HETEROCYCLES, Vol. 20, No. 6, 1983

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

Harjit Singh*, Sunil K. Aggarwal and Nageshwar Malhotra
Department of Chemistry, Guru Nanak Dev University,
Amritsar - 143 005, India

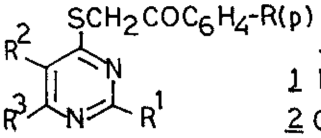
Abstract : ω-(2-Methyl-4-quinazolinylthio or 2,6-dimethyl-4-pyrimidinylthio or 4-oxo-2-quinazolinylthio)acetophenones on treatment with hydrochloric or perchloric acid provide 2,5-diaryl-1,4-dithiins.

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.

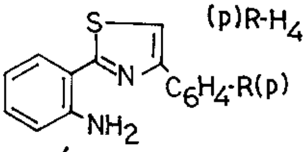
ω-(4-Quinazolinylthio)acetophenones 1 on heating with hydrochloric or perchloric acid furnish 2-(o-aminophenyl)thiazoles 4.[3] But ω-(2-methyl-4-quinazolinylthio)-acetophenones 2(R=H), formed from 2-methylquinazolin-4(3H)-thione and phenacyl bromide, on a similar reaction, gave two products. The product, m.p. 110-112°C, $M^{+\cdot}$, m/e 268, analysed for $C_{16}H_{12}S_2$. From its n.m.r. signals at δ6.52 (s, 2H, =$\overset{|}{C}$-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=CH_3, OCH_3) gave the corresponding 5(R=CH_3,OCH_3) (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.

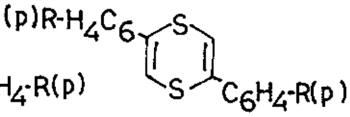
ω-(4-Oxo-6-methyl-2-pyrimidinylthio)acetophenones with aq. acid have been reported to provide 5 ($R=H, CH_3$)[5]. It has been found that analogous quinazoline derivatives, ω-(4-oxo-2-quinazolinylthio)acetophenones on similar reaction provide 5 ($R=H, Cl, CH_3, OCH_3, Br$) (Table) and quinazolin-2,4(1H,3H)-dione.



	R^1	R^2	R^3
1	H	$-C_4H_4-$	
2	CH_3	$-C_4H_4-$	
3	CH_3	H	CH_3



4



5

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

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

Compound*(5)	Yield(%) a	Yield(%) b	Yield(%) c	m.p. (°C)	Lit[6] m.p. (°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-quinazolinylthio)acetophenones, 2 and 3 respectively.

ACKNOWLEDGEMENT : We thank C.S.I.R., India for financial assistance.

REFERENCES

1 H. Singh, P. Singh, and K. Deep, Chem. & Ind., 1981, 252.

2 E.J. Corey and K.C. Nicolaou, J. Am. Chem. Soc., 1974, 96, 5614

3 H. Singh, C.S. Gandhi, and M.S. Bal, Heterocycles, 1980, 14, 3; Indian J. Chem; 1981, 20B, 17.

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.

5 T.B. Johnson, R.C. Moran, and E.F. Kohmann, J. Am. Chem. Soc., 1913, 35, 447.

6 C.M. Buess, V.O. Brandt, R.C. Srivastava, and W.R. Carper, J. Het. Chem., 1972, 9, 887.

Received, 7th January, 1983