1-(3-Methyl-2-buten-1-yloxy)-2-(phenylthio)-1-octene (4c) (from **2a** and 1-bromo-3-methyl-2-butene in THF, preferably with 1 equiv of dicyclohexyl-18-crown-6): R_f 0.75 on silica in 2:1 benzene/petroleum ether; NMR (CCl_4) δ 0.9 (m, 3, CH_3), 1.3 (m, 8, CH_2), 1.77 (s, 3, CH_3), 1.85 (s, 3, CH_3), 2.25 (m, 2, $C{=}CCH_2$), 4.37 (d, 2, OCH_2), 5.4 (m, 1, $C{=}CHCH_2$), 6.52 (s, 1, $C{=}CHOR$), 7.17 (m, 5, C_6H_5); IR (neat) 1580, 1630 cm^{-1} ($C{=}C$). Anal. Calcd for $C_{19}H_{28}OS$: C, 74.95; H, 9.27; S, 10.53. Found: C, 75.05; H, 9.07; S, 10.67.

2-Benzyl-2-(phenylthio)octanal (3d) (from **2a** and benzyl bromide in cyclohexane/benzene): R_f 0.7 in 1:3 ether/petroleum ether; NMR ($CDCl_3$) δ 0.85 (m, 3, CH_3), 1.2–1.4 (m, 10, $(CH_2)_5$), 2.97, 3.01 (s, s, 2, $PhCH_2$), 7.15, 7.25 (s, s, 10, C_6H_5), 9.38 (s, 1, CHO). Anal. Calcd for $C_{21}H_{26}OS$: C, 77.25; H, 8.03; S, 9.82. Found: C, 77.15; H, 8.31; S, 9.60.

2-Methyl-2-(phenylthio)octanal (3e) and 1-Methoxy-2-(phenylthio)-1-octene (4e) (from **2a** and methyl iodide in THF, isomer mixture not separated): NMR (CCl_4) δ 0.88 (m, 3, CH_3, **3e** + **4e**), 1.17 (s, $C{-}CH_3$, **3e**), 1.3 (m, CH_2, **3e** + **4e**), 2.0 (m, ~1, $C{=}CCH_2$, **4e**), 3.56, 3.61 (s, s, ~1, ~0.5, **4e**, *E* and *Z*), 6.24, 6.38 (s, s, ~0.35, ~0.15, **4e**, *E* and *Z*), 7.08 (m, ~2.5, C_6H_5, **4e**), 7.20 (s, ~2.5, C_6H_5, **3e**), 9.15 (s, ~0.5, CHO, **3e**).

Acknowledgment. We thank the National Science Foundation for support, Grant No. CHE77-11283.

Registry No. 1a, 81447-38-3; **1b**, 81447-39-4; **1c**, 66080-30-6; **1d**, 81447-40-7; **1e**, 67808-83-7; **2a**, 81447-41-8; **2b**, 81447-42-9; **2c**, 55064-98-7; **2d**, 81456-91-9; **2e**, 81447-43-0; **3a**, 81447-44-1; **3b**, 81447-45-2; **3c**, 81456-92-0; **3d**, 81447-46-3; **3e**, 81447-47-4; **4a**, 81447-48-5; **4c**, 81447-49-6; (*E*)-**4e**, 81447-50-9; (*Z*)-**4e**, 81447-51-0; allyl bromide, 106-95-6; (*E*)-crotyl bromide, 29576-14-5; 1-bromo-3-methyl-2-butene, 870-63-3; benzyl bromide, 100-39-0; methyl iodide, 74-88-4.

Oxidation of Ionol by Silver(I)

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Received December 2, 1981

Silver(I) salts have long served the organic chemist as versatile, yet mild, one-electron oxidizing agents.[1] ϵ°_{red} for Ag^+ (aq) is +0.80 V. Several years ago we began investigating the reaction of Ag(I) with alkoxide ions in hopes of studying the chemistry of silver alkoxides. We found[2] that Ag(I) does indeed react instantaneously and irreversibly with all alkoxides studied, but the silver alkoxides proved highly unstable at 25 °C (though somewhat more stable at −78 °C). For example, reactions of Ag(I) with methoxide in methanol or ethoxide in ethanol at 25 °C gave metallic silver in quantitative yield. Oxidation products deriving from the alkoxy fragment eluded identification, though the obvious ones (aldehydes, etc.) were specifically excluded. When the solvent in the above reactions was changed to THF or when the oxide was phenoxide or *tert*-butoxide, the reactions proved even less tractable.[2] Our frustration at being unable to identify the products from the (presumed) alkoxy radicals has led us to investigate the Ag(I) oxidation of oxides which would give either persistent free radicals or products characteristic of these intermediates. BHT (2,6-di-*tert*-butyl-4-methylphenol, ionol, **1**) is just such a compound.

