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Note

Furan derivatives

LII. The gas chromatography of α,β-unsaturated sulphones of the 5-nitrofuran series

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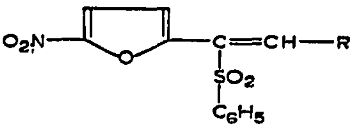
In a previous paper[1], we described a method for the preparation of saturated sulphones of the 5-nitrofuran series with the active methylene group localized between the 5-nitrofuran residue and the SO_2–R group, where R = alkyl, aryl or a heterocyclic ring. As we found, these sulphones undergo a condensation reaction with carbonyl compounds and thus make possible the direct synthesis of 1,1,2-trisubstituted derivatives of ethylene —α,β-unsaturated sulphones of the 5-nitrofuran series. By the condensation of 5-nitrofurfurylphenylsulphone with aldehydes of the benzene series we prepared the corresponding 1-(5-nitro-2-furyl)-1-phenylsulphonyl-2(X-phenyl)ethylenes (I)[2], and with 5-X-2-furaldehydes the 1-(5-nitro-2-furyl)-1-phenylsulphonyl-2-(5-X-2-furyl)ethylenes (II)[3].

The question of the geometric isomers and various conformers in these noncoplanar systems, together with the mechanism of their formation, is discussed elsewhere[2–4].

These 1,1,2-trisubstituted derivatives of ethylene (A) were previously unknown and are interesting from the point of view of both biological activity and physico-chemistry, so that chromatographic studies were thought to be useful.



(A)

R = aldehyde residue

The main purpose of this work was to investigate how to distinguish analytically α,β-unsaturated sulphones of the 5-nitrofuran series. We also studied the effect of substituents on the retention times.

EXPERIMENTAL

Preparation of compounds[1–4]

The starting 5-nitrofurfurylphenylsulphone was prepared by the reaction of 5-nitrofurfuryl nitrate with sodium benzenesulphinate.

Procedure A (derivatives I–XIV). Piperidine (0.5 ml) and ammonium acetate (3.0 g; 0.04 mole) were added to a mixture of 5-nitrofurfurylphenylsulphone (5.4 g; 0.02 mole) and the corresponding aldehyde (0.02 mole) in acetic acid (50 ml), the mixture was refluxed for 5 h, poured on to ice (150 g) and the precipitate was filtered and dried. The crude product was extracted with chloroform and the extract was boiled with charcoal, filtered and concentrated to a small volume. The addition of diethyl ether or light petroleum precipitated the product, which was contaminated with a small amount of starting sulphone. The product was purified by chromatography on an alumina column (16×2 cm, Brockmann activity II), usually using *n*-hexane–ethyl acetate (2:3) as eluent.

Procedure B (derivative XV). A mixture of 5-nitrofurfurylphenylsulphone (2.7 g; 0.01 mole), 5-nitro-2-furaldehyde (2.8 g; 0.02 mole) and acetic anhydride (25 ml) was refluxed for 4 h, cooled in a salt–ice mixture, and the precipitate (unreacted starting sulphone) was filtered off. The filtrate was treated with hydrochloric acid (20 ml; 1:1), the mixture was stirred for 1 h and then poured on to crushed ice (100 g). The precipitate was filtered, washed with diethyl ether and purified chromatographically as described in procedure A.

Gas chromatography

The instrument used was a Hewlett-Packard 7620 A research gas chromatograph with a dual hydrogen flame-ionisation detector. A 183 × 0.2 cm steel column packed with Diatoport (80–100 mesh) and coated with 10% UCW 98 silicone gum was used. The flow-rate of the carrier gas (nitrogen) was 20 ml/min. The injector port and detector temperatures were 250° and 270°, respectively, while the column temperature was programmed between 150 and 300° at 8° min.

The retention indices (I) were calculated graphically or from the equation given

TABLE I

RETENTION TIMES (t_R) AND RETENTION INDICES (I) RELATIVE TO *n*-PARAFFINS OF 1-(5-NITRO-2-FURYL)-1-PHENYLSULPHONYL-2-(X-PHENYL)ETHYLENE

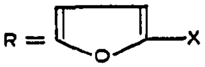
R =


No.	*X*	*m.p.* (°C)	t_R (*min*)	I
I	H	136–138	20.18	2418
II	3-Cl	117–120	21.15	2492
III	4-Cl	132–134	22.01	2555
IV	3,4-Cl_2	176–178	24.13	2700
V	4-I	154–157	14.63	1917
VI	4-NO_2	157–158	17.35	2213
VII	4-CN	154–156	12.77	1727
VIII	4-OCH_3	171–172	9.79	1451

by Kováts[5]. For the graphical determination of retention indices, we used the group of paraffins from C_6 to C_{28}, which were chromatographed on UCW 98 under the same conditions.

TABLE II

RETENTION TIMES (t_R) AND RETENTION INDICES (I) RELATIVE TO *n*-PARAFFINS OF 1-(5-NITRO-2-FURYL)-1-PHENYLSULPHONYL-2-(5-X-FURYL)ETHYLENE



No.	*X*	*m.p.* (°*C*)	t_R (*min*)	*I*
IX	H	115–116	19.23	2351
X	CH_3	113–115	19.74	2386
XI	S-CH_3	124–125	23.20	2638
XII	Br	115–117	20.48	2441
XIII	I	131–132	23.14	2634
XIV	$COOCH_3$	140–142	7.96	1301
XV	NO_2	165–167	14.47	1900

RESULTS

The results in Tables I and II confirm that gas chromatography is a suitable method for the determination of 1-(5-nitro-2-furyl)-1-phenylsulphonyl-2-(X-phenyl)-ethylene and 1-(5-nitro-2-furyl)-1-phenylsulphonyl-2-(5-X-furyl)ethylene. They also show that electron-accepting substituents decrease the value of t_R while substituents with an electron-donor effect shift t_R to higher values.

From this work, it follows that one can apply the method of determination of retention indices described earlier[5,6] to the study of α,β-unsaturated sulphones of the 5-nitrofuran series.

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