CYCLOPROPANES OF 5-NITROFURAN SERIES*

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5-Nitrofurfuryl trichloromethyl sulphone (*I*) was reacted with paraformaldehyde in methanol in the presence of piperidine as catalyst to give 1-(5-nitro-2-furyl)-1-trichloromethylsulphonyl-2-(5-nitro-2-furyl)cyclopropane. This substance was also obtained from 1-(5-nitro-2-furyl)-1-trichloromethylsulphonyl-2-(5-nitro-2-furyl)ethylene and diazomethane. The reaction products were characterized by IR, UV, ^{1}H-NMR and mass spectral data.

So far, little attention has been paid to cyclopropanes substituted by 5-nitro-2-furyl group. Sasaki and coworkers[1,2] synthesized such derivatives by 1,3-dipolar cycloadditions of either 5-nitro-2-furyldiazomethane to acryloylamide or diazomethanes to 5-nitro-2-furylacrylic acid followed by thermal decomposition of pyrazolines formed. Diazomethane was employed in preparation of a similar derivative[3]. 5-Nitrofurfurylsulphones having at the SN_2 group an alkyl or aryl are relatively strong C-acids and, as we ascertained, condense with aromatic and heterocyclic aldehydes only to furnish the corresponding α,β-unsaturated sulphones of 5-nitrofuran series[4–6]. The same products were obtained from sulphone *I*, which reacts unlike the above-mentioned sulphones not only with aromatic, but also with aliphatic aldehydes. This paper deals with reaction of paraformaldehyde with sulphone *I* (ref.[7]) under catalysis of piperidine; cyclopropane *II* (ref.[8]) was isolated and identified from the reaction mixture (Scheme 1). In addition, tarry products and piperidinium chloride were isolated from the reaction mixture; the latter could be formed by Ramberg–Bäcklund reaction[9–11] and also by a direct nucleophilic attack of the base (piperidine) to trichloromethyl group[11]. The same cyclopropane *II* was obtained by reaction of diazomethane with 1-(5-nitro-2-furyl)-1-trichloromethylsulphonyl-2-(5-nitro-2-furyl)ethylene (*III*) (ref.[12,13]). Configurations at $C_{(1)}$ and $C_{(2)}$ of cyclopropane *II* were deduced on the basis of ^{1}H-NMR spectral evidence. Protons of nonequivalent furan rings were ascribed by means of the INDOR technique ($^3J_{1,2} = {}^3J_{3,4} = 4$ Hz). Coupling constants of protons H_A, H_B, H_C were determined by decoupling of the respective interactions. Their values ($^2J_{A,B} = {}^3J_{A,C} = 7{\cdot}5$ Hz geminal or *trans* interaction and $^3J_{B,C} = 10{\cdot}3$ Hz *cis* interaction) correspond to known ones of cyclopro-

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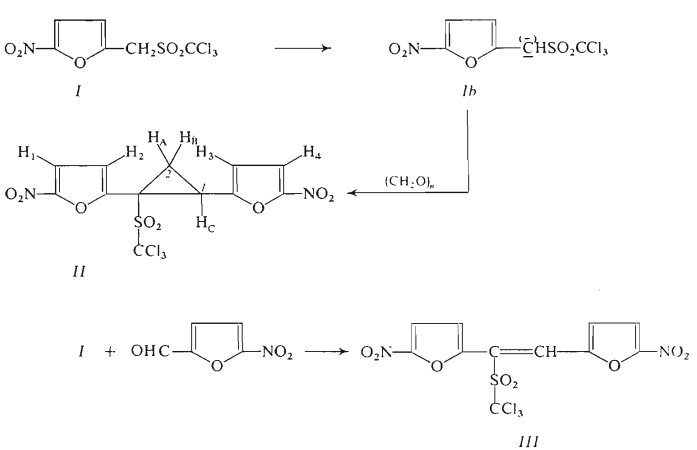

SCHEME 1

pane protons[14-17]. The structure of derivative *II* was further supported by IR and mass spectral data.

