equipped with a glass liner. The apparatus was flushed with N_2, sealed, and heated to 140 °C for 24 h. The pressure rose to 140 psi. After cooling, the apparatus was opened, the brown solution was transferred to a round-bottom flask, and the excess carbon disulfide was removed under vacuum. The dark residue was chromatographed over silica gel (30:1 weight ratio of silica gel to mixture) with benzene as eluent. The trithiones **1** are the first materials to elute followed in certain cases by the narrow dark bands corresponding to the tetrathiafulvalenes.

4-Phenyl-1,3-dithiole-2-thione. From 0.41 g (4.0 mmol) of phenylacetylene and 0.34 g (1.0 mmol) of bis(2,2,6,6-tetramethylpiperidine) disulfide, 0.19 g (45%) of trithione was obtained and recrystallized from ethanol: mp 117 °C (lit.[10] mp 117–118 °C); IR (KBr) 3100, 1485, 1445, 1055, 1045, 890, 740, 675 cm^{-1}; NMR (CS_2) δ 6.95 (1, s), 7.32 (5, s); mass spectrum, *m/e* (relative intensity) 210 (76), 134 (100), 121 (13), 102 (14), 91 (24), 90 (23), 77 (14).

4-*tert*-Butyl-1,3-dithiole-2-thione. From 0.33 g (4.0 mmol) of *tert*-butylacetylene and 0.40 g (1.0 mmol) of bis(2,2,6,6-tetramethylpiperidine) disulfide, 1.4 g (99%) of trithione was obtained and recrystallized from diethyl ether: mp 90 °C; IR (KBr) 2980, 1465, 1365, 1250, 1050, 1035, 898, 800, 655 cm^{-1}; NMR (CCl_4) δ 1.33 (9, s), 6.55 (1, s); mass spectrum, *m/e* (relative intensity) 190 (98), 175 (100), 113 (17), 70 (89), 69 (77), 58 (100).

Anal. Calcd for $C_7H_{10}S_3$: C, 44.21; H, 5.26; S, 50.52. Found: C, 44.11; H, 5.43; S, 50.18.

4-Carboethoxy-5-phenyl-1,3-dithiole-2-thione. From 3.48 g (20.0 mmol) of ethyl phenylpropiolate and 1.18 g (5.0 mmol) of bis(morpholine) disulfide, 1.4 g (99%) of trithione was obtained and recrystallized from diethyl ether: mp 92 °C; IR (KBr) 3000, 1740, 1540, 1450, 1260, 1205, 1090, 1080, 1025, 755, 690 cm^{-1}; NMR (CCl_4) δ 1.12 (3, t, J = 8.0 Hz), 4.10 (2, q, J = 8.0 Hz), 7.32 (5, s); mass spectrum, *m/e* (relative intensity) 282 (82), 178 (18), 166 (14), 145 (36), 134 (82), 133 (45), 121 (36), 89 (100), 77 (27).

Anal. Calcd for $C_{12}H_{10}O_2S_3$: C, 51.06; H, 3.54; S, 34.04. Found: C, 51.18; H, 3.64; S, 33.98.

Methyl 1,3-Dithiole-2-thione-4-carboxylate and 4,4′(5′)-Bis(carbomethoxy)-$\Delta^{2,2'}$-bi-1,3-dithiole. From 1.68 g (20.0 mmol) of methyl propiolate and 1.18 g (5.0 mmol) of bis(morpholine) disulfide, 0.63 g (67%) of trithione was obtained and recrystallized from benzene: mp 104 °C; IR (KBr) 3060, 1730, 1560, 1475, 1290, 1200, 1070, 1055, 735 cm^{-1}; NMR (CCl_4) δ 3.88 (3, s), 7.85 (1, s); mass spectrum, *m/e* (relative intensity) 192 (100), 161 (18), 134 (18), 133 (23), 116 (45), 76 (64), 64 (68), 57 (100), 45 (82).

Anal. Calcd for $C_7H_6O_4S_3$: C, 31.25; H, 2.08; S, 50.00. Found: C, 31.47; H, 2.15; S, 49.86.

