Carbon Disulfide. IV. Reaction with Active Methylene Compounds. The Formation of 3,5-Bismethylene-1,2,4-trithiolanes[1]

PETER YATES AND THOMAS R. LYNCH
Department of Chemistry, Lash Miller Chemical Laboratories, University of Toronto, Toronto 5, Ontario

Received October 1, 1970

The three-sulfur compounds formed on oxidation of the β-keto dithio acids prepared by the reaction of active methylene compounds with base and carbon disulfide have been shown to be 3,5-bis(acylmethylene)-1,2,4-trithiolane derivatives. In several cases, two of the three possible geometrical isomers have been isolated and provisional stereochemical assignments have been made. The i.r. and u.v. spectra of the trithiolanes have been compared with those of corresponding 2,4-bis(acylmethylene)-1,3-dithietane derivatives (desaurins) and interpreted in terms of a strong conjugative interaction between the sulfur atoms and carbonyl groups.

Il a été démontré que les composés contenant des trois atomes du soufre et formés par oxydation des acides dithio β-cétoniques obtenus lors de la réaction du sulfure de carbone avec de la base et des composés contenant des méthylènes actifs sont des dérivés du bis(acylméthylène)-3,5 trithiolane-1,2,4. Dans plusieurs cas, deux des trois isomères géométriques possibles ont été isolés et des configurations stéréochimiques provisoires ont pu être attribuées. Les spectres infrarouge et ultraviolet des trithiolanes ont été comparés à ceux des dérivés bis(acylméthylène)-2,4 dithiétane-1,3(désaurines) correspondants et ont été interprétés en termes d'une interaction conjugative forte entre les atomes de soufre et les groupes carbonyles.

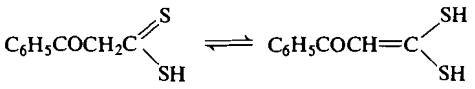
Canadian Journal of Chemistry, 49, 1477 (1971)

Introduction

In the course of our investigation of the desaurins (1), it was observed that during recrystallization of benzoyldithioacetic acid (**1**), the product obtained by treatment of acetophenone with base and carbon disulfide, an insoluble yellow material was obtained. This gave on further recrystallization yellow needles, m.p. 236–238° (dec.), with the formula $C_{18}H_{12}O_2S_3$.

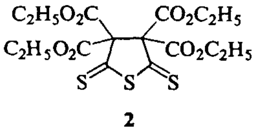
Many years ago Wenzel (2, 3) had observed the formation of compounds containing three sulfur atoms when the sodium derivatives of active methylene compounds, such as diethyl malonate, were treated in carbon disulfide with bromine or iodine. These compounds were assigned structures of type **2** and were considered to arise via oxidation by the bromine of the salts of dithioacetic acids analogous to **1**.

Subsequently, Kelber (4) found that oxidation of the disodium salt of **1** with ammonium persulfate gave a three-sulfur compound, $C_{18}H_{12}O_2S_3$, m.p. 206–207°; he also obtained this compound by oxidation of **1** with iodine followed by recrystallization of the crude product from high boiling solvents, when hydrogen sulfide was eliminated. More recently, Gompper and Töpfl (5) have reinvestigated the oxidation by bromine, iodine, and ammonium persulfate of the disodium salts of dithio acids derived by reaction of active methylene compounds with carbon disulfide. In some cases they again obtained three-sulfur compounds, but in others two-sulfur compounds were isolated. The latter were shown to be desaurins (**3**)[2] (1); the former were assigned structures of type **4** on the basis of their chemical properties and the similarity of their spectra with those of the desaurins.

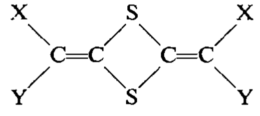


$$C_6H_5COCH_2C(=S)SH \rightleftharpoons C_6H_5COCH{=}C(SH)_2$$

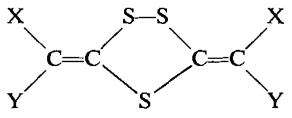
1



2



3



4

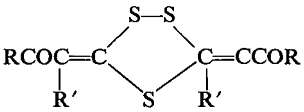
---

[1] For Paper III see ref. 1*a*.

[2] In this and subsequent structures, no assignment of configuration is implied, unless specifically discussed.

TABLE 1. The n.m.r. spectra of 3,5-bismethylene-1,2,4-trithiolanes

Compound*



Compound*	R	R'	Solvent†	δ (p.p.m.)
19	$(CH_3)_3C$	Cl	C	1.33(s)
23	$(CH_3)_3C$	H	C	1.20(s, 18H), 6.95(s, 2H)
27*a*	*p*-$CH_3C_6H_4$	H	C	2.42(s, 6H), 7.29(d, J = 8.5 Hz, 4H) 7.48(s, 1H), 7.68(s, 1H) 7.89(d, J = 8.5 Hz, 4H)
27*b*	*p*-$CH_3C_6H_4$	H	S	2.47(s), 7.54(d, J = 8.5 Hz) 7.75(s), 7.98(d, J = 8.5 Hz)
28*a*	C_6H_5	H	C	7.5(m, 8H), 8.0(m, 4H)
28*b*	C_6H_5	H	S	7.9(m)
29*a*	C_6H_5	C_6H_5	C	7.3(m)
29*b*	C_6H_5	C_6H_5	S	7.40(br s)
30	Mesityl	H	C	2.17(s, 12H), 2.30(s, 6H), 6.83(s, 6H)

*See text for stereochemical assignments.
†C, Deuteriochloroform; S, 96% sulfuric acid.

Among the cases investigated by Gompper and Töpfl was that of the disodium salt of **1**; this on treatment with bromine gave in high yield a yellow crystalline compound, $C_{18}H_{12}O_2S_3$, m.p. 216–220° (dec.). We found that on repeated recrystallization from toluene the m.p. of the product formed in this reaction is raised to 236–238° (dec.) and that this m.p. is undepressed on admixture of the product with that obtained during our recrystallization of **1**; the spectra of the two products were also identical. It is thus clear that these products are the same and probable that our product was formed by air-oxidation during the recrystallization.

We embarked on a fuller study of these three-sulfur compounds for several reasons. First, to provide further evidence for the assignment of structure; although the spectral data excluded structures of type **2** for these compounds, they did not definitively establish structures of type **4**. Second, to examine the possibility of stereoisomerism among these compounds. Third, to examine in detail the relationship between their spectra and those of the desaurins.

Reactions and Structures of the Three-sulfur Compounds

The compound whose chemistry has been examined most extensively is that derived from pinacolone. This was prepared in 34% yield by the general method of Gompper and Töpfl (5) with the use of ammonium peroxydisulfate as oxidant. It was shown to have the molecular formula $C_{14}H_{20}O_2S_3$ by elemental analyses and mass spectrometry. Its n.m.r., i.r., and u.v. spectra are given in Tables 1–3; they are in accord with the assignment of a structure of type **8** and will be discussed subsequently.

Reduction of this substance with zinc and acetic acid gave three products. One was shown to be ethyl *t*-butyl ketone (**5**) by its i.r. and n.m.r. spectra and by the m.p. of its 2,4-dinitrophenylhydrazone.

