Carbon Disulfide. II. Reaction with Active Methylene Compounds. The Structures of the Desaurins[1,2]

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The desaurins, high-melting, neutral compounds formed by the reaction of active methylene compounds with base and carbon disulfide, have been shown to be derivatives of 2,4-bismethylene-1,3-dithietane.

On a montré que les désaurines, des composés neutres, à points de fusion élevés provenant de la réaction du sulfure de carbone avec de la base et des composés contenant des méthylènes actifs, sont des dérivés du bisméthylène-2,4-dithiétane-1,3.

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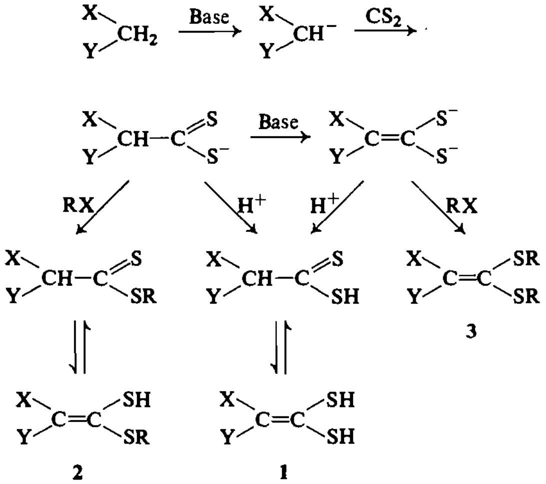
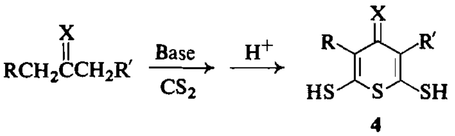
Introduction

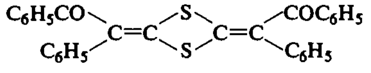
The reactions of active methylene compounds with carbon disulfide in the presence of bases have been observed to give both acidic and neutral products. The former have been shown to be dithio acids of type **1**; these acids have often been isolated as their more stable alkyl derivatives **2** and **3** (Scheme 1) (3–9). If an activating group is flanked on both sides by methylene groups, acidic products of type **4** (and/or tautomers) can also be formed (eq. 1) (*6b*, 10).



Scheme 1

[1] 

The first report of the formation of a neutral compound by the reaction of an active methylene compound with carbon disulfide in the presence of a base is that of Norton and Oppenheim (11), who obtained a yellow product from the reaction of ethyl acetoacetate with carbon disulfide and zinc or lead oxide. Subsequently, Meyer and Wege (12) obtained a related compound by the reaction of deoxybenzoin with four equivalents of potassium hydroxide in carbon disulfide. The product was a high-melting, golden-yellow crystalline solid, that was identical with a compound formed on treatment of the sodio derivative of deoxybenzoin with thiophosgene (13). Meyer (14) showed that this compound has the molecular formula $C_{30}H_{20}O_2S_2$ and suggested that it has structure **5**.[4] He dubbed this class of compounds desaurins on account of their color [*des*oxybenzoin + *aur*um (L., gold)].



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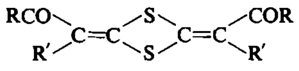

6

Analogs of **5** were subsequently prepared by treatment of compounds of type $ArCOCH_2Ar'$ and $ArCOCH_2CH_3$ with carbon disulfide and base (15, 16). Desaurins were also obtained by

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[1] For Paper I see ref. 1.

[2] A preliminary report on part of this work has appeared (2).

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

pyrolysis of the dibenzoyl derivatives or heavy metal salts of dithio acids of type **1** (16); pyrolysis of the acids themselves gave the desaurins, but in very poor yields. Recently, Gompper and Töpfl (7*a*) have obtained desaurins directly from compounds of type **1** by treatment with acylating agents or with oxidizing agents (bromine, iodine, or ammonium persulfate). However, the latter agents give rise to products containing three sulfur atoms in some cases (7*a*, 17). These reactions are related to the earlier observations by Wenzel (18) of the formation of desaurins and three-sulfur compounds on treatment of active methylene compounds with bromine in carbon disulfide.

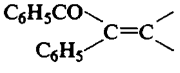
The structural type **6** originally proposed by Meyer (14) for the desaurins has found general acceptance by most other workers [*cf.*, however, Wenzel (18*b*)]. However, the assignment of **6** rested almost solely on the elemental composition and molecular weights of the compounds. The only degradative studies, those of Wachter (19) on the desaurin from deoxybenzoin, were performed under vigorous conditions and provided little structural information. The present work was undertaken to establish the structures of the desaurins and to investigate further the chemistry of this interesting group of compounds.

Reactions and Structures of the Desaurins

The desaurin from deoxybenzoin was prepared by the procedure of Meyer and Wege (12), and the molecular formula, $C_{30}H_{20}O_2S_2$, previously assigned to it was confirmed by elemental analysis and mass spectrometry (1). Its i.r. and u.v. spectra [λ_{max}(KBr) 6.17μ; λ_{max}($CHCl_3$) 266 (ε 22 900) and 419 mμ (ε 38 100)] showed the presence of one or more highly conjugated carbonyl groups.[5] It was found to be highly resistant to acid hydrolysis; after treatment with a boiling solution of concentrated hydrochloric acid in dioxane for 50 h, 96% of the desaurin was recovered.

Oxidation with chromic acid in acetic acid gave >3 molar equivalents of benzoic acid, demonstrating that no ring closure on the phenyl rings occurs in the formation of the desaurin. Oxidation of the desaurin with potassium permanganate in boiling acetone or ozonolysis in dichloromethane at 0° gave benzil and benzoic acid. The formation of these products is in accord with the presence of the structural feature **7** in **5** (21).

Reaction of the desaurin with zinc in boiling acetic acid for 50 h gave 2-phenylpropiophenone (**8**), *erythro*-1,2-diphenyl-1-propyl acetate (**9**) (22), and *trans*-1,2-diphenylpropene (**10**) (23). The formation of these products is again in accord with the presence of one or more groupings of type **7** in the desaurin molecule. Moreover, the desaurin was found to be stable to the action of zinc and acetic acid at room temperature, which makes it most unlikely that thione groups or disulfide linkages are present.



