bicyclic compound readily binds to Co(II)-**2.** The observed ESR transitions were: toluene (80 K), $g_x = 2{,}38$, $g_y = 2.24$, $g_z = 2.00$; $a^{\mathrm{Co}} = 105$ G, 97.7×10^{-4} cm^{-1}; $a^{\mathrm{N}} = 20$ G, 18.7 $\times 10^{-4}$ cm^{-1}. Particularly informative is the appearance of only three superhyperfine lines on the high field ESR transition indicating that only one nitrogen atom binds to the Co(II) ion. Thus, facile isomerization of the cis isomers in the presence of Co(II)-**2** is probably due to the formation of a dπ-pπ bond between the metal ion and the bound nitrogen atom. Electronic delocalization of this type would have the effect of reducing the double bond character of the azo linkage itself and thus facilitate the isomerization to the stable trans isomer.

Finally, a toluene solution containing 1.4 μM Co(II)-**2** and 14 μM trans Ni(II)-**1** was irradiated as before using 5017 Å radiation.[20] The fact that no isomerization was observed under these conditions taken with the ESR results is supportive of the energy releasing process shown in Scheme I. Thus, the photoreaction transforms a sterically incumbered ligand, trans Ni(II)-**1,** into a good donor group, cis Ni(II)-**1** which subsequently binds to Co(II)-**2.** This bis macrocyclic complex is unstable and rapidly decomposes to give trans Ni(II)-**1,** Co(II)-**2,** and heat. All efforts to trap and examine the unusual intermediate bis macrocyclic complex have been unsuccessful to date.[21]

The overall efficiency of converting photoenergy into thermoenergy for the system described in this report is low.[22] However, since the metallomacrocyclic framework gives rise to strong metal dependent absorptions in the visible region, the compounds can be viewed as polychromic absorbers. The combination of this feature with the ability to attach other higher energy acceptor molecules to the macrocyclic framework enhances the possibility of using this type of macrocyclic structure in an efficient photo-thermo conversion process. We are continuing to study the forward light driven reaction as a function of both the coordinated metal ion and the structure of the covalently bound acceptor molecule. At the same time the effects of various chemical agents on the energy releasing step are being explored.

Acknowledgment. We wish to thank Mr. Abbas Pezeshk for his assistance in determining the ESR spectra of the complexes. We also wish to thank the Syracuse University Institute for Energy Research for their support of this project.

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(7) The compounds **1** (52% yield) and Ni(II)-**1** (60% yield) gave acceptable analytical and mass spectral data: *m/e*, calcd (obsd), **1,** 553 (553); Ni(II)-**1** 609 (609). ^{1}H (NMR) ($CDCl_3$), **1** δ 2.02 (s, 6 H), 2.17 (s, 6 H), 4.90 (s, 1 H), 7.0–8.3 (m, 17 H) 12.25 (s, 1 H), 13.88 (s, 1 H); Ni(II)-**1** δ 1.83 (s, 6 H), 2.05 (s, 6 H), 4.83 (s, 1 H), 6.5–8.5 (m, 17 H).
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(11) All irradiation experiments were done using a Spectra Physics Model 166-03 argon ion laser with a Spectra Physics Model 375 dye laser for the long wavelength studies. The solutions, which were run in duplicate, were thoroughly degassed before irradiating. Typical irradiation conditions employed a laser intensity of about 20 mW for durations of under 2 min. Using these conditions no degrading of the compound in solution could be observed. Longer irradiation times and higher powers lead to some decomposition as evidenced by the inability of the irradiated solution to completely return to its original spectral properties. The observed quantum yields were referenced against a ferric oxalate actiometer; C. A. Parker, "Photoluminescence of Solutions", Elsevier, New York, N.Y., 1968, p 208. Difference spectral techniques were used to measure the amount of cis Ni(II)-**1** present after irradiation. The quantum yield value was obtained on solutions containing <3% of cis Ni(II)-**1** Φ_{5017} trans → cis 3.3×10^{-2}; pps 76% trans.
(12) Thin layer conditions. Silica gel (C_6H_6); R_f trans Ni(II)-**1** 0.55, cis Ni(II)-**1** 0.25.
(13) The first-order rate constant for the cis to trans isomerization of azobenzene is 1.6×10^{-6} s^{-1}; R. J. W. LeFevre and J. Northcott, *J. Chem. Soc.*, 867 (1953).
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(20) Although Co(II)-**2** is an intensely absorbing compound this ratio of the complexes produces an absorption spectrum essentially identical with that shown in Figure 1b.
(21) Irradiation of toluene glasses (80 K) containing Co(II)-**2** and trans Ni(II)-**1** have not yielded the five-coordinate Co(II)-**2**, cis Ni(II)-**1** adduct. The ESR parameters of such an irradiated glass are identical with those described in the text for Co(II)-**2** in toluene.
(22) At 5017 Å only about 0.1% of the energy input is returned as heat. The low efficiency is directly attributable to both the nonsensitized nature of the light driven photoreaction and the low thermo yield of the cis-trans azo isomerization.

