## Effect of the conditions of the formation of the crystalline phase of 1-hydroxy-5,5-dimethyl-2,4-diphenyl-3-imidazoline-3-oxide on the direction of its reaction with phenyllithium

V. A. Reznikov\* and L. B. Volodarsky

Novosibirsk Institute of Organic Chemistry, Siberian Branch of the Russian Academy of Sciences, 9 prosp. Acad. Lavrent'eva, 630090 Novosibirsk, Russian Federation. Fax: +7 (383 2) 354 752

The course of the heterogeneous reaction of 1-hydroxy-5,5-dimethyl-2,4-diphenyl-3imidazoline 3-oxide with PhLi is dependent on the conditions of the formation of the crystalline phase of the starting compound. This compound can be isolated mainly in the cyclic or in the chain tautomeric forms.

Key words: 3-imidazoline 3-oxide, ring-chain tautomerism.

We have shown previously<sup>1</sup> that the reaction of imidazoline (1) with PhLi yields acyclic hydroxylamino oxime (2). This is due to the fact that solid 1 exists as the acyclic tautomer 1b (cf. Ref. 2), as evidenced by the fact that the reaction with PhLi is virtually heterogeneous. When we attempted to reproduce this reaction with another specimen of the same compound 1, it unexpectedly gave 2-imidazoline (3) in 80 % yield, instead of compound 2, i.e., judging from the structure of the reaction product, this specimen of the starting compound 1 existed as the cyclic tautomer 1a. According to the literature data, compound 1 exists in DMSO only in the acyclic tautomeric form 1b (see Ref. 3), whereas in an ethanolic solution, both tautomeric forms are observed.<sup>2</sup> Therefore, one may believe that compound 1 can exist either in the cyclic form or in the open form depending on the conditions under which its crystalline phase formed.

In the study of the reactions of various specimens of compound 1 with PhLi under identical conditions we showed that the direction of this reaction is actually considerably dependent on the conditions of the preliminary treatment of the starting compound. For example, when the reaction is carried out with compound 1 recrystallized from ethanol (specimen a), acyclic hydroxylamino oxime 2 is practically the only reaction product. The reactions with 1 recrystallized from ethyl acetate (specimen b) or prepared by reprecipitation from dimethyl sulfoxide by water (specimen c) afford approximately equal amounts of compounds 2 and 3; and when the reaction is carried out with the material prepared by water (specimen d), cyclic compound 3 is almost the



only product. Thus, one may argue that recrystallization of compound 1 can lead to a change in the tautomeric composition of the starting compound and, as a consequence, to a change in the direction of its reaction with PhLi.

The IR spectra of specimens b-d in KBr are similar, and, therefore, they cannot be used for quantitative evaluation of the ratio between the tautomeric forms. The IR spectrum of specimen *a* contains the same bands as those of specimens b-d, however, their intensities are different. The most characteristic is the region in which the bands corresponding to the vibrations of the multiple bonds of the phenylnitrone group are manifested. For

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example, the IR spectrum of specimen *a* exhibits a set of bands at 1587, 1575<sup>\*</sup>,<sup>1</sup> 1565, and 1500 cm<sup>-1</sup> in this region, and the spectrum of specimen *b* contains the bands at 1587, 1570, and 1545<sup>\*</sup> cm<sup>-1</sup>. The IR spectra of CHCl<sub>3</sub> solutions of all of the specimens are identical. The melting points of the specimens of 1 also cannot indicate their tautomeric composition, since there is no correlation between the melting points and the ratio between the reaction products. This may be due to the fact that the tautomeric composition of the substance can change at the instant of melting. The melting points vary from 189–193 °C (*a*) to 202–203 °C (*b*) depending on the procedure of the preparation.

It should be noted that the reaction of any of specimens a-d with an excess of phenylmagnesium bromide affords acyclic hydroxylamino oxime 2 in  $\approx 75$  % yield. Under these conditions, the reaction occurs somewhat more slowly, which is probably results in the change in the tautomeric composition of the deprotonated form of the starting compound and is caused by the fact that the selectivity of PhMgBr toward phenylketonitrone group of form **1a** and phenylaldonitrone group of form **1b** is higher than that of PhLi.

Thus, by varying the nature of the reactant or the conditions under which the crystalline phase of compound 1 forms, one can direct the addition of an organometallic compound at the formation of either 2-imidazoline 3 or acyclic hydroxylamino oxime 2.

## Experimental

IR spectra were recorded on a Specord M-80 spectrometer in KBr pellets (the concentration was 0.25 %) and CHCl<sub>3</sub> solutions (at a concentration of 5 %). Compound **1** was prepared by the known procedure.<sup>2</sup> Specimen *a* was prepared by recrystallization from ethanol, m.p. 190–193 °C, *b* was obtained by recrystallization from ethyl acetate, m.p. 202–203 °C, *c* was obtained by reprecipitation from dimethyl sulfoxide by water, m.p. 195–197 °C, and *d* was prepared by reprecipitation from ethanol by water; a part of this material melts at 183 °C and the rest melts at 193–195 °C (*cf.* Ref. 2: m.p. 162–164 °C (from ethanol)). Compounds **2** and **3** were identified by a comparison with authentic samples synthesized according to the previously reported procedure.<sup>1,4</sup>

Reaction of 3-imidazoline 3-oxide (1) with phenyllithium (cf. Ref. 1). Imidazoline 1 (1.7 g, 6 mmol) was added portionwise over a period of 15 min to a stirred solution of phenyllithium prepared from phenyl bromide (3.2 mL, 15 mmol) and lithium (0.42 g, 30 mmol) in 30 mL of anhydrous ether. The reaction was carried out in an argon atmosphere. The mixture was stirred for 30 min at 20 °C, and 20 mL of water was added. In the case of specimen a, the organic phase was separated and the aqueous phase was extracted with ether (2×20 mL). The combined extract was dried with MgSO<sub>4</sub>, the solvent was evaporated, the residue was washed with hexane, and the precipitate of hydroxylamino oxime 2 was filtered off. Yield 1.73 g (80 %), m.p. 139-141 °C (from a hexane-ethyl acetate, see Ref. 1: m.p. 139-141 °C). In the case of specimens b-d, the precipitate of imidazoline 3 was washed with water and dried. The yield of 3 was  $\approx 0.8$  g (40 %, specimens b and c) or 1.65 g (80 %, specimen d), m.p. 218-219 °C (from a heptane-ethyl acetate mixture, 1 : 1, see Ref. 4: 218-219 °C). The filtrate (for b and c) was extracted with ether, and the extract was dried with MgSO4 and concentrated. The residue was washed with 5 mL of hexane, and the precipitate of hydroxylamino oxime 2 was filtered off, yield  $\approx 0.7$  g (33 %).

Reaction of 3-imidazoline 3-oxide (1) with phenylmagnesium bromide. Imidazoline 1 (specimen a-d) (1.7 g, 6 mmol) was added portionwise over a period of 15 min to a stirred solution of phenylmagnesium bromide prepared from phenyl bromide (2.5 mL, 24 mmol) and magnesium (0.58 g, 24 mmol). The mixture was stirred for 3 h at 20 °C, and 15 mL of a 10% aqueous solution of NH<sub>4</sub>Cl was added to it. The organic phase was separated, and the aqueous phase was extracted with ether (2×20 mL). The combined extract was dried with MgSO<sub>4</sub>, the solvent was evaporated, the residue was washed with hexane, and the precipitate of hydroxylamino oxime 2 was filtered off. Yield ≈1.6 g (75 %).

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<sup>\*</sup> The most intense band.