FACILE OXIDATION OF 2-OXO-1,4,6-TRISUBSTITUTED 1,2,3,6-TETRAHYDROPYRIMIDINES WITH CHLORANIL

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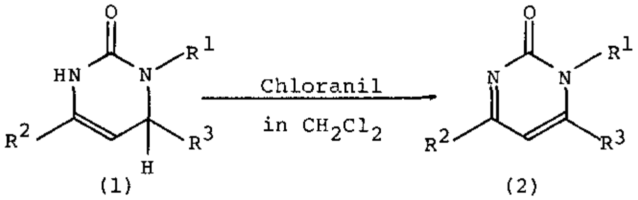
Abstract 2-Oxo-1,4,6-trisubstituted 1,2,3,6-tetrahydropyrimidines (**1a**-**1h**) were easily oxidized with 2,3,5,6-tetrachloro-1,4-benzoquinone(chloranil) to afford the corresponding 1,4,6-trisubstituted 2(1H)-pyrimidinones (**2**) in good yields.

2(1H)-Pyrimidinones have been supplied by the reaction of ureas with acetylacetone1), the condensation of acetylenic ketones with ureas2), the reaction of diimines with ethyl chloroformate.3) However, the only two attempts to prepare 2(1H)-pyrimidinones by oxidation of 2-oxo-tetrahydropyrimidines with potassium permanganate and manganese dioxide were carried out by Hardtmann4) and Coppola5), respectively, to the best of our knowledge.

In this paper, we wish to report on the reaction of 2-oxo-1,4,6-trisubstituted 1,2,3,6-tetrahydropyrimidines with various oxidizing agents. 2-Oxo-1,4,6-trisubstituted 1,2,3,6-tetrahydropyrimidines (**1**) were prepared from the reduction of 1,4,6-trisubstituted 2(1H)-pyrimidinones (**2**) with sodium borohydride in the presence of trimethyl borate. 2-Oxo-1-phenyl-4,6-dimethyl-1,2,3,6-tetrahydropyrimidine (**1a**) was treated with manganese dioxide or potassium ferricyanide to recover the starting material. Further, we tried oxidation of **1a** with potassium permanganate or potassium permanganate in the presence of phase transfer catalysis, $PhCH_2\overset{+}{N}Et_3Cl^-$, to give intractable mixture in both cases. On the contrary, **1a** was smoothly oxidized with chloranil to afford the corresponding 1-phenyl-4,6-dimethyl-2(1H)-pyrimidinone (**2a**) in 96% yield. The oxidation was carried out as follows. Chloranil (1.2 mmol) was added to the solution of 2-oxo-tetrahydropyrimidine (**1a**, 1 mmol) in dichloromethane (20 ml). The mixture was stirred for an hour at room temperature and the yield was determined by lpc. The oxidation of other 2-oxo-tetrahydropyrimidines (**1b**-**1h**) was

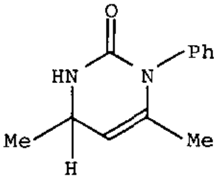
Table 1



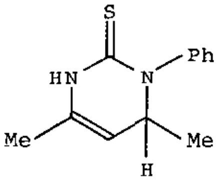
(1) (2)

	R^1	R^2	R^3	Yield(%)*
a	C_6H_5-	CH_3-	CH_3-	96
b	p-$CH_3C_6H_4$-	CH_3-	CH_3-	94
c	m-$CH_3OC_6H_4$-	CH_3-	CH_3-	98
d	m-ClC_6H_4-	CH_3-	CH_3-	92
e	m-$CH_3C_6H_4$-	CH_3-	CH_3-	96
f	C_6H_5-	C_6H_5-	CH_3-	99
g	C_6H_5-	CH_3-	C_6H_5-	88
h	CH_3-	CH_3-	C_6H_5-	88

*Determined by lpc.



(3)



(4)

performed in the same manner as described above and the yields were summarized in Table 1. 2-Oxo-1-phenyl-4,6-dimethyl-1,2,3,4-tetrahydropyrimidine (3) was also oxidized with chloranil to yield 2(1H)-pyrimidinone (2a), but the oxidation product couldn't be obtained in the case of 2-thioxo-1-phenyl-4,6-dimethyl-1,2,3,6-tetrahydropyrimidine (4).

From these results, we found that 2-oxo-1,4,6-trisubstituted 1,2,3,6-tetrahydropyrimidines were easily oxidized with chloranil in high yields.

References

1) A. Novacek, Collect. Czech. Chem. Comm., 1968, 33, 3919.

2) F. G. Badder, F. H. Al-Hajjar, and N. R. El-Rayyes, J. Heterocyclic Chem., 1978, 15, 105.

3) J. Barluenga, M. Tomas, V. Rubio, and V. Gotor, Chem. Comm., 1979, 675.

4) G. E. Hardtmann and H. Ott, U.S.P. 3,663,698 (1972).

5) G. M. Coppola, J. D. Fraser, G. E. Hardtmann, B. S. Huegi, and F. G. Kathawala, J. Heterocyclic Chem., 1979, 16, 545.

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