brought to room temperature and diluted with ether. Conventional ether–water workup afforded the crude oil, which was purified by high-pressure LC (ethyl acetate). The solvent was removed under reduced pressure to yield 300 mg (87%) of a light yellow solid, which was recrystallized (pentane) to afford (1*S*,4*R*)-diol **9c**: tan crystals, mp 63–65 °C; pure by TLC (R_f 0.37, ether), ^{1}H and ^{13}C NMR.

(1*R*,4*S*,7*E*)-1,4-Dihydroxy-*A*-homo-19-nor-9,10-secocholesta-5,7-diene, 8c. The 1-acetoxy-4-benzoyloxy isomer **8a** (90.2 mg, 0.165 mmol) in 5% KOH–methanol (11 mL) was heated at 70 °C for 2 h under a nitrogen atomosphere. The usual water–ether workup afforded an orange oil (61.1 mg), which was chromatographed (high-pressure LC, ethyl acetate). The resulting white crystals were recrystalized in pentane to afford the pure (1*R*,4*S*)-diol **8c**: mp 112–114 °C; pure by TLC (R_f 0.32, ether), ^{1}H and ^{13}C NMR; 54.4 mg (82%).

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Registry No. 1 benzoate, 2174-12-1; **3e**, 75896-12-7; **3f**, 75896-13-8; **4e**, 75947-25-0; **4f**, 75946-86-0; **7a**, 75896-14-9; **7b**, 75896-15-0; **7c**, 75896-16-1; **8a**, 75896-17-2; **8c**, 75946-87-1; **9b**, 75896-18-3; **9c**, 75946-88-2.

Supplementary Material Available: Spectral and analytical data for **3e,f**, **4e,f**, **7a–c**, **8a,c**, and **9b,c** (10 pages). Ordering information is given on any current masthead page.

Aldehydes from Nitriles. Formation of *N*-Alkylnitrilium Ions and Their Reduction to *N*-Alkylaldimines by Organosilicon Hydrides

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A two-step procedure for the partial reduction of nitriles to aldehydes under mild reaction conditions is presented. This approach involves the N-alkylation of nitriles in dichloromethane solution and reductive capture of the resulting nitrilium ions to *N*-alkylaldimines with an organosilicon hydride such as triethylsilane or tri-*n*-hexylsilane. Mild hydrolysis of the aldimines produces aldehydes in generally good-to-excellent yield. Use of both triethyloxonium tetrafluoroborate and isopropyl chloride–iron(III) chloride reagents to effect alkylation is reported. Selective reduction of the nitrile function in polyfunctional substrates is possible with this technique. Over reduction to amines does not occur. Close control of reducing agent and reaction temperatures is not required. Attempts to effect reduction of nitrile–boron trifluoride complexes with triethylsilane were unsuccessful, even at elevated temperatures.

Organic nitriles are often available as starting materials, thus synthetic routes leading directly from them to less readily available aldehydes are frequently quite useful. Such transformations generally take the form of partial reduction of the nitrile to an aldimine followed by hydrolysis of the aldimine to the aldehyde (eq 1).[1,2] One of

$$\mathrm{RC{\equiv}N \rightarrow RCH{=}NR' \rightarrow RCH{=}O} \qquad (1)$$

the oldest variations of this potentially attractive synthetic route is the Stephen reaction.[3] It is usually limited to reactions involving aromatic nitriles and is sometimes undependable.[4] Other methods employ various metal hydrides as reducing agents such as lithium trialkoxyaluminohydrides,[5] sodium dialkylaluminohydrides,[6,7] and diisobutylaluminum hydride.[8] These reagents, while generally useful, are strong reducing agents which must be used wiith caution to prevent over reduction or reduction of other functional groups present.

We have studied an alternative general approach for the conversion of the nitrile functionality to the formyl group in which the nitrile function is selectively "activated" prior to reduction. Nitriles may be alkylated to form electron-deficient *N*-alkylnitrilium ions which are much more susceptible to nucleophilic attack at carbon than are their parent nitriles.[9,10] For example, although nitriles themselves resist reduction by sodium borohydride, this reagent completely reduces the derived *N*-alkylnitrilium ions to the corresponding secondary amines in high yields.[11,12]

Our choice of a mild reducing agent for nitrilium ions was triethylsilane. Organosilicon hydrides are able to effect the reduction of a wide variety of carbocations by selective transfer of hydride from silicon to electron-deficient carbon.[13] Under the proper conditions, organosilicon hydrides are such mild reducing agents that neutral species are not reduced by them and even unusually stable car-

