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(31) Baker silica gel, chromatographic quality, deactivated with 10% H_2O and containing 0.5% by weight Du Pont 609 Phosphor: B Leov and M. Goodman, *Chem. Ind.* (*London*), 2026 (1967).

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Cyano Adducts of 1-Substituted Pyridinium Salts[1a]

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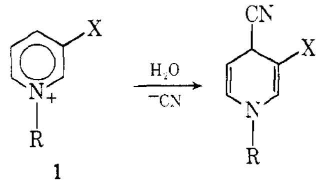
The isolation and characterization of several cyano adducts **11a–e** of 1-substituted pyridinium salts **10** is described. These represent the first examples of this type of compound. In addition, the first Reissert-like compound (**12a**) from pyridine is reported. Contrary to earlier suggestions, the title compounds are relatively stable. An explanation of the stability on the basis of interaction of the N substituent with the reactive dihydropyridine ring is presented.

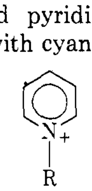
The synthesis of stable, simple dihydropyridines has received increased attention recently.[2] Such compounds are of interest theoretically[2,3] and as precursors in synthetic applications.[2,4]

It has been shown that cyanide reacts with 1,3-disubstituted pyridinium salts **1** to afford the corresponding 4-cyano adducts **2**.[2] Only salts related to **1** yield isolable products.[2] That adducts of other salts were not observed was assumed to be due both to the low electrophilicity of the salt and the lack of resonance stabilization of the corresponding cyano adduct which is only possible in species such as **2**.[5]



R = alkyl
X = CONH$_2$, CO$_2$Me,
CN, COMe, COPh

While 3-unsubstituted pyridinium salts **3** had been found to be unreactive with cyanide,[5] related reactions are known. Thus, the corresponding quinolinium adducts (**4**, **5**) have been known for many years,[6,7] while 1-alkoxy- and 1-amidopyridinium salts **6** yield transient cyano adducts which decompose with loss of an alcohol or amide to produce cyanopyridines.[8] In contrast to Gauthier's results, cyano adduct **7** was found to be stable in DMSO.[9]



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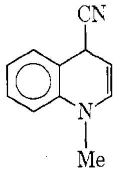
R = alkyl, aryl, acyl



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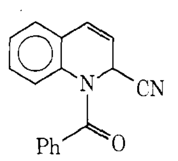

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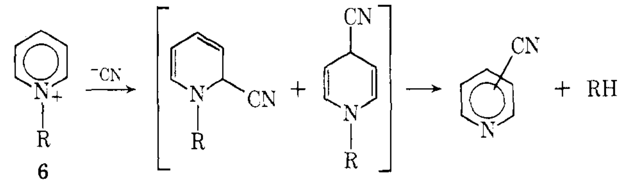
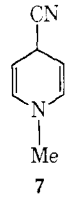


R = OR, RNCOR′



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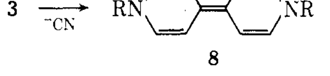
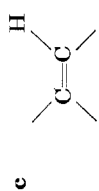
Within the last several years it has been reported that **3** (R = alkyl or aryl) reacts with cyanide to afford dihydrobipyridine **8** or its oxidized derivatives.[10,11] Although



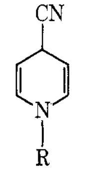
8

Table I
Properties of 4-Cyano-1,4-dihydropyridines (11)[a]

