Preparation of 4 and 5 by Phase-Transfer Method. To the ester **3** (0.90 g, 5.0 mmol) in benzene (4.5 mL) were added benzyltriethylammonium chloride (50 mg, 0.22 mmol) and 50% aqueous KOH (50 mL). The mixture was stirred vigorously at room temperature and chloroform (8 mL) was added dropwise over a period of 2 h. The reaction mixture was stirred for 48 h, diluted with ether, and acidified with 6 N HCl. The ethereal layer was separated and the aqueous layer was extracted with ether (3×). The combined ethereal solutions were washed with water and brine, dried over $MgSO_4$, and concentrated. Chromatography proceeded as described in the text.

X-ray Analysis. The crystals of **5** have triclinic symmetry, space group $P\bar{1}$. The unit cell which has the dimensions a = 7.603 (2), b = 12.292 (4), c = 6.961 (2) Å, α = 97.77 (3), β = 99.09 (3), and γ = 93.38(2)° contains two molecules of **5** yielding a calculated density of 1.39 g/cm^3.

Data were collected on a Syntex-P2$_1$ diffractometer, using graphite-monochromated Cu Kα radiation (λ = 0.71069 Å) in the $\theta/2\theta$ mode in the range 3° ≤2θ ≤ 135° at scan speeds of 2.93–29.30°/min, depending on the intensity of the reflection. Lorentz and polarization factors were applied and an empirical absorption correction was made (μ = 43.66 cm^{-1} for Cu Kα radiation). After the data reduction 2104 independent reflections ($I \geq 2\sigma(I)$) were retained for the refinement of the structure.

The position of the two chlorine atoms was determined by heavy atom methods; the residual atoms including hydrogen were located in difference maps. The hydrogen atoms together with individual isotropic temperature factors were included in the refinement. For all other atoms anisotropic temperature factors were introduced.

After several cycles the refinement converged to a final value of R = 0.046. In the last cycle of refinement the shifts for all parameters divided by their standard deviations were smaller than 0.02. A final difference map showed no electron density higher than 0.26 e/Å^3.

Acknowledgment. D.S. gratefully acknowledges a grant of the Deutsche Forschungsgemeinschaft supporting his stay at Harvard. The X-ray equipment used in this study was generously supplied by Professor W. N. Lipscomb, and the cost of the research was defrayed by National Science Foundation Grants CHE-7719899 (to W. N. Lipscomb) and CHE-782599 (to R. B. Woodward).

Registry No. **3**, 75558-37-1; **4**, 75558-38-2; **5**, 75558-39-3; **6**, 75558-40-6; phenyl(bromodichloromethyl)mercury, 3294-58-4.

Supplementary Material Available: Atomic coordinates, temperature factors, bond lengths, and bond angles (4 pages). Ordering information is given on any current masthead page. A table of observed and calculated structure factors is available from D.S.

Reduction of the Nitro Group versus Insertion in the C–O Bond of 3-Nitrobenzofuran by Ynamines. Synthesis and X-ray Crystal Structure Determination of a 1-Benzoxepin and a Quinoline 1-Oxide

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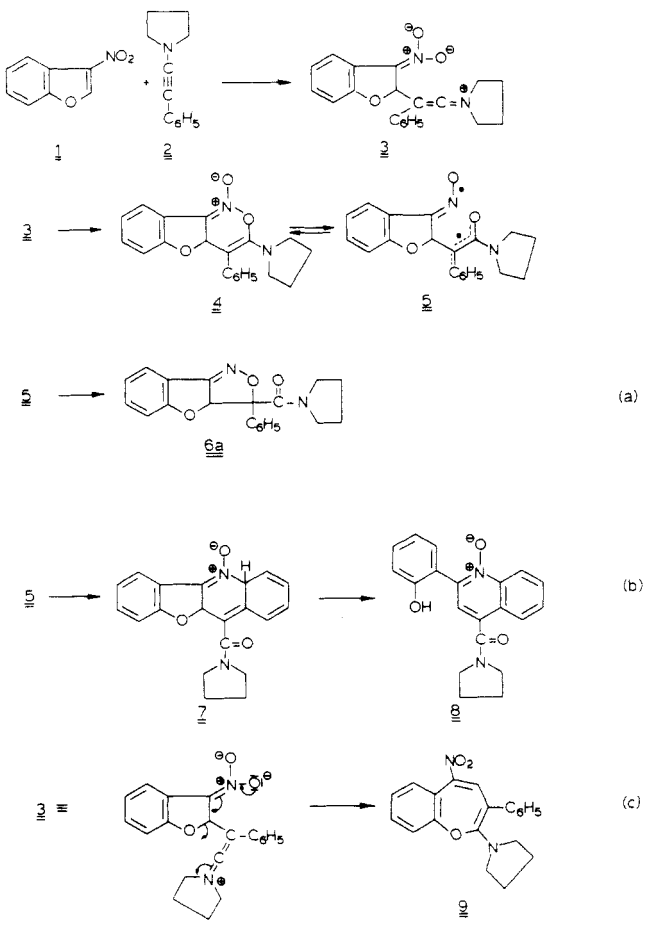
Received July 17, 1980

