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The product formed by the reaction of azibenzil (2-diazo-2-phenylacetophenone) with carbon disulfide has been shown to be 2-(α -phenylphenacylidene)-5,5-diphenyl-1,3-dithiolan-4-one (9).

On démontre que le produit de la réaction entre l'azibenzil (diazo-2 phényl-2 acétophénone) et le sulfure de carbone est la (α -phénylphénylacylidène)-2 diphényl-5,5 dithiolanone-1,3,4 (9).

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The reaction of carbon disulfide with azibenzil (2-diazo-2-phenylacetophenone, 1) was first described by Meyer (4). He found that when a solution of 1 in carbon disulfide was boiled under reflux, a yellow crystalline product, $C_{29}H_{20}O_2S_2$, was formed readily in high yield. Basic hydrolysis of this material was found to give benzoic, phenylacetic, and diphenylacetic acids, together with another acid that was considered to be thiobenzilic acid (2). On this basis Meyer proposed 3 as the structure of the reaction product.

and 347 mµ (ε 13 800) and very strong end absorption. These spectra strongly suggested the presence of the part structure 5; they may be compared with the spectra of 6 (5*a*): λ_{max} 6.20 µ; 257 (ε 10 700) and 350 mµ (ε 15 800).⁴ A further spectroscopic analogy supports this conclusion: a set of strong bands in the 7.4–7.9 µ region of the i.r. spectra of the product C₂₉H₂₀O₂S₂, compound 6, the desaurin 7⁵ (5), and both the trithiolane 8 and one of its *cis* isomers (1).



In our hands Meyer's experimental results were reproduced, except that in the basic hydrolysis 2,2,5,5-tetraphenyl-3,4-dithiaadipic acid (4) was isolated rather than 2. This product is doubtless produced by air oxidation of 2, and the structural implications of its formation are the same as for 2. However, the i.r. and u.v. spectra of the compound $C_{29}H_{20}O_2S_2$ were not in accord with structure 3. Its i.r. spectrum showed bands at 5.86(s), 5.98(w), and 6.17 μ (mw), in addition to bands associated with the phenyl ring vibrations. Its u.v. spectrum showed maxima at 254 (ϵ 17 000)

¹For Paper IV see ref. 1.

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> ²Preliminary reports of this work have appeared (2, 3). ³Lash Miller Chemical Laboratories, Department of Chemistry, University of Toronto, Toronto 5, Ontario.



Given the part structure 5, two structures must be considered for the compound $C_{29}H_{20}O_2S_2$, *viz.* 9⁶ and 10. Of these, 9 may be preferred on the



⁴The differences in these spectra may be attributed to the presence of an additional chromophore in the compound $C_{29}H_{20}O_2S_2$.

⁵The stereochemical assignment for the desaurin is provisional (5).

⁶No stereochemical assignment is implied by this and subsequent structures, unless specifically discussed.

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basis of the formation of products with geminal phenyl groups in several of the degradation reactions of the compound $C_{29}H_{20}O_2S_2$ now to be discussed.

It may first be noted that the products obtained on basic hydrolysis can readily be interpreted in terms of structure 9 (Scheme 1).⁷

Acidic hydrolysis of the compound $C_{29}H_{20}O_2$ -S₂ gave diphenylacetic acid, deoxybenzoin, and sulfur, products whose formation can again be readily interpreted in terms of structure **9** (Scheme 2).

<u>Desulfurization of the compound $C_{29}H_{20}O_2S_2$ </u> ⁷This and the following schemes are illustrative only; it is clear that many variations in detail are possible. with deactivated Raney nickel in ethanol gave principally ethyl diphenylacetate and α -methyldeoxybenzoin (11), together with a small amount of diphenylmethane. These products could arise from 9 as shown in Scheme 3; alternatively, ethyl diphenylacetate could be formed via diphenylketene.

Reduction of the compound $C_{29}H_{20}O_2S_2$ with zinc in boiling acetic acid gave a colorless dihydro product, whose i.r. spectrum showed a broad band at 5.94 μ . Its u.v. spectrum had a maximum at 252 m μ (ϵ 15 900), and its p.m.r. spectrum showed an AB signal system (δ 4.62 and 5.28, J =11 Hz, 2H). Basic hydrolysis gave deoxybenzoin and diphenylacetic acid, and desulfurization with

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-COCH(C₆H₅)₂

C₂H₅OH

,H

∕sh

(C₆H₅)₂CHCO₂C₂H₅

C₆H₅CO

C₆H₅

C₆H₅

[H]

C₀H₅∕

+

C = C

[H]

EtOH

(C6H5)2CHCO2C2H5

C₆H₅CO

C₆H₅CO

C₆H₅

11

+

C6H₂SH

[H]

Снсн₃

C₆H₅COCHCH₃ Ċ₆H₅ 11

Raney nickel in ethanol gave ethyl diphenylacetate, methyldeoxybenzoin (11), and a trace of 1,1,2,2-tetraphenylethane. These data can be interpreted in terms of structure 12 for the dihydro product, derived by reduction of the ethylenic double bond of the α , β -unsaturated carbonyl system of 9. The broad carbonyl-stretching band can be assigned to overlapping absorption of the benzoyl and thio lactone groups, and the u.v. maximum to the former group.⁸ The degradation products can arise by the routes shown in Scheme 4 (the formation of the tetraphenylethane as a minor product on treatment with Raney nickel is probably related to the formation of diphenylmethane from 9, proceeding via the diphenylmethyl radical).

Ozonolysis of the compound $C_{29}H_{20}O_2S_2$ followed by hydrolytic work-up gave benzil and benzoic acid, together with a small amount of diphenylacetic acid. When reductive work-up with zinc and hot aqueous acetic acid was used, the neutral product was benzoin rather than benzil. The formation of benzoic acid from a compound with the structural feature 13 can proceed via benzoic anhydride, whose formation finds analogy, for example, in the ozonolysis of 14 (7). The failure to isolate more than small amounts of geminal diphenyl derivatives may be due to the incorporation of water-soluble sulfonic acid residues. Evidence was obtained that indicated the formation of sulfuric acid in the reaction, but this accounted for only a small fraction of the sulfur in the starting material.



Oxidation of the compound $C_{29}H_{20}O_2S_2$ with perphthalic acid led to the formation of a compound $C_{29}H_{20}O_3S_2$. Since this product regenerates the compound $C_{29}H_{20}O_2S_2$ on treatment with zinc and acetic acid at room temperature, it is highly probable that it has been formed without skeletal change. Three structures then come into consideration on the basis of structure 9 for the



compound $C_{29}H_{20}O_3S_2$, viz., 15, 16, and 17. Of these 17 may be rejected, since it is most unlikely that the electron poorer of the two sulfur atoms of **9** would undergo preferential attack by peracid. Treatment of the compound $C_{29}H_{20}O_3S_2$ with aqueous ethanolic sodium hydroxide gave benzophenone and the desaurin 7. The formation of these products can be interpreted in terms of structure 16 as shown in Scheme 5. The cleavage of the sulfenic acid 18 to give thiobenzophenone finds analogy in the observation that the disulfide 4 undergoes partial conversion to thiobenzophenone (20) in aqueous base (8); the further conversion of 20 to benzophenone with aqueous ethanolic sodium hydroxide has also been observed previously. The conversion of the thicketene 19 to the desaurin 7 may well not involve simple dimerization, but may proceed via attack of hydroxide or methoxide ion to give a β -keto thio acid or ester as an intermediate (cf. ref. 5b).

