Reactions of Pyrrole with Isothiocyanates. Preparation and Reactions of *N*-Ethoxycarbonylpyrrole-2-thiocarboxamide and 2-Thiopyrrole-1,2-dicarboximide

E. P. PAPADOPOULOS

Department of Chemistry, University of New Mexico, Albuquerque, New Mexico 87106

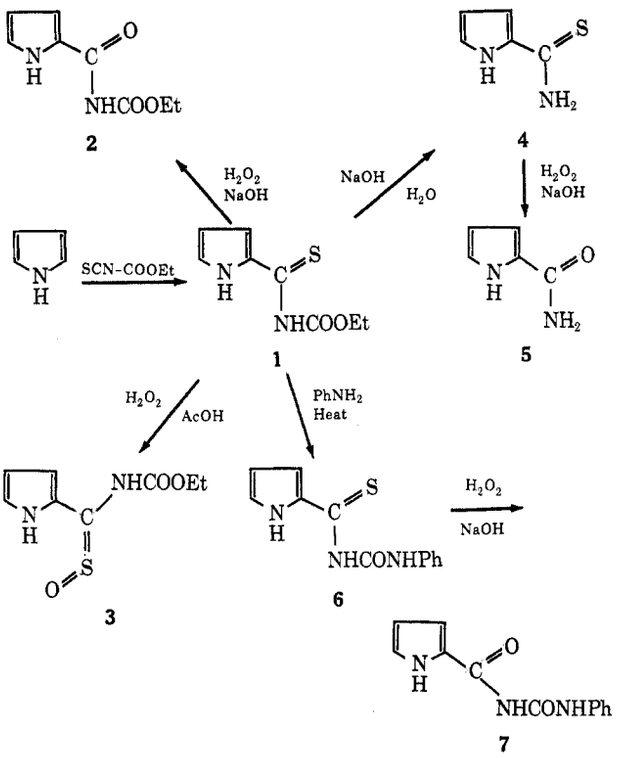
Received September 1, 1972

The reaction of pyrrole with ethoxycarbonyl isothiocyanate yields *N*-ethoxycarbonylpyrrole-2-thiocarboxamide (**1**), which is converted to 2-thiopyrrole-1,2-dicarboximide (**14**) by treatment with hot quinoline. Starting with pyrrolylpotassium, *N*-ethoxycarbonylpyrrole-1-thiocarboxamide (**24**) and 1-thiopyrrole-1,2-dicarboximide (**34**) are similarly obtained. Compounds **1**, **14**, and **24** are convenient and versatile sources of a variety of monocyclic and bicyclic thioamides, thioamide *S*-oxides, and amidines of pyrrole.

Nitrogen-substituted pyrrole-2-carboxamides[1] and thioamides[2] are useful synthetic intermediates because they allow formation of a new heterocyclic ring fused to the original pyrrole ring.[3,4] To supplement the results of a recent study of the preparation and reactions of *N*-ethoxycarbonylpyrrole-2-carboxamide and pyrrole-1,2-dicarboximide,[4] an investigation of the corresponding thio derivatives of pyrrole was undertaken.

N-Ethoxycarbonylpyrrole-2-thiocarboxamide (**1**) is obtained in high yield when pyrrole is allowed to react with ethoxycarbonyl isothiocyanate. The structure assignment is supported by the ir spectrum of the product, which shows absorption due to NH at 3350 and 3325 cm^{-1}, carbonyl at 1765 and 1740 cm^{-1},[5] and thiocarbonyl at 1120 cm^{-1}.[6] In agreement, the nmr spectrum displays three one-proton multiplets centered at δ 6.2, 6.8, and 7.0, characteristic of 2-substituted pyrrole derivatives of this type,[4,7] as well as two singlets at δ 8.7 and 9.9 for the imide and pyrrole NH protons, respectively. Oxidation of **1** with alkaline hydrogen peroxide yields the expected *N*-ethoxycarbonylpyrrole-2-carboxamide (**2**),[4] but treatment with hydrogen peroxide in acetic acid leads to *N*-ethoxycarbonylpyrrole-2-thiocarboxamide *s*-oxide (**3**). The ir spectrum of this compound lacks the C=S absorption band at 1120 cm^{-1} and displays, instead, a strong *S*-oxide band at 960 cm^{-1}.[8]

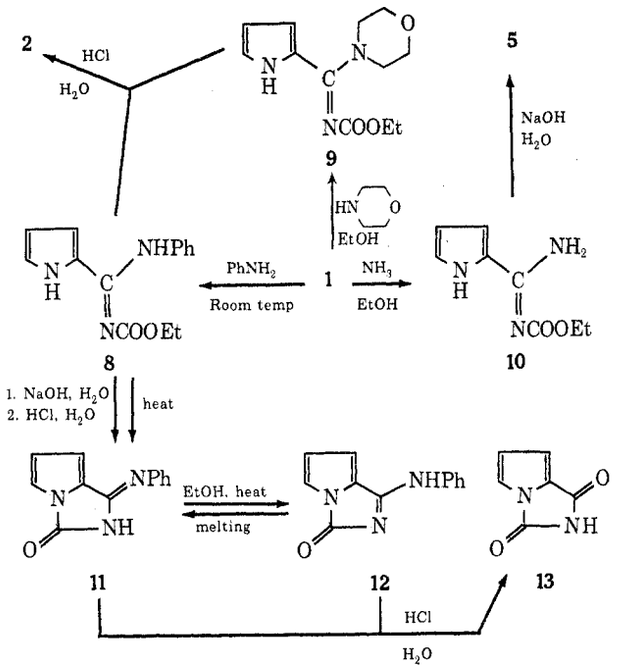
Compound **1** shows considerable reactivity toward nucleophilic reagents at both carbonyl and thiocarbonyl groups. Thus, heating with aqueous sodium hydroxide hydrolyzes the ester group with loss of CO_2 and formation of pyrrole-2-thiocarboxamide (**4**) in excellent yield. Brief boiling with aniline results in substitution at the carbonyl and yields *N*-phenylcarbamoylpyrrole-2-thiocarboxamide (**6**), which is readily oxidized to the known *N*-phenylcarbamoylpyrrole-2-carboxamide (**7**)[4] by hydrogen peroxide. On the other hand, prolonged standing at room temperature of a mixture of **1** and aniline leads to reaction at the thiocarbonyl with elimination of H_2S and formation of *N'*-ethoxycarbonyl-*N*-phenylpyrrole-2-carboxamidine (**8**). The ir spectrum of this compound contains C=O and C=N stretching bands at 1630 and 1570 cm^{-1}, respectively. In view of the low-frequency carbonyl absorption, the α,β-unsaturated ester structure **8** is likelier than that of the tautomeric carbamate.[9] This conclusion is supported by an inspection of the ir spectrum of the corresponding morpholine derivative **9** (obtained when **1** is boiled briefly with ethanolic morpholine) for which similar tautomerism is not possible. In this case the C=O band appears at 1650 cm^{-1} and the C=N band at 1570 cm^{-1}. The formation of *N*-ethoxycarbonylpyrrole-2-carboxamide (**2**) upon hydrolysis of either **8** or **9** by dilute hydrochloric acid is consistent with the structures formulated for these compounds.



It is interesting to note that a different product is obtained when hydrolysis of **8** is attempted by treatment with hot, aqueous NaOH, followed by acidification. This compound, which also results from the thermal decomposition of **8**, may be recrystallized unchanged from benzene or toluene, but is converted to an isomer upon recrystallization from methanol or ethanol. Either of the two isomers is hydrolyzed

(1) A. Treibs and W. Ott, *Justus Liebigs Ann. Chem.*, **577**, 119 (1952).
(2) E. Bullock and R. J. Abraham, *Can. J. Chem.*, **37**, 1391 (1959).
(3) (a) E. P. Papadopoulos and H. S. Habiby, *J. Org. Chem.*, **31**, 327 (1966); (b) E. P. Papadopoulos, *ibid.*, **31**, 3060 (1966).
(4) E. P. Papadopoulos, *ibid.*, **37**, 351 (1972).
(5) In chloroform solution, the two bands merge into one, at 1760 cm^{-1}, with a weak shoulder at 1730 cm^{-1}.
(6) E. Spinner, *J. Chem. Soc.*, 1237 (1960).
(7) L. R. Smith, A. J. Speziale, and J. E. Fedder, *J. Org. Chem.*, **34**, 633 (1969).
(8) W. Walter and H. P. Kubersky, *Justus Liebigs Ann. Chem.*, **694**, 70 (1966).
(9) Compare with C=O stretching frequencies in carbamates: 1720 cm^{-1} in PhNHCOOEt, 1740 and 1765 in **1**, 1770 cm^{-1} in **2**.

readily to pyrrole-1,2-dicarboximide (**13**) by hot, dilute hydrochloric acid.

