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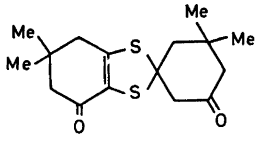
Enethiols. VIII.* 3-Mercapto-5,5-dimethyl-2-cyclohexen-1-one ("Thiodimedone") and Derivatives. Thermal and Photochemical Rearrangements

L. DALGAARD and S.-O. LAWESSON

Department of Organic Chemistry, Chemical Institute, Aarhus University, DK-8000 Aarhus C, Denmark

Reaction of 3-chloro-5,5-dimethyl-2-cyclohexen-1-one with Na_2S gave 3-mercapto-5,5-dimethyl-2-cyclohexen-1-one (RSH). Subsequent alkylation of RSH (Na^+ salt) gave the sulfides RSR′ (R′ = CH_3-, $CH_2=CHCH_2-$, $CH_3CH=CHCH_2-$, and CH_3COCH_2-). Similarly RSH (Tl^+ salt) yielded RSR′ (R′ = $HC\equiv CCH_2-$) while RSH (Bu_4N^+ salt) gave (R′ = $H_2C=C=CH-$) by alkylation with $HC\equiv CCH_2Br$. Allylic sulfides (RSR′) underwent thio-Claisen rearrangement and cyclization at about 140 °C in quinoline to 2,6,6-trimethyl-4-oxo-2,3,4,5,6,7-hexahydrobenzothiophene (when R′ = $CH_2=CHCH_2-$) and 2,3,6,6-tetramethyl-4-oxo-2,3,4,5,6,7-hexahydrobenzothiophene (when R′ = $CH_3CH=CHCH_2-$). Rearrangement in acetic anhydride gave 3-acetylthio-2-allyl-5,5-dimethyl-2-cyclohexen-1-one (when R′ = $CH_2=CHCH_2-$). Photolysis of RSR′ (R′ = $CH_2=CHCH_2-$, $CH_3CH=CHCH_2-$, $PhCH_2-$, $CH_3C(O)-$, and $H-$) gave RSSR and a 1,3-dithiole:



This product was obtained in 79 % yield by photolysis of RSSR. Photolysis of RSR′ (R′ = phenyl) gave 3,3-dimethyl-5-oxo-2,3,4,5-tetrahydrodibenzothiophene.

In previous papers dealing with the thermal [1-5] and photochemical [1] behaviour ($Z-E$ isomerization [1,2] and thio-Claisen rearrangements [1-5]) of α,β-unsaturated sulfides, open chain compounds were investigated. As part of this study it seemed desirable to investigate enethiols and sulfides having the corresponding mercapto- and alkylthio group placed in the β-position of an α-β-unsaturated carbonyl compound, but in which intramolecular H-bonding of the enethiol is excluded. Thiodimedone (3-mercapto-5,5-dimethyl-2-cyclohexen-1-one) and the 3-alkylthio derivatives were thought to be suitable representatives of such compounds. 3-Mercapto-5,5-dimethyl-2-cyclohexen-1-one and most of its derivatives were conveniently prepared from the 3-chloro-2-cyclohexen-1-one (for relevant literature, see Refs. 6 – 15). Results on synthesis, thermolysis, and photolysis of these compounds are the subject of the present work.

Synthesis of 3-mercapto-5,5-dimethyl-2-cyclohexen-1-one (thiodimedone) and derivatives (Fig. 1). Dimedone *1*, when treated with PCl_3 gave *2*,[16] which by further reaction with Na_2S gave *3* and small amounts of *4*. Acidification, alkylation or oxidation of the water solution of *3* yielded thiodimedone *5*, the sulfides *6* – *9*, or the disulfide *13*, respectively. Preparation of the unsoluble thallium(I) salt of *5* suspended in HMPA followed by alkylation with 2-propynyl bromide resulted in the formation of the 2-propynyl sulfide *10*. When alkylation was performed in a homogeneous mixture, consisting of the tetrabutylammonium salt of *5* dissolved in CH_2Cl_2 and 2-propynyl bromide, the allenyl sulfide *11* was formed. The acetyl derivative *12* was prepared from acetyl chloride and *5* dissolved in pyridine. Treatment of *1*

* Part VII. See Ref. 1.

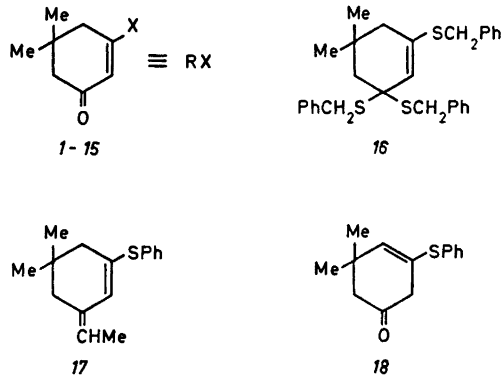


Fig. 1. Compounds *1-18*. 1 (ROH), *2* (RCl), 3 ($RS^{\ominus}$), *4* (RSR), *5* (RSH), *6* ($RSCH_3$), *7* ($RSCH_2CH=CH_2$), *8* ($RSCH_2CH=CHCH_3$), *9* ($RSCH_2COCH_3$), *10* ($RSCH_2C{\equiv}CH$), *11* ($RSCH=C=CH_2$), *12* ($RSCOCH_3$), *13* (RSSR), *14* (RSPh), *15* ($RSCH_2Ph$).

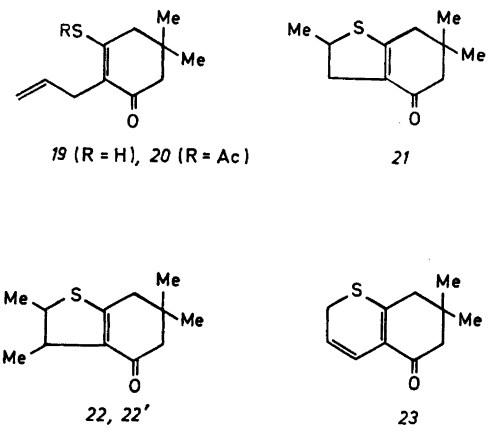
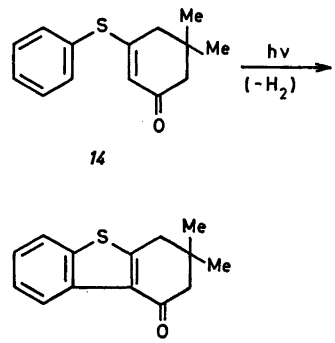


Fig. 2. Compounds *19-23*.

with the appropriate thioles gave the sulfides *14* [7] and *15* [7] together with the thioacetal *16*. When *14* was reacted with ethyllithium a 1,2-addition followed by elimination took place resulting in the formation of *17*, while treatment of *14* with $LiNH_2/NH_3$ gave partly isomerization to *18* (see also Refs. 17, 18).