One of the other products was a colorless, crystalline solid, $C_{14}H_{20}S_2$. Its i.r. spectrum showed a weak band at 6.15 μ, characteristic of ethylenic or aromatic bonds, and a doublet at 7.18 and 7.32 μ, assignable to *t*-butyl groups. Its n.m.r. spectrum exhibited two singlets at δ 1.40 (18H) and

TABLE 2. The i.r. spectra of the 3,5-bismethylene-1,2,4-trithiolanes

Compound*	Medium†	λ_{max} (μ)
19	C	6.25
23	C	6.18, 6.26(sh)
27*a*	N	6.23, 6.25, 6.43
27*b*	N	6.26, 6.42
28*a*	N	6.21, 6.26, 6.40
28*b*	N	6.26, 6.39
29*a*	N	6.25, 6.35, 6.44
29*b*	N	6.25, 6.35, 6.44
30	N	6.21, 6.29
36‡	U	6.19

*See Table 1 for structures of compounds.
†N, Nujol mull; C, chloroform; U, unspecified.
‡Reference 16.

TABLE 3. The u.v. spectra of 3,5-bismethylene-1,2,4-trithiolanes

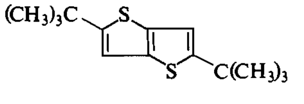
Compound*	Solvent†	λ_{max} (mμ) (ε)
19	D	241(15 100), 352(19 500)
23	E	241(17 800), 339(19 500)
27*a*	C	282(21 400), 361(sh, 34 700) 378(39 800), 392(sh, 35 500)
27*b*	C	282(22 900), 372(sh, 32 400), 389(35 500)
28*a*	E	220(22 900), 268(21 400) 364(sh, 30 200), 378(33 900)
28*b*	E	228(20 900), 268(27 500) 370(sh, 28 800), 382(29 500)
29*a*	C	265(21 900), 392(32 400)
29*b*	C	265(25 100), 395(33 900)
30	E	247(10 000), 355(12 000)
36	E	232(15 200), 347(19 800)

*See Table 1 for structures of compounds.
†C, Chloroform; D, dioxane; E, 95% ethanol.

6.82 (2H). The high field signal could tentatively be assigned to two *t*-butyl groups in equivalent chemical environments; the position of the signal suggested that these groups might be attached to an aromatic ring system. The low field signal could then be due to two protons attached directly to this system in equivalent chemical environments. These spectral data, the origin of the compound, and the fact that its molecular formula requires the presence of a total of five double bonds and/or rings, suggested that it might be 2,5-di-*t*-butylthieno[3,2-*b*]thiophene (**6**).

$(CH_3)_3CCOCH_2CH_3$

5



6

$(CH_3)_3CCOCH_2CH_2SCH_2CH_2COC(CH_3)_3$

7

Strong confirmatory evidence for the presence of the ring system was provided by the u.v. spectrum which exhibited maxima at 269 (ε 17 400) and 280 mμ (ε 12 600), while the parent compound, thieno[3,2-*b*]thiophene, has u.v. maxima at 259 (ε 12 600), 268 (ε 10 000), and 278 mμ (ε 10 000) (7). The related thieno[2,3-*b*]thiophene and thieno[2,3-*c*]thiophene systems, however, give u.v. spectra (8, 9) that differ markedly from the spectrum of the product.

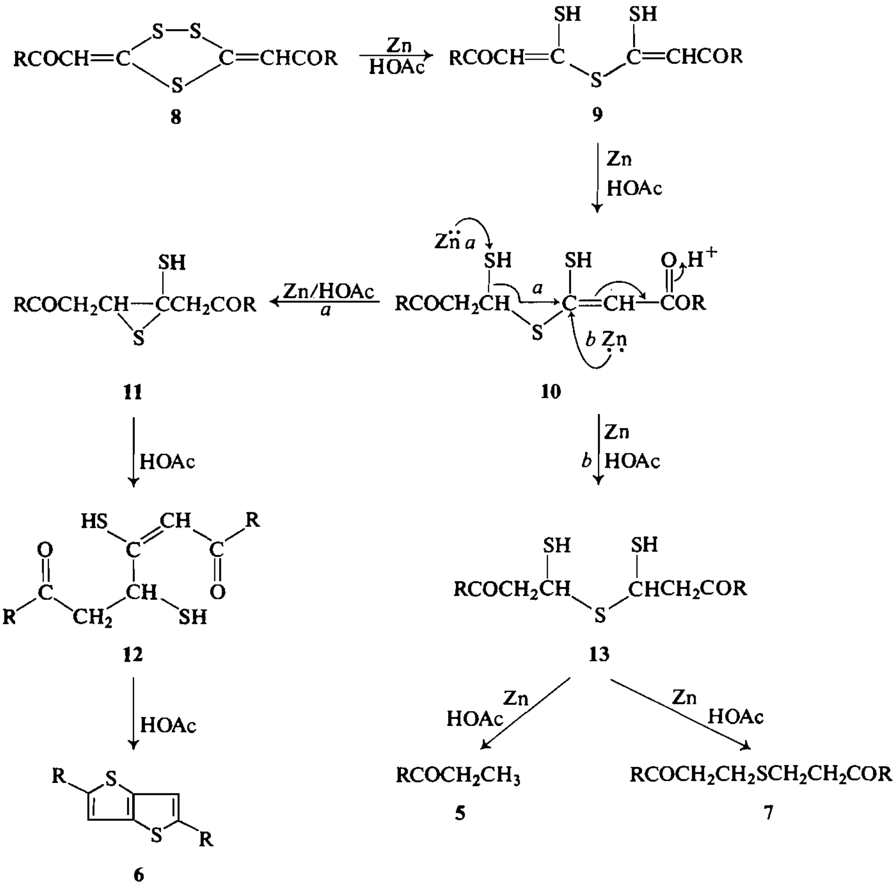
Conclusive evidence for the presence of the thieno[3,2-*b*]thiophene system was afforded by the observation (10) that *t*-butylation of the parent compound gave, *inter al.*, a compound whose i.r. and n.m.r. spectra and m.p. were identical with those of our product; a mixture m.p. point showed no depression.[3] Given this proof of the nature of the aromatic nucleus of the compound $C_{14}H_{20}S_2$, the only structures other than **6** that can be entertained are the corresponding 2,3- and 3,5-di-*t*-butyl derivatives. The former is most unlikely to give the simple n.m.r. spectrum observed for this compound, and both, unlike **6** (*vide infra*), could arise only by a complex series of rearrangements. Structure **6** is thus preferred for this product.

The third reduction product was an oil, which gave a yellow bis-2,4-dinitrophenylhydrazone, $C_{26}H_{34}N_8O_8S$. The formula of the oil was thus indicated to be $C_{14}H_{26}O_2S$, indicating that it is acyclic and has no double bonds other than those of the two carbonyl groups. Its i.r. spectrum showed a single carbonyl-stretching band at 5.84 μ. Its n.m.r. spectrum in carbon tetrachloride solution showed two singlets at δ 1.14 (18H) and 2.67 (8H); this simplicity was deceptive, however, since in benzene solution the lower-field signal appeared as a symmetrical multiplet at δ 2.62. On the basis of these data, structure **7** is assigned to this product; this was confirmed by the fact that on desulfurization with Raney nickel it gave **5**.

