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(10) Photochemically produced carbonyl ylides were trapped in the middle sixties by Ullman, but these ylides were derived from a highly specific, n,π^* singlet excited-state precursor. Cf. E. F. Ullman and W. A. Henderson, Jr., *J. Am. Chem. Soc.*, **88**, 4942 (1966), and references therein.

(11) While this work was in progress, Professor G. Griffin kindly informed me of his group's success in trapping photochemically generated carbonyl ylides. Cf. (a) G. W. Griffin, I. Lev, and K. Ishikawa, Vth IUPAC Symposium on Photochemistry, Enschede, The Netherlands, July 21–27, 1974, Contr. Paper No. 20, p 62; (b) G. W. Griffin, N. E. Brightwell, K. Ishikawa, I. Lev, and S. Satra, VIIth International Conference on Photochemistry, Edmonton, Canada, Aug. 7–13, 1975, Abstr. I-1; (c) G. W. Griffin, K. Ishikawa, and I. Lev, 27th Southeast-31st Southwest Regional Meeting of the American Chemical Society, Memphis, Tenn., Oct. 29–31, 1975, Abstr. 443; (d) I. J. Lev, K. Ishikawa, N. S. Bhacca, and G. W. Griffin, *J. Org. Chem.*, preceding paper in this issue. Professor R. Huisgen has also recently described trapping of photochemically generated carbonyl ylides.[7c]

(12) Photolyses performed by dissolving 1 mmol of stilbene oxide in 10.0 ml of organic solvent. Solutions were deaerated with argon in quartz tubes, capped and irradiated with 2537-Å lamps in a Rayonet reactor (New England Ultraviolet Co.) for 15 min. Analyses were performed by VPC (5% QF-1) using an added external standard. Only trace amounts of benzaldehyde could be detected under these conditions.

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(19) The assignment of structure and configuration of adducts **3** and **4** rests on their characteristic spectral properties (NMR, ir, *m/e*) as well as chemical conversion of **3a** to **3b** and **4a** to **4b** with sodium methoxide.[20] Photolyses were performed by irradiating deareated solution containing ~0.75 mmol of stilbene oxide and ~1.9 mmol of olefin in 10.0 ml of solvent with 16–2537-Å lamps in a Rayonet reactor. Complete reaction product analyses will be presented in our full paper.

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(23) Irradiations were performed on deaerated solutions of ~1 mmol of stilbene oxide, ~2.5 mmol of methyl acrylate, 2.0 ml of acetone, and 10.0 ml of acetonitrile or benzene contained in a Pyrex test tube mounted next to a Hanovia 450-W high pressure mercury arc lamp.

(24) Attempted sensitization of **1a** in the presence of methyl acrylate with acetophenone gave no reaction (capable of producing acrylate triplets only).[25]

(25) G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *J. Am. Chem. Soc.*, **86**, 3197 (1964).

(26) L. Salem, *J. Am. Chem. Soc.*, **96**, 3486 (1974).

(27) Addition of *trans,trans*-2,4-hexadiene to reaction solutions failed to inhibit THF adduct formation or to change isomer ratios. Although several factors may be responsible for the lack of stereospecificity obtained in ring opening of stilbene oxides upon direct irradiation, one possibility is that the singlet excited oxirane could undergo partial intersystem crossing to the excited triplet state followed by stereorandomization of adduct formation.

(28) K. N. Houk, J. Sims, R. E. Duke, Jr., R. W. Strozier, and J. K. George, *J. Am. Chem. Soc.*, **95**, 7287–7300 (1973); K. N. Houk, J. Sims, C. R. Watts, and L. J. Luskus, *ibid.*, **95**, 7301–7315 (1973).

(29) Similar experiments by earlier workers have apparently also failed to trap carbonyl ylides with simple olefins.[1-4]

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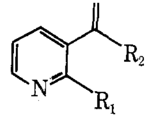
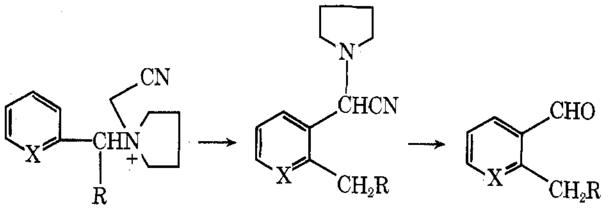
Synthesis of 2,3-Disubstituted Pyridines. Ortho-Formylation and Ortho-Acylation of 2-Alkylpyridines

Summary: A general synthesis of 2-alkyl-3-acylpyridines and 2-alkyl-3-formylpyridines via [2,3]-sigmatropic rearrangements of α-pyrrolidinyl-2-alkylpyridines is described; the initially obtained α-cyanoamine can be hydrolyzed to an aldehyde, reductively cleaved to an amine, or alkylated and hydrolyzed to a ketone.

