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## Some Chemical Aspects of Tetrahydro-1-thiopyran-4-one Derivatives

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3,5-Diarylmethylene-2,6-diphenyltetrahydrothiopyran-4-thiones, 2, reacted with two or four moles of bromine to form 3-arylmethylene 5-bromoarylmethylene-2,6-diphenyltetrahydrothiopyran-4-thione, 3, and 3-arylmethylene-5-bromoarylmethylene-2,6-dibromo-2,6-diphenyltetrahydrothiopyran-4-thione, 5, respectively. Compound 2a reacted with amines giving 2,6-diphenyl-5-iminophenylmethyl-3-phenylmethylenetetrahydrothiopyran-4-thiones, 6. Diphenyldiazomethane and 9-diazofluorene converted 2a into 4-diphenylethylene-2,6-diphenyl-3,5-diphenylmethylenetetrahydrothiopyran, 7, and 2,6-diphenyl-3,5-diphenylmethylene-4-(9-fluorenylidene) tetrahydrothiopyran, 8, respectively. Compounds 2 with copper-bronze afforded 3,3',5,5'-tetraarylmethylene-2,2',6,6'-tetraphenyl-1,1-thio-4,4'-dipyranylidenes, 9.

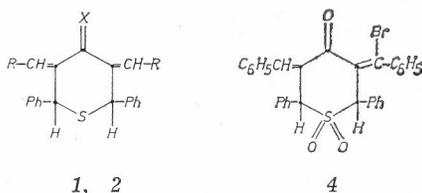
### INTRODUCTION

Many pyrone derivatives are known to be useful as intermediates in the pharmaceutical industry.<sup>1,2</sup> In continuation of our previous work<sup>3,4</sup> dealing with the synthesis and reactions of 3,5-diarylmethylene-2,6-diphenyltetrahydrothiopyran-4-ones, 1, the present paper reports the reaction of 1 with P<sub>4</sub>S<sub>10</sub> giving the corresponding 4-thione derivatives 2. The behaviour of 2 towards bromine, amines, diazoalkanes and copper-bronze has now been investigated. The newly synthesized compounds have been bacteriologically screened.

### RESULTS AND DISCUSSION

The 3,5-diarylmethylene-2,6-diphenyltetrahydrothiopyran-4-ones (1a-c) were prepared by condensing 2,6-diphenyltetrahydrothiopyran-4-one with aldehydes in alkaline medium.<sup>5</sup>

The action of P<sub>4</sub>S<sub>10</sub> on compounds 1a—c afforded the corresponding thiones 2a—c. The IR spectra of 2a—c displayed absorption bands at 1255, 1230 and 1245 cm<sup>-1</sup> for the C=S group and showed no absorption for C=O group. The <sup>1</sup>H—NMR spectrum of 2a showed signals at 3.7 ppm (s, 2, CH—S—CH) and 6.8—7.7 ppm (m, 22, benzyldiene and phenyl protons). The MS of 2a showed the molecular ion peak (M<sup>+</sup>) at m/e 460. Moreover oxidation of 2a with hydrogen peroxide gave 1a.<sup>3</sup>



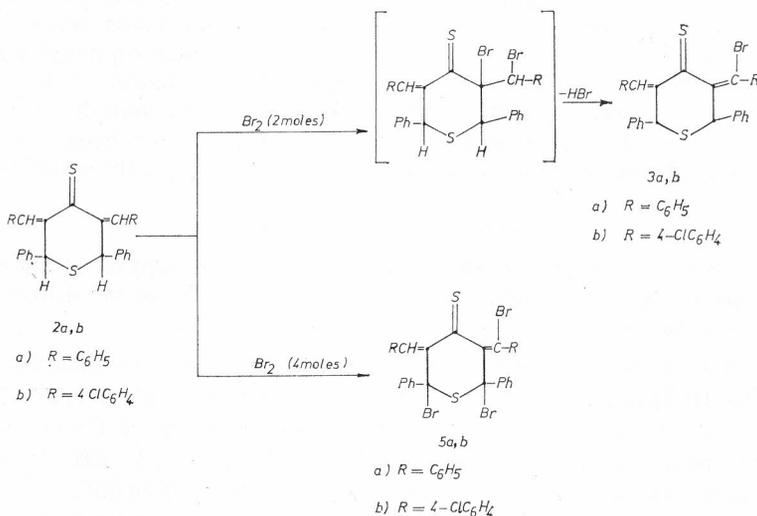
	X	R		X	R
1a	O	C <sub>6</sub> H <sub>5</sub>	2a	S	C <sub>6</sub> H <sub>5</sub>
1b	O	C <sub>6</sub> H <sub>4</sub> Cl- <i>p</i>	2b	S	C <sub>6</sub> H <sub>4</sub> Cl- <i>p</i>
1c	O	C <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub> - <i>p</i>	2c	S	C <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub> - <i>p</i>

