## 4,4-DIMETHYL-4,5-DIHYDRO-1,2-DITHIOLO-[3,4-c]QUINOLINE-1-THIONES IN 1,3-DIPOLAR CYCLOADDITION REACTIONS WITH ACETYLENIC DIPOLAROPHILES

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The behavior of 4,4-dimethyl-4,5-dihydro-1,2-dithiolo[3,4-c]quinoline-1-thiones in the 1,3-dipolar cycloaddition reaction with acetylenic dipolarophiles has been studied. The rate of cycloaddition is reduced along with the decrease of electron-deficiency of the triple bond. Substituted 4-(1',3'-dithiol-2'-ylidene)-1,2-dihydroquinoline-3-thiones were shown to be the reaction products. On using a twofold excess of acetylenedicarboxylic acid dimethyl ester, adducts of composition 1 : 2 were formed which occured to be substituted 1',3'-dithiole-2'-spiro-1-(5,6-dihydrothiino[2,3-c]quinolines).

Simple 1,2-dithiole-2-thiones may act as 1,3-dipoles in 1,3-dipolar cycloaddition reactions, however the authors of [1-3] give inconsistent information on both the structure of the products formed and on the regioselectivity of the process.

We have studied the 1,3-dipolar cycloaddition of acetylenic dipolarophiles to 4,4-dimethyl-4,5-dihydro-1,2-dithiolo[3,4-c]quinoline-1-thiones (Ia-f). Results of thin layer chromatography have shown that acetylenedicarboxylic acid dimethyl ester adds to all dithiolethiones Ia-f in the cold on simply mixing the reactants in benzene, toluene, or chloroform. The time for complete cycloaddition was 20-30 h and depended little on the nature of the substituent in the aromatic ring ( $\mathbb{R}^1$ ) or on the nitrogen atom of the hydroquinoline fragment ( $\mathbb{R}^2$ ).



I, II a  $R^1 = R^2 = H$ ; b  $R^1 = Me$ ,  $R^2 = H$ ; c  $R^1 = OMe$ ,  $R^2 = H$ ; d  $R^1 = H$ ,  $R^2 = Me$ ; e  $R^1 = H$ ,  $R^2 = COMe$ ; f  $R^1 = H$ ,  $R^2 = COPh$ 

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	Chemical shift, δ, ppm						
Com- pound	gem-Me <sub>2</sub> (6H, s or two s)	R۱	R²	4'(5')-R <sup>3</sup> * <sup>2</sup>	H <sub>arom</sub> , m		
lla	1,45	*	5,62 (1H, s)	3,85 (6H, s)	6,857,75 (4H)		
IIb	1,47	2,32 (3H, s)	5,67 (1H, s)	3,89 (6H, s)	6,737,25 (3H)		
llc	1,46	3,72 (3H, s)	5,65 (1H, s)	3,90 (6H, s)	6,757,47 (3H)		
IId	1,35	*	2,72 (3H, s)	3,88 (6H, s)	6,787,81 (4H)		
Ile	1,45	*	2,05 (3H, s)	3,90 (6H, s)	6,808,05 (4H)		
llf	1,70	*	7,077,40 (5H, m)	3,90 (6H, s)	6,808,00 (4H)		
Illa	1,44 1.52	*	2,70; 2,75 (two s)	-*	6,727,90 (10H)		
IIIb	1,48 1,57	*	5,45; 5,49 (1H, two s)	3,75; 3,79 (3H, two s, COOMe)	6,707,85 (9H)		
IIIc	1,32 1,50	*	5,60; 5,68 (1H, two s)	1,33; 1,39 (3H, two t, OCH <sub>2</sub> C <u>H</u> <sub>3</sub> ) 4,07; 4,17 (2H, two m, OCH <sub>2</sub> )	6,657,21 (9H)		
IIId	1.35 1,54	2,31; 2,39 (3H, two s)	5,62; 5,80 (1H, two s)	1,31; 1,36 (3H, two t, OCH <sub>2</sub> C <u>H<sub>3</sub>)</u> 4,03; 4,12 (2H, two m, OC <u>H<sub>2</sub>CH<sub>3</sub>)</u>	6,707,05 (8H)		
Ille	1,33 1,52	2,72 (3H, s)	*	*	6,587,23 (14H)		

TABLE 1. <sup>1</sup>H NMR Spectral Characteristics of Substituted 4-(1',3'-Dithiol-2'-ylidene)-1,2-dihydroquinoline-3-thiones (II), (III)

\* Signal is within the multiplet signal of the  $H_{arom}$  protons. \*<sup>2</sup> For compounds IIa-f 4'-R<sup>3</sup> = 5'-R<sup>3</sup> = COOMe.

