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1,3-DIPOLAR CYCLOADDITION OF ETHYL PROPIOLATE TO 4,4-DIMETHYL-4,5-DIHYDRO-1,2-DITHIOLO-[5,4-*c*]QUINOLINE-1-THIONES

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The interaction of ethyl propiolate with 4,4-dimethyl-4,5-dihydro-2,3-dithiolo[3,4-c]quinoline-1-thiones leads to 1,3-dithiol-2-ylidenes, 1,6,6a(λ^4)-trithiapentalene, or thiino[2,3-c]quinolines depending on the conditions.

Keywords: 1,3-dithiol-2-ylidene, 2,3-dithiolo[3,4-*c*]quinoline-1-thione, thiino[2,3-*c*]quinoline, 1,6,6a(λ^4)-trithiapentalenes, 1,3-dipolar cycloaddition.

As a continuation of studies on the heterocyclization reaction in condensed 1,2-dithiol-3-thionedihydroquinolines [1] we have carried out the interaction of 4,4-dimethyl-4,5-dihydro-2,3-dithiolo[3,4-*c*]-quinoline-1-thiones **1a,b** with ethyl propiolate.

It is known that simple 1,2-dithiol-3-thiones may react with dipolarophiles both with opening of the 1,2-dithiol ring by a 1,3-dipolar cycloaddition and by fission of the thioketone bond by a [2+2] cycloaddition with subsequent recyclization [2-4]. The direction, the character of the cycloaddition, the form, and the number of products formed depends on the reaction conditions.

We have established that the cycloaddition of ethyl propiolate to compounds **1a,b**, depending on the conditions used (solvent, temperature), may proceed fairly selectively in any of the directions indicated. Thus on boiling equimolar quantities of the reactants in chloroform the reaction takes place as the usual 1,3-dipolar cycloaddition with opening of the 1,2-dithiol ring and the formation of 4-(4-carbethoxy-1,3-dithiol-2-ylidene)-2,2-dimethyl-6-R-1,2,3,4-tetrahydroquinoline-3-thiones **2a,b**, the structures of which were confirmed by data of ^{1}H NMR and mass spectroscopy.

Signals appeared in the ^{1}H NMR spectrum of compound **2a** (Table 1), together with quinoline ring signals, for the ethoxy group as a triplet at 1.48 and a quintet at 4.46 ppm, and also a signal for the one quasiaromatic proton of the 1,3-dithiol ring at 8.02 and 8.34 ppm. Splitting of the latter into two singlets is evidently caused by the existence of compounds **2a,b** as *E* and *Z* isomers (Table 2).

High temperature interaction of ethyl propiolate with thiones **1a,b** in boiling xylene occurs with fission of the thioketone bond and subsequent recyclization with the formation of 5-R-2(3)-carbethoxy-9,9-dimethyl-8,9-dihydroquino[3,4-b]-1,6,6a(λ^4)-trithiapentalenes **3a,b**.

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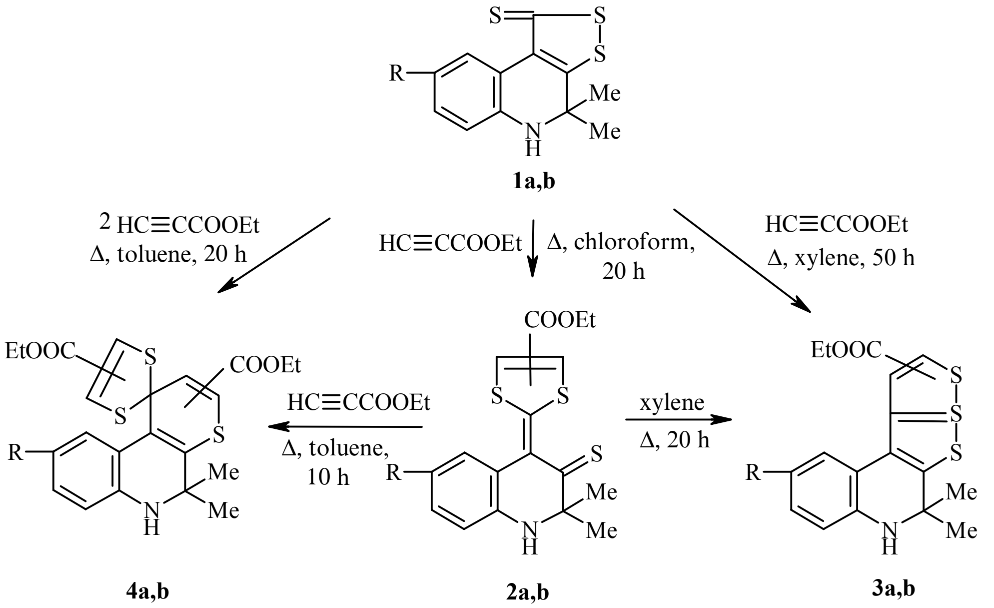
TABLE 1. ^{1}H NMR Spectra of Compounds **2-4**

Compound	Chemical shifts, δ, ppm						
	CMe$_2$, (s, 6H)	ArMe, (s, 3H)	COOCH$_2$CH$_3$		NH (s, 1H)	H arom., m (Σ H)	C=CH, s
			CH$_3$, t	CH$_2$			
2a	1.49	—	1.48 (3H)	4.46 (m, 2H)	5.98	6.3-7.6 (4H)	8.02; 8.34, (1H)
2b	1.46	2.32	1.39 (3H)	4.36 (m, 2H)	5.49	6.31-7.58 (3H)	7.98; 8.39, (1H)
3a	1.51	—	1.36 (3H)	4.35 (m, 2H)	6.02	6.82-7.64 (4H)	9.01 (1H)
3b	1.48	2.34	1.38 (3H)	4.32 (m, 2H)	5.86	6.84-7.49 (3H)	9.08 (1H)
4a	1.41	—	0.85; 1.32 (2 × 3H)	3.95, q; 4.18, q (2 × 2H)	6.01	6.6-7.1 (4H)	7.48; 7.88 (2H)
4b	1.48	2.21	0.89; 1.29 (2 × 3H)	3.93, q; 4.21, q (2 × 2H)	5.69	6.5-7.0 (3H)	7.35; 7.77 (2H)



