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A Selective Synthesis of 3,5-Diphenyl-1,2,4-Oxadiazole by a Reaction of Bezylcobaloxime with Alkyl Nitrite

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Benzyl ligand of Benzylbis(dimethylglyoximato)pyridine cobalt complexe was selectively converted to 3,5-diphenyl-1,2,4-oxadiazole by a reaction with alkyl nitrite under irradiation of visible light. The reaction proceeds via an in situ formation of an oxime and a nitrile oxide.

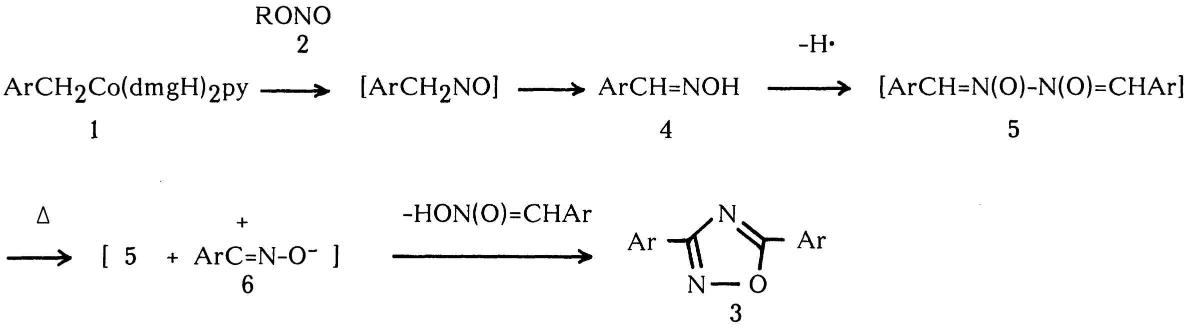
Alkylbis(dimethylglyoximato)cobalt complexes, cobaloximes, are not only a vitamin B_{12} model1) but also useful radical trapping and alkyl radical generating reagents.2) The selective and mild transformation of the alkyl ligand by the homolytic manner has been noted in connection with organic syntheses.3) We have reported4,5) some reactions of alkylcobaloxime with organic and inorganic compounds under irradiation conditions to investigate the reactivity of the photoactivated alkylcobaloximes. Nitrogen oxides are reactive gases but are scarcely used in synthetical applications.6) In the case of the reaction of alkylcobaloxime with nitrogen monoxide (NO),5) it had been demonstrated that the selectivity for the formation of the products between the oxime and the alkyl nitrate was controlled by the nature of its alkyl ligand and the reaction conditions.

In this paper, we investigate the reaction of cobaloximes having a benzylic ligand with alkyl nitrite as a NO precursor, demonstrating a direct conversion method of the benzylic ligand to 3,5-diaryl-1,2,4-oxadiazoles.

Benzylbis(dimethylglyoximato)pyridine cobalt 1 (100 mM) was reacted with benzyl nitrite 2 (300 mM) in dichloromethane under an irradiation with tungsten lamp (400 W) for 20 h at 35 ° C under an argon atmosphere. After the reaction, the organic products were separated from the reaction mixture on a silica gel column eluting with dichloromethane.

The benzyl ligand of 1 was selectively converted to 3,5-diphenyl-1,2,4-oxadiazole 3 in 57% yield. When the reaction is carried out under the conditions at the lower concentration of 2 (100 mM), benzaldehyde oxime 4 is selectively produced in 42% yield. By use of alkyl nitrites such as ethyl nitrite other than 2, both the yield and the selctivity for the formation of the oxadiazole are decreased. The irradiation accelerates the proceeding of this reaction. Nitrosylcobaloxime and chlorocobaloxime were isolated after the reaction. In addition, other alkylcobaloximes such as p-tolylmethylcobaloxime and 1-naphthylmethylcobaloxime can be converted to corresponding 3,5-diaryl-1,2,4-oxadiazoles in ∿ 50% yields.

A proposed reaction course is summarized in Scheme 1. In the first step of this reaction, the photoactivated benzylcobaloxime 1 is reacted with alkyl nitrite 2, giving oxime 4 as well as the reaction with NO.5) The hydrogen abstraction of 4 by a radical species such as an alkoxyl radical or NO is succesively occurred, forming benzaldehyde azine N,N'-dioxide 5 which partially decomposed to benzonitrile oxide 6. The dipolar cycloaddition of 5 with 6 gives oxadiazole 3 as suggested in the previous report.7)



Scheme 1.

In confirmation of above reaction course, oxime 4 was reacted with nitrite 2, giving oxadiazole 3 in 70% yield. In addition, cobaloxime 1 was reacted with 2 in the presence of phenylacetylene as a dipolarophile, giving 3,4-diphenyl-isoxazole (12%) and 3,5-diphenyl-isoxazole (12%) besides 3 (34%), which suggests the in situ formation of nitrile oxide 6.

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