ARYLHYDRAZONES OF 5-NITROFURFURYL DICHLOROMETHYL SULFONE*

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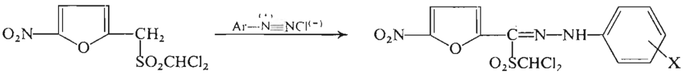
X-Phenylhydrazones of α-dichloromethylsulfonyl-5-nitro-2-furaldehydes ($X = H$, 4-CH_3, 4-OCH_3, 4-Cl, 4-Br, 4-$COOC_2H_5$, 4-COOH, 4-NO_2, 3-NO_2) were prepared by condensation of aryldiazonium salts with 5-nitrofurfuryl dichloromethyl sulfone in ethanolic sodium acetate. IR, UV and ^1H-NMR spectra of the synthesized substances were interpreted.

Sulfones substituted with a 5-nitrofurfuryl group, having an active methylene attached directly to the furan ring, are relatively strong C-acids and easily afford carbanions which condense with aromatic, heterocyclic and some of them also wiht aliphatic aldehydes. Our previous papers showed the possibilities to use these sulfones in syntheses of substituted ethylenes[1-6], and cyclopropanes of 5-nitrofuran series[7]. Compounds containing an active methylene group also react with diazonium salts to furnish arylhydrazones. So far, reactions of some aryl and alkyl sulfones $ArSO_2CH_2CN$ and RSO_2CH_2COX ($X = OH$, NH_2, OC_2H_5) ref.[8,9], as well as sulfones with a methylene group localized between two SO_2 groups[10] were investigated. α-Alkoxy-β-keto sulfones react with diazonium salts to afford the corresponding azo compounds[11].

We synthesized X-phenylhydrazones of α-dichloromethyl-sulfonyl-5-nitro-2-furaldehyde *II*, which can be obtained from 5-nitrofurfuryl dichloromethyl sulfone (*I*) and aromatic diazonium salts according to Scheme 1.



I *II*

SCHEME 1

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* Part CXXVII in the series Furan Derivatives; Part CXXVI: This Journal *44*, 2417 (1979)

The reactions were carried out in ethanolic solution of the sulfone in the presence of sodium acetate in 35 – 50% yields (calculated on the starting sulfone). Attempts to evaluate the synthesized compounds as precursors of nitrilimines *via* elimination of dichloromethanesulfinic acid by means of triethylamine or pyridine failed; this reaction resulted in formation of tarry products.

Physical constants of the synthesized compounds are listed in Table I. Characteristic data of UV and ^{1}H-NMR spectra are summarized in Table II. Absorption bands in the IR region appeared in 1547 to 1550 cm^{-1} ($\nu(NO_2)_{as}$) and 1144 to 1146 cm^{-1} ($\nu(SO_2)_s$) ranges, whereas those ascribable to $\nu(SO_2)_{as}$ and $\nu(NO_2)_s$ were overlapped and appeared between 1347 and 1355 cm^{-1}. Vibrations of C=N and NH groups were seen at 1602 to 1607 and 3328 to 3337 cm^{-1}. All substances revealed a narrow weak band in the 876 to 880 cm^{-1} range belonging to a furan ring. UV spectra of arylhydrazones *III* – *XI* displayed four absorption bands at 208 – 218, 239 – 259,

TABLE I

Characteristic Data of X-Phenylhydrazones of α-Dichloromethylsulfonyl-5-nitro-2-furaldehyde

Compound X	Mol. formula (mol. weight)	M.p., °C (yield, %)	Calculated/Found % S	 % N
III H	$C_{12}H_9Cl_2N_3O_5S$ (378·2)	175—177 (51)	8·48 8·34	11·11 11·19
IV 4-CH_3	$C_{13}H_{11}Cl_2N_3O_5S$ (392·2)	178—180 (42)	8·18 8·21	10·71 10·93
V 4-OCH_3	$C_{13}H_{11}Cl_2N_3O_6S$ (408·2)	171—172 (37)	7·84 7·79	10·29 10·40
VI 4-Cl	$C_{12}H_8Cl_3N_3O_5S$ (412·6)	183—185 (40)	7·75 7·78	10·18 10·25
VII 4-Br	$C_{12}H_8Cl_2BrN_3O_5S$ (457·1)	172—173 (40)	7·00 6·98	9·19 9·08
VIII 4-COOH	$C_{13}H_9Cl_2N_3O_7S$ (422·2)	202—204 (52)	7·58 7·50	9·95 10·14
IX 4-$COOC_2H_5$	$C_{15}H_{13}Cl_2N_3O_7S$ (450·3)	162—165 (36)	7·11 7·08	9·33 9·41
X 4-NO_2	$C_{12}H_8Cl_2N_4O_7S$ (423·2)	172—174 (46)	7·56 7·67	13·23 13·25
XI 3-NO_2	$C_{12}H_8Cl_2N_4O_7S$ (423·2)	181—183 (48)	7·56 7·54	13·23 13·42

