

# 3,3'-Carbonylbis[5-phenyl-1,3,4-oxadiazole-2(3H)-thione]: A Novel, Reactive, and Versatile Condensing Agent for Amide, Ester, Thiol Ester, Urea, Carbonate, Polyamide, and Polyurea Syntheses

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A novel condensing agent, 3,3'-carbonylbis[5-phenyl-1,3,4-oxadiazole-2(3H)-thione] (**3**), was readily prepared by the reaction of 5-phenyl-1,3,4-oxadiazole-2(3H)-thione with trichloromethyl chloroformate in benzene. The reagent **3** was found to be very useful for the one-pot or direct preparation of amide, ester, thiol ester, urea, and carbonate under mild conditions. The one-pot or direct polycondensation of several dicarboxylic acids with aromatic diamines and of aromatic diamines using **3** proceeded smoothly at ambient temperature to produce high-molecular-weight polyamides and polyureas, respectively.

Heterocyclic amides, such as imidazolides,<sup>1–5</sup> pyrazolide,<sup>6</sup> triazolide,<sup>7</sup> and oxadiazolides,<sup>8</sup> are very useful and popular condensing agents for the preparation of amides, esters, ureas, carbonates, and particularly peptides by a one-pot or direct procedure. The acylation or coupling reaction by the use of these reagents, however, takes a relatively long period. They also are generally very sensitive even to atmospheric moisture and must be handled with special cautions. The studies on the more reactive and even hydrolytically stable condensing agents have been successfully progressed.<sup>9–18</sup>

In the preceding article, we demonstrated that *N*- and *S*-acyl derivatives of 5-aryl-1,3,4-oxadiazole-2(3H)-thiones are novel highly reactive acylating agents for the synthesis of amide and polyamides under mild conditions.<sup>19,20</sup> This finding prompted us to develop further a novel condensing agent, 3,3'-carbonylbis[5-phenyl-1,3,4-oxadiazole-2(3H)-thione] (**3**), for the synthesis of amide and polyamides from carboxylic acids via *N*-acyl derivatives of 5-phenyl-1,3,4-oxadiazole-2(3H)-thione (**1**) as an active intermediate. This reagent might be also expected to be highly reactive for nucleophiles such as amines and alcohols.

We now report that amide, ester, thiol ester, urea, carbonate, and polyamides and polyureas with moderate to high molecular weights can be easily obtained from carboxylic acids and/or the corresponding nucleophiles by a one-pot or direct procedure using **3** under mild conditions.

**oxadiazole-2(3H)-thione** (**3**). A novel and versatile condensing agent, 3,3'-carbonylbis[5-phenyl-1,3,4-oxadiazole-2(3H)-thione] (**3**), was conveniently prepared by the reaction of 5-phenyl-1,3,4-oxadiazole-2(3H)-thione (**1**) with trichloromethyl chloroformate (**2**) in a 1 : 1 molar ratio in benzene under reflux conditions (Scheme 1).

The reagent **3** is a pale yellow crystalline solid melting at 202 °C and has excellent hydrolytic stability compared with conventional condensing agents. Hence, this can be easily handled. The condensing agent **3** may be kept for a long period of time under atmospheric pressure.

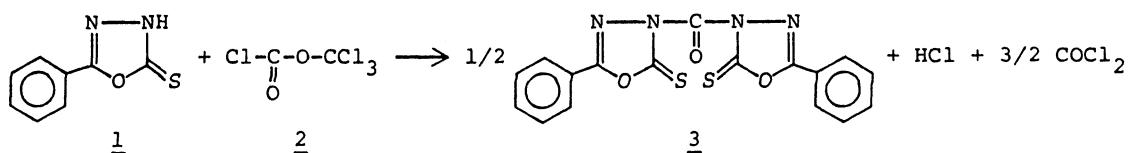
The structure of **3** was assigned on the basis of infrared (IR) spectroscopy and elemental analysis. The IR spectrum exhibited a strong carbonyl absorption at 1760 cm<sup>-1</sup> and a thiocarbonyl stretching absorption at 1355 cm<sup>-1</sup>.

