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A MECHANISTIC APPROACH TO THE PHOTO-AMINATION OF CYCLOHEXANE WITH HYDRAZINE[1]

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Abstract—The UV light-induced amination of cyclohexane with hydrazine in a liquid phase at room temperature has been further studied. In addition to the cyclohexylamine produced, bicyclohexyl and cyclohexylhydrazine were detected as by-products. The presence of bicyclohexyl suggests a radical mechanism for the reaction. In spite of the formation of a small amount of cyclohexylhydrazine in this reaction, cyclohexylamine seems to be produced exclusively by coupling of $\cdot NH_2$ with $\cdot C_6H_{11}$, because no appreciable amount of cyclohexylamine was detected in the photodecomposition products of cyclohexylhydrazine with or without hydrazine under similar conditions used for the photoamination. A probable mechanism is discussed.

THE UV light-induced amination of cyclohexane with hydrazine in a liquid phase at room temperature forming cyclohexylamine in 45% yield under optimum conditions of 0·0103 M hydrazine, 0·0195 M cyclohexane and 40 hr irradiation has been reported previously. One of the by-products was cyclohexanol formed by the oxidation with dissolved oxygen.

The photodecomposition of hydrazine forming ammonia, hydrogen and nitrogen[3] has been explained by either the N–N[4] or N–H bond fission[5] in the primary process.

[N–N fission]

$$H_2N\text{–}NH_2 \overset{h\nu}{\rightleftarrows} H_2N\text{–}NH_2^* \longrightarrow 2\cdot NH_2 \tag{1}$$

$$\cdot NH_2 + H_2N\text{–}NH_2 \longrightarrow NH_3 + N_2 + H_2 + \cdot H \tag{2}$$

$$H\cdot + H_2N\text{–}NH_2 \longrightarrow \cdot NH_2 + NH_3 \tag{3}$$

[N–H fission]

$$H\text{–}NHNH_2 \longrightarrow H\cdot + \cdot NHNH_2 \tag{4}$$

$$H\cdot + H\text{–}NHNH_2 \longrightarrow \cdot NHNH_2 + H_2 \tag{5}$$

$$2\cdot NHNH_2 \longrightarrow 2NH_3 + N_2 \tag{6}$$

$$2\cdot NHNH_2 \longrightarrow N_2 + H_2 + H_2NNH_2 \tag{7}$$

Consequently, it is probable that the present photoamination with hydrazine is also initiated by an analogous process. Therefore, in the initial cleavage of the N–N bond, cyclohexylamine may be formed directly by coupling of amino and cyclohexyl

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radicals. On the other hand, in the initial cleavage of the N–H bond, the disproportionation of cyclohexylhydrazyl radical, $C_6H_{11}NHNH$; to cyclohexylamine (similar to Eq. 6) may be important.

The present paper describes the detection of by-products formed in the photoamination of cyclohexane with hydrazine.

RESULTS AND DISCUSSION

Bicyclohexyl was detected by means of gas chromatography as the main by-product in the high boiling fraction of the reaction products indicating a radical nature of the photoamination.

If the reaction is initiated by the N–H bond fission, cyclohexylhydrazine should be one of the products and it was detected by TLC after 20 hr, although the detection by gas chromatography failed probably because of its instability at high temperature.

In order to obtain evidence for the photodecomposition of cyclohexylhydrazine forming cyclohexylamine, the photolysis of cyclohexylhydrazine in t-butanol with and without the addition of hydrazine was carried out. The gas chromatographic analysis of the decomposition products showed that no appreciable amount of cyclohexylamine was produced even after irradiation for 40 hr in the presence of hydrazine whereas cyclohexylhydrazine was almost completely decomposed after 40 hr if no hydrazine was added. It was assumed that photodecomposition was suppressed by the inner-filter effect of hydrazine (0·1 M solution in t-butanol) having absorption band at wavelength below 270 mμ similar to that of cyclohexylhydrazine. No other by-products such as cyclohexene, cyclohexanone, cyclohexanone oxime and dicyclohexylamine were detectable by gas chromatography.