Our recent work on thermal reactions of electron-rich 1-aminoacetylenes (ynamines) with electron-deficient 1-nitroalkene systems[1,2] and nitro-substituted heteroaromatics[3] has revealed a remarkable variety of reaction products. The reactions of ynamines and 1-nitroalkenes provide cyclobutenes as well as 2,3-dihydroazete 1-oxides,[1,4] which are derived from a cyclic nitronate intermediate. With 3-nitrobenzo[*b*]thiophene and 4-nitroisothiazole the reaction products are cyclobutene derivatives and *C*-carbamoyl-*N*-heteroaryl nitrones.[3] The reaction of 3-nitrobenzofuran with 1-(diethylamino)propyne led to a benzofuro[3,2-*c*]isoxazole.[5]

Scheme I



We now report that the course of the reaction of 3-nitrobenzofuran (**1**) with ynamines depends on the structure of the ynamine. 1-Phenyl-2-(1-pyrrolidinyl)acetylene (**2**) reacted with 3-nitrobenzofuran (**1**) in benzene to give a mixture of products, from which three crystalline compounds were isolated by preparative TLC (Scheme I). The analytical and spectral data of the compound which was eluted second clearly showed that it was the benzofuro[3,2-*c*]isoxazole **6a**, (mp 214–216 °C, 12% yield), analogous to the product **6b** obtained from the reaction of **1** with 1-(diethylamino)propyne.[5] The ^{13}C NMR spectroscopic data in particular provide convincing evidence for the structure of **6a** (see Table I).

(1) A. D. de Wit, M. L. M. Pennings, W. P. Trompenaars, D. N. Reinhoudt, S. Harkema, and O. Nevestveit, *J. Chem. Soc., Chem. Commun.*, 993 (1979).
(2) M. L. M. Pennings and D. N. Reinhoudt, *Tetrahedron Lett.*, 1781 (1980).
(3) D. N. Reinhoudt and C. G. Kouwenhoven, *Recl. Trav. Chim. Pays-Bas*, **95**, 67 (1976).
(4) Independent studies have shown that a conrotatory ring opening of these 2,3-dihydroazete 1-oxides leads to the formation of *C*-carbamoyl-*N*-heteroaryl or -vinyl nitrones (to be published).
(5) A. D. de Wit, W. P. Trompenaars, D. N. Reinhoudt, S. Harkema, and G. J. van Hummel, *Tetrahedron Lett.*, 1779 (1980).

0022-3263/81/1946-0172$01.00/0 © 1981 American Chemical Society

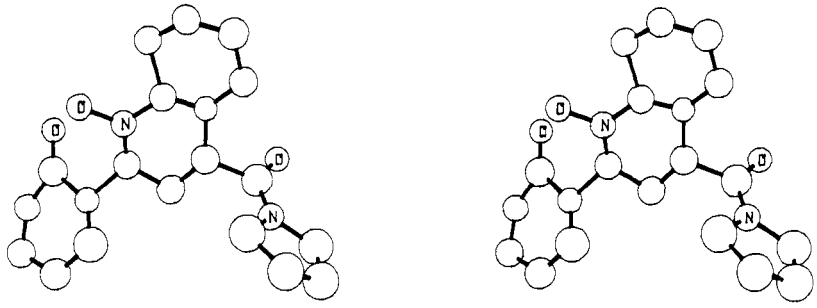


Figure 1. Stereoscopic view of compound 8.