**Reaction of 3 with Benzoic Acid (4), Isophthalic Acid (7a), and Adipic Acid (7b).** In order to clarify the reactivity of **3** for carboxylic acids and the reaction pathway for the synthesis of amide, ester, thiol ester, and polyamides, the reaction of **3** with benzoic acid (**4**) was carried out in a variety of solvents including chloroform, tetrahydrofuran (THF), *N,N*-dimethylacetamide (DMA), *N,N*-dimethylformamide (DMF), and *N*-methyl-2-pyrrolidone (NMP) at room temperature (ca. 15 °C) for 2 h in the presence or absence of pyridine as a tertiary base to form benzoate ion.

The condensing agent **3** reacted rapidly with **4** with the liberation of carbon dioxide and gave active amide intermediate, 5-phenyl-3-benzoyl-1,3,4-oxadiazole-2(3H)-thione<sup>19</sup> (**5**), in good yields (Table 1, Scheme 2). The use of pyridine was somewhat effective for the

## Results and Discussion

### Preparation of 3,3'-Carbonylbis[5-phenyl-1,3,4-

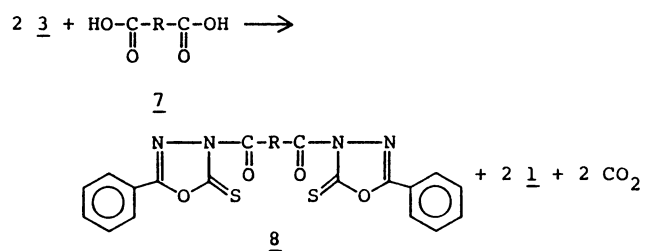
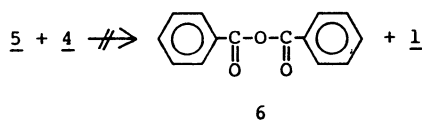
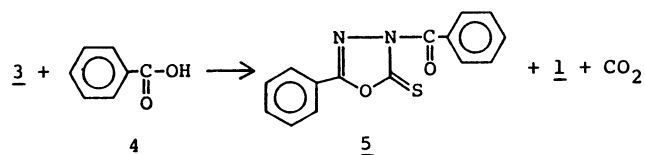


Scheme 1.

Table 1. Preparation of Active Amides **5**, **8a**, and **8b** Using Condensing Agent **3**

| Carboxylic acid | Reaction conditions <sup>a)</sup> |                       |           | Product   |            |
|-----------------|-----------------------------------|-----------------------|-----------|-----------|------------|
|                 | Solvent<br>mL                     | Base<br>mmol          | Time<br>h | Type      | Yield<br>% |
| <b>4</b>        | CF <sup>b)</sup> (4)              | Py <sup>c)</sup> (1)  | 2         | <b>5</b>  | 90         |
| <b>4</b>        | THF(4)                            | Py(1)                 | 2         | <b>5</b>  | 89         |
| <b>4</b>        | DMA(4)                            | None                  | 2         | <b>5</b>  | 88         |
| <b>4</b>        | DMA(4)                            | Py(1)                 | 2         | <b>5</b>  | 91         |
| <b>4</b>        | DMF(4)                            | None                  | 2         | <b>5</b>  | 92         |
| <b>4</b>        | DMF(4)                            | Py(1)                 | 2         | <b>5</b>  | 96         |
| <b>4</b>        | NMP(2)                            | None                  | 2         | <b>5</b>  | 94         |
| <b>4</b>        | NMP(2)                            | Py(1)                 | 2         | <b>5</b>  | 99         |
| <b>4</b>        | NMP(2)                            | TEA <sup>d)</sup> (1) | 2         | <b>5</b>  | 68         |
| <b>7a</b>       | DMA(8)                            | Py(2)                 | 4         | <b>8a</b> | 89         |
| <b>7a</b>       | DMF(8)                            | Py(2)                 | 4         | <b>8a</b> | 91         |
| <b>7a</b>       | NMP(4)                            | None                  | 4         | <b>8a</b> | 93         |
| <b>7a</b>       | NMP(4)                            | Py(2)                 | 2         | <b>8a</b> | 74         |
| <b>7a</b>       | NMP(4)                            | Py(2)                 | 4         | <b>8a</b> | 98         |
| <b>7b</b>       | NMP(4)                            | None                  | 4         | <b>8b</b> | 94         |
| <b>7b</b>       | NMP(4)                            | Py(2)                 | 4         | <b>8b</b> | 97         |