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Table I. Reduction of Nitrilium Ions Derived from Triethyloxonium Tetrafluoroborate Alkylation of Nitriles

nitrile	aldehyde product	% yield[a]
1-pentanonitrile	pentanal	71[b]
2-methylpropanonitrile	2-methylpropanal	85[b]
2,2-dimethylpropanonitrile	2,2-dimethylpropanal	61[b]
1-cyanoadamantane	1-formyladamantane	83[b]
cyanocyclopropane	formylcyclopropane	79[b]
1-carbethoxy-1-cyanocyclopropane	1-carbethoxy-1-formylcyclopropane	[c]
3-phenylpropenonitrile	3-phenylpropenal	54
phenylethanonitrile	phenylethanal	41[b,d]
benzonitrile	benzaldehyde	90[b]
2-carbethoxybenzonitrile	2-carbethoxybenzaldehyde	0
4-methylbenzonitrile	4-methylbenzaldehyde	92
4-methoxybenzonitrile	4-methoxybenzaldehyde	85
4-chlorobenzonitrile	4-chlorobenzaldehyde	61
4-nitrobenzonitrile	4-nitrobenzaldehyde	21
4-acetobenzonitrile	4-acetobenzaldehyde	0[d]
4-formylbenzonitrile	terephthaldehyde	0[d]
1,4-dicyanobenzonitrile[e]	4-formylbenzonitrile terephthaldehyde	60 7
1-naphthonitrile	1-naphthaldehyde	84[b]

[a] Unless otherwise stated, 2 equiv of $Et_3O^+BF_4^-$ and 1.2 equiv of Et_3SiH were used and material balance was accounted for in recovered nitrile. [b] Yield of isolated 2,4-dinitrophenylhydrazone derivative. [c] Trace of aldehyde by VPC; 92% recovery of nitrile. [d] Polymer formed. [e] 5 equiv of $Et_3O^+BF_4^-$ and 2.25 equiv of Et_3SiH used.

bocations are reduced only slowly or not at all.[14] As anticipated, we have found that triethylsilane does efficiently reduce *N*-alkylnitrilium ions to *N*-alkylaldimines. Subsequent hydrolysis yields the corresponding aldehydes (eq 2).[15]

$$RC{\equiv}N + R'X \longrightarrow RC\overset{+}{\equiv}NR'\ X^- \xrightarrow{Et_3SiH} RCH{=}NR' \xrightarrow{H_2O} RCH{=}O \qquad (2)$$

Results and Discussion

The direct N-alkylation of nitriles to form *N*-alkylnitrilium ions has been effected in a variety of ways, some of which are more suitable to convenient synthetic applications than others.[11,12,16-30] For reasons of economy, availability, and safety we chose Meerwein's triethyloxonium tetrafluoroborate[31] as the alkylating agent in our initial studies.

Nitrilium Salts from Nitriles and Triethyloxonium Tetrafluoroborate. A solution of *N*-ethylnitrilium tetrafluoroborate was prepared following the method of Borch[11] by holding 1 equiv of nitrile and 2 equiv of the oxonium salt in dichloromethane at reflux for 3–4 days. The resulting solution was then rapidly added at room temperature to a slight excess (~10–20 mol%) of triethylsilane dissolved in dichloromethane.[32] Stirring was continued for 0.5–5 h. Addition of water, followed either by steam distillation or heating for 1 h, afforded aldehyde products (Table I). Addition of solid anhydrous potassium carbonate instead of water to the reduced nitrilium ion solutions yielded *N*-ethylaldimines.

The only volatile silicon product observed was triethylfluorosilane. It did not interfere with product isolation. Even when a large (2- to 3-fold) excess of triethylsilane was used, the product yields were not affected. Under these conditions, unreacted excess triethylsilane could be recovered.

Solutions of some of the more reactive nitrilium ions, such as those derived from unhindered alkylnitriles or 4-nitrobenzonitrile, refluxed vigorously when added to triethylsilane. Most reductions appeared to be complete within 1 h. An exception to this was the behavior of the *N*-ethylnitrilium ion derived from 1-cyanoadamantane. Aqueous quenching 1 h after addition of the nitrilium solution to the triethylsilane produced a 35% yield of 1-formyladamantane together with a 47% yield of the nitrilium salt hydrolysis product, *N*-ethyl-1-adamantanecarboxamide. A total reduction time of 5 h at reflux was required to produce the aldehyde in the yield shown in Table I. Steric hindrance in this nitrile presumably slows down the rate of hydride transfer to the nitrilium ion.

Not surprisingly, 4-formylbenzonitrile and 4-acetobenzonitrile gave only dark, polymeric material when subjected to the reaction conditions.[33,34] Phenylethanonitrile also yielded a small amount of polymeric material in addition to aldehyde product. In the majority of cases summarized in Table I, however, the remainder of the reactant not converted into aldehyde product could be accounted for as recovered nitrile. This was somewhat unexpected, for if the initial conversion to nitrilium ion were complete, then the only byproducts expected upon workup would be *N*-ethylcarboxamides derived from the hydrolysis of any *N*-ethylnitrilium ions not reduced by triethylsilane.[16]

In order to clarify this point, a sample of *N*-ethylbenzonitrilium tetrafluoroborate was prepared, isolated, and purified.[16] Subsequent reduction of this salt by addition to triethylsilane in dichloromethane produced a quantitative yield of benzaldehyde upon hydrolysis and workup. It thus seems that variations in the relative amounts of aldehyde product and recovered nitrile are best understood in terms of the rather slow establishment of the equilibrium position of eq 3. The comparative yields

$$RC{\equiv}N + Et_3O^+BF_4^- \rightleftarrows RC\overset{+}{\equiv}NEt\ BF_4^- + Et_2O \qquad (3)$$