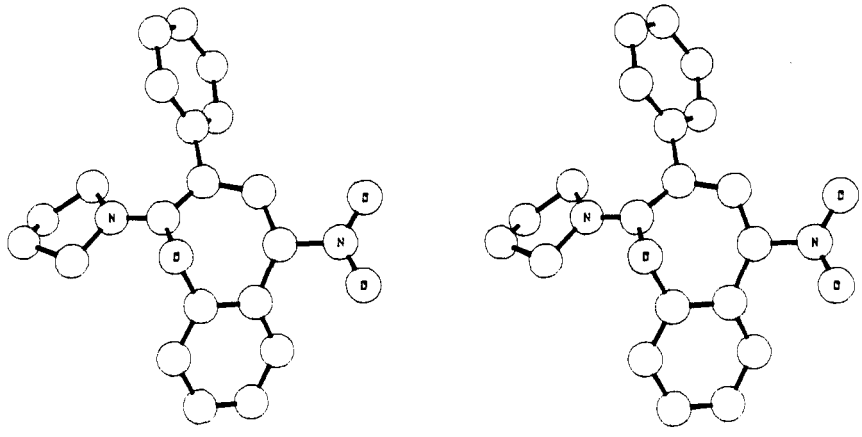
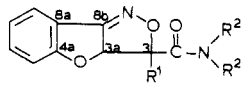


Figure 2. Stereoscopic view of compound 9.

Table I. ^{13}C NMR Data ($CDCl_3$, ppm) of the 3,3a-Dihydrobenzofuro[3,2-*c*]isoxazoles 6a and 6b

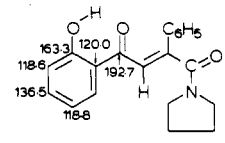


	6a, $R^1 = C_6H_5$; $R^2R^2 = (CH_2)_4$	6b, $R^1 = CH_3$; $R^2 = C_2H_5$
C=O	169.4 (s)	169.8 (s)
C-4a, C-8b	166.2 (s), 165.1 (s)	168.2 (s), 167.3 (s)
C-8a	114.7 (s)	115.4 (s)
C-5	112.9 (d)	113.2 (d)
C-3a	96.5 (d)	96.6 (d)
C-3	96.9 (s)	94.6 (s)

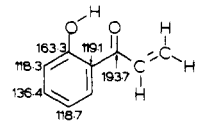
Mass spectrometry of the yellow crystalline material which was eluted last showed that it was also a 1:1 reaction product. Spectroscopic data excluded possible nitrone or cyclobutene structures and the presence of a carbamoyl group (IR, ^1H, and ^{13}C NMR spectroscopy) ruled out the oxazine derivative 4. A single-crystal X-ray determination showed that the compound was the quinoline 1-oxide 8 (mp 166–169 °C, 35% yield) (Figure 1).

The red crystalline compound which was eluted first still contained a nitro group, as indicated by the strong absorptions at 1520 and 1230 cm^{-1} in its IR spectrum. Mass spectrometry proved that this compound was another 1:1 reaction product and ^1H and ^{13}C NMR spectroscopy showed the absence of a carbamoyl group. An X-ray structure determination showed that the compound was the 1-benzoxepin 9 (mp 176–178 °C, 27% yield) (Figure 2).

On prolonged contact with silica gel or on standing in chloroform solution exposed to the atmosphere, the 1-benzoxepin 9 decomposed to give a yellow crystalline compound which had a molecular formula of $C_{20}H_{19}NO_3$, as shown by elemental analysis and mass spectrometry. The presence of a carbamoyl function was shown by ^1H and ^{13}C NMR spectroscopy. Comparison of the ^{13}C NMR values of this compound with those given for the parent 2′-hydroxyacrylophenone 12[6] confirmed that the decomposition product was 2′-hydroxy-3-phenyl-3-(1-pyrrolidinylcarbonyl)acrylophenone (11) (mp 161–163 °C).