a) Reaction was carried out with 1 mmol of **4**, **7a**, or **7b** using 1 and 2 mmol of **3** for **4** and for **7a** and **7b**, respectively, at room temperature. b) CF: chloroform. c) Py: pyridine. d) TEA: triethylamine.



Scheme 2.

formation of **5**. No definite effect of medium on the reaction was, however, observed. Probable active intermediate benzoic anhydride (**6**) was not detected nor isolated entirely from the reaction mixtures. The use of triethylamine was attempted in place of pyridine, but was found less suitable as a base.

Similarly, active bisamide intermediates, 3,3'-isophthaloylbis[5-phenyl-1,3,4-oxadiazole-2(3*H*)-thione]<sup>19)</sup> (**8a**) and 3,3'-adipoylbis[5-phenyl-1,3,4-oxadiazole-2(3*H*)-thione]<sup>19)</sup> (**8b**), were both isolated in quantitatively from the condensation of **3** with isophthalic acid (**7a**) and adipic acid (**7b**), respectively (Table 1, Scheme 2).

Active amide intermediates **5**, **8a**, and **8b** obtained here were identified by melting point and IR spectroscopy. They, the actual acylating agents, have been characterized by high reactivity toward aminolysis.

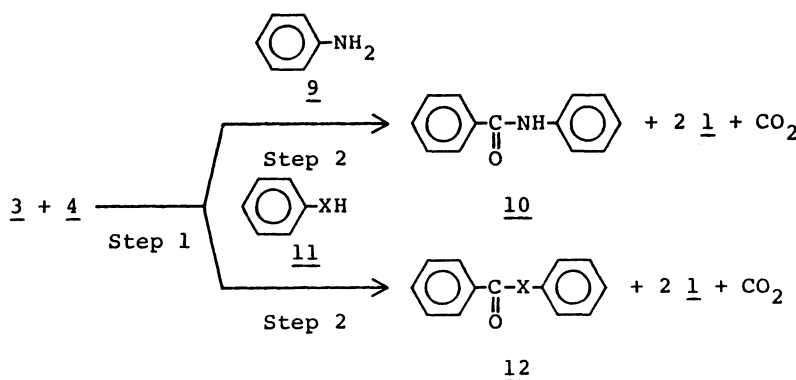
**Preparation of Benzanilide (10), Phenyl Benzoate (12a), and S-Phenyl Benzothioate (12b).** Based on these results, we first studied the preparation of benzanilide (**10**), phenyl benzoate (**12a**), and S-phenyl benzothioate (**12b**) from benzoic acid (**4**) and aniline (**9**), phenol (**11a**), and thiophenol (**11b**), respectively, by a one-pot procedure using **3**. This efficient procedure consists of reacting **3** with **4** in chloroform, THF, DMA, DMF, or NMP at ambient temperature for 2 h in the presence or absence of pyridine affording **5** as an active intermediate (step 1) and subsequently with the respective nucleophiles at that temperature for a prescribed period (step 2).

The reaction with **9** as a nucleophile proceeded smoothly even without pyridine to furnish amide **10** in high yields (Table 2, Scheme 3). NMP as a solvent was somewhat more favorable than the others in the preparation of **10**. Both the reactions with **11a** and **11b** progressed much more slowly, but almost quantitative conversions to ester **12a** and thiol ester **12b** could be achieved in 2 and 8 d, respectively (Table 2, Scheme 3). An increase in the reaction temperature above 50 °C in step 2, however, accelerated dramatically the alcoholysis of **5**. Esterification at room temperature required an equimolar quantity of pyridine and above to nucleophiles **11a** and **11b**.

