REACTION OF 5-NITROFURFURYLTRICHLOROMETHYL SULFONE WITH ALIPHATIC ALDEHYDES. SYNTHESIS OF BUTADIENES AND CYCLOBUTENES RELATED TO 5-NITROFURAN

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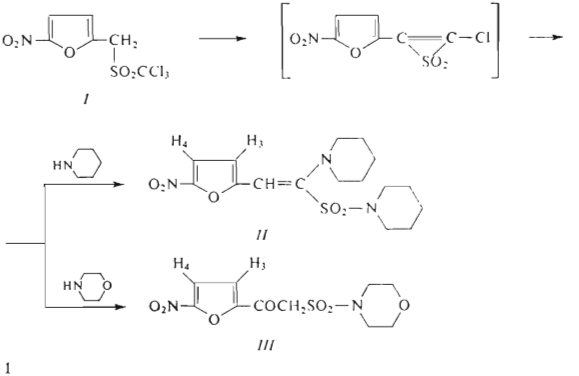
5-Nitrofurfuryltrichloromethyl sulfone (*I*) reacts with piperidine or morpholine to give 1-(5-nitro-2-furfuryl)-2-piperidyl-2-piperidinosulfonylethylene (*II*) or 5-nitro-2-furoylmorpholinosulfonylmethane (*III*). α,β-Unsaturated sulfones, obtained by condensation of the sulfone *I* with aliphatic aldehydes, containing an acidic hydrogen at α-carbon (RCH_2CHO, $R=CH_3$, C_2H_5, C_6H_5), undergo an allylic rearrangement by the action of pyridine, triethylamine or tributylamine to yield butadienes or cyclobutenes derived from 5-nitrofuran. The mechanism of formation of the respective products is proposed and the spectral data (^{1}H NMR, IR, UV and mass spectra) are interpreted.

5-Nitrofurfuryl sulfones of general formula $5\text{-}NO_2\text{—}C_4H_2O\text{—}CH_2\text{—}SO_2R$ ($R=CH_3$, $CHCl_2$, C_6H_4X) are relatively strong CH-acids reacting only with aryl-, heteroaryl or 2-furaldehydes to form α,β-unsaturated sulfones[1–4]. 5-Nitrofurfuryltrichloromethyl sulfone readily reacts not only with aromatic or heterocyclic aldehydes to afford α,β-unsaturated sulfones[5], but also with aliphatic aldehydes under catalysis of piperidine to give the respective cyclopropanes. The reaction mechanism has already been reported[6,7].

This paper deals with reactions of 5-nitrofurfuryltrichloromethyl sulfone (*I*) and its condensation products with aliphatic aldehydes in the presence of bases as catalysts. The sulfone *I* treated with basic catalysts containing an active hydrogen yields products of Ramberg–Bäcklund reaction[8,9] *II* and *III* at room temperature (Scheme 1).

The first step of this reaction involves the formation of a carbanion by a base; this carbanion eliminates Cl^- in an intramolecular reaction to give an unstable thiirane-1,1-dioxide turning into thiirene-1,1-dioxide. An accompanying feature of this step is the precipitation of piperidinium or morpholinium chlorides. Thiirene-1,1-dioxide formed as an intermediate reacts with the base (piperidine, morhpoline to yield *II* or *III*. The latter was formed during the work-up with water. The suggested reaction mechanism is in accordance with the experience with the reaction course of Ramberg–Bäcklund reaction of trichloromethylalkyl sulfones[10]. Formation of different pro-

ducts during this reaction indicates that the strength of the base plays a decisive role. Attempts to isolate cyclic sulfones failed also with changing temperature: at 80 to 100°C (dioxane) the reaction products resinate, at −20–0°C almost no reaction occurred.