The formation of these products is more difficult to interpret in terms of structure 15 in that the segment of the molecule that would have to serve as the source of the desaurin is in too high an oxidation state, while that which must serve as the source of the benzophenone is in too low an oxidation state. Furthermore, the i.r. and u.v. spectra of the compound $C_{29}H_{20}O_3S_2$ are in better accord with structure 16. Thus, its i.r. spectrum (CHCl₃) showed carbonyl-stretching bands at 5.83 and 5.97 μ that may be assigned to the thio lactone and benzoyl carbonyl groups in 16, respectively. The conversion of the thio ether function to a sulfoxide function should inhibit the

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⁸Thiol esters have absorption maxima at *ca*. 235 mµ (ε 4000) (6) and thus the thio lactone absorption would be expected to be masked by the maximum due to the benzoyl group and the intense end absorption.





interaction of this sulfur atom with the benzoyl carbonyl group and also partially inhibit the interaction of this carbonyl group with the ethylenic double bond, thus accounting for the fact that the carbonyl-stretching band due to the benzoyl group occurs at a wavelength only slightly longer than that observed for simple benzoyl groups [cf. methylenedeoxybenzoin (21): $\lambda_{max}(CCl_4)$ 5.95 μ (10)].⁹ The sulfoxide function could also be responsible for the observed small hypsochromic shift of the thio lactone band relative to that of 9. Finally, it may be noted that a strong band occurs at 9.27 μ , close to the range assigned to the sulfoxide group (9). On the other hand, it is unlikely that the benzoyl group in structure 15 would have its carbonyl-stretching band at longer wavelength than that for simple benzoyl compounds, and it would be expected that the thio lactone carbonylstretching band would occur at longer rather than shorter wavelength than that for 9.

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The u.v. spectrum of the perphthalic acid oxidation product showed a maximum at 263 mµ (ϵ 23 400) with a shoulder at 287 mµ (ϵ 16 500). This spectrum is in good accord with structure 16; the considerable hypsochromic shift relative to the long wavelength maximum in the spectrum of 9 being again attributable to inhibition of the interaction between the thio ether sulfur atom and the α , β -unsaturated carbonyl system upon oxidation of this sulfur to a sulfoxide function. The spectrum may be compared with that of **21**, which shows a maximum at 247 m μ (ϵ 20 900) (10). Although models are lacking for the epoxy ketone structure **15**, it seems unlikely that this would show such strong absorption at 287 m μ .

CH2 C6H5COCC6H5 21

Thus, although no single observation rigorously excludes structure 15, the weight of the evidence favors the assignment of structure 16. It may be noted that in simpler cases it has been found that oxidation of vinyl sulfides with peracids gives sulfoxides rather than epoxides (11).

As pointed out earlier, the formation of geminal diphenyl derivatives in several of the degradation reactions of the compound $C_{29}H_{20}O_2S_2$ favors the assignment of 9 rather than 10 as its structure. However, most of these reactions were carried out under vigorous conditions, and the possibility existed that the residue 22 arose by rearrangement of the residue 23. Furthermore, in none of the degradation reactions had products been isolated that provided direct evidence of the environment of both sulfur atoms. A very mild method of degradation was therefore sought.



 $^{{}^{9}}As$ has been noted earlier, it is anticipated that the other sulfur atom would not interact strongly with the α , β -unsaturated carbonyl system because of its incorporation into a thio lactone function.

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Treatment with propy lamine in chloroform solution at room temperature provided such a method. The reaction mixture rapidly assumed a bright red color, which slowly faded; further addition of amine resulted in regeneration of the red color until 2 molar equivalents had been added. The characteristic odor of hydrogen sulfide indicated its formation during the reaction. Two compounds were isolated by fractional crystallization of the product mixture.

The lower melting, more soluble compound, $C_{18}H_{19}NOS$, is assigned structure 24 on the following basis. On treatment with dilute aqueous sodium hydroxide at room temperature, it slowly dissolves, after which an oily product separates from solution. The latter product was shown to be the thio amide 25 by direct comparison with a sample prepared from the reaction of benzylmagnesium chloride with propyl isothiocyanate. Acidification of the basic solution from the hydrolysis reaction gave benzoic acid. Thus the compound $C_{18}H_{19}NOS$ must be a benzoyl derivative of 25; the only such derivative that would be expected to be base-soluble is 24, which could form the anion 26 (Scheme 6). In accord with this assignment, a solution of the compound rapidly gave a black precipitate when treated with mercuric oxide, indicating the presence of a thiocarbonyl group (12).

The spectroscopic data for compound 24 are in good accord with the assigned structure and show that this compound has the preferred conformation 24*a* in solution. Its i.r. spectrum showed a single carbonyl-stretching band at 5.98 μ , assigned to the hydrogen-bonded benzoyl carbonyl group in 24*a*; it also showed a band at 3.01 μ (with shoulder at 2.95 μ) attributable to a hydrogen-bonded N—H stretching vibration (the shoulder may result from the presence of conformations other than 24*a*). Its u.v. spectrum in methanol showed maxima at 249 (ε 15 900) and 265 mµ (infl., ε 12 300), attributable to the benzoyl and thio amide groups, respectively [*cf.* thioacetamide λ_{max} (EtOH) 265 mµ (ε 13 800) (13)].



When the u.v. spectrum was recorded in methanolic sodium methoxide these maxima were shifted to 273 (ε 7800) and 340 mµ (ε 15 100), a change that can be attributed to formation of the anion **26**. Its p.m.r. spectrum showed signals at δ 0.9(t), 1.55(m), and 3.42(m), assigned to the *N*propyl protons, a singlet at 6.30, assigned to the benzylic proton, multiplets at 7.33 and 8.05, assigned to the phenyl protons, and a broad signal at 9.30, in good accord with the presence of a strongly hydrogen-bonded thio amide proton.

The spectral data exclude the possibility that 24 exists in solution as the enethiol tautomer 24b. This would be expected to show i.r. and u.v. bands at much longer wavelengths than those observed (1, 5, 10). Further, the p.m.r. spectrum of such a species would be expected to show a signal at $\delta \gg$ 10, due to chelate-type hydrogen bonding. Although β -keto dithio acids and their derivatives



SCHEME 7

often exist to a significant extent as the corresponding enethiol tautomers (5, 10), it is not surprising in the present case that 24a should be favored over 24b. Gompper and Schaefer (14) have found that the β -keto thioamide 27 exists in the solid state in the unenolized form 27a, and that in solution in chloroform the tautomer ratio 27a:27b is 6:4. It would be expected in the case of



24 that the unenolized form 24a would be considerably more favored than in the case of 27a, both because 24a derives additional stabilization from hydrogen bonding and because 24b is destabilized more than 24a by steric interactions between the phenyl groups.

