CHEMISTRY LETTERS, pp. 201-204, 1973. Published by the Chemical Society of Japan

CHEMISTRY OF NITROSOIMINES. IV.[1] REACTIONS OF 3-SUBSTITUTED 2-NITROSOIMINO-2,3-DIHYDROBENZOTHIAZOLES WITH GRIGNARD REAGENTS

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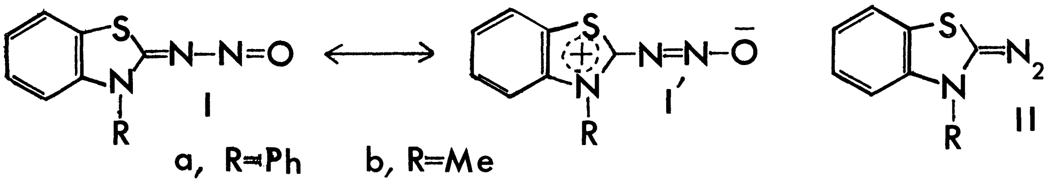
Reactions of 3-substituted 2-nitrosoimino-2,3-dihydrobenzothiazoles (I) with Grignard reagents gave three kinds of major products depending on the structure of Grignard reagents: the corresponding 2,2-diaryl compounds with arylmagnesium bromides by extrusion of nitrosoimino group, 2-monosubstituted compounds with bulky Grignard reagents, and 2-benzylidenehydrazono derivative with benzylmagnesium chloride, respectively.

Nitrosoimines are usually unstable,[1,2] but the nitrosoimines such as 3-substituted 2-nitrosoimino-2,3-dihydrobenzothiazoles (I)[3] are stabilized by a large contribution of a resonance structure (I').[1a]

In a series of investigation on the nitrosoimines, we have tried the reduction of I with lithium aluminum hydride, expecting to prepare the diazo compound (II). The results have shown that the nucleophilic attack by hydride ion occurred at the C_2 position and at the nitrogen atom of the nitroso group.[4] Similar type of reaction of I is expected with other nucleophiles.

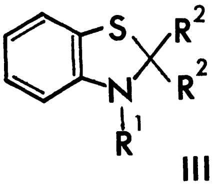
This paper describes the selective reaction of I with Grignard reagents, which strongly depends on the structure of Grignard reagents.



a, R=Ph b, R=Me

Ia (0.03 mol) was added portionwise to an ice-cooled ethereal solution (150 ml) of phenylmagnesium bromide (0.15 mol) with stirring under nitrogen. The reaction took place exothermally with vigorous evolution of gas. Stirring was continued at room temperature for further 2-3 hr after the addition. Products were separated by column chromatography on silica gel after usual work-up. 2,2,3-Triphenyl-2,3-dihydrobenzothiazole$^{5)}$ (IIIa; 48%, mp 191.5-192.5°C) and 3-phenyl-2-phenylhydrazono-2,3-dihydrobenzothiazole (IVa; 17%, mp 157-158°C) were eluted as major products with benzene and CH_2Cl_2-$CHCl_3$ (1:1), respectively.

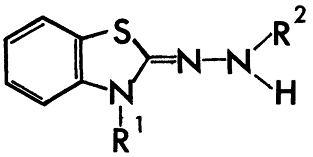
Similar reaction of p-tolylmagnesium bromide with Ib gave IIIb (66%, mp 141.0-141.5°C) and IVb (12%, mp 155.0-156.5°C).



III

a, $R^1=R^2=Ph$

b, $R^1=Me$ $R^2=p\text{-}MeC_6H_4$



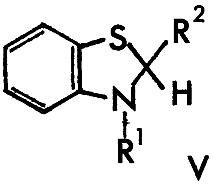
IV

a, $R^1=R^2=Ph$

b, $R^1=Me$ $R^2=p\text{-}MeC_6H_4$

c, $R^1=Ph$ $R^2=t\text{-}Bu$

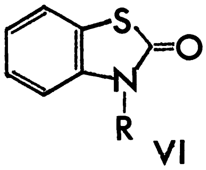
d, $R^1=Me$ $R^2=Me_3C_6H_2$



V

a, $R^1=Ph$ $R^2=t\text{-}Bu$

b, $R^1=Me$ $R^2=Me_3C_6H_2$



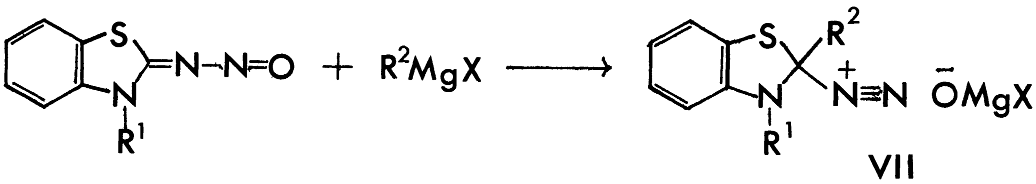
VI

a, R=Ph

b, R=Me

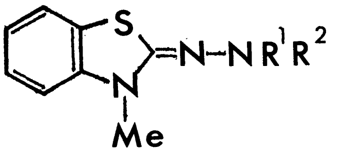
Reaction of bulky t-butylmagnesium chloride with Ia gave Va (50%, mp 61-62 °C), in which only one t-butyl group was introduced on the C_2 position because of steric hindrance, IVc (15%, mp 161.0-162.0°C) and the thiazolone (VIa; 22%, mp 76-77°C). Reaction of mesitylmagnesium bromide with Ib gave an analogous result and the yields of Vb (mp 222.0-223.5°C), IVd (mp 152.0-154.5°C) and VIb (mp 76-77°C) were 46, 18 and 10%, respectively.

The formation of III and V probably involves a diazonium compound (VII) as an intermediate. In the case of t-butylmagnesium chloride, the gas evolved was identified as nitrogen by means of mass spectrometry and the amount of nitrogen was equivalent to that of the sum of Va and VIa. This fact supports the intermediacy of the diazonium compound (VII).



VII

On the other hand, reaction of benzylmagnesium chloride with Ib under the same conditions gave azine (VIII[3b]; 44%, mp 162.0-163.0°C) and hydrazone (IX; 19%, mp 116.5-117.5°C); no compound which corresponds to III or V was obtained in this case.



VIII R^1R^2=PhCH=

IX R^1=R^2=$PhCH_2$

The structure of known compounds was confirmed by the melting points and spectral data, and all new compounds were identified by the elemental analyses and spectral data.

It is noteworthy to mention that arylmagnesium bromide and bulky Grignard reagents react mainly at the C_2 position, while benzylmagnesium chloride does exclusively at the nitrogen atom of the nitroso group. The substitution on the C_2 position of I with bulky Grignard reagents and arylmagnesium bromides is useful as a preparative method of 2-monosubstituted and 2,2-disubstituted 2,3-dihydr benzothiazoles, respectively, for the sake of fairly good yields of the products.

References

1) For preceding papers of this series, see: a) K. Akiba, I. Fukawa, N. Nomura, and N. Inamoto, Bull. Chem. Soc. Japan, 45, 1867 (1972). b) K. Akiba and N. Inamoto, Chem. Commun., 1973, in press.

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3) a) H. Passing, J. Prakt. Chem., 153, 1 (1939). b) E. Besthorn, Ber., 43, 1519 (1910).

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5) For the syntheses of analogous compounds, see: H. Larive, A. J. Chambonnet, and J. Metzger, Bull. Soc. Chim. Fr., 1963, 1675.

(Received December 26, 1972)