Compd	R	Yield, %	Solvent	Nmr spectra, chemical shift, τ H₂	H₃	H₄	R	Ir max (KBr), cm⁻¹	Uv max (CHCl₃), nm (ε)	Decomposition point, °C
11a	4-Pyridyl	79	$(CD_3)_2CO$	3.0 (d, *J* = 9.0 Hz)	5.0 (m)	5.5 (m)	2.85 (d, 2, *J* = 5.0 Hz), 1.50 (d, 2, *J* = 5.0 Hz)	2230, 1690	289 (8000), 345 (300)	75–80
11b	DNP[b]	92	$(CD_3)_2SO$	2.2 (m)	2.7 (m)	3.5 (m)	1.4 (m, 1), 1.0 (m, 1), 0.5 (m, 1)	2220, 1670	240 (sh, 18,000),[e] 290 (sh, 10,000),[e] 375 (10,300)[e]	100
11c		50	$CDCl_3$	3.5 (d, *J* = 7.0 Hz)	5.2 (m)	5.6 (m)	4.0 (d, 1, *J* = 14.5 Hz), 3.40 (d, 1, *J* = 14.5 Hz), 2.6 (s, 5)	2240, 1685	315 (23,000)	75
11d	TAG[c]	63	$CDCl_3$	3.7 (d, *J* = 7.5 Hz)	5.3 (m)	5.5 (m)	7.9 (q, 12), 6.2 (m, 1), 5.7 (m, 3), 4.7 (m, 3)	2235, 1760, 1690	280 (2400)	140
11e	CH_2OMe	24	$CDCl_3$	3.8 (d, *J* = 7.5 Hz)	5.5 (m)	5.5 (m)	6.7 (s, 3), 5.6 (s, 2)	2250,[d] 1685[d]	243 (2600), 286 (2000)	
11g	CH_2OAc	Trace	$CDCl_3$	3.8 (d, *J* = 7.5 Hz)	5.4 (m)	5.6 (m)	7.8 (s, 3), 5.25 (s, 2)			
11h	CH_2CN	Trace	$CDCl_3$	3.9 (d, *J* = 7.0 Hz)	5.3 (m)	5.7 (m)	5.9 (s, 2)			
11i	CH_2CO_2Et	Trace	$CDCl_3$	4.0 (d, *J* = 7.5 Hz)	5.6 (m)	5.6 (m)	8.7 (t, 3, *J* = 7), 6.2 (s, 2), 5.7 (q, 2, *J* = 7 Hz)			

[a] Acceptable elemental analyses were obtained for **11a–e**. [b] DNP = 2,4-dinitrophenyl. [c] TAG = tetracetylglucosido. [d] Neat. [e] CH_3CN.

there are several possible mechanisms,[10,11b] the initial reaction in each is the formation of a 4-cyano adduct **9.** We now wish to report several examples of **9** which are



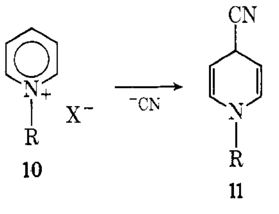
9

R = alkyl, aryl

relatively stable and can be readily isolated. These adducts represent a new class of simple dihydropyridines.

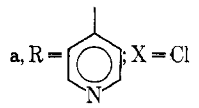
Results

When aqueous solutions of pyridinium salts **10a–e** were treated with sodium cyanide, the corresponding 4-cyano adducts **11** were obtained. The yields ranged from 24% for **11e** to 92% for **11b** as shown in Table I. Since reaction

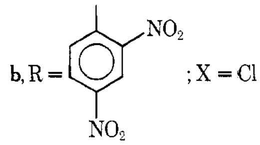


10

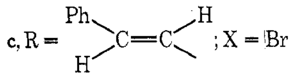
11



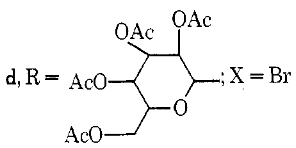
a, R = ; X = Cl



b, R = ; X = Cl



c, R = ; X = Br



d, R = ; X = Br

e, R = CH_2OMe; X = Cl
f, R = Ph; X = Cl
g, R = CH_2OAc; X = Br
h, R = CH_2CN; X = Cl
i, R = CH_2CO_2Et; X = Cl
j, R = CH_2Ph; X = Br

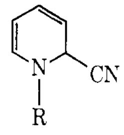
times of greater than 2 hr afforded impure **11e** and pyridinium salts dimerize in the presence of cyanide, presumably *via* a cyano adduct as described above, further efforts to obtain a higher yield of **11e** were not made.

