

Furan derivatives. CLIV.

Synthesis of 5-nitrofuran type cyclopropanes by a reaction of diazomethane with α,β -unsaturated sulfones

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Reaction of diazomethane with 1-(5-nitro-2-furoyl)-1-phenylsulfonyl-2-(4-X-phenyl)ethylenes in tetrahydrofuran at 0–5°C yielded the corresponding 1-(5-nitro-2-furoyl)-1-phenylsulfonyl-2-(4-X-phenyl)cyclopropanes (X = CN, F, Cl, NO₂). The formation of pyrazolines, the possible intermediates of the cycloaddition reaction, has not been observed under the applied reaction conditions.

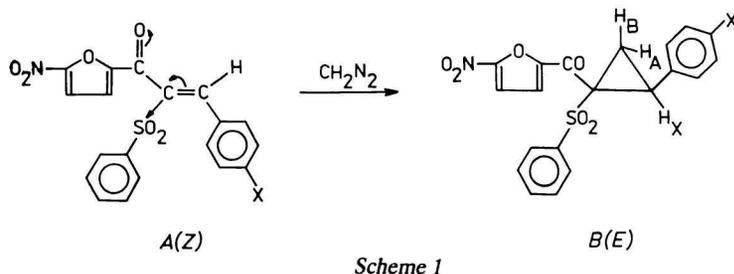
Реакцией диазометана с 1-(5-нитро-2-фурил)-1-фенилсульфонил-2-(4-X-фенил)этиленами в тетрагидрофуране при 0–5°C образуются соответствующие 1-(5-нитро-2-фурил)-1-фенилсульфонил-2-(4-X-фенил)циклопропаны (X = CN, F, Cl, NO₂). В указанных условиях не было замечено образование пиразолинов как возможных промежуточных продуктов реакции циклоаддиции.

Diazomethane reacts with double bonds by 1,3-dipole cycloaddition reaction to give pyrazoline derivatives [1, 2]. In addition to activating multiple bonds, electron-withdrawing groups direct the addition in that the carbon atom of diazomethane is linked to the β carbon, with respect to the activating group, of the multiple bond. Some α,β -unsaturated sulfones react with diazomethane to give, depending upon the structure of the sulfone and orientation of diazomethane, typical and nontypical pyrazolines [3].

We have found [4] that the addition of diazomethane to 1-(5-nitro-2-furyl)-1-phenylsulfonyl-2-(4-X-phenyl)ethylenes yields 1-pyrazolines which thermally decompose to tetrasubstituted ethylenes and not to the corresponding cyclopropanes. On the other hand, strongly polar 1-(5-nitro-2-furyl)-1-trichloromethylsulfonyl-2-(4-X-phenyl)ethylenes containing more electron-withdrawing trichloromethylsulfonyl group, instead of the phenylsulfonyl residue, yield directly cyclopropane derivatives by way of untermiated stepwise mechanism [5].

The aim of the present work was to perform reactions of diazomethane with another type of strongly polar, nonplanar α,β -unsaturated sulfones — chalcones of

5-nitrofuran type *A*, and to find whether pyrazolines or cyclopropanes would be the reaction products. Syntheses and the proof of *Z* configuration of the starting trisubstituted ethylenes have been described [6] (Scheme 1)



It follows from elemental analyses of products and spectral data for crude reaction mixtures that trisubstituted cyclopropane derivatives *B* were formed exclusively under the applied reaction conditions (see Experimental).

Physicochemical and spectral characteristics of cyclopropane derivatives are summarized in Tables 1—3. The presence of a cyclopropane ring is evident from the bands present at $3153\text{--}3150\text{ cm}^{-1}$ ($\nu(\text{CH})$) and $1083\text{--}1079\text{ cm}^{-1}$ (skeletal vibrations) in the i.r. spectra. The u.v. spectra show three absorption bands, the last of which shows but slight hypsochromic shift (5—10 nm) compared to the starting ethylenes, confirming thus their nonplanarity [6]. The cyclopropane protons appear in the ^1H -n.m.r. spectra as an ABX system. The nonequivalent H_A and H_B methylene protons are split into a pair of doublets by the geminal interaction and *cis* and *trans* interaction with the methine proton H_X . The chemical shifts (H_A : δ

Table 1
Synthesized 1-(5-nitro-2-furyl)-1-phenylsulfonyl-2-(4-X-phenyl)cyclopropanes