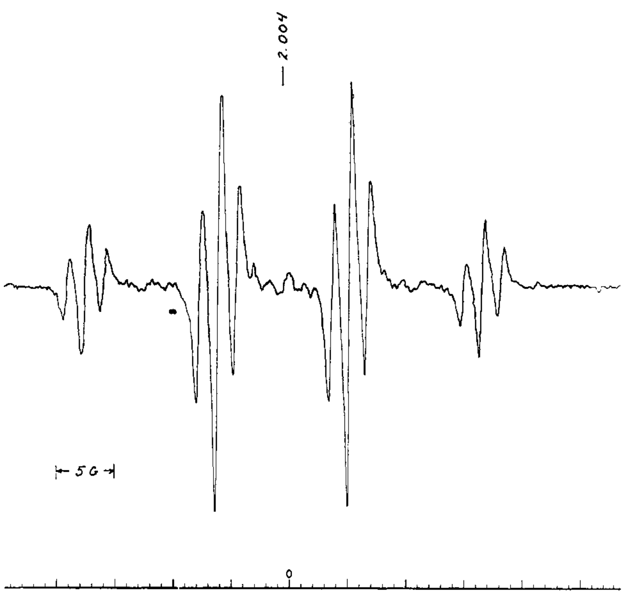
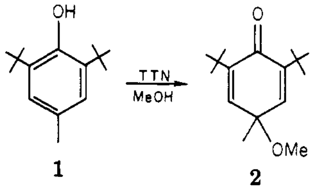


Figure 1. ESR spectrum of the supernatant from the oxidation of the conjugate base of **1** with Ag(I).

The literature reports hundreds of studies of the reaction of **1** with a wide variety of oxidizing agents. Although Ag_2O has been used to convert catechols to quinones[3] and oxidize 2,6-dimethylphenol,[4] we were unable to find reports on the oxidation of **1** with Ag(I). These are, nonetheless, recent reports of related oxidations of **1**. For example, while **1** reacts with $KMnO_4$ to give over a dozen products,[5] it reacts cleanly with thallium(III) nitrate to give **2**.[6] Most relevant to our work is the oxidation of **1** with DDQ, which is summarized in Scheme I.[7] Compounds **4** and **6** were isolated, the former being somewhat unstable; evidence for the intermediacy of **5** came from its ultraviolet spectrum (λ_{max} 284 nm, log ε 4.45) and the formation of **6**. Support for the involvement of phenoxy radical **3** came from the solid-state ESR spectrum of **4**, which exhibited a four-line pattern.



1 **2**

Results

A methanol solution containing equimolar amounts of **1** and Ag(I) was essentially stable at room temperature. After the solution was left standing for 17 days, a perceptible silver mirror had formed, but this constituted less than 5% of the silver present.[8] In sharp contrast, when **1** was first converted to its conjugated base, it reacted instantaneously with 1 mol equiv of Ag(I) to give a grayish-black precipitate and a nearly colorless supernatant. The precipitate proved to be Ag, formed in quantitative yield. Examination of the supernatant by ESR spectros-

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(1) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis", Wiley, New York, 1967, and later volumes in the series.

(2) R. S. Macomber, J. C. Ford, and J. H. Wenzel, *Synth. React. Inorg. Met.-Org. Chem.*, 7(2) 111 (1977).

(3) See, for example, R. Wellstatter and A. Pfannensteil, *Ber. Dtsch. Chem. Ges.*, **37**, 4744 (1904).

(4) B. O. Lindgren, *Acta. Chem. Scand.*, **14**, 1203 (1960); the major product (15%) was 2,6-dimethyl-4-(2,6-dimethylphenoxy)phenol.

(5) B. M. Benjamin, V. R. Raaen, E. W. Hagaman, and L. L. Brown, *J. Org. Chem.*, **43**, 2986 (1978).