Table 2. One-Pot Preparation of Amide **10**, Ester **12a**, and Thiol Ester **12b** Using Condensing Agent **3**

| Amine or alcohol | Reaction conditions  |                  |                              | Product    |                  |
|------------------|----------------------|------------------|------------------------------|------------|------------------|
|                  | Step 1 <sup>a)</sup> |                  | Step 2 <sup>b)</sup><br>Time | Type       | Yield<br>%       |
|                  | Solvent<br>mL        | Pyridine<br>mmol |                              |            |                  |
| <b>9</b>         | CF(4)                | 1                | 2h                           | <b>10</b>  | 85               |
| <b>9</b>         | THF(4)               | 1                | 2h                           | <b>10</b>  | 89               |
| <b>9</b>         | DMA(4)               | 1                | 2h                           | <b>10</b>  | 86               |
| <b>9</b>         | DMF(4)               | 1                | 2h                           | <b>10</b>  | 96               |
| <b>9</b>         | NMP(2)               | 0                | 2h                           | <b>10</b>  | 91               |
| <b>9</b>         | NMP(2)               | 1                | 2h                           | <b>10</b>  | 99               |
| <b>11a</b>       | CF(4)                | 2                | 4d                           | <b>12a</b> | 99 <sup>c)</sup> |
| <b>11a</b>       | THF(4)               | 2                | 4d                           | <b>12a</b> | 91               |
| <b>11a</b>       | DMA(4)               | 2                | 4d                           | <b>12a</b> | 85               |
| <b>11a</b>       | DMF(4)               | 2                | 4d                           | <b>12a</b> | 91               |
| <b>11a</b>       | NMP(2)               | 0                | 4d                           | <b>12a</b> | Trace            |
| <b>11a</b>       | NMP(2)               | 0                | 12h <sup>d)</sup>            | <b>12a</b> | 89               |
| <b>11a</b>       | NMP(2)               | 1                | 4d                           | <b>12a</b> | 99 <sup>c)</sup> |
| <b>11a</b>       | NMP(2)               | 2                | 1d                           | <b>12a</b> | 67               |
| <b>11a</b>       | NMP(2)               | 2                | 2d                           | <b>12a</b> | 95               |
| <b>11b</b>       | NMP(2)               | 0                | 8d                           | <b>12b</b> | Trace            |
| <b>11b</b>       | NMP(2)               | 2                | 8d                           | <b>12b</b> | 86               |

a) Reaction was carried out with 1 mmol of **3** and **4** for 2 h at room temperature. b) Reaction was carried out with 1 mmol of **9**, **11a**, or **11b** at room temperature unless otherwise noted. c) A trace amount of **5** was contained. d) Reaction was carried out at 50 °C.



**Preparation of *N,N'*-Diphenylurea (**14**) and Diphenyl Carbonate (**16**).** The direct aminolysis and alcoholysis of **3** were next investigated to demonstrate the feasibility of the reactions for urea and carbonate formations, respectively. The reactions of **3** with twice-molar amounts of **9** and **11a** were conducted using chloroform, THF, DMA, DMF, and NMP as media at ambient temperature for a predetermined duration in the presence or absence of pyridine.

As shown in Table 3, **3** underwent aminolysis within a short time in the solvents to provide excellent yields of *N,N'*-diphenylurea (**14**) (Scheme 4). The use of NMP significantly affected the reaction rate of the aminolysis. Thus, the direct aminolysis of **3** is a facile, high-yield reaction which can be used for the synthesis of polyureas. The direct alcoholysis of **3** leading to diphenyl carbonate (**16**) took place relatively slow and required prolonged reaction time (much more than 8 d) for its completion (Table 3, Scheme 4). Raising the reaction temperature favored markedly the alcoholysis. Alcoholysis at room temperature required an equimolar quantity of pyridine to **11a**.

