(sublimes). An additional 1–2 g of less pure product may be obtained from the filtrate: ir (KBr) ν_{max} 3420 (broad, w), 3030 (w–m), 1743 (s), 1625 cm^{-1} (s); nmr (D_2O) δ 2.63 (s, 6, methyls), 6.85 (s, 1, ring H); uv (H_2O) λ_{max} (log ϵ) 213 nm (3.97), 293.5 (3.79); uv (H_2O, pH > 7) λ_{max} (log ϵ) 226 nm (3.78), 289.5 (3.72), compare with 2-hydroxypyridine, uv (H_2O) $\lambda_{max}^{pH>7}$ (log ϵ) 230 nm (4.00), 295 (3.80),[9] which has a large contribution made to its structure by the 2-one tautomer.

Anal. Calcd for $C_6H_9ClN_2O$: C, 44.87; H, 5.65; Cl, 22.08. Found: C, 44.91; H, 5.61; Cl, 21.86.

***cis*-2-Oxo-4,6-dimethyl-1,3-diazacyclohexane (2).**—A mixture of the pyrimidine hydrochloride 1 (12.28 g, 0.076 mol) and 1.0 g of 10% palladium on carbon in 80 ml of distilled water containing a few drops of concentrated hydrochloric acid was hydrogenated (3–4 atm) in a Parr apparatus at room temperature until uptake of hydrogen had ceased (*ca.* 4 hr). The mixture was filtered as soon as possible and the filtrate was concentrated to dryness at reduced pressure to leave a colorless, clear, viscous oil which crystallized exothermically when kept under high vacuum. The crystalline mass was broken up and dried *in vacuo* overnight. The crude product (12.7 g) was recrystallized from a 1:1 mixture of ethyl acetate and tetrahydrofuran (THF) and dried *in vacuo*. The colorless, crystalline product (10.7 g), mp 110–118°, contained included solvent (10–15% solvent by weight) and was a single stereoisomer (nmr). Doubly sublimed material was clear, sparkling needles: mp 250–252° dec (strong sublimation); ir (KBr) ν_{max} 3220 (NH, s), 3075 (NH, m), 1670 cm^{-1} (C=O), s); nmr (acetone-d_6–D_2O) δ 1.32 (d, 6, methyls, J = 6.3 Hz), 1.37 (d of t, 1, axial H, J_{ab} = 13.4 Hz, J_{ax} = 11.0 Hz), 2.21 (d of t, 1, equatorial H, J_{bx} = 3.8 Hz), 3.80 (m, 2, methine), NH protons were absent due to deuterium exchange.

Anal. Calcd for $C_6H_{12}N_2O$: C, 56.22; H, 9.44. Found: C, 56.08; H, 9.25.