The formation of the three reduction products **5**, **6**, and **7** from the three-sulfur compound can readily be interpreted in terms of the assignment

---

[3] We thank Professor S. Gronowitz, University of Lund, for undertaking this synthesis and carrying out the mixture m.p. determination.

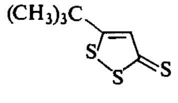


R = C(CH$_3$)$_3$

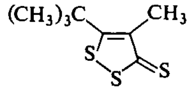
SCHEME 1

to it of a structure, **8**, of the type proposed by Gompper and Töpfl (Scheme 1). Reduction of the disulfide link would lead to **9**, which would give **10** on reduction of one of the α,β-unsaturated carbonyl systems (or of its thione tautomer). Reductive carbon–carbon bond formation as in path *a* could then lead to **11**,[4] which after ring cleavage to **12** followed by dehydration would give **6**. Alternatively, **10** could undergo reduction of its remaining α,β-unsaturated ketone system (or of its thione tautomer) to give **13**, which on further reduction would give **5** and **7**.

Reaction of the three-sulfur compound with phosphorus pentasulfide in boiling xylene gave a compound $C_7H_{10}S_3$, m.p. 69.0–69.5°. This product showed no bands in the 5–6.5 μ region of its i.r. spectrum. Its n.m.r. spectrum showed two singlets at δ 1.43 (9H) and 7.18 (1H). These data showed the product to be 5-*t*-butyl-1,2-dithiole-3-thione (**14**) (11). This structural assignment was corroborated by the similarity of the product's u.v. spectrum with that of **15** (12). The yield of **14** was 56%, based on the formation of 2 mol from 1 mol of the original three-sulfur compound. This reaction can again be readily interpreted in terms of the assignment of structure **8** to the latter compound (Scheme 2). Conversion of the diketone in the usual fashion to the corresponding dithione **16** could be followed by processes (**17** and **18**, arrows) that lead to two molecules of **14**.



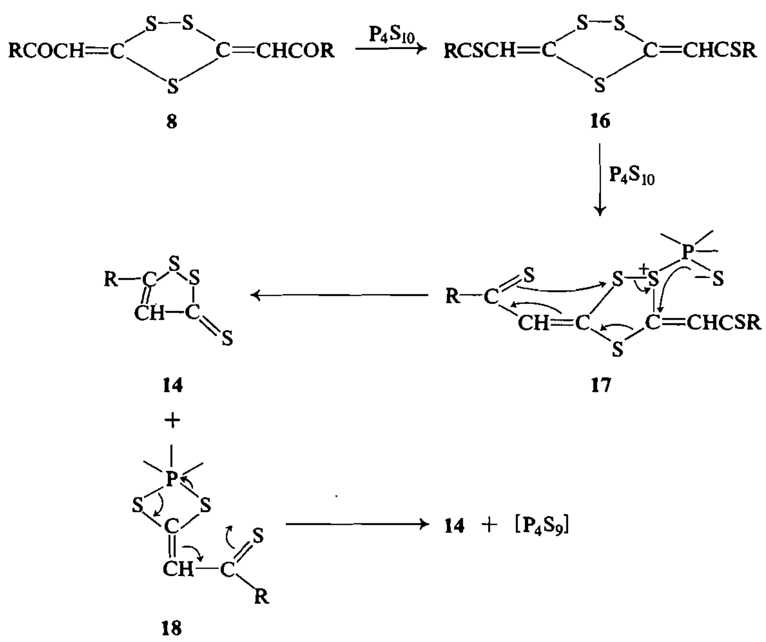
14



15

---

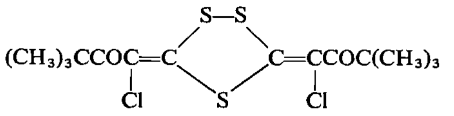
[4] *Cf.* the occurrence of C—C bond formation in the nickel reduction of the desaurin derived from deoxybenzoin (1).



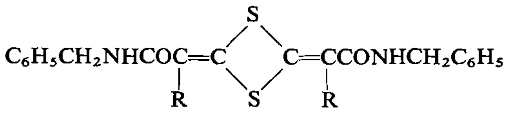
R = $C(CH_3)_3$

SCHEME 2

Reaction of **8** with phosphorus pentachloride gave a product, $C_{14}H_{18}Cl_2O_2S_3$. The u.v. spectrum of this product indicated that the original chromophore was intact (*vide infra*). Its n.m.r. spectrum showed only a singlet at δ 1.33. These data are clearly in accord with the assignment to this product of structure **19**, in which the vinyl hydrogen atoms are replaced by chlorine atoms. A related substitution reaction has been reported recently (13) in which treatment of the desaurin **20** with bromine gives **21**.

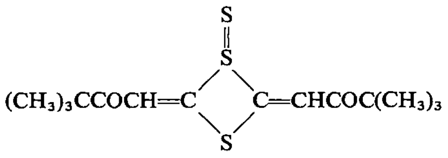


19

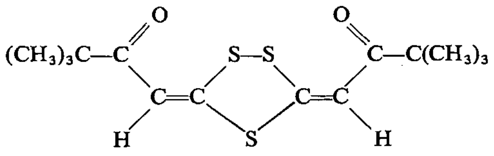


20 R = H
21 R = Br

Thus, these reactions of the three-sulfur compound from pinacolone can all be interpreted in terms of structure **8**. The only possible alternative appears to be the 2,4-bismethylene-1-thiono-1,3-dithietane, **22**. However, branched bonding at sulfur is unlikely in the present case. Such bonding appears to occur only in cases where the sulfur atom to which the branch is attached is also bonded to highly electronegative atoms (14). The assignment of structure **8** has subsequently been confirmed by an X-ray crystallographic study by Nyburg and Mellor (15), which has shown the compound to have the structure, configuration, and conformation shown in **23**.



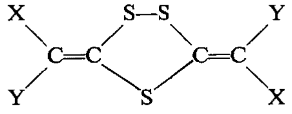
22



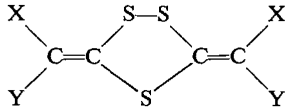
23

Compounds with the gross structure **4** can exist as three geometrical isomers: *trans* (**24***a*), *cis*$_2$

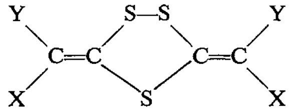
(**24*b***), and *cis*$_1$ (**24*c***).[5] As expected on the basis of the assignment of the *cis*$_2$ configuration **23** to the trithiolane from pinacolone, this compound shows a single vinyl proton signal in its n.m.r. spectrum (Table 1). The n.m.r. spectrum of the crude product and that of a sample recovered after solution of the pure product in 96% sulfuric acid and quenching on ice showed an additional, weak signal at δ 7.10, indicating the presence of a second geometrical isomer. Attempts to isolate this were unsuccessful, however.