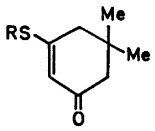
Thermal rearrangements of allylic derivatives. 3-Allyloxy-2-cyclohexen-1-one has been shown [19] to undergo Claisen rearrangement at 190-210 °C. Similarly the 3-allylthio analogues do undergo thio-Claisen rearrangement. Rearrangement in the presence of *p*-toluenesulfonic acid resulted in the formation of 2-allyl-3-mercapto-5,5-dimethyl-2-cyclohexen-1-one *19*, which cyclisized partly during distillation. When the reaction was performed in boiling acetic anhydride, 3-acetylthio-2-allyl-5,5-dimethyl-2-cyclohexen-1-one *20* was isolated. Rearrangement in quinoline at 160 °C yielded the hexahydrobenzothiophene *20*. The 2-butenyl derivative rearranged to *21* somewhat slower under similar conditions. Heating of the 2-propynyl (*10*) and the allenyl (*11*) sulfides in quinoline or pyridine resulted mostly in tarry material However, the 2H-thiapyran *23* could be isolated in a reasonably pure state by rearrangement of *10*.

Photolysis of 3-mercapto-5,5-dimethyl-2-cyclohexen-1-one and sulfide derivatives. Photolysis of the compounds *5*, *7*, *8*, *12*, and *15* (Table 1) did not yield the expected [23-24] 2+2 cycloadducts. Irradiation of the enethiol *5* gave the disulfide *13* which is an ordinary type of product in photolysis of thiols,[25] the 1,3-dithiole *24* and the 1,4-dithiane *25*. The allyl *7*, 2-butenyl *8*, and the benzyl *15* derivatives gave *13* and *24* in variable ratios. In one experiment when *15* was irradiated traces of PhCHO arising from the benzyl group were detected along with *13*. The acetyl derivative *12* yielded *13* and *24* together with EtOAc upon photolysis in EtOH. As might be expected the phenyl derivative *14* did not undergo cleavage reaction at the R-S bond, but instead an intramolecular cyclization-oxidation reaction (eqn. 1) took place, giving the tetrahydrodibenzothiophene *26* in poor yields. Similar reactions have been observed for other types of divinyl sulfides.[26,27] In



(1)

Table 1. Photolysis of 3-mercapto-5,5-dimethyl-2-cyclohexen-1-one and derivatives. Conditions and product distribution.

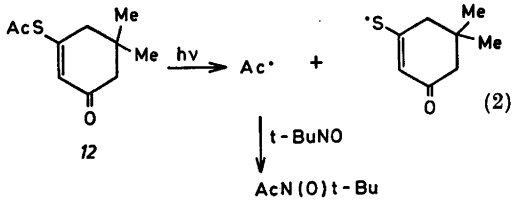


Compound	R	Starting material g (mmol)	Solvent (175–200 ml)	Reaction time (h)	Light [a] source (nm)	Recovered g (%)	*5*, g (%)	*24*, g (%)	Compound, g (%)
5	H	1.52(9.75)	hexane	44	300 py.	0	0.624(41)	0.332(22)	*25*, 0.129(9)
13		5.00(16.0)	EtOH	18	254 qu.	0.26(5)		3.95(79)	
7	$CH_2CH=CH_2$	2.45(12.5)	cyclohexane	16	300 qu.	1.11(45)		trace	
8	$CH_2CH=CHCH_3$	0.75(3.57)	EtOH	19	300 qu.	1.49(61)	0.165(11)		
12	Ac	4.97(25.2)	EtOH	33	254 qu.	0.248(28)	1.08(28)	2.3(59)	EtOAc (GLC)
14	Ph	2.34(10.1)	acetone [b]	72	300 qu.	1.08(46)			*26*, 0.092(4) diacetone-alcohol, 8.5 g
14	Ph	4.56(19.7)	ether [b]	110	300 qu.	3.60(79)			*26*, 0.109(2.4)
14	Ph	3.70(16.0)	dioxan	67	300 py.	1.58(43)			*26*, 0.184(5)
15	$PhCH_2$	2.46(10.00)	ether	11	300 qu.	1.49(61)	0.165(11)		
15	$PhCH_2$	0.80(3.25)	hexane	36	300 py.	0.22(28)	0.10(20)	0	PhCHO, trace

[a] λ_{max} of "Rayonet RS" mercury arcs. Reaction vessel: qu.=quartz, py.=pyrex.
[b] 1 l.

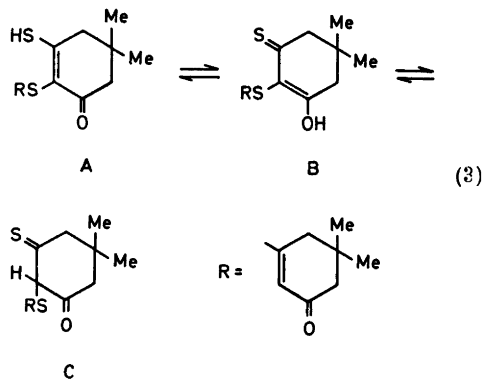
order to find out if *24* could be formed from *13* this compound was irradiated at 254 nm in ethanol. It turned out [28] that *24* was produced in high yields (79 %) and crystallized directly from the solvent. Also sunlight caused this conversion (*13*→*24*) in solution, while in the solid state *13* was quite stable. The possibility that the rearrangement was thermally induced was ruled out, as no conversion was observed when *13* was boiled in ethanol in the dark. More severe conditions (*i.e.* heating in HMPA in the presence of $KHSO_4$)[29,30] which have brought about 3,3-sigmatropic rearrangements of other divinyl-disulfides,[29–32] gave only tar.

