major part of the solvent stabilization should be manifest during the dissociation rather than the formation of the ion pairs. This should be true as (a) it is the step where most of the charge separation is being effected (as the distance between the ions increases), (b) a partial desolvation of at least one side of each reagent must occur during the formation of the ion pair, while no such impediment to the dissociation of the solvated ion pair exists, and (c) the significant stabilization that each counterion affords the other in the ion pair lowers the chemical activity of the ions thereby making additional stabilization less necessary.

The results of this study lead us to suggest, within limits, that variation of substituents are likely to have a greater effect upon formation than dissociation of ion pairs, while variation of solvent is likely to have the reverse order of importance. The overall rate of the substitution reaction, although limited by one or the other of the two processes under consideration, will often depend upon the relative rates of reaction of the ion pairs vs. the return to starting reagent. The results of this study cannot, therefore, be easily compared with overall rates.

Acknowledgment. This work was supported, in part, by PSC-BHE Grant No. 13120 from the City University of New York.

Registry No. 1a, 350-50-5; **1b**, 16473-39-5; **3a**, 78514-46-2; **3b**, 78514-47-3.

Reaction of Pyrrolidone with Phosphorus Pentachloride

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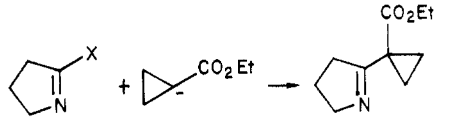
In the course of attempts to prepare the cyclopropylimine **2**[1] according to eq 1, a pyrroline more reactive than



(1)

1 2

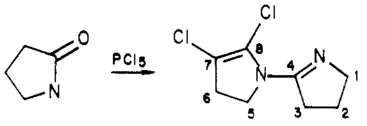
the imino ether **1** (X = OCH_3) was desired. An obvious possibility was the chloropyrroline **1** (X = Cl).[2] Indeed, when pyrrolidone and phosphorus pentachloride were allowed to react, the same compound reported earlier[2] was obtained; however, the proton NMR spectrum did not match the expected structure. In addition, sodium methoxide in refluxing methanol had no effect on the compound and alcoholic silver nitrate gave no silver chloride. The sample turned brown when exposed to the air for a week but was stable under nitrogen either in a desiccator or a freezer. Combustion analysis and the mass spectrum established the molecular formula as $C_8H_{10}N_2Cl_2$.

Table I. ^1H and ^{13}C NMR Parameters for Compound **3**[a]

position	^1H chemical shift	apparent H-H coupling, Hz	^{13}C chemical shift
1	3.43	7.2	54.9 (t)
2	1.79	7.2, 8.2	23.8 (t)
3	2.68	8.2	32.6 (t)
4			162.9
5	3.88	9.3	48.2 (t of t)
6	2.57	9.3	31.1 (t of t)
7			109.1
8			126.6

[a] Chemical shifts are in parts per million relative to Me_4Si.

The structure of this novel compound was unambiguously established as **3** (eq 2) by examination of its proton



(2)

3

and carbon NMR spectra (Table I) and by selective homo- and heteronuclear decoupling experiments. The 200-MHz proton spectrum displayed five signals of equal intensity (two protons each)—four triplets at 3.88 (H-5, J = 9.3 Hz), 3.43 (H-1, J = 7.2 Hz), 2.68 (H-3, J = 8.2 Hz), and 2.57 ppm (H-6, J = 9.3 Hz) and a "pentuplet" at 1.79 ppm (H-2, J = 7.2 and 8.2 Hz). Irradiation of the signal assigned to H-5 collapsed the signal assigned to H-6 to a singlet and vice versa. Irradiation of either the signal assigned to H-1 or the signal assigned to H-3 reduced the pentuplet to a triplet, whereas irradiation of the pentuplet at 1.79 reduced the signals assigned to H-1 and H-3 to singlets. This clearly established the presence of the two- and three-methylene fragments in structure **3**. The chemical shifts of the various protons are fully consistent with the positions to which they are assigned. Also, the proton NMR spectrum did not show any signal attributable to N-H. The proton-decoupled 50-MHz ^{13}C spectrum of **3** showed eight lines: five NOE enhanced signals in the aliphatic region [54.9 (C-1), 48.2 (C-5), 32.6 (C-3), 31.1 (C-6), and 23.8 ppm (C-2)], each of which is a triplet in a coupled spectrum, and three weak signals from nonprotonated carbons in the sp^2 region [162.9 (C-4), 126.6 (C-8), and 109.1 ppm (C-7)], which remain singlets in the coupled spectrum. The aliphatic carbons were unambiguously assigned by a series of selective decoupling experiments in which irradiation of each individual proton signal collapsed the corresponding carbon multiplet to a singlet. Examination of a high-resolution coupled carbon spectrum revealed numerous long-range C–H couplings. For example, C-5 and C-6 are actually triplets of triplets. Selective decoupling of individual hydrogens with low decoupler power removed only these long-range couplings and was particularly useful in confirming the assignments of the three nonprotonated sp^2 hybridized carbons. Again, the carbon chemical shifts are completely consistent with the structural assignments presented.

