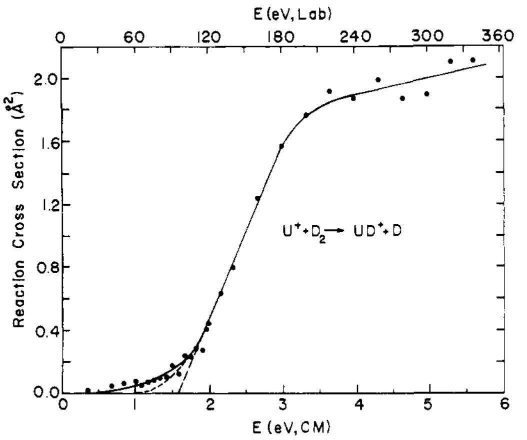

Figure 1. Variation of experimental cross section with relative kinetic energy in the center of mass frame (lower scale) and the laboratory frame (upper scale) for reaction 1. The solid curve is an approximate fit to the experimental points. The straight dashed line (– –) is a linear extrapolation of the data in the threshold region. The curved dashed line (- - -) is the threshold behavior predicted by Chantry's analysis at a temperature of 400 K.

Table I. Proton Affinities of Selected Atomic and Molecular Species

Species	Ionization potential (eV)	Proton affinity (kcal/mol)	Ref for proton affinities
Li	5.39[e]	193 ± 5	*a, b*
Mg	7.64[e]	187 ± 5	*b, d*
Hg	10.44[e]	128 ± 5	*b, d*
U	6.19[f]	238 ± 4	This work
NMe_3	7.87[g]	222 ± 2	*g*
PMe_3	8.01[g]	224 ± 2	*g*
NEt_3	7.42[h]	229 ± 2	*c*
LiOH		241 ± 2	*i*
NaOH		248 ± 2	*i*
KOH		263 ± 2	*i*
CsOH		270 ± 2	*i*

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and target gas masses. The corrected threshold for reaction 1 is 1.7 ± 0.1 eV giving a homolytic bond dissociation energy, $D(UD^+)$, of 2.95 ± 0.10 eV for UD^+ dissociating to U^+ and D. A similar analysis of reaction 2 yields a value of 3.0 ± 0.3 eV, in excellent agreement. An average value of $D(UD^+)$ = 3.0 ± 0.2 eV is thus determined. In this analysis it is assumed that $T\Delta S$ is approximately zero for reaction 1 and $\Delta H_{400\,K} = \Delta H_{298\,K}$.

To obtain the proton affinity of uranium, the substitution of protium (H) for deuterium (D) must be made. The difference in bond dissociation energies for the two isotopes, $D(UD^+) - D(UH^+)$, is estimated to be 1.7 kcal/mol, leading to the value, $D(UH^+)$ = 2.9 ± 0.2 eV. Using eq 3,[5] where IP refers to the ionization potential of the indicated species, the proton affinity of uranium is calculated to be 238 ± 4 kcal/mol.

$$PA(U) = D(UH^+) + IP(H) - IP(U) \qquad (3)$$

The derived value for PA(U) is compared to other available atomic and molecular proton affinities in Table I. Uranium clearly has the highest base strength of any atomic species for which reliable thermodynamic data are available. It is stronger than any organic monodentate base reported to date. Only the alkali hydroxides have a higher basicity. The high proton affinity of uranium is a result of a low ionization potential and a moderately high homolytic bond dissociation energy.

The base strength of uranium suggests that interactions between the metal and acidic species should be quite strong. Utilization of this fact could lead to the formation of new uranium complexes involving both cationic acids and neutral Lewis acids (e.g., UBF_3). The high basicity of uranium may also have implications for the mechanisms of oxidative addition reactions involving this species. Specifically, it is suggested that the heterolytic reaction scheme, process 4, may be the preferred mechanism for bond insertion reactions.[6]

$$U + XY \rightarrow [UX^+ + Y^-] \rightarrow XUY \qquad (4)$$

The methodology developed here should be generally applicable to the determination of gas phase proton affinities for many atomic species. Related experiments are underway in our laboratory to determine a range of metal-hydrogen homolytic bond dissociation energies from which atomic base strengths can be directly evaluated.