EXPERIMENTAL

Melting points were measured on a Kofler hot stage and are uncorrected. ^{1}H-NMR spectra recorded with a Tesla BS 487 B spectrometer operating at 80 MHz at 50°C in hexadeuterioacetone or hexadeuteriodimethyl sulphoxide with hexamethyldisiloxane as internal reference substance are given on δ scale in ppm. Decoupling was measured in hexadeuteriodimethyl sulphoxide at 26°C. Mass spectra were taken with an AEI MS 902 S spectrometer, IR spectra with a UR-20 (Zeiss Jena) spectrophotometer in KBr, electronic absorption spectra with a Specord UV VIS (Zeiss Jena) apparatus in methanol at $3-5 \cdot 10^{-5}$ M in a 1-cm cell; reading accuracy ± 1 nm.

1-(5-Nitro-2-furyl)-1-trichloromethylsulphonyl-2-(5-nitro-2-furyl)cyclopropane (*II*)

a) Piperidine in portions (0·1 ml each, 0·8 ml total) was added during 24 h to a stirred mixture of sulphone *I* (3·08 g, 0·01 mol) and paraformaldehyde (0·7 g, 0·02 mol) in methanol (20 ml) at 20°C when the carbanion *Ib* was consumed. The mixture was stirred for 70 h and then allowed

to stand for 36 h. The residue after evaporation of the solvent was separated on a silica gel (150/250, 3 × 30 cm) column chloroform being the eluant. First fractions afforded after crystallization from acetone the compound *II* (0·2 g, 9%), m.p. 210–212°C, further fractions contained the sulphone *I* and tarry products. For $C_{12}H_7Cl_3N_2O_8S$ (445·6), M^+ 444 for ^{35}Cl, calculated: 7·19% S, 24·9% Cl, 6·28% N; found: 7·35% S, 24·5% Cl, 6·30% N.

b) Piperidine in portions (0·2 ml each, 2·3 mol total) was added to a solution of *I* (3·08 g, 0·01 mol) and paraformaldehyde (0·7 g, 0·02 mol) in methanol (20 ml) under occasional stirring at room temperature during 11 days. The separated substance was filtered off and the filtrate after evaporation of the solvent was chromatographed on a 3 × 30 cm column packed with alumina (Brockmann, activity grade II) with acetone–chloroform 1 : 1. First fractions gave substance *II* (0·3 g, 13%), m.p. 214°C (acetone). The substance which was filtered off was identified by elemental analysis and IR spectrum as being piperidinium chloride (1 g, m.p. 244°C, ref.[18] m.p. 244–245°C).

c) Diazomethane (0·75 g) in ether (50 ml) was added to a solution of compound *III* (2·2 g 5 mmol) in tetrahydrofuran (35 ml) at 0°C. At this temperature a successive separation of crystals has occurred during 12 days (2·08 g, 92%). Crystallization from acetone afforded substance *II*, m.p. 211–212°C. IR: $\nu(CH_2)_{cycl}$ 3045 cm^{-1}, $\nu_{as}(NO_2)$ 1500, 1530 cm^{-1}, $\nu_s(NO_2)$ 1355 cm^{-1}, $\nu_{as}(SO_2)$ 1340 cm^{-1}, $\nu_s(SO_2)$ 1155 cm^{-1}, ν_s(C—O—C) 1027 cm^{-1}; mass spectrum *m/e*: 444 ($C_{12}H_7Cl_3N_2SO_8$, 10%, M^+ for ^{35}Cl), 327 ($C_{11}H_7N_2SO_8$, 14%, M—CCl_3), 311 ($C_{11}H_7N_2SO_7$, 37%, M —$OCCl_3$), 279 ($C_{11}H_7N_2O_7$, 78%, M—CCl_3—SO), 140 ($C_5H_2NO_4$, 100%), 115 (C_9H_7, 69%). ^{1}H-NMR spectrum (Fig. 1): 7·49 (d, H_1), 6·98 (d, H_2), 6·80 (d, H_3), 7·45 (d, H_4), 2·91 (t, H_A), 2·69 (dd, H_B), 3·97 (dd, H_C); UV spectrum (methanol); 209 nm (log ε 4·32), 238 nm (i, log ε 3·97), 305 nm (log ε 4·36).

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