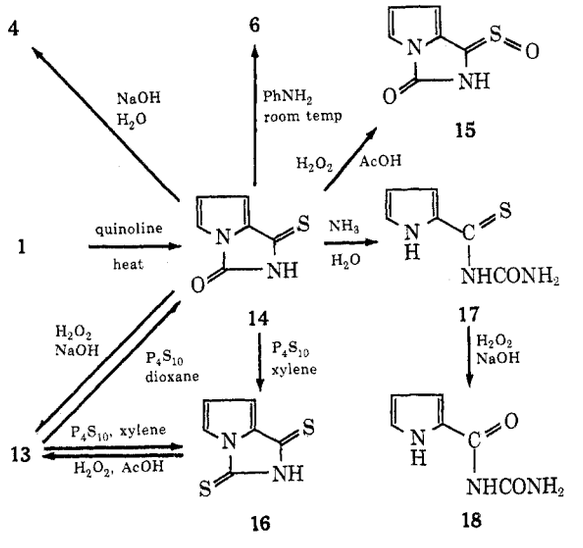


On the basis of ir spectral data, the structure of 1-phenyliminopyrrolo[1,2-*c*]imidazol-3(2*H*)-one (**11**) has been assigned to the initial hydrolysis product, and that of the tautomeric phenylamino derivative **12** to the isomerization product. The ir spectrum of **11** indicates absorption due to C=O at 1780 cm^{-1},[10] and to C=N at 1670 cm^{-1}. In the spectrum of **12**, the corresponding bands appear at 1720 and 1640 cm^{-1}. The lower frequency bands in the case of the latter tautomer are consistent with the conjugation of C=O, as well as the endocyclic position of C=N.[11] In support, the ir spectrum of the analogous morpholine derivative **19**, in which the C=N is by necessity endocyclic, exhibits a C=O band at 1730 cm^{-1} and a C=N band at 1600 cm^{-1}. Of the two tautomer, **11** appears to be the more stable one, because melting converts **12** into **11** but leaves **11** unchanged. Similarly, **12** is converted into **11** upon dissolution in chloroform. This is indicated by the fact that both tautomers give the same ir spectrum in $CHCl_3$ solution showing absorption due to C=O and C=N at 1780 and 1680 cm^{-1}, respectively. There is excellent agreement between the above considerations concerning the structures and ir spectra of tautomers **11** and **12** and the analogous observations made in the cases of 2-iminopyrrolidin-5-ones and 2-amino-Δ^1-pyrrolin-5-ones.[12]

The action of ammonia on **1** is similar to that of aniline and morpholine. Heating of **1** with ethanolic ammonia yields *N'*-ethoxycarbonylpyrrole-2-carboxamidine (**10**). Both ir (C=O at 1680 and C=N at 1620 cm^{-1}) and nmr (broad singlet for $-NH_2$ at δ 8.9) spectra of this compound are fully consistent with the structure assigned to it. Although it resists acid hydrolysis, **10** is readily converted to pyrrole-2-carboxamide (**5**) by hot, aqueous NaOH.

In analogy with the earlier observed behavior of **2**,[4] when **1** is heated with quinoline it undergoes cyclization resulting in elimination of EtOH and formation of 2-thiopyrrole-1,2-dicarboximide (**14**). The ir spectrum of this compound contains carbonyl and thiocarbonyl bands at 1760 and 1150 cm^{-1}, respectively. Its nmr spectrum displays multiplets centered at 6.6, 7.0, and 7.4, for the pyrrole ring protons, and a very broad signal centered at δ 12.3 for the NH proton. The structure formulated for **14** finds support in its formation from pyrrole-1,2-dicarboximide (**13**) by treatment with phosphorus pentasulfide, as well as in its oxidation to **13** by alkaline hydrogen peroxide. By the action of hydrogen peroxide in acetic acid, **14** is converted into 2-thiopyrrole-1,2-dicarboximide *S*-oxide (**15**). An inspection of the ir spectra shows that the spectrum of **15** retains the C=O band at 1770 cm^{-1}, but displays an *S*-oxide band at 1020 cm^{-1}, instead of the C=S band at 1150 cm^{-1} in the spectrum of **14**. Prolonged treatment with P_4S_{10} in refluxing xylene converts both **13** and **14** into pyrrole-1,2-dithiodicarboximide (**16**). The ir spectrum of this compound is characterized by a strong C=S band at 1130 cm^{-1} and the absence of any bands in the carbonyl region. As expected, its nmr spectrum corresponds very closely to that of **14**. Treatment with hydrogen peroxide in acetic acid oxidizes **16** to the dicarboximide **13**.

Nucleophilic reagents attack **14** at either the carbonyl or the thiocarbonyl group. In the first instance, the thiohydantoin ring opens between carbonyl and pyrrole nitrogen, yielding derivatives of pyrrole-2-thiocarboxamide, in complete analogy with the behavior of pyrrole-1,2-dicarboximide (**13**).[4] Thus, treatment with aqueous NH_3 converts **14** to *N*-carbamoylpyrrole-2-thiocarboxamide (**17**). The identification of this compound is based on its spectra (ir, C=O at 1730 cm^{-1}, C=S at 1130 cm^{-1}; nmr, $-NH_2$ at δ 7.8 and 9.1, imide NH at δ 10.8, pyrrole NH at δ 11.7) and its oxidation to the known *N*-carbamoylpyrrole-2-carboxamide (**18**)[4] by hydrogen peroxide. In a similar manner, the action of an excess of aniline on **14** leads to *N*-phenylcarbamoylpyrrole-2-thiocarboxamide (**6**). The analogous ring opening caused by aqueous NaOH proceeds with loss of CO_2 and yields pyrrole-2-thiocarboxamide (**4**). Reac-



(10) Compare with the following C=O stretching frequencies: 1760 cm^{-1} in **14**, 1795 in **13**.

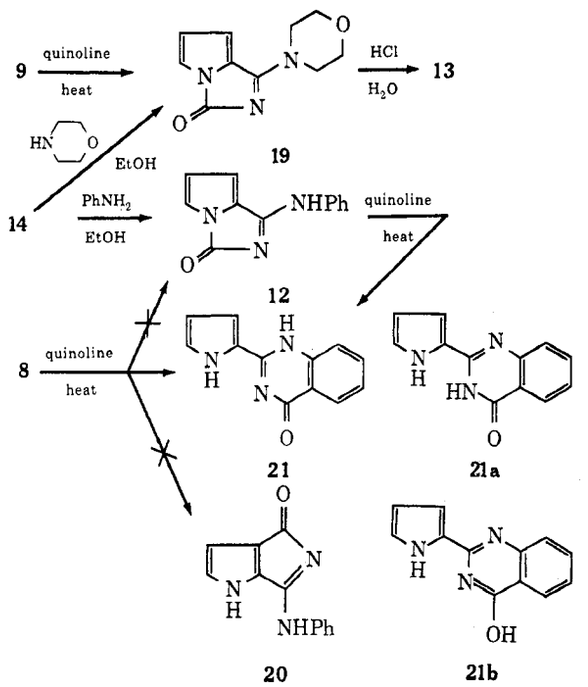
(11) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," 2nd ed, Wiley, New York, N. Y., 1962, p 269.

(12) A. Foucaud and P. Plusquellec, *Bull. Soc. Chim. Fr.*, 3813 (1968).

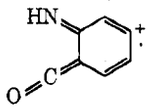
tion at the thiocarbonyl is observed when **14** is treated with a dilute solution of a primary or secondary amine in ethanol and results in replacement of sulfur by an imino group. In this way, treatment with ethanolic aniline yields 1-phenylaminopyrrolo[1,2-*c*]imidazol-3-one (**12**), which, as seen earlier, is also obtained by hydrolysis of the amidine **8**.

A similar reaction between **14** and morpholine in dilute ethanolic solution gives 1-morpholinopyrrolo-[1,2-*c*]imidazol-3-one (**19**). Like **12**, this compound is hydrolyzed by hot, dilute hydrochloric acid to pyrrole-1,2-dicarboximide (**13**).

A cyclization analogous to that involved in the formation of **14** from **1** is observed when the morpholine derivative **9** is heated with quinoline to form **19**. It is of interest to note that the same treatment with hot quinoline fails to convert amidine **8** to **11** or **12**. Instead, an isomer is obtained for which structure **20** or **21** (or a tautomer of either) may reasonably be suggested. The ir spectrum of the product, displaying a sharp NH band at 3420 cm^{-1}, a carbonyl band at 1680 cm^{-1}, and a C=N band at 1600 cm^{-1}, does not allow a choice to be made. However, the presence in it of a



band at 770 cm^{-1}, which is absent from the spectrum of **8**, may be taken to indicate an ortho-disubstituted benzene ring. The nmr and mass spectra, on the other hand, support the structure of 2-(2-pyrrolyl)quinazolin-4(1*H*)-one (**21**) or its 3-H tautomer **21a**.[13] In the nmr spectrum, in addition to two one-proton multiplets centered at δ 6.4 and 7.2, a third multiplet is sufficiently discernible at δ 7.5 (among the signals of the benzene ring protons) to establish the pattern which is characteristic of 2-monosubstituted pyrroles. Furthermore, two multiplets adding up to one proton and centered at δ 8.2 and 8.3 indicate a benzene proton peri to a carbonyl.[14a] There is no evidence for the presence of a significant amount of tautomer **21b**. The mass spectrum exhibits peaks at *m/e* 39 ($C_3H_3^+$), 66 (pyrrolyl ion), 92 (cyanopyrrole ion), and 119 (i), which are consistent

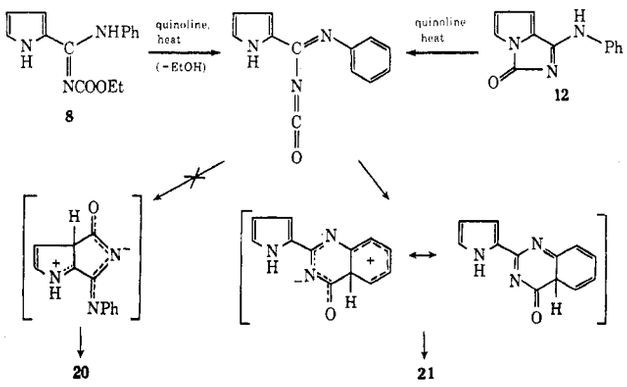


i

with structure **21**, but not with **20**.[14b] Noteworthy is the absence of a peak at *m/e* 77 (phenyl ion), which is prominent in the spectrum of the isomeric phenylamino derivative **12**.

