SYNTHESIS OF TRISUBSTITUTED ETHYLENES OF THE FURAN SERIES BASED ON 5-METHOXYCARBONYL-2-FURFURYL TRICHLOROMETHYL SULFONE*

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Condensation of 5-methoxycarbonyl-2-furfuryl trichloromethyl sulfone with 4-X-benzaldehydes (X = H, OH, OCH_3, $N(CH_3)_2$, Cl, I, CN) or 5-Y-2-furaldehydes (Y = H, NO_2) in acetic acid in the presence of ammonium acetate and piperidine afforded the corresponding 1-(5-methoxycarbonyl-2-furyl)-1-trichloromethylsulfonyl-2-arylethylenes (*IIa*—*IIj*). Structure of these new compounds is discussed on the basis of their UV, ^1H-NMR and IR spectra.

In our previous studies we described the synthesis of several 5-nitrofurfuryl sulfones[1-6] of the general formula $5\text{-}NO_2C_4H_2OCH_2SO_2R$, where R = C_6H_5, CH_3, $CHCl_2$ or CCl_3. These compounds are relatively strong C-acids which enable a direct synthesis of trisubstituted ethylenes by condensation with aromatic[2] and heterocyclic[3-6] aldehydes. 5-Nitrofurfuryl sulfones, containing the strongly electron-accepting CCl_3 group bonded to the sulfonyl group, react also with aliphatic aldehydes to give the corresponding cyclopropane derivatives of the 5-nitrofuran series[7,8].

Our present study shows that α,β-unsaturated sulfones (trisubstituted ethylenes of the furan series) can be synthesized also using other 5-substituted furfuryl derivatives, which, however, must contain a strongly electron-accepting group bonded to the sulfone moiety.

The derivatives *IIa*–*IIj* were synthesized according to Scheme 1. The starting sulfone was prepared in 45% yield from 5-methoxycarbonyl-2-furfuryl bromide[9] by reaction with sodium trichloromethylsulfinate[10] in sulfolane. When chloride was used instead of the starting bromide, the yield of the sulfone did not exceed 5%. The unsaturated sulfones *II* were obtained by condensation of the sulfone *I* with aldehydes in acetic acid, using piperidine and ammonium acetate as catalyst (except the case of *IIj*, whose preparation was accompanied by formation of tars) in 27–37% yields. These yields were substantially lower than those achieved in condensation of 5-nitro-2-furfuryl trichloromethyl sulfone with the same aldehydes[6]. On the other

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hand, it was shown experimentally that a $COOCH_3$ group in the position 5 of the furan nucleus and a trichloromethyl group bonded to the SO_2 group additionally enhance the acidity of the methylene hydrogens. If the trichloromethyl group is replaced by a phenyl group, the corresponding 5-methoxycarbonyl-2-furfurylphenyl sulfone does not undergo the condensation reaction with aromatic aldehydes. The data on the synthesized compounds are given in Table I and II.

In order to find out whether the condensation affords only one stereoisomer

TABLE I

Properties of the Trisubstituted Ethylenes *IIa*—*IIj*

Compound Y X	M.p., °C (yield, %)	Formula (mol.w.)	Calculated/Found		
			% S	% Cl	% N
IIa	133—135	$C_{15}H_{11}Cl_3O_5S$	7·83	25·96	—
H	(28)	(409·7)	7·69	25·48	—
IIb	188—190	$C_{15}H_{10}Cl_3NO_7S$	7·05	23·39	3·08
NO_2	(37)	(454·7)	7·03	23·50	3·34
IIc	164—169	$C_{16}H_{10}Cl_3NO_5S$	7·38	24·47	3·22
CN	(35)	(434·7)	7·29	24·58	3·28
IId	147—149	$C_{15}H_{10}Cl_3IO_5S$	[a]	[a]	—
I	(32)	(535·6)	[a]	[a]	—
IIe	134—139	$C_{15}H_{10}Cl_4O_5S$	7·22	31·94	—
Cl	(27)	(444·0)	7·08	31·69	—
IIf	199—202	$C_{15}H_{11}Cl_3O_6S$	7·53	24·99	—
OH	(28)	(425·7)	7·40	24·82	—
IIg	135—137	$C_{16}H_{13}Cl_3O_6S$	7·29	24·19	—
OCH_3	(27)	(439·7)	7·17	24·14	—
IIh	171—174	$C_{17}H_{16}Cl_3NO_5S$	7·08	23·49	3·09
$N(CH_3)_2$	(28)	(452·7)	7·03	23·36	3·39
IIi	134—138	$C_{13}H_9Cl_3O_6S$	8·02	26·61	—
H	(31)	(399·7)	7·74	26·53	—
IIj	184—185	$C_{13}H_8Cl_3NO_8S$	7·21	23·92	3·14
NO_2	(35)	(444·6)	7·12	23·84	3·31

[a] For this compound the percentage of carbon and hydrogen was determined; calculated: 33·64% C, 1·88% H; found: 32·56% C, 1·83% H.