Compound	X	Formula	M	Calculated/found			Yield %	M.p. °C
				% C	% H	% N		
I	CN	$\text{C}_{21}\text{H}_{14}\text{N}_2\text{O}_6\text{S}$	422.35	59.72	3.34	6.63	80	162—163
				59.20	3.10	6.20		
II	F	$\text{C}_{20}\text{H}_{14}\text{FNO}_6\text{S}$	415.32	57.83	3.32	3.37	64	148—149
				57.25	3.35	3.32		
III	Cl	$\text{C}_{20}\text{H}_{14}\text{NO}_6\text{SCl}$	431.75	55.63	3.27	3.24	75	178—179
				55.50	3.18	3.35		
IV	NO_2	$\text{C}_{20}\text{H}_{14}\text{N}_2\text{O}_6\text{S}$	442.34	54.30	3.19	6.33	82	184—185
				54.13	3.02	6.42		

Table 2

Characteristic i.r. and u.v. spectral data observed for the synthesized substances

Compound	$\nu_{\text{as}}(\text{CH}_2)$ ν_{skel}	$\nu(\text{C}=\text{O})$	$\nu_{\text{as}}(\text{NO}_2)$ $\nu_{\text{s}}(\text{NO}_2)$	$\nu_{\text{as}}(\text{SO}_2)$ $\nu_{\text{s}}(\text{SO}_2)$	$\lambda_{\text{max}}/\text{nm}$ ($\log \epsilon$)		
I	3152	1679	1550	1324	210	215	282
	1079		1354	1152			
II	3153	1678	1550	1320	211	219	290
	1082		1352	1150			
III	3150	1677	1552	1322	210	220	280
	1079		1358	1152			
IV	3153	1678	1552	1320	212	216	289
	1083		1354	1151			

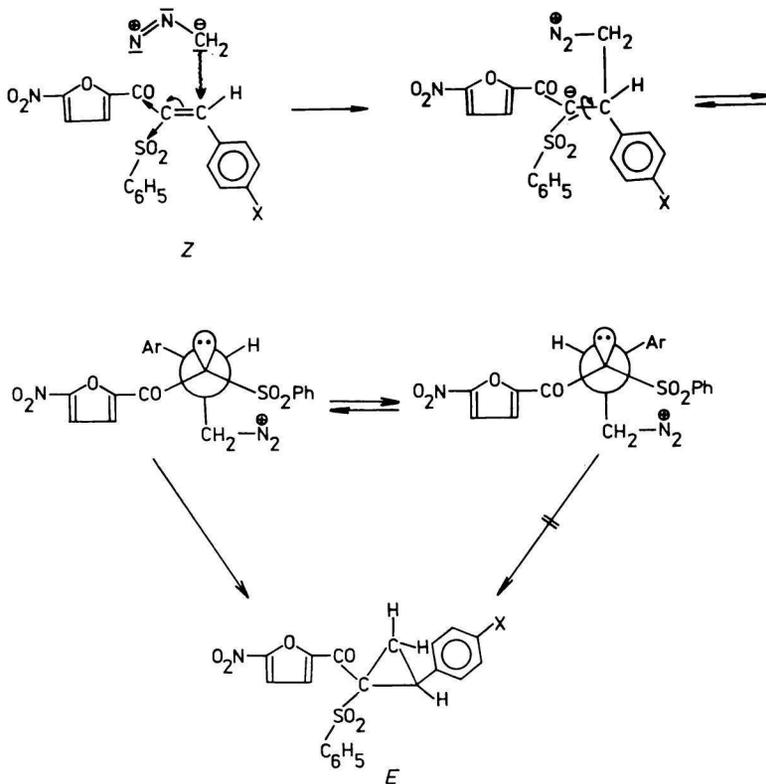
Table 3

Table shifts (p.p.m.) and coupling constants (Hz) for relevant protons of the synthesized substances

Compound	H_4	H_3	H_a	H_b	H_A	H_B	H_X	
	$J_{3,4}$			$J_{a,b}$	J_{AX}	J_{BX}	J_{AB}	
I	7.85	7.61	7.37	8.2	7.69	5.05	4.84	4.54
	4.0				8.18	4.84	2.61	9.80
II	7.80	7.59	7.22	8.5	6.96	4.93	4.86	4.50
	4.0				7.71	4.86	3.58	9.80
III	7.84	7.66	7.14	8.5	7.31	5.02	4.74	4.49
	4.0				8.19	4.74	3.30	9.50
IV	7.82	7.58	7.20	8.5	6.75	4.96	4.82	4.51
	4.0				7.95	4.82	2.95	9.70

4.93—5.05 p.p.m., H_B : δ 4.74—4.86 p.p.m., and H_X : δ 4.49—4.54 p.p.m.), coupling constants, larger values for *cis* than for *trans* interactions (J_{AB} 9.5—9.8 Hz, J_{AX} 7.71—8.19 Hz, J_{BX} 2.61—3.58 Hz), and the multiplicity of the signals observed in the ^1H -n.m.r. spectra of the synthesized substances (Table 3) agree well with the data reported for cyclopropanes [7, 8].