The second compound isolated from the aminolysis of the compound $C_{29}H_{20}O_2S_2$ was found to have the formula $C_{34}H_{36}N_2O_2S_3$. It is assigned structure 28 on the basis of the following data. Reduction with either Raney nickel or zinc and acetic acid gave 2 molar equivalents of the amide 29, whose structure was established by direct comparison with a sample prepared from diphenylacetyl chloride and propylamine (Scheme 7). The compound $C_{34}H_{36}N_2O_2S_3$ was insoluble in dilute aqueous sodium hydroxide and failed to give a sodium nitroprusside test, indicating the absence of sulfhydryl groups (15); it also failed to react with mercuric oxide, indicating the absence of thione groups (12). The sulfur atoms must then be present as sulfide or polysulfide linkages joining two residues related to 29. The removal of all three sulfur atoms by treatment with zinc and acetic acid can then only be interpreted in terms of the structural assignment 28 or the closely related branched trisulfide 30. Although the latter

structure cannot be excluded rigorously, structure 28 is preferred since branched bonding at sulfur appears to occur only in those cases in which the sulfur atom to which the branch is attached is also bonded to a highly electronegative atom (16).

 $+ n-C_3H_7NH_2$

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$$\begin{array}{c} S \\ (C_{6}H_{5})_{2}C - S - S - C(C_{6}H_{5})_{2} \\ n - C_{3}H_{7}NHCO \\ CONHC_{3}H_{7} - n \\ 30 \end{array}$$

The i.r. and u.v. spectra of the compound C₃₄H₃₆N₂O₂S₃ are in good accord with the assignment of structure 28. The former showed all the bands of 29 and no others of appreciable intensity. This is in agreement with expectation since neither C-S nor S-S single bonds give rise to bands of high intensity (17). The u.v. spectrum showed no clear cut maxima but medium intensity absorption at 300 mµ rising steadily to high intensity end absorption with an inflection at ca. 270 m μ (ϵ 6500). In appearance it is strikingly similar to the u.v. spectrum of dibenzyl disulfide (18), although greater in intensity. It can be interpreted in terms of overlap of absorption due to geminal phenyl groups (19) and the trisulfide group (cf. ref. 20).

The three-sulfur compound 28 must have arisen in a secondary reaction after the primary aminolysis (Scheme 8). Its precursor is clearly the thiol 31. It could be formed from this via air oxidation to the disulfide 32 (cf. the formation of the disulfide 4 during the hydrolysis of 9) followed by attack of hydrosulfide ion (the formation of hydrogen sulfide during the reaction has already been noted) to give 33 and oxidative coupling of this with 31; alternatively, 33 might arise via oxidative coupling of 31 with hydrogen sulfide. The yield of 28 was only 39%, and it is possible that the reaction mixture also contained 32 and the tetrasulfide corresponding to 33.

The formation of 24 and 31 on treatment of the

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 $(\mathbf{R} = \mathbf{C}\mathbf{H}_{2}\mathbf{C}\mathbf{H}_{2}\mathbf{C}\mathbf{H}_{3})$



compound $C_{29}H_{20}O_2S_2$ is readily interpretable in terms of structure 9 for that compound as shown in Scheme 9. This scheme accounts for the formation of a red-colored species during the course of the reaction, the anion 35 of the β -keto dithio ester 34. The hydrogen sulfide observed to be formed could arise by reaction of 24 or 35 with propylamine (*cf.* ref. 21).

The isolation of the product 28 from a reaction carried out under such mild conditions supports the earlier conclusion that a geminal phenyl grouping is present in the compound $C_{29}H_{20}O_2S_2$ and that its structure is better represented by 9 than by 10.

The choice of structure 9 was finally vindicated by an alternative synthesis of the compound $C_{29}H_{20}O_2S_2$, albeit in very low yield, by the route shown in Scheme 10. This route was adopted in analogy to that used for the synthesis of 6 (5). The product obtained in this way was identical in all respects with that formed in the reaction of azibenzil with carbon disulfide.

The degradative and synthetic evidence presented in favor of the assignment of structure 9 do not exclude the closely related structure 36, a valence bond isomer of 9 containing a tetracovalent sulfur atom. This might account for the apparent ¹⁰ relatively low intensity of the band assigned to the carbonyl-stretching vibration of the benzoyl group in 9. However, X-ray crystallographic studies in related cases of compounds with the *s*-cis grouping 37 have shown that although the S—O distances are considerably

¹⁰No quantitative intensity measurements have been made; cf. refs. 1 and 5.

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shorter than the sum of the van der Waals' radii of sulfur and oxygen, they are appreciably longer than the normal S—O covalent bond length (22). Furthermore, Kapecki and Baldwin (23) have concluded from extended Hückel molecular orbital calculations that covalent bonding between sulfur and oxygen is negligibly weak in related cases. Thus structure 9 is considered to be the best representation of the compound $C_{29}H_{20}O_2S_2$, although there may be weak bonding between the oxygen atom of the benzoyl group and one of the sulfur atoms.¹¹



A variety of pathways can be envisaged for the formation of 9 from azibenzil and carbon disulfide. All must involve at some stage the rearrangement of one of the two azibenzil residues that are incorporated into the product. In one type of mechanism this is accomplished by a Wolff rearrangement of azibenzil to diphenylketene. However, it has been found that addition of diphenylketene to the reaction mixture of azibenzil and carbon disulfide does not increase the yield of the product, and it thus appears unlikely that diphenylketene is an intermediate. An alternative type of mechanism is illustrated in Scheme 11. Electrophilic attack by carbon disulfide on azibenzil could give **38**; loss of nitrogen would then give 39. Alternatively, this could be formed via 40, whose formation would find analogy in the reaction of aliphatic diazo compounds with thiones (24). Reaction of 39 with a second molecule of azibenzil would give 42, either directly or via 41. Elimination of nitrogen from 42 accompanied by phenyl group migration would give $9.^{12}$

The reaction of two other α -diazo ketones with carbon disulfide have been reported recently. 3-Diazo-2-butanone (43) was found to react with carbon disulfide to give a product, C₉H₁₂O₂S₂, that was originally assigned structure 44 by analogy with the case of azibenzil (25). However, its structure was subsequently shown to be 45 by



X-ray crystallography (22b). It is possible to interpret this behavior in terms of Scheme 11. In the case of 3-diazo-2-butanone the rearrangement corresponding to the step $42 \rightarrow 9$ requires the migration of a methyl group rather than a phenyl group as in the case of azibenzil. It may be anticipated that such a migration will be less ready,

¹¹It should be reemphasized here that the geometry depicted about the ethylenic double bond in 9 is arbitrary and no evidence is available regarding the configuration or conformation of the product.