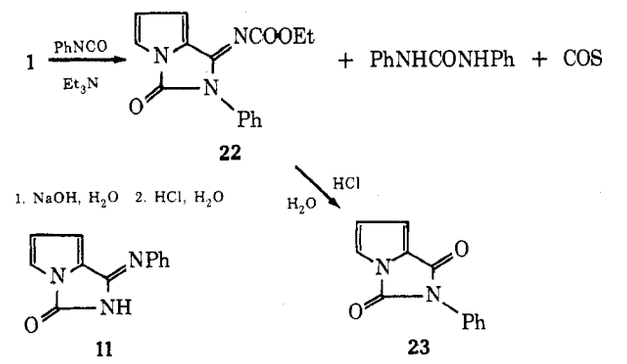
As shown in Scheme I, the formation of quinazolinone **21** from carboxamidine **8** may be accounted for by a re-

SCHEME I



action path in which initial loss of ethanol, resulting in formation of an isocyanate group, is followed by cyclization. Such a path is supported by the observation that **21** is also formed when **12** is heated with quinoline. The fact that electrophilic attack by the isocyanate group on the benzene ring (leading to **21**) is preferred over attack on the pyrrole ring (leading to **20**) may be attributed to the greater stability of the intermediate formed in the former case.

In earlier work,[4] it was found that *N*-ethoxycarbonylpyrrole-2-carboxamide (**2**) reacts with phenyl isocyanate, in the presence of triethylamine, to yield *N*-phenylpyrrole-1,2-dicarboximide (**23**). When the thio



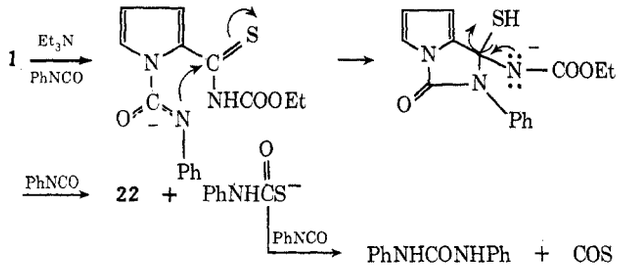
derivative **1** is treated similarly, it reacts in a different manner to form 1-ethoxycarbonylimino-2-phenylpyr-

(13) The formation of quinazolin-4(3*H*)-ones by thermal decomposition of amidines analogous to **8** is a known reaction: (a) R. Shah and M. B. Ichaporia, *J. Chem. Soc.*, 431 (1936); (b) R. Gompper, H. E. Noppel, and S. Schaefer, *Angew. Chem., Int. Ed. Engl.*, **2**, 686 (1963).

(14) (a) S. C. Pakrashi, J. Bhattacharyya, L. F. Johnson, and H. Budjikiewicz, *Tetrahedron*, **19**, 1011 (1963). (b) Q. N. Porter and J. Baldas, "Mass Spectrometry of Heterocyclic Compounds," Wiley-Interscience, New York, N. Y., 1971, pp 325–333, 482.

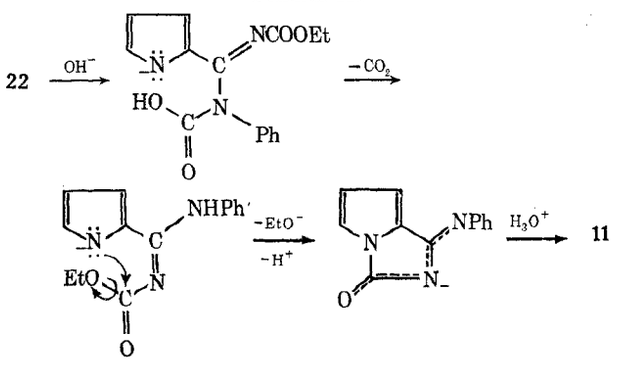
rolo[1,2-c]imidazol-3-one (22), together with *N,N'*-diphenylurea and carbonyl sulfide. The formation of these products may be accounted for by the reaction path shown in Scheme II.

SCHEME II



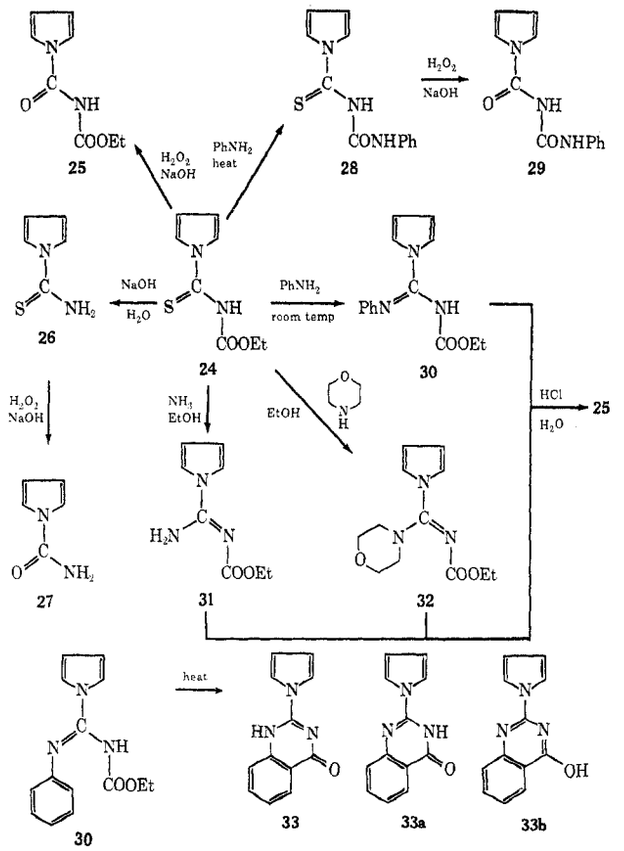
The structure assigned to compound 22 is consistent with its ir spectrum, which displays two carbonyl bands, at 1780 and 1700 cm^{-1}. The nmr spectrum confirms the retention of the ethoxycarbonyl group with typical triplet and quartet signals at δ 1.3 and 4.4. It further exhibits the characteristic pyrrole CH multiplets at δ 6.9, 7.2 and 8.0, as well as a singlet at δ 7.8 for the phenyl protons. Additional support for structure 22 is found in the formation of *N*-phenylpyrrole-1,2-dicarboximide (23) upon hydrolysis with hot, concentrated hydrochloric acid. It is interesting to note that hydrolysis of 22 by hot aqueous NaOH yields the phenylimino derivative 11. It appears that an initial ring opening is followed by loss of CO_2 and a new ring closure, as shown in Scheme III.

SCHEME III



As expected,[3,4] treatment of the potassium salt of pyrrole with ethoxycarbonyl isothiocyanate leads to reaction at the ring nitrogen and formation of *N*-ethoxycarbonylpyrrole-1-thiocarboxamide (24). In many respects, the reactivity of this compound parallels that of its isomer 1. Thus, it is oxidized readily to *N*-ethoxycarbonylpyrrole-1-carboxamide (25)[4] by hydrogen peroxide, although it fails to be converted to an *S*-oxide analogous to 3. Its alkaline hydrolysis proceeds with decarboxylation to yield pyrrole-1-thiocarboxamide (26), which is oxidized to pyrrole-1-carboxamide (27)[4] by hydrogen peroxide. Momentary boiling with aniline converts 24 into *N*-phenylcarbamoylpyrrole-1-thiocarboxamide (28), identified by its oxidation to the known *N*-phenylcarbamoylpyrrole-1-carboxamide (29).[4] Treatment with aniline, at room temperature, or with hot ethanolic ammonia or morpholine gives the corresponding pyrrole-1-carboxamidine derivatives 30, 31, and 32 which are hydrolyzed by dilute hydrochloric acid to *N*-ethoxycarbonylpyrrole-1-carboxamide (25). Ir and nmr spectra of 24–32 (Scheme IV) are fully

SCHEME IV

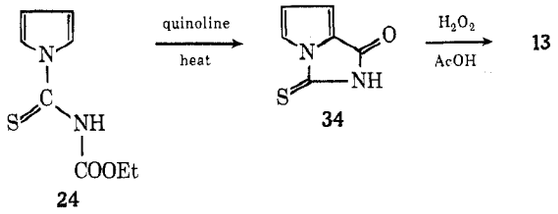


consistent with their proposed structures. For the product of the reaction with aniline at room temperature, the relatively high C=O stretching frequency (1725 cm^{-1}, Nujol mull) supports the structure of *N*-ethoxycarbonyl-*N'*-phenylpyrrole-1-carboxamidine (30), rather than that of the tautomeric α,β-unsaturated ester. The opposite must be true for this compound in solution, because the carbonyl band of the spectrum in $CHCl_3$ appears at 1650 cm^{-1}. For the earlier considered, isomeric pyrrole-2-carboxamidine derivative 8, in contrast, the C=O band appears at the same position (1630 cm^{-1}) both in emulsion and in solution spectra.