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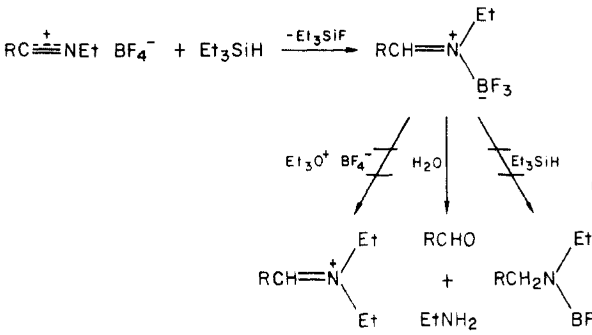
of aldehyde products obtained from 4-methyl- and 4-nitrobenzonitrile (Table I) reflect the different equilibrium positions of the respective alkylations. 1-Carbethoxy-1-cyanocyclopropane is probably not alkylated appreciably under these conditions. It is also of interest to note that even when 5 equiv of triethyloxonium salt were used in conjunction with the reduction of 1,4-dicyanobenzene, only a 7% yield of the doubly reduced product terephthaldehyde was obtained. The major product obtained in this experiment was the monoreduction product 4-cyanobenzaldehyde (60%), with the remainder being recovered starting material.

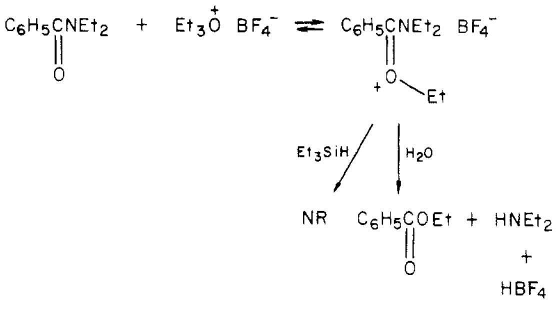
Although we did not explore this possibility, it seems reasonable that the alkylation equilibrium might be shifted more favorably by the use of increased amounts of oxonium salt.[35] The 100 mol % excess of triethyloxonium salt which was used did not appear to interfere with the reduction step either by competing with nitrilium ion as a hydride recipient[36] or by alkylating the aldimine intermediate to form an *N*,*N*-diethylimmonium ion. The only amine product observed after hydrolysis was ethylamine. The aldimine intermediates must exist as BF_3 adducts prior to hydrolysis.[37] Because such adducts should resemble protonated imines in having very little aminocarbenium ion character,[38] it is not surprising that further hydride transfer to give *N*-ethyl amine products does not occur (eq 4).[39]



(4)

Reagents such as lithium triethoxyaluminohydride,[40,41] sodium diisobutylaluminohydride,[6] and diisobutylaluminum hydride[8,42] cause the reduction of either nitriles or *N*,*N*-dialkylamides to aldehydes under essentially identical reaction conditions. In order to compare the selectivity of the present method to that of others, *N*,*N*-diethylbenzamide was subjected to the same reaction conditions as were the nitriles in Table I. The only product obtained was ethyl benzoate (84%); no trace of benzaldehyde was seen.

This result is understandable if the resonance-stabilized cation which results from *O*-alkylation of the amide[43] has so little carbenium ion character that it will not act as a receipient of hydride from triethylsilane. Such cations are known to undergo hydrolysis to esters (eq 5).[44] It is noteworthy that this same cation does undergo complete reduction to diethylbenzylamine when treated with $NaBH_4$ in ethanol.[45]



(5)

Attempted Reduction of BF_3–Nitrile Complexes. Because of the apparent slow and sometimes incomplete conversion of different nitriles into *N*-ethylnitrilium ions by the action of triethyloxonium tetrafluoroborate, several alternative methods for enhancing the electrophilic character of the nitrile carbon were explored. Boron trifluoride complexes of aldehydes and ketones are known to undergo rapid reduction by organosilicon hydrides.[46] Boron trifluoride complexes of nitriles are readily formed, are well characterized,[47] and appear to be more susceptible to nucleophilic attack at the nitrile carbon than are the parent nitriles.[48] For those reasons, reduction of such complexes by triethylsilane seemed worth investigating (eq 6).

$$RC\equiv N + BF_3 \rightarrow RC\equiv N^+{-}BF_3^- \xrightarrow{Et_3SiH} RCH{=}NBF_2 + Et_3SiF \quad (6)$$

Introduction of boron trifluoride gas into a dichloromethane solution of benzonitrile resulted in the immediate formation of the boron trifluoride–benzonitrile complex.[49] Complex formation was verified by the ca. 0.25-ppm downfield shift of the aromatic proton signals in the NMR spectrum of the solution after admission of the Lewis acid. However, addition of triethylsilane to the solution of nitrile–Lewis acid complex did *not* result in reduction as hoped for (eq 6). Even after 4 days, aqueous workup of the reaction mixture yielded only recovered nitrile (NMR and VPC analyses). The reaction was rerun in a pressure vessel maintained at 200 °C overnight, but again only recovered benzonitrile was obtained. From these studies it was concluded that boron trifluoride–nitrile complexes are not sufficiently electrophilic to act as recipients of hydride from the very weakly nucleophilic organosilicon hydrides.

