

213° dec. Recrystallization of a sample from acetonitrile gave pure **3**, mp 212–213° dec.

Anal. Calcd for $C_4H_4N_2OS_3$: N, 14.6; S, 49.9. Found: N, 14.6; S, 49.4.

Hydrolysis of 3.—A mixture of 4.5 g (0.023 mol) of **3**, 10 ml of concentrated HCl, and 20 ml of ethanol was heated to the reflux temperature. The mixture turned homogeneous, but solids deposited on continued reaction at the reflux temperature. After heating for 2.5 hr, the mixture was cooled and filtered. The residue was washed chloride free with water and dried, yield 2.5 g, mp 200° dec. A mixture melting point with an analytical sample of **1** was not depressed. The ir spectrum was identical with that of **1**. Therefore, a 71% yield of isopertthiocyanic acid was recovered.

3-Amino-5-thione-1,2,4-dithiazole Hydrochloride (2).—A mixture of 20.0 g of isopertthiocyanic acid (**1**) and 2 l. of acetonitrile was refluxed for 2 hr and allowed to cool overnight. The mixture was filtered; 5.3 g (0.035 mol) of **1** remained in solution. To the solution, at room temperature, was added HCl gas for 40 min. Solids precipitated which were filtered, washed with acetonitrile, and dried, yield of **2** 3.0 g (46%), mp 190° dec. Attempts to recrystallize **2** regenerated **1**.

Anal. Calcd for $C_2H_3ClN_2S_3$: Cl, 18.9; N, 15.0; S, 51.5. Found: Cl, 18.4; N, 15.2; S, 51.0.

To a solution of 0.08 g (0.01 mol) of sodium bicarbonate in 10 ml of water was added in small portions 0.18 g (0.01 mol) of **2**. Immediate gas evolution occurred, and the mixture was stirred at room temperature for 30 min. The mixture was filtered, and the residue was washed with water and then air-dried to give 0.12 g (80%) of **1**, mp 200° dec. A mixture melting point with an analytical sample of **1** was not depressed. The ir spectra of the two samples of **1** were identical.

N-Phenyl-N'-(5-thione-1,2,4-dithiazyl-3)urea (4).—A mixture of 75.0 g (0.50 mol) of **1** and 59.5 g (0.50 mol) of phenyl isocyanate in 3 l. of dioxane was refluxed for 3.5 hr. After cooling, the mixture was filtered, and the residue was washed with dioxane until the filtrate was colorless. Drying the product at 100° under vacuum gave 105.0 g of a yellow solid, mp 227–229° dec. Recrystallization from dimethylformamide followed by washing the product with ethyl ether gave 61.0 g (45%) of pure **4**, mp 220–221° dec.¹² An additional recrystallization did not change the melting point. Cooling the mother liquor gave an additional 10.0 g (8%) of pure **4**, mp 220–221° dec.

Anal. Calcd for $C_9H_7N_3OS_2$: C, 40.2; H, 2.6; N, 15.6; S, 35.7. Found: C, 40.3; H, 2.7; N, 15.7; S, 35.2.

Registry No.—**1**, 14453-29-3; **2**, 23405-39-2; **3**, 23405-40-5; **4**, 23405-41-6.

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(12) The higher melting point of the crude product is undoubtedly due to the presence of unreacted isopertthiocyanic acid (**1**). Compound **1** melts with decomposition at 202°.

Studies of Organoindium Compounds. The Reaction of Triethylindium with an Excess of Phenyl Isocyanate