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(6) This type of scheme has been proposed by T. Marks, unpublished results, to explain the insertion reactions of thorium.

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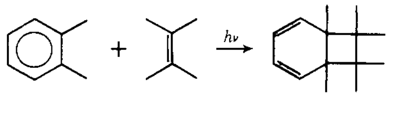
Photochemical Addition of Aromatic Aldehydes to 1,3,5-Cycloheptatriene, a $6\pi_s + 2\pi_s$ Photocycloaddition

Sir:

According to the Woodward-Hoffmann rule of conservation of orbital symmetry, concerted $6\pi_s + 2\pi_s$ cycloadditions are photochemically allowed processes but thermally "forbidden."[1,2] While there are several examples of $6\pi_s + 2\pi_s$ thermal cycloadditions reported in the literature,[3-7] the only examples of $6\pi_s + 2\pi_s$ photocycloadditions reported are additions of a benzenoid system to an olefin with the excited benzenoid system functioning as the 6π-component.[8-10] The adducts formed from such photocycloadditions contain a four-membered ring derived from two adjacent positions of the benzenoid ring and the olefin (reaction 1).[11] In connection with our interest in the



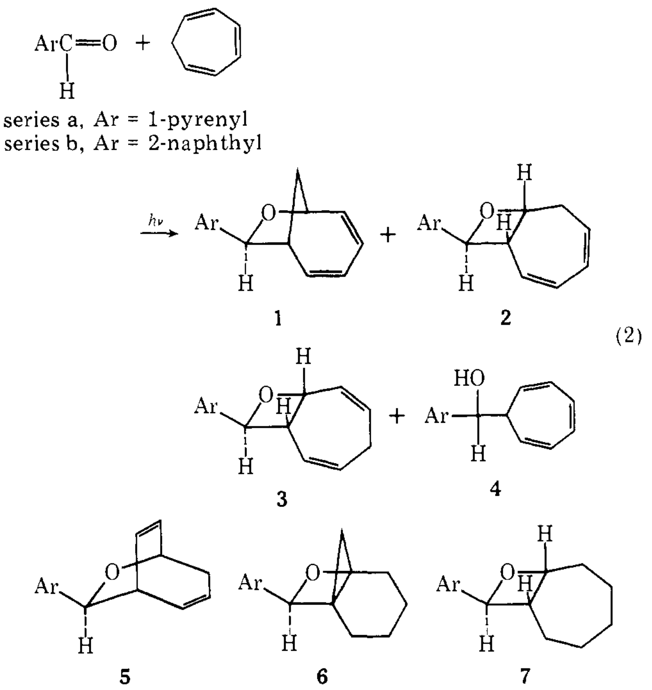
(1)

Table I. Products and Derivatives from the Photocycloaddition of Aromatic Aldehydes to 1,3,5-Cycloheptatriene

Compound[a]	% yield	Mp, °C	IR (intensity),[b] cm^{-1}	UV ($\epsilon \times 10^4$),[c] nm
1a	44[d]	129–130	1080 (s), 1070 (s), 1025(s)	344 (4.63), 275 (4.96), 241 (6.59)
2a	16[d]	118–119	980 (s)	343 (4.40), 276 (5.04), 242 (6.92)
3a	16[d]	108–110	965 (m)	343 (3.69), 275 (3.32), 241 (5.37)
4a	18[e]	137–138	3380 (s)	341 (4.84), 275 (5.21), 242 (7.37)
6a		161–162	1065 (s)	341 (4.82), 274 (5.65), 240 (8.11)
7a		153–154	995, 965 (s)	342 (4.76), 274 (5.59), 241 (7.69)
1b	25[d]	62–64	1040 (s)	265 (0.92), 220 (7.96)
2b	25[d]	67–68	975, 965, 945 (s)	274 (0.70), 225 (9.96)
3b	21[d]	—[f]	—	—
4b	21[e]	64–66	3430 (s)	264 (0.78), 224 (9.59)
6b	—	63–65	1070 (s)	274 (0.54), 225 (11.5)
7b	—	60–61	995 (s), 955 (m)	274 (0.54), 226 (11.1)

