------ Raf. J. Sci., Vol. 22, No.3 pp 57- 61, 2011------

Synthesis of some Aryl sulfonamide Compounds from o-Nitrotoluene

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(Received 18/ 10 / 2010 ; Accepted 14 / 3 / 2011)

ABSTRACT

2-Nitro-4-Methyl benzene sulphonyl chloride (I) has been prepared through sulphonation reaction from chlorosulphonic acid and o-nitrotoluene. Then compound (I) was allowed to react with primary and secondary amines to give a number of sulfonamide compounds (II_{1-14}).

The synthesized compounds were identified depending on the physical and spectral data.

Keyword: sulfonamide compounds.

تحضير بعض مركبات الاريل سلفوناميد من اورثو-نايتروتولوين

الملخص

حضر كلوريد - 2-نايترو-4-ميثل بنزين سلفونيل (I) مـن خلال تفاعل السلفنة بين كلورو حامض السلفونيك وo-نايتروتولوين، بعدها فوعل المركب (I) مع الامينات الاولية والثانوية لإعطاء عدد من مركبات السلفوناميد (II_{1-14}).

شخصت الصيغ التركيبية للمركبات المحضرة بالاعتماد على البيانات الفيزياوية والطيفية.

الكلمات المفتاحية : مركبات السلفوناميد .

INTRODUCTION

Arylsulfonamide compounds were known to possess various biological activities, sulfonamides are synthetic antimicrobial agents which act as competitive inhibitors of the enzyme dihydropteroate synthetase (DHPS) (wikipedia, 2009).

Hypoglycemic sulfonamides used in the treatment of type 2 diabetes mellitus (loub, 2007). Some sulfonamide detective like u,z- Bisarylsufonyl Hydrazine used in antineoplastic , anti- inflammatory , antitubercular (Mohammed *et al*., 2006).

Benzothiazolyl benzene sulfonamide used in cerebro and cardiovascular Dilating agents (Ahmed, 2006), therefore many investigators reported the synthesis of this type of compounds due to the importance of this compound in the medical, industrial and other fields. The norbornem sulfonamide used to prepared Romp Polymer which have more stable

polymers (Kasyan, 2001). Also some sulfonamide derivatives used herbicides (Guuny *et al*., 1999), the common method for the synthesis is by hinsbery reaction which include react primary or secondary amines with sulfonylchloride in the presence of pyridine (R.T Marrson *et al*., 1973).

EXPERIMENTAL

Melting points were determined using electrothermal 9300 Engineering Ltd apparatus and are uncorrected. IR. spectra were recorded by FT-IR spectrophotometer model Tensor 27-Bruker Co. German 2003 as (KBr) disc. UV. spectra were obtained by Shimadzu UV-VIS recording UV-1650 PC spectrophotometer using absolute ethanol as solvent.

Preparation of 2-Nitro-4- Methyl benzene sulphonyl chloride (I) (N. C. Rose, 1970):

To O- nitrotoluene (sul, 0.073 mole), chlorosulfonic acid (10 m, , 0.15 mole) was added. The mixture was reflected fo 30 mintues. Then cooled in an ice bath, poured into 100 g of crushed ice, then extracted with (2 x 20 ml) diethylether. The ether layer was stirred vigorously with 25 ml ammonium hydroxide. The stirring was continued to complete the precipitation, the solid material was separated by filteration, washed with cold water, air dried, recrysttallized from water to give yield 707. of the titled product with mp (25-30 ̊C) (Rose, 1970).

The spectral data of compound (I) showed the following characteristic absorption bands:

υ N=O 1522 cm^{-1} (s)	assymetric stretching of No2 Group
υ N=O 1330 cm^{-1} (s)	symmetric stretching of No2 Group
υ S= O 1298 cm^{-1} (m)	assymetric stretching of So2 Group
υ S= O 1164 cm^{-1} (s)	symetric stretching of So2 Group
υ C=-C 1613 & 1478 cm^{-1}	

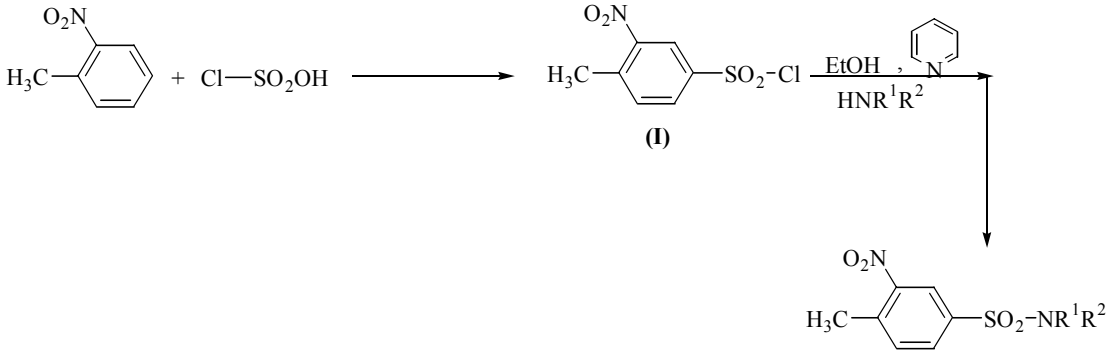
The UV spectrum show bonds at X max (abs. Etoh) 278 nm .