The structures of the products were established on the basis of spectroscopic information. An infrared band was noted at 1680–1690 cm^{-1} which has been found to be diagnostic for simple 1,4-dihydropyridines.[1a,12] A M^+ peak was observed for each adduct except **11b,** indicating that the compounds were indeed covalent and not ionic. The nmr spectra (Table I) are consistent with the assigned structures and related 1,4-dihydropyridines.[1a,2,4a,12] The observed ultraviolet spectra (Table I) likewise give good agreement with previously published results.[2,4a,12]

The reactions of **10f–i** with cyanide were only partially successful. Reaction of **10f** with cyanide furnished **11f,** which was free from dihydrobipyridine 8 (R = Ph) by infrared and mass spectroscopy.[13] However, as soon as the solid was dissolved, an intense green solution of phenylviologen cation radical was formed. It is known that cyanide induces the dimerization of **10f** to 8 (R = Ph) which is oxidized to the cation radical in solution.[11a] Even with short reaction times, **11f** could not be obtained pure.

Salts **10g–i** yielded less than 5% of the corresponding adducts **11** on exposure to cyanide. The structures were assigned by nmr (Table I) and mass spectroscopy. A small amount of uncharacterized polymeric material was obtained from **10j** and cyanide.

The successful preparation of the above cyano adducts encouraged us to attempt the synthesis of the pyridine analogs of Reissert compounds **5**. Popp[14] has prepared a large number of such compounds by mixing the appropriate acid chloride and quinoline in methylene chloride with aqueous sodium cyanide and stirring the resulting mixture for several hours. This technique was utilized in the attempted synthesis of **12**. Thus, when pyridine, ethyl chloroformate, and cyanide were combined as above, 1-carbethoxy-2-cyano-1,2-dihydropyridine (**12a**) was obtained in 25% yield. The elemental analysis and spectral data are consistent with the assigned structure. An infrared absorption at 1650 cm^{-1}, which has been found to be characteristic of 1,2-dihydropyridines,[1a,12] was noted. A M$^+$ peak at m/e 178 was observed. The observed λ_{max} at 302 nm is consistent with that of similar 1-acyl-1,2-dihydropyridines,[4a,15] as is the nmr spectrum.[4a,15,16]



12

a, R = CO_2Et
b, R = $CONMe_2$
c, R = PhCO
d, R = $PhSO_2$
e, R = NO_2PhCO
f, R = o-NO_2PhSO_2
g, R = MeCO
h, R = Me_3Si
i, R = NO
j, R = CN

The attempted syntheses of **12b–j** were unsuccessful. The reactions led to uncharacterized mixtures of starting material, hydrolysis products of the acid chloride, or polymeric materials. The nmr spectra of the crude mixture from the attempted synthesis of **12i** and **12j** suggested the presence of a small amount of 2-cyanopyridine. While mass spectral data indicated that the desired **12d**, **12f**, **12i**, and **12j** were not obtained, a peak was observed at m/e 104 as expected for cyanopyridine. These data suggest that in these cases some of the desired product was formed but decomposed with loss of RH (R = $PhSO_2$, o-NO_2PhSO_2, NO, CN) in a manner analogous to the 1-alkoxy- and 1-amidopyridinium salts described above. No evidence for either cyano adducts or cyanopyridine was observed in the other reactions.

It is known that benzoyl chlorides react with cyanide in the presence of pyridine to afford a complex mixture of products which does not contain pyridine.[17] Such a mixture was obtained from benzoyl chloride, p-nitrobenzoyl chloride, and probably dimethylcarbamoyl chloride.

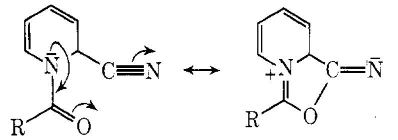
The reaction of ethyl chloroformate and dimethylcarbamoyl chloride, which is known to form a stable salt with pyridine,[18] with cyanide and pyridine was investigated in other systems in an effort to achieve the desired result. Thus, the reagents were combined in methanol, tetrahydrofuran, dichloromethane, and dichloromethane and 1 equiv of $SbCl_5$. However, **12b** was not obtained nor was their any evidence for cyanopyridine observed. While **12a** was obtained in all cases except in the presence of $SbCl_5$, the yield was no better. In addition, Popp's method with reaction times up to 16 hr still gave the same yield of **12a** and afforded none of the desired **12b**.