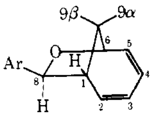
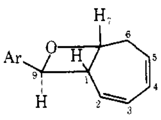
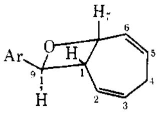
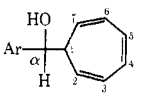
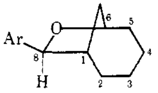
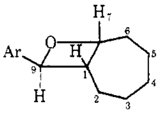
[a] Satisfactory elemental analysis was obtained for all crystalline compounds. [b] In KBr pellet. [c] In methanol. [d] Estimated by NMR of appropriate chromatographic fractions. [e] Isolated yield. [f] Not isolated in crystalline form.

chemistry of exciplexes and photocycloadditions, we investigated the photocycloaddition of aromatic aldehydes to 1,3,5-cycloheptatriene and found that 8-*exo*-aryl-7-oxabicyclo[4.2.1]nona-2,5-diene, **1**, is formed as a major product, together with oxetanes **2** and **3** and the arylcycloheptatrienylcarbinol **4** (reaction 2). All these products were formed with a high degree of regioselectivity, if not regiospecifically. The $4\pi_s + 2\pi_s$ adduct **5** and analogous compounds were not detected in the reaction mixture. The formation of **1** may thus constitute the first finding of a concerted $6\pi_s + 2\pi_s$ photocycloaddition of a nonbenzenoid 6π-system.



A solution of an aromatic aldehyde (3-13 mmol) and cycloheptatriene (10-15% by volume) in benzene (120 mL) was irradiated with a conventional Hanovia Hg-arc with an appropriate filter.[12] The progress of reaction was followed by the disappearence of aromatic aldehyde by chromatography. The product mixture was separated by adsorption chromatography on neutral alumina (activity IV). Due to their similar properties, **2** and **3** could be separated only by repeated chromatography. The photoaddition is illustrated with 1-pyrenecarboxaldehyde and 2-naphthaldehyde, because they form well-defined crystalline products. Qualitative results were also

Table II. NMR Data of Compounds 1a–7a[a]