Bromination of **2a** and **2b** with two moles of bromide afforded 3-benzylidene-5-bromophenylmethylene-2,6-diphenyltetrahydrothiopyran-4-thione (**3a**) and 5-bromophenylmethylene-3-(4-chlorophenylmethylene)-2,6-diphenyltetrahydrothiopyran-4-thione (**3b**) respectively, (Scheme 1).

The UV spectrum of **3a** showed that the main absorption band at  $\lambda_{\max}$  280 nm ( $\log \epsilon = 4.0$ ) is like that of **2a**, which indicates that the same conjugation is present in **2a** and **3a**.

The IR spectrum of **3a** showed characteristic bands at 1235 cm<sup>-1</sup> for C=S,<sup>6a</sup> 1605 cm<sup>-1</sup> for C=C<sup>6b</sup> and 1080 cm<sup>-1</sup> for C=C—Br<sup>6b</sup> groups.

Oxidation of **3a** with hydrogen peroxide in acetic acid yield 3-benzylidene-5-bromophenylmethylene-2,6-diphenyl-1,1-dioxotetrahydrothiopyran-4-one (**4**). The IR spectrum of **4** exhibited absorption bands at 1675 cm<sup>-1</sup> for C=O, 1295 and 1155<sup>-1</sup> (SO<sub>2</sub>) and 1055 cm<sup>-1</sup> (C=C—Br).

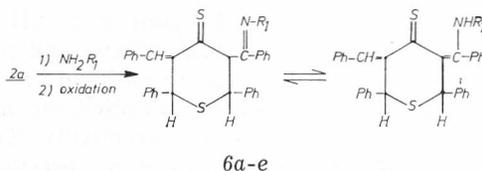


Scheme 1

Bromination of *2a* and *2b* using four moles of bromine, however afforded 5-bromophenylmethylene-2,6-dibromo-2,6-diphenyl-3-phenylmethylenetetrahydrothiopyran-4-thione (*5a*) and 5-(4-chlorophenylbromomethylene)-3-(4-chlorophenylmethylene)-2,6-dibromo-2,6-diphenyltetrahydrothiopyran-4-thione (*5b*) respectively.<sup>7</sup>

In the <sup>1</sup>H—NMR of *5a* there are no signals for 2,6-methylene protons up to 6.9 ppm and its UV spectrum showed the main absorption band at  $\lambda_{\max}$  300 nm (log  $\epsilon = 4.1$ ). Its IR spectrum displayed absorption bands at 1235 cm<sup>-1</sup> and 1050 cm<sup>-1</sup> characteristic for C=S and C=C—Br groups.

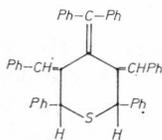
Compound *2a* underwent 1,4-addition<sup>8</sup> with aliphatic amines, hydrazine hydrate and hydroxylamine followed by air oxidation to give 5-iminophenylmethyl thiones *6a—c*, 2,6-diphenyl-5-hydrazonophenylmethyl-3-phenylmethylenetetrahydrothiopyran-4-thione (*6d*) and 2,6-diphenyl-5-oximinophenylmethyl-3-phenylmethylenetetrahydrothiopyran-4-thione, (*6e*) respectively.



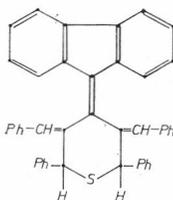
a) R<sub>1</sub> = CH<sub>3</sub>; b) R<sub>1</sub> = C<sub>2</sub>H<sub>5</sub>; c) R<sub>1</sub> = CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>; d) R<sub>1</sub> = NH<sub>2</sub>; e) R<sub>1</sub> = OH.