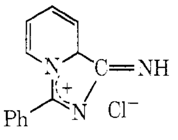
Discussion

Position of Attack. It is unclear why 1-alkyl- and 1-arylpyridinium salts (**10**) afforded 4-cyano adducts (**11**) while 1-carboethoxypyridinium chloride furnished a 2-cyano adduct (**12a**). Identical behavior is observed in the quinolinium system (**4**, **5**). However, again there is no explanation for this dichotomy, although it has been suggested that the carbonyl function guides the cyanide to the 2 position.[7]

It has been established that 2-cyano adducts (kinetic product) rearrange to the more stable (thermodynamic product) 4-cyano adducts, at least for compounds similar to **2**.[2] Since it has been shown that the 1,4-dihydropyridine structure is about 2 kcal/mol more stable than the 1,2-dihydropyridine structure,[3] it is reasonable that the 4-cyano adducts (**11**) should represent the products from thermodynamic control.

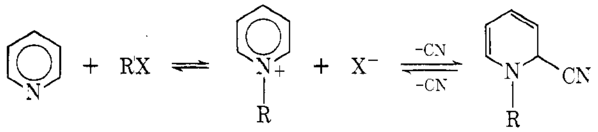
A wide variety of enolate anions and related species have been observed to attack the 4 position of 1-acylpyridinium salts.[19a] However, evidence of initial attack at the 2 position in some cases has been reported.[19b] The stability of 2-cyano adducts[7] as opposed to 4-cyano adducts may be due to a favorable interaction between the carbonyl and cyano groups as shown. This interaction has been suggested to account for the stability of **13**.[19c]





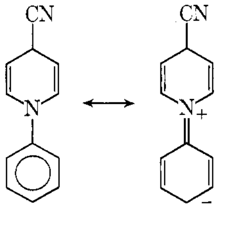
13

Unreactive Pyridinium Salts. The lack of reactivity of 1-acylpyridinium salts might be due to two factors. First, formation of the salt is an equilibrium reaction[20] which could be coupled to an equilibrium between salt and adduct[2] as shown. Unfavorable equilibria for either reaction would make it difficult to obtain the desired cyano adducts **12**. A second difficulty encountered is attack of cyanide or other nucleophiles (H_2O), not on the ring, but at R to give acyl cyanides and related compounds.[17,21] However, 1-acylpyridinium salts have been found to react with several different nucleophilic species to furnish dihydropyridines,[19a] which implies that conditions might be found which would allow the isolation of the corresponding cyano adducts.



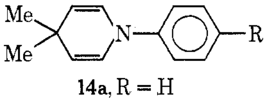
The apparent lack of reactivity of **10g–j** is presumably due to relatively low electrophilicity of the salt. Other workers have noted this behavior.[5,9]

Stability of the Adducts. Since simple dihydropyridines are generally unstable[2] and cyanide was predicted to be unreactive toward simple salts like **10**,[5] yet the adducts **11a–e** and **12a** are readily obtained, there are obviously some stabilizing factors in these compounds. Resonance stabilization as shown below is obviously one factor.



Such resonance interaction would decrease the electron density of the reactive dihydropyridine, thus minimizing the importance of decomposition reactions usually observed with simply dihydropyridines.

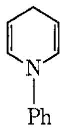
This explanation is completely analogous to the stabilizing effect of substituents at the 3 and 5 positions which are capable of electron withdrawal by resonance interaction (*i.e.*, **2**).[2,5] Kosower[12c] has interpreted the uv spectra of 1-aryl-1,4-dihydropyridines **14** in terms of resonance interaction between the substituents and the electron pair on nitrogen. The resistance of 1-phenyl-1,4- and 1,2-dihydropyridines (**15a** and **15b**) to reduction by sodium borohydride has been attributed to conjugation of the phenyl and dihydropyridine rings.[23]



