represents a good nuclophile since it has alone pair of electrons which attacks carbonyl group of aldehyde to get N- substituted hemiaminol first then schiff's bases.I.R.[7] spectra showed no absorption at 3300, 3410 cm^{-1} indicating the disappearance of NH_2 group , band at revealed the presence of C= N group, aromaticty and substituted groups in all the preapared compounds revealed the characterized bands in their i.r. spectra (table2) U.V.[7] spectra approved the structures of the prepared schiff's bases.

Absorption at 321.0 nm in related to n-π^* transition for no bonded electrons

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of S,O,N heteroatoms in the compounds, absorption at 282,245 nm are related to π-π^*transition.Red shifts are noticed in many compounds due to conjugation and chromophor groups (table3).an extra work was added considering the nuelophiliaty of thiol group to react with α-bromo- ethylacetate in allcaline media to get thion ion.SN2 mechanism[1] is considered in this work since the bromine represents a good leaving group(conjugated base to strong acid).This mechanism involves attack of the entering nucleophile the electrophilie carbonatism at the opposite side of leaving group, resulting an inversion of configuration at the reaction site [2]

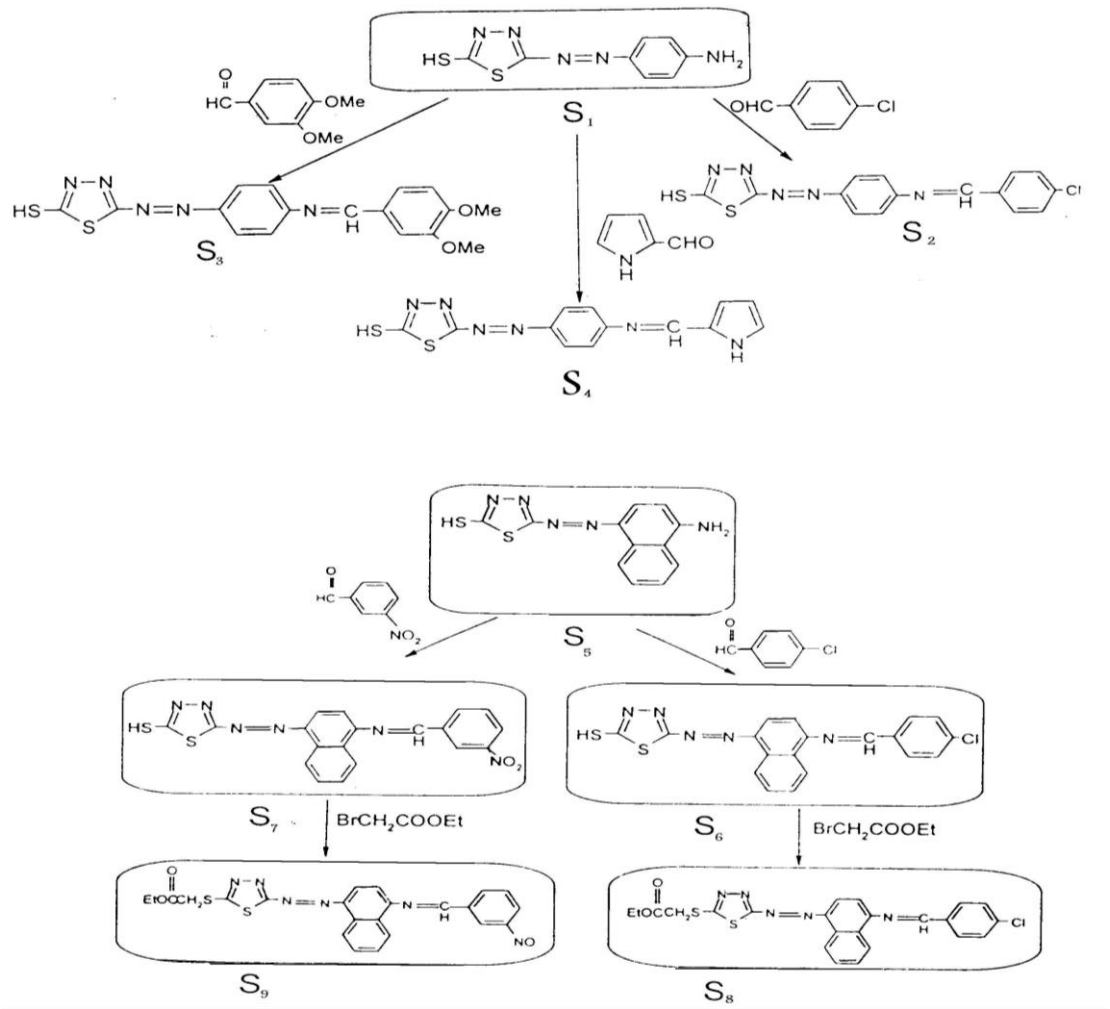

Fig. - 1 -

Experimental:

All chemicals used in this work were highest analytical grad. Melting points were determined by start scientific melting point (SMP).U.V. spectra were recorded with Hitachi- U.V. 2000 spectrophotometers .I.R. spectra were recorded with Pye- Unicame sp3100 spectrophotometer.

1- All the schiff's bases compounds are prepared as according to the following general procedure. azo compound (0.01 mole), aromatic

aldehyde (0.01 mole) and absolute ethanol (20 ml) in a round bottomed flask are refluxed with stirring for 3 h. the mixture was cooled to room temp and filtered. Re crystallization from chloroform gave the desired products (table 1).