The IR spectrum of *6a* displayed absorption bands characteristic of C=N at 1620 cm<sup>-1</sup> and C=S at 1230 cm<sup>-1</sup>. The <sup>1</sup>H—NMR of *6a* showed signals at 2.5 ppm (s, 3, N—CH<sub>3</sub>), 3.7 ppm (s, 2, CH—S—CH) and 6.8—7.9 ppm (m, 21, benzylidene and phenyl protons). The MS of *6a* showed the molecular ion peak (M<sup>+</sup>) at m/e 489. The ions at m/e 476 (M<sup>+</sup>—CH<sub>3</sub>) 456 (M<sup>+</sup>—SH) and 412 (M<sup>+</sup>—Ph) were also observed.

Refluxing of diphenyldiazomethane and 9-diazofluorene with *2a* in benzene afforded 3,5-dibenzylidene-2,6-diphenyl-4-diphenylmethylenetetrahydrothiopyran (*7*) and 3-,5-dibenzylidene-4-(9-fluorenylidene)-2,6-diphenyltetrahydrothiopyran (*8*) respectively.



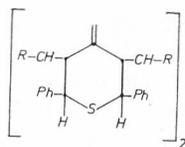
7



8

The <sup>1</sup>H—NMR spectra of *7* and *8* showed a singlet (2H) at 3.7 ppm (CH—S—CH) and multiplets 32 H (*7*) and 30 H (*8*) at 6.7—8.1 ppm for the phenyl and benzylidene protons. The MS of *7* and *8* showed the molecular ion peaks (M<sup>+</sup>) at m/e 591 and 592, respectively.

Compound 2a and 2c reacted with copper-bronze in anhydrous boiling xylene to give the thiopyranylidene derivatives: 2,2',6,6'-tetraphenyl-3,3',5,5'-tetraphenylmethylene-1,1'-thio-4,4'-dipyranlydene, (9a) and 2,2',6,6'-tetraphenyl-3,3',5,5'-tetra(p-methoxyphenylmethylene)-1,1'-thio-4,4'-dipyranlydene, (9b) respectively.



9

- a) R = C<sub>6</sub>H<sub>5</sub>  
b) R = 4-ClC<sub>6</sub>H<sub>4</sub>

The <sup>1</sup>H-NMR of 9b showed signals at 3.7 ppm (s, 2, CH—S—CH), 3.85 ppm (s, 6, 2 OCH<sub>3</sub>) and 6.8—8.0 ppm (m, 20, benzylidene and phenyl protons) and the IR spectra of 9a and 9b displayed absorption bands at 1640 and 1645 cm<sup>-1</sup> (C=C), respectively. The MS of 9a and 9b exhibited the molecular ion peaks at m/e 428 (1/2 M.<sup>+</sup>) and m/e 488 (1/2 M.<sup>+</sup>), respectively. The ions at m/e 351 (1/2 M.<sup>+</sup>—Ph) and 381 (1/2 M.<sup>+</sup>—C<sub>6</sub>H<sub>5</sub>OCH<sub>3</sub>—p) were observed in the spectra of 9a and 9b respectively.

#### Cleavage by Sulphur and Thionyl Chloride

It has been reported<sup>8-11</sup> that at higher temperatures, certain ethylenes are susceptible to cleavage by sulphur and thionyl chloride. Thus, when compounds 7, 9a and 9b were fused with sulphur above their melting points, compound 2a (in case of 7 and 9a) and 2c (in case of 9b) were obtained. Compound 7 when boiled with thionyl chloride gives the ketochlorides 4,4-dichloro-2,6-diphenyl-3,5-dibenzylidene-tetrahydrothiopyran and dichlorodiphenyl methane. These ketochlorides give rise to 1a as well as benzophenone on hydrolysis. Similarly 9b was cleaved by thionyl chloride yielding 1c in a quantitative yield.

#### Biological Activity

The above compounds were screened against six organisms representative for Gram positive (*Micrococcus tetragenus*, *Staphylococcus citreus* and *Streptococcus faecalis*) and Gram negative (*Salmonella species*, *Pseudomonas aerogena* and *Escherichia coli*) bacteria using a modified Cup-test assay technique.<sup>12,13</sup> It appears that compound 2b has inhibited the growth of *Salmonella* species at concentrations of 100 μg/ml and compound 5b was active against *Escherichia coli* at 100—10 μg/ml.

