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REACTION OF CHROMOUS CHLORIDE WITH 3-NITROFLAVENES. A NOVEL SYNTHESIS OF FLAVONOLS

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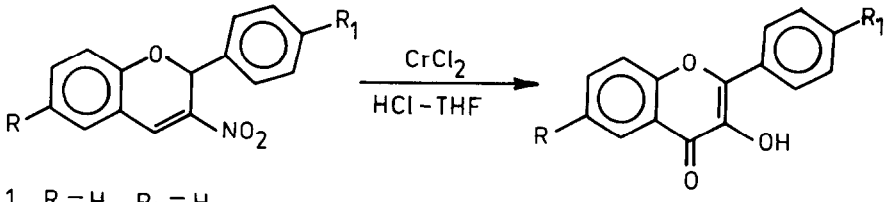
Summary : Reaction of Chromium(II) chloride with 3-nitroflavene yields flavonol.

Chromous chloride is a versatile and very useful reagent for a variety of selective reductions[1,2]. There are very few reports in the literature on the reduction of nitro compounds with chromous chloride[3-6]. We have recently reported a smooth photoconversion of 3-nitroflavene[7] to the corresponding 3-hydroxyflavone[8]. However chemical conversion of similar type is hitherto unknown. Thus it was decided to explore the behaviour of chromous chloride towards 3-nitroflavene in view of chromous chloride catalysed transformation of steroidal nitro olefins to α-hydroxy oximes[3]. We now report the reaction of 3-nitroflavenes (1-4) with chromous chloride to give flavonols (5-8) in high yields.



1. R = H , R_1 = H
2. R = H , R_1 = OMe
3. R = OMe , R_1 = Me
4. R = OMe , R_1 = OMe

5. R = H , R_1 = H
6. R = H , R_1 = OMe
7. R = OMe , R_1 = Me
8. R = OMe , R_1 = OMe

In a typical reaction, to a solution of 3-nitroflavene (2 mmol) in tetrahydrofuran (15 ml) chromous chloride solution[1] (80 ml) was added under nitrogen atmosphere at ambient temperature and the reaction mixture was left at this temperature for 8-10 min. Little work up and chromatography over silica gel afforded the flavonol in 60-65% yield. Further purification was achieved by crystallization from methanol. The identity of the reported compounds were established by comparing with authentic samples prepared by unambiguous methods[8,9] spectral and analytical data.

However the mechanistic details of this reaction are not known. Further work on this novel reaction is in progress.

References

1. M. Fieser, L. F. Fieser, Reagents for Organic Synthesis, Vol.1, John Wiley and Sons, Inc., New York, 1967, p.149.
2. J. R. Hanson, Synthesis, 1974, 1.
3. J. R. Hanson, E. Premuzic, Tetrahedron Lett. 1966, 5441, Tetrahedron, 1967, 23, 4105.
4. J. R. Hanson, J. D. Organ, J. Chem. Soc. (C), 1970, 1182.
5. Yasuo Akita, Mihoko Inaba, Hisako Uchida, Akihiro Ohta, Synthesis, 1977, 792.
6. S. S. Ranganathan, B. B. Singh, J. Chem. Soc. (D), 1970, 218.
7. T. Sakakibara, M. Koezuka, R. Sudoh, Bull. Chem. Soc. Japan, 1978, 51, 3095.
8. T. Sudhakar Rao, A. K. Singh, G. K. Trivedi, Heterocycles, 1984, 22, 1377.
9. T. Sudhakar Rao, S. R. Deshpande, H. H. Mathur, G. K. Trivedi, Heterocycles, 1984 (in press).

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