24*a*

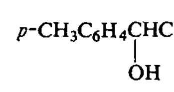


24*b*



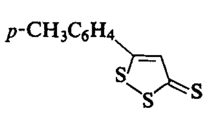
24*c*

More success was met in the case of the product from *p*-methylacetophenone. Two isomeric trithiolanes, $C_{20}H_{16}O_2S_3$, were obtained. The major product was insoluble in chloroform and had m.p. 251–252°, while the minor product was chloroform–soluble and had m.p. 213.5–214.5°. The i.r. and u.v. spectra of these products (Tables 2 and 3) were in accord with the assignment of structures analogous to that of the trithiolane from pinacolone. Furthermore, reduction of the higher-melting isomer with zinc and acetic acid followed by lithium aluminum hydride gave 1-*p*-tolyl-1-propanol (**25**), confirming the assigned carbon skeleton, and treatment with phosphorus pentasulfide gave a product, $C_{10}H_8S_3$, whose spectra (see Experimental) showed it to be **26**, the analog of **14**.



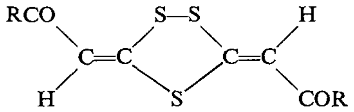
$p\text{-}CH_3C_6H_4\underset{\displaystyle OH}{\underset{|}{C}}HCH_2CH_3$

25

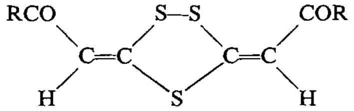


26

The n.m.r. spectrum (CDCl$_3$) of the lower-melting isomer (Table 1), showed in addition to signals attributable to the *p*-tolyl protons, two singlets at δ 7.48 and 7.68 that can be assigned to the vinyl protons. This isomer must therefore be the *trans* compound **27*a***, since this is the only one of the three isomers of type **24*a*–*c*** that has chemically non-equivalent vinyl protons. The two *p*-tolyl rings in **27*a*** also are non-equivalent; however the difference between their environments must be too small to lead to differentiation of their proton signals. The n.m.r. spectrum of the higher-melting isomer could not be taken in conventional solvents because of its insolubility. Its spectrum in 96% sulfuric acid showed in addition to *p*-tolyl proton signals a singlet at δ 7.75 attributable to the vinylic protons. This is in accord with the assignment to it of either a *cis*$_2$ or *cis*$_1$ structure, each of which has chemically equivalent vinyl protons.[6] No firm basis for choice between their two structures is available, but the *cis*$_2$ structure **27*b*** is provisionally assigned by analogy with **23**.



27*a* R = $p\text{-}CH_3C_6H_4$
28*a* R = C_6H_5



27*b* R = $p\text{-}CH_3C_6H_4$
28*b* R = C_6H_5

When the lower melting isomer was heated under nitrogen at 225° it was converted to the higher-melting isomer. The observation that thermal interconversion of one isomer to another can occur and that the higher-melting isomer is favored provides some evidence that this isomer has the *cis*$_2$ rather than the *cis*$_1$ structure. For it has been found that in this type of compound there is an attractive interaction between the oxy-

---

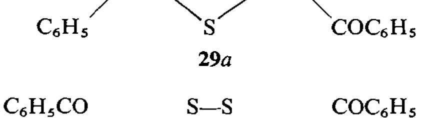
[5] In the general case the designations *cis*$_1$ and *cis*$_2$ are arbitrary. However for all the cases examined by us, X = RCO ≠ Y, and we define **24*b*** as *cis*$_2$ (RCO groups *cis* to two-sulfur bridge) and **24*c*** as *cis*$_1$ (RCO groups *cis* to one-sulfur bridge).

[6] The use of sulfuric acid as solvent leads to the possibility of isomerization in solution (*vide supra*); however, in this case there was no spectral evidence of such isomerization, and the higher-melting isomer was recovered unchanged on quenching the solution on ice.

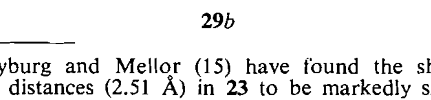
gen and sulfur atoms (1, 15),[7] and it may be anticipated that the cis_2 isomer will be more stable than the cis_1 isomer because the two oxygen atoms interact with a common sulfur atom in the latter case while in the former they interact with two different sulfur atoms.

The observation that two isomeric trithiolanes are formed from *p*-methylacetophenone led us to reexamine the case of acetophenone. As has been discussed previously, the major product, $C_{18}H_{12}O_2S_3$, has m.p. 236–238° (dec.). Work-up of the mother liquors from the crystallization of this compound led to the isolation of a more soluble, isomeric compound, m.p. 167.5–168.5°. The vinylic proton signals in the n.m.r. spectra of both isomers are embedded in the aromatic proton multiplets and do not serve to distinguish between the isomers in this case. A tentative assignment of stereostructures **28***a* and *b* to the lower- and higher-melting isomers is made on the basis of the m.p. and solubility relationships and analogy with **23**. The fact that the lower-melting isomer resolidified above its m.p. and melted again with decomposition at *ca.* 225° strongly indicates that thermal conversion of the lower- to the higher-melting isomers occurs in this case also.

A third instance of the formation of two stereoisomeric trithiolanes was observed in the case of deoxybenzoin. The major product, $C_{30}H_{20}O_2S_3$, m.p. 277–278° (dec.), was accompanied by a minor, isomeric, more soluble product, m.p. 219–220°. Since these products lack vinyl hydrogen atoms, the *trans* isomer cannot be recognized by n.m.r. spectroscopy. A tentative assignment of stereostructures **29***a* and *b* to the lower- and higher-melting isomers, respectively, is again made on the basis of the m.p. and solubility relationships and analogy with **23**.



29*a*



29*b*

From mesityl methyl ketone only a single trithiolane, $C_{24}H_{24}O_2S_3$, was obtained. Its n.m.r. spectrum (Table 1) showed a single low-field singlet attributable to superimposition of the signals due to both the vinylic and phenyl protons. Thus this is most probably a *cis* stereoisomer and it is provisionally assigned the stereostructure **30** by analogy.

We conclude this discussion of the reactions and structures of the 3,5-bismethylene-1,2,4-trithiolanes by noting that two reactions have been reported in which these compounds are converted to desaurins, *i.e.*, 2,4-bismethylene-1,3-dithietanes (**3**) (1). Wenzel (3) observed that saponification of the trithiolane **31** with sodium hydroxide in ethanol followed by acidification gave the desaurin **33**.[8] This transformation most probably involves the reductive cleavage of the disulfide linkage by the alcoholic base (*cf.* Scheme 1, **8** → **9**) to give **32** followed by closure to the desaurin with elimination of sulfide ion (Scheme 3).

More recently, Kirby (16) has converted the trithiolane **36** to the desaurin **37** by treatment with boiling triethyl phosphite. The trithiolane **36** was obtained by an analogous, novel method, *viz.*, reaction of triethyl phosphite with the tetrathiane **35** at room temperature (or by heating **35** in boiling toluene). The tetrathiane **35** (16, 17) was obtained by reaction of **34**, the adduct of biacetyl and trimethyl phosphite with carbon disulfide (Scheme 4).