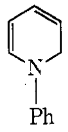
14a, R = H

b, R = NO_2

c, R = CN



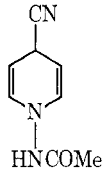
15a



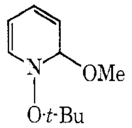
15b

The stability of **11d** and **11e** is unique. Since no resonance interactions are possible, perhaps inductive electron withdrawal is responsible for stabilizing the adducts. However, this does not explain why **11g**–**i** are not equally as stable. Tetracetylglucosido (TAG) is particularly effective in stabilizing the dihydropyridine ring.[24] As judged from its decomposition point and inertness upon recrystallization, **11d** appears to be the most stable adduct isolated. Wallenfels[25] has reported that TAG's stabilizing effect is due to inductive electron withdrawal which makes the pyridinium salt highly electrophilic and, therefore, highly reactive with nucleophiles.[25] In the corresponding dihydropyridine, the electron-withdrawing effect by TAG reduces the electron density of the ring, thus making oxidation (and presumably dimerization, etc.) more difficult relative to other 1-alkyl (or related) dihydropyridines.[25b]

Compounds **16** and **17** have been isolated, although they readily decompose to the corresponding pyridines.[26,27]



16



17

The limited stability of these compounds is also presumably due to inductive electron withdrawal.

While one can envision some stabilization due to inductive effects, it is not easy to understand why they are apparently so important in compounds with ether substituents (**11d**, **11e**). The possible biological implications of the tremendous stabilizing ability of TAG are obvious.

Experimental Section[28]

1-(4-Pyridyl)-4-cyano-1,4-dihydropyridine (11a). A solution of 3.0 g (15.6 mmol) of **10a** (Aldrich) in 35 ml of water was outgassed for 10 min with nitrogen. The addition of potassium cyanide (2.0 g, 30.0 mmol) caused a red solid to precipitate. The flask was stoppered and left in the dark overnight at room temperature. The solid was collected and dried under vacuum to afford 2.25 g (79%) of red **11a**: mass spectrum (70 eV) *m/e* (rel intensity) 183 (M^+, 15), 182 (21), 157 (30), 79 (15), 78 (19), 27 (100), 26 (17).

A solution of 1.15 g (5 mmol) of **10a** hydrochloride (Aldrich) and 0.42 g (5 mmol) of sodium bicarbonate in 20 ml of water was filtered[29] and purged with nitrogen for 30 min. To this solution was added 0.49 g (10 mmol) of sodium cyanide. The solution was stirred for 15 min while being flushed with nitrogen. The resulting red solid was collected, washed well with water, and dried under vacuum to afford 0.49 g (53%) of **11a**.[30]

1-(2,4-Dinitrophenyl)-4-cyano-1,4-dihydropyridine (11b).[31] After a solution of **10b** (1.40 g, 5 mmol) in 20 ml of water was purged with nitrogen for 30 min, sodium cyanide (0.49 g, 5 mmol) was added. The solution was stirred under nitrogen for 5 min to afford a brown solid, which was collected and dried under vacuum to yield 1.25 g (92%) of **11b**: mass spectrum (70 eV) *m/e* (rel intensity) 184 (70), 79 (82), 78 (100), 27 (40).

1-(*trans*-2-Styryl)-4-cyano-1,4-dihydropyridine (11c). After a solution of 0.54 g (1.93 mmol) of **10c** hydrate[32] in 10 ml of water was purged with nitrogen for 5 min, sodium cyanide (0.15 g, 3.06 mmol) was added. The solution was shaken for 1 min, then kept under nitrogen for 5 min, and finally extracted with chloroform (2 × 15 ml). The extracts were dried ($MgSO_4$) and concentrated to afford 0.20 g (50%) of **11c**: mass spectrum (70 eV) *m/e* (rel intensity) 208 (M^+, 2), 182 (25), 103 (13), 79 (13) 77 (12), 28 (100), 27 (41).

1-Tetracetylglucosido-4-cyano-1,4-dihydropyridine (11d). A solution of 2.71 g (5.53 mmol) of **10d**[33] in 10 ml of water was layered with 20 ml of methylene chloride. To the stirred mixture was added dropwise over 20 min 10 ml of water containing 0.50 g (10.2 mmol) of sodium cyanide. After the resulting mixture was stirred for 10 min, the layers were separated and the water layer was extracted with 20 ml of methylene chloride. The extracts were combined, dried (sodium carbonate), and concentrated under vacuum to yield 1.51 g (63%) of brown, crystalline solid. Recrystallization of 0.50 g from acetone–water afforded 0.25 g of tan plates of **11d**: mass spectrum (70 eV) *m/e* (rel intensity) 436 (M^+, 1) 79 (44), 43 (100), 27 (56).