Various methods were used in order to determine the mechanisms of the observed photochemical reactions. A hexane solution of the acetyl derivative *12* and 2-methyl-2-nitrosopropane was irradiated at 254 – 300 nm in the ESR spectrograph. The formation of *N*-acetyl-*N*-(*t*-butyl)nitroxide ($a_N = 8$ gauss) [33] indicated that the primary photochemical process was a cleavage of *12* into acetyl and thiyl radicals (eqn. 2). However, no well defined signal from the thiyl radical or trapped thiyl radical could be observed. Also attempts to trap radicals by photolysis of the disulfide *13* were fruitless. The conversion of *13* irradiated with monochromatic light (254 and 300 nm) was measured by the change of the UV spectrum. The change of the UV spectrum obtained in ethanol differed



(2)

clearly from that obtained in $CHCl_3$. In both solvents the absorption at 277 nm disappeared with about equal rates. However, in ethanol an absorption at 350 nm appeared quickly, reached a maximum and then faded out. In $CHCl_3$ only comparatively weak absorption at 350 nm was found. It is believed that different tautomers (eqn. 3) of the same intermediate are formed when the solvent is changed, thus giving rise to different UV-spectra. For comparison, it should be pointed out that *5* showed a behaviour similar to the intermediate in eqn. 3 as *5* revealed absorption at 342 nm in ethanol and DMSO, while in $CHCl_3$ this band was comparatively weak. The suggested intermediate (M) represented by structure A, B, and C in eqn. 3 might be formed by a radical chain process initiated by light (eqn. 4). The propagation step (eqn. 5) consists of a thiyl radical attack on C-2 of *13* (RSSR), giving M and another thiyl radical. This means that the rate of disappearance of *13* is dependent on the concentration of *13*. Measurement of the quantum yield ($\Phi = 0.1$) for disappearance of *13* showed no such dependence on [RSSR], and it seems therefore reasonable to suggest another mechanism. The reaction could proceed through reactions in which two thiyl radicals combine to give M either as free radicals or in a solvent cage (eqn. 7). Finally a concerted [1,3]-sigmatropic process could be suggested (eqn. 8). The conversion of M to *24* might be a thermal cyclisation reaction, but more likely a photochemical process, because it explains the change of the UV spectrum in EtOH. The absorption at 350 nm, ascribed to M, did not change on standing in the dark, while irradiation caused a change as described above.



(3)

Initiation:

$$RSSR \rightarrow RSSR^* \rightarrow 2\ RS\cdot \quad (4)$$

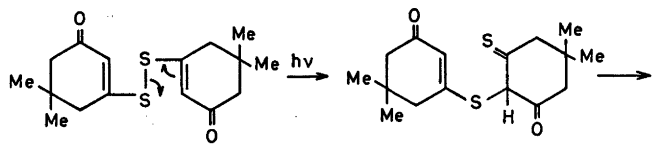
Propagation:

$$RS\cdot + RSSR \xrightarrow{k_1} M + RS\cdot \quad (5)$$

$$\Phi I = -dC/dt = k_1[RS\cdot][RSSR] \quad (6)$$

$$2\ RS\cdot \rightarrow M \quad (7)$$

$$RSSR \rightarrow RSSR^* \rightarrow M \quad (8)$$



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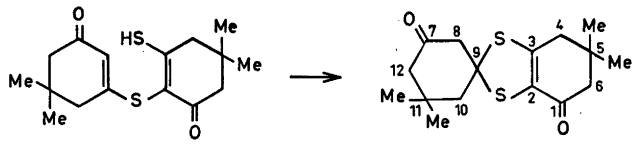
(9)



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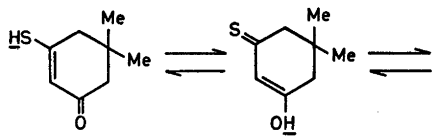
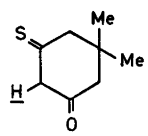
SPECTROSCOPY

Tautomerism of thiodimedone. In principle thiodimedone *5* can exist as the monomeric keto-enethiol (D), thioketo-enol (E), and the ketothioketo (F) structures (eqn. 10). In concentrated solutions or neat also dimer structures



5 (D) 5 (E)

(10)



5 (F)

analogous to the findings for 1,3-cyclohexandione and dimedone should be considered likely.[36,37] The IR spectrum of thiodimedone showed absorption at 2520 cm^{-1} and a broad band at 1680 cm^{-1} assigned, respectively, to the mercapto and the α,β-unsaturated keto group of the keto-enethiol (D). This was the only tautomer detectable by NMR. The signal at δ 6.05 was assigned to the vinyl proton, as an allylic coupling to the protons on C-4 was observed. The broad signal at δ 4.23 could be attributed to a mercapto proton, excluding an enolic proton, which was expected to reveal a signal at lower field (δ 9 – 13). The broadening of this signal was ascribed to proton exchange. Contrary to what is often found for enethiols, no coupling between the proton of the mercapto group on C-3 and the protons on C-4 was present. The structural requirement for a maximum coupling is that the bondings between the hydrogens obtain a planar zig-zag framework, as found for enethiols possessing an intramolecular chelated structure.[38] As only energetical less important intermolecular hydrogen bonding can occur in thiodimedone, the rotation about the C – S bond is less restricted, and the coupling decreases to zero. The UV spectrum of thiodimedone obtained in hexane showed absorption at 268 nm, ascribed to the $\pi - \pi^*$ transition of the α,β-unsaturated keto chromophore, present in the keto-enethiol (A). When the solvent was changed to EtOH or DMSO absorption maxima at 282 and 340 nm were observed. On going from an α,β-unsaturated ketone to the thione the $\pi - \pi^*$ absorption is shifted about 80 nm.[39–42] The strong absorption of 340 nm must therefore arise from structure *5*E. The structure *5*F cannot be excluded because saturated thioketones have only weak absorption above 300 nm and the observed one is strong.

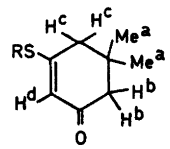
Identification of other compounds. The spectroscopic data of 3-alkylthio derivatives of thiodimedone are shown in Table 3 (NMR) and Table 4 (IR and UV). These compounds gave rise to an IR absorption in the range of 1650 – 1680 cm^{-1} due to an α,β-unsaturated carbonyl group and a band at 1570 – 1595 cm^{-1} corresponding to a carbon-carbon double bond. The UV spectra of compounds *7* – *10*, *15* showed

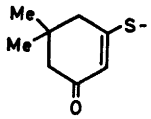
Table 2. Rate of disappearance ($-\Delta C/\Delta t$) of compound *13*, measured by the change in UV absorbance (ΔAbs) for various concentrations (C) of *13*.