Spectra of the 3,5-Bismethylene-1,2,4-trithiolanes[9]

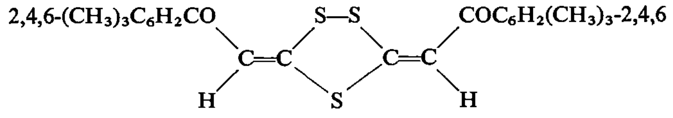
Aspects of the n.m.r. spectra of the trithiolanes have already been discussed in the discussion of stereochemistry. It remains here to comment that the expected relationship between the vinylic proton signals in the spectra of the alkyl ketone **23** and the aryl ketones **27***b* and **28***b* holds in that the former appears at δ 6.95, while the latter are shifted to lower field (δ 7.4–7.7). Further, the mesityl ketone **30** more closely resembles the alkyl ketone than the other aryl ketones in this respect, as anticipated to result from a considerable departure from coplanarity of the mesityl and α,β-unsaturated carbonyl systems (18). It is of interest to note that the vinylic proton signals of

---

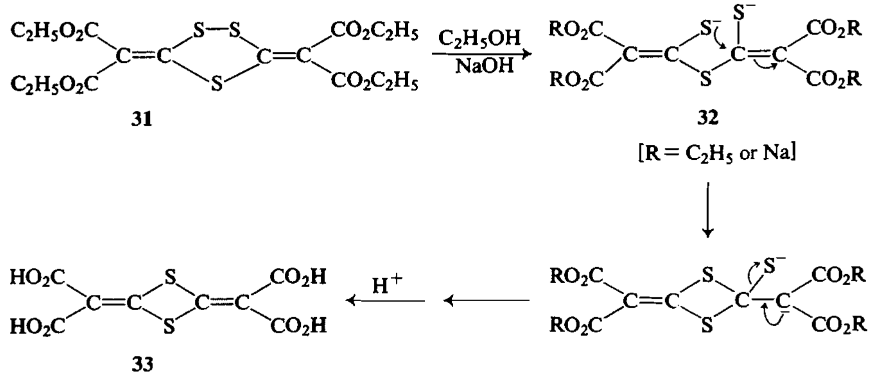
[7] Nyburg and Mellor (15) have found the shortest S—O distances (2.51 Å) in **23** to be markedly smaller than the sum of the van der Waals' radii of sulfur and oxygen (*cf.* ref. 1).

[8] The desaurin was originally considered to be a cyclobutane-1,2-dithione on the basis of the erroneous assignment of structure **2** to the trithiolane (3).

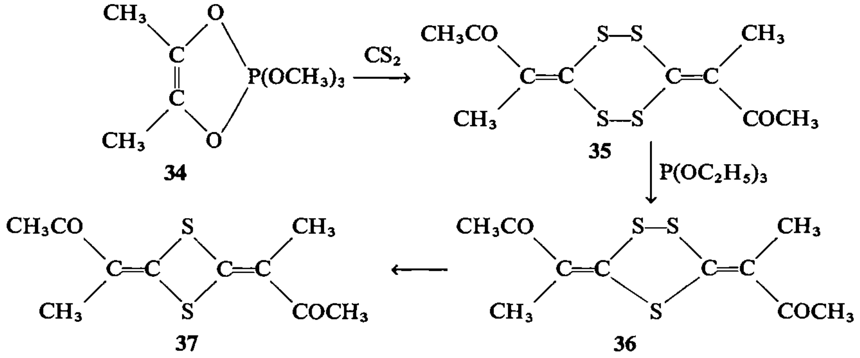
[9] For a discussion of the mass spectra of several 3,5-bismethylene-1,2,4-trithiolanes see ref. 6.



30

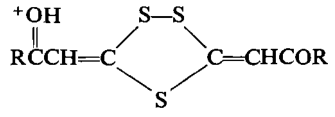


SCHEME 3

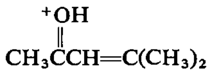


SCHEME 4

27*b* and **28***b* in sulfuric acid are only at slightly lower field than those of **27***a* and **28***a* in deuteriochloroform. Presumably, the species present in the sulfuric acid solutions are cations of type **38** (or the corresponding dications). Protonation of simple α, β-unsaturated ketones normally causes a shift of 0.6–1.0 p.p.m. to lower field of the α-vinylic proton signal (19, 20), *e.g.* protonated mesityl oxide (**39**) shows this signal at δ 6.96 (19) (Δδ = 1.0). The n.m.r. data in the present case indicate that the positive charge is more extensively delocalized, thus reducing the effect on the vinylic proton.



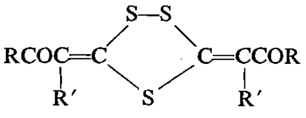
38



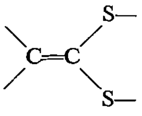
$CH_3\overset{+OH}{\overset{\|}{C}}CH{=}C(CH_3)_2$

39

Bands in the 5–6 μ region of the i.r. spectra of the trithiolanes are listed in Table 2. These bands resemble those in this region in the spectra of the desaurins (1) in that the carbonyl-stretching bands are at unusually long wavelength and often appear to be unusually weak. The trithiolanes **23** and **36** of type **40** (R′ = H or alkyl) have their carbonyl-stretching band at 6.18–6.19 μ.[10] This represents a significant shift to longer wavelength relative to the corresponding desaurins. It is possible that this shift is related to the fact that the S—O distance in the trithiolane **23** has been found to be shorter than that in one of the desaurins (15). In more general terms, the geometry of the trithiolanes may be more favorable for delocalization of the unshared electrons on sulfur than that of the dithietanes. It is noteworthy that the carbonyl-stretching band of **19**, in which the vinylic hydrogen atoms of **23** are replaced by chlorine atoms, is shifted to 6.25 μ. In the case of cyclic enones substitution of chlorine for α-vinyl hydrogen usually causes a shift of the carbonyl-stretching band to lower wavelength (21). The present result can be interpreted as due to the existence of **19** in an *s-cis* conformation; the dipoles of the carbon–halogen bonds would then facilitate the stretching of the carbonyl bonds, in contrast to their effect in the *s-trans* cyclic enones.



40 R = alkyl
41 R = aryl



42

As in the case of the desaurins, the carbonyl-stretching bands of compounds of type **27** and **28** with an aryl group in conjugation with the carbonyl group (**41**) are moved to longer wavelength. Again they occur at longer wavelength than in the case of the corresponding desaurins. Their range cannot readily be defined because of overlap with aromatic stretching vibrations; the lower wavelength limit, however, is 6.21 μ. Compound **30**, the mesityl derivative falls at this lower limit as expected, due to departure from coplanarity of the aryl rings and the carbonyl groups (18). Another feature of the trithiolane spectra that resembles those of the desaurins is the occurrence of strong or very strong bands in the region 6.8–7.2 μ.[11] These are probably similar in origin to strong bands observed in the 6.5–7.0 μ region of the spectra of the desaurins and related two-sulfur compounds (1, 22). These have been assigned by Jensen and Henriksen (22) to the ν_1 vibration of the grouping **42**. As previously noted (1), this assignment must be considered as provisional because strong bands due to aromatic C—C stretching and aliphatic C—H bending vibrations can also occur in this region.

