Experimental. Phytanic acid (5 g, prepared as previously described) was dissolved in chloroform (35 ml) and mixed with concentrated sulphuric acid (25 ml) and sodium azide (8 g). After refluxing the mixture for 5 h, the chloroform was removed by suction, and the residue made alkaline with sodium hydroxide. The liberated amine which was extracted with petroleum ether, remained as a pale brown, oily liquid after removal of the solvent (yield 3 g). The corresponding amine sulphate could readily be prepared; it was a white solid, soluble in ethanol but insoluble in acetone and water, m.p. 201°.

To a solution of the free amine (3 g) in 20 % acetic acid — 1 % HCl (100 ml) was added sodium nitrite (0.6 g in 5 ml of water). After 15 min at room temperature the evolution of nitrogen had ceased. The oil which separated was extracted with petroleum ether, and the ether extract was washed with dilute sodium hydroxide and then with water. After removal of the solvent, a pale yellow oil remained (yield 2 g). Gas chromatographic analysis demonstrated that the product consisted of several components other than the expected pristanol. No attempt was made however, to purify the fatty alcohol further before the oxidation step.

The crude pristanol (2 g) was oxidized with chromic acid in acetic acid, and pristanic acid was isolated using the same method as previously described for synthesis of phytanic acid. (Yield of crude pristanic acid 0.7 g). Gas chromatographic analysis of the crude acid (methylated) showed one major peak, comprising about 70 % of the sample and four smaller peaks. The contaminating substances could be removed by preparative thin layer chromatography of the crude pristanic acid on plates of Silica gel G, using petroleum ether, b.p. 60°—80°:diethyl ether:methanol:acetic acid (90:10:3:1) as solvent. The remaining acid was about 99 % pure estimated by gas chromatography of the methyl ester. This ester had relative retention time 0.63 (methyl phytanate =1) at 185° on 6 ft × 1/8 in. columns of 8 % BDS on Chromosorb W. Mass spectrometric analysis of the purified product (as methyl ester) on a LKB-9000 instrument showed a parent ion at m/e 312, and with large fragments at m/e 88, 101, 129, 157, 222, and 281. The mass spectrum of our product was in all parts identical to that of methyl pristanate recently published by Hanson and Morrison.

We are indebted to Dr. R. Ryhage, Stockholm, for carrying out the mass spectrometric analysis.


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Studies of Isothioanilotropines

I. On the Structure of the Products Formed from 2-Aryl-4,4-diphenyl-1,3-oxathiolan-5-ones and Concentrated Sulfuric Acid

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On treatment of various 2-aryl-4,4-diphenyl-1,3-oxathiolan-5-ones (I) with conc. sulfuric acid and dilution with water, Bistrzyck et al., isolated yellow compounds formulated as 9,10-endosulfido-9,10-dihydroanthracenes (II).

\[
\begin{align*}
\text{C}_6\text{H}_5\text{S} & \quad \text{(I)} \\
\text{H} & \quad \text{R} \\
\text{H} & \quad \text{R} \\
\text{H} & \quad \text{R} \\
\text{C}_6\text{H}_5 & \quad \text{S} \\
\end{align*}
\]

Later, Dufraisse et al. showed by comparison of the Raman spectra of 1,3-diphenylsobenzofuran and that of the product from I (R = C\(_6\)H\(_4\)) that the latter probably should be formulated as 1,3-diphenylsobenzothiophene (III, R = C\(_6\)H\(_4\)). Almost twenty years later, however, Hartough reported that the primary products of Bistrzycki et al. had the struc-

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ture II, although they rearranged to III in acetic acid. To eliminate this ambiguity, we have reinvestigated the compounds formed from I (R = C₆H₄, p-CH₃C₆H₄, o-, m-, and p-CIC₆H₄, m-NO₂C₆H₄, p-BrC₆H₄, with exception of the latter previously investigated by Bistrzycki et al.) and have concluded that in all cases the primary products are isobenzenothiophenes (III). Our assignments are based on the NMR spectra and chemical evidence.

The 60 Mc/s NMR spectrum of the compound derived from (I, R = C₆H₄) showed only a rather complicated multiplet centered at 2.55 τ. In a 100 Mc/s spectrum, two bands at 2.90—3.05 τ and 2.10—2.25 τ were observed, each consisting of seven lines symmetrically displayed around the center of the multiplet. The integration of the spectrum showed each of these bands to correspond to two protons. On spin-spin decoupling by double irradiation at 2.94 τ, the pattern at low field was reduced to a singlet at 2.18 τ. The pattern and the spin-spin decoupling showed the spectrum to be of spin type A₂B₂, which was in accordance with the four protons in the quinoid benzene ring of structure III. Between the A and the B patterns, a complex multiplet was situated; integration showed it to correspond to ten protons. This signal must be due to the protons of the two phenyl groups placed in positions 1 and 3. Structure II would not be reconcilable with the observed spectrum. We also recorded the spectrum of 1,3-diphenylisobenzo[1,2]-benzofuran and found a similar pattern, except that only two lines of the septet at low field could be detected in a 60 Mc/s spectrum, because differences in chemical shifts caused this pattern to be placed in the same region as the signal from the phenyl protons. The septet at high field was not obscured.