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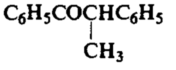
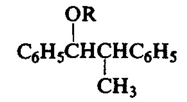


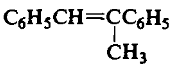
$C_6H_5CO\underset{CH_3}{\underset{|}{C}H}C_6H_5$

8



$C_6H_5\overset{OR}{\overset{|}{C}H}\underset{CH_3}{\underset{|}{C}H}C_6H_5$

9 R = $COCH_3$
11 R = H



$C_6H_5CH{=}\underset{CH_3}{\underset{|}{C}}C_6H_5$

10

Treatment of the desaurin with Raney nickel in boiling dioxane also gave **8** together with *erythro*-1,2-diphenyl-1-propanol (**11**) (23). The same products were obtained when old sponge nickel catalyst was used; however, when fresh sponge nickel catalyst was used, a different product was obtained. This was a colorless crystalline compound, $C_{30}H_{22}O_2$, with a strong band at 5.91 μ in its i.r. spectrum and medium or weak bands at 6.25, 6.33, and 6.45 μ; its u.v. spectrum showed maxima at 249 (ε 31 600) and 291 mμ (ε 17 400), and its p.m.r. spectrum showed signals at δ 6.05 (s, 1H), 6.26 (s, 1H), 7.1–7.5 (m, 18H), 7.9–8.1 (m, 2H). It formed an orange 2,4-dinitrophenylhydrazone. These data suggested the presence of a benzoyl group attached to an sp^3 carbon atom, and a furan ring (24). The desulfurization product was cleaved by ethanolic potassium hydroxide to give benzoic acid and an oily product, $C_{23}H_{18}O$. This did not show a strong band in the carbonyl-stretching region of its i.r. spectrum, but retained a medium band at 6.45 μ, attributable to a furan ring. The cleavage product was oxidized by potassium permanganate to a ketone, $C_{23}H_{16}O_2$, that was characterized as its 2,4-dinitrophenylhydrazone. The spectra of the ketone [6.08 μ; 263 (ε 18 600) and 344 mμ (ε 19 100)] indicated that it was highly conjugated, a feature that was confirmed by the position of the long wavelength maximum in the u.v. spectrum of its 2,4-dinitrophenylhydrazone [418 mμ (ε 26 900)]. More vigorous oxidation with potassium permanganate

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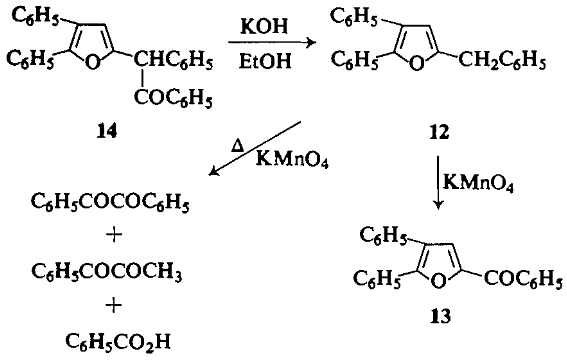
[5] The i.r. and u.v. spectra of the desaurins are discussed in detail in Paper III of this series (20).

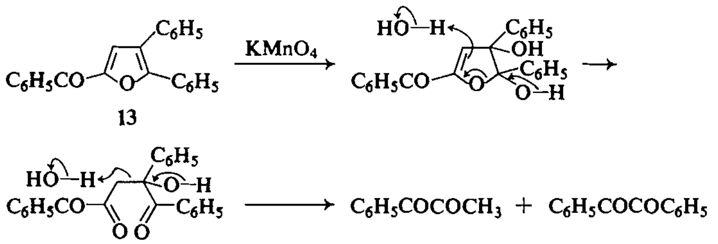


SCHEME 2

gave benzoic acid, benzil, and 1-phenyl-1,2-propanedione. These data establish the structure of the cleavage product as **12**; the ketone formed on mild oxidation is formulable as **13** (see Scheme 2). The desulfurization product itself can then be formulated as **14**, its cleavage to **12** finding close analogy in the cleavage of 2,2-diphenylacetophenone by ethanolic potassium hydroxide to diphenylmethane and benzoic acid (25). The products formed on vigorous oxidation of **12** can be interpreted as arising via hydroxylation of **13** (Scheme 3).

The formation of **14** from the desaurin can be rationalized in terms of structure **5** by a route of the type shown in Scheme 4. The formation of a new carbon–carbon bond during desulfurization reactions with nickel has been observed in other cases (26), and the proximity of the carbon atoms involved in **5** could undoubtedly represent a favorable factor for the occurrence of such a reaction in the present case.

The chemical reactions of the desaurin from deoxybenzoin discussed thus far can all be interpreted in terms of structure **5**; the only alternative structure that could possibly provide a basis for their interpretation and might be in accord with the spectroscopic data is **15**. This differs from **5** in possessing one rather than two carbonyl groups, and means were therefore sought to establish the number of carbonyl groups present in the desaurin. This could not be done by the preparation of simple derivatives, because of the very low solubility of the desaurin in organic solvents. Advantage was therefore taken of its solubility in concentrated sulfuric acid to subject it to a Schmidt reaction in this medium by the addition of sodium azide. Two isomeric yellow products, $C_{30}H_{21}O_2S_2N$, were obtained, whose i.r. spectra were very similar. These spectra showed weak bands at 2.96–2.97 μ, and bands in the carbonyl-stretching region at 6.02–6.03 and 6.14 μ, and are in good accord with the assignment to the products of structures of type **16** or **17**. The u.v. spectra of the products confirmed the retention of the desaurin nucleus in these products (20). The very close similarity of their spectra suggested that they are *cis*- and *trans*-stereoisomers of either **16** or **17**, rather than structural



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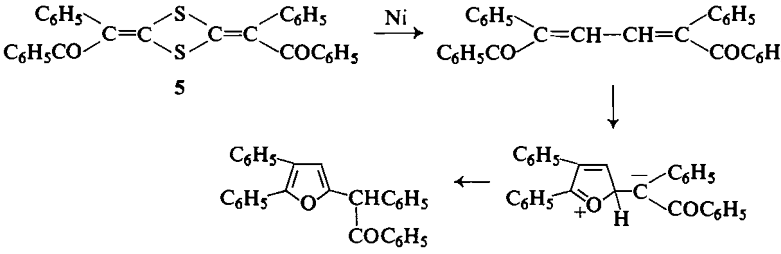
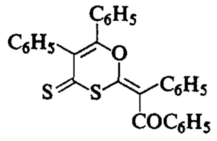


SCHEME 4



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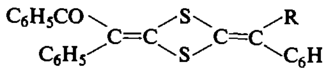


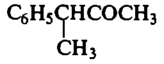
16 R = $CONHC_6H_5$
17 R = $NHCOC_6H_5$

isomers. Structure **16** can be assigned on the basis of the mass spectrum of one of the isomers, which shows, in addition to the molecular ion peak at *m/e* 491 (42%), a peak at *m/e* 399 (47%) corresponding to the ion $(M\text{-}C_6H_5NH)^+$. The formation of these amides that possess a second carbonyl group that gives rise to a carbonyl-stretching band in a similar position to that of the desaurin itself can readily be interpreted in terms of structure **5**, but not of structure **15**.