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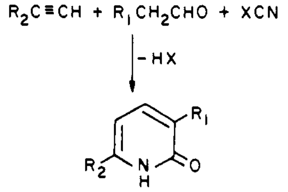
A New Synthesis of 2-Pyridones. Solution Thermolysis of Propargylic Pseudoureas

Sir:

The 2-pyridone ring is an important structural feature of a number of natural alkaloids,[1,2] and several pharmacologically active series of compounds.[3] In this communication we report an experimentally simple, and mechanistically novel, new synthesis of substituted 2-pyridones. The formal construction of the 2-pyridone ring which is possible by this new methodology is illustrated below. The highly convergent nature of this approach and the availability of the precursor components[4] are features which make this a noteworthy addition to existing methodology.[5]



The approach is illustrated in Scheme I. Base catalyzed condensation[6] of secondary propargylic alcohols and 1-cyanopyrrolidine[7] at 0–25 °C produced pseudoureas **1** in yields (crude) in excess of 85%. These intermediates were not puri-

Scheme I

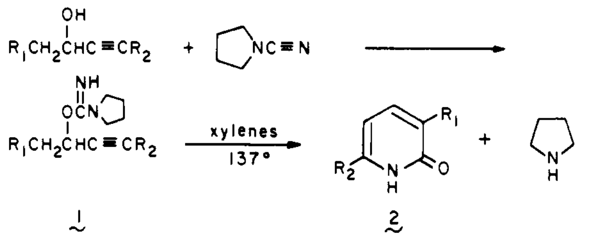
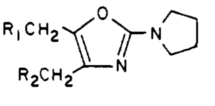


Table I. Propargylic Pseudourea Route to Substituted 2-Pyridones (**2**)

R_1	R_2	Thermolysis conditions[a] (h)	2-Pyridone Mp, °C	2-Pyridone Yield[b]
$(CH_3)_3C$	$(CH_3)_3C$	12	273-274	68 (83)
CH_3	n-C_3H_7	24	60-61	79
n-C_3H_7	n-C_3H_7	24	41-41.5	64
C_6H_5	$(CH_3)_3C$	12	217-218	63 (74)
H	$(CH_3)_2CH$	72	129-131[c]	58
C_6H_5	C_6H_5	24	258-260[d]	29 (34)
C_2H_5	H	24	120-121[e]	12

[a] A xylene solution (0.03-0.05 M) of the crude pseudourea was heated at reflux, under nitrogen, for the indicated time. [b] Overall yields (from the propargylic alcohol) of recrystallized 2-pyridone. Purification was achieved by recrystallization and/or chromatography on silica gel. The yields have not been optimized in any case. Yields in parentheses are based on consumed alcohol. [c] Lit. mp 129-130 °C: N. K. Kochetkov, *Dokl. Akad. Nauk SSSR*, **84**, 289 (1952). [d] Lit. mp 260-261 °C: D. Muenznen, H. Lattan, and H. Schubert, *Z. Chem.*, **7**, 278 (1967). [e] Reported by: N. F. Hall and M. R. Springle, *J. Am. Chem. Soc.*, **54**, 3469 (1932); however, no data were given.

