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Reactions of Isothiocyanates with Cyanothioformamides. Cyclization of 5-Imino-4-thioxo-2-imidazolidones and 5-Imino-2,4-imidazolidinedithiones to 5,7-Dihydrodiimidazo[4,5-*b*:4′,5′-*e*]pyrazine-2,6(1*H*,3*H*)-diones and -dithiones[1]

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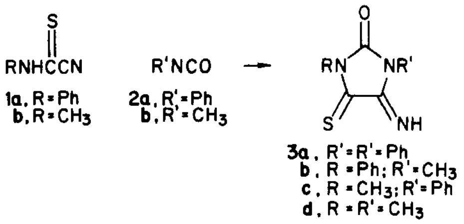
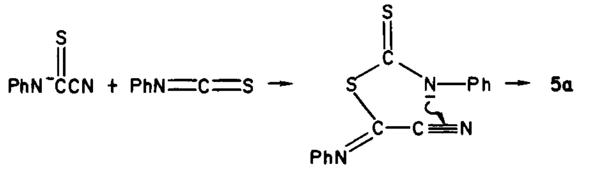
N-Methyl- or *N*-phenylcyanothioformamide (**1a**,**b**) reacts with methyl or phenyl isocyanate to provide 5-imino-1,3-disubstituted-4-thioxo-2-imidazolidinones **3a**–**d**. Methyl or phenyl isothiocyanate with **1a**,**b** gives 5-imino-1,3-disubstituted-2,4-imidazolidinedithiones **6** or 5-(phenylimino)-4-imino-2-thiazolidinethiones **5**, depending upon the reaction conditions and the reactants. **6a**,**c**,**d** react with *o*-phenylenediamine to give 1*H*-imidazo-[4,5-*d*]quinoxaline-2(3*H*)-thiones **11a**–**c**. Both **3** and **6** cyclize to diimidazopyrazine derivatives (**12**, **13**, **14**, **15**) at around 200 °C. From unsymmetrically substituted reactants (**3b**,**c**; **6c**), two isomeric products are obtained.

We have reported that cyanothioformanilide (**1a**) reacts with both phenyl isocyanate (**2a**) and phenyl isothiocyanate (**4a**) to form derivatives of imidazolidinetrione (**3**, **6**).[3] These assignments were based on previous reports of the reactions of isocyanates with both cyanoformamides[4] and cyanothioformamides[5] and the assumption that isothiocyanates would react qualitatively in the same way. However, during an investigation of subsequent reactions of these products it became clear that the product from phenyl isothiocyanate and cyanothioformanilide did not have structure **6a** analogous to **3a** from phenyl isocyanate but was the diiminothiazole derivative **5a**.[6] A more extensive study of the reactions of cyanothioformamides and isothiocyanates thus seemed in order. We report here the reactions of both methyl and phenyl isocyanates and isothiocyanates with *N*-methyl- and *N*-phenylcyanothioformamides under various conditions.

Reactions of both methyl and phenyl isocyanates with either *N*-methyl- or *N*-phenylcyanothioformamide **1** gave high yields of the expected 5-imino-4-thioxo-2-imidazolidinones **3**. Only the 1,3-diphenyl derivative **3a** has been previously reported.[5]



However, a different picture emerges in the reactions of methyl and phenyl isothiocyanate. The product reported earlier[3] from cyanothioformanilide and phenyl isothiocyanate was yellow and on the basis of its reaction with dimethyl acetylenedicarboxylate[6] may now be assigned the 4,5-diiminothiazolidine structure **5a**. This product results from nucleophilic attack by the sulfur atom of the ambident anion from the cyanothioformanilide. It was rationalized that the polar, protic ethanol–water–triethylamine system because of coordination with the nitrogen would render sulfur the more effective nucleophile. We hoped that generation of the free, uncoordinated



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[1] Part 8 of the series "Heterocyclic Ring-Closure Reactions". Part 7: Ketcham, R.; Schaumann, E.; Niemer, T. *Synthesis* **1980**, 869.