When heated 20–30° above its melting point, compound 30 loses ethanol and yields 2-(1-pyrrolyl)-quinazolin-4(1*H*)-one (33) or its 3-H tautomer 33a. This remarkably easy and clean transformation is analogous with the formation of the isomeric quinazolinone 21, when 8 is boiled with quinoline, but contrasts with the conversion of 8 into 11 by simple thermal decomposition.

Compared with the ir spectrum of 21, that of 33 lacks a strong, sharp NH band, but retains the C=O and C=N bands at essentially the same positions (1675 and 1615 cm^{-1}, respectively). The nmr spectrum of 33 displays two triplets at δ 6.4 and 7.8, which are characteristic of 1-monosubstituted pyrroles, as well as two multiplets, centered at δ 8.1 and 8.2, which indicate a benzene proton peri to a carbonyl.[14a] There is only a weak, diffuse signal, centered at about δ 12.5, for the NH proton. As in the case of 21, there is no evidence

supporting the presence of a significant amount of tautomer **33b**.



Rather unexpectedly, brief boiling of **24** with quinoline causes ring closure at position 2 of the pyrrole ring and yields 1-thiopyrrole-1,2-dicarboximide (**34**). The elimination of EtOH is indicated by the nmr spectrum of the product, which displays only three one-proton multiplets (centered at δ 6.6, 6.9, and 7.6) for the ring protons, in addition to a very broad signal (centered at δ 12.5) for the NH proton. The ir spectrum contains a carbonyl band at 1750 cm^{-1} and a thiocarbonyl band at 1140 cm^{-1}. Oxidation of this compound with hydrogen peroxide in acetic acid gives pyrrole-1,2-dicarboximide (**13**). No *S*-oxide analogous to **15** is isolated.

Experimental Section[15]

***N*-Ethoxycarbonylpyrrole-2-thiocarboxamide** (**1**).—A mixture of 16.8 g (0.25 mol) of pyrrole and 32.8 g (0.25 mol) of ethoxycarbonyl isothiocyanate,[16] both ice-cold, was swirled occasionally and cooled as needed to prevent its temperature from rising above 40°. Within about 1 hr the mixture had solidified, whereupon it was allowed to stand overnight. Following repeated washing of the product with petroleum ether (bp 60–90°), there was obtained 46.2 g (93%) of **1**, mp 95–98°. Recrystallization from aqueous ethanol gave the pure compound in the form of yellow crystals: mp 98.5–99.5°; ir 3350, 3325, 1765, 1740, 1535, 1510, 1340, 1210, 1120, 1070, 1025, 900, 870, 750, 695, and 620 cm^{-1}; nmr ($CDCl_3$) δ 1.3 (t, 3, J = 7 Hz, $-CH_3$), 4.2 (q, 2, J = 7 Hz, $-OCH_2-$), 6.2 (m, 1, pyrrolyl CH), 6.8 (m, 1, pyrrolyl CH), 7.0 (m, 1, pyrrolyl CH), 8.7 (s, 1, imide NH), and 9.9 (s, 1, pyrrolyl NH).

Anal. Calcd for $C_8H_{10}O_2N_2S$: C, 48.46; H, 5.08; N, 14.13. Found: C, 48.65; H, 5.20; N, 13.92.

Oxidation of 1 to *N*-Ethoxycarbonylpyrrole-2-carboxamide (**2**).—To an ice-cold solution of 0.50 g of **1** in 5 ml of absolute ethanol was added 1.0 g of anhydrous sodium carbonate and 5 ml of hydrogen peroxide (30%). The mixture was kept in an ice–water bath for 15 min, and at room temperature for a further 2 hr. Dilution with water and filtration yielded 0.25 g of **2**, mp 136–137°, raised to 138–140° by recrystallization from CH_2Cl_2 (lit.[4] mp 140–141°).

***N*-Ethoxycarbonylpyrrole-2-thiocarboxamide *S*-Oxide** (**3**).—Hydrogen peroxide (30%, 10 ml) was added in portions to an ice-cold mixture of 3.0 g of **1**, 3.0 g of sodium acetate, and 20 ml of acetic acid. When the resulting solution was allowed to stand at room temperature, a precipitate was formed within a few minutes. Dilution with water and filtration gave 3.0 g (94%) of **3**, mp 124.5–125.5° dec. An analytical sample was obtained by recrystallization from ethyl acetate as yellow crystals: mp 125–126° dec; ir 3240, 3150, 1720, 1560, 1525, 1400, 1270, 1240, 1140, 1080, 1040, 1000, 960, 860, 835, 750, 660, 600, and 470 cm^{-1}; nmr δ 1.3 (t, 3, J = 7 Hz, $-CH_3$), 4.4 (q, 2, J = 7 Hz, $-OCH_2-$), 6.6 (m, 1, pyrrolyl CH), 7.5 (m, 2, pyrrolyl CH), 10.8 (s, 1, NH), and 13.2 (s, 1, NH).

Anal. Calcd for $C_8H_{10}O_3N_2S$: C, 44.85; H, 4.71; N, 13.07. Found: C, 44.66; H, 4.72; N, 13.22.

(15) Melting points were determined in a Thomas-Hoover apparatus with use of a calibrated thermometer. A Perkin-Elmer Model 337 infrared spectrophotometer was used to take infrared spectra in Nujol. Nmr spectra were obtained on a Varian A-60A spectrophotometer using solutions in hexadeuteriodimethyl sulfoxide (unless otherwise indicated) with tetramethylsilane as internal standard. Known compounds were identified by comparison of their ir and nmr spectra with those of authentic samples, as well as by mixture melting point determination.

(16) R. W. Lamon, *J. Heterocycl. Chem.*, **5**, 837 (1968).

Pyrrole-2-thiocarboxamide (**4**). **A. By Hydrolysis of 1.**—A solution of 2.0 g of **1** in 10 ml of 10% aqueous sodium hydroxide was heated on the steam bath for 10 min. Cooling and filtration yielded 1.2 g (92%) of **4**, as pale yellow crystals: mp 161–162, raised to 162–164° by recrystallization from toluene (lit.[17] mp 162–164°); ir 3340, 3280, 3170, 1625, 1530, 1420, 1310, 1110, 1090, 1060, 970, 890, 880, 845, 750, 700, 600, 580, and 445 cm^{-1}; nmr δ 6.2 (m, 1, CH), 7.0 (m, 2, CH), 9.1 (s, 2, $-NH_2$), and 10.0–11.7 (very broad s, 1, pyrrolyl NH).

B. By Hydrolysis of 14.—Upon dissolution of 0.50 g of **14** in 5 ml of 10% aqueous sodium hydroxide, a solid started precipitating almost at once. Filtration, after 15 min, yielded 0.35 g (85%) of **4**, mp 160–162° raised to 161–163° by recrystallization from toluene.

Oxidation of 4 to Pyrrole-2-carboxamide (**5**).—To an ice-cold suspension of 0.50 g of **4** in 5 ml of 20% aqueous sodium hydroxide was added gradually 5 ml of hydrogen peroxide (30%) and the resulting mixture was kept in an ice–water bath for 10 min. When the reaction flask had been allowed to stand at room temperature for a few minutes, a vigorous reaction took place with evolution of gas and formation of a white precipitate. A cooling treatment followed by filtration yielded 0.30 g of **5**, mp 173–176° (lit.[18] mp 176.5°).

***N*-Phenylcarbamoylpyrrole-2-thiocarboxamide** (**6**). **A. From 1.**—A mixture of 1.0 g of **1** and 5 ml of aniline was boiled for about 1 min and the resulting solution was cooled and then filtered. Following washing of the precipitate with carbon tetrachloride, there was obtained 1.1 g (92%) of **6**, mp 211–212°. Recrystallization from ethanol yielded the pure compound in the form of yellow crystals: mp 213–214°; ir 3380, 3225, 3150, 1700, 1600, 1560, 1330, 1230, 1110, 1060, 980, 890, 860, 750, 690, 565, 520, and 505 cm^{-1}; nmr δ 6.3 (m, 1, pyrrolyl CH), 7.0–7.7 (m, 7, phenyl and pyrrolyl CH), 11.2 (s, 1, NH), 11.8 (sharp s superimposed on broad signal, 2, NH).