(6) A. Mckillop, D. H. Perry, M. Edwards, S. Antus, L. Farkas, M. Nogradi, and E. C. Taylor *J. Org. Chem.*, **41**, 282 (1976).

(7) H.-D. Becker, *J. Org. Chem.*, **30**, 982 (1965).

(8) We have found that photolysis of this solution gives a much more rapid deposition of silver metal. The details of these experiments, as related to some earlier work,[9] will be reported later.

(9) R. S. Macomber, S. Carr, P. Boudjouk, and C. Kapfer, *J. Org. Chem.*, **45**, 356 (1980).

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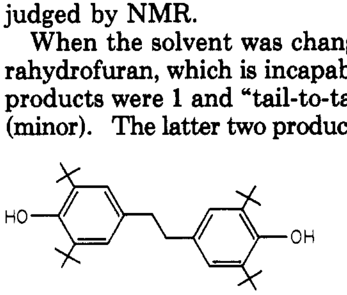
copy provided a well-resolved quartet of triplets (Figure 1), exactly as would be predicted for **3** (g = 2.004, a = 11.3 G, 1.5 G). The signal decayed to ca. 10^{-3} of its original intensity after 50 min at 23 °C. During this period a UV spectrum of the solution exhibited λ_{max} 278 nm with ϵ 2.1 × 10^3 based on the amount of **1** originally present.[10] TLC analyses of the supernatant showed two major components and traces of three or four other compounds. One of the major components had R_f identical with **1**. ^{1}H NMR examination of the residue left after evaporation of the supernatant confirmed the presence of **1**; all the remaining lines could be assigned to **6** as the other major component. The minor components must, therefore, account for less than 5% of the total mass of soluble product. Compound **6** was isolated by fractional crystallization and found to have the previously reported[7] melting point. The mass of the supernatant residue accounted for >94% of the **1** originally present.

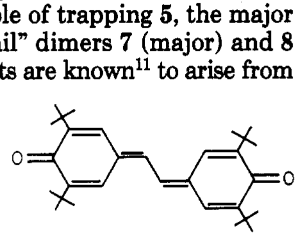
These results indicate that the oxidation of the conjugate base of **1** by Ag(I) at 25 °C proceeds by a mechanism very similar to that shown in Scheme I for DDQ. Apparently, at 25 °C coupling product **4** is not formed in significant yield (vide infra). Instead, disproportionation of **3** occurs, and the resulting quinone methide **5** is rapidly converted to **6**.

Oxidation of the phenoxide at −78 °C was somewhat more complex. Addition of Ag(I) gave a reddish-tan suspension which darkened to black after 1 h at −78 °C. After 20 h at 25 °C, analysis as described above showed that silver precipitated quantitatively, but the supernatant was orange, becoming cherry red upon evaporation. Trituration with ether gave a stable yellow solution, TLC of which was quite similar to the one described above, except that there was a yellow spot at R_f 0.49. UV examination showed maxima of 267 and 394 nm with relative intensity 6:4. The yellow compound was a minor component (<10%), as judged by NMR.

When the solvent was changed from methanol to tetrahydrofuran, which is incapable of trapping **5**, the major products were **1** and "tail-to-tail" dimers **7** (major) and **8** (minor). The latter two products are known[11] to arise from "dimerization" of **5**. Further, the R_f values for **7** (0.54) and **8** (a yellow spot at 0.49) identified them as the minor products in the methanol reaction.



7



8

These observations lend support to our previous deductions[2] regarding the oxidation of alkoxides and related compounds by silver(I). While neutral alcohols and phenols are essentially stable toward silver(I), their corresponding conjugate bases are instantaneously oxidized at room temperature by what appears to be a simple electron-transfer mechanism. The efficacy of silver oxide and Tollen's reagent as oxidizing agents can probably be attributed to their basicity, which converts the neutral substrate to its conjugate base, a better electron donor.

At −78 °C the reaction again proceeds via **3** (though preliminary formation of the silver phenoxide **9** is not ruled out), which decomposes slowly to **1** and **5** (Scheme II). Although most of **5** is trapped as **6**, a small fraction survives long enough to dimerize to **7** and **8**. In THF all of the quinone methide **5** is converted to **7** and **8**. In none of these reactions was a significant amount of **4** detected, though its formation may account for one of the minor TLC spots.