[2] (a) Gomal University. (b) University of California. (c) Institut für Organische Chemie, Universität Hamburg. (d) Mineralogische Petrographishes Institut, Universität Hamburg.

[3] Ketcham, R.; Schaumann, E. *J. Org. Chem.* **1980**, *45*, 3748.

[4] Dieckmann, W.; Kämmerer, H. *Ber. Dtsch. Chem. Ges.* **1905**, *38*, 2977; **1907**, *40*, 3737.

[5] Papadopoulos, E. P. *J. Org. Chem.* **1979**, *44*, 3858.

[6] Khattak, I.; Ketcham, R. *J. Chem. Soc., Chem. Commun.* **1983**, 260.

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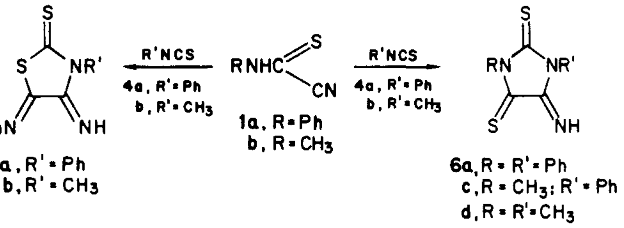
nucleophile in an aprotic environment might leave the more electronegative nitrogen the better nucleophile. By using catalytic amounts of NaH and crown ether[7] in THF, we obtained the red dithione **6a** as the only isolable product.[8] Thus, in this case one can control the selectivity of the reaction site on the ambident nucleophile.

However, by using different substituents in either the cyanothioformamide and/or the isothiocyanate the balance between sulfur and nitrogen nucleophilicity is displaced so that these reactions give only a single product irrespective of the reaction conditions. Thus, cyanothioformanilide and methyl isothiocyanate gave only the yellow thiazole derivative **5b**, which results from nucleophilic attack by sulfur on the isothiocyanate under a variety of conditions including NaH, crown ether, and THF. The reaction of *N*-methylcyanothioformamide with either phenyl or methyl isothiocyanate on the other hand gave only the red-orange imidazoles **6c** and **6d**, respectively, even under protic, polar conditions. Thus, the less electrophilic methyl isothiocyanate reacts only with the sulfur nucleophile in the more stable, less nucleophilic anion from cyanothioformanilide. The more basic anion from *N*-methylcyanothioformamide always reacts at nitrogen.



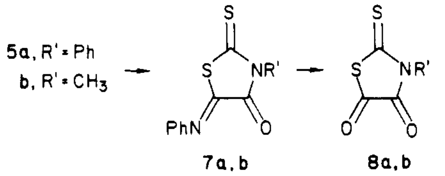
5a, R' = Ph
b, R' = CH$_3$

1a, R = Ph
b, R = CH$_3$

6a, R = R' = Ph
c, R = CH$_3$; R' = Ph
d, R = R' = CH$_3$

The diimino compounds **5a** and **5b** and the imino thiones **6a,c,d** were further characterized by ^{13}C NMR. The diimines **5a** and **5b** have only one ^{13}C NMR resonance (191.3 and 191.6 ppm, respectively) assignable to a thiocarbonyl carbon, whereas the dithiones **6a,c,d** each have two high-field resonances (179.4–181.2 ppm) assignable to thiocarbonyl carbons.