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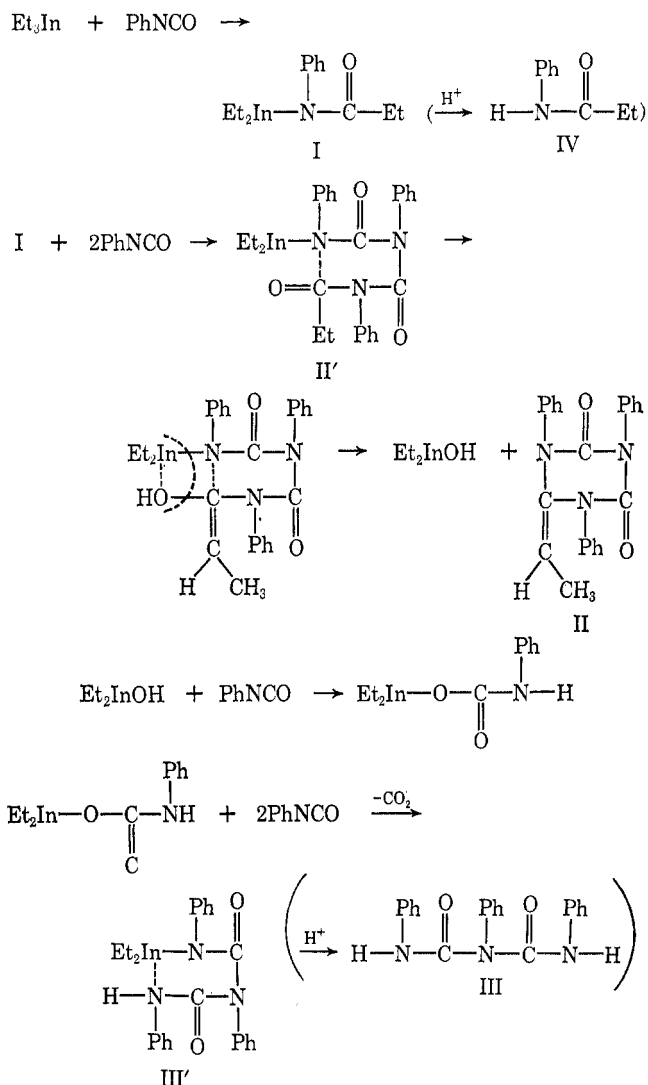
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In a previous paper, we reported the reaction of triethylindium with an equimolar amount of phenyl isocyanate to give N-diethylindium-N-phenylpropionamide (**I**, 89%) and a small amount of unknown compounds.¹

In this paper we describe the reaction of triethylindium with an excess of phenyl isocyanate to give 2,4-dioxo-6-ethylidene-1,3,5-triphenylhexahydro-1,3,5-triazine (**II**), N,N',N''-triphenylbiuret (**III**), N-phenylpropionamide (**IV**), and 2,4-dioxo-6,6-diethyl-1,3,5-triphenylhexahydro-1,3,5-triazine (**V**). Although many organometallic compounds have been known to catalyze the trimerization of isocyanates,² the type of reaction described here has never been observed for other organometallic compounds. The results are shown in Table I and the probable reaction scheme is presented below (Scheme I).

SCHEME I



In the reaction of triethylindium and phenyl isocyanate in a 1:3 molar ratio, the yields of **II** and **III** were low and that of **IV** was moderate, but, in the case of a 1:6.3 molar ratio, the yields of **II** and **III** increased and that of **IV** decreased remarkably. These changes in the yield of products with different molar ratios can be reasonably explained by assuming that **I** is formed at first and is then consumed by the successive insertion of

(1) H. Tada, K. Yasuda, and R. Okawara, *J. Organometal. Chem.*, **16**, 215 (1969).

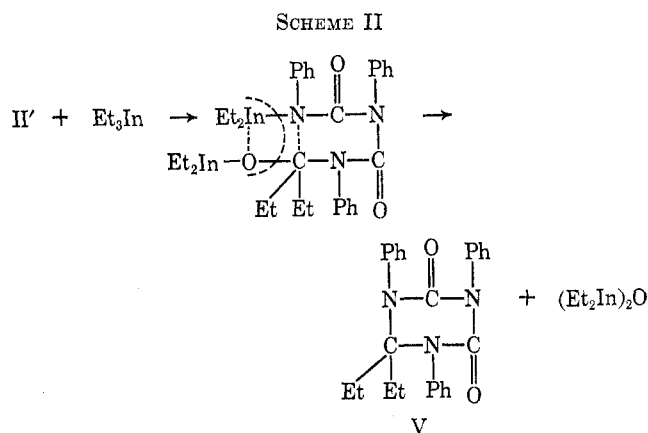
(2) (a) A. J. Bloodworth and A. G. Davies, *J. Chem. Soc.*, 6858 (1965); (b) S. Herbstman, *J. Org. Chem.*, **30**, 1259 (1965); (c) J. G. Noltes and J. Boersma, *J. Organometal. Chem.*, **7**, P6 (1967).

