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SULFOLENES IN REACTIONS WITH SOME 1,3-DIPOLAR REAGENTS

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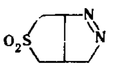
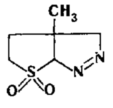
UDC 547.779.1'735'735'228.3

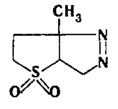
We have shown that 3-sulfolenes (I) and 2-sulfolenes, like other cyclic olefins, are capable of undergoing 1,3-dipolar cycloaddition. Thus at 15-20°C sulfolene I reacts with diazomethane to give II, which is stable on storage and even when it is heated in acetonitrile (at 60° for 7 h). 3-Methyl-3-sulfolene does not react with CH_2N_2. 2-Sulfolene reacts vigorously with CH_2N_2, but the reaction product decomposes rapidly in air. 2-Methyl-2-sulfolene practically does not react with CH_2N_2, whereas its 3-methyl-2-sulfolene isomer forms III in 40% yield. The PMR spectrum of III (in hexametapol) contains a 6-H signal at 6.3 ppm with J = 1.5 Hz. The doublet character is apparently due to the long-range coupling with 3-H or 5-H. The 6-H signal in the spectrum of alternative structure IV should be in the form of a triplet.



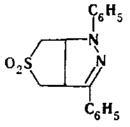
II



III



IV



V

3-Oxo-4-methylsulfolene reacts with CH_2N_2 quantitatively to give 3-methoxy-4-methyl-2-sulfolene [1]. 1,3-Diphenylnitrilimine (from benzoyl chloride phenylhydrazone and triethylamine) reacts with sulfolene I to give V.

EXPERIMENTAL

A solution of 2.8 g (0.024 mole) of sulfolene I in 10 ml of dioxane and a solution of 2.7 g (0.071 mole) of CH_2N_2 in ether were mixed. After 13 days, the amorphous flakes were removed by filtration, the filtrate was concentrated, and the crystals were removed by filtration and washed successively with ether and hot benzene to give 3.32 g (90%) of white crystals of 5,5-dioxo-3H-3a,4,6,6a-tetrahydrothieno[3,4-c]pyrazole (II) with mp 129-130°. A similar procedure was used to obtain 1.6 g (34%) of 6,6-dioxo-3H-3a-methyl-3a,4,5,6a-tetrahydrothieno[2,3-c]pyrazole (III) with mp 167-169.5° (from ethanol). The filtrate was worked up to give 1.6 g of starting 3-methyl-2-sulfolene with mp 77-78°. Typical IR spectrum (of a mineral oil suspension, UR-10 spectrometer): 1560 (N=N); 1305-1315, 1115-1150 cm^{-1} (SO_2).

A solution of 2.7 g (0.071 mole) of CH_2N_2 in ether was added in portions at 7-10° to a solution of 3.5 g (0.024 mole) of 3-oxo-4-methylsulfolane in 10 ml of dioxane. After 24 h, the mixture was worked up as in the preceding experiment to give 3.8 g (99%) of 3-methoxy-4-methyl-2-sulfolene with mp 58.5-60° (from ethyl acetate).

A 6-g (0.058 mole) sample of $(C_2H_5)_3N$ was added in a CO_2 atmosphere to a solution of 6 g (0.05 mole) of sulfolene I and 11.5 g (0.05 mole) of benzoyl chloride phenylhydrazone in 100 ml of dioxane, and the mixture was stirred at 15-20° for 2 h and at 60° for 11 h. The precipitated $(C_2H_5)_3N \cdot HCl$ was removed by filtration, and the

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filtrate was evaporated to give 6.3 g (40%) of 1,3-diphenyl-5,5-dioxo-3a,4,6,6a-tetrahydrothieno[3,4-c]pyrazole with mp 247-249° (from acetone). IR spectrum (KBr): 2900, 2800 (CH_2, CH), 1680 (C=N), 1280, 1150 cm^{-1} (SO_2).

The results of elementary analysis for C, H, N, and S were in agreement with the calculated values.

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ORIENTATION OF MESO-FORMYLATION IN METAL COMPLEXES OF ETIOPORPHYRIN-1

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UDC 547.749:541.49:543.422.25.6'51'544

It has recently been shown [1, 2] that the introduction of a second formyl group in the meso position of the porphyrin ring is possible in the Vilsmeier formylation of cobalt and copper complexes of octalkylporphyrins. It has been assumed [1] that a mixture of positional isomers of meso-diformyletioporphyrins is formed in the formylation of the Co complex of etioporphyrin, but the isolation and establishment of the structures of the individual compounds have not been accomplished. Attempts to carry out the reaction under similar conditions with the Co complex of octaethylporphyrin were unsuccessful because of the formation of a complex mixture of unidentifiable products [2]. However, only the meso-formyl- and α,γ-diformyloctaethylporphyrins were isolated and completely identified in the case of formylation of the Cu complex of octaethylporphyrin, on the basis of which conclusions were drawn regarding the direction of electrophilic substitution at the meso-carbon atoms in the porphyrin molecules.

We have established that the corresponding α,γ-diformyl- (I), α,β-diformyl- (II), and α,γ,β-triformyletioporphyrin (III) complexes are formed in 70-80% overall yields in the reaction of the Cu and Ni complexes of etioporphyrins for 3-4 h and of its Co complex for 5-10 min with $POCl_3$/DMF in dichloroethane at 50-60°. After demetallation of the complexes by treatment with concentrated sulfuric acid, the mixture of free phorphyrins was separated into individual compounds by means of thin-layer chromatography (TLC) on a loose layer of silica gel, and their structures were proved by means of their PMR and mass spectra. From the mass-spectral data for III it can be concluded that a small amount of $\alpha,\beta,\gamma,\delta$-tetraformyletioporphyrin, which is present in a sample of porphyrin III as an impurity, is also formed in the reaction.

The yields and ratios of the formylporphyrins formed are approximately identical in the case of all of the investigated etioporphyrin complexes. Thus porphyrin I was obtained in 25-30% yield, II was obtained in 43-46% yield, and III was obtained in 3-4% yield. The introduction of a second formyl group in the adjacent meso position of the porphyrin ring is consequently more preferable than introduction in the opposing position. This fact indicates the necessity for review and refinement of the theoretical concepts regarding the orientation of electrophilic substitution in the porphyrin series.

A characteristic feature of the electronic spectra of porphyrins II and III is the practically complete disappearance of the traditional (for porphyrins) four bands in the visible region and pronounced broadening of the "Soret band"; this indicates considerable distortion of the plane of the porphyrin ring of these compounds. Thus, for II, λ_{max}, nm ($\varepsilon \cdot 10^{-3}$) in chloroform: 427 (102), 609 (7.3), 683 sh (5.12); for III, 431 (103), 630 (7.35), 694 sh (5.27). The spectrum of porphyrin I [λ_{max}, nm ($\varepsilon \cdot 10^{-3}$): 411.5 (190), 512 (7.05), 550 sh (6.2), 581 (7.34), 646 (5.15), and 666 sh (4.0)] coincides practically completely with the literature data [2] for α,γ-diformyletioporphyrin [λ_{max}, nm ($\varepsilon \cdot 10^{-3}$): 410 (126), 509 (6.76), 549 sh (6.02), 578 (6.92), and 646 (4.78)].

Institute of Biophysics of the Ministry of Public Health of the USSR, Moscow. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 10, pp. 1427-1428, October, 1976. Original article submitted April 2, 1976.