Anal. Calcd for $C_{12}H_{11}ON_3S$: C, 58.75; H, 4.52; N, 17.14. Found: C, 58.92, H, 4.42; N, 17.00.

B. From 14.—A mixture of 1.0 g of **14** and 5 ml of aniline was allowed to stand at room temperature for 18 hr. Dilution with carbon tetrachloride and filtration yielded 0.80 g (50%) of **6**, mp 207–209°, raised to 212–214° by recrystallization from ethanol.

Oxidation of 6 to *N*-Phenylcarbamoylpyrrole-2-carboxamide (**7**).—Hydrogen peroxide (30%, 3 ml) was added to 0.20 g of **5** and two crushed pellets of sodium hydroxide in 10 ml of ethanol, and the resulting mixture was allowed to stand in an ice–water bath for 1 hr. Following addition of another 3 ml of hydrogen peroxide, the reaction mixture was kept cold for a further 2 hr. It was then diluted with water, acidified, and filtered. There resulted 0.10 g of **7**, mp 250–252°. After recrystallization from ethanol, the melting point became 256–257° (lit.[4] mp 257–257.5°).

***N'*-Ethoxycarbonyl-*N*-phenylpyrrole-2-carboxamidine** (**8**).—A solution of 10 g of **1** in 30 ml of aniline was stirred magnetically, at room temperature, for 6 days. Removal of the excess of aniline by evaporation in a current of air and recrystallization of the residue from aqueous ethanol yielded 8.3 g (91%) of **8**, mp 98–100°. The pure compound was obtained as colorless crystals by further recrystallization from aqueous ethanol: mp 99.5–100.5°; ir 3250–3125, 1630, 1570, 1320, 1260, 1230, 1130, 1100, 1050, 930, 910, 880, 810, 750, 700, 690, and 605 cm^{-1}; nmr δ 1.1 (distorted t, 3, J = 7 Hz, $-CH_3$), 4.0 (distorted q, 2, J = 7 Hz, $-OCH_2-$), 6.2 (m, 1, pyrrolyl CH), 6.5–6.7 (m, 1, pyrrolyl CH), 7.0–7.5 (m, 6, phenyl and pyrrolyl CH), 9.3 and 9.8 (s, 1, PhNH–), and 11.5 (s, 1, pyrrolyl NH).

Anal. Calcd for $C_{14}H_{15}O_2N_3$: C, 65.35; H, 5.88; N, 16.33. Found: C, 65.50; H, 5.91; N, 16.51.

Hydrolysis of 8 to 2.—A mixture of 0.50 g of **8** and 5 ml of dilute hydrochloric acid was heated on the steam bath for 0.5 hr. Cooling of the product in an ice–water bath caused the precipitation of 0.20 g of **2**, mp 136–138°. Recrystallization from CH_2Cl_2 raised the melting point to 139–141°.

***N'*-Ethoxycarbonyl-*N*,*N*-oxybisethylenepyrrole-2-carboxamidine** (**9**).—A solution of 2.0 g of **1** and 5 ml of morpholine in 10 ml of absolute ethanol was boiled for 3 min and, after it had been cooled, it was diluted with cold water and the inner surface of the flask was scratched with a glass rod to induce crystallization.

(17) T. P. Sycheva, Z. A. Pankina, and M. N. Shchukina, *Zh. Obshch. Khim.*, **33**, 3654 (1963); *Chem. Abstr.*, **60**, 8012*h* (1964).

(18) E. Fischer and D. D. Van Slyke, *Chem. Ber.*, **44**, 3166 (1911).

Filtration yielded 1.8 g (72%) of **9**, mp 148–150°, and recrystallization from benzene gave the pure compound in the form of colorless crystals: mp 149–150°; ir 3200, 1650, 1570, 1300, 1260, 1210, 1180, 1125, 1110, 1040, 945, 900, 890, 870, 850, 805, 730, 610, and 510 cm^{-1}; nmr δ 1.0 (t, 3, J = 7 Hz, $-CH_3$), 3.4 (m, 4, morpholine $-CH_2NCH_2-$), 3.7 (m, 4, morpholine $-CH_2OCH_2-$), 3.9 (q, 2, J = 7 Hz, $-OCH_2-$), 6.2 (m, 1, pyrrolyl CH), 6.3 (m, 1, pyrrolyl CH), 6.9 (m, 1, pyrrolyl CH), and 11.3 (s, 1, NH).

Anal. Calcd for $C_{12}H_{17}O_3N_3$: C, 57.36; H, 6.82; N, 16.72. Found: C, 57.38; H, 6.94; N, 16.65.

Hydrolysis of 9 to 2.—A mixture of 0.30 g of **9** and 3 ml of dilute hydrochloric acid was heated on the steam bath for 25 min. Chilling of the product yielded 0.10 g of **2**, mp 138–140°.

***N'*-Ethoxycarbonylpyrrole-2-carboxamidine (10).**—A solution of 2.0 g of **1** in 10 ml of absolute ethanol saturated with ammonia at 0° was placed in a pressure bottle and heated on the steam bath for 1 hr. It was then cooled, diluted with water, and extracted with ether. Following a drying treatment ($MgSO_4$), evaporation of the ether solution to dryness yielded 1.6 g (89%) of **10**, mp 129–133°. The pure compound was obtained by recrystallization from water as light tan crystals: mp 136–137°; ir 3320, 3200, 1680, 1620, 1575, 1510, 1300, 1260, 1210, 1140, 1110, 1100, 1040, 970, 950, 890, 810, 750, 595, and 530 cm^{-1}; nmr δ 1.2 (t, 3, J = 7 Hz, $-CH_3$), 4.1 (q, 2, J = 7 Hz, $-OCH_2-$), 6.2 (m, 1, pyrrolyl CH), 7.0 (m, 1, pyrrolyl CH), 7.1 (m, 1, pyrrolyl CH), 8.9 (s, 2, $-NH_2$), and 11.6 (s, 1, pyrrolyl NH).

Anal. Calcd for $C_8H_{11}O_2N_3$: C, 53.03; H, 6.12; N, 23.19. Found: C, 53.23; H, 6.14; N, 23.11.

Hydrolysis of 10 to Pyrrole-2-carboxamide (5).—A mixture of 0.50 g of **10** and 10 ml of 10% aqueous sodium hydroxide was boiled for 15 min. A cooling treatment followed by filtration yielded 0.20 g of **5**, mp 173–175°, raised to 175–176° by recrystallization from aqueous ethanol.

1-Phenyliminopyrrolo[1,2-*c*]imidazol-3(2*H*)-one (11). A. By Hydrolysis of 8.—A mixture of 2.0 g of **8** and 10 ml of 10% aqueous sodium hydroxide was boiled until initial dissolution of the solid had been followed by formation of a new precipitate (about 1 min). The resulting mixture was cooled, then diluted with water and filtered. The solid material thus obtained was suspended in a small amount of water and acidified with dilute hydrochloric acid. A new filtration yielded 1.3 g (81%) of **11**, mp 165–166°, and recrystallization from benzene afforded the pure compound as pale yellow crystals: mp 168–168.5°; ir 1780, 1670, 1590, 1430, 1330, 1225, 1180, 1070, 1045, 910, 780, 735, 695, 625, 515, and 510 cm^{-1}; nmr δ 5.6 and 6.8 (m, 1, 3-pyrrolyl CH), 6.4 (m, 1, 4-pyrrolyl CH), 7.0–7.6 (m, 6, phenyl and 5-pyrrolyl CH), and 11.3 (s, 1, NH).

Anal. Calcd for $C_{12}H_9ON_3$: C, 68.24; H, 4.30; N, 19.89. Found: C, 68.04; H, 4.29; N, 20.02.

B. By Thermal Decomposition of 8.—Melted **8** (0.50 g) was kept at 145–155° (internal temperature) until evolution of EtOH had practically ceased (2–3 min). Upon cooling, there was obtained 0.35 g (85%) of crude **11**, mp 158–168°.

Hydrolysis of 11 to Pyrrole-1,2-dicarboximide (13).—A mixture of 0.50 g of **11** and 5 ml of dilute hydrochloric acid was heated on the steam bath for 0.5 hr. Cooling of the product followed by filtration yielded 0.30 g of **13**, mp 206–210°. After recrystallization from ethanol, the melting point of the product became 209–211° (lit.[4] mp 209–211°).

1-Phenylaminopyrrolo[1,2-*c*]imidazol-3-one (12). A. From 11.—Recrystallization of crude **11** from methanol or ethanol gave **12** in the form of light yellow crystals: mp 167.5–168.5°; ir 3290, 3170, 1720, 1640, 1580, 1520, 1400, 1340, 1280, 1230, 1175, 1085, 1070, 1040, 910, 870, 855, 795, 760, 745, 710, 680, 580, and 510 cm^{-1}; nmr, same as for **11**.

Anal. Calcd for $C_{12}H_9ON_3$: C, 68.24; H, 4.30; N, 19.89. Found C, 68.36; H, 4.50; N, 20.11.