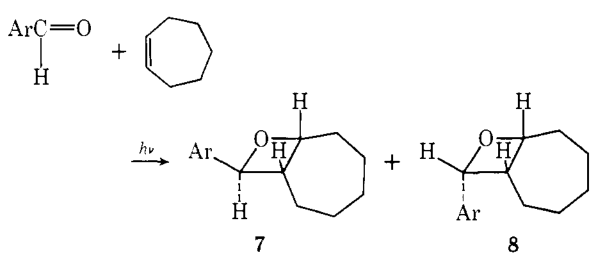
Compound	Proton	δ (ppm)	J, Hz
1a 	$C_{9\alpha}$	2.17	$J_{gem} = 13$
	$C_{9\beta}$	2.49	$J_{gem} = 13, J_{1,9\beta} = J_{6,9\beta} = 6.5$
	C_1	2.81	$J_{1,2} = J_{1,9\beta} = 6.5, J_{1,8} = 2.5$
	C_6	5.00	$J_{5,6} = J_{6,9\beta} = 6.5$
	C_{3-5}	6.00–6.19	Multiplets, 3 H
	C_8	6.32	$J_{1,8} = 2.5$
	C_2	6.50	$J_{1,2} = 6.5, J_{2,3} = 8$
	Aromatic	7.97–8.22	Multiplets, 9 H
2a 	$C_{6\beta}$	2.68	Broad doublets, $J_{gem} = 13$
	$C_{6\alpha}$	3.10	Multiplet
	C_1	3.71	$J_{1,7} = 9, J_{1,9} = 7$
	C_7	5.39	$J_{1,7} = J_{6\alpha,7} = 9, J_{6\beta,7} = 3$
	C_{2-5}	6.20	Broad singlet, 4 H
	C_9	6.78	$J_{1,9} = 7$
	Aromatic	8.00–8.44	Multiplets, 9 H
3a 	C_4	3.00	Broad singlet, 2 H
	C_1	3.85	Broad quartet
	C_7	5.55	$J_{1,7} = 10$
	C_2	5.72	$J_{1,2} = 4.5, J_{2,3} = 11$
	C_3	5.93	$J_{3,4\alpha} = J_{3,4\beta} = 5.5, J_{2,3} = 11$
	C_{5-6}	6.00	Singlet, 2 H
	C_9	6.52	$J_{1,9} = 7$
	Aromatic	7.92–8.42	Multiplets, 9 H
4a 	O–H	2.40[b]	Broad singlet
	C_1	2.54	$J_{1,2} = J_{1,7} = 6, J_{1,8} = 7$
	C_2	5.20	$J_{1,2} = 6, J_{2,3} = 9$
	C_7	5.77	$J_{1,7} = 6, J_{6,7} = 9$
	C_α	5.97	$J_{1,\alpha} = 7$
	C_3	6.08	$J_{2,3} = 9, J_{3,4} = 5$
	C_6	6.32	$J_{5,6} = 5, J_{6,7} = 9$
	C_{4-5}	6.63	Multiplet, 2 H
	Aromatic	7.96–8.28	Multiplets, 9 H
6a 	C_{2-5}, and $_9$	1.51–2.40	Multiplets, 10 H
	C_1	2.61	$J_{1,2\alpha} = J_{1,2\beta} = 4, J_{1,9\beta} = 9$
	C_6	5.03	Broad doublet, $J_{6,9\beta} = 9$
	C_8	5.85	Singlet
	Aromatic	7.95–8.08	Multiplets, 9 H
7a 	C_{2-6}	1.20–2.33	Multiplets, 10 H
	C_1	3.00	Multiplet
	C_7	5.10	Multiplet
	C_9	6.32	$J_{1,9} = 6$
	Aromatic	7.93–8.49	Multiplets, 9 H

[a] Compounds 1b–7b exhibit similar NMR spectra, except that the benzylic proton is at a higher field, e.g., C_8-proton of 1b is at δ 5.58 ppm ($J_{1,8}$ = 1 Hz) relative to that of 1a at 6.32 ppm. Values are in $CDCl_3$. [b] This value is variable depending on experimental conditions.

obtained with 1-naphthaldehyde, benzaldehyde, and 9-anthraldehyde. The results are summarized in Table I. Compounds **1–3** were characterized by their elemental analysis, conventional spectroscopic analyses, and their conversion into respective tetrahydroderivatives (**6** and **7**) to be 1:1 cycloadducts of the aldehyde to the triene. The structure of these adducts may be determined by high resolution NMR spectroscopy with spin decoupling at 270 MHz. All cycloadducts of an aromatic aldehyde to cycloheptatriene will have two ring juncture protons, an allylic proton which is vicinal to the benzylic proton and an α-ethereal proton. Ring juncture protons in $6\pi_s + 2\pi_s$ adducts (**1**) are both vicinal to the methylene bridge protons (C_9-protons in **1**) but are not coupled with each other, ring juncture protons in $2\pi_s + 2\pi_s$ adducts (**2** and **3**) are vicinal to each other, and ring juncture protons in $4\pi_s + 2\pi_s$ adducts (**5**) are isolated from each other. The NMR data of **1a–3a** formed from 1-pyrenecarboxaldehyde are presented in Table II.