 $^{^{12}}$ It is not excluded that the processes depicted in Scheme 11 occur in a more concerted fashion.

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and, if the intermediate corresponding to 42 is formed reversibly from that corresponding to 41, an alternative pathway could be traversed from the latter, leading to the formation of 45 (Scheme 12).

12). Baldwin and Kapecki (26) have investigated the reaction of p-fluorobenzoyl-p-fluorophenyl-diazomethane (46) with carbon disulfide. They obtained as the major product a compound

 $C_{29}H_{16}F_4O_2S_2$, analogous in composition to **9** and **45**. They concluded that this product was better represented by structure **47**, analogous to **9**, than by a structure analogous to **45**, on the basis of its ¹⁹F n.m.r. spectrum, which showed three signals with an intensity ratio of 1:1:2 in both tetrahydrofuran and bromoform solution [*cf.* **45**, which shows in its p.m.r. spectrum four methyl proton signals (25)]. The preferential for-

p-FC₆H₄COCN₂C₆H₄F- $p \xrightarrow{CS_2}$





mation of **47** can again be interpreted in terms of the above rationale.

Experimental

Solutions in organic solvents were dried over anhydrous sodium sulfate, unless otherwise indicated. The i.r. spectra were taken in chloroform solution unless otherwise indicated.

Reaction of Azibenzil with Carbon Disulfide (4). Formation of 9

Azibenzil (22.0 g, 106 mmol), prepared by the method of Nenitzescu and Salomonica (27), was dissolved in carbon disulfide (120 ml, 1.99 mol). The solution was boiled under reflux for 36 h. Carbon disulfide was removed by heating the solution on the steam bath at water aspirator pressure until the product began to crystallize. The mixture was then cooled in an ice bath, and the product was filtered. It was washed with ether and recrystallized from carbon disulfide to give 9 as a pale yellow crystalline solid (22.5 g, 92%), m.p. $154-155^{\circ}$ [lit. (4) m.p. $153-154^{\circ}$]; λ_{max} 5.86, 5.98 (w), 6.17 μ (mw); λ_{max} (CHCl₃) 254 (ϵ 17 000), 347 m μ (ϵ 13 800).

Anal. Calcd. for $C_{29}H_{20}O_2S_2$: C, 74.97; H, 4.34; S, 13.80. Found: C, 74.83; H, 4.46; S, 13.71.

Compound 9 was recovered unchanged after treatment with yellow mercuric oxide in boiling benzene for 30 min and with boiling 2% alcoholic silver nitrate for 15 min.

Basic Hydrolysis of 9

A mixture of 9 (12.0 g, 25.8 mmol) and a solution of potassium hydroxide (16.0 g, 285 mmol) in 95% ethanol (50 ml) was boiled under reflux for 7 h. It was cooled to room temperature, diluted with a four-fold excess of water, and acidified to pH 1 with concentrated hydrochloric acid, when hydrogen sulfide was evolved. The mixture was heated on the steam bath for a few minutes, cooled, neutralized with aqueous 10% sodium bicarbonate, and filtered. The filtrate was acidified (pH ca. 1) and extracted three times with ether. The combined ethereal extracts were dried and evaporated on the steam bath to give a solid (10.4 g). This was extracted three times with petroleum ether (b.p. 30-60°). The red oil (4.8 g) that remained undissolved was extracted with benzene. Evaporation of the benzene from this extract afforded a white solid (100 mg), m.p. 194-196° (dec.). This product was soluble in aqueous 5% sodium bicarbonate with evolution of carbon dioxide and after several recrystallizations from carbon disulfide had m.p. 199.5-200.5° dec.; $\lambda_{max}(KI)$ 5.99 μ .

Anal. Calcd. for $C_{28}H_{22}O_4S_2$. H_2O (mol. wt. 504): C, 66.64; H, 4.80; S, 12.71. Found (neut. equiv. 247): C, 66.32; H, 4.76; S, 13.13.

The m.p. of authentic 2,2,5,5-tetraphenyl-3,4-dithiaadipic acid (4) (vide infra) was undepressed on admixture with this product; the i.r. spectra of the two samples were identical.

An ethereal solution of diazomethane (5.9 mmol) was added to a solution of the degradation product (100 mg, 2.0 mmol) in dioxane. The dioxane was evaporated at oil pump pressure on the steam bath, and the resulting methyl ester was crystallized from benzene: m.p. 130.5–131.5°; λ_{max} 5.79 µ.

Anal. Calcd. for $C_{30}H_{26}O_4S_2$: C, 70.01; H, 5.09; S, 12.46. Found: C, 69.65; H, 5.08; S, 12.12.

The m.p. of the methyl ester was undepressed on admixture with authentic dimethyl 2,2,5,5-tetraphenyl-3,4dithiaadipate (*vide infra*); the i.r. spectra of the two samples were identical.

The petroleum ether - soluble fraction from the basic hydrolysis of 9 weighed 5.0 g. Examination of the i.r. spectra of this fraction in both carbon disulfide and chloroform corroborated Meyer's earlier observation (4) that this was a mixture of benzoic and phenylacetic acid. Quantitative analysis by means of i.r. spectroscopy demonstrated that it was composed of 2.2 g (70%) of benzoic acid and 2.8 g (80%) of phenylacetic acid.

It was subsequently found that such drastic conditions are not necessary to effect the basic hydrolysis of 9, which was completely hydrolyzed in a 2.5% sodium hydroxide solution in dioxane-water at room temperature overnight.

2,2,5,5-Tetraphenyl-3,4-dithiaadipic Acid (4)

2,2,5,5-Tetraphenyl-3,4-dithiaadipic acid was prepared by the method of Becker and Bistrzycki (28) from thiobenzilic acid (28) in 70% yield; m.p. 192.0–193.5° (dec.).

Dimethyl 2,2,5,5-Tetraphenyl-3,4-dithiaadipate

Dimethyl 2,2,5,5-tetraphenyl-2,4-dithiadipate was prepared by reaction of 4 with ethereal diazomethane as above; m.p. 130.5–131.5°.

Acidic Hydrolysis of 9

Compound 9 (10.0 g, 21.5 mmol) was added to a mixture of glacial acetic acid (300 ml), concentrated sulfuric acid (50 ml), and water (50 ml). The mixture was boiled under reflux for 2 days, poured into water (2 l), and extracted six times with ether. The combined ethereal extracts were extracted with aqueous 5% sodium bicarbonate until carbon dioxide was no longer evolved. The sodium bicarbonate extract was acidified to pH ca. 1 with concentrated hydrochloric acid and extracted six times with ether. Both the acidic and neutral fractions were dried and evaporated to dryness on the steam bath.

