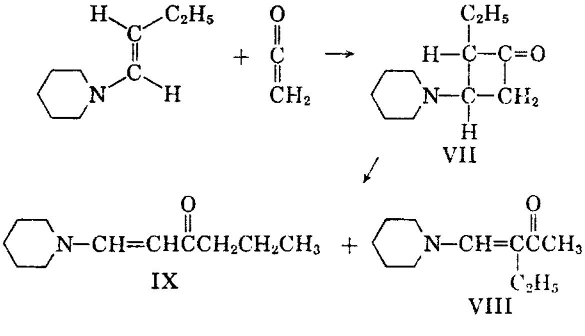
Ketene and *N*-(1-butenyl)piperidine in hexane reacted at −20° to give 2-ethyl-3-piperidinocyclobutanone (VII), as evidenced by the infrared maximum at 5.65 μ. Rearrangement of VII occurred during distillation to give a 70% yield of a mixture of 2-ethyl-1-piperidino-1-buten-3-one (VIII) and 1-piperidino-1-hexen-3-one (IX) that was not separated by fractional distillation. The mixture had a boiling point of 137° (0.3 mm.), n_D^{22} 1.5544, infrared maxima at 6.05, 6.25, and 6.38 μ. An estimate made from the NMR spectrum showed the mixture to be about two parts of IX to one part of VIII. *Anal.* Calcd. for $C_{11}H_{19}NO$: C, 72.9; H, 10.5; N, 7.8. Found: C, 72.7; H, 10.5; N, 7.7.



The thermally unstable cyclobutanones, III, V, and VII, were treated with lithium aluminum hydride to give the corresponding cyclobutanols, which showed no tendency to undergo a ring-opening reaction.

The cycloaddition of other ketenes and enamines has been observed; this work will be described in greater detail at a later date.

Research Laboratories
Tennessee Eastman Co.
Division of Eastman Kodak Co.
Kingsport, Tenn.

R. H. Hasek
J. C. Martin

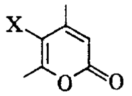
Received August 18, 1961

The Reaction of Enamines with Ketene

Sir:

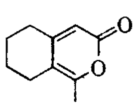
We wish to report the results of our initial studies of the reaction of enamines with ketene. Treatment of 4-*N*-pyrrolidino-3-penten-2-one with three molar equivalents of ketene in ether at 0° and chromatography of the reaction mixture after evaporation of the solvent afforded 5-acetyl-4,6-dimethylcoumalin (Ia) (52%), m.p. 72.8–73.4° (C, 65.10; H, 5.69), $\lambda_{max}^{C_2H_5OH}$ 296 mμ (ε 6090).

Similarly, ethyl 3-*N*-pyrrolidinocrotonate reacted with ketene to produce ethyl isodehydroacetate (Ib) (35%), m.p. 18–20° (C, 61.42; H, 6.13), $\lambda_{max}^{C_2H_5OH}$ 247 mμ (ε 6530), 294 mμ (5240), which was identical to a sample prepared by the procedure of Wiley and Smith.[1] 1-*N*-Pyrrolidinocyclohexene reacted with excess ketene to produce II (16%), m.p. 82.0–84.5° (C, 72.93; H, 7.21), $\lambda_{max}^{C_2H_5OH}$ 312 mμ (ε 6800). The NMR spectra of the α-pyrones are in agreement with the proposed structures. These results are particularly interesting in view of the observations that diketene reacts with enamines to form γ-pyrones.[2,3]



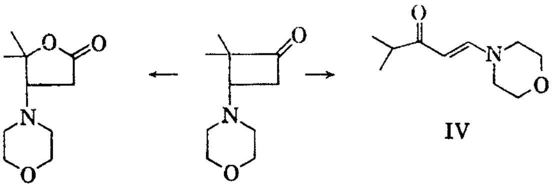
Ia. X = $CH_3\overset{\overset{O}{\|}}{C}$

b. X = $C_2H_5O\overset{\overset{O}{\|}}{C}$



II

The reaction of 1-*N*-morpholinoisobutene with ketene follows a different course. When either pentane or ether is the solvent, the product isolated is 2,2-dimethyl-3-*N*-morpholinocyclobutanone (III) (75%), m.p. 41.1–42.2° (C, 65.73; H, 9.38; N, 7.71). Compound III rearranges readily on warming to 4-methyl-1-*N*-morpholino-1-butene-3-one (IV), identical to a sample prepared from morpholine and ethynyl isopropyl ketone.[4] Treatment of III with aqueous hydrogen peroxide produced a lactone (48%), m.p. 103.4–104.3° (C, 60.41; H, 8.63; N, 7.10) which is assigned structure V. Hasek and Martin[5] have shown that ketene and dimethylketene react with enamines derived from aldehydes to yield the corresponding cyclobutanones. The rearrangement of these adducts has also been observed.



Department of Chemistry
Massachusetts Institute of Technology
Cambridge 39, Mass.

Glenn A. Berchtold
George R. Harvey
G. Edwin Wilson, Jr.

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(1) N. R. Smith and R. H. Wiley, *Org. Syn.*, **32**, 76 (1952).

(2) S. Hünig, E. Benzing, and K. Hübner, *Chem. Ber.*, **94**, 486 (1961).

(3) B. B. Millward, *J. Chem. Soc.*, 26 (1960).

(4) This sample was kindly supplied by Prof. N. J. Leonard of the University of Illinois.

(5) R. H. Hasek and J. C. Martin, *J. Org. Chem.*, **26**, 4775 (1961).