B. From 14.—A solution of 1.0 g of **14** and 5 ml of aniline in 50 ml of absolute ethanol was stirred magnetically, at room temperature, for 48 hr. At the end of this period, filtration yielded 0.50 g (36%) of **12**, mp 163–165°. Longer reaction times and/or increased concentration of aniline led to higher yields of less pure product.

Hydrolysis of 12 to 13.—As described for the hydrolysis of **11**, from 0.50 g of **12** and 5 ml of dilute hydrochloric acid, there was obtained 0.20 g of **13**, mp 209–212°.

2-Thiopyrrole-1,2-dicarboximide (14). A. From 1.—A mixture of 5.0 g of **1** and 15 ml of quinoline was heated in a 25-ml erlenmeyer flask until the temperature of the escaping vapor reached 170–180°. The resulting tarry material was cooled, then mixed with cold, dilute hydrochloric acid, and extracted with ether. After it had been washed with water, treated with charcoal, and dried ($MgSO_4$), the ether solution was evaporated to dryness to yield 3.3 g (87%) of **14**, mp 135–138°. Recrystallization from aqueous ethanol gave the pure compound in the form of orange-red crystals: mp 140–141.5°; ir 3200, 1760, 1550, 1400, 1300, 1200, 1150, 1060, 1010, 890, 750, 700, 690, 660, 620, and 475 cm^{-1}; nmr δ 6.6 (m, 1, CH), 7.0 (m, 1, CH), 7.4 (m, 1, CH), and 12.3 (broad s, 1, NH)

Anal. Calcd for $C_6H_4ON_2S$: C, 47.35; H, 2.65; N, 18.41. Found: C, 47.46; H, 2.60; N, 18.29.

B. From 13.—A mixture of 0.50 g of **13**, 2.0 g of phosphorus pentasulfide, and 25 ml of dioxane was refluxed for 1 hr. After it had been cooled, the reaction mixture was diluted with 200 ml of ether and filtered. The resulting ether solution was washed with water, treated with decolorizing charcoal, dried ($MgSO_4$), and evaporated to dryness. Recrystallization of the residue from carbon tetrachloride gave 0.30 g (50%) of **14**, mp 138–139.5°.

Oxidation of 14 to 13.—To an ice-cold solution of 0.30 g of **14** and one crushed pellet of sodium hydroxide in 10 ml of absolute ethanol was added 5 ml of hydrogen peroxide (30%) and the resulting mixture was kept in an ice–water bath for 2 hr. After dilution with water to 50 ml and acidification with dilute hydrochloric acid, the solution was saturated with sodium chloride and extracted with ether. The extract was washed with saturated brine, treated with charcoal, dried ($MgSO_4$), and evaporated to dryness to yield 0.10 g of **13**, mp 208–211°.

2-Thiopyrrole-1,2-dicarboximide *S*-Oxide (15).—To an ice-cold mixture of 1.0 g of **14**, 1.0 g of sodium acetate, and 10 ml of acetic acid was added 5 ml of hydrogen peroxide (30%), in five portions. Upon standing at room temperature, the orange-red solid went into solution and a new, yellow precipitate was formed. Dilution with water followed by filtration yielded 0.9 g (82%) of **15**, mp 150–150.5° dec. An analytical sample was obtained by recrystallization from ethanol as yellow crystals: mp 150.5–151° dec; ir 3280, 3130, 1770, 1550, 1400, 1300, 1240, 1200, 1175, 1050, 1020, 955, 900, 820, 780, 740, 710, 690, 630, 580, and 480 cm^{-1}; nmr δ 6.7–7.0, 7.4 (m, 2, CH), 7.8 (m, 1, CH), and 12.9 (broad s, 1, NH).

Anal. Calcd for $C_6H_4O_2N_2S$: C, 42.85; H, 2.40; N, 16.66. Found: C, 42.91; H, 2.61; N, 16.86.

Pyrrole-1,2-dithiodicarboximide (16). A. From 14.—The mixture obtained when 1.0 g of **14**, 4.0 g of phosphorus pentasulfide, and 50 ml of xylene had been refluxed for 25 hr was cooled, diluted with 400 ml of ether, and filtered. Following treatment with decolorizing charcoal and anhydrous magnesium sulfate, the ether solution was evaporated to dryness, and the resulting residue was recrystallized from carbon tetrachloride to yield 0.60 g (55%) of pure **16** as dark purple crystals: mp 183–184°; ir 3150 (broad), 1550, 1410, 1320, 1240, 1205, 1130, 1040, 1000, 895, 820, 735, 650, 520, and 440 cm^{-1}; nmr δ 6.6 (t, 1, J = 3 Hz, CH), 7.1 (d, 1, J = 3 Hz, CH), 7.5 (d, 1, J = 3 Hz, CH), and 13.7 (s, 1, NH).

Anal. Calcd for $C_4H_4N_2S_2$: C, 42.83; H, 2.40; N, 16.66. Found: C, 42.79; H, 2.66; N, 16.72.

B. From 13.—To a mixture of 1.0 g of **13**, 4.0 g of phosphorus pentasulfide, and 30 ml of xylene, which had been refluxed for 24 hr, was added another 4.0 g of phosphorus pentasulfide and the refluxing was continued for a further 41 hr. Following the same procedure as in the previous preparation, there was obtained 0.70 g (64%) of **16**, mp 180–184°.

Oxidation of 16 to 13.—A mixture of 0.30 g of **16**, 0.30 g of sodium acetate, 3 ml of acetic acid, and 3 ml of hydrogen peroxide (30%) was allowed to stand at room temperature for 24 hr. At the end of this period, a further 3 ml of hydrogen peroxide was introduced into the reaction mixture, which was then allowed to stand for an additional 24 hr. Dilution with water followed by extraction with ether yielded a solution, which was washed with water and aqueous sodium bicarbonate, dried ($MgSO_4$), and evaporated to dryness. Trituration of the residue with petroleum ether (bp 30–60°) yielded 0.050 g of **13**, mp 210–212°.

***N*-Carbamoylpyrrole-2-thiocarboxamide (17).**—Brief (4–5 min) standing of a solution of 1.0 g of **14** in 2 ml of concentrated aqueous ammonia resulted in the formation of a precipitate which was collected by filtration. The yield was 0.80 g (73%) of **17**, mp 169–171°. The pure compound was obtained in the form of yellow crystals by recrystallization from water: mp 171–172°; ir 3390, 3370, 3250, 1730, 1580, 1540, 1330, 1280, 1130,

1060, 1035, 960, 885, 850, 840, 745, 580, 565, 540, and 450 cm^{-1}; nmr δ 6.3 (m, 1, CH), 7.3 (m, 1, CH), 7.4 (m, 1, CH), 7.8 and 9.1 (broad singlets, 2, $-NH_2$), 10.8 (s, 1, imide NH), and 11.7 (s, 1, pyrrole NH).

Anal. Calcd for $C_6H_7ON_3S$: C, 42.59; H, 4.17; N, 24.83. Found C, 42.75; H, 4.21; N, 24.62.

Oxidation of 17 to *N*-Carbamoylpyrrole-2-carboxamide (18).—Hydrogen peroxide (30%, 5 ml) was added in one portion to an ice-cold solution of 0.20 g of **17** and two pellets of NaOH in a mixture of 5 ml of ethanol and 1 ml of water. Following standing of 1–2 min in an ice–water bath, the mixture was acidified with dilute hydrochloric acid and filtered. There was obtained 0.12 g of **18**, mp 239–240° (lit.[4] mp 240–241°).

1-Morpholinopyrrolo[1,2-*c*]imidazol-3-one (19). A. From 9.—A mixture of 2.0 g of **9** and 3 ml of quinoline was boiled in a 25-ml erlenmeyer flask until the temperature of the escaping vapor reached 150–160°, and then it was cooled and filtered. There resulted 1.5 g (94%) of **19**, mp 180–182°. An analytical sample, colorless crystals obtained by recrystallization from carbon tetrachloride, melted at 184–185°: ir 1730, 1600, 1530, 1410, 1350, 1290, 1270, 1230, 1195, 1165, 1115, 920, 880, 770, 740, 725, 685, 620, 590, and 535 cm^{-1}; nmr δ 3.9 (s, 8, morpholine CH), 6.6 (t, 1, J = 3 Hz, pyrrolyl CH), 7.0 (d, 1, J = 3 Hz, pyrrolyl CH), and 7.7 (d, 1, J = 3 Hz, pyrrolyl CH).

Anal. Calcd for $C_{10}H_{11}O_2N_3$: C, 58.53; H, 5.40; N, 20.48. Found: C, 58.57; H, 5.43; N, 20.53.

B. From 14.—A solution of 1.0 g of **14** and 0.60 g of morpholine in 30 ml of absolute ethanol was allowed to stand at room temperature for 2 hr. Filtration yielded 0.50 g of **19**, mp 184–185°, and an overnight stay of the filtrate afforded a further 0.10 g of material having the same melting point (total yield 46%).