#### EXPERIMENTAL

IR spectra were determined as KBr pellets with Unicam SP 1200 spectrophotometer. UV spectra were recorded in ethanol solution with Unicam SP 8000 recording spectrophotometer. <sup>1</sup>H NMR spectra were obtained on a Varian EM-360 spectrophotometer in CDCl<sub>3</sub> with TMS as the internal reference. MS 7070 F mass spectrometer operating at 70 ev using direct inlet. All melting points are uncorrected.

*Reaction of 3,5-Diarylmethylene-2,6-diphenyltetrahydrothiopyran-4-ones (1a—c) with P<sub>4</sub>S<sub>10</sub>*

Compound 1a-c (0.01 mol) was refluxed with P<sub>4</sub>S<sub>10</sub> (0.01 mol) in 10 ml of anhydrous xylene for 4 hrs. The solvent was evaporated and the residue crystallised to give 2a-c (Table I).

*Oxidation of 3,5-Dibenzylidene-2,6-diphenyltetrahydrothiopyran-4-thione (2a) with Hydrogen Peroxide*

Hydrogen peroxide (50 ml, 35% vol.) was added to 2a (0.01 mol) in 20 ml of acetic acid. The mixture was left for 2 days at room temperature. The 1a separated as solid in 82% yield had m. p. and mixed m. p. with authentic sample of 1a of 124 °C.

*Action of Bromine on 2a, b*

*Reaction with 2 moles of bromine*

Bromine (0.01 mol) in 20 ml of acetic was added dropwise with stirring to 2a, b (0.005 mol). The mixture was refluxed for 6 hrs, concentrated, cooled and crude 3a, b was filtered off and crystallised to give pure 3a, b. (Table I).

*Reaction with 4 moles of bromine*

Bromine (0.02 mol) in 30 ml of acetic acid was added dropwise with stirring to 2a, b (0.005 mol). The mixture was refluxed for 6 hrs, concentrated and cooled. The solid obtained was filtered off and crystallised to give 5a, b. (Table I).

*Oxidation of 3-Benzylidene-5-Bromophenylmethylene-2,6-diphenyltetrahydrothiopyran-4-thione (3a) with Hydrogen Peroxide*

Hydrogen peroxide (50 ml, 35% vol.) was added to 3a (0.01 mol) in 20 ml of acetic acid. The mixture was left for 2 days at room temperature. The solid that separated was filtered off and crystallised to give 3-benzylidene-5-bromophenylmethylene-1,1-dioxo-2,6-diphenyl-tetrahydrothiopyran-4-one (4) (Table I).

*Reaction of 3,5-Benzylidene-2,6-diphenyltetrahydrothiopyran-4-thione (2a) with Amines*

A mixture of 2a (0.01 mol) and the appropriate amines (0.01 mol) in 20 ml of ethonol was refluxed for 5 hrs. The ethanol was distilled off and the residue crystallised to give pure 6a-e. (Table I).

*Reaction of 3,5-Dibenzylidene-2,6-diphenyltetrahydrothiopyran-4-thione (2a) with Diphenyldiazomethane and 9-Diazofluorenes*

A mixture of 2a (0.01 mol) and diazoalkane (0.015 mol) in 20 ml of anhydrous benzene was refluxed for 4 hrs. The mixture was concentrated and cooled. The solid obtained was crystallised to give 7 and 8. (Table I).

*Reaction of 2a, c with Copper-bronze*

A mixture of 2a or 2c (0.01 mol), copper-bronze (3 g) and 20 ml of anhydrous xylene was refluxed for 6 hrs under nitrogen. The solution was filtered while hot. The filtrate was evaporated under reduced pressure and the residue formed crystallised to give 9a and 9b, respectively.

9a: yield 89%, m. p. (petrol. ether) 150 °C, analysis Calcd. for C<sub>62</sub>H<sub>48</sub>S<sub>2</sub>: C, 86.9; H, 5.61; S, 7.5. Found: C, 86.8; H, 5.49; S, 7.6%.