1–4 a R = H, **b** R = Me

The presence of a 1,6,6a(λ^4)-trithiapentalene structure in products **3a,b** was confirmed unequivocally by data of ^{1}H NMR and mass spectroscopy. In the ^{1}H NMR spectra of compounds **3a,b**, in difference to thiones **2a,b**, the signal for the quasiaromatic proton of the trithiapentalene ring is displaced into the low field region to 9.0-9.2 ppm, which is characteristic of the structure proposed. The mass spectra of compounds **3a,b** also have a characteristic fragmentation, differing from the mass spectra of adducts **2a,b** [5]. In the latter there are ions formed by fission of a molecule of the dipolarophile, which are absent from the former.

Boiling dihydrodithioloquinolinethiones **1a,b** with ethyl propiolate in toluene leads to a mixture of products **2** and **3**, from which they were isolated successfully in pure form only in insignificant yield by column chromatography.

It was shown by additional investigations that pentalenes **3a,b** may be obtained by boiling thiones **2a,b** in xylene. It is evident that such a rearrangement is possible on catalysis by various sulfur-containing compounds (elementary sulfur, the initial 1,2-dithiol-3-thione, etc) and occurs by the mechanism described previously through the stage of radical addition of sulfur at the polarized methylene bond [6].

TABLE 2. Characteristics of Compounds **2-4**

Compound	Empirical formula	Found, % Calculated, %				mp, °C	Yield, %
		C	H	N	S		
2a	$C_{17}H_{17}NO_2S_3$	56.32 56.20	4.71 4.68	3.89 3.86	27.69 26.45	126-127	65
2b	$C_{18}H_{19}NO_2S_3$	57.15 57.29	4.97 5.04	3.68 3.71	26.03 25.46	131-132	67
3a	$C_{17}H_{17}NO_2S_3$	56.28 56.20	4.64 4.68	3.79 3.86	26.52 26.45	181-182	53
3b	$C_{18}H_{19}NO_2S_3$	57.24 57.27	5.03 5.07	3.79 3.71	25.38 25.48	149-150	48
4a	$C_{22}H_{23}NO_4S_3$	57.34 57.27	4.90 4.99	3.01 3.04	20.89 20.82	122-123	71
4b	$C_{23}H_{25}NO_4S_3$	58.26 58.11	5.27 5.26	2.89 2.95	20.26 20.21	151-152	78

It was established that compounds **2a,b**, having a free α,β-unsaturated thioketone fragment, unlike compounds **3a,b**, participate in the diene synthesis reaction. On boiling them in toluene with an equimolar amount of ethyl propiolate 2,2-dimethyl-4'(5'),9(10)-dicarbethoxy-1',3'-dithiol-2'-spiro-8-(2,3-dihydro-8H-thiino[2,3-*c*]quinolines) **4a,b** were formed, which were also obtained directly from 1,2-dithiole-3-thiones **1a,b** on boiling the latter with a twofold excess of ethyl propiolate. The structure of adducts **4a,b** was confirmed by their ^{1}H NMR spectra, in which, unlike the ^{1}H NMR spectra of compounds **2a,b**, there were two sets of signals for two carbethoxy groups and two singlets for the quasiaromatic protons.

EXPERIMENTAL

A check on the progress of reactions and the homogeneity of the substances obtained was effected by TLC on Silufol UV 254 plates, eluent was chloroform. The ^{1}H NMR spectra were taken on a Bruker AC-300 (300 MHz) instrument in DMSO-d_6, internal standard was TMS. Mass spectra were taken on an LKB 9000 instrument, energy of ionizing electrons was 70 eV.

4-(4-Carbethoxy-1,3-dithiol-2-ylidene)-2,2-dimethyl-6-R-1,2,3,4-tetrahydroquinoline-3-thiones 2a,b. Ethyl propiolate (0.01 mol) was added to a solution of compound **1** (0.01 mol) in chloroform (30 ml), and the mixture was boiled for 20 h. The solvent was then removed, and the residue crystallized from isopropanol.

5-R-2(3)-Carbethoxy-9,9-dimethyl-8,9-dihydroquino[3,4-*b*]-1,6,6a(λ^4)-trithiapentalenes 3a,b. A. Ethyl propiolate (0.01 mol) was added to a solution of compound **1** (0.01 mol) in xylene (30 ml), and the mixture boiled for 50 h, after which the solvent was distilled off, and the residue crystallized from isopropanol.

B. Compound **2** (0.005 mol) in xylene (30 ml) was boiled for 20 h. The solvent was then distilled off, and the residue crystallized from isopropanol.

4'(5'),9(10)-Diethoxycarbonyl-2,2-dimethyl-1',3'-dithiolo-2'-spiro-8-(2,3-dihydro-8H-thiino[2,3-*c*]-quinolines) 4a,b. A. Ethyl propiolate (0.01 mol) was added to a solution of compound **1** (0.01 mol) in toluene, and the mixture boiled for 10 h. The solvent was then distilled off, and the residue crystallized from isopropanol.

B. A mixture of compound **1** (0.01 mol) and ethyl propiolate (0.02 mol) in toluene was boiled for 20 h, the solvent was distilled off, and the residue crystallized from isopropanol.

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