

HETEROCYCLES IN ORGANIC SYNTHESIS. PART V¹. A SYNTHESIS OF
2,5-DIARYL-1,4-DITHIINS

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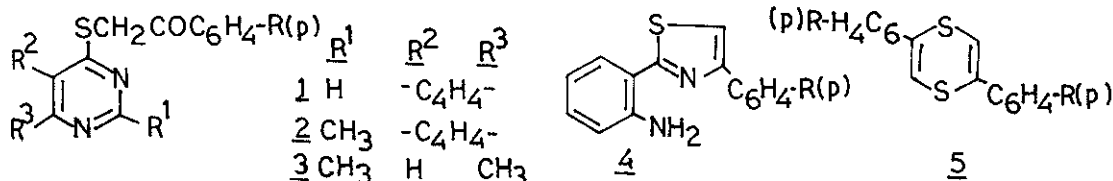
Abstract : ω -(2-Methyl-4-quinazolinylthio or 2,6-dimethyl-4-pyrimidinylthio or 4-oxo-2-quinazolinylthio) acetophenones on treatment with hydrochloric or perchloric acid provide 2,5-diaryl-1,4-dithiins.

Activating and leaving group properties of heterocycles in appropriate precursors have been used for *in situ* generation and intramolecular cyclisation of bifunctionalised organic intermediates and these operations constitute a methodology of immense synthetic consequence.² Here ω -(2-methyl-4-quinazolinylthio or 2,6-dimethyl-4-pyrimidinylthio or 4-oxo-2-quinazolinylthio) acetophenones with aqueous acids have furnished 2,5-diaryl-1,4-dithiins evidently through the generation and intermolecular condensation of bifunctionalised species, ω -mercaptoacetophenones.

ω -(4-Quinazolinylthio) acetophenones **1** on heating with hydrochloric or perchloric acid furnish 2-(o-aminophenyl) thiazoles **4**.³ But ω -(2-methyl-4-quinazolinylthio)-acetophenones **2** (R=H), formed from 2-methylquinazolin-4(3H)-thione and phenacyl bromide, on a similar reaction, gave two products. The product, m.p. 110-112°C, M⁺, m/e 268, analysed for C₁₆H₁₂S₂. From its n.m.r. signals at δ 6.52 (s, 2H, =C-H), 7.30-7.55 (m, 10H, ArH) and the absence of carbonyl absorption band in the i.r. spectrum, the compound was assigned the structure 2,5-diaryl-1,4-dithiin **5** (R=H).⁴ The second product was found to be 2-methylquinazolin-4(3H)-one. Likewise ω -(2-methyl-4-quinazolinylthio) acetophenones **2** (R=CH₃, OCH₃) gave the corresponding **5** (R=CH₃, OCH₃) (Table).

Thus the lack of quinazolinyl C-2 hydrolytic extrusion in ω -(2-methyl-4-quinazolinylthio) acetophenones **2**, probably because of steric hindrance at C-2 for attack of water, results in an alternate hydrolytic nucleophilic substitution of thioacetophenone side chains to form mercaptoacetophenones which through bimolecular condensation provide **5**.

ω -(4-Oxo-6-methyl-2-pyrimidinyl thio)acetophenones with aq. acid have been reported to provide 5 ($R=H, CH_3$)⁵. It has been found that analogous quinoxaline derivatives, ω -(4-oxo-2-quinoxalinyll thio)acetophenones on similar reaction provide 5 ($R=H, Cl, CH_3, OCH_3, Br$) (Table) and quinoxalin-2,4(1H,3H)-dione.



ω -(2-Pyridyl thio)acetophenone in conc. hydrochloric acid remains unchanged, indicating that under acidic conditions, quinoxalinones are better leaving groups than pyridones. In order to investigate the generality of this character of diazinones, ω -(2,6-dimethyl-4-pyrimidinyl thio)acetophenones 3 ($R=H, CH_3, OCH_3, Cl, Br$) have been heated in conc. hydrochloric or perchloric acid and corresponding 5 (Table) along with 2,6-dimethylpyrimidin-4(3H)-one are formed.

TABLE : 2,5-Diaryl-1,4-dithiins 5

Compound * (<u>5</u>)	Yield (%)			m.p. (°C)	Lit ⁶ m.p. (°C)
	a	b	c		
$R=H$	55	55	50	110-12	116-17
$R=CH_3$	65	45	45	136-37	136-37
$R=OCH_3$	60	50	45	131-34	136-37
$R=Br$	65	-	60	153-55	159-60
$R=Cl$	60	-	55	152-53	150-51

* All these compounds gave satisfactory spectral/elemental analysis and a,b,c correspond to the yields obtained from the reactions of ω -(4-oxo-2-quinoxalinyll thio)acetophenones, 2 and 3 respectively.

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- 4 On repeating the reaction of 1 ($R=H$) with conc. hydrochloric or perchloric acid, 5 ($R=H$) (10%) was found to be formed along with 4.
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