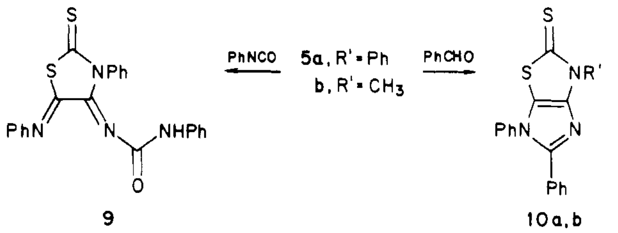
5a was reported[3] to give two hydrolysis products; the structures for which are now seen to be **7a** and **8a**. The latter is identical with the substance prepared from *N*-phenyldithiocarbamate and oxalyl chloride,[9a] while the former appears to have been prepared from 3-phenyl-2-thioxo-4-thiazolidone and nitrosobenzene[10] (no melting point). **5b** gives a similar sequence of hydrolysis products **7b** and **8b** in which, again, the second is identical with the known product from *N*-methyldithiocarbamate and oxalyl chloride.[9b] The reaction product of **5a** with phenyl isocyanate[3] may now be revised to **9**.


5a, R' = Ph
b, R' = CH$_3$

7a,b

8a,b

It is also necessary to comment on the cyclization reaction of the diimines with benzaldehyde which are now seen to be **10a,b**. Thus, these compounds have the expected resonance for the thiocarbonyl group at 186.1 ppm and other resonances at 135.6–149.2 ppm for the three heteroaromatic ring carbons. **10b** is best prepared by simply heating the diimine **5b** with excess benzaldehyde under reflux rather than the BF$_3$-catalyzed reaction used for **10a**.



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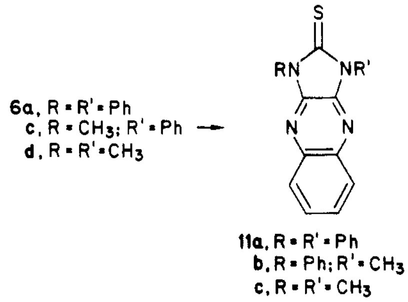
5a, R' = Ph
b, R' = CH$_3$

10a,b

A chemical characterization of the three iminodithiones **6a,c,d** was afforded by cyclization with *o*-phenylenediamine[5] to give the imidazoglyoxalines **11a–c**. Loss of the elements of ammonia and hydrogen sulfide is consistent with the proposed structures.


6a, R = R' = Ph
c, R = CH$_3$; R' = Ph
d, R = R' = CH$_3$

11a, R = R' = Ph
b, R = Ph; R' = CH$_3$
c, R = R' = CH$_3$

All of the compounds that contain a 5-imino 4-thione grouping, (**3a–d** and **6a,c,d**) partially resolidify at 180–200 °C, indicating formation of high-melting tricyclic product.[3] **6a**, as would be expected, gives a better yield (20%) of the thermolysis product than was obtained earlier[3] from the diimine **5a**. The latter provided the tricyclic system only when heated with phenol or hydroquinone where it apparently underwent partial rearrangement to the imino thione **6a**, which in turn led to the low yield of tricyclic product.

Attempts to improve the yields by using potential sulfur scavengers such as trivalent phosphorus compounds or solvent systems capable of oxidation (nitrobenzene) or reduction (catechol) provided no improvement in yields. In spite of these limitations it was felt that because of the ready availability of the starting materials[3,5] and the novelty of the reaction and its products that further study would be of interest.

Reaction of dimethyl- or diphenyl-substituted starting materials **3a,d**; **6a,d** afforded, as anticipated, a single product. The dithiones **13a,b** are bright yellow and fluoresce bright green in solution. The diones **12a,b** are almost colorless and fluoresce less obviously. On the basis of these reactions, a pathway which involved attack by each NH nitrogen on the C$_4$-thiocarbonyl carbon of the reacting partner, followed by loss of the elements of H$_2$S$_2$, seemed reasonable.

