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SYNTHESIS OF 2,6-DI-p-METHOXYPHENYL-1-THIA-4-PYRANONE AND 2,6-DI-p-METHOXYPHENYL-3,5-DICHLORO-1-THIA-4-PYRONE AND THEIR REACTIVITY TOWARDS CARBONYL REAGENTS.

BY

Ibrahim El-Sayed El-Kholy and Fathi Kamel Rafla
Department of Chemistry, Faculty of Science,
Alexandria University, Alexandria, EGYPT, U.A.R.

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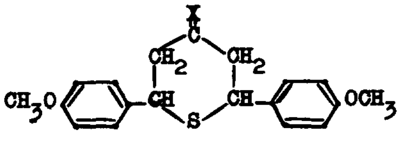
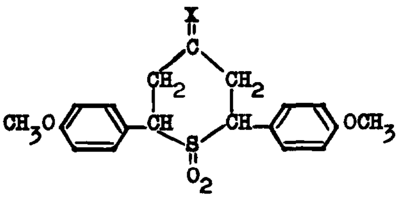
Addition of hydrogen sulphide to di-p-methoxybenzal acetone in slightly alkaline medium, afforded 2,6-di-p-methoxyphenyl-1-thia-4-pyranone (I,X=O) in excellent yield. I (X=O) was characterised by oximation to I (X=N.OH) with hydroxylamine in boiling ethanol or pyridine. I (X=O) was also oxidised by hydrogen peroxide in acetic acid forming a sulphone, $C_{19}H_{22}O_7S$, m.p. 140°(decomp.), containing hydrogen peroxide of crystallisation like polysubstituted thiophenes[1]. It was converted by crystallisation to the free hydrogen peroxide sulphone II (X=O) which gave with hydroxylamine in ethanol an oximino-derivative II (X=N.OH).



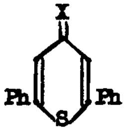
(I)



(II)

Two isomeric 2,6-diphenyl-1-thia-4-pyranones have been synthesised by Arndt and his co-workers[2] who succeeded in converting them to 2,6-diphenyl-1-thia-4-pyrone (III,X=O) and 2,6-diphenyl-3-chloro-1-thia-4-pyrone (IV,X=O) by the action of phosphorus pentachloride. It has now been found, that 2,6-di-p-methoxyphenyl-1-thia-4-pyranone (I,X=O) and phosphorus pentachloride (4 moles) in dry benzene afforded 2,6-di-p-methoxyphenyl-3,5-dichloro-1-thia-4-pyrone (V,X=O) in good yield together with an unidentified material (crude m.p. 125-137°), which gave a picrate.

This novel reaction appears particularly interesting since it provides a convenient and a simple synthetic route to 3-chloro- and 3,5-dichloro-2,6-diaryl-1-thia-4-pyrones .



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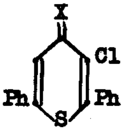

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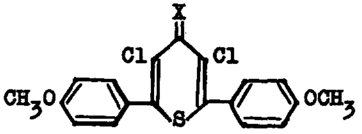


(V)

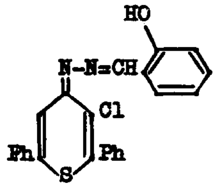
2,6-Diphenyl-1-thia-4-pyrone (III,X=O)[2] gave a stable picrate while 2,6-diphenyl-3-chloro- (IV,X=O)[2] and 2,6-di-p-methoxyphenyl-3,5-dichloro-1-thia-4-pyrone (V,X=O) failed to give this general reaction. Further, by the action of phosphorus pentasulphide on V (X=O), we have prepared its 4-thio-analogue V (X=S).

Like diaryl-1,4-thiopyrones[3], the 1-thia-4-thiopyrones III (X=S)[4], IV (X=S)[3,4], and V (X=S) were readily converted by hydroxylamine in ethanol into the corresponding -1-thia-4-pyrone oximes III (X=N.OH)[4], IV (X=N.OH)[5], and V (X=N.OH) in quantitative yield.

Moreover, whereas 2,6-diphenyl-1,4-pyrone[6] yielded 1-hydroxy-2,6-diphenyl-4-pyridone and 2,6-diphenyl-4-pyrone oxime with hydroxylamine in ethanol, the three -1-thia-4-pyrones III (X=O) , IV (X=O) , and V (X=O) were recovered unchanged after prolonged refluxing in the same solvent.

When this reaction was carried out in pyridine the corresponding oximes III (X=N.OH) and IV (X=N.OH) were obtained as the sole products. However, V (X=O) failed to react under similar conditions.

The reaction of hydrazine hydrate with 2,6-diphenyl-1,4-pyrone[6] and its 4-thio-analogue involves ring opening with the formation of the pyrazole derivative. We have now found that hydrazine hydrate and phenylhydrazine react readily with IV (X=S) and V (X=S) giving the corresponding hydrazones and phenylhydrazones IV (X=N-NH$_2$ & or N-NHPh) and V (X=N-NH$_2$ & or N-NHPh) without affecting the -1-thia-4-pyrone ring. The hydrazone IV (X=N-NH$_2$) was characterised by giving N,N'-hydrazine derivatives VI and VII with salicylaldehyde and cis-2,6-diphenyl-1-thia-4-pyranone[7], respectively.



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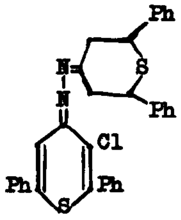
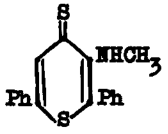


(VII)



(VIII)

When 2,6-diphenyl-3-chloro-1-thia-4-thiopyrone IV (X=S) was reacted with 33% methylamine in ethanol, we did not obtain the expected anil but isolated 2,6-diphenyl-3-(methylamino)-1-thia-4-thiopyrone (VIII) in 85% yield . Using 25% dimethylamine instead of methylamine, IV (X=S) was hydrolysed on prolonged boiling to the oxo-analogue IV (X=O).

The following table shows a list of the correctly analysed compounds and their physical properties. Spectroscopic data of these compounds will be discussed in a subsequent publication.

TABLE.

Compound	D	Shape and colour	Melting point
I (X=O)	B	Needles	181-182°
I (X=N.OH)	B	"	184-185°
II (X=O)	B-L	Aggregate prisms	214-215°(decomp.)
II (X=N.OH)	M	Needles	254-255°(decomp.)
III (X=O) picrate	M	Yellow needles	171°(decomp.)
III (X=N.OH)picrate	M	" "	199°(decomp.)
IV† (X=S)	B-L	Brown needles	170°
IV* (X=N.OH)	B-M	Yellow needles	239°(decomp.)
IV (X=N-NH_2)	B-L	" "	168°
IV (X=N-NHPh)	M	Orange needles	170°(decomp.)
V (X=O)	E	Needles	186-187°
V (X=S)	B-M	Green plates	204°
V (X=N.OH)	B	Needles	183°(decomp.)
V (X=N-NH_2)	B-L	Pale yellow needles	168°
V (X=N-NHPh)	B-L	Yellow needles	173°(decomp.)
VI	B-M	" "	180-181°
VII	B-M	" "	210°
VIII	B-L	Brick-red needles	197-198°

B = Benzene ; D = Solvent of crystallisation ; E = Ethyl acetate ; L = Light petroleum (b.p. 50-70°) ; M = Methanol ; † = Recorded m.p. 155°(Ref. 4) ; * = Recorded m.p. 167°(Ref. 5).

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