The stereochemistry of **1** and its tetrahydro derivative **6** may be assigned by the value of J between the C_8-proton (benzylic) and C_1-proton (ring juncture). It is clear from the examination of molecular models that the dihedral angle between the C_1-proton and endo-C_8-proton is approximately 90° while that between the C_1-proton and exo-C_8-proton is approximately 20°. Since values of $J_{1,8}$ for **1a, 1b, 6a,** and **6b** are 2.5, 1.0, 0.0, and 0.0 Hz, respectively, the results clearly indicate that **1** is 8-*exo*-aryl-7-oxabicyclo[4.2.1]nona-2,5-diene.[13]

The structures of **2** and **3** were determined partially by their IR spectra (965–995 cm^{-1}, oxetane),[14] the presence of a 1,3-diene system in **2** and the absence of it in **3**, their NMR data (coupling between two C_6-protons with a C_7-proton in **2**), and their conversion to a single tetrahydro derivative **7**. Since the Paterno-Büchi reaction of polynuclear aromatic aldehydes and simple olefins proceeds mainly via their $^1n,\pi^*$ state and is regioselective,[15] authentic samples of **7a** and **7b** may be prepared by the photocycloaddition of 1-pyrenecarboxaldehyde and 2-naphthaldehyde to cycloheptene (reaction 3). Indeed, only two major adducts were formed in each reaction, **7** and **8**, and **7a** thus prepared is identical in all respects with the hydrogenation product of **2a** and **3a**. Their respective stereochemistry may be assigned again on the basis of their J values in NMR. It is known that J values of vicinal cis-protons in oxetanes are larger than the corresponding trans-protons.[16] For **7** and **8**, the values of $J_{1,9}$ are 6.0 Hz and 8.0 Hz, respectively. Therefore, the result suggests that the stereochemistry between C_7-, C_1-, and C_9-protons in **7** is cis-anti as indicated.

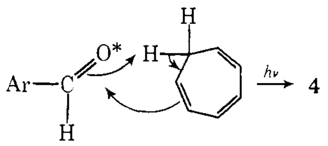


(3)

7 **8**

Abstraction of an activated hydrogen atom by photoexcited carbonyl compounds is a well-known photochemical process,[17] and abstraction of C_7–H of 1,3,5-cyclohepatatriene by excited aromatic aldehyde would give an Ar–ĊH–OH and a cycloheptatrienyl radical. It is unlikely that **4** was formed from the free radical recombination of these two radicals, since other radical recombination products such as dicycloheptatrienyl and 1,2-diaryl glycols were not detected in the reaction mixture. It is probable that **4** may be formed by an insertion of excited aldehyde to a C_7–H bond in cycloheptatriene or a concerted ene-reaction (reaction 4) which is known to occur concurrently with many photocycloadditions.[2]

These photochemical reactions of 1-pyrenecarboxaldehyde



(4)

and cycloheptatriene proceed with an appreciable quantum efficiency as indicated by the value of $\phi_{\text{-ArCHO}}$ at 365 nm of 0.13 ± 0.01. The reaction of 1-naphthaldehyde and cycloheptatriene closely parallels that of 2-naphthaldehyde; the products were characterized by spectroscopic methods but not isolated in crystalline form. Although **1** is also formed in the photochemical reaction of 9-anthraldehyde and the triene, the reaction was complicated by the addition of the triene to the meso positions of the anthracene nucleus.[18] Preliminary results on the addition of benzaldehyde to the triene indicated that **1–3** were also formed regioselectively but in very low quantum efficiency.[19] Our results clearly indicate that the photocycloaddition of aromatic aldehydes to cycloheptatriene is a general phenomenon. Since the fluorescence of polynuclear aromatic aldehydes is quenched by the triene, e.g., the Stern–Volmer constant for fluorescence quenching of 1-pyrenecarboxaldehyde by the triene is 5.0 M^{-1}, this reaction proceeds most likely via the singlet excited state of aromatic aldehydes. The Paterno-Büchi Reaction of simple phenyl carbonyl compounds is known to proceed via the $^3n,\pi^*$ state and a stepwise mechanism with a triplet biradical intermediate to give oxetanes with no selectivity in their stereochemistry.[15,20] The high regioselectivity and stereoselectivity of this reaction is in direct contrast to such a mechanism but is equally compatible with a concerted mechanism or a stepwise mechanism involving a singlet biradical intermediate.[21] Since only photocycloadducts allowed by the Woodward–Hoffmann rule are formed in this reaction, the formation of **1** may represent the first finding of a concerted $6\pi_s + 2\pi_s$ photocycloaddition of a nonbenzenoid 6π-system.