$C \times 10^7$ mol/cm³	ΔAbs	$-\Delta C \times 10$/[a] mol/cm³	Δt (s)	$-\frac{\Delta C}{\Delta t} \times 10^{11}$ mol/cm³ s
0.645	0.29	1.45	180	8.06
1.30	0.23	2.30	300	7.67
1.94	0.25	3.45	420	8.23
3.23	0.21	5.25	720	7.23
3.87	0.23	6.90	900	7.67
6.45	0.29	14.50	1800	8.05

[a] ΔC corresponds to 16–23 % conversion of *13*. $\Delta C = \Delta\text{Abs}/\Delta\varepsilon$, where $\Delta\varepsilon$ is the difference between the molar absorbance of compound *13* ($\varepsilon = 21\,400$) and that of compound *24* ($\varepsilon = 1400$) at 277 nm.

Table 3. ^{1}H NMR chemical shift (δ values) and coupling constants (J Hz) of 3-mercapto-5,5-dimethyl-2-cyclohexen-1-one and derivatives. The solvent is CCl_4.



Compound	R	δ_a	δ_b	δ_c	δ_d	δ_e	δ_f	J_{cd}	J_{ef}
5	H[e]	1.05(s)	2.13(s)	2.39(d)	6.05(t)	4.23(s)		1.30	
13		1.06(s)	2.19(s)	2.39(d)	6.03(t)				
7	$\overset{e}{CH_2}=\overset{e}{CH}\text{-}\overset{f}{CH_2}$-	1.05(s)	2.13(s)	2.26(d)	5.73(t)	5.1–6.2(m)	3.46(br.d)		6
8[a]	$\overset{g}{Me}\overset{e}{CH}=\overset{e}{CH}\overset{f}{CH_2}$-	1.05(s)	2.14(s)	2.25(d)	5.73(t)	5.2–9(m)	3.42(br.d)		6
9[b]	$\overset{e}{MeCO}\overset{f}{CH_2}$-	1.05(s)	2.24(s)	2.36(d)	5.78(t)	2.32(s)	3.76(s)		
10	$\overset{e}{HC}\equiv\overset{f}{CCH_2}$-	1.06(s)	2.17(s)	2.30(d)	5.82(t)	2.35(t)	3.60(d)		2.4
11	$\overset{e}{H_2C}=\overset{f}{C}=CH$-	1.08(s)	2.15(s)	2.27(d)	6.18(t)	5.06	5.88	1.30	6.6[c]
12	$\overset{e}{MeCO}$-	1.10(s)	2.20(s)	2.50(d)	6.24(t)	2.37(s)			
14	$\overset{e}{Ph}$-	1.04(s)	2.12(s)	2.33(d)	5.42(t)	7.47(s)			
15	$\overset{e}{Ph}\overset{f}{CH_2}$-	1.02(s)	2.12(s)	2.24(d)	5.82(t)	7.28(s)	3.94(s)		

[a] $\delta_g(J_{eg}\text{Hz}) = 1.74(5)$. [b] Solvent $CDCl_3$. [c] AB_2 spin system.

Table 4. IR and UV spectra of 3-mercapto-5,5-dimethyl-2-cyclohexen-1-one and derivatives.

Compound	IR ν_{max} (cm^{-1}) $\nu_{C=O}$	$\nu_{C=C}$	Other	Conditions	UV,[a] λ_{max} nm (log ε)
5	1680(br.s)	1595	2520(w,br,)	CCl_4	282(4.12), 340(3,74) [b] 268(4.11), 300–310(w) [c] 269, 314(w) [d] 279, 342 [e] 273, 313(w) [f] 280
4	1660(s)	1580(s)		$CHCl_3$	232(3.96), 278(3.97), 313(3.90)
13	1650(s)	1580(s)		KBr	277(4.33)
7	1660(s)	1580(s)		film	288(4.24)
8	1660(s)	1580(s)		CCl_4	293(4.26)
9	1730(s) 1670(s)	1590(s)		CCl_4	287(4.20)
10	1660(s)	1590(s)	3300(m) 3250(m)	film	287(4.22)
11	1660(s)	1590(s)	1930(w)	film	297(4.15)
12	1705(s) 1670(s)	1590(s)		film	226(3.93), 277(3.96)
14	1660(s)	1580(s)		KBr	294(4.20)
15	1660(s)	1570(s)		KBr	282(4.30)
19	1655(s)	1600(s)	2530(m)	film	290, 350(shoulder)
20	1715(s) 1685(s)	1645(w) 1605(w)		film	232, 255, 278
21	1660(s)	1605(s)		film	312(4.13)
22	1660(s)	1600(s)		film	312(4.09)
23	1650(s)	1550(m)		film	

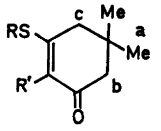
[a] The solvent is EtOH, unless otherwise stated. [b] Solvent: Hexane, [c] ether, [d] DMSO, [e] MeCN, [f] $CHCl_3$.

absorption at 287–292 nm which is ascribed to a $\pi-\pi^*$ transition of the conjugated system. The compounds *4*, *11*, *14* which were further conjugated with an additional carbon-carbon double bond showed a $\pi-\pi^*$ transition at somewhat longer wavelength *i.e.* in the range of 294–313 nm. The disulfide *13* and the acetyl *12* derivatives absorbed at shorter wavelength, namely at 277 nm, than the above mentioned compounds. The spectroscopic data of the products obtained by rearrangement of 3-allylthio and 3-(2-butenyl) derivatives are shown in Table 5 (NMR) and Table 6 (IR and UV). The UV absorptions of the hexahydrobenzothiophenes were found at 312 nm which are about 25 nm higher than the corresponding bands of the starting materials. This is in agreement with the bathochromic effect exhibited by an α-substituent on α,β-unsaturated carbonyl chromophore.