***meso-N,N'*-Dicarbethoxy-2,4-diaminopentane (3).**—The cyclic urea solvent-inclusion complex [29.4 g, 0.2 mol (*ca.* 25.6 g of pure urea)] was heated to reflux in 200 ml of 40% aqueous sulfuric acid (w/w). After reflux was attained (150° oil bath), five 22.0-ml portions of concentrated sulfuric acid (96–98%) were cautiously added at 30-min intervals through the top of the condenser. The mixture (*ca.* 60% in H_2SO_4) was heated at 160° for 4 days with stirring. It was cooled, diluted with 200 ml of 2-propanol, and poured into a mixture of *ca.* 3000 ml of THF and *ca.* 500 ml of dry ether.[10] The supernatant liquid was decanted and saved and the dense oil was rinsed with 200-ml portions of THF until it became a highly viscous, immobile deposit (usually two to five washings). The washings were combined with the supernatant solution and 200–300 ml of dry ether was added to force out more of the oil. Again the solvent was decanted and the oil was rinsed with THF (smaller portions). The crude diammonium salt was thus obtained and was not purified further. The cloudy oil was dissolved in 75 ml of distilled water and neutralized with *ca.* 9.0 g of sodium hydroxide (pH 8–9) with cooling and stirring. Ether (75 ml) was added, and to the stirred mixture kept at 10–15° was then added dropwise 36.0 g of ethyl chloroformate, followed by dropwise addition of 90 ml of 15% aqueous sodium hydroxide. The mixture was stirred for 1 hr at room temperature and diluted with 150 ml of ether, and the layers were separated. The aqueous phase was extracted with two 75-ml portions of ether and the combined ethereal extracts were washed with 25 ml of distilled water and dried ($MgSO_4$). Stripping of the solvent furnished 26–28 g (*ca.* 55%) of colorless dicarbamate, mp 94–95.5°. Recrystallization from hexane–ethyl acetate (prisms, mp 94–95.5°) followed by sublimation provided an analytical sample, mp 95–96°. Noteworthy is the fact that the dicarbamate, even before recrystallization, contained no detectable amount (<5%) of *dl* compound (nmr; also note melting point constancy), reinforcing the claim that the cyclic urea was stereochemically homogeneous: ir (KBr) ν_{max} 3325 (NH), 1682 cm^{-1} (C=O); nmr ($CDCl_3$) δ 1.17 (d, 6, methyls, J = 6.7 Hz), 1.22 (t, 6, ethoxy methyls, J = 7.0 Hz), 1.57 [1.43 (b), 1.70 (a)] (t of q_{ab}, J = 13.6 Hz, $J_{ax} \cong J_{ay}$ = 7.0–7.2 Hz, $J_{bx} \cong J_{by}$ = 6.5–6.8 Hz), 3.72 [d of d of d of q, methine, J (NH–CH) = 7.2–7.5 Hz], 4.12 (q, 4, ethoxy methylenes, J = 7.0 Hz), 4.80 (broad d, 2, NH, J = 7.2–7.5 Hz). The pattern for the methenyl and methinyl protons, excluding J (NH–CH) and J (CH_3–CH), represented an abxy system in which the chemical shifts of x and y were accidentally coincident. The *dl* dicarbamate prepared from predominantly *dl* diamine dihydrochloride[1] gave an nmr spectrum similar to that of **3**. The methylene resonance at 1.53 ppm, however, could be used to distinguish it from the meso isomer: nmr ($CDCl_3$) δ 1.17, 1.23, 1.53, 3.72, 4.12, 4.82.

Anal. Calcd for $C_{11}H_{22}N_2O_4$: C, 53.64; H, 9.00. Found: C, 53.54; H, 8.87.

***meso*-2,4-Diaminopentane (4).**—The diammonium salt, obtained as described above, was made strongly alkaline with *ca.* 25% aqueous sodium hydroxide (enough to dissolve most of the precipitated salts) and the resulting mixture was extracted with five equal volume portions of ether. The combined ethereal extracts were dried (Na_2SO_4, then $CaSO_4$) and carefully concentrated. The concentrate was dried over crushed KOH pellets overnight and carefully distilled at *ca.* 70 mm through a Vigreux column. After removal of a forerun, essentially pure[11] 4 distilled, bp 78–81° (70 mm) [lit.[1] bp 60–61° (22 mm)], $n^{22}D$ 1.4388. The yield of diamine from 4.52 g of 2 was 0.9–1.0 g (25–30%). The *N,N'*-dibenzoyl derivative of 4 recrystallized from dilute ethanol had mp 194.5–195.5° (lit.[1] mp 193–194°). A sample of the diamine purified by preparative glc had the following properties: ir (thin film) ν_{max} 3360 (NH), 3285 (NH, d), 2965, 2930, 1600, 1457, 1376, 1142, 1060, 905, 870, 818 cm^{-1}; nmr ($CDCl_3$) δ 1.09 (d, 6, methyls, J = 6.5 Hz), 1.35 (t, 2, methylene, J = 6.8 Hz), 1.39 (s, 4, NH), 3.05 [hextet (d of d of q), 2, methine]. The nmr spectrum of chiefly *dl* diamine[1] was similar to that of 4, but clearly distinguishable by the fact that the methine protons resonated at 3.00 ppm: nmr ($CDCl_3$) δ 1.08, 1.32, 1.52, 3.00.

Registry No.—**1**, 34289-60-6; **2**, 34289-61-7; **3**, 34289-62-8; **4**, 29745-96-8.