Experimental Section

The following spectrometers were used: ^{1}H NMR, Varian T-60 (downfield from internal Me_4Si); ESR, Varian E104 (g referred to external Cr^{3+} in MgO[12]); UV, Unicam SP 800 (methanol solutions).

Oxidation of 1 in Methanol. A stock solution of **1** (A) was prepared by diluting 540.7 mg **1** to 10.00 mL with sieve-dried absolute methanol; the resulting concentration was 0.246 M. Saturated methanolic silver nitrate (B) was prepared by mixing 400 mg of $AgNO_3$ with 10.0 mL of dry methanol, shaking overnight, and then decanting to remove undissolved silver nitrate and a small amount of precipitated silver. The concentration of silver(I) was determined gravimetrically by treating an aliquot with chloride ion; it was found to be 0.19 M. Sodium methoxide solution (C) was prepared by allowing 110 mg of clean, freshly cut sodium metal to react with 25 mL of anhydrous methanol. After cooling, the solution was titrated against standard HCl, exhibiting a concentration of 0.147 M.

In a typical reaction, 0.90 mL of solution A (0.22 mmol of **1**) was pipetted into a weighed centrifuge tube, and 1.50 mL of solution B (0.22 mmol) was added. To this solution was added portionwise a total of 1.17 mL of solution C (0.22 mmol). After each portion, the mixture was centrifuged. Addition of 2 additional drops of solution C caused no further precipitation. The supernatant was examined by ESV and UV as described in the text. The black precipitate was washed with 2 mL of hot methanol and dried to give 25.2 mg of silver[13] (theoretical, 23.8 mg). The washings were combined with the supernatant, and the resulting solution was evaporated to dryness, leaving 69.2 mg of a colorless semisolid (theoretical for a 1:1 mixture of **1** and **6**, 51.7 mg; theoretical for $NaNO_3$, 18.7 mg; total, 70.4 mg). The residue was triturated with warm ether. (The insoluble material dissolved completely in water.) The ether solution was evaporated, leaving 48.6 mg of a colorless semisolid. TLC of this residue (EM silica gel plates eluted once with benzene and visualized with iodine) showed two major spots centered at R_f 0.58 and 0.27, with trace spots at 0.12, 0.21, 0.38, and 0.53. Compound **1** has an R_f of 0.58 under these conditions. ^{1}H NMR of the evaporated supernatant (CCl_4) showed peaks for **1** [δ 1.39 (s, 18 H), 2.20 (s, 3 H), 4.80 (s, 1 H), 6.78 (s, 2 H)] and **6** [δ 1.36 (s, 18 H), 3.23 (s, 3 H), 4.23 (s, 2 H), 5.00 (s 1 H), 6.94 (s, 2 H)] in nearly equal amounts.[14] Slow evaporation of a carbon tetrachloride solution of this residue gave crystals of **6**, mp 99.5–101 °C [lit.[7] 98–99 °C], which had R_f 0.27 and an ^{1}H NMR identical with that described above.

Oxidation of 1 in THF. To a solution of 178.2 mg (0.814 mmol) of **1** in 4.0 mL of dry THF at 25 °C was added 1 equiv of methyllithium (1.4 M in ether),[15] followed by a solution of 168.7 mg (0.814 mmol) of silver perchlorate in 4.0 mL of dry THF. There was an immediate precipitation of black silver, which was isolated by filtration (dry mass 84.7 mg, 100%). The initially colorless filtrate became bright yellow over 5 min, and later it became orange. TLC analyses showed major spots at 0.58 (**1**), 0.54 (**7**), and 0.49 (**8**), with a minor spot at 0.21 (**4**?). Evaporation of the filtrate and recrystallization from carbon tetrachloride gave the less soluble **8** as red-orange crystals (ca. 20 mg) which, after a second recrystallization from benzene, had mp 310–312 °C (lit.[11] 314–315 °C) and gave a yellow TLC spot at 0.49. Crude **7** (ca. 30 mg) was obtained from the concentrated mother liquor. One recrystallization from ethanol gave pale yellow[16] crystals: mp 174–176 °C (lit.[11] 174–175 °C); ^{1}H NMR δ 1.40 (s, 36 H), 2.75 (s,

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(10) The UV spectrum of **1** has a poorly resolved double maximum at 277 and 284 nm with ϵ 2.8 × 10^3 in isooctane: "Selected Ultraviolet Spectral Data", API Research Project 44, no. 270; see also ref 7.