Nitrilium Salts from Nitrile–$FeCl_3$ Complexes and Isopropyl Chloride. A number of years ago, Meerwein and co-workers reported a rather simple and direct synthesis of *N*-alkylnitrilium tetrachloroferrate salts through the reaction of nitrile–$FeCl_3$ complexes with excess amounts of alkyl chlorides.[16] As the successful use of this method has been reported by others,[26,50] we investigated this approach as a means of preparing nitrilium ions for subsequent reduction to aldimines by organosilicon hydrides.

Although *N*-*tert*-butylnitrilium tetrachloroferrate salts are formed rapidly and in high yield from the interaction

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[35] Attempts to shift this equilibrium (eq 3) to the right by removal of diethyl ether under mild conditions were not successful.

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Table II. Reduction of Nitrilium Ions Derived from Alkylation of Nitriles by Isopropyl Chloride-Iron(III) Chloride

nitrile	aldehyde product	% yield[a]
1-cyanoadamantane	1-formyladamantane	91,[b] 93[c]
cyanocyclopropane	formylcyclopropane	77,[b] 100[c]
1-carbethoxy-1-cyanocyclopropane	1-carbethoxy-1-formylcyclopropane	53[d]
3-phenylpropenonitrile	3-phenylpropenal	56
benzonitrile	benzaldehyde	87,[c,e] 92[c]
2-carbethoxybenzonitrile	2-carbethoxybenzaldehyde	42[c]
4-methylbenzonitrile	4-methylbenzaldehyde	88,[c,e] 87[c]
4-methoxybenzonitrile	4-methoxybenzaldehyde	57,[c,e] 64[c]
4-chlorobenzonitrile	4-chlorobenzaldehyde	53,[c,e] 60[c,f]
4-nitrobenzonitrile	4-nitrobenzaldehyde	97,[e] 94
4-acetobenzonitrile	4-acetobenzaldehyde	[g]
1,4-dicyanobenzene	4-formylbenzonitrile	0,[e,h] 19,[c,h] 0,[c,i] 0[c,j]
	terephthaldehyde	0,[e,h] 1,[c,h] 78,[c,i] 78[c,j]

[a] Unless otherwise stated, method B (see text) was used with 1.0 equiv of $FeCl_3$, excess isopropyl chloride, and 1.25 equiv of Et_3SiH; material balance accounted for in recovered nitrile. [b] Yield of isolated 2,4-dinitrophenyl hydrazone derivative. [c] Yield by VPC using internal standard. [d] Tri-*n*-hexylsilane used as reducing agent. [e] Method A used (see text). [f] Obtained 24% recovered nitrile and 16% 4-chlorobenzoic acid. [g] Only polymer obtained. [h] 1 equiv of $FeCl_3$, 1.25 equiv of Et_3SiH. [i] 2 equiv of $FeCl_3$, 3 equiv of Et_3SiH. [j] $FeCl_3$ increased to 2.4 equiv.

of nitrile–$FeCl_3$ complexes with excess *tert*-butyl chloride, under our reaction conditions in dichloromethane they tended to undergo decomposition. For that reason, we chose to use the more stable *N*-isopropylnitrilium salts. In our initial studies, the nitrilium salts were produced by heating equimolar quantities of the nitrile and anhydrous iron(III) chloride in a large (7- to-10-fold) excess of isopropyl chloride. The alkylation reactions were in most cases complete within the first hour,[16] but the reaction mixtures were allowed to remain at reflux overnight to assure complete alkylation throughout the entire series of reactants examined (eq 7 and 8). The excess isopropyl

$$\mathrm{RC{\equiv}N + FeCl_3 \rightarrow RC{\equiv}N^+{-}\bar{F}eCl_3} \quad (7)$$

$$\mathrm{RC{\equiv}N^+{-}\bar{F}eCl_3 + (CH_3)_2CHCl \rightarrow RC{\equiv}N^+{-}CH(CH_3)_2\ \bar{F}eCl_4} \quad (8)$$

$$\mathrm{RC{\equiv}N^+{-}CH(CH_3)_2\ \bar{F}eCl_4 + Et_3SiH \rightarrow RCH{=}NCH(CH_3)_2 + Et_3SiCl + FeCl_3} \quad (9)$$