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Direct Formylation and Acylation of Pyridine via Pentacarbonyliron

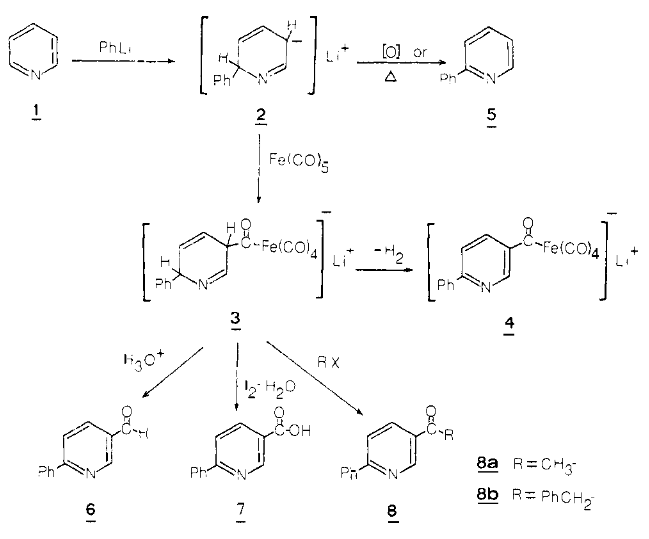
Sir:

A wide variety of β-substituted pyridines and their derivatives have found important uses, e.g., in biological studies,[1] mechanistic investigations,[2] as insecticides,[3] anticorrosion formulations,[4] intermediates in organic and pharmaceutical synthesis, and as potentially useful drugs. Some aryl pyridine-2-carboxaldehydes and their derivatives have been investigated for their potential antitumor activity,[5] but aryl 3-(or 5-)pyridinecarboxaldehydes have not been evaluated because their preparation, like other β-substituted derivatives,[6] has been a problem. In fact, Friedel-Crafts acylation, which is so facile in benzene, has to date *not* been successfully carried out with pyridine. While there have been recent reports of formylation and acylation procedures to prepare 2,3-disubstituted pyridines via [2,3]-sigmatropic rearrangements of α-pyrrolidinyl-2-alkylpyridines,[7] and via the rearrangement of azasulphonium salts of 2-aminopyridines,[8] there have been no reports of a direct formylation or acylation of the β-position of pyridine using pentacarbonyliron. Pentacarbonyliron has been used for formylation and acylation in benzenoid systems.

Thus, it is known that aryl- and alkyllithium compounds react with pentacarbonyliron at low temperature to give unstable lithium acylcarbonylferrates, which are useful precursors for the synthesis of aromatic aldehydes[9] and ketones.[10] Acyltetracarbonylferrates, which can also be obtained from other reactions (e.g., between acid chlorides and $Na_2Fe(CO)_4$), were used for the preparation of aldehydes, ketones, and carboxylic acid derivatives.[11] While benzene derivatives have been prepared via such reactions, the preparation of pyridine aldehydes using pentacarbonyliron is unknown.