In addition, 0.16 g (10%) of bidithiole was obtained and recrystallized from ligroin (70–90 °C): mp 240 °C (lit.[11] mp 244–245 °C); IR (KBr) 3080, 1722, 1440, 1250, 1200, 1160, 1050, 939, 829, 765, 730 cm^{-1}; mass spectrum, *m/e* (relative intensity) 320 (100), 204 (68), 161 (29), 105 (36), 101 (32), 76 (59).

Dimethyl 1,3-Dithiole-2-thione-4,5-dicarboxylate and Tetramethyl [$\Delta^{2,2'}$-Bi-1,3-dithiole]-4,4′,5,5′-tetracarboxylate. From 1.14 g (8.0 mmol) of dimethyl acetylenedicarboxylate and 0.69 g (2.0 mmol) of bis(2,2,6,6-tetramethylpiperidine) disulfide, 0.17 g (33%) of trithione was obtained and recrystallized from a mixture of toluene and hexane: mp 89 °C (lit.[11] mp 87 °C): IR (KBr) 1750, 1725, 1550, 1425, 1250, 1100, 1085, 1010, 920, 760 cm^{-1}; NMR (CCl_4) δ 3.86 (s); mass spectrum, *m/e* (relative intensity) 250 (100), 219 (22), 191 (22), 174 (26), 107 (48), 76 (49), 59 (96), 45 (28).

In addition, 0.11 g (13%) of bidithiole was obtained and recrystallized from methanol: mp 169–170 °C (lit.[5] mp 169–170 °C); IR (KBr) 1740, 1710, 1570, 1440, 1262, 1020 cm^{-1}; NMR (CCl_4) δ 3.85 (s); mass spectrum, *m/e* (relative intensity) 436 (100), 404 (11), 377 (30), 332 (22), 261 (50), 100 (17), 88 (44), 59 (55), 44 (44).

Registry No.—**3**, 75-15-0; 4,4′(5′)-bis(carbomethoxy)-$\Delta^{2,2'}$-bi-1,3-dithiole, 51751-18-9; tetramethyl [$\Delta^{2,2'}$-bi-1,3-dithiole]-4,4′,5,5′-tetracarboxylate, 26314-39-6.

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Phthalimido Phenylcarbamate: A New Isocyanate Generator

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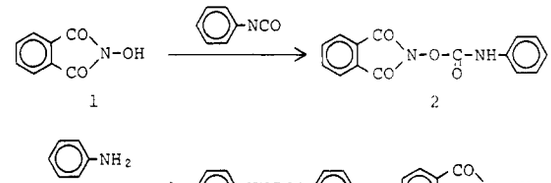
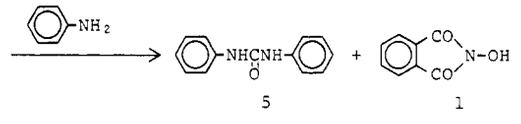
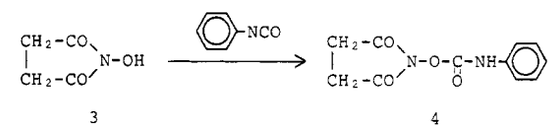
N-Hydroxyphthalimide (**1**) is an interesting compound as it has a unique acidic hydroxy group, and its alkylation[1-6] and esterification[7,8] have been reported in the literature. Regarding other reactions of **1**, however, very little has been published. As a result of our current interest in reactions of imide derivatives, we have recently examined the reaction of **1** with phenyl isocyanate. The reaction gives rise to the formation of a new type of urethane linkage which is expected to regenerate phenyl isocyanate on heating. The urethane compound would be a relatively stable solid which could be more easily handled with safety than the isocyanate, and moreover it could form a stable mixture with nucleophiles in solid state at ambient temperatures. These properties are especially useful in coating chemistry. We now wish to report the synthesis of phthalimido phenylcarbamate (**2**) and its potential as an isocyanate generator, comparing them with those of succinimido phenylcarbamate (**4**).