However, thermolysis of the three unsymmetrically substituted starting materials **3b,c**;**6c** provided not one but two isomeric products. These can only be the centrosymmetric structures (C_{2h}, **12c** and **13c**) and the isomeric structures having a second plane of symmetry (D_{2h}, **14** and **15**) (Chart I). In order for the latter substances to be formed, C$_4$ and C$_5$ in **3b,c** and **6c** must lose their original identity so that the *N*-methyl (and *N*-phenyl) groups can end up on the same side of the molecule (D_{2H}) or on the opposite sides of the molecule (C_{2h}). We suggest initial loss of sulfur to form the imino carbene A. This then could rearrange to the isomeric imino carbene B via a formally antiaromatic intermediate (or transition state) 2-azirine.[11,12]

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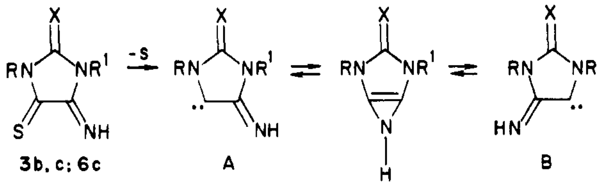
[7] Gokel, G. W.; Durst, A. D. *Synthesis* **1976**, 168.

[8] This approach was first suggested by J. F. Stearns, private communication.

[9] (a) Ritter, W. *Tetrahedron Lett.* **1967**, 4593. (b) Hahnkamm, V.; Gattow, G. *Naturwissenschaften* **1968**, *55* (12), 650.

[10] Hirohashi, R. *Chiba Daigaku Kogakubu Kenkyu Hokoku* **1972**, *23* (44), 169–237.



Thus, A + A or B + B would give the centrosymmetric C_{2h} products **12c** and **13c** whereas A + B would give the D_{2h} products **14** and **15**.

While it is possible to speculate on the identities of the isomeric products (**12**, **14**; **13**, **15**) on the basis of physical properties and spectroscopic data this seemed tenuous at best. Thus, we carried out an X-ray crystallographic examination of the high-melting dimethyldiphenyl dione, which was the major product from **3b** or **3c**. This substance clearly has the centrosymmetric structure **12c**.

Having established this, it is now possible on the basis of melting point and NMR studies to assign the centrosymmetric structure to the higher melting dithione **13c**. The *N*-methyl groups of the centrosymmetric dione **12c** absorb at $\delta = 3.54$ ppm and those of the D_{2h} product **14** absorb at $\delta = 3.62$ ppm. It is assumed that the same relative positions for the *N*-methyl group in **13c** and **15** would be observed so that the centrosymmetric dithione structure **13c** may be assigned to the higher melting isomer having $\delta = 3.82$ ppm and the lower melting product having $\delta = 3.95$ ppm has the D_{2h} structure **15**. The dithiones **13**, and **15** invariably have higher melting points than the similarly constituted diones **12** and **14**, a fact which in retrospect may be attributed to the higher polarization of the thione compared with the carbonyl group.