1-Methoxymethyl-4-cyano-1,4-dihydropyridine (11e). Pyridine and chloromethyl methyl ether were combined to afford 1-methoxymethylpyridinium chloride (**10e**). A solution of **10e** (3.6 g, 22.5 mmol) in 20 ml of water was layered with 70 ml of methylene chloride and outgassed with nitrogen for 5 min. To the stirred mixture was added under nitrogen 10 ml of water containing 1.1 g (22.5 mmol) of sodium cyanide. After stirring for 2 hr under nitrogen, the mixture was poured into ether and the solution was washed with water. The ether was dried ($MgSO_4$) and concentrated to afford 0.8 g (24%) of green oil **11e**: mass spectrum (70 eV) *m/e* (rel intensity) 150 (M^+, 50), 124 (25), 119 (100), 45 (90). The oil darkened on standing.

Attempted Synthesis of 1-Phenyl-4-cyano-1,4-dihydropyridine (11f). A solution of 0.96 g (5.0 mmol) of **10f**[34] in 20 ml of water was purged with nitrogen for 15 min. Sodium cyanide (0.49 g, 10.0 mmol) was added and the flask was stoppered. After standing at room temperature in the dark overnight, impure **11f** as a waxy, brown solid (0.13 g) was obtained. Solutions of this material exhibited the characteristic uv spectrum of phenylviologen cation radical:[11c] ir (neat) 2230 (CN), 2120, 1680 cm^{-1} (1,4-dihydropyridines); mass spectrum (70 eV) *m/e* (rel intensity) 182 (M^+, 74), 181 (86), 156 (100), 77 (47), 27 (76).

Anal. Calcd for $C_{12}H_{10}N_2$: C, 79.12; H, 5.49; N, 15.38. Found: C, 78.68; H, 5.26; N, 11.55.

A solution of 0.85 g (4.50 mmol) of **10f** in 5 ml of water was layered with 20 ml of methylene chloride and purged with nitrogen for 10 min. To the stirred mixture under nitrogen was added dropwise over 10 min 5 ml of water containing 0.32 g (6.50 mmol) of sodium cyanide. After 10 min the layers were separated and the aqueous layer was extracted with 20 ml of methylene chloride. The extracts were dried (K_2CO_3) and concentrated to afford 0.3 g of brown solid. The infrared and mass spectra were identical with those above. Solutions of the solid again exhibited the spectrum of phenylviologen cation radical.

1-Acetoxymethyl-4-cyano-1,4-dihydropyridine (11g). Pyridine and bromomethyl acetate were mixed in ether to afford **10g**. A solution of **10g** (2.3 g, 10 mmol) in 10 ml of water was layered with 35 ml of methylene chloride and outgassed with nitrogen for 5 min. Sodium cyanide (0.5 g, 10 mmol) in 10 ml of water was added and the reaction was carried out as in the synthesis of **11e** above to yield a small amount of green oil **11g** which darkened on standing: mass spectrum (70 eV) *m/e* 119, 104, 93, 79, 78, 57, 26; ir ($CHCl_3$) 2270 (CN), 1705 cm^{-1}; uv max ($CHCl_3$) 240, 290 nm (sh).

1-Cyanomethyl-4-cyano-1,4-dihydropyridine (11h). Chloroacetonitrile and pyridine were added to THF to afford 1-cyanomethylpyridinium chloride (**10h**). Sodium cyanide (0.2 g, 4 mmol) and 0.6 g (4 mmol) of **10h** were allowed to react as above to afford a small yield of green oil **11h** which darkened on standing: mass spectrum (70 eV) *m/e* 119, 79, 57, 49, 47, 44, 26; ir ($CHCl_3$) 2285 (CN), 2205 (CN), 1685 cm^{-1} (1,4-dihydropyridines); uv max ($CHCl_3$) 243, 290 nm (sh).