The carbamate **2** was prepared from *N*-hydroxyphthalimide (**1**) and phenyl isocyanate in dry dioxane or dimethylacetamide. The succinimide derivative **4** was synthesized from *N*-hydroxysuccinimide (**3**) similarly.

The thermal stability of **2** was examined by means of thermogravimetric analysis at a heating rate of 5 °C/min in air, and it was found that **2** decomposed with two-step weight loss. The first weight loss observed between 97 and 170 °C accounted for 45% of the initial weight, which was in good agreement with the theoretical value (42%) for the loss of phenyl isocyanate. The infrared spectrum of the solid obtained after the first weight loss was identical with that of the authentic **1**. Compound **2** was therefore thought to start regenerating phenyl isocyanate from around 100 °C in the solid state. Compound **4**, on the other hand, showed no two-step weight loss, probably on account of the volatility of the decomposed species. The weight loss started at 129 °C.

In order to evaluate its potential as an isocyanate generator, **2** was subjected to reaction with aniline at various temperatures. A dichloromethane solution containing equimolar amounts of **2** and aniline started to deposit diphenylurea (**5**) after about 4 h at room temperature (ca. 25 °C). Under these

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Table I. Reaction of 2 or 4 with Aniline

Solvent (bp, °C)	Reaction time, h	Reaction of 2 yield, % 5	1	Reaction of 4 yield, % 5	3
Dioxane (101)	4	96	90	89	54
Benzene (80)	4	85	86	98	45
Acetone (56)	4	84	90	89	36
Dichloromethane (40)	10	42	*a*	73	*b*

[a] A mixture of 1 and unreacted 2 was obtained. [b] A mixture of 3 and unreacted 4 was obtained.

conditions, **5** was isolated in 5% yield after 48 h. The reaction was then carried out in dioxane, benzene, acetone, and dichloromethane at their boiling temperatures, and the products, diphenylurea (**5**) and *N*-hydroxyphthalimide (**1**), were isolated by fractional recrystallization. Table I summarizes the results of the reactions in the four solvents. Compound **4** was similarly treated with aniline, and the results are included in Table I. As shown in the table, **5** was isolated in good yield from **2** in dioxane, benzene, or acetone despite the small scale reaction. When dichloromethane was used as a solvent, however, the yield of **5** was much lower and a mixture of **1** and unreacted **2** was obtained, presumably because of the low boiling temperature of the solvent. Compound **4** also gave **5** in good yield, even in dichloromethane, which suggests that **4** is more reactive toward aniline than **2**.

The reactivity of **2** and **4** was then compared by the reaction of equimolar amounts of **2**, **4**, and aniline. After repeated fractional recrystallization, the expected five compounds were isolated in yields as follows: **5**, 96%; **1**, 39%; **3**, 30%; **2**, 48%; and **4**, 30%. The fact that more **2** was recovered than **4** seems to support the idea that **4** is more reactive than **2**, though the isolated amount of **3** is less than that of **1** due to the difficulty in recrystallization of **3**.[9] This is in good accordance with the tendency of a compound with a more acidic leaving component to show better reactivity in the amide-forming nucleophilic substitution reaction;[10] pK_a values of **1** and **3** are 7.0[11] and 6.0,[12] respectively. Although both **2** and **4** were thus shown to be good isocyanate generators, **2** was considered to be a better one in terms of the ease in recovering the starting *N*-hydroxy compound.

Experimental Section

Melting points were determined on a Mel-Temp apparatus and are uncorrected. IR spectra were recorded on a Jasco IR-G spectrometer. NMR spectra were obtained on Jeol JNM-MH-60 or Hitachi R-24 spectrometers. Elemental analyses were performed by Shonan Bunseki Center, Kanagawa, Japan.

Materials. *N*-Hydroxyphthalimide (**1**) was prepared according to the procedure reported by Mazur and Plume.[13] *N*-Hydroxysuccinimide (**3**) was synthesized by the method of Anderson, Zimmerman, and Callahan.[14] All of the solvents that were used were dried by the usual manner.