Based on the charge distribution in the 1,3-dipolar fragment of the dithiolethiones Ia-f we assigned the structure of 4',5'-dimethoxycarbonyl-1',3'-dithiol-2'-ylidene-2,2-dimethyl-1,2-dihydroquinoline-3-thiones (IIa-f) to the products of their interaction with acetylenedicarboxylic acid dimethyl ester. This was confirmed by their spectral characteristics (Table 1).

Boiling in benzene for 20-30 h was sufficient to complete the cycloaddition of dithiolethiones Ia-f to alkyl esters of acetylenedicarboxylic and phenylpropiolic acids, but extended boiling in toluene (more than 100 h) was necessary for phenyl- and diphenylacetylene. This is seemingly caused by decrease of electron deficiency on the acetylenic bond on replacing an ester by phenyl group in the series:

The cycloaddition products of unsymmetrical acetylenic dipolarophiles to dithiolethione I are mixtures of two isomers (A and B). We drew this conclusion since all the adducts of this type melt over a wide temperature range (up to 5°C) and there was a double set of signals for all protons in their <sup>1</sup>H NMR spectra. The intensity ratio of the signals was 4:1 to 3:1 (Table 1). It is therefore possible to assign the structure 4'(5')-R-5'(4')-phenyl-1',3'dithiol-2'-ylidene-2,2-methyl-1,2-dihydroquinoline-3-thiones (IIIa-d) to the reaction product of symmetrical acetylenes with dithiolethione I. In accordance with the charge distribution in the dipolarophiles the major product is isomer A and the minor -B.



III a  $R^1 = R^3 = H$ ,  $R^2 = Me$ ; b  $R^1 = R^2 = H$ ,  $R^3 = COOMe$ ; c  $R^1 = R^2 = H$ ,  $R^3 = COOEt$ ; d  $R^1 = Me$ ,  $R^2 = H$ ,  $R^3 = COOEt$ ; e  $R^1 = Me$ ,  $R^2 = H$ ,  $R^3 = Ph$ 

When studying the cycloaddition of acetylenedicarboxylic acid dimethyl ester to dithiolethiones Ia-f we have discovered that using an excess of dipolarophile and heating, a further bright yellow-coloured spot was observed on the thin layer chromatogram, in addition to the cherry-red spot of the desired cycloaddition product. We linked the appearance of this spot with the possible formation of products of diene synthesis at a ratio of 1:2. On the basis of <sup>1</sup>H NMR spectral data (Table 2) we assigned the structure 4',5'-dimethoxycarbonyl-1',3'-dithiole-2'-spiro-1-(5,5-dimethyl-2,3-dimethyloxycarbonyl-5,6-dihydrothiino[2,3-c]quinolines) (IVa-f) to these products. These compounds were synthesized in up to 85% yield on boiling of equimolar quantities of compounds IIa-f and acetylenedicarboxylic acid dimethyl ester in benzene or toluene for 10-15 h. They may also be obtained directly from dithiolethiones Ia-f by heating with a twofold excess of this dipolarophile in toluene. During the reaction the mixture changes from orange (compounds Ia-f) to cherry (compounds IIa-f) and then to bright yellow (compounds IVa-f), thus enabling the reaction to be followed visually.