We now wish to report the first direct formylation (and other carbonylation reactions) of pyridine via pentacarbonyliron; in particular, the "one-flask" synthesis of 2-aryl-5-pyridinecarboxaldehyde and other carbonyl derivatives from pyridine. Pyridine was carefully added to an ethereal solution of phenyllithium at room temperature and under an atmosphere of argon. The resulting suspension of solids **2**[6c] was taken up in dry tetrahydrofuran (THF) and cooled to −65 °C. After addition of an equimolar amount of pentacarbonyliron in THF, the mixture (containing intermediate **3** or **4**) was allowed to gradually warm to room temperature. Hydrolysis with saturated, aqueous ammonium chloride gave after purification 2-phenylpyridine (**5**) (18%) and 2-phenyl-5-pyridinecarboxaldehyde (**6**) (46%). When acetic acid was used for the hydrolysis, 73% yield of **6** was obtained. **6:** mp 58–59 °C; NMR ($CDCl_3$) δ 7.72 (complex multiplet, pyridine C-3, C-4 and phenyl 7 H), 9.15 (singlet, pyridine C-6 1 H), 10.13 (singlet, aldehydic 1 H). Anal. ($C_{12}H_{19}NO$) C, H, N.[12] If the mixture (containing **3** or **4**) was oxidized with iodine, 2-phenylpyridine-5-carboxylic acid (**7**) (50%) was isolated; the use of methyl iodide (RX = CH_3I) or benzyl bromide (RX = $PhCH_2Br$) instead of iodine resulted in the production of 2-phenyl-5-acetylpyridine[13] (**8a**) (32%) or 2-phenyl-1-(6-phenyl-3-pyridinyl)ethanone (**8b**) (24%), respectively. **8b:** mp 122–123 °C; NMR ($CDCl_3$) δ 4.31 (singlet, benzyl 2 H), 7.90 (complex multiplet, pyridine C-3, C-4 and phenyl 12 H), 9.29 (singlet, pyridine C-6 1 H). Anal. ($C_{19}H_{15}NO$) C, H, N.[12] In addition to the acid and ketones, 2-phenylpyridine was also isolated. 2-Phenylpyridine has been found in other reactions involving **2**. Dihydropyridinyl structures such as **2** are easily aromatized via thermolysis or oxidation.[6c]

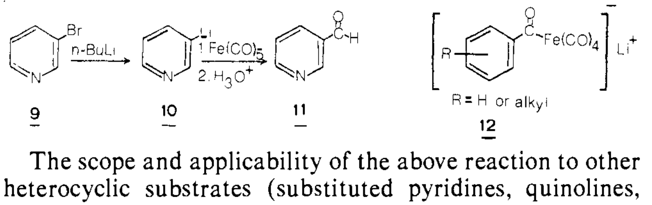
Scheme I



We have isolated 3-pyridinecarboxaldehyde (**11**) from the reaction of 3-pyridinyllithium (**10**) and pentacarbonyliron, but preliminary experiments gave a poor yield (5%). 3-Pyridinyllithium was prepared from 3-bromopyridine and *n*-butyllithium.[15] Thus, this reaction is feasible but under these conditions it is not a useful synthetic procedure. In fact, if 3-bromopyridine (instead of pyridine) were to be used as a starting compound, other higher yield synthetic methods have been reported.[16]

We have not been able to characterize the intermediate **3** (or **4**) responsible for the formation of the aldehyde, ketones, and carboxylic acid. However, the infrared spectrum of the reaction mixture after adding pentacarbonyliron to a solution of phenyllithium-pyridine intermediate **2** gave a characteristic R-C(=O)Fe absorption at 1635 cm^{-1} which is not associated with either the reagents or products. **4** is a more likely immediate precursor, because the related lithium benzoyltetracarbonylferrates (**12**) give aromatic aldehydes[9] and ketones[10] on treatment with aqueous acid and benzylbromide, respectively. Irrespective of the actual structure of the intermediate, we have provided a direct formylation and acylation of pyridine using pentacarbonyliron.

Scheme II



The scope and applicability of the above reaction to other heterocyclic substrates (substituted pyridines, quinolines, isoquinolines, and naphthyridines), and other metal carbonyls are being investigated.

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