Phthalimido Phenylcarbamate (2). To a solution of 1.14 g (7 mmol) of **1** in 20 mL of dry dioxane was added 0.76 mL (0.83 g, 7 mmol) of phenyl isocyanate and then a drop of dibutyltin dilaurate as catalyst. The solution was stirred at room temperature, and precipitation began to take place in 4 h. The stirring was discontinued after 6 h, and the solvent was removed under reduced pressure. The resulting crystalline solid was recrystallized from dichloromethane–petroleum ether to give 1.86 g (94%) of colorless granular crystals. On rapid heating, **2** melted at 175–178 °C: IR (KBr) 3240, 1775, and 1735 cm^{-1}; NMR (Me_2SO-d_6) δ 6.90–7.50 (m, 5, C_6H_5–N), 7.75–7.90 (m, 4, $C_6H_4(CO)_2N$), and 8.45 (broad s, 1, NH). Anal. Calcd for $C_{15}H_{10}N_2O_4$: C, 63.83; H, 3.57; N, 9.93. Found: C, 64.22; H, 3.80; N, 9.68.

Succinimido Phenylcarbamate (4). Starting from 0.806 g (7 mmol) of *N*-hydroxysuccinimide and 0.75 mL (0.83 g, 7 mmol) of phenyl isocyanate, 1.41 g (86%) of **4** was obtained as colorless plates after recrystallization from chloroform–petroleum ether. On rapid heating, **4** melted at 149–154 °C; IR (KBr) 3240, 1775, and 1715 cm^{-1}; NMR (Me_2SO-d_6) δ 2.75 (s, 4, CH_2CH_2), 6.93–7.43 (m, 5, C_6H_5), and 7.45 (broad s, 1, NH). Anal. Calcd for $C_{11}H_{10}N_2O_4$: C, 56.41; H, 4.30; N, 11.96. Found: C, 56.12; H, 4.20; N, 12.13.

Reaction of 2 and Aniline. To a solution of 0.846 g (3 mmol) of **2** in 8 mL of dry acetone was added 0.285 mL (0.29 g, 3.1 mmol) of aniline. The solution was heated at reflux for 4 h and evaporated under reduced pressure to give a slightly yellow solid. It was washed with petroleum ether to remove the unreacted aniline and then recrystallized from dioxane to give 0.51 g of **5** as colorless needles. The filtrate was concentrated under reduced pressure, and the residual solid was fractionally recrystallized from dioxane–petroleum ether to give an additional 0.05 g of **5**, 0.08 g of a mixture of **5** and **1**, and 0.44 g (90%) of **1**. The total yield of **5** was 0.56 g (84%), mp 241–242 °C (lit.[15] mp 241–242 °C).

Succinimide derivative **4** was treated with aniline in the same way. The dried mixture was washed with water to remove **3**, which was recrystallized from ethyl acetate.

Reaction of a Mixture of 2 and 4 with Aniline. To a solution of 0.846 g (3 mmol) of **2** and 0.703 g (3 mmol) of **4** in 8 mL of dry acetone was added 0.273 mL (0.279 g, 3 mmol) of aniline. After heating the solution for 4 h, the solvent was removed under reduced pressure. The residual solid was fractionally recrystallized from chloroform–hexane to give 0.608 g (96%) of **5**, 0.189 g (39%) of **1**, 0.105 g (30%) of **3**, 0.403 g (48%) of **2**, and 0.211 g (30%) of **4**.

Registry No.—**1**, 524-38-9; **2**, 60506-34-5; **3**, 6066-82-6; **4**, 23583-11-1; **5**, 102-07-8; phenyl isocyanate, 103-71-9; aniline, 62-53-3.

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Oxidative Acetoxylation of Anisole by Ceric Ammonium Nitrate in Acetic Acid[1]

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Substitution of hydrogen atoms in aromatic compounds by acyloxy groups via oxidative routes is being given considerable attention in view of the mechanistic implication as well as of the synthetic potential.[2,3]

We have shown that ceric ammonium nitrate (CAN) in acetic acid is a suitable reagent for the functionalization of polymethylbenzenes.[4] Substitution of benzylic C–H bonds was the only reaction observed with all the substrates investigated, with the sole exception of mesitylene, for which nu-

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