TABLE I
RESULTS OF THE REACTION OF TRIETHYLINDIUM WITH PHENYL ISOCYANATE

| Reactants | | | Products ^a | | | |
|--------------------|--------------------|----------------|-----------------------|----------------|----------------|----------------|
| EtsIn, g (mmol) | PhNCO, g (mmol) | Molar ratio | II, g (%) | III, g (%) | IV, g (%) | V, g (%) |
| 1.34 (6.63) | 2.37 (19.96) | 1:3 | 0.50 (20.4) | 0.45 (20.5) | 0.60 (60.7) | 0.10 (3.8) |
| 1.70 (8.42) | 6.33 (53.2) | 1:6.3 | 2.00 (64.3) | 1.30 (46.6) | 0.00 (0.00) | 0.40 (11.9) |

^a Calculation of yields are based on the amount of triethylindium used.

two molecules of isocyanate³ and that the residual phenyl isocyanate is consumed by both I and diethylindium hydroxide.⁴ The reaction of I (prepared by another route) with 5.3 mol of phenyl isocyanate gave II and III in good yield without formation of V. This result supports the scheme in which II is formed from I and the participation of the resulting, not yet characterized, triethylindium fragment, probably diethylindium hydroxide, to form III'.⁵ Considering that V was not obtained in the reaction of I with isocyanate,⁶ it is reasonable to suppose that V was formed from the reaction of II' and triethylindium, as shown below (Scheme II).



Experimental Section

General preparative methods were described in the previous paper.¹

Reaction of Triethylindium with Phenyl Isocyanate. A. In the Molar Ratio of 1:3.—When phenyl isocyanate (2.37 g, 19.96 mmol) in *n*-hexane (20 ml) was treated with triethylindium (1.34 g, 6.63 mmol) in *n*-hexane (20 ml) with stirring at 0°, carbon dioxide containing a small amount of ethane was slowly evolved.⁷ After 20 hr the precipitate was filtered off, washed with *n*-hexane, and fractionally recrystallized from acetone, yielding II and V. Data for II follow: mp 226°; ir (Nujol) 1732, 1690, and 1673 cm⁻¹ (C=O and C=C); nmr (CH₂Cl₂) τ

2.63 (multiplet, aromatic protons), 5.66 (quartet, methine proton), and 9.00 (doublet, $J = \text{CHCH}_3 = 7.2$ Hz, methyl protons) of relative intensity 15:1:3; mass spectrum m/e 369 (M⁺, C₂₃H₁₉N₃O₂).

Anal. Calcd for C₂₃H₁₉N₃O₂: C, 74.77; H, 5.18; N, 11.37; mol wt, 369. Found: C, 74.68; H, 5.24; N, 11.36; mol wt, 353 (0.403% in benzene).

Data for V follow: mp 222°; ir (KBr) 1707, and 1669 cm⁻¹ (C=O); nmr (CH₂Cl₂) τ 2.56 (singlet, aromatic protons), 2.63 (singlet, aromatic protons), and 8–9 (multiplet, A₃B₂-type ethyl protons) of relative intensity 10:5:10; mass spectrum m/e 399.5 (M⁺, C₂₅H₂₅N₃O₂).

Anal. Calcd for C₂₅H₂₅N₃O₂: C, 75.16; H, 6.31; N, 10.52; mol wt, 399.5. Found: C, 74.66; H, 6.48; N, 10.42; mol wt, 385 (0.797% in CH₃CN).