(11) R. H. Bauer and G. M. Coppinger, *Tetrahedron*, 19, 1201 (1963).

(12) W. Low and E. L. Offenbacher, *Solid State Phys.*, 17, 135 (1965).

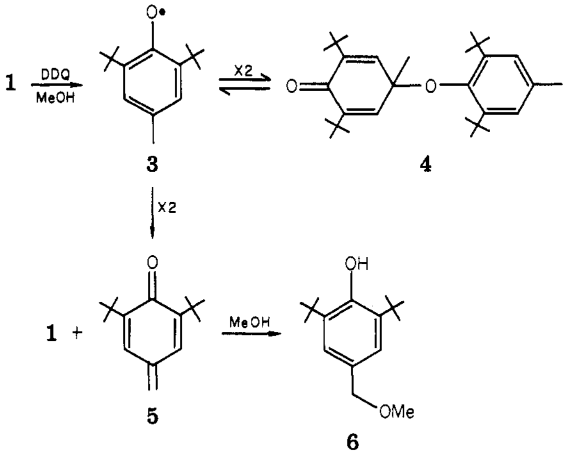
(13) Purity of silver determined by dissolving in hot nitric acid followed by precipitation as AgCl.[2]

(14) Different runs gave ratios of 1:6 varying from 54% (**1**) to 44% (**1**).

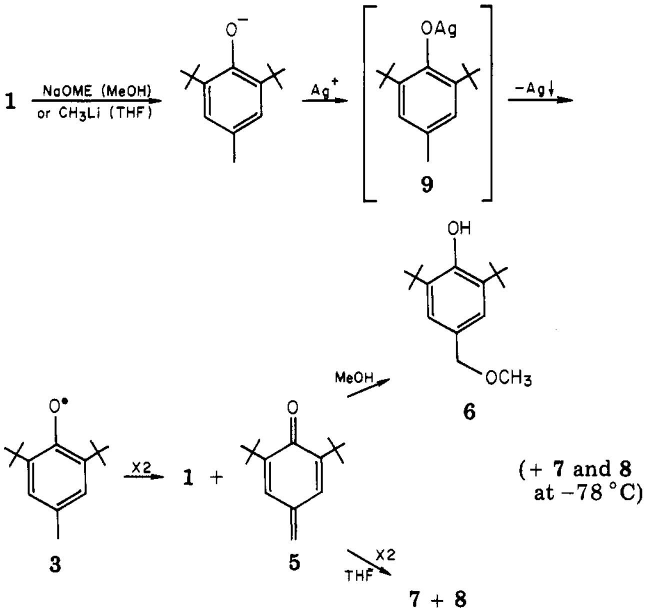
(15) The equivalence point was determined by collecting the evolved methane.

(16) The yellow color was due to a trace of **8**, confirmed by TLC.

Scheme I



Scheme II



4 H), 4.75 (br s, 2 H), 6.80 (s, 4 H); TLC R_f 0.54.

Acknowledgment. The author expresses his gratitude to Professors Albert Bobst and Estel Sprague of this department for their help in obtaining and interpreting the ESR spectrum and to one of the referees for calling our attention to ref 4.

Registry No. 1, 17688-83-4; 3, 6858-01-1; 4, 2179-51-3; 5, 2607-52-5; 6, 87-97-8; 7, 1516-94-5; 8, 809-73-4; Ag(I), 14701-21-4.