Acknowledgment.—We thank Mrs. Carol Folk at the University of Pennsylvania for 100-MHz proton nmr spectra.

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[9] See R. M. Silverstein and G. C. Bassler, "Spectrophotometric Identification of Organic Compounds," Wiley, New York, N. Y., 1968, p. 168.

[10] (a) The object at this point in the preparation is to separate the salt as a viscous, dense oil. The exact amount of solvent in the mixture may be variable; thus it is recommended that only 150 ml of 2-propanol be used initially. If the dense phase is too voluminous, then more 2-propanol may be added. The oily deposit should not be very voluminous and should show signs of increased viscosity. (b) This *work-up* is a variation of a general one[7] in which acetone was employed. Use of acetone in our case resulted in only 24–30% yield of dicarbamate **3**. We found that this was due to the formation of the *gem*-diamine, 2,2,4,6-tetramethyl-1,3-diazacyclohexane (by rapid condensation of acetone with the disalt), which was isolated pure by preparative glc (after treating the mixture of diammonium salts with aqueous alkali and extracting with ether): ir (thin film) ν_{max} 3370 (broad NH), 3275 cm^{-1} (NH); nmr ($CDCl_3$) δ 0.95 (broad s, 2, NH), 1.05 (d, 6, methyls, J = 6.3 Hz), 1.31 and 1.35 (pair of s, 6, *gem*-methyls), 1.78 (d of t, methylene, possibly one-half of an ab pattern centered at 1.34 ppm with δ_{ab} = 26 ± 2 Hz, J_{ax} = 12 ± 2, J_{bx} = 2.7, and J_{ab} = 13 Hz), 3.00 [m (d of d of q), 2, methines, 11 lines were observed of the hypothetical 13-line pattern which would be expected if the above postulated parameters were valid with J_{ax} = 12 Hz]. Reaction of this compound with 2,4-dinitrophenylhydrazine reagent gave acetone 2,4-DNP which was identical with the authentic material. *Anal.* Calcd for $C_8H_{18}N_2$: C, 67.55; H, 12.76. Found: C, 67.68; H, 12.58.

[11] No contaminants other than water (*ca.* 3%) were present in the final product. The diamine is very hygroscopic and sensitive to carbon dioxide. A more lengthy purification, which supplies an anhydrous product, is provided in ref 1.

Photochemistry of 2-Phenyloxazolo[4,5-c]pyridine. Photoalkylation by Diethyl Ether

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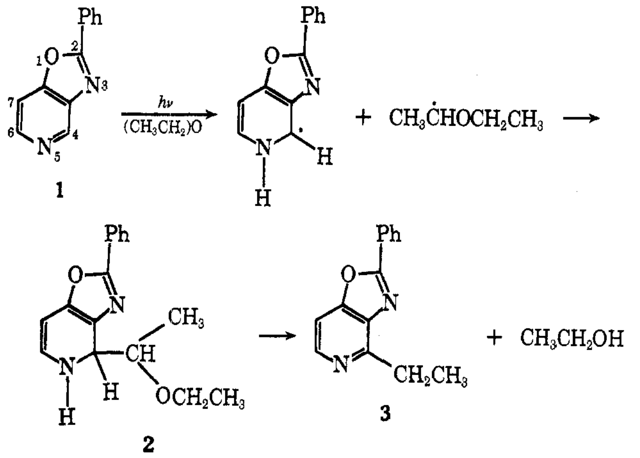
Photoalkylation of various aromatic nitrogen heterocycles has been observed in a variety of alcoholic solvents.[1–7] In general these photoalkylations occur most readily with condensed ring systems such as quinoline. Alkylation by ethers is much rarer and generally involves complete incorporation of the ether moiety.[8] However, from the present work and previous work by a number of different investigators[9,10] it is becoming increasingly apparent that participation of the solvent (generally *via* formation of solvent-derived radicals) is a fairly general phenomenon.

We now report a novel example of C-ethylation of a nitrogen heterocycle by the solvent diethyl ether. Irradiation of a dilute solution of 2-phenyloxazolo[4,5-*c*]pyridine (**1**) in ethanol-free diethyl ether and work-up of the resultant complex mixture by preparative layer chromatography resulted in isolation of the alkylated product **3** in reasonable yield. We suggest that this product arises as shown in Scheme I.