Examination of the i.r. spectra of the trithiolanes suggests that the carbonyl-stretching bands have unusually weak intensities relative to other bands in the spectra, as in the case of the desaurins (1). Measurement of the integrated absorption intensity for **27*a*** in chloroform solution gave a value of 4.17, *i.e.*, 2.09 per carbonyl group, and for **27*b*** in a potassium bromide disc a value of 2.24, *i.e.*, 1.12 per carbonyl group.[12] These values are comparable with those for benzophenone in chloroform and in a potassium bromide disc, *i.e.*, 2.35 and 1.20, respectively. The apparent abnormal weakness of the carbonyl-stretching bands observed on qualitative examination of the spectra is presumably due to the presence of unusually strong bands in other regions of the spectra and the fact that most of the spectra were recorded in the solid state.[13] In the case of planar chromophores, conjugation with an ethylenic double bond or aromatic ring brings about an increase in the carbonyl-stretching band intensity (23, 25). While the positions of the carbonyl-stretching bands of **27*a*** and ***b*** show a considerably higher degree of conjugation than that in benzophenone, their integrated intensities per carbonyl group are slightly lower than the intensity of the carbonyl-stretching band of benzophenone. Thus, there does in fact appear to be a significant reduction in intensity relative to simple conjugated ketones when carbonyl groups are conjugated with the grouping **42**. As for the desaurins (1), this may be due to an interaction through space between the sulfur and oxygen atoms (15) in these compounds.

The u.v. maxima of the trithiolanes are listed in Table 3. The spectra of compounds **19**, **23**, and **36**

---

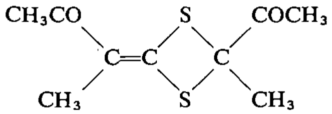
[10] The actual range may extend to slightly longer wavelength, since the shoulder at 6.26 μ in the spectrum of **23** suggests that the carbonyl-stretching band in this case may be split (*cf.* ref. 1).

[11] Although most of the spectra were recorded in Nujol mulls, it is clear that strong absorption due to the sample is superimposed on the Nujol absorption in this region.

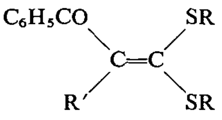
[12] See ref. 1 for details of these integrated intensity measurements; the values are given in absorbance units (23), *i.e.*, 1×10^4 mol^{-1} l cm^{-2}.

[13] It has previously been found that absorptivities are less in the solid state than in solution (24).

of type **40** (R′ = H, CH_3, or Cl) have a high intensity long wavelength maximum at 339–352 mμ (ε 19 500 – 19 800) and another maximum at 232–241 mμ (ε 15 100 – 17 800). These may be compared with the spectra of analogous desaurins which have maxima at 350–370 mμ (ε 28 700 – 29 500) and *ca.* 242 mμ (ε 1440–2510) (1, 16), and of the related compound **43**, which has maxima at 317 (ε 8950) and 243 mμ (ε 5360) (16, 26). The relationship among these spectra is consistent with transmission of delocalization through one or more of the sulfur atoms in the trithiolanes, but to a lesser extent than in the desaurins (13, 16). This reduction most probably reflects reduced transmission through the disulfide linkage relative to that through the single sulfide linkage. The relationship among the spectra of **19**, **23**, and **36** is in accord with expectation in that substitution of alkyl groups or chlorine atoms for vinylic hydrogen atoms leads to a bathochromic shift of the long wavelength maximum.



43



44 R = CH_3 or $(CH_2)_n$

The stereoisomers of the trithiolanes **27**, **28**, and **29** of type **41** show maxima in their u.v. spectra at 378–395 mμ (ε 29 500 – 35 500) and 265–282 mμ (ε 21 400 – 27 500). The bathochromic and hyperchromic shifts of the long wavelength maxima relative to those of the trithiolanes of type **40** clearly reflect the additional conjugation of the carbonyl groups with the phenyl groups. Again, the spectra give evidence of transmission of delocalization through one or more of the sulfur atoms [*cf.* the spectra of the related compounds of type **44**: λ_{max} 344–350 mμ (ε 15 800 – 22 900) and 257–263 mμ (ε 7940 – 14 500) (1)], but indicate that this is less than in the case of the related desaurins [λ_{max} 392–419 mμ (ε 38 100 – 49 000) and 266–274 mμ (ε 17 000 – 22 900) (1)]. The relationship among the spectra of the stereoisomers of **27**, **28**, and **29** is analogous to that in the case of the related desaurins in that substitution of phenyl groups for vinylic hydrogen atoms leads to a bathochromic shift of the long wavelength maximum. The relationship between the spectra of each pair of stereoisomers indicates that the *cis* isomers have long wavelength maxima at somewhat longer wavelengths than the corresponding *trans* isomers; the relationship is clouded, however, by the fact that the long wavelength maxima can show shoulders at either shorter or longer wavelength.

The trithiolane **37** of type **41**, but with R = mesityl, has a u.v. spectrum that more closely resembles the spectra of the trithiolanes of type **40** than the spectra of the other trithiolanes of type **41**. This difference is readily attributable to the usual marked departure from coplanarity of the aryl ring and the carbonyl group in mesitoyl derivatives (18).

Experimental

Melting points were taken on a Fisher-Johns micro hot stage and are corrected. Solutions in organic solvents were dried over anhydrous sodium sulfate. The n.m.r., i.r., and u.v. spectroscopic data for the trithiolanes are listed in Tables 1–3 in the text.

Preparation of the Trithiolane 23 (≡ 8) from Pinacolone

Pinacolone (5.00 g, 50.0 mmol) was added dropwise to a stirred suspension of sodamide (1.95 g, 50.0 mmol) in anhydrous ether (40 ml) cooled in ice. When anion formation was complete, carbon disulfide (1.50 ml, 25.0 mmol) was added slowly. The bright yellow precipitate that formed was dissolved by the addition of methanol (5 ml). Ammonium peroxydisulfate (5.70 g, 25 mmol) in water was then added slowly, and, when the addition was complete, the solution was stirred for a further 0.5 h and filtered. The solid was dissolved in chloroform, the solution was filtered and dried, and the solvent was removed to give **8** (**23**) as a pale yellow solid (1.34 g, 34%), m.p. 202–204°. Five crystallizations from chloroform–hexane gave fine, very pale yellow needles, m.p. 211.5–212.5°.

Anal. Calcd. for $C_{14}H_{20}O_2S_3$: C, 53.12; H, 6.37; S, 30.39. Found: C, 53.23; H, 6.22; S, 30.24.

Reduction of 8 with Zinc and Acetic Acid

A mixture of **8** (6.80 g, 21.5 mmol), zinc dust (21.3 g, 325 mg-atoms), and glacial acetic acid was boiled under reflux with stirring for 5 h. After cooling, the reaction mixture was diluted with ether and filtered, and the filtrate was washed with water until free of acetic acid. The ethereal solution was dried, and the solvent was removed by careful distillation until only a few milliliters remained. The residual solvent and the volatile product were removed by distillation at 80° (10 mm) into a series of Dry Ice traps. Distillation of the material in the traps gave ethyl *t*-butyl ketone (**5**; 1.78 g, 36%), b.p. 120–125°, identified by its i.r. and n.m.r. spectra, and the formation of a 2,4-dinitrophenylhydrazone, m.p. 144.5–146° [lit. (27) m.p. 143.5–144.5°].

