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## A New Method for the Preparation of Isothiocyanates from Amines Using 1,1'-(Thiocarbonyldioxy)dibenzotriazole

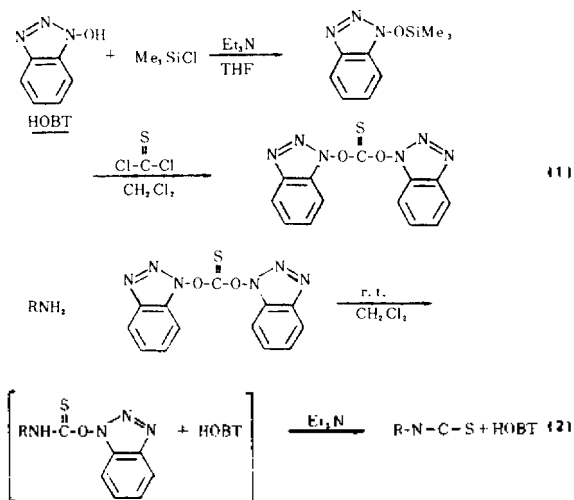
Heung Chang and Sunggak Kim\*

Department of Chemistry, Korea Advanced Institute of Science and Technology, Seoul 131. Received July 1, 1986

As part of our continuous efforts toward the development of new reactive thionocarbonates as condensing reagents and thiocarbonyl transfer reagents,<sup>1</sup> we wish to report the preparation of 1,1'-(thiocarbonyldioxy)dibenzotriazole, its explosive nature, and its use for the preparation of isothiocyanates from amines.

First, the reaction of 1-hydroxybenzotriazole with an equimolar amount of thiophosgene in the presence of 2 equiv of triethylamine or pyridine in methylene chloride at room temperature was tried but no desired product was obtained. However, as shown in eq. 1, 1,1'-(thiocarbonyldioxy)dibenzotriazole was prepared by treatment of 1-trimethylsilyloxybenzotriazole<sup>2</sup> with an equimolar amount of the thiophosgene in methylene chloride at 0°C for 1 h. The reagent was obtained in essentially quantitative yields (90-98%) as a faint yellow crystalline solid.

It is noteworthy that the reagent is violently exploded at 114°C<sup>3</sup> and also we have experienced one violent explosion during the preparation of the reagent.<sup>4</sup> Thus, proper safety precautions should be made to prepare the reagent and to carry out the reactions. Furthermore, the explosive nature of the similar type of the reagent, 1,1'-(carbonyldioxy)dibenzotriazole<sup>5</sup>, has been independently observed by us and others.<sup>6</sup>



Reaction of benzylamine with 1,1'-(thiocarbonyldioxy)dibenzotriazole in methylene chloride at room temperature did not afford benzyl isothiocyanate, presumably yielding

Table 1. Preparation of Isothiocyanates from Amines<sup>a</sup>

Amine	Time, min	Yield, % <sup>b,c</sup>
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> NH <sub>2</sub>	5	88
CH <sub>3</sub> CH <sub>2</sub> CH(NH <sub>2</sub> )CH <sub>3</sub>	10	89
(CH <sub>3</sub> ) <sub>2</sub> CNH <sub>2</sub>	45	84
CH <sub>2</sub> =CHCH <sub>2</sub> NH <sub>2</sub>	5	86
c-c <sub>6</sub> H <sub>11</sub> NH <sub>2</sub> <sup>c</sup>	10	95
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> NH <sub>2</sub>	5	93
C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	5	95
p-Cl-C <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	5	97
p-CH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	5	84
p-NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	30	93

<sup>a</sup> The reaction was carried out with an equimolar mixture of an amine, triethylamine, and 1,1'-(thiocarbonyldioxy)-benzotriazole in methylene chloride at room temperature. <sup>b</sup> The isolated yields after Kugelrohr distillation or crystallization. <sup>c</sup> c-C<sub>6</sub>H<sub>11</sub> indicates cyclohexyl group. <sup>d</sup> Physical and spectroscopic data of the products were in accord with reported data.