9b: yield 75%, m. p. (ethanol) 177 °C, analysis calcd. for C<sub>66</sub>H<sub>56</sub>O<sub>4</sub>S<sub>2</sub>: C, 81.2; H, 5.74; S, 6.6. Found: C, 81.0; H, 5.7; S, 6.5%.

TABLE I  
Physical and Analytical Data for Compounds 2-8

Comp.	Yield m. p/°C		IR/cm <sup>-1</sup>	UV λ/mμ (log ε)	<sup>1</sup> H-NMR ppm	Formula (mol. wt)	Analysis					
	(cryst.)	%					Calcd.:	Found:	%C	%H	%S	%N
2a	90 (methanol)	115	1590,1255	288 (4.2)	3.7(s,2H,CH-S-CH), 6.8-7.7(m,2H,Ph & benzylidene)	C <sub>31</sub> H <sub>24</sub> S <sub>2</sub> (460.)	80.87 (80.93)	5.22 (5.14)	13.91 (14.12)	—	—	—
2b	81 (methanol)	180	1590,1230	300 (4.0)	3.7(s,2H,CH-S-CH), 6.8-7.9(m,20H,Ph & benzyl)	C <sub>31</sub> H <sub>23</sub> Cl <sub>3</sub> S <sub>2</sub> (529.6)	70.32 (70.18)	4.16 (4.01)	12.10 (12.23)	—	—	Cl, 13.42 (13.30)
2c	77 (ethanol)	218	1600,1245	295 (4.4)	3.7(s,2H,CH-S-CH), 3.85(s,6H,2-OCH <sub>3</sub> ), 6.9-8.0(m,20H,Ph & benzyl)	C <sub>33</sub> H <sub>28</sub> O <sub>2</sub> S <sub>2</sub> (520.7)	76.15 (76.03)	5.38 (5.49)	12.31 (12.50)	—	—	—
3a	81 (ethanol)	201	1605,1235 1080	280 (4.0)	3.7(s,2H,CH-S-CH), 6.7-7.9(m,21H,Ph & benzyl)	C <sub>31</sub> H <sub>23</sub> BrS <sub>2</sub> (539.6)	69.02 (68.89)	4.27 (4.41)	11.87 (12.02)	—	—	Br, 14.84 (14.63)
3b	67 (methanol)	188	1610,1240 1080	290 (3.9)	3.7(s,2H,CH-S-CH), 6.9-8.0(m,19H,Ph & benzyl)	C <sub>31</sub> H <sub>21</sub> BrCl <sub>2</sub> S <sub>2</sub> (608.6)	61.18 (60.94)	3.45 (3.36)	10.53 (10.50)	—	—	Br, 13.15 (13.02)
4	69 (Petrol- ether)	219	1675,1295 1055	230 (3.7)	5.1(s,2H,CH-SO <sub>2</sub> -CH), 6.8-8.0(m,21H,Ph & benzyl)	C <sub>31</sub> H <sub>23</sub> BrO <sub>3</sub> S (555.5)	67.03 (67.20)	4.14 (3.96)	5.77 (6.02)	—	—	Br, 14.41 (14.19)
5a	65 (benzene)	237	1235,1050	300 (4.1)	6.9-7.9(m,21H,Ph & benzyl)	C <sub>31</sub> H <sub>21</sub> Br <sub>3</sub> S <sub>2</sub> (697.6)	53.37 (53.32)	3.01 (3.18)	9.18 (9.04)	—	—	Br, 34.43 (34.81)
5b	59 (benzene)	255	1240,1080	295 (4.0)	6.8-8.0(m,19H,Ph & benzyl)	C <sub>31</sub> H <sub>19</sub> Br <sub>3</sub> Cl <sub>2</sub> S <sub>2</sub> (766.6)	48.56 (48.34)	2.48 (2.36)	8.36 (8.16)	—	—	Br, 31.33 (30.90)