The acidic fraction, which contained much acetic acid, was kept in a vacuum desiccator over potassium hydroxide pellets until the odor of acetic acid was absent. It was crystallized from aqueous ethanol to give colorless crystals of diphenylacetic acid (3.10 g, 68%), m.p. 145–147°, undepressed on admixture with an authentic sample. The neutral fraction yielded sulfur (1.30 g, 94%) as yellow needles, m.p. 116–118.5° [lit. (29) m.p. of monoclinic sulfur, 119°]. Its identity was confirmed by the fact that it burned with a blue flame, liberating sulfur dioxide and leaving no residue. The remainder of the neutral fraction (5.30 g) showed all the bands of deoxybenzoin in its i.r. spectrum. It was converted to its 2,4-dinitrophenylhydrazone by the method of Shriner *et al.* (30). This was recrystallized from ethyl acetate to give orange crystals (3.60 g, 50%), m.p. 200-201°, undepressed on admixture with an authentic sample of the 2,4-dinitrophenylhydrazone of deoxybenzoin.

Desulfurization of 9 with Raney Nickel

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The W-2 Raney nickel catalyst was prepared by the method of Mozingo (31). This was deactivated by a modification of the procedure of Spero *et al.* (32). The W-2 Raney nickel catalyst (50.0 g) was washed twice by decantation with acetone and heated in boiling acetone (150 ml) under reflux for 2 h. The catalyst was then washed twice by decantation with ethyl acetate, heated in boiling ethyl acetate (150 ml) under reflux for 2 h, and washed twice by decantation with ethanol.

The deactivated W-2 Raney nickel catalyst (50.0 g, 1.78 g-atoms) was suspended in ethanol (250 ml), **9** (5.00 g, 10.8 mmol) was added, and the mixture was boiled under reflux in a nitrogen atmosphere for 24 h. Examination of the i.r. spectrum of an aliquot of the reaction mixture showed that all of the starting material had been consumed. The mixture was filtered free of the catalyst and evaporated to dryness on the steam bath at water aspirator pressure to give an oil (4.70 g).

A solution of this oil (4.35 g) in petroleum ether (b.p. $30-60^\circ$; 75 ml) was chromatographed on Merck alumina (150 g). The column was developed with petroleum ether, and 50 ml fractions were collected. Fractions 1 and 2 gave diphenylmethane (190 mg), which was purified by vacuum distillation; b.p. 70-75° (1 mm); n_D^{24} 1.5761. This was identified by its characteristic odor and the identity of its i.r. spectrum with that of an authentic sample; n_D^{24} 1.5763.

Further elution of the column gave an oil (fractions 13-15). One gram of this oil was subjected to a series of seven successive chromatographic separations. In each case Merck alumina (40 g) was used, and 10 ml fractions were collected. The oil was thus separated into two components. The i.r. spectra of these two compounds were identical in every respect to those of methyldeoxybenzoin and ethyl diphenylacetate.

To corroborate the identification of these products, the oil (1.00 g) was heated for 3 h with boiling aqueous 5% sodium hydroxide (25 ml) and ethanol (10 ml) under reflux. The reaction mixture was diluted three-fold with water and extracted three times with ether to give the neutral fraction. The aqueous layer was acidified to pH ca. 1 with concentrated hydrochloric acid and extracted three times with ether to give the acidic fraction. Both fractions were dried and evaporated to dryness on the steam bath. The acidic fraction was crystallized from aqueous thanol to give diphenylacetic acid (300 mg, 66%), m.p. 144–145.5°, undepressed on admixture with an authentic sample; the i.r. spectra of the two samples were identical.

The neutral fraction (410 mg, 73%) was a colorless oil. This was converted to its 2,4-dinitrophenylhydrazone by the method of Shriner *et al.* (30). The orange crystalline product was recrystallized from ethyl acetate: m.p. $151.5-152.5^{\circ}$, undepressed on admixture with an authen-

tic sample of the 2,4-dinitrophenylhydrazone of methyldeoxybenzoin (*vide infra*).

When W-6 Raney nickel catalyst (33) was used for the desulfurization in place of the less reactive deactivated W-2 Raney nickel catalyst, a product mixture of different composition was obtained. Reaction with 9 (5.00 g) yielded 640 mg of diphenylmethane, and the amount of methyldeoxybenzoin was greatly reduced. The product mixture was separated by chromatography and vacuum distillation. Ethyl diphenylacetate was isolated and crystallized from aqueous ethanol: m.p. 57–58°, undepressed on admixture with an authentic sample; the i.r. spectra of the two samples were identical.

Methyldeoxybenzoin 2,4-Dinitrophenylhydrazone

Methyldeoxybenzoin was prepared by the method of Meyer and Oelkers (34) in 65% yield; b.p. 140–145° (5 mm); λ_{max} 5.95, 7.28 μ (m). It was converted to its 2,4-dinitrophenylhydrazone by the method of Shriner *et al.* (30); m.p. 151.5–152.5°.

Anal. Calcd. for $C_{21}H_{18}O_4N_4$: C, 64.60; H, 4.65; N, 14.35. Found: C, 64.78; H, 4.86; N, 14.81.

Reduction of 9 by Zinc and Acetic Acid.

Formation of **12**

To a boiling solution of 9 (1.00 g, 2.15 mmol) in glacial acetic acid (15 ml), zinc dust (1.00 g, 15.3 mg-atoms) was added with swirling over a period of 20 min. The solution was filtered, and three drops of concentrated hydrochloric acid were added to the filtrate (pH ca. 1). The solution was added to a large excess of water, and the mixture was extracted with dichloromethane. The extract was washed three times with saturated aqueous sodium bicarbonate and three times with water, dried, and evaporated on the steam bath. The residual oil (700 mg) was crystallized from benzene – petroleum ether (b.p. 30–60°) to yield 12 (140 mg, 14%) as a colorless, crystalline solid, m.p. 209.5–210.5°; λ_{max} 5.94 μ (br), λ_{max} (EtOH) 252 m μ (ϵ 15 900); δ (CDCl₃) 4.62 (d, J = 11 Hz, 1H), 5.28 (d, J = 11 Hz, 1H), 7.2–7.5 (m, 18H), 7.67 (m, 2H).

Anal. Calcd. for $C_{29}H_{22}O_2S_2$: C, 74.67; H, 4.75; S, 13.72. Found: C, 74.69; H, 5.03; S, 13.90.

Although the i.r. spectrum of the oil showed only the bands of the reduction product **12**, attempts to obtain further crystalline product from it failed.

Basic Hydrolysis of 12

A mixture of 12 (1.00 g, 2.15 mmol) and a solution of potassium hydroxide (1.50 g, 26.7 mmol) in 95% ethanol (10 ml) was boiled under reflux for 7 h. The reaction mixture was diluted with water, acidified to pH ca. 1 with concentrated hydrochloric acid, heated on the steam bath for 10 min, and allowed to cool to room temperature. It was then extracted three times with ether, and the combined ethereal extracts were extracted three times with aqueous 5% sodium bicarbonate. The bicarbonate extract was acidified with concentrated hydrochloric acid to pH ca. 1 and extracted three times with ether to obtain the acidic fraction. Both acidic and neutral fractions were dried and evaporated on the steam bath.