11

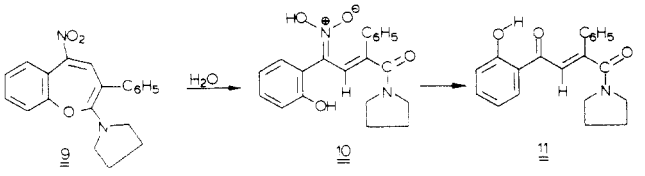


12

The formation of 8 and 9 from 1 and 2 can be explained by the presence of the 2-substituted phenoxy group, a potential leaving group, and the phenyl group in the 1,4-dipolar intermediate 3, which is initially formed by nucleophilic addition of the ynamine 2 to the C_2–C_3 double bond of the "pseudo" nitroalkene 1 (Scheme I). Different reaction pathways can be proposed to explain the formation of 6, 8, and 9, starting from this 1,4-dipolar intermediate (3). Firstly, a C–O bond can be formed to give the (not isolated) 4a*H*-benzofuro[3,2-*c*][1,2]oxazine derivative 4 in a similar way to that formed in the reaction of 1-nitrocyclopentene with the ynamine 2.[2] Homolytic fission of the weak N–O bond in 4 gives the diradical 5 which then rearranges, by formation of a second C–O bond, to yield the benzofuro[3,2-*c*]isoxazole 6 (Scheme I, route a). This reaction pathway is the one observed with 1 and 1-(diethylamino)propyne.[5] A deviation of this pathway, which is not possible with 1-(diethylamino)propyne, involves attack at the ortho position of the phenyl group to give the thermally unstable dihydrobenzofuro[3,2-*b*]-quinoline 1-oxide (7) which then undergoes aromatization

(6) R. Visser and A. A. Deetman, private communication.

Scheme II



by cleavage of the C–O ether linkage and a hydrogen transfer reaction to give **8** (Scheme I, route b). The second type of reaction of the 1,4-dipolar intermediate **3** is the *intra*molecular alkylation of the furan oxygen atom with simultaneous or subsequent cleavage of the ether linkage of the benzofuran ring to give the 1-benzoxepin **9** (Scheme I, route c).

In both the formation of **8** and **9** the effect of the 2-substituted phenoxy group as a good leaving group is evident. Similar types of insertion reactions of ynamines in the C–O bonds of 2,2-bis(trifluoromethyl)-1,3-dioxolan-4-ones and 1,3-oxazolidin-5-ones have been reported by Burger et al.[7] and of phthalic anhydride and phthalide by Höfle and Steglich.[8] The X-ray structure determination of **9** proves that insertion had taken place in the C—O bond and not in the C=C bond. The latter type of insertion would result from a (2 + 2)-cycloaddition reaction[9] followed by a ring enlargement to the oxepin as was found in the reaction of 3-(1-pyrrolidinyl)benzofuran with dimethyl acetylenedicarboxylate.[10] In addition Abramovitch et al.[11] have reported the ring expansion of 3-substituted 1,2-benzoisothiazole 1,1-dioxides to 1,2-benzothiazepines 1,1-dioxides by insertion of an ynamine in the C=N bond.

A possible mechanism for the formation of **11** is shown in Scheme II: hydrolysis of **9** gives the nitronic acid **10** which is further hydrolyzed (Nef reation[12]) to give the acrylophenone **11**.

From a synthetic point of view, the formation of 1-benzoxepins by insertion of a vinyl group in a benzofuran offers a useful addition to the few available methods for the synthesis of these 12π-electron heterocycles.[10,13] Further, the formation of the quinoline 1-oxide **8** from an ynamine and a nitroalkene possessing a good leaving group may open a simple route for the synthesis of aza aromatics.

Experimental Section

Melting points were determined with a Mettler FP1 apparatus and are uncorrected. ^{1}H NMR and ^{13}C NMR spectra ($CDCl_3$) were recorded with a Varian XL-100 spectrometer (Me_4Si as internal standard). Mass spectra were obtained with a Varian Mat 311A spectrometer. Elemental analyses were carried out by the Element Analytical Section of the Institute for Organic Chemistry TNO, Utrecht, The Netherlands, under supervision of W. J. Buis.

3-Nitrobenzofuran (1). This compound was prepared by nitration of benzofuran according to Kaluza and Perold:[14] mp 149–150 °C (lit.[14] mp 149.5 °C); ^{1}H NMR δ 8.60 (s, 1 H, H-2), 8.30–8.05 (m, 1 H, H-4), 7.70–7.30 (m, 3 H, H-5,6,7).

1-Phenyl-2-(1-pyrrolidinyl)acetylene (2). This compound was sythesized from 1-chloro-2-phenylacetylene[15] and 1-pyrrolidinyllithium according to the procedure described in ref 3: bp 100–102 °C (0.1 torr) [lit.[3] 103–104 °C (0.2 torr)]; ^{1}H NMR δ 7.40–7.05 (m, 5 H, Ph H), 3.50–3.20 (m, 4 H, pyrr H(α)), 2.05–1.70 (m, 4 H, pyrr H(β)).