When substituents were introduced in the 2-phenyl group of I, the two symmetrical patterns in the NMR spectra of the reaction products were not altered, but the chemical shifts were a little different. The two septets, however, always corresponded to four protons. The signal from the phenyl protons was different in the spectra of the compounds investigated. Hence the 2-phenyl group of the oxathianolone could not be incorporated into the isobenzenothiophene nucleus, but had to be one of the substituents in positions 1 or 3.

If the compounds III were boiled with maleic anhydride in xylene, compounds of type IV (Table 1) were formed.

![Diagram](image)

**Table 1.**

<table>
<thead>
<tr>
<th>R</th>
<th>Yield %</th>
<th>M.p. °C</th>
<th>Formula</th>
<th>Analyses</th>
</tr>
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<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Calc.</td>
</tr>
<tr>
<td>C₆H₄</td>
<td>78</td>
<td>249—250d</td>
<td>C₆H₄H₂Oₛ</td>
<td>74.99</td>
</tr>
<tr>
<td>p-CIC₆H₄</td>
<td>65</td>
<td>221—222d</td>
<td>C₆H₄H₁₀Clₛ</td>
<td>68.75</td>
</tr>
<tr>
<td>p-BrC₆H₄</td>
<td>60</td>
<td>228—229d</td>
<td>C₆H₄H₁₀Brₛ</td>
<td>62.20</td>
</tr>
<tr>
<td>p-CH₂C₆H₄</td>
<td>94</td>
<td>230—232d</td>
<td>C₆H₄H₁₀Oₛ</td>
<td>75.57</td>
</tr>
</tbody>
</table>

be written as the polar mesomeric form (V), a thioacarbonyllylde formally analogous to the carbonylylde discussed by Huisgen. The structure (II) with its fully aromatic benzene rings does not offer opportunity for any of these additions.

The solutions of I in conc. sulfuric acid were in all cases deep red violet, and this colour disappeared when the solutions were poured into water. Apparently the colour was not caused by free radicals since no paramagnetic species were detectable by EPR spectroscopy. Further investigation of the reaction mechanism is in progress.

Experimental. The 60 Mc/s spectra were recorded on a Varian A 60 and the 100 Mc/s spectrum on a Varian HA 100. All spectra were obtained from approx. 20 % solutions in CDCl₃ with TMS as internal standard.

2. (4- Bromophenyl)-4,4- diphenyl-1,3- oxathiolan-5-one. This compound was prepared by the method described by Bistrzycki et al. with the modification that conc. sulfuric acid was used as the condensing agent. The compound was recrystallised from ethanol; m.p. 117—118°C, yield 85 %. (Found: C 61.50; H 3.71; S 7.89. Calc. for C₁₁H₁₄BrO₃S: C 61.50; H 3.66; S 7.75).

The other oxathiolanones have been described by Bistrzycki et al. 1,4,7

1. (4- Bromophenyl)-3- phenylisobenzothiophen.
2. (4- Bromophenyl)-4,4- diphenyl-1,3- oxathiolan-5-one (1 g) was dissolved in conc. sulfuric acid (20 ml). The deep red solution was allowed to stand at room temperature for 20 h. It was then poured on to 150 g of ice, the yellowish green solution was extracted with 3 x 75 ml of chloroform, the extract was dried over sodium sulfate and evaporated to dryness in vacuo, and the residue was recrystallised from a mixture of 90 % acetone and 10 % ethanol; m.p. 135—136°C, yield 37 %. (Found: C 85.35; H 3.61; S 8.74. Calc. for C₁₂H₁₂Br₂S: C 85.70; H 3.59; S 8.75).

The other isobenzothiophenes used were prepared with the modifications of the Bistrzycki procedure exemplified above.

Maleic anhydride adducts (Table 1). 1,3-Diarylisobenzothiophenes (0.001 mole) were mixed with maleic anhydride (0.001 mole) and refluxed in xylene for 4 h in an atmosphere of carbon dioxide. Upon cooling, the adducts crystallised. The products were extracted several times with hot water on the filter to remove unreacted maleic anhydride. The compounds were recrystallised from xylene to give faint yellowish-green crystals.

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