The solvent and the slight excess of phenyl isocyanate (0.1 g recovered as ethyl-*N*-phenylcarbamate) were removed from the filtrate under reduced pressure. The remaining solid was dissolved in *n*-hexane. Addition of methanol (2 ml) gave a white precipitate immediately, which was filtered off, washed with *n*-hexane, and recrystallized from methylene chloride, yielding III: mp 147° (lit.⁸ mp 147–148°); ir (KBr) 3322 (NH), 1707, and 1674 (C=O); nmr (CH₂Cl₂) τ 1.09 (broad singlet, amide proton) and 2.7 (multiplet, aromatic protons) of relative intensity 2:15.

Anal. Calcd for C₂₀H₁₇N₃O₂: C, 72.49; H, 5.17; N, 12.68; mol wt, 331. Found: C, 72.54; H, 5.09; N, 12.89; mol wt, 323 (1.085% in benzene).

The filtrate was hydrolyzed by aqueous hydrogen chloride, giving *N*-phenylpropionamide (IV), mp 107° (lit.⁹ mp 105°), whose ir spectrum was identical with that of an authentic sample.

B. In the Molar Ratio of 1:6.3.—The above procedure was followed. Unreacted phenyl isocyanate was recovered as ethyl-*N*-phenylcarbamate (1.70 g).

Preparation of *N*-Diethylindium-*N*-phenylpropionamide (I).—When triethylindium (1.26 g, 6.24 mmol) in *n*-hexane (15 ml) was added to *N*-phenylpropionamide (0.93 g, 6.24 mmol) suspended in *n*-hexane (30 ml), ethane was evolved. After the clear solution had been heated under reflux for 1 hr, the solvent was removed under reduced pressure to give I (2.00 g), whose ir spectrum and melting point were identical with those of an authentic sample.¹

Reaction of *N*-Diethylindium-*N*-phenylpropionamide (I) with Phenyl Isocyanate in the Molar Ratio of 1:5.3.—When phenyl isocyanate (3.94 g, 33.1 mmol) in *n*-hexane (15 ml) was treated with *N*-diethylindium-*N*-phenylpropionamide (I, 2.00 g, 6.24 mmol) in *n*-hexane (45 ml), carbon dioxide was slowly evolved, and, after the usual treatment, II (1.50 g, 65%) and III (2.0 g, 96%) were obtained. Unreacted phenyl isocyanate was recovered as ethyl-*N*-phenylcarbamate (1.5 g).

Registry No.—Triethylindium, 923-34-2; phenyl isocyanate, 103-71-9; II, 23405-35-8; III, 2645-39-8; V, 23405-37-0.

Acknowledgment.—Thanks are due to Professor C. R. Dillard of Brooklyn College of the City University of New York for his help in improving our manuscript.

(7) Gas analysis was performed by glpc (2-m column packed with activated charcoal using helium as carrier gas).

(8) B. Kuhn and E. Henschel, *Chem. Ber.*, **21**, 504 (1888).

(9) C. G. Rerick and J. H. Bornmann, *J. Amer. Chem. Soc.*, **35**, 1284 (1913).

(3) Triethylindium did not react with isocyanate dimer and trimer.

(4) (a) It has been reported that triethylsilanol reacts with isocyanate to give the corresponding triethylsilyl carbamates,^{4b} and that tributyltin *N*-ethylcarbamate reacts with phenyl isocyanate, giving *N*-ethyl-*N'*-phenyltributylstannylurea and carbon dioxide.^{4c} These results lend some support to the scheme to form biuret from diethylindium hydroxide and phenyl isocyanate. (b) V. V. Atakhin, I. P. Losev, and K. A. Andrianov, *Dokl. Akad. Nauk SSSR*, **113**, 581 (1957); *Chem. Abstr.*, **51**, 14582 (1957). (c) A. J. Bloodworth and A. G. Davies, *J. Chem. Soc., C*, 229 (1966).

(5) If bisdiethylindium oxide is formed from diethylindium hydroxide by dehydration, the water should react with the remaining phenyl isocyanate (*cf.* Experimental Section) to give *N,N'*-diphenylurea, but we could not obtain urea in these reactions. Consequently, the possibility of the participation of bisdiethylindium oxide to form biuret as in the case of bistrityltin oxide^{4c} was eliminated.

(6) In this case, there was no triethylindium present.