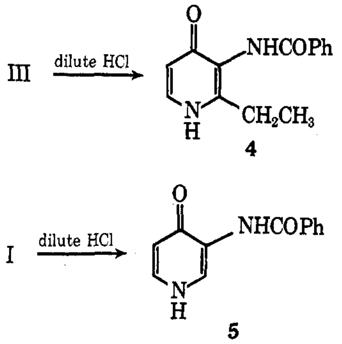
SCHEME I



The gross structure of **3** was deduced readily from the analytical and spectral data and the exact location of the ethyl substituent on the pyridine nucleus was assigned by careful comparison of the nmr spectrum of **3** with that of **1**; the spectrum of **3** showed the absence of a signal due to H_4 which was easily discernible in the spectrum of **1**.

Additional conformation of the assigned structure **3** was obtained by hydrolytic opening of the oxazole ring of **3** to give the substituted pyridone **4** which was compared with the pyridone **5** resulting from similar treatment of **1**.

Control experiments verified that the source of the ethyl substituent in **3** was not trace amounts of ethanol present in the ether used for the photolysis. The ether used for the irradiation contained less than 0.001% ethanol (vpc) and ethanol production was observed (vpc) as the irradiation progressed (the final concentration of ethanol was $\sim$0.002%).



One of the fractions from the preparative layer chromatography of the resultant photolysate, which could not be obtained in a pure state, has been assigned the structure **2** primarily on the basis of the observed spectral properties of this nonhomogeneous fraction. Formation of this product as the primary product of the irradiation is quite consistent with the work of Stermitz[4] on the photoalkylation of nitrogen heterocycles by alcohols. In the present case, however, the ether moiety is incorporated entirely, and subsequently a molecule of ethanol is eliminated; the net result is introduction of an ethyl group from diethyl ether onto the heterocyclic ring with the concomitant production of ethanol. The intermediate **2** probably arises by initial abstraction of the labile hydrogen atom of diethyl ether and resultant radical coupling as shown in Scheme I. Even though we feel that we have sufficient evidence to invoke the dihydropyridine **2** as the precursor of the alkylated product **3**, we do not have any evidence which permits us to characterize this transformation as either thermal or photochemical.

The present work suggests caution in using diethyl ether as solvent for irradiations of nitrogen heterocycles even though we do not know how general this photoalkylation process might be. It is not impossible that this procedure might be a general method for ether cleavage under very mild conditions.

Experimental Section[11]

Irradiation of 2-Phenyloxazolo[4,5-*c*]pyridine (1).—A solution of 2-phenyloxazolo[4,5-*c*]pyridine[12] (1.00 g, 5.10 mmol) in 400 ml of ethanol-free ether (see below) was irradiated for 41 hr using a medium-pressure Hanovia 450-W lamp contained in a water-cooled quartz immersion well containing a Corex filter sleeve. Within 5 min of the start of the irradiation a colorless precipitate formed on the immersion well and the solution emitted a blue fluorescence. As the reaction progressed it was necessary to intermittently clean the immersion probe of insoluble material. The progress of the reaction was monitored by thin layer chromatography (tlc).

Upon completion of the photolysis (as evidenced by tlc), the insoluble material (300 mg) was removed by filtration and the filtrate was evaporated to leave a residual yellow oil. This complex mixture was separated by preparative layer chromatography (plc) using 20 × 100 cm silica gel plates (six developments with

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[9] P. L. Kumler and R. A. Dybas, *J. Org. Chem.*, **35**, 125 (1970).

[10] T. R. Evans in "Energy Transfer and Organic Photochemistry," P. A. Leermakers and A. Weissberger, Eds., Wiley-Interscience, New York, N. Y., 1969, pp 311-320.

[11] Melting points were obtained on a Thomas-Hoover apparatus and are reported uncorrected. Ir spectra were measured using a Beckman IR-20-A; uv spectra were measured with a Beckman DB recording spectrophotometer. Nmr spectra were taken on a Varian Associates A-60 spectrometer; spectra were recorded in deuteriochloroform solution (unless noted otherwise) and chemical shifts are reported in τ (parts per million) relative to tetramethylsilane as internal standard. Vpc used a Varian-Aerograph Model 700 chromatograph.