Reaction of 2-Amino-3-cyano-4-methylfuran as a Dienamine and a Diene

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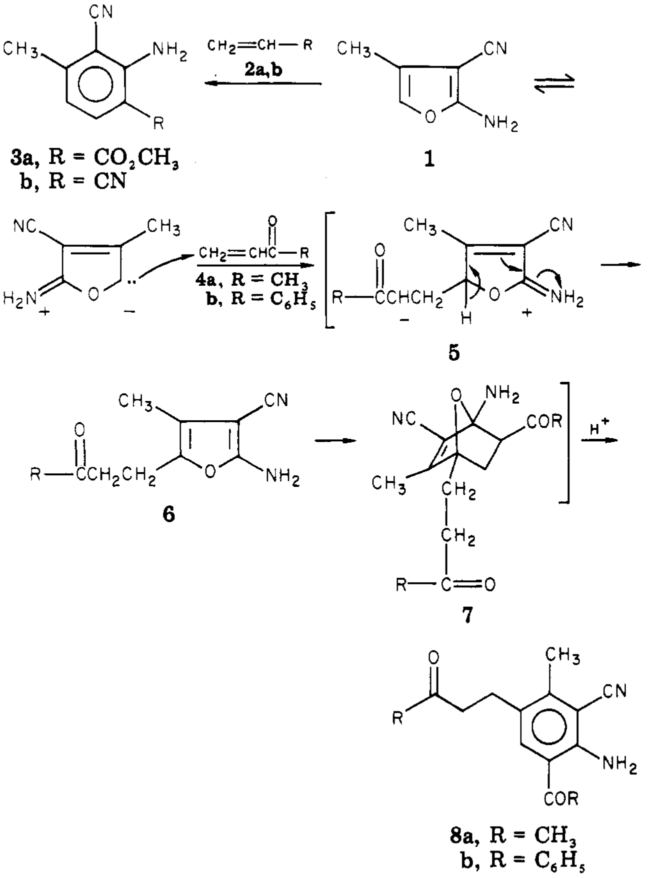
Received December 7, 1981

Scheme I



Previous studies in the use of furan *o*-aminonitriles as precursors for the synthesis of anthranilic acid derivatives and condensed heterocyclic compounds have shown [1] that 4,5-disubstituted 2-amino-3-cyanofurans react with various olefins in a Diels–Alder fashion. This reaction has now been extended to 2-amino-3-cyano-4-methylfuran (1)[2] with comparable results with methyl acrylate and acrylonitrile (Scheme I). However, 1 was observed to undergo a novel enamine reaction[3] when treated with methyl or phenyl vinyl ketones (Scheme I). The dienamine tautomer adds to the vinyl ketone by Michael addition,[6] leading to the

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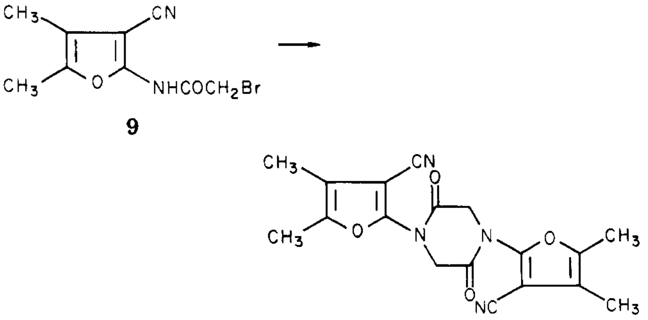
[1] Nixon, W. J., Jr.; Garland, J. T.; Blanton, C. D., Jr. *Synthesis* **1980**, 56.

[2] Gewald, K. *Chem. Ber.* **1966**, *99*, 1002.

[3] Furan an pyrrole *o*-aminonitriles have been shown[4] by NMR spectroscopy to behave as dienamines in trifluoroacetic acid with electrophilic addition at C_5. In one case, C-acylation of a furan *o*-aminonitrile (i.e., 2-amino-3-cyano-4,5-dimethylfuran) was claimed[4] to occur via the enamine, which was subsequently converted to a furo[2,3-*b*]pyrrole derivative. In fact, N-acylation was observed, and the product previously designated as a furopyrrole[4] was shown[5] to be *N,N'*-bis(3-cyano-4,5-dimethyl-2-furyl)-2,5-diketopiperazine:



Upon mild acidic hydrolysis, compound 9[4] gave the starting 4,5-dimethyl-2-amino-3-cyanofuran, whereas a peak at 352 in the mass spectrum supported the diketopiperazine assignment for **10**.

[4] Wie, C. T.; Sunder, S.; Blanton, C. D., Jr. *Tetrahedron* Lett. **1968**, 4605.

[5] Nixon, W. J., Jr. Ph.D. Dissertation, University of Georgia, July, 1972.

[6] Bergmann, E. D.; Ginsburg, D.; Pappo, R. *Org. React.* **1959**, *10*, 179.

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