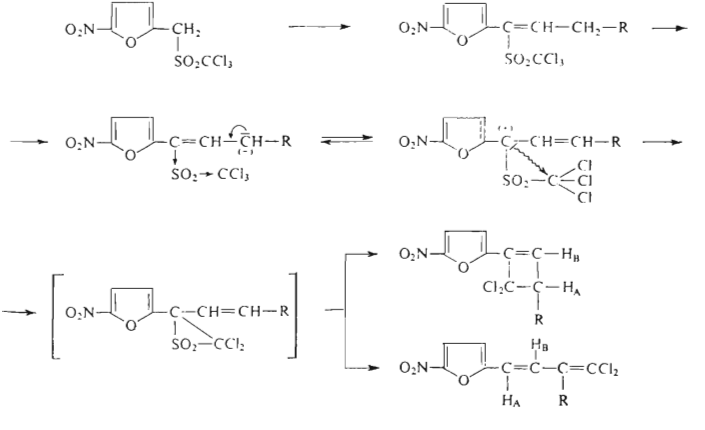


I

II

III

SCHEME 1



SCHEME 2

As we have already reported[7], reaction of the sulfone *I* with aliphatic C_1-C_3 aldehydes catalyzed by piperidine in dioxane leads at 80–100°C to cyclopropanes *via* addition of the starting sulfone carbanion to an α,β-unsaturated, transiently formed sulfone. This was isolated if the condensation was catalyzed with pyridine and the aldehyde used was acetaldehyde. Higher aliphatic aldehydes give rise to butadiene or cyclobutene derivatives related to 5-nitrofuran instead of α,β-unsaturated sulfones. Scheme 2 illustrates the suggested reaction mechanism involving an allylic rearrangement induced Ramberg–Bäcklund reaction. The provisionally formed α,β-unsaturated sulfones having an alkyl at the β-carbon cleave a proton due to a strong polarization of the multiple bond which is associated with an acidification of hydrogens at α′-carbon; the carbanion originating in this way becomes stabilized by an allylic rearrangement followed by the Ramberg–Bäcklund reaction. This step is accompanied by elimination of Cl^- and formation of an unstable thiirane-1,1-oxide. During this reaction, leading to the corresponding cyclobutenes or butadienes, sulfur dioxide is freed. The ratio of products is condition dependent (temperature, reaction time) and the yields vary within 20–30%.

Derivatives of cyclobutene are thermally and photochemically unstable and decompose during storage, as well. On the other hand, butadiene derivatives are stable. The reaction products were isolated providing that propanal, butanal and phenylethanal were the aldehydes. The first two afforded both cyclobutenes and butadienes

TABLE I

Physical constants and elemental analyses of compounds *IV–VIII*

Compound R	Formula M_r	M.p., °C (yield, %)	Calculated/Found	
			% C	% N
IV CH_3	$C_9H_7Cl_2NO_3$ (248·1)	55–56 (21·5)	28·59 28·47	5·65 5·59
V CH_3	$C_9H_7Cl_2NO_3$ (248·1)	136–137·5 (27)	28·59 28·61	5·65 5·60
VI C_2H_5	$C_{10}H_9Cl_2NO_3$ (262·1)	liquid (25)	27·06 27·20	5·34 5·16
VII C_2H_5	$C_{10}H_9Cl_2NO_3$ (262·1)	134–136 (27·5)	27·06 27·10	5·34 5·40
VIII C_6H_5	$C_{14}H_9Cl_2NO_3$ (310·1)	126–128 (24)	22·87 22·90	4·52 4·45

which were chromatographically separated, the third gave the corresponding cyclobutene and a greater amount of an unidentified oil. Cyclobutenes and butadienes could not be isolated from the reaction with methanal, whilst ethanal yielded the already mentioned α,β-unsaturated sulfone. Higher C_6-C_{10} aldehydes gave both types of products in small amounts; these were not isolated but unequivocally identified by the ^{1}H NMR spectra of the reaction mixture.