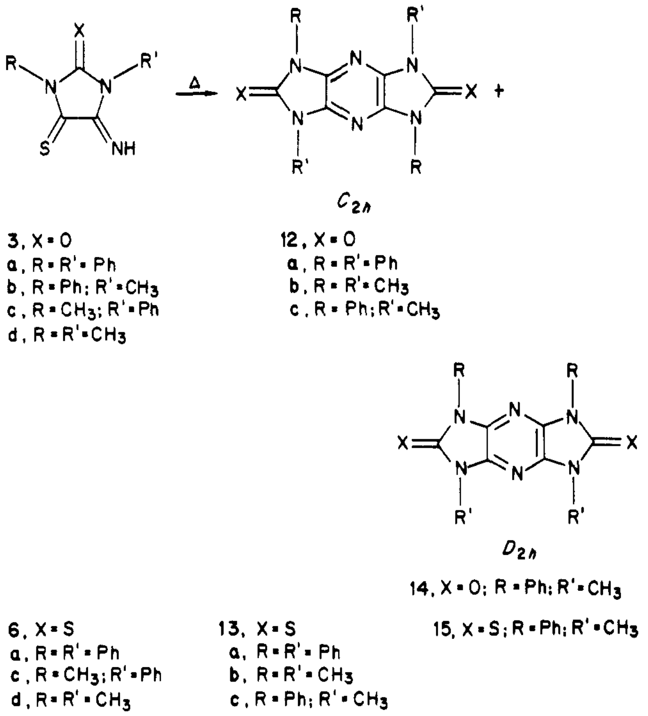
Experimental Section

Reagents were commercially available unless otherwise noted. Melting points were taken on a Fischer-Johns melting point block and are uncorrected. NMR spectra were taken on a Varian FT-80 spectrometer in $CDCl_3$ and are reported in δ units relative to Me_4Si. ^{13}C NMR spectra were measured on a Bruker WP60 or WH270 spectrometer in $CDCl_3$. Elemental analyses were conducted at the microanalytical laboratory at the Chemistry Department, University of California, Berkeley or the analytical laboratory at the University of Hamburg. All new compounds reported gave acceptable combustion analyses. Mass spectra were determined on a Kratos MS-25 spectrometer.

Reactions of Cyanothioformamides with Isocyanates. Cyanothioformanilide (**1a**)[13] and *N*-methylcyanothioformamide (**1b**)[1] were prepared as previously described. The reactions of these substances with the isocyanates **2a,b** were carried out in benzene (**3d**) or toluene as previously described[3,5] (for **3a**) using triethylamine as catalyst.

1-Methyl-3-phenyl-5-imino-4-thioxo-2-imidazolidinone (3b), mp 131–133 °C, was obtained in 69% yield: ^1H NMR δ 9.29 (NH), 7.44–7.50 (Ph), 3.77 (CH_3).

Chart I



1-Phenyl-3-methyl-5-imino-4-thioxo-2-imidazolidinone (3c), mp 120–122 °C, was obtained in 76% yield: ^1H NMR δ 9.57 (NH), 7.45 (Ph), 3.71 (CH_3).

1,3-Dimethyl-5-imino-4-thioxo-2-imidazolidinone (3d), mp 62–64 °C, was obtained in 56% yield: ^1H NMR δ 9.19 (C=O, (N_3 CH_3), 3.28 (N_1 CH_3).

Reactions of Cyanothioformamides with Isothiocyanates. Equivalent amounts of cyanothioformamide (**1a,b**) and isothiocyanate (**4a,b**) in 95% ethanol were treated with 0.1 equiv of triethylamine. After standing at room temperature for 0.5 to 0.4 h, the reaction mixture was refrigerated for several hours. The products were collected and washed with cold ethanol.

3-Phenyl-4-imino-5-(phenylimino)-2-thiazolidinethione (5a): ^{13}C NMR δ 191.3 (C_2), 149.7 and 160.5 (C_4, C_5), 120.4–135.2, 147.6.

3-Methyl-4-imino-5-(phenylimino)-2-thiazolidinethione (5b) was obtained in 59% yield and recrystallized from $CHCl_3$–hexane: mp 115–117 °C; ^1H NMR δ 9.46 (NH), 7.54–7.43 (Ph), 3.46 (CH_3); ^{13}C NMR δ 191.6 (C_2), 150.0, 159.9 (C_4, C_5), 32.0, 120.7–129.5, 147.9.

1-Phenyl-3-methyl-5-imino-2,4-imidazolidinedithione (6c) was obtained in 81% yield and recrystallized from $CHCl_3$–hexane: mp 135–137 °C; ^1H NMR δ 9.42 (NH), 3.77 (CH_3), 7.39–7.55 (Ph); ^{13}C NMR δ 179.4, 180.5 (C_2, C_4), 156.4 (C_5), 33.1, 129.1, 133.9.

1,3-Dimethyl-5-imino-2,4-imidazolidinedithione (6d) was obtained in 45% yield and recrystallized from hexane: mp 72–73 °C; ^1H NMR δ 9.34 (NH), 3.68, 3.55 (Me); ^{13}C NMR δ 180.0, 181.2 (C_2, C_4), 155 (C_5), 32.8, 30.2.