The neutral fraction (330 mg, 79%) showed all of the bands of deoxybenzoin in its i.r. spectrum. A 2,4-dinitrophenylhydrazone of this fraction was made (30) and crystallized from ethanol: m.p. 200-201°, undepressed

upon admixture with authentic deoxybenzoin 2,4-dinitrophenylhydrazone.

The acidic fraction (420 mg, 91%), whose i.r. spectrum was identical with that of diphenylacetic acid, was crystallized from aqueous ethanol to yield colorless crystals of diphenylacetic acid, m.p. $145-146^{\circ}$, undepressed on admixture with an authentic sample.

Desulfurization of 12 with Raney Nickel

A mixture of 12 (1.00 g, 2.14 mmol), W-2 Raney nickel catalyst (31) (2.00 g), and ethanol (50 ml) was stirred under a nitrogen atmosphere for 2 days. The mixture was filtered, and the filtrate was stripped of ethanol on a steam bath under vacuum. The resulting oil had an i.r. spectrum identical with that of the oil from the Raney nickel desulfurization of 9. It was heated with a boiling mixture of aqueous 5% sodium hydroxide (15 ml) and ethanol (3 ml) for 3 h. After cooling to room temperature, the mixture was poured into a three-fold excess of water and extracted with ether to give the neutral fraction. The aqueous layer was acidified with ether three times to give the acidic fraction. Both fractions were dried and evaporated on the steam bath.

The acid fraction on crystallization from aqueous ethanol gave diphenylacetic acid (160 mg, 36%) m.p. 144– 146°, undepressed on admixture with an authentic sample.

Lixiviation of the partially crystalline neutral fraction with ethanol yielded *sym*-tetraphenylethane (30 mg) as colorless crystals, m.p. $210-211^{\circ}$ after recrystallization from benzene. The m.p. was undepressed upon admixture with authentic *sym*-tetraphenylethane.

Excess ethanol was evaporated from the filtrate to give an oil (400 mg, 89%) whose i.r. spectrum showed all of the bands of methyldeoxybenzoin. Its 2,4-dinitrophenylhydrazone was prepared (30) and crystallized from ethanol; m.p. 151–152.5°. A mixture melting point with an authentic sample of the 2,4-dinitrophenylhydrazone of methyldeoxybenzoin showed no depression.

Ozonolysis of 9

A solution of 9 (1.00 g, 2.15 mmol) in dichloromethane (50 ml) was cooled to 0° , and maintained at this temperature throughout the ozonolysis. Ozone from a Welsbach ozonizer was bubbled through the solution for 3 h.The ozonide was decomposed by the addition of water (20 ml). The dichloromethane was removed under water aspirator pressure, first at room temperature and finally on the steam bath. The aqueous solution was extracted four times with ether, and the combined ethereal extracts were extracted six times with aqueous 5% sodium hydroxide. The ethereal layer was dried and evaporated on the steam bath to give the neutral fraction. The aqueous layer was neutralized with concentrated hydrochloric acid to pH ca. 1 and extracted four times with ether. The combined ethereal extracts were dried and evaporated on the steam bath to give the acidic fraction.

The original aqueous solution was allowed to stand at room temperature until it had evaporated. The residue (150 mg) was dissolved in water to give an acidic solution (pH ca. 1). Neutralization of this solution to the methyl red end-point with aqueous 5% barium hydroxide gave a precipitate of barium sulfate (20 mg).

The neutral fraction (630 mg) was distilled at 100°

(1 mm) to give an oil (410 mg) that showed all of the bands of benzil in its i.r. spectrum. This was treated with 2,4dinitrophenylhydrazine reagent (30), and the product was crystallized from ethanol to give benzil 2,4-dinitrophenylhydrazone, m.p. 194–195°, undepressed on admixture with an authentic sample.

The acidic fraction (170 mg) was sublimed at 50° (1 mm) for 6 h. The sublimate (110 mg) was crystallized from water to give benzoic acid, m.p. 120–121.5°, undepressed on admixture with an authentic sample. Distillation of the sublimation residue from the acidic fraction at 150° (1 mm) gave an oil (30 mg). This oil showed all of the bands of diphenylacetic acid in its i.r. spectrum; however, it contained benzoic acid since all of the bands of the latter were also present in the spectrum.

In another ozonolysis, the ozonide was decomposed with zinc and acetic acid by the method of Noller and Adams (35). Glacial acetic acid (10 ml) was added to the ozonide, and the dichloromethane was removed at water aspirator pressure and room temperature. Ether (40 ml) was added, and the mixture was stirred and treated with zinc dust (1.00 g) and three drops of water. Further zinc dust (9.00 g) was added in small portions, followed by water (1 ml). The mixture was boiled under reflux until it gave a negative test with starch-iodide paper (ca. 15 min). It was then filtered, and the zinc salts were washed several times with ether. The combined filtrate and washings were washed several times with aqueous 10% sodium carbonate and once with water. The sodium carbonate extract was acidified to obtain the acidic fraction. The ethereal layer was dried and evaporated on the steam bath to give the neutral fraction (250 mg), which was crystallized from benzene to give benzoin, m.p. 132-134°, undepressed on admixture with an authentic sample; the i.r. spectra of the two samples were identical.

Oxidation of 9 with Perphthalic Acid. Formation of 16

Compound 9 (5.00 g, 10.8 mmol) was added to a solution of perphthalic acid (33.5 mmol) in ether (500 ml). The mixture was stirred at room temperature for 2 days. The solution was evaporated at water aspirator pressure without the application of external heat. The residue was digested with chloroform (250 ml) that had stood over anhydrous sodium sulfate for 3 h. The mixture was filtered, and the filtrate was evaporated to dryness. The product was crystallized from ethanol to give 16 (4.10 g, 79%), m.p. 148-150° (dec.); λ_{max} 5.83, 5.97 µ; λ_{max} 263 (ϵ 23 400), 287 mµ (sh, ϵ 16 000).

Anal. Calcd. for $C_{29}H_{20}O_3S_2$: C, 72.47; H, 4.20; S, 13.35. Found: C, 72.28; H, 4.19; S, 13.14.

Reduction of 16 with Zinc and Acetic Acid

A mixture of 16 (82 mg, 0.17 mmol), acetic acid (10 ml), and zinc dust (39 mg, 0.70 mmol) was stirred at room temperature for 30 min. The solution was decanted into ether (30 ml), and the ethereal solution was washed twice with water, three times with aqueous 5% sodium bicarbonate, and again with water. It was dried over anhydrous magnesium sulfate and evaporated to give a yellow glass (80 mg). This was crystallized from ether to give 9 as pale yellow crystals (10 mg, 13%), m.p. 153–155°. One recrystallization from carbon disulfide gave material, m.p. 153.5–155°, undepressed on admixture with an authentic sample of 9, the i.r. spectra of the two samples were identical.