On the basis of these data, it seems reasonable that in the initial step of photodecomposition of hydrazine, only the N–N bond fission is important and that the photoamination in the presence of hydrazine may occur as shown in the following reaction scheme:

$$H_2N\text{-}NH_2 \overset{h\nu}{\rightleftarrows} H_2N\text{-}NH_2^* \longrightarrow 2\cdot NH_2 \tag{1}$$

$$RH + \cdot NH_2 \text{ (or } \cdot NHNH_2 \text{ or other radicals)} \longrightarrow R\cdot + NH_3 \text{ (or } H_2NNH_2 \text{ etc.)} \tag{8}$$

$$R\cdot + \cdot NH_2 \longrightarrow R\text{-}NH_2 \tag{9}$$

The mechanism which involves the preliminary fission of the N–H bond of cyclohexylhydrazine is less probable, since no appreciable amount of cyclohexylamine was detected in the photolysis of cyclohexylhydrazine.

EXPERIMENTAL

Materials. Cyclohexane, hydrazine and t-butanol were purified as previously reported.[5]

Bicyclohexyl was prepared by photochlorination of cyclohexane[6] with UV light (Toshiba SHL-100 UV), b.p. 64·0–66·0°/60 mm, n_D^{25} 1·4598 (lit.[7] n_D^{25} 1·4600); yielding cyclohexyl chloride which was converted to bicyclohexyl by a Würtz reaction in cyclohexane, b.p. 113·0–114·0°/25 mm, n_D^{20} 1·4765 (lit.[8] n_D^{20} 1·4795). The IR spectrum of bicyclohexyl was identical with that in the literature.[8]

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Cyclohexylhydrazine. Cyclohexyl bromide was prepared by the gradual addition of Br_2 to cyclohexane heated under reflux and irradiated with a 100 W Tungsten Lamp, b.p. 71·0–72·0°/33 mm (lit.[9] 71·0–72·0°/32 mm), n_D^{25} 1·4875 (lit.[10] n_D^{25} 1·4917). It was converted into cyclohexylhydrazine by reaction with hydrazine according to a modified Westphal's procedure, b.p. 89·0–91·0°/20 mm (lit.[12] b.p. 75°/11 mm), m.p. of its hydrochloride 108·0–109·5° (lit.[13] 110°). Cyclohexylhydrazine showed IR peaks (KBr disk) at 3340, 1620, 890 and 865 cm^{-1} corresponding to the N–H bond and at 2930, 2860 and 1460 cm^{-1} corresponding to the C–H bond.

The detection of bicyclohexyl. Unreacted cyclohexane and solvent were carefully removed under moderately red. press. and the remaining bicyclohexyl was detected by gas chromatography employing a Yanagimoto Model GCG-220 operated with a 1·0 m × 4 mm stainless steel column packed with silicone DC 550 (30 wt.%) on Celite 545 of 80–100 mesh using He as a carrier gas (54 ml/min) at 152°. A comparison of the retention time for an authentic specimen with that of the sample obtained proved the presence of bicyclohexyl.

The detection of cyclohexylhydrazine. A sample solution was spotted on a chromatoplate (20 cm × 20 cm) spread with Merck silica gel G in a thickness of 0·75 mm. (a) After being developed with MeOH, the chromatoplate was sprayed with 50% H_2SO_4 aq and dried at 100°. The spot corresponding to cyclohexylhydrazine emitted fluorescence by UV light, whereas the spots of other material such as cyclohexylamine, cyclohexanol and hydrazine emitted no fluorescence. The R_f value of cyclohexylhydrazine was 0·12. (b) After being developed with a mixture of MeOH–conc HCl (7:3), the chromatoplate was sprayed with an EtOH solution of 2% picryl chloride and exposed to the vapour of ammonia. A red spot of cyclohexylhydrazine and a blue spot of hydrazine[14] were observed. The R_f value of cyclohexylhydrazine was 0·72. The similarity between the colour and R_f values for the sample and authentic material established its identity.

The photolysis of cyclohexylhydrazine. A solution of 0·05 M cyclohexylhydrazine in t-butanol (30 ml) with and without hydrazine (in a concentration of 0·1 M) was irradiated in a quartz tube (30 × 300 mm) with a rubber stopper using Toshiba UV Lamp (H-400-P) without filter at a distance of 20 cm at room temp. for 20–40 hr. The detection of cyclohexylamine was done by means of gas chromatography as described previously.[3]

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