The composition and the molecular weight of the 1,3-dithiole *24* were determined to be $C_{16}H_{22}O_2S_2$ (M = 310) from the elemental analysis and the mass spectrum, respectively. The ^1H NMR spectrum showed signals at δ 1.05–1.15 δ 2.25–2.48, and δ 3.02 with the relative intensity of 1:4:6, while the IR spectrum showed strong bands at 1705, 1660, and 1560 cm^{-1}. Several structures, which were compatible with these data, could be drawn. Among the most plausible suggestions are those, which maintain the carbon skeleton and the positions of substituents of the starting material. However, an unambiguous choice could be made from the ^{13}C-noise decoupled and the off resonance NMR spectra, which are shown in Table 6. The assignment of the signals was based on the data given for the chemical shifts and C–H coupling constants of cyclohexanone [43] and cyclohexenone.[44] Approximate values of the C–H coupling constants were determined from the residual splittings, using the expression given by Ernst,[45] and shown to be of the same size as for methylene groups of cyclohexane.[45]

Compound *25* was shown to have the composition $C_{16}H_{24}O_2S_2$ (molecular weight 312)

Table 5. ^{1}H NMR chemical shift (δ values in ppm relative to TMS) and coupling constants of 2-alkyl-3-mercapto-5,5-dimethyl-2-cyclohexen-1-one and derivatives.



Compound	Solvent	R	R′	δ_a	δ_b	δ_c	δ_d	δ_e	δ_f	δ_g	J_{de}	J_{ef}	J_{eg}	J_{fg}	J_{cf}	J_{cg}
19	(CCl_4)	$H^d\,\overset{e}{CH_2}=\overset{f}{CH}-\overset{g}{CH_2}-$						3.09 (br.d)								
20	($CDCl_3$)	$Ac^d\,CH_2=CH-CH_2-$		1.09 (s)	2.36 (s)	2.69 (br.)	2.50 (s)	3.23 (br.d)	4.8	−6.05 (m)						
21	(CCl_4)	R= $-\overset{e}{CH}(Me^d)-\overset{f,g}{CH_2}-$	=R′			2.33 (t)	1.38 (d)	3.83 (m)	3.08 (m)	2.66 (m)	6.75	8.92	5.74	−15.78[a]	2.36	2.04
22	(CCl_4)	R= $-\overset{e}{CH}(Me^d)-\overset{f}{CH}(Me^g)-$	=R′	0.78 (s)	2.05 (s)	1.97 (br.s)	1.11 (d)	1.19 (d)	2.7	−3.5 (m)	7.0			6.5		
22′		80 %(22)+20 %(22′)		0.78 (s)	2.05 (s)	1.97 (br.s)	1.07 (d)	1.05 (d)	2.5	3.5 (m)	7.0			7.0		
22	(C_6D_6)			1.07 (s)	2.12 (s)	2.33 (br.s)	1.35 (d)	1.11 (d)	2.9	3.5 (m)						
22′				1.07 (s)	2.12 (s)	2.33 (br.s)	1.36 (d)	0.99 (d)	2.9	3.5 (m)						
23[b]	(CCl_4)	R= $-\overset{d}{CH_2}-\overset{e}{CH}=\overset{f}{CH}-$	=R′	1.03 (s)	2.24 (br.s)	2.34 (br.s)	3.42 (q)	5.45 (m)	6.57 (m)		5.1	10.15			0.9	

[a] Rel. sign. [b] J_{df}= 1.6 Mz.

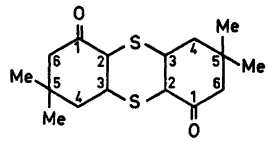
Table 6. ^{13}C NMR data of the noise and off resonance decoupled spectra of compound *24* (*cf.* p. 1081). Chemical shifts (δ values in ppm, relative to TMS) and approximate coupling constants (J_{CH} Hz) evaluated from the expression [44]

$J_{CH}{}^{r} = 2\pi \Delta\nu J_{CH}/\gamma H_2$

Relative intensities of lines (I). The solvent is $CDCl_3$.

	Me	Me	Me	Me	C5(11)	C11(5)	CH_2	CH_2	CH_2	CH_2	CH_2	C9	C2	C3	C1	C7
δ	27.4	28.6	29.4	30.2	35.3	35.9	40.5	49.3	50.5	53.2	57.4	66.9	128.9	152.5	190.0	204.0
I(rel)	206	185	188	203	198	132	171	169	193	206	157	14.7	60	90	90	198
J(Hz)	122±3	122±3	122±3	122±3	–	–	129±5	129±5	129±5	129±5	129±5	–	–	–	–	

Table 7. ^{13}C NMR data of the noise and off resonance decoupled spectrum of compound *25*.



Chemical shifts (δ values in ppm, relative to TMS) and relative intensities of lines (I). The solvent is $CDCl_3$.

	Me	Me	C5	C3	C4	C2	C6	C1
δ	28.3	34.9	39.7	48.4	49.4	54.7	54.8	213
I	162	155	59	112	119	74	211	30
Multiplicity	q	q	s	d	t	d	t	s

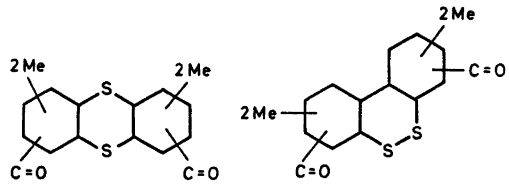
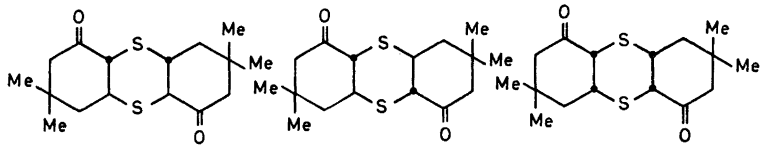


Fig. 3. Possible structures for the photo-dimer *25*.

as determined by the mass spectrum. The noise decoupled ^{13}C NMR spectrum showed 8 signals (Table 7) from the 16 carbon atoms, indicating magnetic equivalent pairs of carbon atoms. The off resonance decoupled spectrum showed the presence of methyl methylene and methine carbon atoms. It was assumed that the carbon skeleton of thiodimedone *5* was maintained in the photo-dimer *25*, which might then have one of the 1,2- or 1,4-dithiane structures shown in Fig. 3. However, the 1,2-dithiane structure was unlikely, as it did not account for the ^1H NMR multiplet signal at δ 3.6 – 4.1 assigned to a pair of equivalent methine protons. The signals due to the methine protons in the α-position to the carbonyl group of the 1,2-dithiane would be found at higher field, *i.e.* at about δ 3. The most probable structures are therefore those represented in Fig. 4, which could not be distinguished based on ground of the available data.