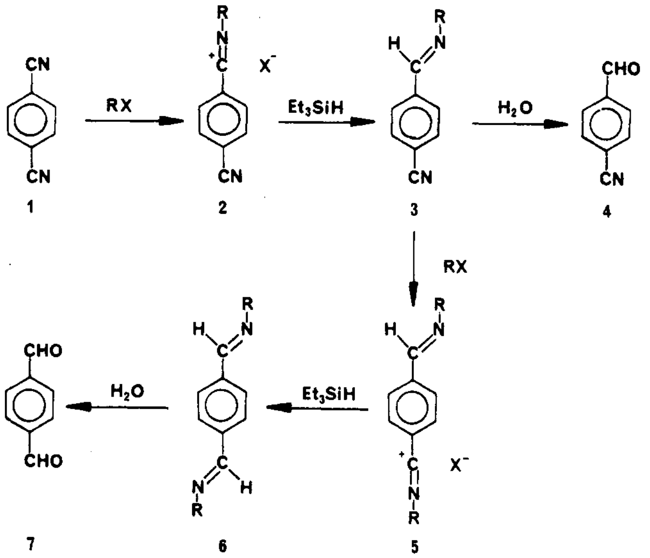
$$\mathrm{RCH{=}NCH(CH_3)_2 \xrightarrow{H_2O} RCHO + (CH_3)_2CHNH_2} \quad (10)$$

$$\mathrm{Et_3SiCl \xrightarrow{H_2O} 0.5(Et_3Si)_2O} \quad (11)$$

chloride was then removed by rotary evaporation, the residual *N*-isopropylnitrilium tetrachloroferrate was dissolved in dichloromethane, and this solution was added to a dichloromethane solution of 1.3 equiv of triethylsilane (eq 9). Following a 1–2-h period of reflux to assure complete reduction, the aldehyde was isolated by steam distillation from the reaction mixture (eq 10). Hexaethyldisiloxane was the silicon-containing product (eq 11).

The yields of aldehyde products obtained by using this technique, denoted method A, are shown in Table II. In order to avoid the necessity of first removing excess isopropyl chloride and then dissolving the residual nitrilium salt in dichloromethane, a variation of this technique was used in which the dichloromethane solvent was simply added at the beginning of the alkylation reaction and the excess isopropyl chloride was allowed to remain in the reaction mixture. This variation, denoted method B in Table II, produced yields of aldehydes which were essentially the same as those obtained by using the less convenient method A.

Scheme I

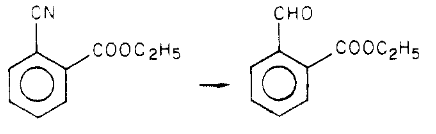


Comparison of Alkylation Methods. Comparison of the results summarized in Tables I and II indicates that, as expected, the isopropyl chloride–iron(III) chloride reagent effects a more rapid and complete alkylation of many nitriles than does triethyloxonium tetrafluoroborate. Use of the former method yielded 4-nitrobenzaldehyde in 97% yield from 4-nitrobenzonitrile, whereas use of triethyloxonium tetrafluoroborate yielded the aldehyde in only 21% yield. The smaller yield in the latter case is presumably a reflection of incomplete alkylation (eq 3).

Particularly illustrative of the difference in the alkylating abilities of the two systems is the behavior of 1,4-dicyanobenzene (**1**, Scheme I). Treatment of this compound with 5 equiv of triethyloxonium tetrafluoroborate in dichloromethane resulted in the formation of a tan solid which dissolved upon addition of triethylsilane to the solution. Aqueous workup yielded only 7% of completely reduced terephthaldehyde product (**7**), together with 60% monoreduction product 4-cyanobenzaldehyde (**4**) and 33% recovered 1,4-dicyanobenzene. From this it is concluded that the intermediate precipitate was most likely the mononitrilium ion **2**, which redissolved upon reduction to the cyano imine **3**. The cyano imine was apparently not alkylated very rapidly by the triethyloxonium tetrafluoroborate to form ion **5**, the precursor to **6** and **7**.

Treatment of **1** with only 1 equiv of iron(III) chloride and excess isopropyl chloride yielded, after reduction and aqueous workup, 19% **4**, 1% **7**, and 80% recovered starting **1**. Quite different results were obtained when the amount of iron(III) chloride used was increased from 1 to 2 equiv. Under these conditions, no 4-cyanobenzaldehyde (**4**) was obtained; the only product besides recovered **1** (27%) was terephthaldehyde (**7**), formed in 73% yield. Increasing the amount of iron(III) chloride to 2.4 equiv raised the yield of **7** to 78%. Those results strongly suggest that, in contrast to the weaker alkylating agent triethyloxonium tetrafluoroborate, iron(III) chloride in combination with isopropyl chloride not only alkylates the relatively nonnucleophilic 1,4-dicyanobenzene to form **2** but also rapidly alkylates the somewhat more nucleophilic nitrile nitrogen of cyanoimine **3** as it is formed to give nitrilium ion **5**.

