

SHORT
COMMUNICATIONS

Reaction of 2-Benzothiazolethione
with C-Ethoxycarbonyl-*N*-phenylnitrilimine*

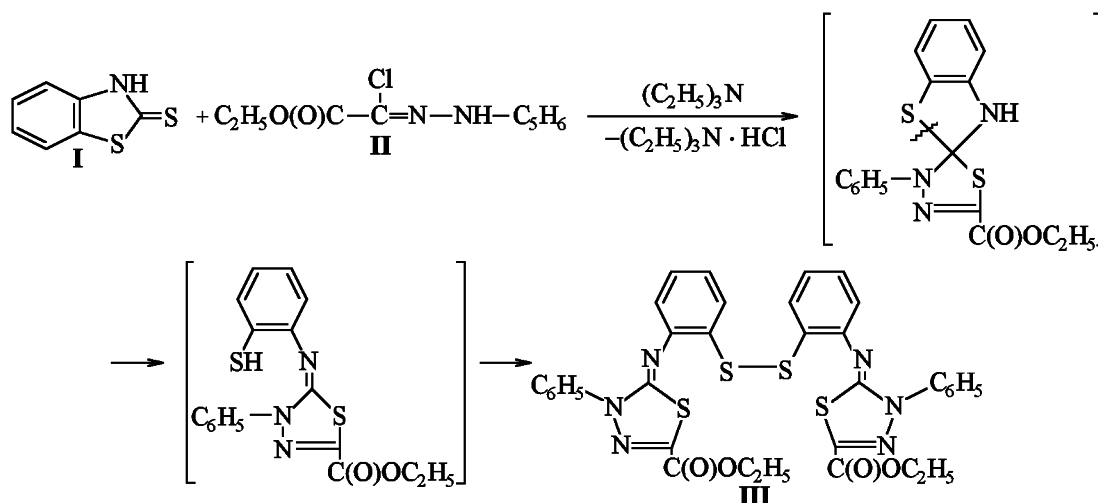
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2-Benzothiazolethione may exist in two tautomeric forms, thiol and thione, depending on the polarity and basicity of the medium [1, 2]. We studied reaction of 2-benzothiazolethione (**I**) with C-ethoxycarbonyl-*N*-phenylnitrilimine (**II**). The reaction starts apparently as 1,3-dipolar cycloaddition involving the exocyclic

bond C=S of 2-benzothiazolethione. Then in the arising benzothiazolespirothiadizole occurs the opening of thiazole ring followed by dimerization yielding 2,2'-bis(2,3-dihydro-3-phenyl-5-ethoxycarbonyl-1,3,4-thiadiazol-2-ylideneaminodiphenyl disulfide (**III**)).



The 1H NMR spectrum of compound **III** contains the characteristic proton signals of ethoxycarbonyl group and aromatic substituents. The ^{13}C NMR data correspond to the assumed structure. In the mass spectra a molecular ion is observed with m/z 712 $[M]^+$ and a fragment ion with m/z 356 $[M/2]^+$. The structure of compound **III** obtained was proved by X-ray diffraction study.

2,2'-Bis(2,3-dihydro-3-phenyl-5-ethoxycarbonyl-1,3,4-thiadiazol-2-ylideneaminodiphenyl disulfide

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(**III**). A solution of 8 mmol of 2-benzothiazolethione, 8 mmol of oxalyl chloride phenylhydrazone ethyl ester and 9 mmol of triethylamine in 50 ml of toluene was boiled for 2 h. The precipitated triethylamine hydrochloride was filtered off (quantitative yield). The filtrate was evaporated at reduced pressure. The residue was ground with ether. The crystals obtained were recrystallized from acetone. Yield of 2,2'-bis(2,3-dihydro-3-phenyl-5-ethoxycarbonyl-1,3,4-thiadiazol-2-ylideneaminodiphenyl disulfide (**III**)) 1.7 g (60%), mp 124–125°C. 1H NMR spectrum, δ , ppm: 1.35 t (6H, CH_3CH_2), 4.40 q (4H, CH_3CH_2), 7.07–7.95 m (18H, H arom). Found, %: C 57.50; H 4.18;

N 12.38; S 18.63. $C_{34}H_{28}N_6O_4S_4$. Calculated, %: C 57.28; H 3.96; N 11.79; S 17.99. 1H (500 MHz) and ^{13}C (125 MHz) NMR spectra were registered on spectrometer Bruker DRX-500 from 20% solutions in $DMSO-d_6$, internal reference HMDS. Mass spectrum was measured on mass spectrometer MKh-1321, vaporizer temperature 120°C, ionizing chamber temperature 200°C, ionizing voltage 70 V.

REFERENCES

1. Stavrovskaya, V.I. and Kolosova, M.O., *Zh. Onshch. Khim.*, 1960, vol. 30, no. 2, pp. 689–694.
2. Safaev, A.S. and Kadyrov, A.K., *Sintez i prevrashcheniya soedinenii ryada piperidina, tiazola i imidazolina* (Synthesis and Transformations of Compounds of Piperidine Series), Tashkent: Fan, 1984, ch. IV.