EXPERIMENTAL

^1H NMR spectra were recorded at 60 MHz on a Varian A-60 spectrometer. The temperature of the 15 – 20 % solutions (w/w) were 33 ± 1 °C. TMS was used as internal reference standard and the chemical shifts are expressed in δ-values and are correct within ± 0.02 ppm. ^{13}C spectra were recorded on a Varian XL-100-15 spectrometer operating in the c.w. mode at 25.2 MHz. Internal field-frequency lock was provided by the ^2H resonance of $CDCl_3$ as solvent. Carbon line positions were measured relative to the carbon resonance of internal TMS. Noise-modulated and single-frequency proton decoupling experiments were performed by means of the Varian Gyrocode spin decoupler. The sample solution was contained in a 12 mm tube. 70 eV mass spectra were obtained on a Bell and Howell CEC 21 – 104 single focussing mass spectrometer. The IR spectra were recorded as 5 % solutions, film,



25

Fig. 4. Compound *25*.

or as KBr pellets on a Perkin-Elmer infracord 137 and the UV spectra on a Bausch & Lomb Spectronic 505 spectrophotometer with EtOH as solvent. B.p's are uncorrected. Analyses were made by Novo Industri A/S, Copenhagen.

General procedure for the preparation of the sodium salt of 3-mercapto-5,5-dimethyl-2-cyclohexen-1-one. An amount of 16 g (0.1 mol) 3-chloro-5,5-dimethyl-2-cyclohexen-1-one, *2*, was dropped to a solution of 25 g (0.1 mol) $Na_2S.9H_2O$ in 25 ml water during 2 h. The mixture was kept at about 60 °C until it became homogeneous after further 2 h. This solution was then extracted with diethyl ether (2 × 10 ml), which after drying and evaporation gave small amounts of bis(5,5-dimethyl-2-cyclohexen-3-yl-1-one)sulfide, *4*. The water solution was then used for further reactions.

3-Mercapto-5,5-dimethyl-2-cyclohexen-1-one, 5. Acidification (0.1 mol) of the solution of the sodium salt of *5* with cold 4 M HCl, extraction with ether, drying and evaporation of the ether gave the crude product, which amounted to 14.8 g (95 %). The yield decreased considerably by distillation at 98 °C/0.1 mmHg; $n_D^{25} = 1.5690$. (Found: C 61.49; H 7.79; S 19.47. $C_8H_{12}OS$ requires: C 61.52; H 7.75; S 20.49).

Bis(5,5-dimethyl-2-cyclohexen-1-on-3-yl)-sulfide, 4. Ether extraction of the water solution of the sodium salt of *5* prepared by the general procedure gave after drying and evaporation 0.656 g (5 %) of m.p. 176–177 °C. (Found: C 68.84; H 7.98; S 11.46 $C_{16}H_{22}O_2S$ requires: C 69.04; H 7.97; S 11.50). MS, *m/e* (%): 280(9), 279(38), 278(51), 264(5), 263(23), 207(8), 196(5,) 195(11), 194(57), 156(9), 155(47), 152(14), 151(16), 141(9), 139(9), 138(15), 137(24), 123(9), 112(11), 111(12), 110(77), 95(9), 93(8), 91(8), 79(23), 77(15), 71(17), 68(100), 56(8), 55(22), 53(22).

Bis-(5,5-dimethyl-2-cyclohexen-1-on-3-yl)-disulfide, 13. To a water solution of 0.1 mol of the sodium salt of *5* prepared by the general method were added (excess) 20 g (0.079 mol) of iodine dissolved in 50 ml THF. After about 2 h at room temp. a saturated solution of $Na_2S_2O_3$ was added until the dark colour disappeared, and the mixture was extracted with CH_2Cl_2. This was then stripped off and the residue treated with ether and water. The ether was dried and evaporated giving 14.1 g (91 %) of crystalline product. M.p. 91 °C (ether). (Found: C 61.95; H 7.16; S 20.21. $C_{16}H_{22}O_2S_2$ requires: C 61.92; H 7.15; S 20.6). MS, *m/e* (%): 310(26), 295(9.2), 279(11), 278(37), 277(100), 255(9.2), 254(39), 253(56), 247(7.4), 246(45), 254(19), 220(11), 212(35), 156(26), 155(33), 100(56), 83(56), 71(32), 67(65), 55(37).

5,5-Dimethyl-3-methylthio-2-cyclohexen-1-one, 6. To the solution prepared by the general method were added 16 g (0.11 mol) MeI. The temp. was kept at about 30 °C. The mixture was then allowed to stir overnight. Extraction with ether, drying evaporation of the solvent yielded 15.1 g (89 %) of crystalline compound, m.p. 35 °C (lit. m.p.[6] 34–37 °C).

3-Allylthio-5,5-dimethyl-2-cyclohexen-1-one, 7. An amount of 15 g (0.12 mol) allyl bromide in 25 ml DMSO was added to the water solution of the 0.1 mol sodium salt of *5*. The temp. was allowed to rise to 45 °C. After 2 h the mixture was cooled and extracted with 15 ml ether, which was then evaporated. Extraction with water of the residue dissolved in light petroleum was repeated. Drying and evaporation and distillation gave 18 g (92 %); b.p. 65 °C/10^{-4} mmHg, $n_D^{25} = 1.5520$. (Found: C 67.34; H 8.21; S 16.11. $C_{11}H_{16}OS$ requires: C 67.32; H 8.22; S 16.31).

3-(2-Butenylthio)-5,5-dimethyl-2-cyclohexen-1-one, 8. An amount of 8 g (0.059 mol) of 2-butenyl bromide was added to 0.05 mol of the water solution of the sodium salt of *5*. Stirring overnight, followed by extraction with ether, drying and evaporation of the ether gave 8.7 g (83 %); b.p. 114–116 °C/0.1 mmHg; m.p. 33–34 °C. (Found; C 68.61; H 8.64; S 15.11. $C_{12}H_{18}OS$ requires: C 68.54; H 8.63; S 15.22).

5,5-Dimethyl-3-(propan-2-on-1-ylthio)-2-cyclohexen-1-one, 9. A water solution of 0.1 mol of the sodium salt of *5* was treated with 11 g (0.12 mol) chloroacetone. The exothermal process was finished within ½ h. Extraction with 50 ml of ether, drying, and evaporation of the solvent gave 14.5 g (68 %) of crystalline product; m.p. 65 °C (ether–light petroleum 1/1). (Found: C 62.47: H 7.74; S 15.21 $C_{11}H_{16}O_2S$ requires: C 62.25; H 7.60; S 15.08).

