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3-PHENYL-2H-THIOPYRAN,1,1-DIOXIDE AND 2H-THIOCHROMEN,1,1-DIOXIDE. SYNTHESIS AND ACIDIC PROPERTIES. (°)

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In the course of our continuing study of cyclic sulfones (1) we have prepared two new members of this class of heterocycles: 3-phenyl-2H-thiopyran,1,1-dioxide (I) and 2H-thiochromen,1,1-dioxide (II). We have investigated in some detail the chemistry of (I) and (II) but we wish to report here only on their synthesis and on the nature of the corresponding anions.

From the reaction of mercaptoacetone with ω-bromo-acetophenone in chloroform solution and in presence of triethylamine, acetonyl-phenacyl-sulfide (III - m.p. 57° from ethanol) (°°) was obtained in 61% yield and subsequently oxidised to the corresponding sulfone (IV - m.p. 119° from ethanol) with potassium permanganate in a bifasic system (water-benzene)(yield 55%). The sulfone IV on heating in acetic acid in presence of sodium acetate underwent cyclization to 3-phenyl-5-oxo-2H-5,6-dihydro-

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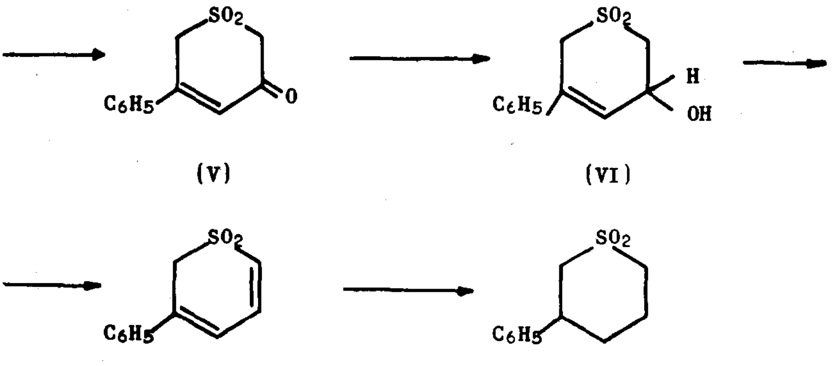
(°) Part III of "Studies on cyclic sulfones". For part II see reference (1)

(°°) Satisfactory analyses for all compounds here reported were obtained. All melting points are uncorrected.

thiopyran,1,1-dioxide (V -m.p. 158° from diluted acetic acid: p.nitrophenylhydrazone m.p. 279° from dimethylformamide. Yield 72%). The keto-sulfone V was reduced with sodium borohydride in diluted ethanol solution to the carbinol VI (thick oil; acetylderivative: m.p. 144°, b.p. 225-227° at 1 mm. Hg) and the latter dehydrated with 85% phosphoric acid at 100° to 3-phenyl-2H-thiopyran,1,1-dioxide (I - m.p. 99-100° from methanol) in 35% yield. Catalytic hydrogenation (Pd/C in methanol) of I yielded the corresponding tetrahydroderivative (VII - m.p. 163° from methanol).

$$\underset{\text{(III)}}{C_6H_5\text{-}CO\text{-}CH_2\text{-}S\text{-}CH_2\text{-}CO\text{-}CH_3} \longrightarrow \underset{\text{(IV)}}{C_6H_5\text{-}CO\text{-}CH_2\text{-}SO_2\text{-}CH_2\text{-}CO\text{-}CH_3} \longrightarrow$$



(V) (VI)

(I) (VII)

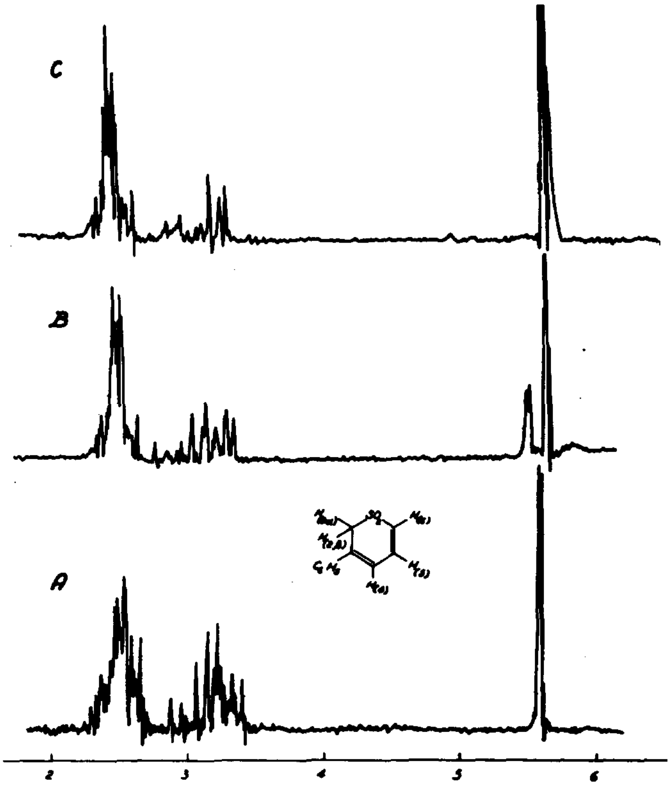
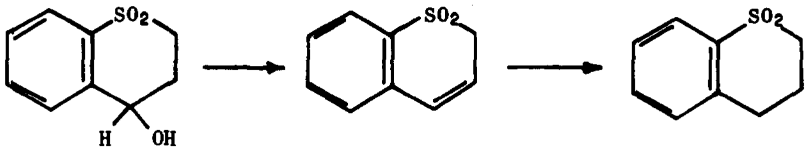


FIG. 1

In the I.R. spectrum of I are present bands related to the sulfone group (1110 and 1270 cm.$^{-1}$) and to the conjugated ethylenic bonds (1560 cm.$^{-1}$). I dissolves in cold diluted aqueous alkalies and the resulting light yellow solutions undergo marked alteration after a short time.