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2% methanol in methylene chloride) and various fractions were removed from the plate and extracted with chloroform in a Soxhlet extractor. One of these fractions gave pale yellow crystals of 4-ethyl-2-phenyloxazolo[4,5-*c*]pyridine (**3**, 192 mg, 17%). Recrystallization from hexane gave colorless crystals: mp 89–90°; ir (KBr) 2980–2850 cm^{-1} (aliphatic CH); uv max (95% EtOH) 282 nm (ϵ 3000); nmr ($CDCl_3$) τ 1.50 (d, J = 8 Hz, 1 H, H_6), 1.6–1.9 (m, 2 H, ortho H's of phenyl), 2.3–2.8 (m, 4 H, meta and para H's of phenyl and H_7), 6.75 (q, 2 H, CH_2), 8.53 (t, 3 H, CH_3); the nmr spectrum lacks the characteristic singlet at τ 0.87 due to H_4 in the starting material.[13]

Anal. Calcd for $C_{14}H_{12}N_2O$: C, 74.98; H, 5.39; N, 12.49. Found: C, 74.73; H, 5.68; N, 11.84.

Another fraction from the plc separation yielded 79 mg of a brown nonhomogeneous oil (at least three spots by tlc) which we believe contains the dihydropyridine derivative **2**: ir (film) 3300 (broad, OH and NH), 2980–2850 cm^{-1} (aliphatic CH); nmr ($CDCl_3$) τ 6.47 (q, 2 H, CH_2CH_3), 8.47 (d, 3 H, CH_3CH), 8.77 (t, 3 H, CH_3CH_3) (although quite complex the above features could be discerned).

3-Benzamido-4-pyridone (5).—A sample of the oxazolopyridine **1** (110 mg, 0.56 mmol) was dissolved in 10 ml of dilute hydrochloric acid and allowed to stand at room temperature for 72 hr. At this stage, colorless needles had formed and they were removed by filtration, washed with water, and air dried. These crystals were shown to be the hydrochloride salt of the pyridinol tautomer of **5** (140 mg, 93%): mp 219–222°; ir (KBr) 3300 (broad, OH), 2800–2300 (broad, NH^+), 1635 cm^{-1} (amide C=O).

Anal. Calcd for $C_{12}H_{13}N_2O_3Cl$ (monohydrate of hydrochloride salt): C, 53.64; H, 4.88; N, 10.42. Found: C, 53.53; H, 4.80; N, 10.49.

The product from above was dissolved in 20 ml of water containing 1 ml of dilute sodium hydroxide, stirred for 10 min, and then acidified with glacial acetic acid; the resulting colorless solid was filtered, washed with water, and air dried. Elution of this material through a short column of alumina with 2% methanol in chloroform (to remove contaminating sodium acetate) resulted in formation of 3-benzamido-4-pyridone (**5**) which was recrystallized from acetone–hexane to give colorless needles: mp 255–256°; ir (KBr) 3360 (NH), 1670 (pyridone C=O), 1635 cm^{-1} (amide C=O); uv max (95% EtOH) 292 nm (sh, ϵ 7340), 275 (8560), 225 (10,700).

Anal. Calcd for $C_{12}H_{10}N_2O_2$: C, 67.28; H, 4.71; N, 13.08. Found: C, 67.20; H, 4.78; N, 12.92.

2-Ethyl-3-benzamido-4-pyridone (4).—A sample of the oxazolopyridine **3** (54 mg, 0.24 mmol) was dissolved in 20 ml of 3 *N* hydrochloric acid and allowed to stand at room temperature for 48 hr. To this solution was added 3 g of alumina and the resultant mixture was evaporated to dryness at reduced pressure. The resultant powder was packed on the top of an 8-in. alumina column and the column was eluted with 2% methanol in chloroform. Evaporation of the eluate and recrystallization from ethanol–hexane gave the pyridone **4** as colorless needles (28 mg, 48%): mp 148–149°, 178–180° (resolidifies above 148° and then melts at 178–180°); ir (KBr) 3340 (NH), 1660 (pyridone C=O), 1624 cm^{-1} (amide C=O); uv max (95% EtOH) 260 nm (ϵ 11,800), 226 (sh, 14,000); high resolution mass spectrum,[14] calcd mol wt 242.1055, found 242.1054.