Basic Hydrolysis of 16

A mixture of compound **16** (1.00 g, 2.09 mmol), ethanol (25 ml), and aqueous 5% sodium hydroxide (25 ml) was boiled under reflux for 3 days. The mixture was poured into an excess of water, acidified to pH ca. 1 with concentrated hydrochloric acid, and extracted three times with ether, with filtration to remove the insoluble yellow precipitate that appeared. This precipitate was crystallized from chloroform to give 7 (220 mg, 45%), m.p. $300.5-302.5^{\circ}$ (dec.), undepressed on admixture with an authentic sample (5b).

The ethereal extract was dried and evaporated to give a liquid (330 mg, 87%) that showed all of the bands of benzophenone in its i.r. spectrum. Its 2,4-dinitrophenylhydrazone was prepared (30) and crystallized from ethyl acetate – ethanol; m.p. 238–240°, undepressed on admixture with an authentic sample of the 2,4-dinitrophenylhydrazone of benzophenone.

Acidic Hydrolysis of 16

A mixture of 16 (1.00 g, 2.09 mmol), ethanol (25 ml), and concentrated hydrochloric acid (25 ml) was boiled under reflux for 2 days. The mixture was poured into a four-fold excess of water and extracted four times with ether, and the combined ethereal extracts were extracted four times with aqueous 10% sodium bicarbonate. The sodium bicarbonate extract was acidified to pH ca. 1 with concentrated hydrochloric acid and extracted four times with ether. These ethereal extracts were combined, dried, and evaporated on the steam bath to give the acidic fraction (160 mg). This was crystallized from aqueous ethanol to give benzilic acid, m.p. 148–149°, undepressed on admixture with an authentic sample; the i.r. spectra of the two samples were identical.

The neutral fraction showed all of the bands of the starting material 16 in its i.r. spectrum.

Reaction of 9 with n-Propylamine. Formation of 24 and 28

To a solution of 9 (5.00 g, 11.0 mmol) in chloroform (50 ml) was added n-propylamine (2.0 ml, 1.4 g, 24 mmol). The pale yellow solution rapidly acquired a bright red color, which faded to pale orange after the solution had stood for 2 h at room temperature, when the characteristic odor of hydrogen sulfide could be detected. Addition of further n-propylamine (0.50 ml, 350 mg, 6.0 mmol) produced only a slight intensification of the orange color. After a further 4 h at room temperature the chloroform and excess amine were removed by evaporation at room temperature and water aspirator pressure. The residual orange oil was dissolved in a small amount of ether, and the solution was stored at -10° . After 2 days the solid (750 mg) that had separated was filtered and washed well with ether; the mother liquor was concentrated and again cooled to -10° . After a further 3 days a second crop of solid (600 mg) was separated as before. The first crop had m.p. 164-166°, and the second had m.p. 166-168°; their i.r. spectra were virtually identical. Combination and recrystallization from benzene-ligroin gave fine colorless needles of 28 (1.30 g, 39%), m.p. 167-168°. Two more recrystallizations from benzene-ligroin gave an analytical sample, m.p. 167–168°; λ_{max} 2.91 (w), 2.94 (sh), 2.98 (sh), 6.01 μ ; λ_{max} (MeOH) ca. 270 m μ (inflexion, ϵ 6500); ϵ_{235} 25 000.

Anal. Calcd. for $C_{34}H_{36}N_2O_2S_3$: C, 68.02; H, 6.03; N, 4.65; S, 15.98. Found: C, 67.87; H, 5.98; N, 4.67; S, 16.20.

A benzene solution of 28 on treatment with yellow mercuric oxide underwent no reaction in 30 min.

Crystallization of the remainder of the original reaction product from ether yielded a yellowish solid (1.05 g) whose i.r. spectrum suggested that it was a mixture. The remaining product was crystallized from ether – petroleum ether by cooling at – 10° to give **24** as a faintly yellow solid (1.20 g, 37%), m.p. 62–64°. Four more recrystallizations from ether – petroleum ether gave fluffy white needles, m.p. 66–67°; $\lambda_{max}(CCl_4)$ 2.95 (sh), 3.01 (m), 5.98 μ ; $\lambda_{max}(MeOH)$ 249 (ϵ 15 900), 265 (inflexion, ϵ 12 300) m μ ; $\lambda_{max}(MeOH-MeONa)$ 273 (ϵ 7800), 340 m μ (ϵ 15 100); δ 0.90 (t, J = 7 Hz, 3H), 1.55 (m, 2H), 3.42 (m, 2H), 6.30 (s, 1H), 7.33 (m, 8H), 8.05 (m, 2H), 9.30 (br, s, 1H).

Anal. Calcd. for C₁₈H₁₉NOS: C, 72.70; H, 6.44; N, 4.71; S 10.76. Found: C, 72.76; H, 6.63; N, 4.52; S, 10.65.

A benzene solution of 24 on treatment with yellow mercuric oxide developed a black precipitate within 10 min.

Reaction of 24 with Aqueous Base

A mixture of **24** (271 mg, 0.91 mmol) and aqueous 5% sodium hydroxide (20 ml) was stirred vigorously at room temperature. After 20 min all but a few crystals had dissolved to give a yellow solution, from which an oil soon began to separate. After 3 h the mixture was extracted with two 20 ml portions of ether. The extracts were combined, dried over anhydrous magnesium sulfate, and evaporated to give a pale yellow oil (105 mg) that crystallized on standing; the i.r. spectrum of this material showed only very weak absorption in the 5.8–6.1 μ region. Two recrystallizations from ether – petroleum ether gave α -phenyl-*N*-*n*-propylthioacetamide (**25**) as colorless needles (49 mg, 28%), m.p. 55.5–57°, undepressed on admixture with an authentic sample (*vide infra*); the i.r. spectra

In another run 24 (192 mg, 0.65 mmol) was stirred for 3 h with aqueous 5% sodium hydroxide (10 ml). After separation of the neutral product, the solution was acidified with hydrochloric acid and extracted with two 20 ml portions of ether. These were dried over magnesium sulfate and evaporated to give an off-white solid (86 mg), whose i.r. spectrum was very similar to that of benzoic acid. Sublimation of the solid at 50° (1 mm) gave colorless crystals (55 mg), m.p. 106–113°. Recrystallization first from aqueous ethanol and then cyclohexane gave benzoic acid as colorless crystals (14 mg, 18%), m.p. 120–122°, undepressed on admixture with an authentic sample.

α -Phenyl-N-n-propylthioacetamide(25)

n-Propyl isothiocyanate was prepared by the method used previously for the preparation of methyl isothiocyanate (36). It was obtained in 73% yield as a colorless liquid, b.p. 150–152° [lit. (37) b.p. 153°]; $\lambda_{max}(CCl_4)$ 4.60 (sh), 4.71 (sh), 4.82 μ .

n-Propyl isothiocyanate was converted to 25 by treatment with benzylmagnesium bromide following the method described by Blicke and Zinnes (38) for the preparation of α -phenyl-*N*-ethylthioacetamide. Com-

pound 25 was obtained in 43% yield as off-white needles, m.p. 51.5-53.5°. Four recrystallizations from ether – petroleum ether gave colorless needles, m.p. 55.5-56.5°; $\lambda_{max}(CCl_4)$ 2.89 (m), 6.25 (w), 6.63, 7.16, 9.36 µ; λ_{max} -(MeOH) 267.5 (ϵ 12 700), 271 (sh, ϵ 12 400) mµ; $\lambda_{max}(MeOH-MeONa)$ 268 (ϵ 11 500), 271 mµ (sh, ϵ 11 300).