Physical constants, elemental analyses and spectral data of cyclobutenes *IV*, *VI*, *VIII* and butadienes *V* and *VII* are listed in Tables I, II and III. All products were also identified by mass spectra. As evident isomeric compounds substantially differ in properties and spectral data. The UV spectrum displayed a noticeable K-band shift (at 390 nm); that of butadienes is up to 70 nm bathochromically shifted when compared with cyclobutenes. This feature indicates that these derivatives have an opened butadiene chain the electrons of which interact with the 5-nitrofuran ring. Cyclobutenes have the K-band absorption at 320 nm, this being in agreement with interaction of one multiple band with the 5-nitrofuran residue[11]. Considerable differences between cyclobutenes and butadienes are seen in the ^{1}H NMR spectra (Table III). Butadienes reveal doublets of protons H_A and H_B (*trans* interaction, J_{AB} = = 16·2 Hz), whereas cyclobutenes have the doublet of H_A split either into a quartet (R = CH_3, J_{AR} = 6·6 Hz) or into a triplet (R = CH_2CH_3, J_{AR} = 6·4 Hz) due to an interaction with the alkyl R. The doublet of H_B is similarly split by a long-range inter-

TABLE II
UV and IR spectral data of compounds *IV*–*VIII*

Compound	λ_{max}, nm (log ε)				$\tilde{\nu}$, cm^{-1}			
					$(C{=}C)_{aliph}$	$(NO_2)_{as}$	$(NO_2)_s$	ring deform.
IV	235 (4·18)	255 (4·19)	320 (3·95)		1 643 1 605	1 535 1 502	1 739 1 357	1 024
V	215 (3·88)	280 (4·23)	390 (4·21)		1 621	1 540 1 510	1 390 1 356	1 025
VI	235 (4·17)	255 (4.19)	320 (3·98)		1 641 1 604	1 536 1 502	1 379 1 356	1 026
VII	215 (3·98)	280 (4·25)	390 (4·23)		1 620	1 526	1 390 1 357	1 022
VIII	208 (4·15)	232 (4·17)	310 (4·52)	320 sh (4·44)	1 603	1 530	1 380 1 352	1 020

action with R (J_{BR} = 1·6 and 1·5 Hz, respectively). The coupling constant H_A and H_B of cyclobutenes is 15·6 Hz). These compounds also display a different fragmentation pattern: *IV*: M^+ (100%), M—Cl (15·3%), M—NO_2 (4·1%); *V*: M^+ (100%), M—Cl (2·7%), M—NO_2 (24·3%); *VII*: M^+ (100%), M—Cl (3·6%), M—NO_2 (16·1%); *VIII*: M^+ (48%), M—Cl (35·6%), M—NO_2 (1%).

EXPERIMENTAL

Spectral Measurements

The IR spectra of 0·02 mol l^{-1} or saturated chloroform solutions were recorded with a UR-20 (Zeiss, Jena) apparatus in 0·02—1 mm-cells. Electron absorption spectra of $2·5—5 . 10^{-5}$ mol l^{-1} methanolic solutions were measured with a specord UV VIS (Zeiss, Jena) spectrophotometer in 100 mm cells; reading accuracy ±1 mm. The ^1H NMR spectra were taken with a Tesla BS 487C instrument operating at 80 MHz in hexadeuterioacetone with tetramethylsilane as an internal reference. Mass spectra were run with an AEI MS 902 S (Manchester) spectrometer at 70 eV.

1-(5-Nitro-2-furyl)-2-piperidyl-2-piperidinosulfonylethylene (*II*), and 5-Nitro-2-furoylmorpholinosulfonylmethane (*III*)

A solution of piperidine or morpholine (10 mmol) in dioxane (20 ml) was dropwise added at room temperature to 5-nitrofurfuryltrichloromethylsulfone (1·55 g, 5 mmol) dissolved in dioxane (30 ml). The solution was stirred for 3 h, the separated piperidinium or morpholinium chloride filtered off, the filtrate concentrated, dissolved in chloroform or dichloromethane, washed with dilute HCl and water and dried over $MgSO_4$. The products were separated and purified on a silica gel (Brockmann II, 100—250 mesh) packed column (200 × 30 mm).

