

Experimental. Phytanic acid (5 g, prepared as previously described⁶) 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 (0.9 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 pristol. No attempt was made however, to purify the fatty alcohol further before the oxidation step.

The crude pristol (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.⁶ (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 Cromosorb 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.⁴

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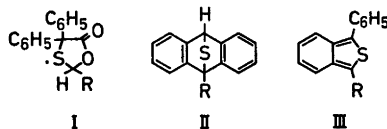
Studies of Isobenzothiophenes

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

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On treatment of various 2-aryl-4,4-diphenyl-1,3-oxathiolan-5-ones (I) with conc. sulphuric acid and dilution with water, Bistrzycki *et al.*^{1,2} isolated yellow compounds formulated as 9,10-endsulfido-9,10-dihydroanthracenes (II).



Later, Dufraisse *et al.*³ showed by comparison of the Raman spectra of 1,3-diphenylisobenzofuran and that of the product from I (R = C₆H₅) that the latter probably should be formulated as 1,3-diphenylisobenzothiophene (III, R = C₆H₅). Almost twenty years later, however, Hartough⁴ reported that the primary products of Bistrzycki *et al.* had the struc-

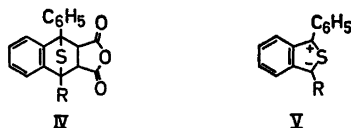
ture II, although they rearranged to III in acetic acid. To eliminate this ambiguity, we have reinvestigated the compounds formed from I ($R = C_6H_5$, $p\text{-}CH_3C_6H_4$, $o\text{-}$, $m\text{-}$, and $p\text{-}ClC_6H_4$, $m\text{-}NO_2C_6H_4$, $p\text{-}BrC_6H_4$, with exception of the latter previously investigated by Bistrzycki *et al.*) and have concluded that in all cases the primary products are isobenzothiophenes (III). Our assignments are based on the NMR spectra and chemical evidence.

The 60 Mc/s NMR spectrum of the compound derived from I ($R = C_6H_5$) 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 A_2B_2 , 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-diphenylisobenzofuran 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.

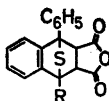
When substituents were introduced in the 2-phenyl group of I, the two symmetrical patterns in the NMR spectra of the reaction products were not altered, but the chemical shifts were a little different. The two septets, however, always corresponded to four protons. The signal from the phenyl protons was different in the spectra of the compounds investigated. Thence the 2-phenyl group of the oxathiolanone could not be incorporated into the isobenzothiophene 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.



The diphenyl compound (IV, $R = C_6H_5$) has been prepared by Wittig⁵ from 1,3-diphenylisobenzothiophene obtained in a different way. The reaction can be considered either as a Diels-Alder addition to the 1,4-dienic system of the thiophene ring or as a 1,3-dipolar cycloaddition, since (III) can

Table 1.



R	Yield %	M.p. °C	Formula	Analyses					
				C		H		S	
				Calc.	Found	Calc.	Found	Calc.	Found
C_6H_5	78	249–250d	$C_{24}H_{16}O_3S$	74.99	74.77	4.20	4.38	8.32	8.26
$p\text{-}ClC_6H_4$	65	221–222d	$C_{24}H_{14}ClO_3S$	68.75	68.67	3.61	3.71	7.66	7.76
$p\text{-}BrC_6H_4$	60	228–229d	$C_{24}H_{14}BrO_3S$	62.20	62.00	3.26	3.42	6.92	6.91
$p\text{-}CH_3C_6H_4$	94	230–232d	$C_{25}H_{18}O_3S$	75.37	75.20	4.55	4.43	8.03	8.09

be written as the polar mesomeric form (V), a thiocarbonylylide formally analogous to the carbonylylide discussed by Huisgen.⁶ 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 $CDCl_3$ 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.*⁷ 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 $C_{21}H_{15}BrO_2S$: C 61.30; H 3.68; S 7.78).

The other oxathiolanones have been described by Bistrzycki *et al.*^{1,2,7}

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 3×75 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 65.35; H 3.61; S 8.74. Calc. for $C_{20}H_{15}BrS$: C 85.70; H 3.59; S 8.78).

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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