1,3-Diphenyl-5-imino-2,4-imidazolidinedithione (6a). Cyanothioformanilide was dissolved in THF and treated with 0.1 equiv each of 18-crown-6 and NaH (57% in oil). One equivalent of phenyl isothiocyanate (**4a**) was then added and the reaction mixture allowed to stand at room temperature for 3–4 h. It was refrigerated for several hours and then evaporated to dryness in a stream of nitrogen. The gummy, greenish black material was extracted repeatedly with ether until no more red product was extracted. The ether solution was treated with charcoal and filtered to remove the gummy blue impurity and then diluted with hexane and concentrated to induce crystallization. After recrystallization from ether–hexane, there was obtained a 45% yield of brick red crystals: mp 135–137 °C; ^1H NMR δ 9.47 (NH), 7.51 (Ph); ^{13}C NMR δ 180.2, 180.3 (C_2, C_4), 156.4 (C_5), 128.2–135.3.

3-Methyl-5-(phenylimino)-2-thioxo-4-thiazolidinone (7b). To 0.47 g (2 mmol) of **5b** in 10 mL of hot 95% ethanol was added 2 mL of 1 N HCl. A transient red color appeared and was followed

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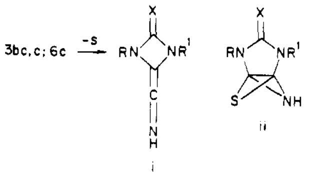
(11) "Pyrolytic Methods in Organic Chemistry"; Academic Press, Inc.: New York, 1980; p 141.

(12) Formation of a ketenimine (i) would also satisfy the structural requirements for an intermediate leading ultimately to the two isomeric products. This could occur via A and B or by a concerted process. Contraction of a five-membered ring to a four-membered should make this process unlikely. Another intermediate (ii) suggested by a referee could also lead to a 2-azirine and the isomeric iminocarbenes by loss of sulfur.



(13) Reissert, A.; Brüggemann, K. *Ber. Dtsch. Chem. Ges.* **1924**, *57*, 981.

by an almost immediate formation of yellow crystals. After standing at room temperature for 2 h, the solid was collected and washed with cold ethanol to give 0.45 g (45%) of product, mp 149–152 °C. Recrystallization from $\mathrm{CHCl_3}$–hexane provided an analytical sample, mp 159–161 °C: ^{1}H NMR δ 7.47–7.11 (m, 5 H, Ar), 3.61 (s, 3 H, $\mathrm{CH_3}$); ^{13}C NMR δ 191.9 (C=S); 161.6, 150.4 (C=O, C=N), 120.8–140.3 (Ar), 31.1 ($\mathrm{CH_3}$); MS, *m/e* (relative intensity) 236 (80, M$^+$).

3-Phenyl-5-(phenylimino)-2-thioxo-4-thiazolidinone (7a) prepared earlier[3] had the following: ^{13}C NMR δ 191.6 (C=S), 161.3, 150.4 (C=O, C=N), 120.8–148.3 (Ar); MS, *m/e* 266 (M$^+$) (lit.[10] no mp).

3-Methyl-2-thioxo-4,5-imidazolidinedione (8b). To 0.47 g (2 mmol) of **5b** in 15 mL of hot 95% ethanol was added 1 mL of concentrated HCl. The reaction mixture was diluted with water to give a cloudy mixture. Filtration removed a small amount of **7b**, mp 154–160 °C. The filtrate was extracted with $\mathrm{CHCl_3}$. Evaporation gave a semicrystaline residue which was recrystallized from pentane: yield 0.20 g (62%); mp 42–45 °C (lit.[9b] mp 44 °C); ^{1}H NMR δ 3.63 (s, $\mathrm{CH_3}$); MS, *m/e* 161 (M$^+$).

3-Phenyl-2-thioxo-4,5-imidazolidinedione (8a) prepared earlier[3] had the following: MS, *m/e* 223; mp 178 °C (lit.[9a] mp 178 °C).