1 - Carboethoxymethyl - 4 - cyano - 1,4 - dihydropyridine (11i). Ethyl chloroacetate and pyridine were combined in THF to yield **10i**. Sodium cyanide (0.7 g, 14 mmol) and 2.8 g (14 mmol) of **10i** were allowed to react as above to furnish a small amount of green oil **11i** which darkened on standing: mass spectrum (70 eV) *m/e* 192 (M^+), 191, 166, 163, 138, 119, 105, 93, 29, 26; ir ($CHCl_3$) 2270 (CN), 1740 (C═O), 1685 cm^{-1} (1,4-dihydropyridine); uv max ($CHCl_3$) 243, 290 nm (sh).

1-Carboethoxy-2-cyano-1,2-dihydropyridine (12a). A solution of 6.3 g (80 mmol) of pyridine and 12.0 g (245 mmol) of sodium cyanide in 40 ml of water was layered with 60 ml of methylene chloride. After the mixture was purged with nitrogen for 5 min, 17.5 g (163 mmol) of ethyl chloroformate was added dropwise (*ca.* 20 min) under nitrogen with stirring. The resulting mixture was stirred for an additional 1 hr, poured into 200 ml of water, and extracted with 200 ml of ether. The extract was concentrated under vacuum, poured into dilute hydrochloric acid (*ca.* 10^{-3} *M*), and extracted with ether. The ether solution was washed with saturated sodium bicarbonate and water, dried, and concentrated under vacuum to afford 3.5 g (25%) of **12a** as a red liquid: ir ($CHCl_3$) 1720 (C═O), 1650 cm^{-1} (1,2-dihydropyridine); uv max ($CHCl_3$) 304 nm; nmr ($CDCl_3$) τ 8.70 (t, 3, J = 7.0 Hz), 5.65 (q, 2, J = 7.0 Hz), 4.35 (m, 3), 3.75 (m, 1) 3.00 (d, 1, J = 7.5 Hz); mass spectrum (70 eV) *m/e* (rel intensity) 178 (M^+, 6), 105 (32), 79 (100), 78 (61).

Anal. Calcd for $C_9H_{10}N_2O_2$: C, 60.67; H, 5.62. Found: C, 60.17; H, 5.74.

Registry No.—**10a**, 22752-98-3; **10b**, 4185-69-7; **10c**, 26154-94-9; **10d**, 51364-78-4; **10e**, 51364-79-5; **10f**, 13958-90-2; **10g**, 51364-80-8; **10h**, 17281-59-3; **10i**, 27032-03-7; **11a**, 51364-81-9; **11b**, 51364-82-0; **11c**, 51364-83-1; **11d**, 51381-70-5; **11e**, 51364-84-2; **11f**, 51364-85-3; **11g**, 51364-86-4; **11h**, 51364-87-5; **11i**, 51364-88-6; **12a**, 51364-89-7.

References and Notes

(1) (a) Taken in part from the Ph.D. Thesis of R. H. R., Drexel University, 1972. (b) NSF Predoctoral Fellow, 1968–1971. (c) Address all correspondence to this author at Department of Chemistry, Virginia Commonwealth University, Academic Center, Richmond, Va. 23220.

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Cycloadition of 1-Azirines to 1,3-Diphenylisobenzofuran and Rearrangement of the Adducts[1]

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1-Azirines 1 and 1,3-diphenylisobenzofuran (2) react smoothly and efficiently in refluxing toluene to afford the simple 1:1 adducts 3, possessing the exo configuration. Two of the adducts, 3a and 3b, were found to rearrange in the presence of neutral alumina, to give the epoxybenzo-2*H*-azepines 20a and 20b. Chemical reactions (water, alcohol, $LiAlH_4$) of the adducts 3 generally involved initial opening of the oxido bridge in a regiospecific manner. When more vigorous conditions were used, rupture of the aziridine ring usually followed.

The role of 1-azirines 1 as dienophilic components in Diels–Alder reactions with cyclopentadienones has recently been demonstrated and developed by us[2-5] and others.[6] The products were 3*H*- or 2*H*-azepines but only indirect evidence for the intermediacy of Diels–Alder adducts (7-norbornanones) was obtained. In an effort to isolate related Diels–Alder adducts, we examined, concurrently with our investigations of the cyclopentadienone system, 1,3-diphenylisobenzofuran (2) as the diene component. In the meantime a note has appeared[7] on this very same reac-