5,5-Dimethyl-3-(2-propynylthio)-2-cyclohexen-1-one, 10. An amount of 1.80 g (11.5 mmol) of *5* was dropped to 3.0 g (12 mmol) of thallium(I) ethoxide dissolved in 25 ml benzene. The solid product was filtered off and washed with benzene and ether, giving an mount of 3.9 g (95 %). Then 3.59 g (10 mmol) of this salt were suspended in 15 ml HMPA and 1.5 g (12.6 mmol) of 2-propynyl bromide were added. The mixture was stirred overnight and extracted with ether and water. The ether was stripped off and extraction was repeated with light petroleum and water. Drying and evaporation of the solvent yielded 1.77 g (89 %) which were distilled quantitatively. B.p. 80 °C/10^{-4} mmHg; $n_D^{25} = 1.5608$; (Found: C 68.23; H 7.04; S 16.23. $C_{11}H_{14}OS$ requires: C 68.02; H 7.27; S 16.5).

3-Allenylthio-5,5-dimethyl-2-cyclohexen-1-one, 11. An amount of 4.62 g (29.5 mmol) of *5* dissolved in 30 ml CH_2Cl_2 was added to 10.5 g (31.0 mmol) of tetrabutylammonium hydrogensulfate and 3 g (75 mmol) of NaOH in 30 ml water. Then 4 g (34 mmol) of 2-propynyl bromide were added and the mixture stirred for 18 h. The CH_2Cl_2 phase was evaporated and the residue was treated with ether and water. Drying and evaporation yielded 4.9 g (86 %) of *11*. However, the yield decreased considerably by distillation which gave 1.58 g of b.p. 70 °C/10^{-4} mmHg; $n_D^{25} = 1.5705$. (Found: C 67.94;

H 7.14; S 15.95. $C_{11}H_{14}OS$ requires: C 68.02; H 7.27; S 16.5).

3-Acetylthio-5,5-dimethyl-cyclohexen-1-one, 12. Acidification and work up (without distillation) of a solution prepared by the general method gave *5* which was then treated with 10 g pyridine and 100 ml ether. An amount of 9 g (0.115 mol) acetyl chloride was dropped to the mixture and after 1 h the pyridinium hydrochloride was filtered off and the residue washed with water. The ether was dried over $NaHCO_3$. Evaporation gave 19 g and distillation yielded 15.82 g (75 %); b.p. 96 °C/0.05 mmHg; $n_D^{25} = 1.5314$. (Found: C 60.79; H 7.13; S 15.80. $C_{10}H_{14}O_2S$ requires; C 60.59; H 7.12; S 16.15).

1,3,3-Tribenzylthio-5,5-dimethyl-1-cyclohexene, 16, and 3-benzylthio-5,5-dimethyl-2-cyclohexen-1-one, 15. Preparation by the method of Campaigne.[7] An amount of 14 g (0.1 mol) of dimedone, *1*, and 24.8 g (0.2 mol) of phenylmethanethiol were mixed in 200 ml ethanol. The solution was saturated with HCl gas. A precipitate of 1.16 g (3.6 %) of *16* was formed (theoretical yield 31.9 g). M.p. 77–82 °C. (Found: C 72.73; H 6.68; S 19.88. $C_{29}H_{32}S_3$ requires: C 73.09; H 6.77; S 20.14). NMR (CCl_4): δ 0.96 (6 H, s), 1.83 (4 H, br.s), 3.53 (2 H, s), 3.70 (4 H, s), 5.18 (1 H, s), 7.22 (15 H, s). IR ν_{max}(KBr) (cm^{-1}) 1590. UV (EtOH) λ_{max} (log ε): 212 (4.46), 252 nm (4.07). The alcohol solution was poured into 300 ml water in which 150 g Na_2CO_3 was dissolved. A precipitate was filtered, and then dissolved, dried and the solvent evaporated, giving 5.5 g (22 %) of *15*. M.p. 84–85 °C. (Found: C 73.11; H 7.29; S 13.11. $C_{15}H_{18}OS$ requires: C 73.14; H 7.37; S 12.99).

Treatment of 3-alkylthio-5,5-dimethyl-2-cyclohexen-1-ones with nucleophiles

3-Ethyliden-5,5-dimethyl-1-phenylthio-cyclohexene, 17. An amount of 11.6 g (0.05 mol) of *14* dissolved in 50 ml THF was treated with 0.05 mol EtLi in 50 ml THF solution at −10 °C. After about 1 h, 15 g (0.106 mol) MeI were added and the mixture allowed to stir for 1 h. The solvent was stripped off and extracted with ether and water. The ether phase was dried and evaporated, giving 12.0 g of a liquid. After a short time it became milky and separated into two layers. The mixture was treated with ether again, dried and the solvent evaporated. Distillation yielded 9.4 g (77 %) of b.p. 123–124 °C/0.2 mmHg; $n_D^{25} = 1.5909$. IR ν_{max}(film) (cm^{-1}) 3050(m), 2900(s), 1570(m). NMR (CCl_4): δ 0.89 and 0.92 (6 H, s), 1.70 (3 H, br. d, 7), 2.02 (4 H, br. s), 5.1–5.5 (1 H, m), 6.24 and 6.56 (1 H, br.s), 7.28 (5 H, br.s.). (Found: C 78.24; H 8.00; S 13.17. $C_{16}H_{20}S$ requires: C 78.65; H 8.25; S 13.1).

5,5-Dimethyl-3-phenylthio-3-cyclohexen-1-one, 18. An amount of 2.32 g (0.01 mol) of *15* dissolved in 10 ml of dry ether was dropped to a suspension of $LiNH_2$ in liq. NH_3 (prepared from 400 mg Li). The NH_3 was evaporated and the residue acidified with H_2O and NH_4Cl. Extraction with ether drying and evaporation of the solvent gave 2.05 g of crude product, which was fractionated on a column, giving 1.85 g (80 %) of starting material and 0.19 g (8 %) of *19*. IR ν_{max}(film) (cm^{-1}) 1710(s). MS, *m/e* (%): 232(56), 219(6), 218(16), 217(100), 189(14), 176(6), 164(10), 156(6), 113(10), 111(12), 110(26), 109(26), 107(56), 95(8), 93(6), 91(8), 81(15), 80(12), 79(68), 78(10), 77(43), 69(10), 67(17), 66(8), 65(15), 55(12), 53(19).