Sir: As part of our studies involving the structure[1] and reactivity[2] of nicotine and various nicotine analogues, we required a series of 2-alkyl-3-acylpyridines (1). Because of the substituent pattern involved and the well-known resistance of pyridine toward Friedel-Crafts alkylation and acylation, compounds generalized by structure **1** are difficult to prepare. We now report a sequence of reactions involving α-cyanoamines in which the α-cyanoamines (1) are the migrating moiety in a Sommelet–Hauser rearrangement; and (2) are utilized as acyl carbanion equivalents to effect alkylations.

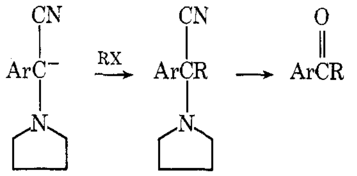


1



2 **4** **3** (1)

a, X = CH, R = H
b, X = N

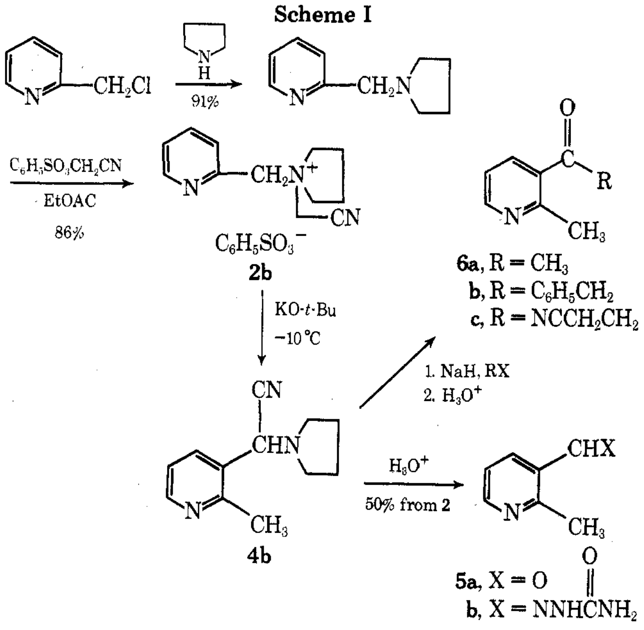


(2)

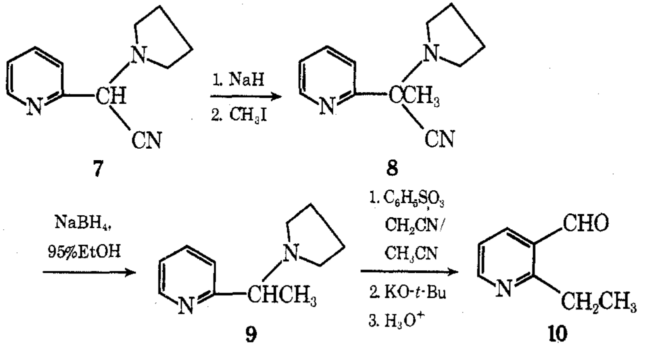
While the synthetic utility of [2,3]-sigmatropic rearrangements is well known in aliphatic and homocyclic chemistry,[3] only one application of this type of reaction in alkylpyridine chemistry has been reported.[4] Recently, Mander and Turner[6] reported the transformation of **2a** with KO-*t*-Bu to *o*-methylbenzaldehyde (**3a**) via the α-cyanoamine **4a**. This rearrangement seemed particularly attractive to us because the α-cyanoamine generated in the reaction was considered capable of undergoing alkylation.[7] In addition, as shown in Schemes I and II, the combination of the alkylation–rearrangement reactions adds remarkable versatility toward the general synthesis of **1**.