Reaction of 3-Nitrobenzofuran (1) with 1-Phenyl-2-(1-pyrrolidinyl)acetylene (2) in Benzene. A solution of 1-phenyl-2-(1-pyrrolidinyl)acetylene (**2**, 0.016 mol) in 15 mL of benzene was added dropwise to a suspension of 3-nitrobenzofuran (**1**, 0.015 mol) in 15 mL of benzene at 10 °C and the mixture was stirred overnight at room temperature. The benzene was removed under reduced pressure and the residue was separated by preparative TLC (silica gel, chloroform/ethyl acetate, 9:1) to yield **9** (27%), **6a** (12%), and **8** (35%), respectively.

3,3a-Dihydro-3-phenyl-3-(1-pyrrolidinylcarbonyl)benzofuro[3,2-*c*]isoxazole (6a): mp 214–216 °C (methanol); ^{1}H NMR δ 6.86 (s, 1 H, H-3a), 7.65–6.75 (m, 9 H, H-5,6,7,8 and Ph H), 3.85–3.40 (m, 3 H) and 2.85–2.65 (m, 1 H, pyrr H(α)), 2.00–1.45 (m, 4 H, pyrr H(β)); ^{13}C NMR δ 169.4 (s, C=O), 166.2 (s) and 165.1 (s) (C-4a and C-8b), 131.2 (s, Ph C-1), 133.6 (d), 128.3 (d), 128.2 (d), 126.4 (d), 123.6 (d) and 122.3 (d) (C-6,7,8 and Ph C), 114.7 (s, C-8a), 112.9 (d, C-5), 96.9 (s, C-3), 96.5 (d, C-3a), 47.3 and 46.6 (t, pyrr C(α)), 26.1 and 23.5 (t, pyrr C(β)); mass spectrum, M^+ calcd 334.132, obsd 334.133.

Anal. Calcd for $C_{20}H_{18}N_2O_3$: C, 71.84; H, 5.43; N, 8.38. Found: C, 71.95; H, 5.38; N, 8.21.

2-(2-Hydroxyphenyl)-4-(1-pyrrolidinylcarbonyl)quinoline 1-oxide (8): mp 166–169 °C (methanol); ^{1}H NMR δ 10.95 (s, 1 H, OH), 8.97 (d, 1 H, H-8), 8.10–6.90 (m, 8 H, H-3,5,6,7 and Ph H), 3.90–3.65 (m, 2 H) and 3.35–3.10 (m, 2 H, pyrr H(α)), 2.20–1.70 (m, 4 H, pyrr H(β)); ^{13}C NMR δ 164.8 (s, C=O), 159.6 (s, Ph C-2), 147.8 (s, C-2), 140.9 (s, C-8a), 136.4 (s, Ph C-1), 125.0 and 120.9 (s, C-4 and C-4a), 132.4 (d), 131.9 (d), 131.1 (d), 129.4 (d), 125.5 (d), 121.6 (d), 120.4 (d) and 120.2 (d) (C-5,6,7,8 and Ph C), 48.6 and 45.9 (t, pyrr C(α)), 25.9 and 24.3 (t, pyrr C(β)); mass spectrum, M^+ calcd 334.132, obsd 334.133.

Anal. Calcd for $C_{20}H_{18}N_2O_3 \cdot 0.25CH_3OH$: C, 71.04; H, 5.59; N, 8.18. Found: C, 71.15; H, 5.58; N, 8.09.

5-Nitro-3-phenyl-2-(1-pyrrolidinyl)-1-benzoxepin (9): mp 176–178 °C (methanol); ^{1}H NMR δ 8.24 (s, 1 H, H-4), 8.10–7.85 (m, 1 H, H-6), 7.50–7.10 (m, 8 H, H-7,8,9 and Ph H), 3.55–3.20 (m, 4 H, pyrr H(α)), 1.95–1.60 (m, 4 H, pyrr H(β)); ^{13}C NMR δ 155.5 (s) and 153.8 (s) (C-2 and C-9a), 140.5 (d, C-4), 138.0 (s) and 136.9 (s) (C-5 and Ph C-1), 126.2 (s, C-5a), 130.2 (d), 129.2 (d) 129.1 (d), 127.9 (d), 126.6 (d), 125.3 (d) and 120.6 (d) (C-6,7,8,9 and Ph C), 100.2 (s, C-3), 50.7 (t, pyrr C(α)), 25.0 (t, pyrr C(β)); mass spectrum, M^+ calcd 334.132, obsd 334.133.