Because of the importance of establishing the presence of two ketonic carbonyl groups in the desaurins, and the possible ambiguity associated with the use of the Schmidt reaction for this purpose, *i.e.*, the possibility of cleavage or additional rearrangement reactions in the strongly acid medium, it was considered desirable to search for a more soluble desaurin, which would undergo derivative formation under mild reaction conditions. Apitzsch (10*a*) has previously reported the formation of an acidic product of type **4** from the reaction of phenylacetone with carbon disulfide and base; we have found that when the reaction is carried out under the conditions used for the preparation of the desaurin from deoxybenzoin, a lemon yellow neutral compound, $C_{20}H_{16}O_2S_2$, is formed whose spectra showed it to be a desaurin (20); it was considerably more soluble in organic solvents than the desaurin from deoxybenzoin.

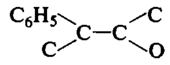
Reduction with zinc and sodium hydroxide gave 1.44 molar equivalents of 3-phenyl-2-butanone (**18**), establishing the presence of *two* C_{10} moieties with structure **19**.

Treatment with 2,4-dinitrophenylhydrazine in ethanolic sulfuric acid gave a mono-2,4-dinitrophenylhydrazone that retained a carbonyl-stretching band in its i.r. spectrum, while treatment with this reagent in aqueous dioxane containing hydrochloric acid gave a bis-2,4-dinitrophenylhydrazone that showed no carbonyl-stretching band in its i.r. spectrum. Further, this desaurin could be converted to a dioxime, $C_{20}H_{18}N_2O_2S_2$, from which the desaurin could be regenerated by acid-catalyzed hydrolysis in the presence of formaldehyde, demonstrating that no skeletal change had occurred in its conversion to the derivative. These data show that the desaurio contains *two* carbonyl groups.

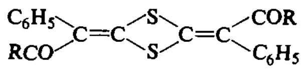


$\underset{\displaystyle CH_3}{C_6H_5CH}COCH_3$

18



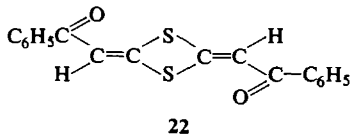
19



20 R = CH_3
21 R = OH

Treatment of the desaurin with sodium hypochlorite converted it to a yellow acidic product, $C_{18}H_{12}O_4S_2$, whose spectra demonstrated that it retained the desaurin nucleus (20). This transformation must involve the conversion of two *C*-acetyl groups to two carboxylic acid groups by haloform reactions; the occurrence of such reactions was confirmed by the isolation of iodoform when the desaurin was treated in basic solution with iodine and potassium iodide. Structure **20**, analogous to **5**, rather than a structure analogous to **15**, can thus be assigned unambiguously to the desaurin; this is in conformance with its p.m.r. spectrum, which shows signals at δ 2.10 (s, 6H) and 7.38 (m, 10H). The structure of the haloform reaction product is then **21**.

The chemical evidence discussed above (27) established that the structures of the desaurins investigated are of type **6**, as originally suggested by Meyer (14*a*). It did not, however, provide information concerning their configuration. This has been obtained in the case of the desaurin from acetophenone by a subsequent X-ray crystallographic study in collaboration with Nyburg and Mellor (28, 29). The desaurin was prepared by the method of Kelber and Schwarz (16) and obtained by slow crystallization from toluene or nitrobenzene as small plates, m.p. 270–272.5° (dec.). A complete three-dimensional X-ray analysis was performed and established the structure, configuration, and conformation of the desaurin as shown in **22**.[6]



22

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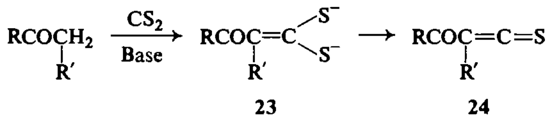
[6] The two α,β-unsaturated carbonyl systems and the two sulfur atoms are essentially coplanar, while the two phenyl rings make an angle of 11° with this plane (29).

[2]



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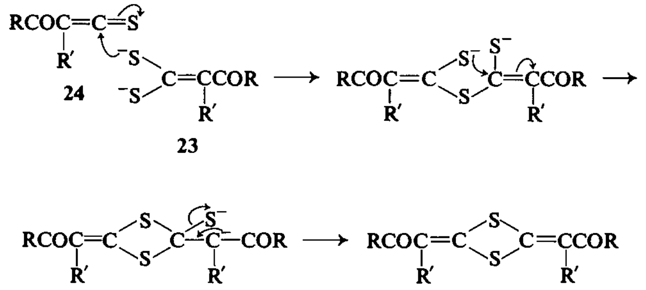

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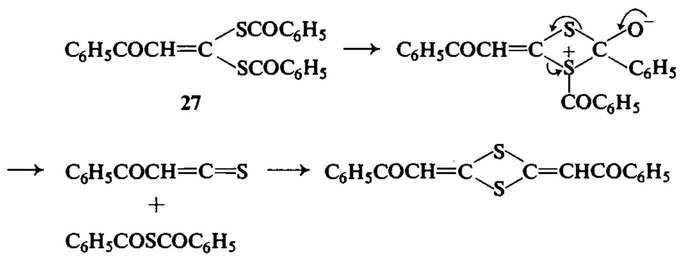
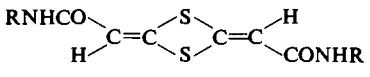


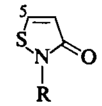
Mechanism of Desaurin Formation

The desaurins are formally dimers of thioketenes, **24**. In the preparation of desaurins by the action of carbon disulfide and bases on active methylene compounds, thioketenes (**24**) could be formed by the elimination of sulfide ion from the dianions **23** (eq. 2). However, formation of the desaurins by dimerization of the thioketenes **24** is unlikely, since the latter would be expected to undergo attack by the nucleophiles present more rapidly than dimerization. The probable pathway, then, would involve attack by **23** on **24** with elimination of sulfide ion (eq. 3). An alternative type of route, without thioketene formation, could involve direct dimerization of **23** followed by elimination of two sulfide ions; however, the dimerization of such dianions is counted improbable on electrostatic grounds (the intervention of the monoanions is also improbable under the highly basic conditions).

Very recently a novel method for the synthesis of the desaurins of type **25** has been reported by Chan, Crow, and Gosney (30), involving treatment of the corresponding *N*-alkyl-3-isothiazolones **26** with bases. These authors also rejected a mechanism for these reactions involving thioketene dimerization for a similar reason to that referred to above. They favored a pathway involving reaction of **26** with its C-5 anion, but did not consider explicitly the possibility of attack of this anion on the thioketene.



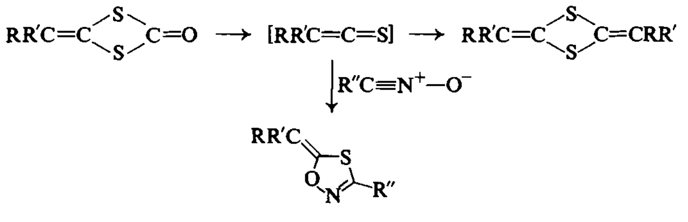
25



26

The formation of desaurins via thermal cleavage of diacyl derivatives of type **27** (16) [or the related alkyl derivatives (7*a*)] may well proceed via thioketene dimerization (*e.g.*, eq. 4); a related pathway could also account for the formation of desaurins by treatment of compounds of type **1** with phthalyl chloride (7*a*).