Hydrolysis of 19 to 13.—A mixture of 0.30 g of **19** and 3 ml of dilute hydrochloric acid was heated on the steam bath for 30 min. Following a cooling treatment, filtration yielded 0.15 g of **13**, mp 208–210°.

2-(2-Pyrrolyl)quinazolin-4(1*H* or 3*H*)-one (21). A. From 8.—A mixture of 2.0 g of **8** and 5 ml of quinoline was placed in a 25-ml erlenmeyer flask and boiled until the temperature of the escaping vapor reached 160–170°. The resulting dark brown liquid was cooled, then mixed with CCl_4 and filtered. There was obtained 1.3 g (81%) of **21**, mp 274–276°. Recrystallization from ethanol yielded the pure compound as colorless needles: mp 277–278°; ir 3420, 1680, 1600, 1540, 1500, 1420, 1320, 1270, 1240, 1165, 1105, 1075, 1050, 1020, 980, 910, 890, 870, 770, 740, 685, 650, 630, 590, 550, 530, and 500 cm^{-1}; nmr δ 6.4 (m, 1, pyrrolyl CH), 7.2 (m, 1, pyrrolyl CH), 7.3–8.3 (m, 5, pyrrolyl and phenyl CH), 11.8 (s, 1, NH), and 12.3 (s, 1, NH).

Anal. Calcd for $C_{12}H_9ON_3$: C, 68.24; H, 4.30; N, 19.89. Found: C, 68.14; H, 4.34; N, 19.88.

B. From 12.—A mixture of 0.30 g of **12** and 3 ml of quinoline was heated to the boiling point, then cooled and diluted with CCl_4. Filtration yielded 0.10 g of **21**, mp 275–277°.

1-Ethoxycarbonylimino-2-phenylpyrrolo[1,2-*c*]imidazol-3-one (22).—Addition of 3 ml of triethylamine to an ice-cold mixture of 2.0 g of **1** and 3.6 g of phenyl isocyanate caused a vigorous reaction to occur with evolution of a gas. After an overnight stay in the refrigerator, the product was mixed with 50 ml of chloroform, and the resulting mixture was filtered to yield 1.0 g of a colorless solid, mp 240–242°, identified as *N*,*N*′-diphenylurea (infrared spectrum, mixture melting point). Evaporation of the filtrate to dryness, followed by trituration of the residue with ethanol and filtration, afforded 1.5 g of **22**, mp 155–162°. The pure compound was obtained in the form of colorless crystals by recrystallization from ethanol: mp 163–164°; ir 1780, 1700, 1650, 1610, 1490, 1280, 1260, 1240, 1165, 1145, 1120, 1010, 830, 795, 750, 700, 690, 640, 620, 610, 580, and 500 cm^{-1}; nmr δ 1.3 (t, 3, J = 7 Hz, $-CH_3$), 4.4 (q, 2, J = 7 Hz, $-OCH_2-$), 6.9 (t, 1, J = 3 Hz, pyrrolyl CH), 7.2 (d, 1, J = 3 Hz, pyrrolyl CH), 7.8 (s, 5, phenyl CH), and 8.0 (d, 1, J = 3 Hz, pyrrolyl CH).

Anal. Calcd for $C_{15}H_{13}O_3N_3$: C, 63.58; H, 4.63; N, 14.84. Found: C, 63.66; H, 4.64; N, 14.72.

The gas evolved in this reaction was identified as carbonyl sulfide in the following manner. It was conducted into a solution of 2 ml of piperidine in 20 ml of dry ether and the precipitate formed (mp 111–112° dec) was recrystallized from dry acetone to yield a colorless, crystalline solid, mp 113–114°. The identity of this as piperidinium 1-piperidinecarbothiolate (lit.[19] mp 117°) was established by comparison with an authentic sample prepared from COS and piperidine in ether.

Hydrolysis of 22. A. To *N*-Phenylpyrrole-1,2-dicarboximide (23).—A mixture of 0.50 g of **22** and 5 ml of concentrated hydrochloric acid was boiled for 1–2 min. Cooling of the product, followed by filtration, yielded 0.30 g of **23**, mp 208–220°, raised to 224–226° by recrystallization from ethanol (lit.[3] mp 226–227°).

B. To 1-Phenyliminopyrrolo[1,2-*c*]imidazol-3(2*H*)-one (11).—Boiling of a mixture of 1.0 g of **22** and 10 ml of 10% aqueous sodium hydroxide for 1–2 min yielded a precipitate, which was collected by filtration, suspended in a small amount of water, and acidified with dilute hydrochloric acid. A new filtration afforded 0.50 g of **11**, mp 165–167°.

***N*-Ethoxycarbonylpyrrole-1-thiocarboxamide (24).**—Pyrrolylpotassium was prepared in a nitrogen atmosphere by the gentle refluxing of a stirred mixture of 40.2 g (0.60 mol) of pyrrole, 100 ml of tetrahydrofuran, and 19.5 g (0.50 g-atom) of potassium, until all of the metal had reacted. Following dilution with 150 ml of solvent and chilling of the slurry in an ice–salt bath, there was introduced a solution of 59.0 g (0.45 mol) of ethoxycarbonyl isothiocyanate in 100 ml of tetrahydrofuran, dropwise, at such a rate that the reaction temperature was kept below 10° (addition time 1.5 hr). The reaction mixture was stirred for a further 0.5 hr, then it was mixed with 2 lb of absolute ether and filtered. The potassium salt thus obtained was dissolved in water, and the resulting solution was washed with ether, chilled, and acidified with acetic acid. Filtration yielded 39.8 g (45%) of crude **24**, mp 77–80°, and recrystallization from petroleum ether (bp 60–90°) afforded the pure compound as yellow needles: mp 80–81°; ir 3210, 1730, 1500, 1320, 1220, 1125, 1095, 1070, 1040, 1015, 970, 880, 795, 755, 735, 685, 630, 600, and 570 cm^{-1}; nmr ($CDCl_3$) δ 1.3 (t, 3, J = 7 Hz, $-CH_3$), 4.3 (q, 2, J = 7 Hz, $-OCH_2-$), 6.3 (t, 2, J = 2 Hz, pyrrolyl CH), 7.4 (t, 2, J = 2 Hz, pyrrolyl CH), and 8.7 (s, 1, NH).

Anal. Calcd for $C_8H_{10}O_2N_2S$: C, 48.47; H, 5.09; N, 14.13. Found: C, 48.70; H, 5.07; N, 14.12.

Oxidation of 24 to 25.—The mixture resulting from the addition of two crushed pellets of NaOH and 1 ml of hydrogen peroxide (30%) to an ice-cold solution of 0.20 g of **24** in 2 ml of ethanol was kept in an ice–water bath for 15 min. A further 1 ml of hydrogen peroxide was then added, and the reaction mixture was allowed to stand at room temperature for an additional 15 min. At the end of this period, acidification yielded 0.050 g of **25**, mp 114–115°. Recrystallization from aqueous ethanol raised the melting point to 120–122° (lit.[4] mp 121.5–123°).

Pyrrole-1-thiocarboxamide (26).—A solution of 0.50 g of **24** in 10 ml of 10% aqueous sodium hydroxide was brought quickly to the boiling point and then heated on the steam bath, under reduced pressure (water aspirator), for 5 min. Following addition of 5 ml of water the heating was continued under suction for a further 5 min. The resulting solution was made ice-cold and weakly acidic to yield 0.25 g (78%) of **26**, mp 157–160°. An analytical sample was obtained as colorless crystals by recrystallization from water: mp 159–160°; ir 3320, 3275, 3150, 1625, 1280, 1115, 1075, 950, 830, 745, 735, 710, 645, 590, 575, and 535 cm^{-1}; nmr δ 6.3 (t, 2, J = 2 Hz, pyrrolyl CH), 7.7 (t, 2, J = 2 Hz, pyrrolyl CH), and 9.1–9.4 (broad, overlapping d, 2, $-NH_2$).

Anal. Calcd for $C_5H_6N_2S$: C, 47.60; H, 4.79; N, 22.20. Found: C, 47.55; H, 4.94; N, 22.32.

Oxidation of 26 to Pyrrole-1-carboxamide (27).—To an ice-cold solution of 0.30 g of **26** in 3 ml of 10% aqueous sodium hydroxide was added 1 ml of hydrogen peroxide (30%) and the resulting mixture was allowed to stand in an ice–water bath for 2–3 min. Filtration yielded 0.15 g of **27**, mp 162–164° (lit.[20] mp 165–166°).

***N*-Phenylcarbamoylpyrrole-1-thiocarboxamide (28).**—A mixture of 0.50 g of **24** and 2 ml of aniline was brought quickly to the boiling point, then cooled and diluted with ethanol. Filtration yielded 0.20 g (32%) of **28**, mp 208–210°. The pure compound was obtained as colorless crystals by recrystallization from 1-butanol: mp 209–210°; ir 3240, 3160, 1685, 1600, 1560, 1300, 1230, 1120, 1050, 1020, 970, 900, 850, 750, 730, 690, 570, 530, and 510 cm^{-1}; nmr δ 6.4 (t, 2, J = 2 Hz, pyrrolyl CH), 7.1–7.7(m, 7, pyrrolyl and phenyl CH), 10.4 (s, 1, NH), and 9.6–11.6 (very diffuse signal, 1, NH).