Treatment of the crystalline quaternary salt **2b** (R = H),[8] prepared via alkylation with cyanomethyl benzenesulfonate[9] (Scheme I), with KO-*t*-Bu in THF–Me_2SO at −10 °C, followed by acid hydrolysis of the crude product, gave (50%) 2-methyl-3-pyridinecarboxaldehyde (**5a**). Treatment of the crude product with semicarbazide hydrochloride gave a 34% yield of semicarbazone **5b**.[10] This procedure represents a considerable improvement over the published synthesis of **5a** which was obtained in 15% yield via a five-step synthesis from ethyl 3-aminocrotonate and 3-ethoxyacrolein diethyl acetal.[10]

Scheme I



Scheme II



Having successfully ortho-formylated 2-picoline, we turned our attention to alkylation of intermediate **4b** to achieve ortho-acylation of 2-picoline. Rearrangement of **2b** (R = H) was carried out as above. After the reaction was complete, as judged by TLC and NMR, 1 equiv of sodium hydride was added followed by 1 equiv of methyl iodide. Acid hydrolysis of the crude product gave 3-acetyl-2-picoline[11] (**6a**, 78%). The corresponding benzyl ketone **6b**[11] was obtained in a similar fashion by alkylation with benzyl bromide (87%). Further investigation showed that this procedure could be simplified by using sodium hydride to effect both rearrangement and alkylation. Thus, the salt **2b** (R = H) was treated with 2 equiv of sodium hydride; after the rearrangement and second anion formation were complete, 3-bromopropionitrile was added followed by acid hydrolysis to give **6c** (48%).

The demonstration that these α-cyanoamines are alkylated with relative ease allows further generalization of this procedure for the preparation of 2-alkyl-3-acylpyridines. Since α-halo-2-alkylpyridines are not readily obtained by direct halogenation of the respective 2-alkylpyridines, the alkylation reaction described above was utilized. The α-cyanoamine **7**, prepared from 2-pyridinecarboxaldehyde, pyrrolidine, and KCN (58%), was treated with sodium hydride and methyl iodide giving **8** which, upon treatment with sodium borohydride in 95% ethanol, underwent reductive cleavage[12,13] to **9** (70% from **7**). Alkylation (Scheme II), rearrangement, and hydrolysis to **10**, isolated as its semicarbazone (10%), were achieved as described above.[14]

The preparation of 2-alkyl-3-acylpyridines using these procedures appears limited only by the nature of those alkyl halides capable of being alkylated by the α-cyanoamine anions.[14] We are currently investigating the scope of these alkylations as well as exploring other transformations of α-cyanoamines which could extend the use of these procedures for the synthesis of more complex heterocyclic systems.

Acknowledgment. We thank Dr. Jerry F. Whidby and Mr. Ron Bassfield for technical assistance.

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(14) Thorough investigation of the product mixture from the alkylation–rearrangement and hydrolysis of **9** indicates that a significant portion of the quaternary salt rearranges via a 1,2 shift; i.e., Stevens rearrangement. We are presently studying the effect of reaction conditions on product composition.

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Protonated Cyclobutadieneiron Tricarbonyl, a σ–π Bonded Cyclobutadiene Hydridoiron Tricarbonyl Cation[1]

Summary: ^{1}H and ^{13}C NMR spectroscopic study of cyclobutadieneiron tricarbonyl in fluorosulfuric acid solution at low temperature shows iron protonation with formation of a static σ–π complex resulting from an unusual π to σ change in the metal–ligand bonding; the observation of the geminal $^1H_4$–Fe–^1H_x (29 Hz) and ^{13}C–Fe–H_x (81.2 Hz) coupling substantiates the proposed structure; evidence of σ–π complex formation was further provided by studies in deuterated fluorosulfuric acid solution.

Sir: The enhanced stability of organometallic carbonyl cations has been well recognized and the nature of metal–ligand bonding in these ions has also been extensively investigated using both spectroscopic methods and quantum mechanical calculations.[2] Brookhart and Harris[3] first reported the π to σ change in metal–ligand bonding yielding stable σ–π complex when bicyclo[6.1.0]nonatrienemolybdenum tricarbonyl was protonated by excess fluorosulfuric acid in SO_2F_2 solution. Evidence for it was also found by Whitesides and Arhart[4] in the case of butadieneiron tricarbonyl complexes. Using ^{13}C