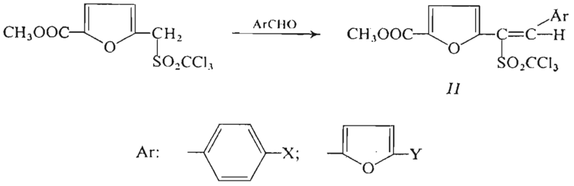
or a mixture of both isomers, we measured the ^{1}H-NMR spectra of crude reaction mixtures. Analysis of the spectral data revealed that only one, non-planar, isomer was formed to which we assigned the *E* configuration. This configurational assignment was based on comparison of UV spectra of the synthesized compounds with that of 1-(5-nitro-2-furyl)-1-trichloromethyl-2-(5-bromo-2-furyl)ethylene. According to X-ray examination[11], this model compound has *E*-configuration and the 5-nitrofuran nucleus deviates by approximately 57° from the double bond plane. The last UV band of this compound is located at 367 nm (log ε 4·06)[6]. The stereochemical reaction

TABLE II

Spectral Data for the Trisubstituted Ethylenes *IIa*—*IIj*

Compound X Y	λ_{max}, nm log ε					$\nu_{(CO)}$	$\delta_{(C=C-H)}$
IIa H	203 (4·45)	226 (4·16)	265 (4·47)	i 291 (4·17)	sh 326 (4·17)	1 728	8·18
IIb NO_2	203 (4·38)	—	i 269 (4·14)	—	345 (3·92)	1 730	8·19
IIc CN	202 (4·22)	—	261 (4·43)	i 283 (4·14)	345 (3·92)	1 732	8·16
IId J	203 (4·37)	240 (4·29)	264 (4·32)	—	327 (4·26)	1 720	8·08
IIe Cl	203 (4·36)	232 (4·20)	267 (4·43)	299 (4·23)	sh 333 (4·13)	1 730	8·12
IIf OH	201 (4·18)	249 (4·21)	—	278 (4·22)	353 (4·30)	1 729	8·08
IIg OCH_3	204 (4·17)	242 (4·23)	—	275 (4·27)	345 (4·35)	1 730	8·10
IIh $N(CH_3)_2$	202 (4·11)	254 (4·11)	—	299 (3·86)	419 (4·40)	1 730	8·01
IIi H	—	—	277 (4·32)	—	351 (4·22)	1 728	7·92
IIj NO_2	202 (4·01)	sh 250 (4·33)		312 (4·15)	384 (4·02)	1 729	7·93

course is thus similar to the situation found for analogous ethylenes of the 5-nitrofurane series[2-6].



SCHEME 1

The UV spectra of most of the synthesized compounds exhibit four absorption bands in the regions 201 – 204 nm, 226 – 254 nm, 260 – 299 nm and 326 – 353 nm. The first three bands can be ascribed to the $\pi \rightarrow \pi^*$ or $n \rightarrow \pi^*$ transitions in the aromatic or furan part of the molecule, conjugated with the ester group. The last absorption band which exhibits a significant hypsochromic shift compared with the planar standard[2] (395 nm; log ε 4·69), proves non-planarity and *E*-configuration of these systems. All the compounds are light-yellow solids except the derivative *IIh*, containing the $N(CH_3)_2$ group, which is orange-coloured and exhibits the last absorption band at 419 nm. This indicates that this compound has a quinoid structure, similarly to the analogous dimethylamino derivatives of the 5-nitrofuran series[6]. The IR spectra display, in addition to bands due to the furan nucleus, characteristic bands due to $\nu(SO_2)_s$ and $\nu(SO_2)_{as}$ in the region 1 150 – 1 160 cm^{-1} and 1 350 – 1 375 cm^{-1}, respectively, the latter band being more affected by the nature of substituent. All the compounds exhibit also very strong bands at 1 728 – 1 732 cm^{-1}, corresponding to $\nu(CO)$ of the ester group. In accord with the UV spectra, their practically constant position proves that the 5-methoxycarbonyl-2-furan moiety deviates from the double bond plane. The chemical shift of the ethylenic proton is 7·90 – 8·12 ppm and does not correlate with σ-Hammett substituent constants.