It is interesting to note that the treatments of **3** with an equimolar amounts of **9** and **11a** also afford high yields of **14** and **16**, respectively. This points to the following pathway (Scheme 4). A half-molar amount of **3** reacts first with **9** and **11a** to form 5-phenyl-3-anilinocarbonyl-1,3,4-oxadiazole-2(3*H*)-thione (**13**) and 5-phenyl-3-phenoxy carbonyl-1,3,4-oxadiazole-2(3*H*)-thione (**15**), respectively. The products **13** and **15** are more reactive than **5** as activated acylating agents and are less stable, and their enhanced reactivities cause them to react more rapidly with unreacted **9** and **11a**, respectively. Therefore, the formation of **13** and **15** is the rate-determining step in the proposed sequence of reactions.

**Synthesis of Polyamides (18a—d).** Facile one-pot amide preparation using the novel condensing agent **3** provides a promising route to polyamides. The polycondensation of dicarboxylic acids **7a** and **7b** with aromatic diamines including 4,4'-oxydianiline (**17a**) and 4,4'-methylenedianiline (**17b**) using **3** was therefore investigated by a one-pot procedure. Thus, the

Table 3. Direct Preparation of Urea **14** and Carbonate **16** Using Condensing Agent **3**

| Amine or alcohol<br>mmol | Reaction conditions <sup>a)</sup> |                  |                  | Product   |                  |
|--------------------------|-----------------------------------|------------------|------------------|-----------|------------------|
|                          | Solvent<br>mL                     | Pyridine<br>mmol | Time             | Type      | Yield<br>%       |
| <b>9</b> (2)             | CF(4)                             | 0                | 2h               | <b>14</b> | 91               |
| <b>9</b> (2)             | THF(4)                            | 0                | 2h               | <b>14</b> | 91               |
| <b>9</b> (2)             | DMA(4)                            | 0                | 2h               | <b>14</b> | 89               |
| <b>9</b> (2)             | DMF(4)                            | 0                | 2h               | <b>14</b> | 93               |
| <b>9</b> (1)             | NMP(2)                            | 0                | 1h               | <b>14</b> | 95 <sup>b)</sup> |
| <b>9</b> (2)             | NMP(2)                            | 0                | 1h               | <b>14</b> | 96               |
| <b>11a</b> (2)           | DMA(4)                            | 2                | 8d               | <b>16</b> | 91               |
| <b>11a</b> (2)           | DMF(4)                            | 2                | 8d               | <b>16</b> | 96               |
| <b>11a</b> (1)           | NMP(2)                            | 1                | 4d               | <b>16</b> | 80 <sup>b)</sup> |
| <b>11a</b> (2)           | NMP(2)                            | 0                | 1d <sup>c)</sup> | <b>16</b> | 86               |
| <b>11a</b> (2)           | NMP(2)                            | 2                | 4d               | <b>16</b> | 85               |
| <b>11a</b> (2)           | NMP(2)                            | 2                | 8d               | <b>16</b> | 97               |

a) Reaction was carried out with 1 mmol of **3** at room temperature unless otherwise noted. b) The yield was calculated on the basis of half-molar quantities of **3**. c) Reaction was carried out at 60°C.