The dimerization of thioketenes has been implicated in related reactions (26*b*, 31) and Dickore and Wegler (31*b*) have trapped the thioketene intermediate with nitrile oxides (Scheme 5). However, Raasch (32) has observed that bis(trifluoromethyl)thioketene dimerizes only very slowly at room temperature in the absence of Lewis bases.



SCHEME 5

Experimental

Melting points were taken on a Fisher–Johns micro hot stage and are uncorrected, unless otherwise indicated. Solutions in organic solvents were dried over anhydrous sodium sulfate.

The Desaurin from Deoxybenzoin (5)

The desaurin was prepared essentially according to the procedure of Meyer and Wege (12). Deoxybenzoin (49.0 g, 0.250 mol) and powdered potassium hydroxide (56.0 g, 1.00 mol) were heated in boiling carbon disulfide (600 ml) under reflux for 8 h. The excess carbon disulfide was removed under reduced pressure, and the solid cake remaining was triturated with water. The suspension was filtered, and the solid was washed with successive small portions of water, alcohol, and ether and air dried to give **5** (23.7 g, 40%) as a bright yellow powder. An additional 2.0 g of the desaurin could be recovered by evaporation of the combined washings to one-half volume.

The desaurin could be purified most conveniently by extraction with chloroform in a Soxhlet apparatus. It crystallized from the hot chloroform as small golden needles, m.p. 300–302° (dec.). An analytical sample was prepared by recrystallization from nitrobenzene, and was dried under reduced pressure at 100° for 10 h; m.p. 300.5–302.5° (dec.).[5]

Anal. Calcd. for $C_{30}H_{20}O_2S_2$: C, 75.60; H, 4.23; S, 13.46. Found: C, 75.81; H, 4.38; S, 13.20.

The desaurin was insoluble in the usual organic solvents at room temperature; at elevated temperatures small amounts could be dissolved in chloroform, dioxane, xylene, and nitrobenzene. It was readily soluble in cold concentrated sulfuric acid to give a deep purple solution, from which it was precipitated unchanged (mixed m.p.) upon addition of water.

Attempted Acid-catalyzed Hydrolysis of 5

The desaurin **5** (1.14 g, 2.39 mmol) was added to concentrated hydrochloric acid (25 ml) and dioxane (50 ml), and the mixture was boiled under reflux for 100 h and filtered. The yellow crystalline solid (1.10 g) was identified as **5** by a mixed m.p.; recovery 96%. The acidic filtrate was extracted with dichloromethane, and the extract was dried, filtered, and evaporated. There was no residue.

Oxidation of 5 with Chromic Acid

The desaurin **5** (1.00 g, 2.10 mmol) was suspended in glacial acetic acid (75 ml), and chromic anhydride (5.00 g, 50 mmol) was added in portions. The mixture was stirred for 15 h at room temperature, then diluted with water (200 ml), and extracted with ether. The ethereal solution was extracted with aqueous 10% sodium hydroxide, washed with water, dried, and filtered. Removal of the solvent gave a gummy solid (0.05 g), whose i.r. spectrum showed it to be largely benzoic acid.

The basic extracts were combined, acidified to p*H* 1, and extracted with four portions of dichloromethane. The combined extracts were dried, filtered, and evaporated by gentle warming on the steam bath to give a white crystalline solid (0.76 g), m.p. 119–120.5°, undepressed on admixture with benzoic acid. The i.r. spectrum of the product was identical with that of benzoic acid. The total yield of benzoic acid was 0.81 g (79%, based on the formation of 4 mol from 1 mol of **5**).

Attempted oxidation of the desaurin with chromic anhydride in concentrated sulfuric acid, or with the chromic anhydride – pyridine complex led only to intractable red tars from which no pure organic compounds could be isolated.

Ozonolysis of 5

A suspension of **5** (1.00 g, 2.09 mmol) in dichloromethane (50 ml) was cooled to 0° in an ice bath. The mixture was maintained at this temperature throughout the ozonization. Ozonized oxygen from a Welsbach Ozonizer was passed through the mixture for 3 h. Additional dichloromethane was added as necessary to maintain the volume of the solution. The ozonide was decomposed by the addition of water (20 ml), removal of the dichloromethane under reduced pressure at room temperature, and heating of the mixture on the steam bath for 0.5 h.

Unconsumed desaurin (0.27 g, 0.564 mmol) was removed by filtration, and the filtrate was extracted with four portions of ether. The aqueous layer was acidified to p*H* 1 with 10% hydrochloric acid and warmed on the steam bath to 80°. Excess dilute aqueous barium chloride was added dropwise, the solution was allowed to cool, and the precipitate of barium sulfate (0.11 g) was collected.

The combined ethereal extracts were partitioned into acid and neutral fractions by extraction with four portions of aqueous 10% sodium hydroxide, combination and acidification of the basic extracts to p*H* 1, and extraction with four portions of dichloromethane. Both organic solutions were dried and stripped of solvent under reduced pressure.

A portion (0.20 g) of the acid fraction (0.25 g) was sublimed at a bath temperature of 55–60° and 2 mm pressure for 5 h. The white crystalline sublimate (0.16 g) was recrystallized from water to give colorless needles (0.12 g), m.p. and mixed m.p. with benzoic acid, 120.5–121.5°. The i.r. spectrum of the product was superimposable on that of benzoic acid.

A portion (0.23 g) of the neutral fraction (0.28 g) was dissolved in cyclohexane and chromatographed on silica gel (15 g). The major fraction, eluted with benzene, was a yellow solid (0.19 g), m.p. 88–92°, whose i.r. spectrum indicated it to be nearly pure benzil. A portion of this material was crystallized from ethanol to give yellow needles, m.p. and mixed m.p. with benzil, 93.5–95°; another portion was converted to the 2,4-dinitrophenylhydrazone by the method of Shriner *et al.* (33), and this was crystallized from ethanol – ethyl acetate; m.p. and mixed m.p. 188–190°.

The yield of benzil was 35%, based on a theoretical yield of 2 mol equiv from unrecovered **5**; that of benzoic acid was 20%, based on a theoretical yield of 4 mol equiv from unrecovered **5**.

Oxidation of 5 with Potassium Permanganate

The desaurin **5** (0.772 g, 1.62 mmol) was mixed with potassium permanganate (5.00 g, 31.6 mmol) in acetone (150 ml), and the mixture was boiled under reflux for 4 h, cooled, and filtered. The brown precipitate was treated with acidified aqueous sodium bisulfite, and the mixture was warmed gently. The desaurin **5** (0.2989 g, 0.627 mmol) was recovered as a yellow, insoluble precipitate.