The non-volatile material (2.2 g) was chromatographed on silica gel. Elution with 2% benzene-pentane gave **6** as a white crystalline solid (0.10 g), m.p. 161.5–162°, after two sublimations at 100° (15 mm); λ_{max}(CCl_4) 6.15 (w), 6.7 (w), 6.85 (m), 7.18 (w), 7.32 μ(w); λ_{max}(C_2H_5OH) 269 (ε 17 400), 280 mμ (ε 12 600); δ (CCl_4) 1.40(s, 9H), 6.82(s, 1H); *m/e* = 252 (mol. ion; 33.5%), 237 (100%), 222 (16.3%), 207 (9%).

Anal. Calcd. for $C_{14}H_{20}S_2$: C, 66.61; H, 7.99; S, 25.41. Found: C, 66.47; H, 7.94; S, 25.24.

The third reduction product, **7**, was obtained as an oil (2.0 g) by elution of the column with 2–5% ether–benzene. Purification was effected by further chromatography followed by molecular distillation at 70° (0.2 mm); λ_{max}(CCl_4) 5.84 (s), 6.76 (m), 7.18 (w), 7.31 μ(m); δ (CCl_4) 1.14 (s, 18H), 2.67 (s, 8H); δ (C_6H_6) 0.93 (s), 2.62 (m).

A bis-2,4-dinitrophenylhydrazone was prepared by the method of Shriner *et al.* (28) and purified by five crystallizations from ethanol – ethyl acetate; m.p. 196–197.5°.

Anal. Calcd. for $C_{26}H_{34}N_8O_8S$: C, 50.47; H, 5.54; N, 18.11; S, 5.18. Found: C, 50.62; H, 5.52; N, 17.86; S, 5.35.

Desulfurization of 7 with Raney Nickel

A mixture of **7** (0.19 g, 0.720 mmol) and W-2 Raney nickel (*ca.* 2 g) in ethanol (15 ml) was boiled under reflux for 3.25 h under a slow stream of nitrogen. Nitrogen was bubbled through the solution for a short time after it had cooled to remove any acetaldehyde present. The solution was filtered, and the filtrate was treated with an excess of 2,4-dinitrophenylhydrazine reagent (28). After standing overnight, the mixture was filtered to give the 2,4-dinitrophenylhydrazone of ethyl *t*-butyl ketone (0.082 g, 20%), m.p. 136–138°. One crystallization from 95% ethanol gave crystals, m.p. 142–143°, undepressed upon admixture with an authentic sample, m.p. 144.5–146°.

Reaction of 8 with Phosphorus Pentasulfide. Formation of 14

A mixture of **8** (0.54 g, 1.70 mmol) and phosphorus pentasulfide (1.00 g, 2.30 mmol) in *p*-xylene (40 ml) was boiled under reflux for 2 h. When cool, the dark solution was washed successively with aqueous 10% potassium hydroxide, aqueous 10% hydrochloric acid, and water and dried. The solvent was removed and the crude product was crystallized from hexane to give **14** as yellow needles (0.37 g, 56%), m.p. 69.0–69.5, after three crystallizations from methanol; λ_{max}($CHCl_3$) 6.84 (m), 7.31 μ(s); λ_{max}(C_2H_5OH) 230 (ε 9600), 246 (ε 5900), 268 (ε 6900), 317 mμ (ε 4400), 408 mμ (11 000); δ ($CDCl_3$) 1.43 (s, 9H), 7.18 (s, 1H).

Anal. Calcd. for $C_7H_{10}S_3$: C, 44.17; H, 5.30; S, 50.54. Found: C, 44.21; H, 5.30; S, 50.46.

Reaction of 8 with Phosphorus Pentachloride. Formation of 19

Compound **8** (0.100 g, 0.316 mmol) was mixed with phosphorus pentachloride (0.150 g, 0.680 mmol) and the mixture was heated at 140–145° under nitrogen for 50 min. Water and chloroform were added to the dark yellow product after it had cooled, and the organic layer was washed several times with water and dried. Removal of the solvent and crystallization of the residue from acetone gave **19** as pale yellow needles (0.040 g, 35%), m.p. 222.5–223.5° after three further crystallizations from acetone.

Anal. Calcd. for $C_{14}H_{18}Cl_2O_2S_3$: C, 43.63; H, 4.71; Cl, 18.40; S, 24.96. Found: C, 43.78; H, 4.75; Cl, 18.50; S, 24.56.

Preparation of the Trithiolanes 27a and b from p-Methylacetophenone

p-Methylacetophenone (6.70 g, 50.0 mmol) in anhydrous ether (10 ml) was converted to a mixture of **27*a*** and ***b*** by the method used for the preparation of **23**. The resulting yellow solid (3.87 g, 80%) was washed with water and methanol, air-dried, and heated briefly in chloroform. The insoluble material was filtered off, and the filtrate was retained. The chloroform-insoluble material was recrystallized five times from toluene to give **27*b***, m.p. 251–252°.

Anal. Calcd. for $C_{20}H_{16}O_2S_3$: C, 62.47; H, 4.19; S, 25.02. Found: C, 62.55; H, 4.49; S, 24.81.

Evaporation of the chloroform filtrates to dryness gave a yellow solid, which was crystallized from benzene to give yellow crystalline clumps, m.p. 210–212° (0.60 g, 13%). Four recrystallizations from benzene gave **27*a***, m.p. 213.5–214.5°.

Anal. Calcd. for $C_{20}H_{16}O_2S_3$: C, 62.47; H, 4.19; S, 25.02. Found: C, 62.73; H, 4.20; S, 24.90.

Compound **27*a*** (0.027 g) was heated at 225° for 3 min. After cooling, the reddish solid was crystallized twice from toluene to give yellow needles (0.018 g, 66%), m.p. 249–251°, undepressed on admixture with **27*b***.

Reduction of 27b. Formation of 25

Compound **27*b*** (3.14 g, 8.10 mmol) and zinc dust (18.5 g) were suspended in glacial acetic acid (50 ml), and the mixture was boiled under reflux with stirring for 6 h. When the mixture had cooled, ether was added, and the acetic acid was removed by washing with water. Removal of the solvent gave a yellow oil (1.94 g) which was chromatographed on silica gel. Fractions eluted with ether–benzene mixtures were combined and evaporated. The product was treated with excess lithium aluminum hydride in anhydrous ether, and the oil obtained was chromatographed on silica gel. Elution with ether–benzene gave 1-*p*-tolyl-1-propanol (**25**) as an oil (0.52 g, 21%): λ_{max}(CCl_4) 2.74 μ(m); δ (CCl_4) 0.82 (t, *J* = 7 Hz, 3H), 1.55 (m, 2H), 2.26 (s, 3H), 4.35 (t, 1H), 7.01 (s, 4H). The identity of this compound was confirmed by comparison of its spectra with those of an authentic sample prepared by reduction of *p*-methylpropiophenone with lithium aluminum hydride.

Reaction of 27b with Phosphorus Pentasulfide. Formation of 26

A mixture of **27*b*** (1.00 g, 2.60 mmol) and phosphorus pentasulfide (2.00 g, 4.60 mmol) in xylene was boiled under reflux for 2 h. When cool, the xylene solution was washed successively with aqueous 10% potassium hydroxide, 10% hydrochloric acid, and water and dried. The solvent was removed to give a reddish residue which was chromatographed on neutral alumina (Woelm). Elution with benzene gave yellow–red oils, which crystallized spontaneously. These were combined and the product was recrystallized from benzene to give yellow crystals (0.757 g, 65%). Five further crystallizations gave **26**, m.p. 119–120°; λ_{max}($CHCl_3$) 6.22 (m), 6.73 (s), 7.10 μ(w); λ_{max}(C_2H_5OH) 230 (ε 12 600), 271 (ε 8300), 327 (ε 21 400), 433 mμ (ε 10 700); δ ($CDCl_3$) 2.40 (s, 3H), 7.42 (s, 1H), 7.23 and 7.55 (dd, J = 8.5 Hz, 4H).