2- Preparation of ethyl { [2- [aryl diazenyl] -1,3,4- thiadiazole-5- yl] thio } acetate (S_8,S_9) .The compounds(S_6,S_7)(0.003 mole), ethanol (15ml) and potassium hydroxide (0.39 gm,0.006 mole) were mixed with stirring in a round bottomed flask equipped with reflux. α- bromoethylacetate was added and the mixture was refluxed for 2h. The crude was cooled, filtered and re crystallized from chloroform to get the pure products. (table 1)

Table (1) Some physical properties of (S_1-S_9) compound

Compound	M.P./C°	Color	γield %	Recrys solvent	M.F
S_2	170-172	Pale brown	76	Chloroform	$C_{15}H_{10}N_5S_2Cl$
S_3	166-168	Pale gray	83	Ethanol	$C_{17}H_{15}N_5O_2S_2$
S_4	80-82	Deep gray	72	Ethanol	$C_{13}H_{10}N_6S_2$
S_6	104-106	Pale brown	74	Ethanol	$C_{19}H_{12}N_5S_2Cl$
S_7	113-115	Pale brown	77	Ethanol	$C_{19}H_{12}N_6OS_2$
S_8	121-123	Deep violent	58	Methanol	$C_{23}H_{18}N_5O_2S_2Cl$
S_9	187-189	Violent	73	Ethanol	$C_{23}H_{18}N_6O_4S_2$

Table (2) I.R. Spectra of Compounds (S_2-S_9)

Comp.	C=N cm^{-1}	C=C Aromatic cm^{-1}	S-H cm^{-1}	C-H Aliphatic cm^{-1}	C-H Aromatic cm^{-1}	Others
S_2	1640	1570,1553	2520-2500	2950-2800	3050-3000	Band at 1150 cm^{-1} represents-OCH_3
S_3	1625	1560,1500	2400	2990-2900	3100-3000	Band at 1235 cm^{-1} indicates presence of C-O-C
S_4	1630-1610	1590,1580	2550		3100-3020	Band at 3220-3160 cm^{-1}represent –NH
S_6	1620	1595,1585	2660	2850-2800	3150 -3000	Band at 760 cm^{-1} belongs to C- Cl
S_7	1660	1580,1550	2600	2850-2800	3050-3000	Two Bands at 1580,1340cm^{-1} represent – NO_2
S_8	1630	1580-1560		2900-2750	3100-3150	Band at 1715 cm^{-1} represent C=O Band at 1130 belongs to C-O cm^{-1} Disappearance of –SH abs. at 2660cm^{-1}
S_9	1630	1580-1560		2890-2800	3090-3070	Band at 1725 represents C=O Disappearance of –SH also at 2600.

Table (3) U.V spectra of compounds (S_2-S_9) ; ethanol as solvent

Comp.	λ nm
S_2	378,305,283,248
S_3	358,381,262
S_4	395,349,266
S_6	358,356,263
S_7	321,282,245
S_8	328,275,220
S_9	347,248

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تحضير بعض قواعد شف من مركبات الازو امين

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الخلاصة:

تفاعل المركب -2-[(4- امينو فنيل) دايزنيايل]- 1 ، 3 ، 4 – ثايادايزول -5- ثايول (S_1) مع مركب بارا كلوروبنزلديهايد ، 3 ، 4 – ثنائي ميثوكسي بنزالديهايد ومركب باسرول -2- كاربوكسي الديهايد فاعطى -5- [{4- (4 – كلوروبنزلدين) امينو} دايزينايل] -1 ، 3 ، 4 – ثايادايازول -2- ثايول (S_2) ، -5- [{ 4 – (3 ، 4 – ثنائي ميثوكسي بنزلدين) امينو } فنيل دايزنيايل] -1 ، 3 ، 4 – ثايادايازول -2 – ثايول (S_3) ، -5- [4- (1 H – بايرول – 2- يل – مثيلين) امينو فنيل] دايزنيايل -1 ، 3 ، 4 – ثايادايازول -2- ثايول (S_4) على التوالي كقواعد شف كذلك وبطريقة مماثلة تفاعل -2- [(4-امينو -1-نافثيل) دايازنيايل] -1 ، 3 ، 4 – ثايايازول -5- ثايول (S_5) مع باراكلوروبنزلديهايد وميتانتروبنزلديهايد ليعطي قواعد شف التالية – 5 [{ 4-(كلوروبنزلدين) امينو] -1- نفثيل }دايزنيل]-1 ، 3 ، 4 – ثايادايازول -2- ثايول (S_6) واعطى -5- [{ 4- (3- نتوبنزلدين) امينو-1- نفثيل } دايزنيايل] -1 ، 3 ، 4 – ثايادايازول -2- ثايول (S_7) . كذلك تفاعل المركبان (S_6 ، S_7) حسب ميكانيكية S_N2 مع خلات بروموانيل للحصول على اثيل [5 { 4- (4- كلورو بنزيلدين امينو) -1 – نفثيل } دايزنيايل] -1 ، 3 ، 4 – ثايادايازول – 2 يل ثايو] خلات (S_8) واثيل [5 { 4 (2- نتروبنزلدين امينو) -1- نفثيل دايزنيايل} -1 ، 3 ، 4 – ثايادايازول -2 يل] خلات (S_9) (شكل رقم 1) .