The filtrate was poured into water, and the solution was extracted five times with ether. The combined ethereal extracts were extracted five times with aqueous 10% potassium hydroxide and once with water. The ethereal solution was dried and filtered, and the solvent was removed under reduced pressure to give a yellow crystalline product, m.p. 92.5–94.5° (0.128 g). This was shown to be benzil by a mixed m.p. determination and comparison of its i.r. spectrum with that of an authentic sample. The yield, based on the formation of 2 mol equiv from the unrecovered desaurin, was 39%.

The combined basic extracts were acidified to p*H* 1 with 10% hydrochloric acid, and the solution was extracted five times with dichloromethane. The extracts were combined, dried, filtered, and evaporated by gentle warming on the steam bath to give a colorless, crystalline mass (0.221 g). This material was sublimed at 50–60° (4–5 mm) for 5 h. The sublimate (0.208 g) had m.p. 119–120.5°. Recrystallization from water gave colorless needles, m.p. and mixed m.p. with benzoic acid, 120.5–121.5°. The i.r. spectrum was identical with that of benzoic acid. The yield, based on the formation of 4 mol equiv from the unrecovered desaurin, was 35%.

Reduction of 5 with Zinc and Acetic Acid

The desaurin **5** (5.00 g, 10.5 mmol) was suspended in glacial acetic acid (150 ml) and a large excess of powdered zinc (*ca.* 30 g) was added. The mixture was boiled under reflux for 50 h, during which time an odor resembling that of carbon oxysulfide was noticed at the top of the condenser. The mixture was cooled and filtered, and the excess zinc was thoroughly washed with acetic acid. The combined filtrate and washings were diluted with water (600 ml), acidified to p*H* 1 with 10% hydrochloric acid, and extracted with three portions of dichloromethane. The extracts were combined, washed three times with aqueous 10% sodium carbonate and once with water, dried, filtered, and evaporated to give a pale yellow-orange, neutral oil (3.94 g). The combined basic washings were acidified to p*H* 1 with 10% hydrochloric acid and extracted with three portions of dichloromethane. The combined extracts were dried, filtered, and evaporated to give a trace of acidic, gummy solid, m.p. 109–116°.

The neutral fraction was dissolved in benzene and chromatographed on alumina (Merck; 100 g) packed in petroleum ether. Early fractions (70% petroleum ether – 30% benzene eluent) crystallized upon evaporation to give a colorless solid (0.14 g), m.p. 57–65°, which after two crystallizations from ethanol gave colorless crystals, m.p. 81–82°, which did not depress the m.p. of authentic *trans*-1,2-diphenyl-1-propene (**10**) (*vide infra*). The two samples had identical i.r. spectra, and each decolorized neutral potassium permanganate in acetone.

Middle fractions (50% petroleum ether – 50% benzene eluent; 0.77 g) gave a product with an i.r. spectrum showing all the bands of methyldeoxybenzoin (**8**). The product was converted to its 2,4-dinitrophenylhydrazone by the method of Vogel (34). After two crystallizations from ethanol – ethyl acetate this had m.p. 153–155°, undepressed on admixture with authentic methyldeoxybenzoin 2,4-dinitrophenylhydrazone (*vide infra*).

Later fractions (benzene eluent; 0.80 g) gave a product that was crystallized twice from ethanol to give transparent squares, m.p. 108–109.5°, identified as *erythro*-1,2-diphenyl-1-propyl acetate (**9**) by a mixed m.p. and i.r. spectral comparison with an authentic sample (*vide infra*).

Stripping of the column with ethanol gave a mixture (0.82 g) whose i.r. spectrum showed bands attributable to **8** and **9** and an unidentified alcohol.

Attempted reduction of the desaurin with the same amounts of reagents at room temperature was unsuccessful.

Methyldeoxybenzoin (8)

Methyldeoxybenzoin was prepared by the method of Meyer and Oelkers (35). A recrystallized sample had m.p. 48–49°; λ_{max}($CHCl_3$) 5.94(s) and 7.28 μ(m).

The 2,4-dinitrophenylhydrazone was prepared by the procedure of Shriner *et al.* (33). Two recrystallizations from ethanol afforded orange prisms, m.p. 153–155° [lit. (36) m.p. 151.5–152.5°].

erythro-1,2-Diphenyl-1-propanol (11) and erythro-1,2-Diphenyl-1-propyl Acetate (9)

A mixture of methyldeoxybenzoin (2.40 g, 11.4 mmol), ethanol (50 ml), and sodium borohydride (0.75 g, 19.8 mmol) was boiled under reflux for 2 h, poured into water (150 ml), and extracted with three portions of dichloromethane. The combined extracts were dried, filtered, and evaporated. An i.r. spectrum of the crude product (2.14 g) revealed complete reduction, as evidenced by the disappearance of all carbonyl absorption.

The crude alcohol was purified by chromatography on alumina (Merck) with ether as eluent. The purified product was crystallized from petroleum ether to give **11** as fine, colorless needles, m.p. 47.5–49° [lit. (37) m.p. 48°]; λ_{max}($CHCl_3$) 2.82(m), 7.24 μ(m).

The acetate **9** was prepared by acetylation of **11** with pyridine – acetic anhydride in the normal fashion, and was crystallized three times from ethanol; m.p. 107–109° [lit. (22) m.p. 109–110°]; λ_{max}($CHCl_3$) 5.78(s), 7.30 μ(m).

trans-1,2-Diphenyl-1-propene (10)

erythro-1,2-Diphenyl-1-propanol (0.65 g, 3.06 mmol) was heated with potassium hydrogen sulfate (2.40 g, 17.6 mmol) at 200° for 0.5 h. The mixture was cooled, water was added, and the solution was extracted with three portions of dichloromethane. The combined extracts were dried, filtered, and evaporated to give the crude alkene (0.53 g). Two recrystallizations from ethanol gave colorless plates, m.p. 80–81.5° [lit. (23) m.p. 81–82°]; $\lambda_{max}(CHCl_3)$ 6.10(w), 7.28 μ(m).

*Reduction of **5** with Nickel. Formation of **14***

(A) Sponge nickel catalyst (Davison; 50.0 g) from a freshly opened bottle was washed 11 times by decantation with dioxane. Dioxane (200 ml) and **5** (5.00 g, 10.5 mmol) were added and the mixture, protected from atmospheric moisture with a calcium chloride drying tube, was boiled under reflux for 50 h. The catalyst was removed by filtration through a sintered glass disc and washed with several portions of boiling absolute ethanol. The combined filtrate and washings were evaporated under reduced pressure at room temperature. The residue was taken up in a small volume of hot ethanol and the solution was allowed to stand for 12 h. Filtration yielded 1.5 g (35%) of **14** as pale yellow needles, m.p. 126–127.5°. Four recrystallizations from ethanol afforded an analytical sample as fine, colorless needles, m.p. 129–130°; $\lambda_{max}(CHCl_3)$ 5.91(s), 6.25(m), 6.33(w), 6.45 μ(w); $\lambda_{max}(C_2H_5OH)$ 249 (ε 31 600), 291 mμ (ε 17 400); $\delta(CDCl_3)$ 6.05(s, 1H), 6.26(s, 1H), 7.1–7.5(m, 18H), 7.9–8.1(m, 2H).

