REACTION OF TETRACYANOETHYLENE OXIDE WITH MESOIONIC 1,3,4-THIADIAZOLO-2-THIONES

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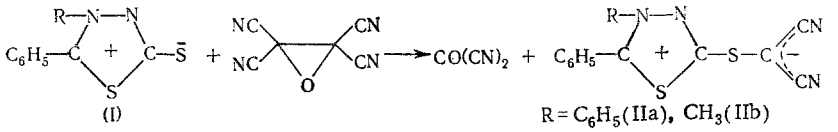
Mesoionic 1,3,4-thiadiazolo-2-thiones are sufficiently nucleophilic to cause disruption of the C–C bond in tetracyanoethylene oxide, with consequent formation of S-diacyanomethylides of 1,3,4-thiadiazolo-2-thiones. The reaction is carried out in boiling alcohol, and this favors decomposition of carbonylcyanide, which is being formed, and thus prevents side reactions



The IR spectrum (IIa, b) does not have an absorption band due to NC=S, while the spectrum of (Ia, b) has a split-band characteristic of the valency vibrations of the cyano group of the cyanomethylide radical, which carries a partially negative charge [2, 3].

This reaction is interesting, since S-dicyanomethylides, in contrast to N-dicyanomethylides [1, 2], usually are only intermediate products in more complex reaction, and furthermore this reaction leads to the formation of mesoionic compound, which has the previously unknown exocyclic structure.

Mesoionic S-dicyanomethylide of 4,5-diphenyl-1,3,4-thiadiazolo-2-thiolium (IIa): yield 37%; mp 121.5°C (from aq alcohol). UV spectrum (CH_3OH, λ_{max}, log ε): 212, 4.55; 241, 4.26; 266 p, 4.11; 308, 4.04; 389 p, 3.91. IR spectrum (KBr, ν, cm^{-1}): 2150, 2185. Found: C 61.12; H 3.11; N 16.86; S 19.00%. $C_{17}H_{10}N_4S_2$. Calculated: C 61.03; H 3.01; N 16.75; S 19.18%.

Mesoionic S-dicyanomethylide of 4-methyl-5-phenyl-1,3,4-thiadiazolo-2-thiolium (IIb): yield 70%; mp 141–142°C (from aq alcohol). UV spectrum (CH_3OH, λ_{max}, log ε): 206, 4.46; 256, 4.01; 298, 4.08; 372 p, 3.90. IR spectrum (KBr, ν, cm^{-1}): 2150, 2180. Found: C 53.49; H 3.04; N 20.75; S 23.36%. $C_{12}H_8N_4S_2$. Calculated: C 52.92; H 2.96; N 20.57; S 23.54%.

LITERATURE CITED

1. W. I. Linn, and E. Ciganek, J. Org. Chem., 34, 2146 (1969).
2. O. Reice and P. Dietrich, Chem. Ber., 96, 3044 (1963).
3. W. I. Linn, O. W. Websber, and R. E. Benson, J. Amer. Chem. Soc., 87, 3650 (1965).

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