3-Methyl-5,6-diphenylimidazo[5,4-*b*]thiazole-2-thione (10b). The diimine **5b** (0.35 g, 1.5 mmol) was heated at 180 °C in an excess of benzaldehyde (1 g, 9.4 mmol) for 45 min. The dark reaction mixture was diluted with ethanol and the solid was collected, washed with ethanol, and recrystallized from $\mathrm{CHCl_3}$–EtOH to give 220 mg, mp 216–218 °C. Chromatography (silica gel/$\mathrm{CHCl_3}$) of the combined mother liquors gave an additional 90 mg, mp 216–218 °C; total yield 310 mg (64%). The analytical sample had the following: mp 217–219 °C; ^{1}H NMR δ 7.29–7.49 (m, 10, Ar), 3.87 (s, 3, $\mathrm{CH_3}$); ^{13}C NMR 184.9 (C=S), 149.1, 145.9, 136.6 ($\mathrm{C_3N_2}$ ring), 115.1–130.0 (Ph), 33.0 ($\mathrm{CH_3}$); MS, *m/e* 323.

Reactions of 5-Imino-2,4-imidazolidinedithiones with *o*-Phenylenediamine. The 5,4-imino thione **6a,c,d** was heated with an excess (1.5 equiv) of *o*-phenylenediamine (recrystallized from water[14]) in methanol for 4 h by which time the initially dark reaction mixture had become lighter. The highly insoluble product (11) precipitated and was collected and recrystallized from $\mathrm{CHCl_3}$-methanol.

1,3-Diphenyl-1*H*-imidazo[4,5-*d*]quinoxaline-2(3*H*)-thione (11a) was obtained in 33% yield: mp 367–368 °C; ^{1}H NMR δ 7.90, 7.62; MS, *m/e* 354.

1-Methyl-3-phenyl-1*H*-imidazo[4,5-*d*]quinoxaline-2-(3*H*)-thione (11b) was obtained in 31% yield: mp 279–280 °C; ^{1}H NMR δ 8.00 (m), 7.61 (m), 3.95 (s); MS, *m/e* 292.

1,3-Dimethyl-1*H*-imidazo[4,5-*d*]quinoxaline-2(3*H*)-thione (11c) was obtained in 40% yield: mp 241–242 °C; ^{1}H NMR δ 7.96 (m), 7.62 (m), 3.85 (s); MS, *m/e* 230.

Thermolysis Reactions. Samples of the imino thiones **3** and **6** were heated to reflux in about 5 parts of phenol for 1 h. Dilution with ethanol or acetone gave crystals of the crude products. For the tetramethyl (**12b**, **13b**) and tetraphenyl products (**12a**, **13a**) simple recrystallization provided the pure products. For the dimethyl, diphenyl substituted products separation was achieved by extracting the crude reaction mixture repeatedly with warm $\mathrm{CHCl_3}$ or $\mathrm{CH_2Cl_2}$. The residue, containing the higher melting C_{2h} product, was recrystallized from DMF. The extract contains about 80% of lower melting and 20% of the high melting product (NMR). Fractional crystallization from $\mathrm{CHCl_3}$–EtOH or partial sublimation (240 °C, 1 mm) eventually gave the pure D_{2h} compound.

5,7-Dihydro-1,3,5,7-tetraphenyldiimidazo[4,5-*b*:4′,5′-*e*]-pyrazine-2,6(1*H*,3*H*)-dione (12a):[3] ^{1}H NMR δ 7.9–7.4 (Ph).

5,7-Dihydro-1,3,5,7-tetramethyldiimidazo[4,5-*b*:4′,5′-*e*]-pyrazine-2,6(1*H*,3*H*)-dione (12b) was obtained in 9% yield (from $\mathrm{CHCl_3}$): mp 305–310 °C; ^{1}H NMR δ 3.51.