Rearrangement of 7

2-Allyl-3-mercapto-5,5-dimethyl-2-cyclohexen-1-one, 19. Traces of *p*-toluenesulfonic acid were added to 5.3 g (27 mmol) of *7* and kept at 100 C for 4½ h in a Vigreaux distillation apparatus. Distillation gave 3 fractions, which consisted of compounds *19* and *21*, as shown by the NMR and IR spectra.

3-Acetylthio-2-allyl-5,5-dimethyl-2-cyclohexen-1-one, 20. An amount of 2.68 g (13.7 mmol) of *7* in 10 ml acetic anhydride was boiled at 140 °C for 2 h. The acetic anhydride was stripped off and the residue dissolved in ether, which was then extracted with 2 M aqueous Na_2CO_3. Drying and evaporation of the ether yielded 2.87 g crude product. 1.40 of this was purified with PLC yielding 0.5 g (38 %) of *20* and 0.26 g of an unidentified mixture. B.p. of *20* 60° C/10^{-4} mmHg; $n_D^{25} = 1.5290$; (Found: C 65.09; H 7.51; S 13.41 $C_{13}H_{18}O_2S$ requires: C 65.53; H 7.61; S 13.41).

2,6,6-Trimethyl-4-oxo-2,3,4,5,6,7-hexahydrobenzothiophene. 21. An amount of 2.05 g (10.4 mmol) of *7* in 5 ml quinoline was heated to 140 °C. After 3 h the starting material was converted. The mixture was extracted with ether and 4 M HCl. The ether layer was dried and evaporated. Crude product amounted to 1.78 g. Distillation gave 0.73 g (36 %) of b.p. 100 °C/0.01 mmHg; $n_D^{25} = 1.5535$; (Found: C 67.26; H 7.92; S 15.99. $C_{11}H_{16}OS$ requires: C 67.32; H 8.22; S 16.31).

Rearrangement of 8

2,3,6,6-Tetramethyl-4-oxo-2,3,4,5,6,7-hexahydrobenzothiophene, 22. An amount of 1.77 g (8.3 mmol) of *8* in 3 ml quinoline was heated for 5 h. Extraction with 4 M HCl and ether gave after drying and evaporation of the ether 1.40 g, which was distilled. B.p. 100 °C/0.01 mmHg, giving 1.17 g of a mixture of 27 % starting material and 73 % product. The experiment was repeated with 0.585 g of this mixture at a temp. of 160 °C and a reaction time of 3 h. Work up as above gave 0.348 g (yield 39 %) of b.p.

100 °C/0.01 mmHg; $n_D^{25} = 1.5420$; (Found: C 67.79; H 8.42; S 14.99. $C_{12}H_{18}OS$ requires C 68.54; H 8.63; S 15.22).

Rearrangement of *10*

7,7-Dimethyl-5-oxo-2,5,6,7,8-pentahydrobenzothiopyran, 23. An amount of 1.19 g (6.2 mmol) of *10* was boiled in 4 ml pyridine for 3½ h. The solvent was evaporated and the residue distilled. B.p. 100 °C/0.01 mmHg; $n_D^{25} = 1.5796$.

General procedure by photolysis of 3-alkylthio- and 3-arylthio-5,5-dimethyl-2-cyclohexen-1-ones. A solution of the compound was irradiated in a "Rayonet RS" photoreactor (for details see Table 1). A flow of dry and oxygen-free N_2 through the solution was maintained during the photolysis. The reaction was followed by UV spectroscopy and TLC. The solvent was evaporated and the residue was fractionated on a silica gel column or plate (about 100 g silica gel/g of product) with benzene – ethyl acetate = 4:1 (w/w) as eluent. However, the mixture obtained by photolysis of *14* was worked up using ether – light petroleum = 1:1 (w/w) as eluent.

The 1,3-dithiole, 24. M.p. 167 – 169 °C; (Found: C 61.90; H 7.12; S 20.63. $C_{16}H_{22}O_2S_2$ requires: C 61.92; H 7.15; S 20.6). NMR ($CDCl_3$): δ 1.05 – 1.15(12 H, 3 s); 2.25 – 2.48 (8 H, br. singlets and AB splittings); 3.02 (2 H, br.s). IR ν_{max}($CHCl_3$) (cm^{-1}), 1710(m-s); 1660(s); 1560(m.) UV ($CHCl_3$) λ_{max} (log ε), 250 (3.71), 350 nm (3.71). MS, *m/e* (%): 310(33), 308(5), 277(5) 256(8), 255(21), 254(68), 253(100), 239(32), 214(8), 213(16), 212(72), 178(20), 156(11), 155(8), 83(48), 55(54).

The 1,4-dithiane, 25. M.p. 172 – 174 °C; NMR ($CDCl_3$): δ 0.93 – 1.1(12 H, br.s); 1.7 – 2.7 (8 H, m); 3.1 – 3.3(2 H, m); 3.6 – 4.1 (2 H, m). IR $\nu_{max}CHCl_3$(cm^{-1}): 1705. MS, *m/e* (%): 312(2), 311(9), 310(4), 309(6), 308(8), 297(18), 282(12), 281(56), 280(40), 279(30), 278(10), 277(17), 263(16), 261(14), 260(75), 248(20), 247(100), 246(14), 245(10), 206(22), 195(40), 181(20), 157(23), 156(67), 155(8), 141(25), 125(77), 97(38), 91(22), 83(56), 55(46), 43(26), 41(53).

3,3-Dimethyl-5-oxo-2,3,4,5-tetrahydrodibenzothiophene, 26. M.p. 100 – 102 °C (Found: C 73.88; H 6.16; S 13.86. $C_{14}H_{14}OS$ requires: C 73.02; H 6.13; S 13.90). NMR (CCl_4): δ 1.15 (6 H, s), 2.36 (2 H, s), 2.90 (2 H, s), 7.1 (3, H, m), 8.50 – 8.65 (1 H, m). IR ν_{max}(KBr) (cm^{-1}) 1650. UV (EtOH): λ_{max} (log ε): 220 (4.08), 243 (3.70), 303 nm (3.48).

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