Structure **3** is the only structure consistent with the molecular formula obtained from elemental analysis and

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(1) This compound has been used as an intermediate in a convergent synthesis of pyrrolizidine alkaloids: Pinnick, H. W.; Chang, Y.-H. *Tetrahedron Lett.* **1979**, 837.

(2) Reportedly prepared from pyrrolidone and phosphorus pentachloride: (a) Tafel, J.; Wassmuth, O. *Chem. Ber.* **1907**, *40*, 2831. (b) Etienne, A.; Correia, Y. *Bull. Soc. Chim. Fr.* **1969**, 3704.

0022-3263/81/1946-4076$01.25/0

mass spectral data and the NMR results described above. Furthermore, Bredereck[3] has reported that lactams react with phosphorus oxychloride and amines to give amidines via O-phosphorylated salts. It is not unreasonable to imagine a similar coupling reaction here.[4]

Experimental Section

Melting points were determined on a Thomas-Hoover capillary tube apparatus and are uncorrected. Infrared spectra were recorded on Perkin-Elmer Model 297 or 599B spectrophotometers. Hydrogen and carbon-13 NMR spectra were obtained on a $CDCl_3$ solution of 3 with a Varian XL-200 NMR spectrometer. Proton spectra were obtained in a few scans, using 12K data points with a sweep width of 2000 Hz and an acquisition time of 3 s and a pulse width corresponding to a flip angle of 30°. Carbon spectra were obtained in a few thousand scans with a sweep width of 10000 Hz, an acquisition time of 0.8 s, and a pulse width corresponding to a flip angle of 35°. Mass spectra were run on a Finnigan 4023 GC/MS. Microanalyses were performed by Atlantic Microlab.

Reaction of Pyrrolidone with Phosphorus Pentachloride. Phosphorus pentachloride (30 g, 0.14 mol) was added over a 10-min period to a stirred solution of 10 g (0.12 mol) of pyrrolidone in 50 mL of dry benzene at room temperature. The reaction mixture was then refluxed for 8 h, cooled, and poured into 100 mL of ice water. Basification of the aqueous layer with 50% sodium hydroxide gave a white solid, which was recrystallized from acetone/water to give 7.5 g (62%) of compound **3**: mp 51–52 °C; IR (KBr) 2960, 2920, 2860, 1620, 1600, 1430 cm^{-1}; mass spectrum, *m/e* (relative abundance) 206 (P + 2, 11), 204 (P, 18), 169 (35), 133 (15), 101 (10), 87 (10), 73 (10), 68 (22), 51 (28), 41 (100).

Anal. Calcd for $C_8H_{10}N_2Cl_2$: C, 46.85; H, 4.91; N, 13.66; Cl, 34.57. Found: C, 46.80; H, 4.95; N, 13.63; Cl, 34.53.

Registry No. 3, 33992-19-7; pyrrolidone, 616-45-5; phosphorus pentachloride, 10026-13-8.

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(3) Bredereck, H.; Bredereck, K. *Chem. Ber.* **1961**, *94*, 2278.

(4) In the absence of additional information, we are hesitant to speculate further on a possible mechanistic pathway.

Acid-Catalyzed Rearrangements of Acetamido-Annelated Cyclobutenes. Formation and Properties of a 1,5-Dihydro-2*H*-azepin-2-one

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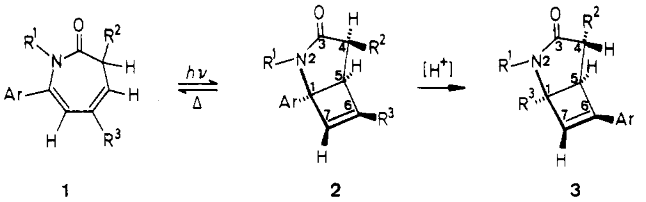
Seven-membered cyclic dienamides (1,3-dihydro-2*H*-azepin-2-ones) 1, in general, are unreactive in their electronic ground state but are prone to undergo photochemical isomerizations.[1] For example, irradiation of 7-aryl-substituted azepinones 1 in aprotic solvents smoothly gives acetamido-annelated cyclobutenes (azabicyclo[3.2.0]heptenones) 2 by intramolecular [2 + 2] cycloaddition.[2] In previous studies, acetamido-annelated cyclobutenes 2 have been shown to be thermally labile, regenerating azepinones 1 at elevated temperature (>200 °C).[3]