Anal. Calcd. for $C_{30}H_{22}O_2$: C, 86.93; H, 5.35. Found: C, 86.94; H, 5.53.

The 2,4-dinitrophenylhydrazone was prepared by the method of Shriner *et al.* (33). Four recrystallizations from ethanol – ethyl acetate gave orange cubes, m.p. 160–162° (dec.).

Anal. Calcd. for $C_{36}H_{26}O_5N_4$: C, 72.71; H, 4.41; N, 9.42. Found: C, 72.65; H, 4.48; N, 9.20.

(B) Reduction of **5** with old Davison sponge nickel catalyst or W-6 Raney nickel (38), by the same procedure as in section A led to a mixture of products, from which no **14** could be isolated.

In a typical reduction desaurin **5** (5.00 g, 10.5 mmol) gave a crude mixture (4.14 g) whose i.r. spectrum showed no absorption at 6.45 μ. A mixture (5.00 g) from two reductions was chromatographed on alumina (Woelm, activity grade 3). From the early fractions (70% petroleum ether – 30% benzene eluent) there was obtained a product (1.78 g) whose i.r. spectrum was very similar to that of methyldeoxybenzoin (**8**). A portion of this material was converted to its 2,4-dinitrophenylhydrazone by the procedure of Shriner *et al.* (33), and this was chromatographed on alumina (Merck). The major fraction gave, after three crystallizations from ethanol – ethyl acetate, orange plates, m.p. 149.5–151°, undepressed on admixture with authentic methyldeoxybenzoin 2,4-dinitrophenylhydrazone.

Later fractions (80% benzene – 20% ether eluent) (0.75 g) from the original chromatogram were combined and rechromatographed on alumina (Merck). Benzene eluted a material which solidified, and whose i.r. spectrum was identical with that of *erythro*-1,2-diphenyl-1-propanol (**11**). Recrystallization from petroleum ether gave fine, colorless needles, m.p. 47–49°.

*Base-catalyzed Hydrolysis of **14**. Formation of **12***

A solution of **14** (0.554 g, 1.34 mmol) in 95% ethanol (25 ml) containing potassium hydroxide (1.50 g, 26.7 mmol) was heated under reflux on the steam bath for 3 h. Water (25 ml) was added, and the solution was cooled and extracted with four portions of dichloromethane. The combined extracts were dried and stripped of solvent under reduced pressure to give a pale yellow oil (0.306 g).

The basic aqueous solution was acidified to p*H* 1 with 10% hydrochloric acid and extracted as above. The acidic product (0.133 g) was obtained as a white crystalline solid, m.p. 119–120.5°, undepressed upon admixture with benzoic acid. The i.r. spectrum of this product was identical with that of benzoic acid.

The neutral oily fraction was purified by chromatography on non-basic alumina (Woelm, activity grade 1) with elution with petroleum ether (b.p. 30–60°). Evaporation of the solvent at 10° under reduced pressure and for 12 h at 0.5 mm gave **12** as a colorless oil; $\lambda_{max}(CHCl_3)$ 6.24(m), 6.34(w), 6.45 μ(m); $\lambda_{max}(C_2H_5OH)$ 225 (ε 23 400), 297 mμ (ε 13 800).

Anal. Calcd. for $C_{23}H_{18}O$: C, 89.00; H, 5.85. Found: C, 88.88; H, 6.28.

*Oxidation of **12** with Neutral Potassium Permanganate. Formation of **13***

A solution of **12** (2.13 g, 6.86 mmol) in anhydrous acetone (50 ml) was stirred with anhydrous magnesium sulfate (2.0 g). A solution of potassium permanganate (0.80 g, 5.06 mmol) in anhydrous acetone (30 ml) was added, and the mixture was stirred at room temperature for 2.5 h. The precipitate of manganese dioxide was filtered off and washed with acetone. The combined filtrate and washings were diluted with water (70 ml), and saturated aqueous sodium bisulfite was added until the pink color was discharged. The resulting solution was acidified with concentrated hydrochloric acid to p*H* 1 and extracted with three portions of ether. The combined ethereal extracts were washed with water and with aqueous 10% sodium bicarbonate, dried, filtered, and evaporated under reduced pressure to give the neutral fraction (1.08 g) as a pale yellow oil. This fraction was dissolved in benzene and chromatographed on alumina (Merck; 50 g). Elution with petroleum ether (b.p. 30–60°) and benzene led to recovery of 0.85 g of colorless oil, which was identified as **12** by its i.r. spectrum. The column was then eluted with dichloromethane to give **13** as a yellow viscous oil (0.18 g); $\lambda_{max}(CHCl_3)$ 6.08(vs), 6.25(m), 6.34(m), 6.62 μ(m); $\lambda_{max}(C_2H_5OH)$ 263 (ε 18 600), 344 mμ (ε 19 100).

Compound **13** was characterized as its 2,4-dinitrophenylhydrazone (33), which was purified by twice eluting it from alumina (Merck) with benzene, followed by three recrystallizations from ethanol – ethyl acetate to give deep orange microcrystals, m.p. 185–186° (dec.); $\lambda_{max}(CHCl_3)$ 290(sh, ε 17 800), 331 (ε 17 400), 418 mμ (ε 26 900).

Anal. Calcd. for $C_{29}H_{20}O_5N_4$: C, 69.04; H, 4.11; N, 11.11. Found: C, 69.02; H, 4.31; N, 10.71.

*Oxidation of **14** with Basic Potassium Permanganate*

A solution of **14** (0.593 g, 1.91 mmol) in acetone (100 ml) was treated with potassium permanganate (1.00 g, 7.97 mmol) and water (10 ml), and the mixture was boiled under reflux for 2.5 h. It was then cooled, acidified with 10% hydrochloric acid to p*H* 1, and treated with aqueous 10% sodium bisulfite (10 ml). After dissolution of the manganese dioxide was complete, the solution was extracted with four portions of dichloromethane. The extracts were combined, washed with four portions of aqueous 10% potassium hydroxide and one of water, dried, filtered, and evaporated to give the neutral fraction (0.172 g).

The combined basic extracts and washings were acidified to p*H* 1 with 10% hydrochloric acid, and extracted with four portions of dichloromethane. The organic extracts were combined, filtered through anhydrous sodium sulfate, and evaporated under reduced pressure to give the acid fraction (0.333 g) as colorless crystals, m.p. 115–118°, undepressed upon admixture with benzoic acid. The i.r. spectrum of the acid fraction was identical with that of benzoic acid.