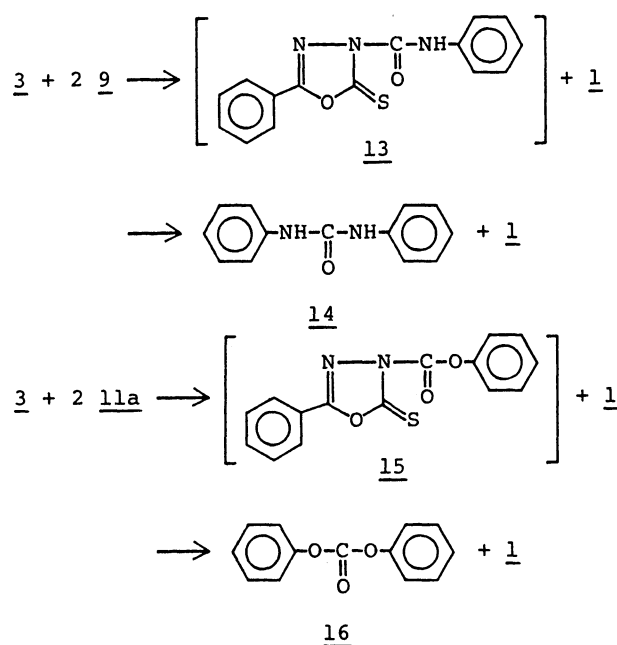


Table 4. One-Pot Synthesis of Polyamides **18a–d** Using Condensing Agent **3**

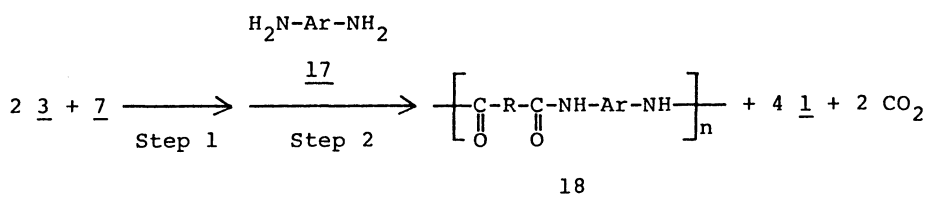
| Carboxylic acid | Amine      | Reaction conditions  |                      | Polymer Type | Polymer |                    | Remark <sup>d)</sup> |
|-----------------|------------|----------------------|----------------------|--------------|---------|--------------------|----------------------|
|                 |            | Step 1 <sup>a)</sup> | Step 2 <sup>b)</sup> |              | Yield   | $\eta_{sp}/c^c)$   |                      |
|                 |            | Pyridine<br>mmol     | Time<br>d            |              | %       | dL g <sup>-1</sup> |                      |
| <b>7a</b>       | <b>17a</b> | 0                    | 1                    | <b>18a</b>   | 92      | 0.13               | P                    |
| <b>7a</b>       | <b>17a</b> | 2                    | 1                    | <b>18a</b>   | 99      | 0.35               | S                    |
| <b>7a</b>       | <b>17a</b> | 2                    | 3                    | <b>18a</b>   | 99      | 0.37               | G                    |
| <b>7a</b>       | <b>17b</b> | 2                    | 1                    | <b>18b</b>   | 99      | 0.29               | G                    |
| <b>7b</b>       | <b>17a</b> | 2                    | 1                    | <b>18c</b>   | 99      | 0.33               | G                    |
| <b>7b</b>       | <b>17b</b> | 2                    | 1                    | <b>18d</b>   | 98      | 0.34               | G                    |

a) Reaction was carried out with 2 mmol of **3** and 1 mmol of **7a** or **7b** in 4 mL of NMP for 5 h at room temperature. b) Polymerization was carried out with 1 mmol of **17a** or **17b** at room temperature. c) Measured at a concentration of 0.5 g dL<sup>-1</sup> in concentrated sulfuric acid at 30°C. d) P: polymer precipitation; S: homogeneous solution; G: apparent gelation.

Table 5. Direct Synthesis of Polyureas **19a** and **19b** Using Condensing Agent **3**

| Amine      | Reaction conditions <sup>a)</sup> |      | Polymer Type | Polymer |                                        | Remark |
|------------|-----------------------------------|------|--------------|---------|----------------------------------------|--------|
|            | Salt <sup>b)</sup>                | Time |              | Yield % | $\eta_{sp}/c^c)$<br>dL g <sup>-1</sup> |        |
| <b>17a</b> | None                              | 1d   | <b>19a</b>   | 98      | 0.26                                   | G      |
| <b>17a</b> | LiOH                              | 1d   | <b>19a</b>   | 99      | 0.78                                   | S      |
| <b>17a</b> | LiCl                              | 1h   | <b>19a</b>   | 99      | 0.67                                   | S      |
| <b>17a</b> | LiCl                              | 1d   | <b>19a</b>   | 99      | 0.87                                   | S      |
| <b>17b</b> | None                              | 1d   | <b>19b</b>   | 97      | 0.24                                   | G      |
| <b>17b</b> | LiCl                              | 1d   | <b>19b</b>   | 99      | 0.68                                   | S      |