The N.M.R. spectrum (°) of I (50 mg. in 0.5 ml. C_3D_6O) has the following features (FIG. 1A): a complex band at 2.2-2.7 τ (aromatic protons); a complex band (ABC system) at 2.8-3.4 τ (vinyl protons); a doublet (J=0.1 c.p.s.) at 6.6 τ (methylene protons). A spectrum of the same sample recorded 30 minutes after addition of D_2O (40% by volume) is represented in FIG.1B: partial reduction of the methylene protons' band, to an extent of about 50%, is visible. Almost complete disappearance (>90%) of the same signal is noticed after 22 hours (FIG. 1C).

2H-thiochromen,1,1-dioxide (II - m.p. 72° from diluted ethanol) was prepared in 93% yield by dehydration of 4-hydroxythiochromane,1,1-dioxide (VIII) (2) on heating with 85% phosphoric acid at 140°C. The structure of II was confirmed by hydrogenation (Pd/C in methanol) to the known 1-thiochromane, 1,1-dioxide (IX) (3).



(VIII) (II) (IX)

In the I.R. spectrum of II are present bands due to the sulfone group (1140 and 1320 cm.$^{-1}$) and to the conjugated ethylenic bond (1610 cm.$^{-1}$). The N.M.R. spectrum of II (70 mg.

(°)- All N.M.R. spectra were recorded on a Perkin Elmer spectrometer mod. R-10 employing T.M.S. as an internal standard.

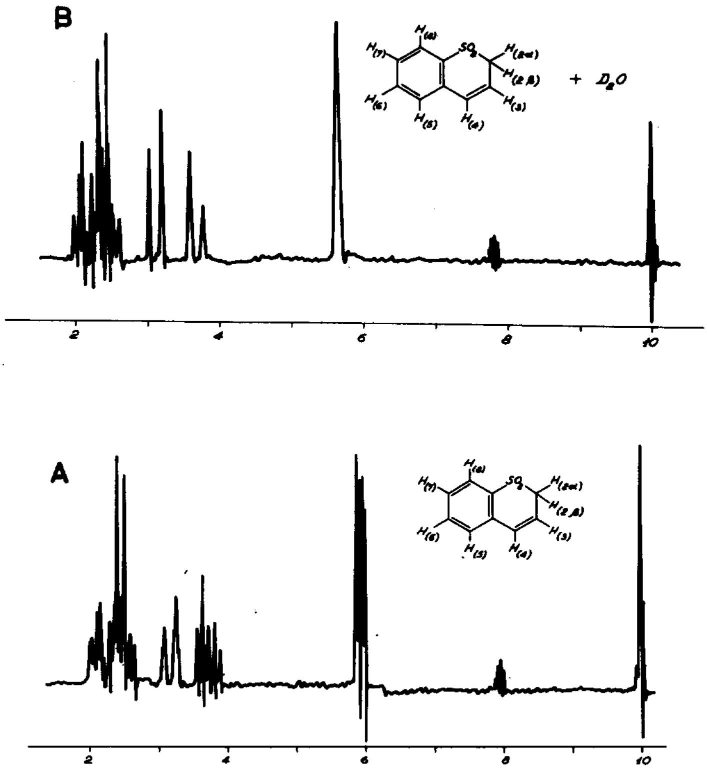
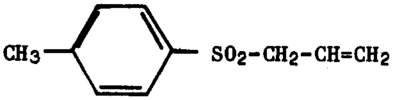


FIG. 2

in 0.4 ml. C_3D_6O) has the following features (FIG. 2A): a complex band at 1.9–2.7 τ (aromatic protons); a typical pattern related to an ABX_2 system: $H_{(4)}$ at 3.2 τ (J_{3-4} =10.5 c.p.s.; J_{2-4} =1.5 c.p.s.); $H_{(3)}$ at 3.72 τ (J_{3-4} = 10.5 c.p.s.;

J_{2-3} =5 c.p.s.); $H_{(2)}$ at 5.90 τ (methylenic protons, double doublet with J_{2-3} = 5 c.p.s.; J_{3-4} = 1.5 c.p.s.). A spectrum of the same sample recorded 24 hours after the addition of 50% D_2O (by volume) shows (FIG. 2B) a complex band at 1.9-2.75 (aromatic protons) and a typical pattern for an AB system with $H_{(4)}$ at 3.2 τ and $H_{(3)}$ at 3.72 τ (J_{3-4} = 10.5 c.p.s.). The spectra in FIG. 1B, 1C, 2B, are evidence that the protons undergoing deuterium exchange in 3-phenyl-2H-thiopyran,1,1-dioxide (I) and in 2H-thiochromen,1,1-dioxide (II) are the ones belonging to the methylene groups.

The cyclic structures of sulfones (I) and (II) are certainly responsible for anions stability at the α-methylene carbon. This conclusion is supported by experiments carried out on p.tolyl-allyl-sulfone (X) (4) in which no deuterium exchange was observed in the same conditions.



(X)

Work on this subject is still in progress and full details will be published elsewhere.

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