The neutral fraction was dissolved in benzene and chromatographed on Florisil. Two distinct yellow bands were developed and eluted with benzene. The first, when freed of solvent, furnished yellow needles (0.082 g), m.p. 91.5–93°, undepressed upon admixture with benzil; its i.r. spectrum was identical with that of benzil. The second gave a yellow oil (0.027 g), whose i.r. spectrum indicated it to be largely 1-phenyl-1,2-propanedione. It was converted *in toto* to its bis-2,4-dinitrophenylhydrazone (0.032 g) (33); this was recrystallized once to give orange micro-crystals, m.p. 153.5–155°, undepressed on admixture with 1-phenyl-1,2-propanedione bis-2,4-dinitrophenylhydrazone [lit. (39) m.p. 155–156°].

Reaction of 5 with Hydrazoic Acid. Formation of 16

The desaurin **5** (0.48 g, 1.00 mmol) was dissolved in concentrated sulfuric acid (50 ml) and sodium azide (0.20 g, 2.3 mmol) was added in small portions. The mixture was allowed to stand for 12 h, and then an additional quantity of sodium azide (0.10 g, 1.2 mmol) was added. After standing for 24 h the color of the solution had changed from an initial intense red–violet to a deep red.

The solution was poured onto ice, the mixture was filtered, and the precipitate was air-dried. This yellow solid was thoroughly triturated with hot ethanol, and the mixture was allowed to cool and then filtered.

The resulting solid (0.22 g) was dissolved in chloroform and chromatographed on alumina (Merck; 50 g). A bright yellow band moved rapidly with chloroform as eluent and gave a fraction, which, after removal of solvent, was obtained as a yellow powder (0.80 g). This was purified by three recrystallizations from chloroform–cyclohexane to give fluffy yellow needles, m.p. 258–259°; *m*/*e* 491 (42), 399 (47), 161 (32), 105 (100).[5]

Anal. Calcd. for $C_{30}H_{21}O_2NS_2$: C, 73.29; H, 4.31; N, 2.85. Found: C, 73.56; H, 4.28; N, 2.70.

A second yellow band that was eluted more slowly with chloroform gave a fraction which, after removal of solvent, yielded small yellow crystals (0.06 g). This product was purified by three recrystallizations from ethanol–water to give yellow micro-crystals, m.p. 210–211°.[5]

Anal. Calcd. for $C_{30}H_{21}O_2NS_2$: C, 73.29; H, 4.31; N, 2.85. Found: C, 73.02; H, 4.33; N, 2.92.

The Desaurin from Phenyl-2-propanone (20)

A mixture of finely powdered potassium hydroxide (56.0 g, 1.00 mol) and phenyl-2-propanone (33.5 g, 0.250 mol) in carbon disulfide (300 ml) was boiled under reflux for 15 h. The excess carbon disulfide was removed under reduced pressure at room temperature, and the residue was treated with water (500 ml). The basic mixture was extracted with four portions of dichloromethane, and the extracts were combined, dried, filtered, and evaporated. The neutral fraction was thus obtained as a dark red tar (22.40 g).

The basic solution was acidified with 20% sulfuric acid at 10°, and extracted three times with dichloromethane. The combined organic extracts were dried over sodium sulfate, filtered, and freed of solvent under reduced pressure to give the acidic fraction as a red-brown tar (12.5 g). A portion (3.0 g) of this acidic material was dissolved in benzene and chromatographed on silica gel (100 g). A light orange band (70% petroleum ether – 30% benzene eluent) was collected and evaporated to give a deep red tar; $\lambda_{max}(CHCl_3)$ 2.84–4.2(w), 6.24(m), 6.44(s), and 6.90 μ(s). The remainder of the acid fraction was dissolved in benzene (200 ml), and the solution was poured into petroleum ether (500 ml) with vigorous stirring to give a curdy light orange precipitate, which on filtration turned to a viscous deep red oil. The i.r. spectrum of the freshly filtered material was compared with that of a sample dried *in vacuo*. The spectra were similar with no extraneous bands unattributable to solvent and the spectrum of the dried sample was indistinguishable from that of the sample obtained by chromatography.

The neutral fraction was dissolved in benzene (50 ml), and chromatographed on alumina (Merck; 500 g). Early fractions (30% benzene – 70% petroleum ether eluent) on evaporation gave dark red oils whose i.r. spectra indicated the presence of large amounts of phenyl-2-propanone. Elution with benzene yielded red oils which solidified either spontaneously or upon trituration with ligroin (b.p. 66–75°). Increasingly polar solvents eluted tars which were not further investigated. The benzene-eluted solid was purified by five recrystallizations from benzene–cyclohexane to give **20** as lemon yellow needles (2.5 g), m.p. 233–233.5°; $\delta(CDCl_3)$ 2.10 (s, 6H), 7.38 (m, 10H).[5]

Anal. Calcd. for $C_{20}H_{16}O_2S_2$ (mol. wt. 352): C, 68.15; H, 4.58; S, 18.20; 2 C—CH_3, 8.53. Found (355 (isothermal distillation)): C, 68.30; H, 4.50; S, 18.23; C—CH_3, 7.34.

The desaurin **20** was readily soluble in hot benzene, ethanol, dioxane, and sparingly soluble in ligroin (b.p. 66–75°). It was soluble in concentrated sulfuric acid to give an orange solution from which it was precipitated by the addition of water.

Reduction of 20 with Zinc and Base

The desaurin **20** (0.50 g, 1.42 mmol) was mixed with zinc dust (3.00 g, 45.9 mg-atoms), sodium hydroxide (5.00 g, 125 mmol), water (150 ml), and ethanol (25 ml), and the mixture was boiled under reflux for 5 days. Fresh zinc dust (1.00 g, 15.3 mg-atoms) and sodium hydroxide (1.00 g, 25 mmol) were added daily.

The reaction mixture was cooled and filtered, and the unchanged zinc was washed with several portions of ethanol. The combined filtrate and washings were diluted with water (100 ml) and extracted with three portions of dichloromethane. The extracts were combined, dried, filtered, and evaporated to give a pale yellow oil (0.30 g), whose i.r. spectrum was very similar to that of 3-phenyl-2-butanone. It was converted *in toto* to its 2,4-dinitrophenylhydrazone (33) to give a product (0.53 g), m.p. 166–169°. Two recrystallizations from ethanol – ethyl acetate afforded orange needles, m.p. 170.5–171.5°, undepressed by admixture with 3-phenyl-2-butanone 2,4-

dinitrophenylhydrazone (*vide infra*), with an i.r. spectrum identical with that of the authentic material.