TABLE III

^1H NMR data (δ, ppm) of compounds *IV*—*VIII*

Compound R	H_3[a]	H_4[a]	H_A	H_B	R			
IV[b]	6·91	7·55	5·84 dq	6·58 dq	3 H	1·85 dd		
V[c]	6·90	7·53	6·84 d	7·48 d	3 H	2·14 s		
VI[d]	6·90	7·53	5·88 dt	6·56 dt	2 H	2·22 m	3 H	1·03 t
VII[e]	6·94	7·54	6·89 d	7·40 d	2 H	2·64 q	3 H	1·13 t
VIII[f]	7·02	7·62	6·68 d	7·34 d	5 H	7·37 m		

[a] Doublet of furan H_3 protons: $J_{3,4}$ = 3·8 Hz, [b] $J_{A,B}$ = 15·6 Hz, $J_{A,R}$ = 6·6 Hz, $J_{B,R}$ = 1·6 Hz; [c] $J_{A,B}$ = 16·2 Hz; [d] $J_{A,B}$ = 15·6 Hz, $J_{A,R}$ = 6·4 Hz, $J_{B,R}$ = 1·5 Hz, $J_{R,R}$ = 7·3 Hz; [e] $J_{A,B}$ = = 16·2 Hz, $J_{R,R}$ = 7·6 Hz; [f] $J_{A,B}$ = 16·1 Hz.

Compound II: yield 22%, m.p. 124–125°C. For $C_{16}H_{23}N_3O_5S$ (369·4) calculated: 11·37% N, 8·68% S; found: 11·20% N, 8·74% S. IR spectrum, cm^{-1}: $\tilde{\nu}$ (C=C) 1 614, $\tilde{\nu}$ $(NO_2)_{as}$ 1 528, $\tilde{\nu}$ $(NO_2)_s$ 1 382, $\tilde{\nu}$ $(SO_2)_{as}$ 1 352, $\tilde{\nu}$ $(SO_2)_s$ 1 166, 1 144. UV spectrum, λ_{max} (log ε): 230 (4·06), 306 (4·03), 405 (3·95). ^{1}H NMR spectrum, δ, ppm: 7·03 (d, H_3), 7·56 (d, H_4), 6·74 (s, =CH), 3·22 m (8 H), 1·63 (m, 12 H, $J_{3,4}$ = 3·8 Hz).

Compound III: yield 27%, m.p. 112–114°C. For $C_{10}H_{12}N_2O_7S$ (304·3) calculated: 9·21% N, 10·54% S; found: 9·14% N, 10·37% S. IR spectrum, cm^{-1}: $\tilde{\nu}$ (C=O) 1 700, $\tilde{\nu}$ $(NO_2)_{as}$ 1 554, $\tilde{\nu}$ $(NO_2)_s$ 1 388, $\tilde{\nu}$ $(SO_2)_{as}$ 1 356, $\tilde{\nu}$ $(SO_2)_s$, 1 168. UV spectrum, λ_{max} (log ε): 225 (4·0), 305 (4·13). ^{1}H NMR spectrum, δ, ppm: 7·66 (d, H_3), 7·8 (d, H_4), 4·76 (s, CH_2), 3·73 (m, 4 H), 3·38 (m, 4 H); $J_{3,4}$ = 3·9 Hz.

Butadienes and Cyclobutenes *IV–VIII*

A solution of an aliphatic aldehyde (10 mmol) and pyridine, or triethylamine, or tributylamine (10 mmol) in dioxane (20 ml) was successively added to a stirred solution of 5-nitrofurfuryltrichloromethyl sulfone (1·55 g, 5 mmol) heated to 60–100°C in dioxane (40 ml). The concentrated solution was then dissolved in chloroform, washed with hydrochloric acid and water, and dried over $MgSO_4$. The products were separated and purified by chromatography on silica gel as in the preceding case.

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