304 – 323 and 395 – 441 nm excepting phenylnitro derivatives revealing an additional band (log ε): *X* at 595 (3·56) and *XI* 508 nm (3·30). The first three bands were due to an electronic transition of the phenyl[12] or 5-nitrofuran moiety of the molecule[13]. The absorption band in the 395 – 441 nm range corresponded to electronic transitions of the whole conjugated system of the molecule (K-band). To answer the question, whether the carbon atom bearing the 5-nitrofuran residue and SO_2CHCl_2 grouping has a planar structure, we synthesized phenylhydrazone of 5-nitro-2-furaldehyde[14] as a model substance. The UV spectrum of this compound also had four maxima at 214, 246, 304 and 453 nm. All arylhydrazones *II* showed a hypsochromic shift of the K-band by 10 – 40 nm toward the absorption maximum at 453 nm; the main representative of substances under investigation displayed a 36 nm shift. This finding let us assume that no planar arrangement was encountered at the very carbon atom

TABLE II

Spectral Data of X-Phenylhydrazones of α-Dichloromethylsulfonyl-5-nitro-2-furaldehyde

Compound	λ_{max}, nm[a] (log ε)				$\delta CHCl_2$ ppm
III	214 sh (4·09)	239 (4·19)	316 (4·33)	417 (4·12)	7·36
IV	213 sh (4·01)	242 (4·13)	323 (4·25)	426 (4·06)	7·34
V	213 sh (4·03)	245 (4·13)	333 (4·19)	441 (4·03)	7·33
VI	209 i (4·03)	244 (4·15)	319 (4·05)	413 (4·09)	7·38
VII	208 i (4·05)	245 (4·15)	320 (4·26)	415 (4·10)	7·38
VIII	218 (4·09)	259 (4·07)	320 (4·29)	412 (4·13)	7·40
IX	217 (4·14)	262 (4·11)	319 (4·34)	407 (4·19)	7·41
X	208 i (4·02)	242 i (4·03)	345 (4·11)	410 (4·23)	7·46
XI	210 i (4·16)	244 i (4·25)	305 (4·33)	395 (4·11)	7·43

[a] i Inflection; sh shoulder.

but, due to a bulky SO_2CHCl_2 group, the 5-nitrofuran ring is distorted from the plain of the $\overset{|}{\underset{|}{C}}=N-$ bond similarly, as with α,β-unsaturated sulfones having a 5-nitrofuran grouping[1,15].

Chemical shifts of the proton of dichloromethyl group (H_a, Table II) are in a satisfactory linear correlation with σ_p Hammett's substituent constants $\varrho = 0{\cdot}12$ ($n = 7$); $r = 0{\cdot}91$. The low ϱ value, however, showed that the transmission of the polar effect of substituent through $Cl_2CH-SO_2-\underset{|}{C}=N-NH-$ grouping is quite weak.

EXPERIMENTAL

Compounds *III—XI*

Sodium acetate (2·5 g) in water (4 ml) was added to a stirred solution of 5-nitrofurfuryl dichloromethyl sulfone[5] (3·6 mmol) in ethanol (30 ml) to which an aqueous solution of the diazonium salt was added during 20—30 min at 0°C. The precipitated product was suction-filtered and crystallized from ethanol.

Spectral Measurements

The IR spectra of saturated solutions were measured with a Zeiss UR-20 spectrophotometer in a *p.a.* grade chloroform in 0·62 mm-NaCl cells. Reading accuracy $\pm 2\,cm^{-1}$. Electronic spectra were recorded with a Zeiss Specord UV-VIS apparatus in methanol; concentration $5 \,.\, 10^{-5}$M, 0·995 cm-cell width, reading accuracy ±1 nm. ^1H-NMR spectra were taken with a Tesla BS-487 C instrument operating at 80 MHz in hexadeuterioacetone, hexamethyldisiloxane being the internal standard.

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