The behavior of both 2-carbethoxybenzonitrile and 1-carbethoxy-1-cyanocyclopropane was of interest because of the opportunity for a variety of complicating intramolecular interactions to occur between the carbethoxy and nitrile groups under the alkylation–reduction conditions. Under conditions of the Stephen reaction ($SnCl_2$, HCl), 2-carbethoxybenzonitrile (**8**) is reported to give 2-carbethoxybenzaldehyde (**9**) in only 11% yield (eq 12).[51] When

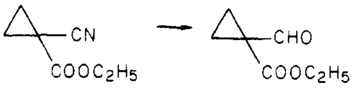


(12)

8 **9**

treated first with triethyloxonium tetrafluoroborate and then triethylsilane, **8** was recovered (92%) and no aldehyde **9** was obtained, probably because the oxonium salt is just not capable of alkylating the nitrile nitrogen of **8**. Use of the isopropyl chloride–iron(III) chloride combination in place of the oxonium salt led to a moderate yield (42%) of aldehyde **9** following workup.

The conversion of 1-carbethoxy-1-cyanocyclopropane (**10**) to aldehyde **11** by the alkylation–silane reduction route was judged a particular challenge because the direct reduction of **10** to **11** (eq 13) has not proved possible with



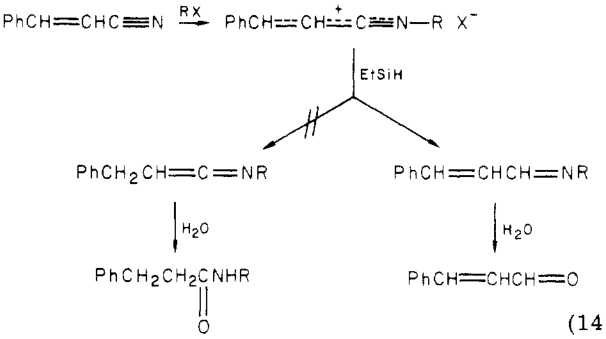
(13)

10 **11**

such commonly used reagents as sodium borohydride, lithium aluminum hydride and some of its alkoxy derivatives, or even diisobutylaluminum hydride.[52] The synthesis of aldehyde **11**, a key intermediate in the synthesis of certain alkaloids, was effected in two steps from nitrile **10** through sodium borohydride reduction of a dihydro-1,3-oxazine intermediate in an overall yield of 39%.[53,54] Attempted alkylation–reduction using triethyloxonium tetrafluoroborate yielded, in our hands, only a 96% recovery of nitrile **10**. However, alkylation using the isopropyl chloride–iron(III) chloride reagent, followed by reaction of the nitrilium ion solution with tri-*n*-hexylsilane in dichloromethane, gave, after aqueous workup, a 53% isolated yield of the aldehyde **11**. Tri-*n*-hexylsilane was used in place of triethylsilane because its final reaction product, hexa-*n*-hexyldisiloxane, has a sufficiently low vapor pressure that separation from the relatively volatile aldehyde product was readily accomplished during product workup.

A case where the triethyloxonium tetrafluoroborate alkylation may be preferred over the use of isopropyl chloride–iron(III) chloride is that in which a polyfunctional substrate may offer a site at which iron(III) chloride may strongly coordinate. A specific example of this is seen in the good yield (85%) of 4-methoxybenzaldehyde obtained from 4-methoxybenzonitrile by using triethyloxonium tetrafluoroborate compared to the relatively lower yields (57–64%) with the combination isopropyl chloride–iron(III) chloride reagent. As the intermediate *N*-alkylnitrilium ion is expected to be quite stable in either case, the lower yield in the latter method probably is caused by complexation of iron(III) chloride at methoxyl oxygen.

It is noteworthy that the α,β-unsaturated nitrilium ions derived from 3-phenylpropenonitrile by either method of alkylation undergo "1,2-addition" to the nitrilium function to yield the α,β-unsaturated aldehyde. The expected product of "1,4-addition", a saturated carboxamide, was not seen (eq 14).



(14)

In summary, it appears that this two-step alkylation–reduction approach to the conversion of nitriles to aldehydes represents a reasonable synthetic alternative to many of the traditional single-step methods. The reaction conditions are mild. Neither temperatures above the boiling point of dichloromethane (41 °C) nor careful regulation of temperature during the reduction step is necessary. Overreduction to amines is not a problem, even when an excess of the mild organosilicon hydride reducing agent is used. Use of either of the two alkylation methods investigated provides reaction conditions which are mild enough that even relatively unstable aldehydes such as 1-formyladamantane and formylcyclopropane are formed and survive without difficulty.

Experimental Section

General Methods. Proton nuclear magnetic resonance spectra were obtained on a Varian T-60A instrument, using tetramethylsilane as an internal standard. Infrared spectra were run by using either a Perkin-Elmer 137 or 621 spectrophotometer. Vapor-phase chromatographic analyses were conducted either on a Varian Aerograph 90-P instrument or on a Hewlett-Packard 5722A instrument equipped with an electronic integrating recorder. Melting points (Thomas-Hoover apparatus) and boiling points are uncorrected.