Anal. Calcd for $C_{12}H_{11}ON_3S$: C, 58.76; H, 4.52; N, 17.13. Found: C, 58.90; H, 4.60; N, 17.20.

(19) J. Parrod, *C. R. Acad. Sci.*, **234**, 1062 (1952).

(20) D. A. Shirley, B. H. Gross, and P. A. Roussel, *J. Org. Chem.*, **20**, 225 (1955).

Oxidation of 28 to *N*-Phenylcarbamoylpyrrole-1-carboxamide (29).—Upon addition of 2 ml of hydrogen peroxide (30%) to an ice-cold mixture of 0.20 g of **28**, two crushed pellets of NaOH, and 2 ml of ethanol, a vigorous reaction took place with formation of a white precipitate. Dilution with water yielded 0.10 g of **29**, mp 221–222°, raised to 229–230° by recrystallization from ethanol (lit.[4] mp 229–230°).

***N*-Ethoxycarbonyl-*N'*-phenylpyrrole-1-carboxamidine (30).**—After a mixture of 2.0 g of **24** and 5 ml of aniline had stood at room temperature for 4 days, the resulting solution was placed on a watch glass and allowed to evaporate to dryness in a current of air. The residue thus obtained was recrystallized from aqueous ethanol to yield 2.2 g (85%) of **30**, colorless crystals, mp 112–114°. Further recrystallization from aqueous ethanol gave the pure compound: mp 114–115°; ir 3330, 1725, 1650, 1590, 1530, 1500, 1340, 1230, 1090, 1070, 1020, 960, 915, 830, 770, 745, 695, 660, 620, 590, 580, and 540 cm^{-1}; nmr δ 1.0 (t, 3, J = 7 Hz, $-CH_3$), 3.9 (q, 2, J = 7 Hz, $-OCH_2-$), 6.3 (t, 2, J = 2 Hz, pyrrolyl CH), 7.0–7.4 (m, 7, pyrrolyl and phenyl CH), and 10.1 (s, 1, NH).

Anal. Calcd for $C_{14}H_{15}O_2N_3$: C, 65.35; H, 5.88; N, 16.33. Found: C, 65.39; H, 5.82; N, 16.41.

Hydrolysis of 30 to 25.—Heating on the steam bath of a mixture of 0.50 g of **30** and 5 ml of dilute hydrochloric acid for 1–2 min resulted in the formation of a heavy oil, which yielded upon cooling 0.30 g of **25**, mp 119–121°, raised to 121–123° by recrystallization from ethanol.

***N'*-Ethoxycarbonylpyrrole-1-carboxamidine (31).**—A mixture of 1.0 g of **24** and 10 ml of absolute ethanol saturated with ammonia at 0° was placed in a pressure bottle and heated on the steam bath for 0.5 hr. The resulting solution was cooled and diluted with water to yield 0.80 g (88%) of **31** as a colorless solid: mp 124–126°, raised to 125–126° by recrystallization from ethanol; ir 3375, 3325, 1670, 1620, 1510, 1320, 1280, 1260, 1210, 1100, 1120, 970, 940, 890, 810, 740, and 690 cm^{-1}; nmr δ 1.3 (t, 3, J = 7 Hz, $-CH_3$), 4.2 (q, 2, J = 7 Hz, $-OCH_2-$), 6.4 (t, 2, J = 2 Hz, pyrrolyl CH), 7.7 (t, 2, J = 2 Hz, pyrrolyl CH), and 9.1 (s, 2, $-NH_2$).

Anal. Calcd for $C_8H_{11}O_2N_3$: C, 53.03; H, 6.12; N, 23.19. Found: C, 53.06; H, 6.14; N, 23.30.

Hydrolysis of 31 to 25.—When a mixture of 0.50 g of **31** and 5 ml of dilute hydrochloric acid had been heated on the steam bath for 20 min, a considerable amount of tar was formed. Chilling of the solution caused precipitation of 0.10 g of **25**, mp 120–121°. After recrystallization from ethanol, the melting point became 121–123°.

***N'*-Ethoxycarbonyl-*N*,*N*-oxybisethylenepyrrole-1-carboxamidine (32).**—A solution of 2.0 g of **24**, 5 ml of morpholine, and 10 ml of absolute ethanol was boiled for 3 min, then chilled and diluted with water to yield 0.60 g (24%) of **32**, mp 109–111°. Recrystallization from carbon tetrachloride afforded the pure compound in the form of colorless crystals: mp 110–111°; ir 1680, 1610, 1310, 1290, 1260, 1250, 1210, 1170, 1120, 1095, 1045, 950, 905, 875, 845, 800, 750, 715, 635, 600, and 520 cm^{-1}; nmr δ 1.0 (t, 3, J = 7 Hz, $-CH_3$), 3.4 (m, 4, morpholine $-CH_2NCH_2-$), 3.7 (m, 4, morpholine $-CH_2OCH_2-$), 3.9 (q, 2, J = 7 Hz, $-OCH_2-$), 6.3 (t, 2, J = 2 Hz, pyrrolyl CH), and 6.9 (t, 2, J = 2 Hz, pyrrolyl CH).

Anal. Calcd for $C_{12}H_{17}O_3N_3$: C, 57.36; H, 6.82; N, 16.72. Found: C, 57.18; H, 6.72; N, 16.77.

Hydrolysis of 32 to 25.—Heating on the steam bath for a few moments of a mixture of 0.40 g of **32** and 5 ml of dilute hydrochloric acid, followed by cooling and filtration, yielded 0.20 g of **25**, mp 120–122°.

2-(1-Pyrrolyl)quinazolin-4(1*H* or 3*H*)-one (33).—When melted **30** (0.40 g) had been kept at 140–150° (internal temperature) for a few minutes (until complete solidification), there resulted 0.30 g (90%) of **33**, mp 266–267°. Recrystallization from ethanol yielded the pure compound in the form of colorless needles: mp 267–268°; ir 1675, 1615, 1570, 1540, 1360, 1340, 1250, 1070, 970, 910, 770, 735, 710, 630, 590, 555, and 505 cm^{-1}; nmr δ 6.4 (t, 2, J = 2 Hz, pyrrolyl CH), 7.8 (t, 2, J = 2 Hz, pyrrolyl CH), 7.3–8.3 (m, 4, benzene ring CH), and 11.7–13.3 (weak, very broad signal, NH).

Anal. Calcd for $C_{12}H_9ON_3$: C, 68.24; H, 4.30; N, 19.89. Found: C, 68.08; H, 4.50; N, 19.65.

1-Thiopyrrole-1,2-dicarboximide (34).—A mixture of 5.0 g of **24** and 5 ml of quinoline was heated in a 25-ml erlenmeyer flask until the temperature of the escaping vapor reached 150–160°. The resulting tarry material was treated as described earlier for **14** to yield 2.2 g (58%) of crude **34**, mp 179–185°. The pure compound was obtained as yellow crystals by recrystallization from toluene: mp 197–198.5°; ir 3150, 1750, 1550, 1300, 1260, 1140, 1055, 1000, 900, 725, 700, 690, 665, 600, 570, and 495 cm^{-1}; nmr δ 6.6 (t, 1, J = 3 Hz, CH), 6.9 (d, 1, J = 3 Hz, CH), 7.6 (d, 1, J = 3 Hz, CH), and 12.5 (broad s, 1, NH).

Anal. Calcd for $C_6H_4ON_2S$: C, 47.36; H, 2.65; N, 18.41. Found: C, 47.56; H, 2.68; N, 18.29.

Oxidation of 34 to 13.—A mixture of 0.50 g of **34**, 0.50 g of sodium acetate, 5 ml of acetic acid, and 3 ml of hydrogen peroxide (30%) was stirred magnetically at room temperature for 24 hr. Following addition of another 2 ml of hydrogen peroxide, stirring was continued for a further 18 hr. At the end of this period, dilution with water yielded 0.20 g of **13**, mp 210–212°.

Registry No.—**1**, 37488-43-0; **3**, 37488-44-1; **4**, 37488-45-2; **6**, 37488-46-3; **8**, 37488-47-4; **9**, 37488-48-5; **10**, 37488-49-6; **11**, 37488-50-9; **12**, 37488-51-0; **13**, 13939-91-8; **14**, 37488-53-2; **15**, 37488-54-3; **16**, 37488-55-4; **17**, 37488-56-5; **19**, 37488-57-6; **21**, 37488-58-7; **22**, 37488-59-8; **24**, 37488-60-1; **26**, 37488-61-2; **28**, 37488-62-3; **30**, 37488-63-4; **31**, 37488-64-5; **32**, 37488-65-6; **33**, 37488-66-7; **34**, 37500-25-7; pyrrole, 109-97-7; ethoxycarbonyl isothiocyanate, 16182-04-0; pyrrole potassium salt, 16199-06-7.

Acknowledgment.—Financial support from the Research Corporation, the Research Allocations Committee of the University of New Mexico, and the Department of Chemistry of the University of New Mexico is gratefully acknowledged.