6a	76 117 (ethanol)	1620,1230	290 (3.9)	2.5(s,3H,CH <sub>3</sub> ), 3.2(s,2H,CH—S—CH), 6.8—7.9(m,2H,Ph & benzyl)	C <sub>32</sub> H <sub>37</sub> NS <sub>2</sub> (489.7)	78.53 (78.44)	5.52 (5.69)	13.09 (13.35)	2.86 (2.81)	—
6b	69 123 (methanol)				C <sub>33</sub> H <sub>39</sub> NS <sub>2</sub> (503.7)	78.73 (78.54)	5.77 (5.63)	12.72 (12.70)	2.78 (2.66)	—
6c	81 132 (benzene)				C <sub>38</sub> H <sub>31</sub> NS <sub>2</sub> (565.7)	80.71 (80.93)	5.49 (5.44)	11.32 (11.44)	2.48 (2.61)	—
6d	77 169 (petrol- ether)	3390,1630 1230	300 (4.0)	3.2(s,1H,CH—C=S), 3.4(s,br,2H,NH <sub>2</sub> ), 3.7(s,2H,CH—S—CH), 6.9—7.9(m,2H,Ph & benzyl)	C <sub>31</sub> H <sub>26</sub> N <sub>2</sub> S <sub>2</sub> (490.7)	75.92 (76.08)	5.31 (5.19)	13.06 (13.02)	5.71 (5.64)	—
6e	70 180 (petrol- ether)	3050—3080 1645,1245	305 (4.1)	3.3(s,1H,CH—C=S), 3.7(s,2H,CH—S—CH), 6.8—7.9(m,2H,Ph & benzyl),109(s,1H, OH)	C <sub>31</sub> H <sub>25</sub> NOS <sub>2</sub> (491.6)	75.76 (75.63)	5.09 (5.12)	13.03 (13.21)	2.85 (2.90)	—
7	69 159 (dioxan)				C <sub>44</sub> H <sub>34</sub> S (594.7)	88.89 (89.03)	5.72 (5.66)	5.39 (5.30)	—	—
8	70 169 (dioxan)				C <sub>44</sub> H <sub>32</sub> S (592.7)	89.19 (89.13)	5.41 (5.60)	5.41 (5.40)	—	—

*Action of Sulphur on 7, 9a and 9b*

One g of each of 7, 9a or 9b was fused with 1 g of sulphur at 180 °C for 2 hrs; the mixture was then cooled and extracted with methanol. 7 gave 2a (m. p. and mixed m. p. 115 °C) and benzophenone, due to the oxidation of the formed thiobenzophenone.

9a: yielded 2a (m. p. and mixed m. p. 150 °C).

9b: yielded 2c (m. p. and mixed m. p. 218 °C).

*Reaction of 3,5-Dibenzylidene-2,6-diphenyl-4-diphenylmethylenetetrahydrothiopyran (7) and 2,2',6,6'-Tetraphenyl-3,3',5,5'-tetra (p-methoxyphenylmethylene)-1,1-thio-4,4-dipyranylidene (9b) with Thionyl Chloride*

A solution of 7 or 9b (0.01 mol) in 10 ml of thionyl chloride was refluxed with stirring for 2 hrs. The solution was cooled and poured into crushed ice. The solid obtained was filtered and crystallised from methanol.

7 gave 1a (m. p. and mixed m. p. 124 °C)<sup>3</sup> and benzophenone and 9 gave 1c (m. p. and mixed m. p. 158 °C).<sup>3</sup>

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## SAŽETAK

## Neki aspekti kemije derivata tetrahidro-1-tiopiran-4-ona

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Reakcijom 3,5-diarilmetilen-2,6-difeniltetrahidrotiopiran-4-tiona (2) sa dva ili četiri mola broma nastaju 3-arilmetilen-5-bromarilmetilen-2,6-difeniltetrahidrotiopiran-4-tion, (3) i 3-arilmetilen-5-bromarilmetilen-2,6-dibrom-2,6-difeniltetrahidrotiopiran-4-tion (5). Supstancija 2 daje reakcijom s aminima 2,6-difenil-5-iminofenilmetil-3-fenilmetilentetrahidrotiopiran-4-tion (6), a reakcijom s difenildiazometanom i 9-diazofluorenom nastaju 4-difeniletilen-2,6-difenil-3,5-difenilmetilentetrahidrotiopiran (7) i 2,6-difenil-3,5-difenilmetilen-4-(9-fluoreniliden)tetrahidrotiopiran (8). U reakciji s bakrom, 2 daje 3,3',5,5'-tetraarilmetilen-2,2',6,6'-tetrafenil-1,1-tio-4,4'-dipiraniliden (9).