a) Polymerization was carried out with 1 mmol of **3** and **17a** or **17b** in 2 mL of NMP at room temperature. b) 5 wt% of the salt to NMP was added. c) Measured at a concentration of 0.5 g dL<sup>-1</sup> in NMP at 30°C.

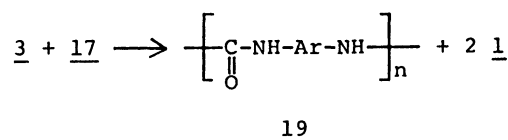


Scheme 5.

activation of the dicarboxylic acids was carried out by the addition of **3** to the respective NMP solutions of **7a** and **7b** at room temperature in the presence or absence of pyridine. After 5 h of stirring the diamine **17a** or **17b** was added, and the mixture was further stirred at that temperature for 1 or 3 d. The polyamides were isolated in the ordinary manner.

As can be seen from the reduced viscosities in Table 4, the corresponding polyamides (**18a–d**) with moderate molecular weights were easily synthesized in quantitative yields with pyridine (Scheme 5). Remarkable effect of pyridine on the polycondensations was observed.

**Synthesis of Polyureas **19a** and **19b**.** In order to further demonstrate the synthetic utility and versatility of the novel condensing agent **3**, it was applied to the synthesis of aromatic polyureas. The direct polycondensation leading to polyureas **19a** and **19b** was con-



Scheme 6.

ducted in solution at ambient temperature for 1 h or 1 d in the presence of **3** using **17a** and **17b** as aromatic diamines. Equimolar amounts of the condensing agent and diamines were used. Polar aprotic solvent NMP was employed as a selected polymerization medium.

Although the polyureas were isolated in excellent yields, the molecular weights remained low, presumably due to the formation of a quasi-gel of polymers (Table 5, Scheme 6). High molecular weights were successfully attained by the addition of inorganic salts

such as lithium hydroxide and lithium chloride to the system in which the polymers remained dissolved.

In conclusion, these experimental results indicate that the novel condensing agent **3** is very useful for the preparation of amide, ester, thiol ester, urea, and carbonate and moderate- to high-molecular-weight polyamides and polyureas under mild conditions. Furthermore, **3** is a crystalline solid and is handled more easily than the conventional condensing agents.

### Experimental

Melting points (mp) were uncorrected. Infrared (IR) spectra were recorded in potassium bromide on a JASCO IR-810 spectrophotometer. 5-Phenyl-1,3,4-oxadiazole-2(3*H*)-thione (**1**) was prepared as reported previously.<sup>21</sup> Trichloromethyl chloroformate (**2**), supplied by Hodogaya Chemical Industries Ltd., was used without further purification. The other reagents and solvents were obtained commercially and were used after purification by the usual manner. The products obtained were identified by spectral comparison and/or mp and mixed mp with the corresponding authentic samples unless otherwise noted.

**3,3'-Carbonylbis[5-phenyl-1,3,4-oxadiazole-2(3*H*)-thione] (3).** A mixture of **1** (17.8 g, 0.1 mol) and **2** (12 mL, 0.1 mol) in benzene (300 mL) was refluxed with stirring for 1 d. The solvent was removed in vacuo and the residue was recrystallized twice from benzene to give pale yellow granular crystals. Yield: 14.9 g (78%). Mp 202 °C (by differential thermal analysis); IR (KBr), 1760 (C=O), 1610 (C=N), and 1355 cm<sup>-1</sup> (C=S).

Found: C, 53.52; H, 2.62; N, 14.76%. Calcd for C<sub>17</sub>H<sub>10</sub>N<sub>4</sub>O<sub>3</sub>S<sub>2</sub>: C, 53.39; H, 2.64; N, 14.65%.