Anal. Calcd. for $C_{11}H_{15}NS$: C, 68.37; H, 7.82; N, 7.25; S, 16.56. Found: C, 68.55; H, 8.01; N, 7.45; S, 16.59.

When a benzene solution of **25** was treated with yellow mercuric oxide a black precipitate developed within 10 min.

Reduction of 28 with Nickel

A solution of **28** (52 mg, 0.087 mmol) in ethanol (20 ml) was boiled under reflux for 20 h with a large excess of sponge nickel catalyst (Davison). The solution was cooled to room temperature, the catalyst was separated by gravity filtration, and the solvent was evaporated at the water aspirator. The residual solid (45 mg) had m.p. 86-88°; crystallization from benzene-ligroin gave α,α -diphenyl-*N*-*n*-propylacetamide (**29**; 28 mg, 64%) as colorless needles, m.p. 94-94.5°. One further recrystallization gave **29** (21 mg), m.p. 94.5–95°, undepressed on admixture with an authentic sample (*vide infra*).

Reduction of 28 with Zinc and Acetic Acid

A solution of **28** (69 mg, 0.120 mmol) in acetic acid (5 ml) was boiled under reflux for 3 h with zinc dust (100 mg). The supernatant solution was poured into ice-water, and the mixture was extracted with three 10 ml portions of ether. The extracts were combined, washed well with aqueous 5% sodium bicarbonate, and dried over anhydrous magnesium sulfate. The ether was evaporated at reduced pressure, and the solid residue was sublimed at 120° (1 mm) to give a white solid (42 mg), m.p. 87-90°. Recrystallization from cyclohexane gave **29** as colorless needles (32 mg, 55%), m.p. 94-94.5°, undepressed on admixture with an authentic sample (*vide infra*).

α, α -Diphenyl-N-n-propylacetamide (29)

The preparation of 29 was accomplished by the general method of Shriner et al. (39). Diphenylacetic acid (500 mg, 2.40 mmol) was dissolved in a large excess of thionyl chloride (10 ml), and the solution was boiled gently under reflux for 30 min. The excess thionyl chloride was evaporated at the water aspirator, and a solution of n-propylamine (1.0 ml, 0.70 g, 12 mmol) in benzene (15 ml) was added to the residual oil. The resulting solution was boiled under reflux for a few minutes, cooled to room temperature, and washed once with 5% hydrochloric acid, once with water, and twice with aqueous 5% sodium hydroxide. Drying over anhydrous magnesium sulfate followed by evaporation of the benzene under reduced pressure gave a tan solid (500 mg). Recrystallization from benzene-ligroin gave 29 as off-white needles (400 mg, 67%) m.p. 94-95°. Six recrystallizations from benzeneligroin gave colorless needles, m.p. 95-95.5°; λ_{max} 2.84 (m), 5.97, 6.66 µ.

Anal. Calcd. for C₁₇H₁₉NO: C, 80.57; H, 7.56; N, 5.53. Found: C, 80.58; H, 7.36; N, 5.58.

Alternative Synthesis of 9

To a stirred suspension of sodium amide (400 mg, 10.0

mmol) in dry benzene (75 ml) was added a solution of deoxybenzoin (2.00 g, 10.0 mmol) in benzene (40 ml), and the mixture was stirred and boiled under reflux under nitrogen for 10 h. The yellow suspension was cooled to room temperature, and to it was added carbon disulfide (0.65 ml, 820 mg, 11.0 mmol). The mixture rapidly acquired a bright red color, which intensified during an additional 24 h of stirring. Addition of a solution of α-chlorodiphenylacetyl chloride (40) (2.70 g, 10.0 mmol) in benzene (20 ml) rapidly discharged the red color, after which the mixture was stirred for 1 h. Dry pyridine (1 ml) was added, and the mixture was boiled under reflux for 5 h, during which time a heavy precipitate formed. The mixture was cooled to room temperature, and the precipitate was filtered and washed with benzene. The benzene was evaporated from the filtrate at reduced pressure leaving a viscous reddish oil. This was triturated with a small amount of ether, and the brownish solution was decanted, leaving a sticky solid (600 mg).

The ethereal solution was evaporated, and the residual oil (3.0 g) was dissolved in benzene – petroleum ether (3:2) and chromatographed on silica gel (Davison, 300-400 mesh; 50 g); 80 ml fractions were collected. Elution with benzene – petroleum ether (9:1) gave fractions that appeared from their i.r. spectra to be largely mixtures of deoxybenzoin and 9. These were combined and rechromatographed on silica gel (50 g). The column was eluted with benzene – petroleum ether (7:3), and 80 ml fractions were collected. Fractions 3 and 4 were combined and recrystallized from carbon disulfide to give a first crop of yellow prisms (97 mg), m.p. 154–156°, and a second crop (57 mg), m.p. 153–155°, undepressed on admixture with 9.

The residue from evaporation of the mother liquors from the recrystallizations was combined with fractions 2. 5, and 6 of the second chromatogram, and this material was again chromatographed on silica gel (18 g). The column was eluted with benzene - petroleum ether (3:2), and 50 ml fractions were collected. Recrystallization of fraction 4 from ether - carbon disulfide gave yellow crystals (14 mg), m.p. 153-155°, while a combination of fractions 3 and 5 gave yellow solid (20 mg), m.p. 142-147°. Trituration of the residues from evaporation of the mother liquors with ether and cooling gave more yellow solid (14 mg), m.p. 151-153°. The last two, low-melting crops were recrystallized from carbon disulfide to give yellow prisms (20 mg), m.p. 154-155°, undepressed on admixture with 9. The i.r. spectra of all four crops were identical with the spectrum of 9; the total combined product (188 mg) represents a yield of 8%.

Reaction of Azibenzil with Carbon Disulfide in the Presence of Diphenylketene

Diphenylketene (5.00 g, 25.7 mmol), prepared by the method of Smith and Hoehn (41), azibenzil (5.72 g, 25.7 mmol), and carbon disulfide (55 ml) were boiled under reflux in a nitrogen atmosphere overnight. The excess carbon disulfide was removed by evaporation on the steam bath at the water aspirator, and the residue was crystallized from acetic acid to give 9 (5.00 g, 84% based on azibenzil alone); m.p. $152-154^\circ$, undepressed on admixture with a sample of 9 prepared by the reaction of azibenzil with carbon disulfide in the absence of diphenyl-ketene. The i.r. spectrum of the product showed all of the bands of 9.

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