The yield of crude ketone based on 2 mol from 1 mol of **20** was 72%; the overall yield of crude 2,4-dinitrophenylhydrazone based on 2 mol from 1 mol of **20** was 57%.

3-Phenyl-2-butanone

3-Phenyl-2-butanone was prepared by the method of Suter and Weston (40).

Its 2,4-dinitrophenylhydrazone (33) was recrystallized from ethanol – ethyl acetate to give fine orange needles, m.p. 173–174° [lit. (41) m.p. 171–172°].

The Mono-2,4-dinitrophenylhydrazone of 20

The mono-2,4-dinitrophenylhydrazone of **20** was prepared by the method of Shriner *et al.* (33). The crude product was purified by elution with benzene from alumina (Merck), and crystallized three times from benzene–ligroin (b.p. 66–75°) to give fluffy, deep red needles, m.p. 250–251°; $\lambda_{max}(CHCl_3)$ 3.01(w), 6.05(m), 6.18(s), 6.27(s), 6.65(s), 6.72(s), 7.36(m), 7.48 μ(s); $\lambda_{max}(CHCl_3)$ 356 (ε 23 400), 450 mμ (ε 22 900).

Anal. Calcd. for $C_{26}H_{20}O_5N_4S_2$: C, 58.63; H, 3.79; N, 10.52. Found: C, 58.75; H, 3.99; N, 10.41.

The Bis-2,4-dinitrophenylhydrazone of 20

The desaurin **20** (0.43 g, 1.28 mmol) was dissolved in dioxane and treated with 2,4-dinitrophenylhydrazine (0.60 g, 3.03 mmol), concentrated hydrochloric acid (1 ml), and water (5 ml). The mixture was warmed briefly on the steam bath to effect complete solution, then allowed to cool and stand at room temperature for 2 weeks. A deep purple–brown solid slowly separated from the solution and was collected from time to time by filtration. The combined, dried solid weighed 0.85 g (93%).

This product was extremely insoluble in all common solvents, including ethyl acetate, chloroform, nitromethane, dimethylformamide, pyridine, and quinoline. Purification was effected by extraction of the powder with boiling pyridine for 0.5 h, filtration of the undissolved solid, and drying at 100° (0.5 mm) for 12 h to give a deep purple-brown powder, m.p. 285–286°; $\lambda_{max}(KBr)$ 6.19(s), 6.32(s), 6.63(s), 6.75 μ(s); $\lambda_{max}(CHCl_3)$ 260 (ε 18 200), 341 (ε 30 000), 505 mμ (ε 21 900).

Anal. Calcd. for $C_{32}H_{24}O_8N_8S_2$: C, 53.92; H, 3.39; N, 15.72. Found: C, 53.92; H, 3.57; N, 15.54.

The Dioxime of 20

The dioxime was prepared in pyridine by the method of Shriner *et al.* (42). Five recrystallizations from ethanol–water afforded yellow needles, m.p. 209.5–210° (dec.); $\lambda_{max}(KBr)$ 3.00(m), 6.17(m), 6.25(w), 6.44 μ(s); λ_{max} (C_2H_5OH) 250 (sh, ε 11 000), 267 (sh, ε 7800), 347 (ε 20 400), 368 mμ (ε 19 500).

Anal. Calcd. for $C_{20}H_{18}O_2N_2S_2$: C, 62.80; H, 4.74; N, 7.33; S, 16.77. Found: C, 62.78; H, 4.78; N, 7.00; S, 16.53.

The dioxime was hydrolyzed in ethanol in the presence of hydrochloric acid and a large excess of 37% aqueous formaldehyde. After being stirred at room temperature for 24 h, the solution was diluted with water, and the product was isolated by filtration. After four recrystallizations from aqueous ethanol, the product was obtained as fine, pale yellow needles, m.p. 232–232.5°, undepressed upon admixture with **20**, and having an identical i.r. spectrum with that of **20**.

Reaction of 20 with Sodium Hypochlorite. Formation of 21

A solution of **20** (0.50 g, 1.42 mmol) in dioxane and a solution of sodium hydroxide (0.70 g) in water (10 ml) were stirred together at room temperature for 1 min. Commercial sodium hypochlorite [Chlorox(5.25% NaOCl): fresh bottle; 10 ml], was added, and stirring was continued for 5 min. Water (100 ml) was added, and the solution was filtered and acidified with 30% hydrochloric acid. The curdy precipitate was filtered, washed thoroughly with water, and air-dried. Purification of the crude product (0.35 g) was effected by one recrystallization from ethyl acetate – cyclohexane, followed by four recrystallizations from 2-butanone-cyclohexane, to give **21** as pale yellow microcrystals, m.p. 298–299° (dec.).

Anal. Calcd. for $C_{18}H_{12}O_4S_2$: C, 60.66; H, 3.39. Found: C, 60.75; H, 3.47.

The sample dissolved in concentrated sulfuric acid to give a yellow brown solution, unchanged on standing.

Reaction of **20** with sodium hypoiodite under a variety of conditions led to mixtures of products in both the acidic and neutral fractions. From the neutral fractions low yields of iodoform, m.p. 117–119°, could be isolated by chromatography on Florisil.

Preparation of the Desaurin from Acetophenone (22)

The desaurin **22** was prepared by the pyrolysis of the mercury salt of benzoyldithioacetic acid (20) according to the method of Kelber and Schwarz (16). The yield of the crude product was 24%. It could also be obtained by pyrolysis of the dibenzoate of benzoyldithioacetic acid in acetophenone. The desaurin was purified by slow recrystallization from toluene or nitrobenzene. Several crystallizations from toluene gave **22** as small plates, m.p. 270–272.5° (dec.) (corrected); λ_{max}(Nujol) 6.18(s), 6.26(m), 6.34(m), 7.26(m), 7.59(m), 8.17(s), 9.80(m), 12.11(m), 12.98(s), 14.4 μ(s); $\lambda_{max}(CHCl_3)$ 274 (ε 17 000), 377 (sh ε 45 700), 392 mμ (ε 49 000).

Anal. Calcd. for $C_{18}H_{12}O_2S_2$: C, 66.64; H, 3.73; S, 19.78. Found: C, 66.66; H, 3.78; S, 19.83.

Rapid crystallization from toluene followed by several recrystallizations gave **22** as small needles, m.p. 237–238° (corrected), with resolidification, followed by remelting with decomposition at *ca.* 265°; λ_{max}(Nujol) 6.18(s), 6.26(m), 6.34(m), 7.26(s), 7.49(m), 8.16(s), 9.80(m), 12.00(w), 12.96(m), 14.39 μ(m); $\lambda_{max}(CHCl_3)$ 273 (ε 18 200), 379 (ε 45 700), and 391 mμ (ε 49 000).

Anal. Calcd. for $C_{18}H_{12}O_2S_2$: C, 66.64; H, 3.73; S, 19.78. Found: C, 66.71; H, 3.77; S, 19.44.

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