Reagent-grade dichloromethane was purified before use.[55] Triethylsilane (Petrarch or PCR) was distilled prior to use. Tri-*n*-hexylsilane (PCR) was used as received. Triethyloxonium tetrafluoroborate was prepared by the method of Meerwein.[31] With the exceptions noted, all nitriles used were commercially available and were analyzed for purity by VPC. 1-Naphthonitrile was prepared from 1-bromonaphthalene.[56] 1-Carbethoxy-1-cyanocyclopropane was prepared by the reaction of ethyl cyanoacetate and 1,2-dibromoethane.[57] 2-Carbethoxybenzonitrile, prepared by the method of Carpino,[58] was kindly supplied by Dr. R. J. Spangler.

All glassware was oven dried, assembled while hot, and allowed to cool under a stream of dry nitrogen. Products were identified by their NMR and IR spectra, by their VPC retention times, and/or by comparison of the melting points of their 2,4-dinitrophenylhydrazone derivatives with literature values.

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Alkylations Using Triethyloxonium Tetrafluoroborate. The following procedure is representative of that normally used for the synthesis of most compounds listed in Table I.

1-Naphthaldehyde. Into a 50-mL flask equipped with a reflux condenser and nitrogen bubbler was placed a solution of 1.84 g (12.0 mmol) of 1-naphthonitrile and 4.70 g (24.8 mmol) of triethyloxonium tetrafluoroborate in 20 mL of dichloromethane. The lemon-yellow nitrilium ion solution was held at gentle reflux under nitrogen for 3 days, after which it was added with magnetic stirring over a 1-min period to a solution of 1.64 g (14.2 mmol) of triethylsilane in 10 mL of dichloromethane contained in a 250-mL three-necked flask. The reaction mixture was held at gentle reflux for 1 h. The flask was then fitted for steam distillation and 10 mL of water was added to the flask contents. Steam was introduced and distillation was continued until ca. 200 mL of distillate was collected. The organic layer of the distillate was separated and the aqueous layer was extracted twice with 40-mL portions of dichloromethane and twice with 40-mL portions of diethyl ether. The extracts were combined with the original organic layer and dried (Na_2SO_4). Removal of volatile materials at reduced pressure gave 1.85 g (99%) of pale-yellow oil which was essentially pure 1-naphthaldehyde by VPC analysis (6.4 mm × 1.5 m 10% Apiezon L on 60/80 Chromosorb W, 225 °C). The oil was stirred with 65 mL of 0.2 M 2,4-dinitrophenylhydrazine reagent[59] to give 3.40 g (84%) of the 2,4-dinitrophenylhydrazone of 1-naphthaldehyde. The bright yellow crystals (from EtOH/EtOAc) had mp 259–260 °C (lit.[60] mp 254 °C).

1-Formyladamantane. The following procedure for the preparation of this compound represents the most rigorous conditions which we found necessary to use. A solution of 1.36 g (8.45 mmol) of 1-cyanoadamantane and 3.21 g (16.9 mmol) of freshly prepared triethyloxonium tetrafluoroborate in 15 mL of dichloromethane was held at gentle reflux for 5 days under dry nitrogen in a 100-mL flask equipped with a reflux condenser. A dry 250-mL flask equipped with an addition funnel and a reflux condenser with Drierite tube was charged with 1.16 g (10 mmol) of triethylsilane dissolved in 10 mL of dichloromethane. The colorless nitrilium ion solution was then added rapidly to the magnetically stirred silane solution over a 1-min period. Stirring was continued at room temperature for 1 h, at which time VPC analysis (Apiezon L, 225 °C) of an aliquot of the reaction mixture quenched with water indicated incomplete reduction. The mixture was therefore held at reflux for an additional 4 h before it was cooled and 10 mL of water was added. The volatile organic material was then steam distilled directly from the reaction flask. The aqueous layer of the steam distillate was extracted with 20 mL of dichloromethane. The combined organic portions were washed once with 25 mL of saturated aqueous sodium bicarbonate solution and once with 25 mL of brine. After the solution was dried ($MgSO_4$) and the volatile materials were removed at reduced pressure, there was obtained 1.31 g of colorless oil which crystallized upon cooling. VPC and IR analyses showed this to contain 89% 1-formyladamantane, 7% 1-cyanoadamantane, and 4% *N*-ethyl-1-adamantanecarboxamide. The overall yield of aldehyde was thus 83%. The 2,4-DNPH derivative had mp 227–228 °C (lit.[61] mp 225–226 °C).