Anal. Calcd for $C_{20}H_{18}N_2O_3$: C, 71.84; H, 5.43; N, 8.38. Found: C, 71.61; H, 5.55; N, 8.23.

Hydrolysis of 9 to 2′-Hydroxy-3-phenyl-3-(1-pyrrolidinylcarbonyl)acrylophenone 11. Upon standing at 30 °C a chloroform solution of the 1-benzoxepin **9** changed in color from deep red to brown. After 14 days the chloroform was evaporated to give an oil which was chromatographed on silica gel (chloroform/ethyl acetate, 9:1) to give, after elution of a trace of the 1-benzoxepin **9**, the acrylophenone **11** (80%): mp 161–163 °C (methanol); yellow needles; ^{1}H NMR δ 8.0–6.85 (m, 10 H, Ph H), 3.90–3.65 (m, 2 H) and 3.35–3.10 (m, 2 H, pyrr H(α)), 2.15–1.70 (m, 4 H, pyrr H(β)); ^{13}C NMR δ 192.7 (s, C=O), 167.4 (s, NC=O), 163.3 (s, C-2′), 152.8 (s, C-3), 136.5 (d, C-4′), 134.0 (s, Ph C-1), 130.8 (d), 129.6 (d), 129.0 (d) and 127.0 (d) (Ph C and C-6′), 120.0 (s, C-1′), 118.8 (d, C-5′), 118.6 (d, C-3′), 117.5 (d, C-2), 46.9 and 45.3 (t, pyrr C(α)), 25.7 and 24.4 (t, pyrr C(β)); mass spectrum, M^+ calcd 321.137, obsd 321.137.

Anal. Calcd for $C_{20}H_{19}NO_3$: C, 74.75; H, 5.96; N, 4.36. Found: C, 74.61; H, 6.05; N, 4.24.

Crystallographic Data and X-ray Structure Analysis of 8 and 9. X-ray intensities of crystals of **8** and **9** were measured with a Philips PW 1100 diffractometer (graphite monochromated radiation). Only small single crystals of both compounds could be obtained, resulting in a large number of weak reflections and quite high standard deviations for the observed ones. Information on the unit cells found and the data collection is presented in Table II. The crystal of **8** slowly decomposed in the course of

(7) K. Burger, A. Meffert, and A. Gieren, *Justus Liebigs Ann. Chem.*, 1037 (1978).
(8) G. Höfle and W. Steglich, *Chem. Ber.*, **105**, 1368 (1972).
(9) 3-Nitrobenzo[*b*]thiophene and 4-nitroisothiazole react with ynamines[3] to give cyclobutenes by (2 + 2) cycloaddition.
(10) D. N. Reinhoudt and C. G. Kouwenhoven, *Tetrahedron Lett.*, 5203 (1972); *Recl. Trav. Chim. Pays-Bas*, **93**, 129 (1974).
(11) R. A. Abramovitch, K. M. More, I. Shinkai, and P. C. Srinivasan, *Heterocycles*, **5**, 95 (1976).
(12) N. Kornblum and R. A. Brown, *J. Am. Chem. Soc.*, **87**, 1742 (1965).
(13) H. Hofmann and H. Westernacher, *Chem. Ber.*, **102**, 205 (1969), and references cited therein.
(14) F. Kaluza and G. Perold, *Chem. Ber.*, **88**, 597 (1955).
(15) F. M. Beringer and S. A. Galton, *J. Org. Chem.*, **30**, 1930 (1965).

Table II. Crystallographic Data of 8 and 9

	8	9
formula	$C_{20}H_{18}N_2O_3 \cdot xCH_3OH$	$C_{20}H_{18}N_2O_3$
radiation used	Mo Kα (0.7107 Å)	Mo Kα (0.7107 Å)
maximum θ, deg	20	20
space group	$P2_1/c$	$Pbca$
a, Å	12.372 (4)	12.879 (4)
b, Å	18.660 (6)	24.923 (8)
c, Å	9.254 (3)	10.962 (4)
β, deg	111.75 (5)	
Z	4	8
no. of refl measured	1964	1537
observed refl ($I > \sigma(I)$)	1129	749
R_w	13.0%	8.3%