fied, but were rearranged directly to the corresponding 2-pyridones in refluxing xylene. As an example, 4-octyn-3-ol (from propionaldehyde and 1-lithio-1-pentyne, THF, −78 °C) was converted to 3-methyl-6-propyl-2-pyridone (**2**, $R_1 = CH_3$, $R_2 = n$-C_3H_7)[8] in 79% isolated yield (71% overall yield from propionaldehyde). Table I summarizes the results we have obtained with seven representative propargylic alcohols. The method is most successful for the preparation of 2-pyridones having an alkyl substituent at carbon-6 (**2**, R_2 = alkyl) and either hydrogen, alkyl, or aryl substitution at carbon-3. When the terminal acetylenic carbon of pseudourea **1** is unsubstituted, or phenyl substituted (R_2 = H or C_6H_5), competing intramolecular addition of the imine nitrogen to the triple bond, to yield ultimately oxazoles **3**,[8] becomes an important side-reaction.[9]



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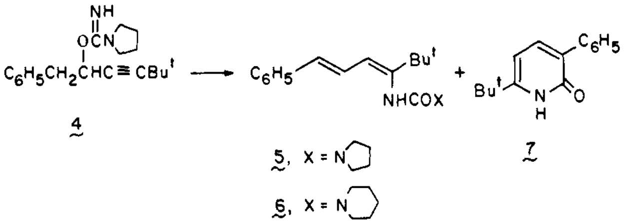
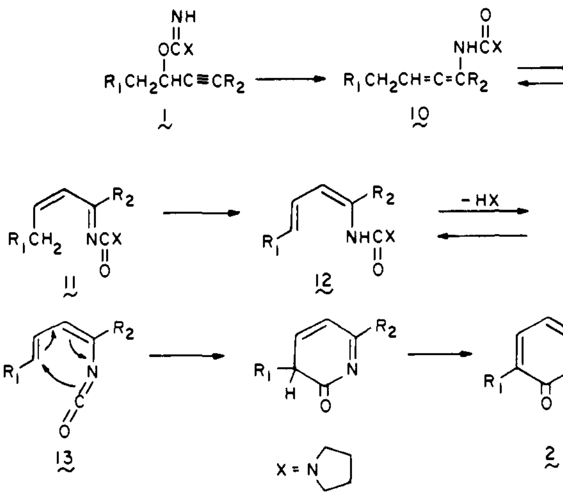
$R_1 = R_2 = C_6H_5$ (39% yield)

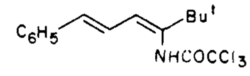
$R_1 = C_2H_5$, R_2 = H (31% yield)

When the thermolysis (xylene, 137 °C) of pseudourea **4** was terminated after 5 h, diene **5** (mp 142-143 °C, 5.2% yield)[8] was isolated in addition to pyridone **7** (59% yield). The stereochemical assignment for **5** follows from ^1H NMR paramagnetic shift experiments (Eu(dpm)$_3$) which gave the largest induced shift for the central vinylic hydrogen, and resolved the vinylic coupling constants (J = 16 and 11 Hz). Treatment of diene **5** at reflux in xylene for 7 h resulted in its quantitative conversion to pyridone **7**. When this conversion was conducted in the presence of piperidine (5 equiv), and the reaction terminated at 2 h, the piperidinylurea **6**[8] (17%) was isolated in addition to recovered **5** (37%) and pyridone **7** (25%). In marked contrast to the smooth conversion of diene **5** to pyridone **7**, the diene trichloroacetamide **8**[10] afforded no trace of pyridone **7** when treated in refluxing xylene for 72 h.



Scheme II





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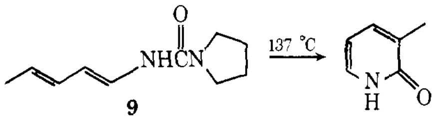
In studies aimed at examining whether the Z-configuration of the diene urea 1,2-double bond is required for efficient conversion to the corresponding 2-pyridone, the (E),(E)-diene **9**[11] was investigated. Treatment of **9** at reflux in xylene resulted in its *slow* conversion (<10% after 19 h by ^1H NMR) to 3-methyl-2-pyridone. After 1 week, 3-methyl-2-pyridone was isolated in 60% yield.