In our previous studies we have found that addition of diazomethane to 5-nitrofurane analogues of the compounds described in this paper depends on the character of the SO_2R group, leading either to pyrazolines[12] ($R = SO_2C_6H_5$) or directly to cyclopropanes[13] ($R = SO_2CCl_3$). Therefore, we carried out this reaction also with 1-(5-methoxycarbonyl-2-furyl)-1-trichloromethylsulfonyl-2-phenylethylene (*IIa*). Unlike its nitrofurane analogue, this compound afforded 1-pyrazoline, containing traces of 2-pyrazoline, as shown by ^1H-NMR and IR spectra. Thus, replacement of a nitro group on the furan nucleus by a methoxycarbonyl group favours the formation of pyrazoline instead of cyclopropane ring. In this case, a synchronous 1,3-cycloaddition of CH_2N_2 takes place because the ethylenic bond is less polar than in the 5-nitrofuran analogues to which the addition proceeds by a stepwise mechanism to give cyclopropane ring[13].

EXPERIMENTAL

5-Methoxycarbonyl-2-furfuryl Trichloromethyl Sulfone (*I*)

A mixture of 5-methoxycarbonyl-2-furfuryl bromide (4·4 g; 0·02 mol), sodium trichloromethylsulfinate (5 g; 0·025 mol) and sulfolane (50 ml) was heated under stirring for 18 h to 40—45°C, poured on crushed ice and stirred until the separated oil became thick. The product was filtered, washed with water and crystallized from methanol, m.p. 102—104°C, yield 3 g (45%). For $C_8H_7Cl_3O_5S$ (321·4) calculated: 9·42% S, 31·23% Cl; found: 9·92% S, 32·37% Cl.

Preparation of Compounds *IIa—IIi*

A stirred mixture of the sulfone *I* (3·2 g; 0·01 mol), the corresponding aldehyde (0·012 mol), acetic acid (50 ml), ammonium acetate (2 g) and piperidine (3—5 drops) was refluxed for 3 h. After pouring on ice the precipitate was filtered, washed with water and dried. The products were purified by chromatography on silica gel (3 × 50 cm column) in chloroform or by crystallisation from methanol (*IIb*, *IIi*) or ethyl acetate (*IIa*, *IIc*).

1-(5-Methoxycarbonyl-2-furyl)-1-trichloromethylsulfonyl-2-(5-nitro-2-furyl)ethylene (*IIj*)

A mixture of *I* (3·2 g; 0·01 mol), 5-nitro-2-furaldehyde (1·4 g; 0·01 mol), acetic acid (0·3 g), piperidine (2—3 drops) and benzene (30 ml) was refluxed for 4 h in a 100 ml flask equipped with an azeotropic separator. The benzene was removed *in vacuo* and the precipitate crystallized twice from methanol; yield 1·5 g (34%) of light-yellow crystals, m.p. 184—185°C.

Addition of Diazomethane to 1-(5-Methoxycarbonyl-2-furyl)-1-trichloromethylsulfonyl-2-phenylethylene (*IIa*)

An ethereal solution of diazomethane (threefold molar excess) was added at 5—10°C to a solution of *IIa* (1·2 g; 0·003 mol) in tetrahydrofuran (20 ml). After standing for 24 h, the separated 3-(5-methoxycarbonyl-2-furyl)-3-trichloromethylsulfonyl-4-phenyl-Δ^1-pyrazoline was filtered and crystallized from acetone, m.p. 90—92° (decomposition). Yield 1·2 g (91%). For $C_6H_{13}Cl_3N_2O_5S$ (451·7) calculated: 7·10% S, 23·55% Cl, 6·20% N; found: 7·15% S, 23·62% Cl, 6·25% N. IR spectrum, cm^{-1}: $\nu(CO)$ 1730, $\nu(N{=}N)$ 1562, $\nu(SO_2)_s$ 1555, $\nu(SO_2)_{as}$ 1355, $\nu(C{-}O{-}C)$ 1025, $\nu(C{-}H)_{def}$ 985; UV spectrum λ_{max} nm (log ε): 203 (4·28), 259 (3·98), 307 (3·87); ^{1}H-NMR spectrum (ppm): $\delta(CH{-}CH_2)$ m 4·55—4·73, m 4·55—4·73, m 5·28—5·47, $J_{CH,CH2} = 5$ Hz.

Spectral Measurements

IR spectra were measured in chloroform on a UR-20 (Zeiss, Jena) spectrophotometer (0·66 mm NaCl cells, concentration 10^{-2}M or saturated solutions). The instrument was calibrated by a polystyrene foil. Electron absorption spectra were taken on a Specord UV VIS (Zeiss) spectrometer;

$3 . 10^{-5}$—$7 . 10^{-5}$M ethanolic solutions, accuracy ±1 nm. ^{1}H-NMR spectra were measured at 25°C on a Tesla BS 487 B (80 MHz) instrument in deuteriochloroform with tetramethylsilane as internal standard.

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