IV a  $R^{1} = R^{2} = H$ ; b  $R^{1} = Me$ ,  $R^{2} = H$ ; c  $R^{1} = OMe$ ,  $R^{2} = H$ ; d  $R^{1} = H$ ,  $R^{2} = Me$ ; e  $R^{1} = H$ ,  $R^{2} = COMe$ ; f  $R^{1} = H$ ,  $R^{2} = COPh$ 

TABLE 2. <sup>1</sup>H NMR Spectral Characteristics of Substituted 1',3'-Dithiole-2'spiro-1-(5,6-dihydrothiino[2,3-c]quinolines) (IV)

Com- pound	Chemical shift, δ, ppm						
	<i>gem</i> -Me <sub>2</sub> (6H, s)	R <sup>1</sup>	R <sup>2</sup>	COOMe, m (12H)	Harom		
	1.46		6 6 2 (111 a)	267 292	676765( <b>4</b> Um)		
Iva	1,46		) 5,63 (TH, S)	3,073,82	0,707,03 (4H, M)		
IVb	1,48	2,34 (3H, s)	5,66 (1H, s)	3,693,86	6,687,29 (3H, m)		
IVc	1,49	3,69 (3H, s)	5,33 (1H, s)	3,723,86	6,296,46 (3H, m)		
IVd	1,39	*	2,64 (3H, s)	3,623,81	6,687,15 (4H, m)		
IVe	1,53	*	2,3 (3H, s)	3,693,81	6,677,18 (4H, m)		
IVf	1,72	*	6,97,4 (5H, m)	3,713,89	6,736,96 (4H, m)		

\* Signal is within the multiplet signal of the H<sub>arom</sub> protons.

		Found, %				mp, ℃	Yield, %	
Com-	Empirical	Calculated, %						
pouna		С	н	N	S	M*		
IIa	C <sub>18</sub> H <sub>17</sub> NO <sub>4</sub> S <sub>3</sub>	<u>53,21</u> 53,05	<u>4,18</u> 4,20	<u>3,60</u> 3,44	. <u>23,25</u> 23,60	<u>407</u> 407.53	<b>17</b> 4175	72
IIb	C19H19NO4S3	<u>54,29</u> 54,13	<u>4,70</u> 4,54	<u>3,39</u> 3,32	<u>22.71</u> 22.82	<u>421</u> 421,56	132133	79
llc	C19H19NO5S3	<u>52,23</u> 52,15	<u>4,19</u> 4,38	<u>3,28</u> 3,20	<u>21,75</u> 21,98	<u>437</u> 437,56	166167	71
IId	C19H19NO4S3	<u>54,32</u> 54,13	<u>4,40</u> 4,54	<u>3,44</u> 3,32	<u>22,69</u> 22,82	$\frac{421}{421,56}$	161162	84
lle	C20H19NO5S3	<u>53,55</u> 53,43	<u>4,41</u> 4,26	<u>3,29</u> 3,12	<u>21,55</u> 21,40	<u>449</u> 449,57	192193	86
llf	C <sub>25</sub> H <sub>21</sub> NO <sub>5</sub> S <sub>3</sub>	<u>58,71</u> 58,69	<u>4,29</u> 4,14	<u>2,79</u> 2,74	<u>19,03</u> 18,80	<u>516</u> 516,64	194195	72
Illa	$C_{20}H_{19}NS_3$	<u>65,18</u> 65,00	<u>5,33</u> 5,18	<u>3,90</u> 3,79	<u>26,17</u> 26,00	<u>369</u> 369,57	8991	25
IIIb	$C_{21}H_{19}NO_2S_3$	<u>60,40</u> 60,69	<u>4,52</u> 4,61	<u>3,24</u> 3,37	<u>23,25</u> 23,14	<u>415</u> 415,60	134136	68
IIIc	$C_{22}H_{21}NO_2S_3$	<u>61,70</u> 61,51	<u>4,80</u> 4,93	<u>3,44</u> 3,26	<u>23,61</u> 22,39	$\frac{429}{429,63}$	179182	72
IIId	C <sub>23</sub> H <sub>23</sub> NO <sub>2</sub> S <sub>3</sub>	<u>62,43</u> 62,27	<u>5,41</u> 5,22	<u>3,29</u> 3,16	<u>21,30</u> 21,68	<u>443</u> 443,66	160164	65
Ille	C <sub>26</sub> H <sub>23</sub> NS <sub>3</sub>	<u>70,21</u> 70,07	<u>5,07</u> 5,20	<u>3,40</u> 3,14	<u>21,33</u> 21,58	<u>445</u> 445,67	1 <b>97</b> 198	38
IVa	$C_{24}H_{23}NO_8S_3$	<u>52,69</u> 52,45	<u>4,40</u> 4,22	<u>2,71</u> 2,55	<u>17,75</u> 17,50	<u>549</u> 549,65	179180	72
IVb	C25H25NO8S3	<u>53,41</u> 53,27	<u>4,61</u> 4,47	<u>2,19</u> 2,47	<u>16,95</u> 17,06	<u>563</u> 563,68	176177	68
IVc	C25H25NO9S3	<u>51,71</u> 51,80	<u>4,49</u> 4,35	<u>2,58</u> 2,42	<u>16,83</u> 16,60	<u>579</u> 579,68	137138	• 68
IVd	C <sub>25</sub> H <sub>25</sub> NO <sub>8</sub> S <sub>3</sub>	<u>53,11</u> 53,27	<u>4,70</u> 4,47	<u>2,59</u> 2,47	<u>17,31</u> 17,06	<u>563</u> 563,68	164165	81
IVe	C <sub>26</sub> H <sub>25</sub> NO <sub>9</sub> S <sub>3</sub>	<u>52,93</u> 52,78	<u>4,41</u> 4,26	<u>2,14</u> 2,37	<u>16,13</u> 16,26	<u>591</u> 591,69	158159	67
IVf	C31H27NO9S3	<u>56,77</u> 56,95	<u>4,33</u> 4,16	<u>2,39</u> 2,14	<u>14,49</u> 14,71	<u>653</u> 653,76	176177	73