Alkylations Using Isopropyl Chloride–Iron(III) Chloride. Method A. 4-Nitrobenzaldehyde. A solution of 0.87 g (5.9 mmol) of 4-nitrobenzonitrile in 30 mL of isopropyl chloride was placed in a 100-mL round-bottomed flask which was equipped with a magnetic stirrer, reflux condenser, and nitrogen bubbler. An ice bath was raised around the reaction flask and 1.0 g (5.9 mmol) of iron(III) chloride was added to the reaction mixture with stirring. The ice bath was removed and the black solution was kept at reflux overnight. The excess isopropyl chloride was removed by rotary evaporation and the residue was dissolved in 15 mL of dichloromethane. The nitrilium salt solution was placed in an addition funnel attached to a 100-mL flask equipped with a reflux condenser and containing a solution of 1.2 mL (7.5 mmol) of triethylsilane in 5 mL of dichloromethane. The nitrilium salt solution was added to the stirred solution in the flask over a 1-min period, causing the mixture to spontaneously reflux for a short while. The mixture was then warmed to maintain reflux for 1 h. At that time, 10 mL of water was added and the apparatus was equipped for steam distillation. The organic portion of the distillate was separated, washed, and dried in the usual manner before volatile components were removed by rotary evaporation to yield 1.65 g of solid residue. Sublimation [50 °C (0.2 torr)] of the residue produced 0.86 g (97%) of product which was shown to be pure 4-nitrobenzaldehyde by NMR and VPC (6.4 mm × 1.8 m glass 10% Carbowax 20M on Anakrom ABS, 80/90, 190 °C) analyses.

Method B. 1-Carbethoxy-1-formylcyclopropane (11). A mixture of 3.35 g (23.9 mmol) of 1-carbethoxy-1-cyanocyclopropane (**10**), 30 mL of isopropyl chloride, 75 mL of dichloromethane, and 5.0 g (29.7 mmol) of anhydrous iron(III) chloride was held at reflux with stirring under nitrogen overnight. The resulting black nitrilium ion solution was then transferred to an addition funnel and added with stirring over a 1-min period to a solution of 7.1 mL (36 mmol) of tri-*n*-hexylsilane in 25 mL of dichloromethane. The reaction mixture was held at reflux for 1 h before 50 mL of water was added and the aqueous mixture held again at reflux for 1 h. The cooled reaction mixture was transferred to a separatory funnel and the organic layer was washed and dried before removal of volatile components. Kugelrohr distillation of the organic residue afforded 1.79 g (53%) of aldehyde **11** product, pure by VPC (Carbowax, 140 °C) and with IR and ^1H NMR spectra consistent with those of a known sample:[52,53] IR 2870, 1725, 1765 cm^{-1}; ^1H NMR (CCl_4) δ 1.30 (t, 3 H), 1.52 (s, 4 H), 4.23 (q, 2 H), 10.12 (s, 1 H).

Acknowledgment. We thank Dr. R. V. Stevens for kindly providing us with information on the synthesis and spectral properties of compounds **10** and **11** and Dr. R. J. Spangler for providing us with information concerning the preparation and spectral properties of compounds **8** and **9** in addition to a generous sample of nitrile **8**. Support by The University of Toledo Faculty Research Awards and Fellowships Program is appreciated.

Registry No. 1-Pentanonitrile, 628-73-9; 2-methylpropanonitrile, 625-28-5; 2,2-dimethylpropanonitrile, 3302-16-7; 1-cyanoadamantane, 23074-42-2; cyanocyclopropane, 5500-21-0; 1-carbethoxy-1-cyanocyclopropane, 1558-81-2; 3-phenylpropenonitrile, 75881-14-0; phenylethanonitrile, 645-59-0; benzonitrile, 100-47-0; 2-carbethoxybenzonitrile, 6525-45-7; 4-methylbenzonitrile, 104-85-8; 4-methoxybenzonitrile, 874-90-8; 4-chlorobenzonitrile, 623-03-0; 4-nitrobenzonitrile, 619-72-7; 4-acetobenzonitrile, 1443-80-7; 4-formylbenzonitrile, 105-07-7; 1-naphthonitrile, 86-53-3; 1,4-dicyanobenzene, 623-26-7; pentanal, 110-62-3; pentanal 2,4-DNP, 2057-84-3; 2-methylpropanal, 78-84-2; 2-methylpropanal 2,4-DNP, 2057-82-1; 2,2-dimethylpropanal, 630-19-3; 2,2-dimethylpropanal 2,4-DNP, 13608-36-1; 1-formyladamantane, 2094-74-8; 1-formyladamantane 2,4-DNP, 18220-81-0; formylcyclopropane, 1489-69-6; formylcyclopropane 2,4-DNP, 36873-36-6; 1-carbethoxy-1-formylcyclopropane, 33329-70-3; 3-phenylpropenal, 104-55-2; phenylethanal, 122-78-1; phenylethanal 2,4-DNP, 2074-04-6; benzaldehyde, 100-52-7; benzaldehyde 2,4-DNP, 1157-84-2; 2-carbethoxybenzaldehyde, 34046-43-0; 4-methylbenzaldehyde, 104-87-0; 4-methoxybenzaldehyde, 123-11-5; 4-chlorobenzaldehyde, 104-88-1; 4-nitrobenzaldehyde, 555-16-8; 4-acetobenzaldehyde, 3457-45-2; terephthaldehyde, 623-27-8; 1-naphthaldehyde, 66-77-3; 1-naphthaldehyde 2,4-DNP, 1773-51-9; triethyloxonium tetrafluoroborate, 368-39-8; triethylsilane, 617-86-7; isopropyl chloride, 75-29-6; iron(III) chloride, 7705-08-0; tri-*n*-hexylsilane, 2929-52-4.

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