Molecular models and data in our other works [5, 9] show that with the bulky substituents (Scheme 1) the *trans* arrangement of the phenylsulfonyl and 4-X-phenyl residue, *i.e.* *E* configuration, is more favourable than the *cis* arrangement. Had diazomethane reacted with the starting ethylenes of *Z* configuration by 1,3-dipolar cycloaddition the formed cyclopropanes would have preserved



Scheme 2

the same configuration of the substituents. Thus, it appears that also here diazomethane reacts with the strongly polarized $>C=C<$ arrangement by untermi-nated stepwise mechanism [5]. In the course of the reaction a rotation around a σ bond of the carbanion formed in the transition state cannot be excluded. In the resulting more favourable conformation an intermolecular S_Ni reaction can then operate and eventually cyclopropanes, having probably *E* configuration (Scheme 2), are formed.

Experimental

1-(5-Nitro-2-furoyl)-1-phenylsulfonyl-2-(4-X-phenyl)ethylenes were prepared by condensations of the corresponding 5-nitro-furan type β -ketosulfones with aromatic aldehydes under the conditions of the modified *Lehnert's* method [10, 11], *i.e.* in tetrahydrofuran or dioxan, and the presence of a catalytic amount of $TiCl_4$.

The i.r. spectra for saturated chloroform solutions were recorded with UR-20 (Zeiss, Jena) spectrophotometer using sodium chloride 0.02 mm cells. The instrument was calibrated against a polystyrene foil. Electronic absorption spectra for $2.5\text{--}5.0 \times 10^{-5}$ M dioxan solutions were measured with Specord UV VIS (Zeiss, Jena) instrument using 1 cm cells. The accuracy of the reading was ± 1 nm. $^1\text{H-N.m.r.}$ spectra for solutions in DMSO-d_6 were obtained at $20\text{--}25^\circ\text{C}$ with a Tesla BS 487C spectrometer using hexamethyldisiloxane as the internal standard.

1-(5-Nitro-2-furoyl)-1-phenylsulfonyl-2-(4-X-phenyl)cyclopropanes (I—IV)

Ethereal diazomethane (3—5 molar excess with respect to the substrate) was added at $0\text{--}5^\circ\text{C}$ to the solution of ethylenes (1—5 mmol) in dry tetrahydrofuran, and the reaction mixture was kept at $0\text{--}5^\circ\text{C}$ for 10 days. After concentration at reduced pressure, the products were obtained by crystallization from acetone or by chromatography on silica gel (100—250 mesh). Physical and spectral characteristics observed for the synthesized substances are given in Tables 1—3.

References

1. Houben, T. and Weyl, T., *Methoden der organischen Chemie*, 4. Auflage, *Stickstoffverbindungen I*, Part 4, p. 804. Thieme, Stuttgart, 1968.
2. Behr, L. C., Fusko, R., and Jarboe, C. H., in *The Chemistry of Heterocyclic Compounds*. (Weissberger, A., Editor.) Vol. 22, *Pyrazoles, Pyrazolines, Indazoles and Condensed Rings*. (Wiley, R. H., Editor.) Interscience, New York, 1968.
3. Parham, W. E., Blake, F. D., and Theisen, D. R., *J. Org. Chem.* 27, 2415 (1967).
4. Jurášek, A., Kováč, J., and Kováč, M., *Collect. Czech. Chem. Commun.* 41, 3391 (1976).
5. Prousek, J., Jurášek, A., and Kováč, J., *Collect. Czech. Chem. Commun.*, in press.
6. Polakovičová, D., Jurášek, A., and Kováč, J., *Collect. Czech. Chem. Commun.*, in press.
7. Müller, Ch., Stier, F., and Weyerstahl, P., *Chem. Ber.* 110, 124 (1977).
8. Aksekov, V. S. and Terenteva, G. A., *Izv. Akad. Nauk SSSR, Ser. Khim.* 3, 623 (1977).
9. Geisbacher, D., Jurášek, A., and Kováč, J., *Collect. Czech. Chem. Commun.* 44, 1984 (1979).
10. Lehnert, W., *Tetrahedron* 28, 663 (1973).
11. Lehnert, W., *Tetrahedron* 30, 301 (1974).

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