The mechanism we currently prefer for this complex transformation is outlined in Scheme II. In analogy with related studies,[6,10] we suggest that the first step is a thermal [3,3]sigmatropic rearrangement of **1** to yield allene **10**. Subsequent tautomerization could then produce the (Z),(E)-diene **12**. The kinetic preference which is observed in this, and related studies,[12] for forming the diene with the Z configuration about the 1,2-double bond is attributed to the second tautomerization (**11** → **12**) occurring via an intramolecular[1,5]sigmatropic hydrogen migration. Apparently, the cis α,β-unsaturated N-acylimine **11** is either the highly favored kinetic tautomer of **10** (preferential protonation at C-2 cis to the C-3 hydrogen), or is in rapid equilibrium with the corresponding trans isomer. Reversible elimination of pyrrolidine from **12** could then afford the diene isocyanate **13**, which would be expected to undergo electrocyclic ring closure to yield ultimately pyridone **2**. Cyclization of diene isocyanates in this manner is precedented.[13] One can surmise from this mechanism that the major requirement for XH is that it be an acceptable leaving group; chloroform is apparently not.

Current investigations are directed toward the application of this methodology in the natural products area, and in the generalization of this transformation to other propargylic derivatives.

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(8) All new compounds were fully characterized by spectral means (^{1}H and ^{13}C NMR, IR, mass) and elemental composition.

(9) We anticipate that this side-reaction will be suppressed (or eliminated) by the use of gas phase (hot tube) pyrolysis techniques. This aspect is under investigation.

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(12) For example, thermolysis of the trichloroacetimidic ester of 3-butyn-2-ol affords (*Z*)-1-trichloroacetamido-1,3-butadiene as the major isomer (kinetic preference 98:2).[10b] Similarly thermolysis of pseudourea **1** (R_1 = CH_3, R_2 = H, xylene, 137 °C, 2 h) affords, in addition to 5-ethyl-4-methyl-2-pyrrolidinyloxazole, a diene (7% yield, ca. 90% pure) which was clearly (^{1}H and ^{13}C NMR) not the (*E*),(*E*)-isomer **9**, but rather the 1-(*Z*),3-(*E*) isomer.

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(14) A. P. Sloan Foundation Fellow, 1975–1977; Camille and Henry Dreyfus Teacher-Scholar Award Recipient, 1976–1981.

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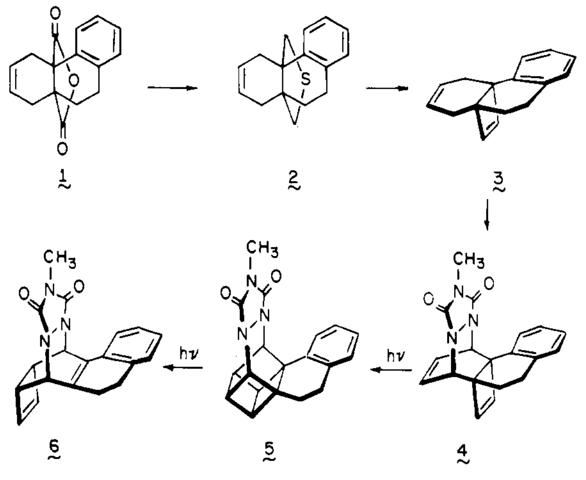
Stereospecific [3,3] Shift of a Cyclobutene Ring Involving Photofragmentation of a 1,8-Bishomocubane as the Relay

Sir:

During recent years, the chemistry of homo- and bishomocubane derivatives, in particular the susceptibility of such compounds to metal-catalyzed rearrangement,[1] has received considerable attention.[2] These highly strained molecules owe their stability in large part to orbital symmetry constraints which preclude simple $[_\sigma 2_s + _\sigma 2_s]$ thermal retrogression.[3-5] Although one might hope to avail himself of the synthetic potential of such cycloreversions by the utilization of photochemical methods, these ring systems have also proven stable to light. In fact, intramolecular photocyclization constitutes their most important method of synthesis. We now report a novel photorearrangement mediated by a 1,8-bishomocubane derivative in which a suitably positioned benzene ring serves as the internal activator. The key feature of the process is a stereospecific [3,3]cyclobutene ring transposition which provides a route along an excited state hypersurface from unsaturated propellanes to cyclooctatetraenes.[6]

In a sequence modeled after that devised earlier for cyclobutene annulation,[9] anhydride **1**[10] was converted to the tetracyclic sulfide **2** in 76% overall yield. Successive treatment of **2** with 1 equiv of *N*-chlorosuccinimide and 2 equiv of monoperphthalic acid gave a mixture of α-chlorosulfones which without purification was subjected to suitable Ramberg-Bäcklund rearrangement conditions (KO-*t*-Bu, THF, reflux, 2.5 h). The resulting hydrocarbon (**3**) could be readily purified by column chromatography on alumina (52% from **2**): (δ, $CDCl_3$) 7.31–7.06 (m, 4), 5.84 (m, 3), 5.64 (d, *J* = 3 Hz, 1), 2.84–2.54 (m, 3), 2.29 (m, 1), 2.01 (m, 2), and 1.87–1.16 (m, 2).

Adduct **4** was obtained from **3** by selective bromination of the cyclohexene double bond (Py·HBr_3, HOAc/CCl_4), twofold dehydrobromination (LiCl, Li_2CO_3, HMPA, 90 °C) to introduce the bicyclo[4.2.0]octatriene part structure, and reaction with *N*-methyltriazolinedione in ethyl acetate at −70 °C (56% overall). That entry of the dienophile had occurred from that surface anti to the cyclobutene ring was suggested by Eu(fod)$_3$-induced shifting experiments and substantiated by the photochemical behavior of **4**.



Irradiation of a benzene-acetone (1:1) solution of **4** through Corex with a 450-W Hanovia lamp for 3 h resulted in conversion to **5**, mp 148–150 °C,[11] and **6**, mp 147–147.5 °C[12] (71 and 25% yields based upon unconsumed **4** after silica gel chromatography). At shorter reaction times, the relative percentages of **6** were appreciably less. Since bishomocubane **5** independently undergoes photofragmentation to **6** under these conditions, it is seen to be the intermediate linking **6** to **4**. The structural assignment to **6** has been firmly established by three-dimensional x-ray crystal structure analysis.

Photoproduct **6** crystallized in the monoclinic space group with a = 11.886 (6) Å, b = 8.453 (2) Å, c = 15.878 (2) Å, and β = 92.54 (3)°. The systematic extinctions conformed to $P2_1/n$ and a density measurement indicated Z = 4 or one molecule of $C_{19}H_{17}O_2N_3$ formed the asymmetric unit. All unique diffraction maxima within the 2θ sphere of 110° were measured using graphite monochromated Cu Kα (1.5418 Å) x rays. A total of 2269 diffraction maxima were surveyed and after correction for Lorentz, polarization, and background effects, 1754 were judged observed ($F_o \geq 3\sigma(F_o)$).

The structure was solved routinely using a multisolution weighted tangent formula approach.[13] Full-matrix least-squares refinements with anisotropic temperature factors for nonhydrogen atoms and isotropic temperature factors for hydrogens smoothly converged to a standard crystallographic discrepancy index of 0.046 for the observed reflections.[14] The computer generated drawing of the final x-ray model, bond distances, and angles which are presented in the supplemental material agree well with generally accepted values; see paragraph at end of paper regarding supplementary material. The cyclobutene ring is clearly joined in exo fashion to the bicyclic ring. There are no abnormally close intermolecular contacts or large residual peaks in a final difference electron density synthesis.

As a test of the regiodisposition of this photorearrangement, dideuteriopropellane **7** was prepared. Its synthesis was accomplished by H/D exchange at the α-chlorosulfone stage