TABLE 3. Characteristics of Compounds Synthesized

\* M was determined mass spectrometrically.

The characteristics of the synthesized compounds IIa-f, IIIa-e, and IVa-f are given in Table 3.

## EXPERIMENTAL

A check on the progress of reactions and the homogeneity of substances obtained was performed by TLC on Silufol UV 254 plates using chloroform as eluent. The <sup>1</sup>H NMR spectra were taken on a Bruker AC-300 instrument (300 MHz) in DMSO-d<sub>6</sub> relative to TMS. Mass spectra were taken on an LKB 9000 instrument, the energy of the ionizing electrons was 70 eV.

The initial dithiolethiones Ia-f were obtained as described previously in [4,5].

4-(4',5'-Dimethoxycarbonyl-1',3'-dithiol-2'-ylidene)-2,2-dimethyl-1,2-dihydroquinoline-3-thiones (IIa-f). Acetylenedicarboxylic acid dimethyl ester (10 mol) was added to solution of dithiolethione Ia-f (10 mol) in chloroform. The reaction mixture was left at room temperature for 20-30 h, the solvent was evaporated under reduced pressure, and the residue crystallized from ethanol.

4-[4'(5')-R-5'(4')-Phenyl-1',3'-dithiol-2'-ylidene]-2,2-dimethyl-1,2-dihydroquinoline-3-thiones (IIIa-d). Equimolar quantities of dithiolethione Ia-f and R<sup>3</sup>-substituted phenylacetylene were boiled for 20-30 h in benzene (when R<sup>3</sup> = COOMe, COOEt) or for 100-120 h in toluene (when R<sup>3</sup> = H, Ph). The solvent was evaporated under reduced pressure, and the residue crystallized from ethanol. 4',5'-Dimethyloxycarbonyl-1',3'-dithiole-2'-spiro-1-(5,5-dimethyl-2,3-dimethyloxycarbonyl-5,6-dihydrothiino[2,3-c]quinolines (IVa-f). A. Equimolar quantities of compounds IIa-f and acetylenedicarboxylic acid dimethyl ester were boiled in benzene for 10-15 h until the solution was decolorized. The solvent was distilled off under reduced pressure, and the residue crystallized from ethanol.

B. A mixture of dithiolethione (Ia-f) (10 mol) and acetylenedicarboxylic acid dimethyl ester (20 mol) was boiled and then subsequently treated in the same way.

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