1 2 3

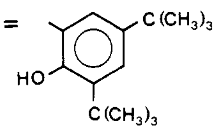
1–3 a: $R^1 = CH_3$

b: $R^1 = n\text{-}C_3H_7$

c: $R^1 = c\text{-}C_6H_{11}$

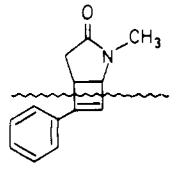
$R^2 = R^3 = C(CH_3)_3$

Ar =



In an attempt to facilitate the thermally induced cycloreversion by acid catalysis,[4] we have now found that acetamido-annelated cyclobutenes 2 can undergo novel transformations which complement the previously known cationic conversions of cyclobutenes, resulting in either ring contraction or ring enlargement and concomitant incorporation of a nucleophile.[5] Thus, refluxing solutions of **2a–c** in benzene in the presence of trifluoroacetic acid (TFA) smoothly gives the isomeric acetamido-annelated cyclobutenes **3a–c**. Isomers **3** differ structurally from starting compounds **2** by substituent interchange at C-1/C-6 and by epimerization at C-4.

As exemplified for the rearrangement product obtained from **2a**, the assignment of strucure **3** is based on the following spectroscopic evidence. In their infrared spectra, both **2a** and **3a** exhibit their carbonyl absorption at similar wavenumber (1665 and 1660 cm^{-1}, respectively), suggesting the rearrangement product to have retained the γ-lactam function. The ultraviolet spectrum of **2a** in ethanol shows the longest wavelength absorption maximum at 284 nm (ϵ 1900), while that of the rearrangment product **3a**, in agreement with extended conjugation, appears at 306 nm (ϵ 4100). Similar UV data [λ_{max} 291 nm (ϵ 4400)] have been reported for the structurally related azabicycloheptenone **4**.[6] Also analogous to **4**, the dominant mass spectral fragmentation of **3a** involves elimination of the arylacetylene moiety (M – 230).



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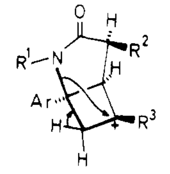

5

The ^1H NMR spectrum of **3a**, by and large, resembles that of **2a**, however, differences in coupling constants indicate the changes in dihedral angles between the protons at C-4, C-5, and C-7 which, as Dreiding molecular models suggest, may be brought about by the change of stereochemistry at C-4 (see Figure 1). Thus, in the ^1H NMR spectrum of the starting material **2a** (whose C-4 *tert*-butyl substituent has been confirmed to be endo oriented),[7] the

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(1) Paquette, L. A. In "Nonbenzenoid Aromatics"; Snyder, J. P., Ed.; Academic Press: New York, 1969; Vol. 1, 249–310.

(2) Becker, H.-D.; Gustafsson, K. *J. Org. Chem.* **1977**, *42*, 2966. Becker, H.-D.; Turner, A. B. *Tetrahedron Lett.* **1979**, 4871.

(3) Chapman, O. L.; Hoganson, E. D. *J. Am. Chem. Soc.* **1964**, *86*, 498. Vogel, E.; Erb, G.; Lenz, G.; Bothner-By, A. A. *Justus Liebigs* Ann. Chem. **1965**, *682*, 1.

(4) Numerous examples of acid-catalyzed reversions of photochemical cycloadditions have been reported in the literature: Hirao, K.; Taniguchi, M.; Yonemitsu, O.; Flippen, J. L.; Witkop, B. *J. Am. Chem. Soc.* **1979**, *101*, 408. Becker, H.-D. *Justus Liebigs Ann. Chem.* **1973**, 1675. Greene, F. D. *Bull. Soc. Chim. Fr.* **1960**, 1356.

(5) Seebach, D. In "Methoden der Organischen Chemie (Houben-Weyl-Müller)", 4th ed.; Georg Thieme Verlag: Stuttgart, 1971; Vol. IV/4, p 422. Cf. also: Paquette, L. A.; Krow, G. R. *Tetrahedron Lett.* **1968**, 2139.

(6) Atherton, F. R.; Lambert, R. W. *J. Chem. Soc., Perkin Trans. 1* **1973**, 1079.

(7) Becker, H.-D.; Gustafsson, K.; Raston, C. L.; White, A. H. *Aust. J. Chem.* **1979**, *32*, 1931.

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