5,7-Dihydro-1,5-dimethyl-3,7-diphenyldiimidazo[4,5-*b*:4′,5′-*e*]pyrazine-2,6(1*H*,3*H*)-dione (12c) was obtained in 15% from **3c** and in 8% from **3d**; mp 370 °C; ^{1}H NMR δ 7.4–7.9 (Ph), 3.54 (Me).

5,7-Dihydro-1,7-dimethyl-3,5-diphenyldiimidazo[4,5-*b*:4′,5′-*e*]pyrazine-2,6(1*H*,3*H*)-dione (14) was obtained in 5% yield from **3c** and 3.5% from **3d**; mp 275–280 °C; ^{1}H NMR δ 7.4–7.9 (Ph), 3.62 (Me).

5,7-Dihydro-1,3,5,7-tetraphenyldiimidazo[4,5-*b*:4′,5′-*e*]-pyrazine-2,6(1*H*,3*H*)-dithione (13a[3]): ^{1}H NMR δ 7.54 (Ph).

5,7-Dihydro-1,3,5,7-tetramethyldiimidazo[4,5-*b*:4′,5′-*e*]-pyrazine-2,6(1*H*,3*H*)-dithione (13b) was obtained in 20% yield (from $\mathrm{CHCl_3}$-EtOH): mp >400 °C (sublimes); ^{1}H NMR δ 3.86 (Me).

5,7-Dihydro-1,5-dimethyl-3,7-diphenyldiimidazo[4,5-*b*:4′,5′-*e*]pyrazine-2,6(1*H*,3*H*)-dithione (13c). The mixture obtained from the pyrolysis was extracted several times with $\mathrm{CHCl_3}$. The residue was recrystallized from boiling DMF to give 15% of **14c**: mp 420 °C; ^{1}H NMR δ 7.60 (Ph), 3.82 (Me).

5,7-Dihydro-1,7-dimethyl-3,5-diphenyldiimidazo[4,5-*b*:4′,5′-*e*]pyrazine-2,6(1*H*,3*H*)-dithione (15). The $\mathrm{CHCl_3}$ extract from above was diluted with ethanol and concentrated to induce crystallization. Recrystallization ($\mathrm{CHCl_3}$–EtOH) or fractional sublimation (~300 °C) gave the pure compound: mp 380 °C in 5% yield; ^{1}H NMR δ 7.49 (Ph), 3.95 (Me).

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Registry No. **1a**, 4955-82-2; **1b**, 13621-47-1; **2a**, 103-71-9; **2b**, 624-83-9; **3a**, 71342-25-1; **3b**, 79174-54-2; **3c**, 97012-42-5; **3d**, 97012-43-6; **4a**, 103-72-0; **4b**, 556-61-6; **5a**, 87606-14-2; **5b**, 97012-44-7; **6a**, 74331-41-2; **6c**, 97012-45-8; **6d**, 72973-61-6; **7a**, 39666-58-5; **7b**, 97012-46-9; **8a**, 17822-34-3; **8b**, 21468-40-6; **10a**, 97012-57-2; **10b**, 97012-47-0; **11a**, 97012-48-1; **11b**, 97012-49-2; **11c**, 97012-50-5; **12a**, 74331-47-8; **12b**, 97012-51-6; **12c**, 97012-52-7; **13a**, 74331-48-9; **13b**, 97012-54-9; **13c**, 97012-55-0; 14, 97012-53-8; **15**, 97012-56-1; PhCHO, 100-52-7; *o*-$\mathrm{(NH_2)_2C_6H_4}$, 95-54-5.

Supplementary Material Available: Crystallographic data for **12c** and tables of bond lengths, bond angles, and atomic coordiantes (7 pages). Ordering information is given on any current masthead page.

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[14] Fieser, L. F.; Fieser, M. "Reagents for Organic Synthesis"; John Wiley and Sons, Inc.: 1976; Vol. 1, p 834.