Preparation of sulfonamide compounds (II $_{1-14}$) (Frank, 1947):

Compound (I) (0.01 mole) was dissolved in absolute ethanol (15 ml), then dry pyridine (5-7 drops) was added to the mixture. The mixture was stirred at room temperature for (15 minutes). Amino compound (0.01 mole) was added gradually with stirring. The stirring was continued for (24 hrs) at room temperature. After the addition of the mixture into a beaker containing crushed ice, precipitate was formed. The precipitate was filtered, washed with cold water and recrystallized from ethanol to yield the synthesized compounds (I_{1-14}). The physical and spectral data were illustrated in Table(1).

RESULT AND DISCUSSION

The previous studies showed that some sulfonamides had pharmaceutical activity. The sulfonamido group take part in giving different biological activities (Wilson *et al.*,1982) (Hanafy *et al.,* 2007). Moreover, the hetrocyclic substituted sulfonamides were found to be the best drugs among sulfa drugs (Moore *et al.,* 1978). Therefore, we described here the possibility of synthesing of sulfonamides containing heterocyclic groups in order to obtain expected biologically active sulfonamides Scheme 1.



Scheme 1

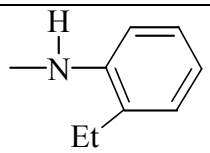
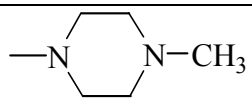
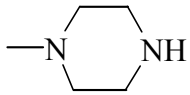
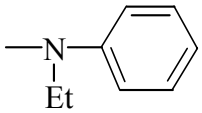
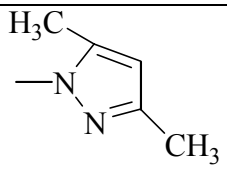
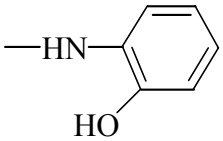
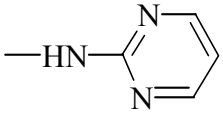
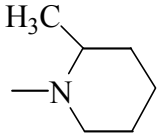
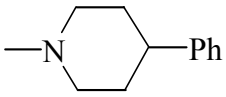
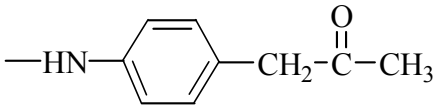
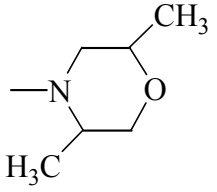
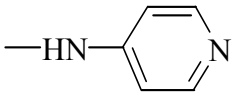
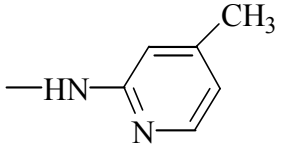
Comp. No.	—NR^1R^2	Comp. No.	—NR^1R^2
II a	 2- ethylaniline	**II h**	 N- methypiperzine
II b	 piperazine	**II i**	 N- Ethyl aniline
II c	 3,5- dimethyporazolen	**II j**	 2-hydroxyaniline
II d		**II k**	
II e		**II l**	
II f	 2,5- dimethylmorptaline	**II m**	
II g	—NH—but n.	**II n**	 4- methyl -2- amino pyridine

Table 1 : physical and spectral data of sulphanomide compounds (II 1-14).

Comp. No.	Yield %	m.p. ˚C	IR. (KBr) cm^{-1}				UV. EtOH λmax (nm)
			υ N=O	υ S=O	υ N-H	others	
II a	85	114-115	1516 1320	1325 1139	 3419	---- ----	268
II b	55	230-233	1512 1314	1362 1155	 3385	---- ----	260
II c	45	149-150	1530 1348	1348 1148		C=N 1617	256
II d	65	208-210	1488 1316	1331 1157	3396	C=N 1624	252
II e	70	169-170	1555 1300	1345 1165			246
II f	82	110-112	1546 1326	1337 1167			250
II g	87	66-67	1527 1338	1338 1174	3455		240
II h	50	120-122	1527 1343	1343 1176			250
II i	80	127-128	1529 1350	1350 1147			244
II j	88	134-136	1514 1331	1340 1142	υ N-H + υ O-H 3430		254
II k	86	80-81	1528 1345	1345 1137			242
II l	76	130-131	1496 1334	1334 1154	3355	υ C=O 1680	260
II m	50	267-270	1491 1318	1338 1150	3391		250
II n	76	257-260	1523 1324	1360 1164	3389		244

The reaction mechanism of benzene sulfonyl chloride with primary and secondary amines was occurred through neuclophilic substitution reaction similar to that of (SN2):

The structural formula of the synthesized sulfonamide compounds (II 1-14) have been investigated according to their physical and spectral data (IR and UV) (Parikh, 1974).

The IR spectra of the synthesized compounds (II 1-14) showed the appearance of two strong absorption bands at the regions (1546-1488) cm^{-1} (1350-1300) cm^{-1} due to the asymmetric and symmetric stretching vibrations of (NO_2) group respectively, also two absorption bands appeared at the regions (1362-1325) cm^{-1} and (1176-1137) cm^{-1} due to

asymmetric and symmetric stretching vibration of (SO_2) group respectively. The broad band at (3455-3283) cm^{-1} is due to stretching vibration of (N-H) bond.

Sometimes, the symmetric stretching vibration band of (NO_2) group was overlapped with the asymmetric stretching vibration of (SO_2) group which appeared as single band at the same region.

The UV. Spectra of synthesized sulfonamide compounds (II 1-14) showed lower λ max. values as compared with compound (I). This is due to the sulfonamido group, which affect the $n \rightarrow \pi^*$ transition leading to decrease the λ ma X values to all the synthesized compounds.

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