Anal. Calcd. for $C_{10}H_8S_3$: C, 53.53; H, 3.59; S, 42.88. Found: C, 53.49; H, 3.56; S, 42.84.

*Preparation of the Trithiolanes **28a** and **b** from Acetophenone*

The method of Gompper and Töpfl (5) was followed, giving the crude product in 65% yield. The material was purified by recrystallization from toluene to give **28*b*** as fine yellow needles, m.p. 236–238° (dec.). The same material was also obtained by recrystallization of a yellow, insoluble, material obtained during the purification of benzoyldithioacetic acid. A mixed m.p. with the material obtained by Gompper and Töpfl's method showed no depression.

Anal. Calcd. for $C_{18}H_{12}O_2S_3$: C, 60.64; H, 3.39; S, 26.99. Found: C, 60.53; H, 3.44; S, 26.77.

The mother liquors from the first method of preparation were stripped of solvent, and the residue was crystallized several times from benzene–hexane to give **28*a***, m.p. 167.5–168.5°.

Anal. Calcd. for $C_{18}H_{12}O_2S_3$: C, 60.64; H, 3.39; S, 26.99. Found: C, 60.71; H, 3.52; S, 26.58.

*Preparation of the Trithiolanes **29a** and **b** from Deoxybenzoin*

Deoxybenzoin (2.00 g, 10.0 mmol) in anhydrous ether (10 ml) was converted to a mixture of **29*a*** and ***b*** by the method used for the preparation of **23**. The resulting yellow precipitate (0.49 g, 38%) was washed with water, air dried, and heated briefly in chloroform. The solution was filtered, and the filtrate was retained. The chloroform-insoluble material (0.40 g, 31%) was crystallized three times from toluene to give **29*b***, m.p. 277–278° (dec.).

Anal. Calcd. for $C_{30}H_{20}O_2S_3$: C, 70.83; H, 3.96; S, 18.91. Found: C, 70.85; H, 3.98; S, 18.60.

Evaporation of the chloroform filtrates gave **29*a***, m.p. *ca.* 213° (0.085 g, 7%). After several recrystallizations from benzene–hexane, this had m.p. 219–220°, with subsequent solidification and remelting at *ca.* 245° (dec.).

Anal. Calcd. for $C_{30}H_{20}O_2S_3$: C, 70.83; H, 3.96; S, 18.91. Found: C, 70.90; H, 4.29; S, 18.85.

*Preparation of the Trithiolane **30** from Mesityl Methyl Ketone*

Mesityl methyl ketone (2.0 g, 12.5 mmol) in anhydrous ether (15 ml) was converted to **30** by the method used for the preparation of **23**. Benzene was added to the reaction mixture, and the organic layer was washed several times with water and dried. The solvent was removed, and the crude product was crystallized from chloroform–hexane to give **30** as small plates (0.38 g, 29%), which after five further crystallizations from chloroform–hexane had m.p. 208.5–210°.

Anal. Calcd. for $C_{24}H_{24}O_2S_3$: C, 65.42; H, 5.49; S, 21.83. Found: C, 65.35; H, 5.52; S, 21.45.

We thank the National Research Council of Canada for generous support of this work and for fellowship support (T.R.L.).

1. (*a*) P. Yates, T. R. Lynch, and D. R. Moore. Can. J. Chem. This issue. (*b*) P. Yates, D. R. Moore, and T. R. Lynch. Can. J. Chem. This issue.
2. G. Wenzel. Ber. **33**, 2041 (1900).
3. G. Wenzel. Ber. **34**, 1043 (1901).
4. C. Kelber. Ber. **43**, 1252 (1910).
5. R. Gompper and W. Töpfl. Chem. Ber. **95**, 2861 (1962).
6. P. Yates, T. R. Lynch, and L. S. Weiler. Can. J. Chem. **46**, 365 (1968).
7. Ultraviolet spectral data. American Petroleum Research Institute No. 44. Serial No. 731.
8. O. Dann and W. Dimmling. Chem. Ber. **87**, 373 (1954).
9. J. Godart. J. Chim. Phys. **34**, 70 (1937).
10. S. Gronowitz. Private communication.
11. A. Thuillier and J. Vialle. Bull. Soc. Chim. Fr. 2187 (1962).
12. R. S. Spindt, D. R. Stevens, and W. E. Baldwin. J. Amer. Chem. Soc. **73**, 3693 (1951).
13. A. W. K. Chan, W. D. Crow, and I. Gosney. Tetrahedron, **26**, 1493 (1970).
14. *Cf.* R. L. Kuczkowski and E. B. Wilson, Jr. J. Amer. Chem. Soc. **85**, 2028 (1963). Q. E. Thompson, M. M. Crutchfield, and M. W. Dietrich. J. Amer. Chem. Soc. **86**, 3891 (1964).
15. S. C. Nyburg. Private communication. I. P. Mellor. Ph.D. Thesis. University of Keele, Keele, England. 1968.
16. A. J. Kirby. Tetrahedron, **22**, 3001 (1966).
17. N. W. Alcock and A. J. Kirby. Tetrahedron, **22**, 3007 (1966).
18. L. L. Ingraham. *In* Steric effects in organic chemistry. *Edited by* M. S. Newman. John Wiley and Sons, Inc., New York, N.Y., 1956. Chapt. 11.
19. N. C. Deno, H. G. Richey, Jr., N. Friedman, J. D. Hodge, J. J. Houser, and C. U. Pittman, Jr. J. Amer. Chem. Soc. **85**, 2991 (1963).
20. P. Yates and P. M. Burke. Unpublished results. P. M. Burke. Ph.D. Thesis. University of Toronto, Toronto, Ontario, 1966.
21. H. N. A. Al-Jallo and E. S. Waight. J. Chem. Soc. B, 73 (1966).
22. K. A. Jensen and L. Henriksen. Acta Chem. Scand. **22**, 1107 (1968).
23. R. N. Jones, D. A. Ramsay, D. S. Keir, and K. Dobriner. J. Amer. Chem. Soc. **74**, 80 (1952).
24. N. E. Sharpless and D. A. Gregory. Appl. Spectrosc. **17**, 47 (1963).
25. G. M. Barrow. J. Chem. Phys. **21**, 2008 (1953).
26. J. A. Kapecki, J. E. Baldwin, and I. C. Paul. Tetrahedron Lett. 5307 (1967); J. Amer. Chem. Soc. **90**, 5800 (1968).
27. F. A. Whitmore, C. I. Noll, and V. C. Meunier. J. Amer. Chem. Soc. **61**, 683 (1939).
28. R. L. Shriner, R. C. Fuson, and D. Y. Curtin. The systematic identification of organic compounds. 5th ed. John Wiley and Sons, Inc., New York, N.Y., 1964. p. 253.