the intensity measurements. A correction for this effect (maximum 10%) was applied. The structures were solved by direct methods (MULTAN 78)[16] and refined by the full-matrix least-squares method (ORFLS).[17] Parameters refined were positional and anisotropic thermal parameters of all nonhydrogen atoms. A final-difference Fourier synthesis for compound 8 revealed two peaks with a distance of 1.5 Å. These peaks were ascribed to methanol, from which compound 8 was recrystallized. Subsequent refinements with inclusion of the carbon and oxygen atoms of the methanol molecule gave rather high temperature factors for both atoms. Therefore a partial occupancy (75%) of the methanol sites was supposed. The refinements now gave reasonable temperature factors, but the C–O distance found (1.7 Å) is too long. Our conclusion is that there is methanol in the crystal lattice, but the quality of our data does not allow us to draw more definite conclusions. A low-temperature X-ray structure determination may resolve the problems. Tables of atomic coordinates, thermal parameters, bond distances, and bond angles have been deposited as supplementary material. The perspective drawings of the structures were made by the ORTEP program.[18]

Registry No. 1, 75420-78-9; 2, 54494-80-3; 6a, 75420-79-0; 6b, 75420-80-3; 8, 75420-81-4; 9, 75420-82-5; 11, 75420-83-6; benzofuran, 271-89-6; 1-chloro-2-phenylacetylene, 1483-82-5; 1-pyrrolidinyllithium, 4439-90-1.

Supplementary Material Available: Tables of atomic coordinates, thermal parameters, bond distances, and bond angles and stereoscopic view of 8·MeOH (5 pages). Ordering information is given on any current masthead page.

(16) G. Germain, P. Main, and M. M. Woolfson, *Acta Crystallogr., Sect. B*, **26**, 274 (1970); P. Main, "Recent Developments in MULTAN" in "Computing in Crystallography", H. Schenk, Ed., Delft University Press, The Netherlands, 1978.
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Thermolysis of *N*-Alkyl-Substituted Phthalamic Acids. Steric Inhibition of Imide Formation

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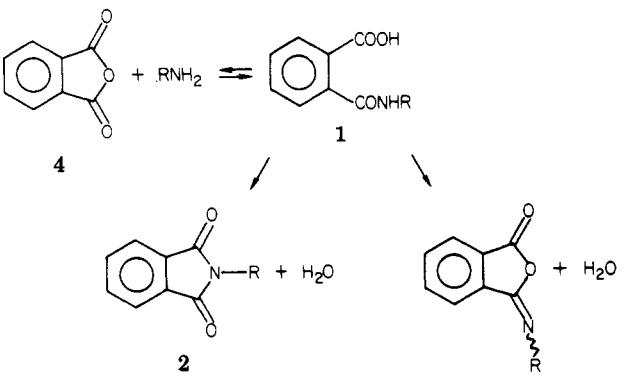
Received April 23, 1980

The dehydration of amic acids, derived from the reaction of cyclic anhydrides with primary amines, to yield imides is a general method for the preparation of this important class of heterocyclic compounds and is of major commercial significance in the conversion of polyamic acids to polyimides.[1] In principle, the thermal ring closure of amic acids can lead to the formation of imides, isoimides, or anhydrides (Scheme I). Numerous reagents have been employed to effect the dehydration of amic acids[2] to imides and isoimides and the partitioning of products between these isomers has been found to depend strongly upon the specific dehydrating agent used as well as on the nature of the amic acid itself.[3-10] In contrast, no detailed study of the relationship between the structure of the amic acid and the initial product distribution obtained in the thermal ring-closure reactions of amic acids has been reported. Furthermore, we have observed that in the reaction of phthalic anhydride with primary aliphatic amines to yield imides in refluxing acetic acid, the amount of excess amine required to optimize the yield of imide is strongly dependent upon the steric bulk of the amine employed. For these reasons, we have undertaken a study of the primary product distribution obtained in the vacuum thermolysis at 200 °C of a series of *N*-alkyl-substituted phthalamic acids in which the steric bulk of the *N*-alkyl substituents has been systematically varied.

Scheme I



Results and Discussion

Phthalimides are known to undergo very slow ring opening in the presence of water or amines while the ring opening of anhydrides and the isomerization of isoimides to imides in the presence of these species are known to occur quite readily.[8,11] Therefore, the thermolysis had to be accomplished under conditions which provided for the rapid removal of water and amine as they formed, in order to avoid these secondary reactions. Although various combinations of temperature and pressure were adequate for this purpose, we found that conducting the thermolyses

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0022-3263/81/1946-0175$01.00/0 © 1981 American Chemical Society