**Reaction of 3 with Benzoic Acid (4).** To a solution of **4** (0.122 g, 1 mmol) and/or pyridine (0.079 g, 1 mmol) in a solvent (2 or 4 mL) was added **3** (0.382 g, 1 mmol) followed by stirring at room temperature for 2 h. The reaction mixture was poured into 1% aqueous sodium hydrogencarbonate (50 mL). The resulting precipitate was collected, washed several times with water, and dried.

**Reaction of 3 with Isophthalic Acid (7a) or Adipic Acid (7b).** The condensing agent **3** (0.764 g, 2 mmol) was added to a solution of **7a** or **7b** (1 mmol) and/or pyridine (0.158 g, 2 mmol) in a solvent (4 or 8 mL). The solution was stirred at ambient temperature for 2 or 4 h, and then poured into 1% aqueous sodium hydrogencarbonate (100 mL). The solid, so formed, was filtered off, rinsed repeatedly with water, and dried.

**Benzanilide (10).** To a stirred solution of **4** (0.122 g, 1 mmol) and/or pyridine (0.079 g, 1 mmol), **3** (0.382 g, 1 mmol) at room temperature was added. After 2 h of the reaction aniline (**9**) (0.093 g, 1 mmol) was added, and the solution was stirred at that temperature for an additional 2 h. The product was isolated by pouring the solution into 1% aqueous sodium hydrogencarbonate (100 mL). It was gathered, washed thoroughly with water, and dried.

**Phenyl Benzoate (12a) and S-Phenyl Benzothioate (12b).** A mixture of **3** (0.382 g, 1 mmol), **4** (0.122 g, 1 mmol), and/or pyridine (1 or 2 mmol) in a solvent (2 or 4 mL) was stirred at ambient temperature for 2 h and phenol (**11a**) or thiophenol (**11b**) (1 mmol) was added. Stirring was further continued at that temperature or 50 °C for 12 h, 1, 2, 4, or 8 d. The

reaction mixture was worked up as reported for **10**.

**N,N'-Diphenylurea (14).** The condensing agent **3** (0.382 g, 1 mmol) was added to a solution of **9** (1 or 2 mmol) in a solvent (2 or 4 mL). This solution was stirred at room temperature for 1 or 2 h followed by treating as described.

**Diphenyl Carbonate (16).** A solution of **3** (0.382 g, 1 mmol), **11a** (1 or 2 mmol), and/or pyridine (1 or 2 mmol) in a solvent (2 or 4 mL) was reacted with stirring at ambient temperature or 60 °C for 1, 4, or 8 d. The work-up of the product was as usual.

Judging from IR and <sup>1</sup>H NMR spectra and the mp, all the products were virtually pure without any purifications.

**Polyamides 18a—d.** The condensing agent **3** (0.764 g, 2 mmol) was allowed to react with **7a** or **7b** (1 mmol) in *N*-methyl-2-pyrrolidone (NMP) (4 mL) in the presence or absence of pyridine (0.158 g, 2 mmol) and stirred at ambient temperature for 5 h. Diamine 4,4'-oxydianiline (**17a**) or 4,4'-methylenedianiline (**17b**) (1 mmol) was then added to this mixture. After 1 or 3 d of stirring at this temperature the polymer was separated by reprecipitation with 1% aqueous sodium hydrogencarbonate (300 mL). It was isolated, rinsed well with hot methanol, and dried. The reduced viscosity was measured at a concentration of 0.5 g dL<sup>-1</sup> in concentrated sulfuric acid at 30 °C.

**Polyureas 19a and 19b.** A mixture of **3** (0.382 g, 1 mmol) and **17a** or **17b** (1 mmol) in NMP or NMP (2 mL) containing 5 wt% of lithium hydroxide or lithium chloride reacted with stirring at room temperature for 1 h or 1 d. The polymerization solution was treated as described for **18**. The reduced viscosity was measured in NMP.

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