Anal. Calcd for $C_{14}H_{14}N_2O_2$: C, 69.41; H, 5.82; N, 11.56. Found: C, 69.72; H, 5.71; N, 11.74.

Detection of Ethanol.—The irradiation of **1** was monitored directly by vpc by withdrawing aliquots from the reaction mixture and analyzing on a 30% FFAP column ($^3/_8$ in., 20 ft, on 50–60 Chromosorb W) at 105°. With a helium flow rate of ~100 ml/min the approximate retention times for various components were the following: air, 3 min; ether, 4 min; ethanol, 21 min. By analyzing standard solutions of ethanol in ether (1.0, 0.1, 0.01, and 0.001% v/v) the lower limits of detectability were determined; it was shown that 0.001% ethanol could easily be detected. At the start of the irradiation the ethanol concentration in the ether used as solvent was less than 0.001%. As the photolysis progressed the buildup of ethanol could easily be observed and at completion of the irradiation (41 hr) the ethanol concentration was 0.002%.

Registry No.—**1**, 34297-84-2; **3**, 34282-21-8; **4**, 34282-22-9; **5**, 34282-23-0; **5** HCl, 34282-24-1; diethyl ether, 60-29-7.

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[13] The nmr spectrum of **1** shows the following features: τ 0.87 (slightly broadened singlet, 1 H, H_4), 1.42 (d, J = 5.5 Hz, 1 H, H_6), 1.6–1.9 (m, 2 H, ortho H's of phenyl), 2.3–2.8 (m, 4 H, meta and para H's of phenyl and H_7).

[14] We thank Dr. Ted R. Evans, Eastman Kodak Laboratories, for this measurement.

The Catalytic Oxidation of Vicinal Diols to α Diketones[1]

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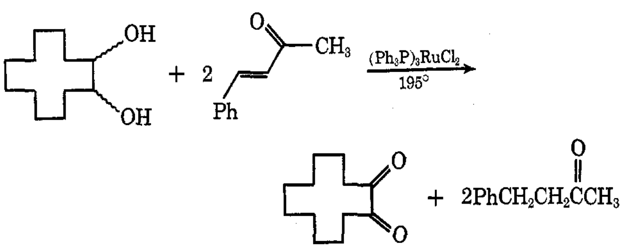
We wish to describe a convenient method for the oxidation of certain vicinal diols to α diketones, based on the ruthenium-catalyzed transfer–hydrogenation reaction reported by Sasson and Blum.[3] α diketones are of value as precursors of acetylenes and dioximes. However, despite interest in substances containing the α-diketone moiety, practical synthetic entries into this class of compounds are restricted to the oxidation of acyloins[4] and α-halo ketones[5] using metal salts or dimethyl sulfoxide, oxidation of ketones with selenium dioxide,[6] and oxidation of olefins with potassium permanganate.[7] Although in principle vicinal diols would appear to be attractive as precursors of α diketones, in practice the direct oxidation of vicinal diols produces α diketones only in erratic yields.[8]

The procedure described here involves the transition metal catalyzed transfer of hydrogen from the diol to a suitable olefinic hydrogen acceptor. Exploration of several metallic catalysts and hydrogen acceptors (Table I) suggests that the combination described by Sasson and Blum, tris(triphenylphosphine)ruthenium dichloride and benzalacetone, is the most effective, although the reaction appears less sensitive to the hydrogen acceptor than to the catalyst. At low conversion of 1,2-cyclododecanediol (**1**) to 1,2-cyclododecanedione (**2**), an appreciable quantity of α-hydroxycyclododecanone (**3**) can be detected in the reaction mixture; **3** is itself smoothly oxidized to **2** under the reaction conditions. Thus, we presume that the overall con-



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[1] Supported by the National Institutes of Health, Grant GM-16020.

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