1-benzotriazolyl benzylthiocarbamate.<sup>7</sup> Direct conversion of benzylamine into benzyl isothiocyanate has been achieved by performing the reaction in the presence of 1 equiv of triethylamine in methylene chloride at room temperature or in toluene at 60°C for 3 h without adding triethylamine. The similar behavior has been noted with 1,1'-thiocarbonyldiimidazole.<sup>8</sup> However, it is of interest that the reaction of 1,1'-thiocarbonyldi-1,2,4-triazole with amines affords 1-(alkylthiocarbonyl)-1,2,4-triazole, which shows no tendency to dissociate isothiocyanates and 1,2,4-triazole in refluxing toluene<sup>9</sup> and in the presence of triethylamine in methylene chloride.<sup>10</sup>

The remaining reactions were carried out in the presence of triethylamine in methylene chloride at room temperature due to the explosive nature of the reagent at an elevated temperature. The preparation of isothiocyanates was performed on a variety of structurally different amines to determine the scope and limitations of the present method and the results are summarized in Table 1. In general, the reaction occurred almost instantly at room temperature for most simple alkyl and aryl amines. Relatively unreactive p-nitroaniline and sterically hindered t-butylamine were smoothly converted into the corresponding isothiocyanates in high yields but required

longer reaction times for completion of the reaction.

In conclusion, we feel that the present method, because of its simplicity, effectiveness, and mildness, will complement a number of previously known methods<sup>11</sup> for this conversion but the explosive nature of 1,1'-(thiocarbonyldioxy)dibenzotriazole limits further applications in various functional group conversions. Furthermore, it is highly recommended that the reaction should be carried out by one-pot procedure without the isolation of 1,1'-(thiocarbonyldioxy)dibenzotriazole for the safety purpose.

### References

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2. 1-Trimethylsilyloxybenzotriazole (b.p. 108-110 °C/0.6 mmHg) was prepared in 93% yield from an equimolar mixture of 1-hydroxybenzotriazole, trimethylsilyl chloride, and triethylamine in tetrahydrofuran at 0°C for 1 h.

3. We have observed that the reagent was instantly and violently decomposed in refluxing toluene.
4. Scratching the flask containing the reagent with a spatular caused violent explosions.
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## Electrochemical Behaviour of Dibenzoylmethane on Mercury Film Electrode in Basic Ethanol-Water Solvent

Jung-Kyoon Chon\*

*Department of Chemistry, Hankuk University of Foreign Studies, Seoul 131. Received July 2, 1986*

During the past two decades the electrochemical reduction of  $\beta$ -diketones has received considerable attention,<sup>1-7</sup> not only because of the numerous possibilities for reduction pathways, but also because of the large number of such compounds readily available and hence of potential synthetic use. Previous investigators<sup>1-7</sup> studied the electrochemical reduction of  $\beta$ -diketones by polarographic experiments. These included a study of 1,3-diphenyl-1,3-propanedione (or dibenzoylmethane), a typical symmetrical  $\beta$ -diketone, which was reported to give three different reduction waves under various conditions, thus suggesting at least three types of products and pathways. Evans<sup>4</sup> reported that three polarographic waves were observed and three reduction products of dibenzoylmethane could be obtained on mercury electrodes in slightly basic (pH < 10.0) ethanol-water solution. However, in more basic (pH greater than 10.0) solution the first two waves were fused to form one composite wave since the waves are quite close to one another on the potential axis. And reduction pathways were also proposed that reduction of the keto form of dibenzoylmethane to dimeric products occurred with two electron transfer process under the potential of the composite wave.

In this investigation cyclic voltammetry and kinetic measurements of electrochemical reduction of dibenzoylmethane on mercury film electrodes in basic ethanol-water solutions were made in order to elucidate the mechanism of the reduction reactions.

The mercury film electrodes were prepared by mere dip-

ping of the platinum wire in mercury pool.<sup>8</sup> All of the experiments were performed in ethanol-water (50% by volume) solvent and the potential data given here are referred to the saturated calomel electrode (SCE). Dibenzoylmethane used in this investigation was found to exist almost entirely in the enol form by the measurement of IR and NMR spectra.

The pK<sub>a</sub> value of the dibenzoylmethane was measured to be 10.4 in 50% ethanol-water solution by pH-metric titration. Thus, the enolate form of dibenzoylmethane will be probably dominant over the enol form in the solution that pH is higher than 10.4.

The cyclic voltammograms of dibenzoylmethane in 0.10 M NaOH/ethanol-water solution were obtained and are shown in Figure 1. And the cyclic voltammetric data with various scan rates in unstirred solution are shown in Table 1. There are two reduction waves in both stirred and unstirred solutions, however in the unstirred solution the second reduction wave was decreased with decreasing scan rates.

Furthermore, the current ratio between two reduction waves ( $i_{p2}/i_{p1}$ ) was increased up to 1.0 with increasing scan rates in unstirred solution but the ratio was measured to be nearly 1.0 and unchanged with scan rates in stirred solution. It seems that the two reduction waves are due to two consecutive reduction steps and the second reduction step is occurring with parallel chemical reaction.

When at the potential region of the first reduction wave the radical species is produced by one electron transfer which will be followed by consecutive one electron transfer or coupl-