Selective Dehalogenation of α-Bromo Sulfoxides by Dicobalt Octacarbonyl on Alumina

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There has been considerable interest in recent years in the use of metal carbonyls, deposited on refractory oxides, for effecting various organic transformations.[2] In some cases, the overall reactions are the same as those observed under homogeneous conditions, except that the reaction conditions are milder and workup is simple. However, in several instances, the heterogeneous process is formally different than the homogeneous one. For example, while triiron dodecacarbonyl on alumina[3,4] or under homogeneous conditions, and dicobalt octacarbonyl on alumina, convert nitroarenes to anilines under gentle conditions, the homogeneous reaction using $Co_2(CO)_8$ affords azobenzenes.[5]

$$ArNO_2 + Co_2(CO)_8/Al_2O_3 \text{ or } Fe_3(CO)_{12}/Al_2O_3 \rightarrow ArNH_2$$

$$ArNO_2 \xrightarrow[Co_2(CO)_8]{C_6H_6,\ 80\ °C} ArN{=}NAr$$

Another useful reaction process is dehalogenation. It has been reported that the dehalogenation of α-halo ketones occurs when using molybdenum hexacarbonyl on alumina.[6] It is known that α-bromo sulfoxides[7] undergo dehalogenation and coupling on exposure to $Mo(CO)_6$ in refluxing 1,2-dimethoxyethane, affording thioacetals.[8] We anticipated that, by using milder conditions, treatment of α-bromo sulfoxides with molybdenum hexacarbonyl on alumina would result in the selective removal of the halogen functionality. However, no reaction occurred when $Mo(CO)_6/Al_2O_3$ was stirred with an α-bromo sulfoxide in tetrahydrofuran.

Cobalt carbonyl on alumina proved to be a useful and selective reagent for the debromination of α-bromo sulfoxides. Treatment of an α-bromo sulfoxide with an equimolar amount of cobalt carbonyl on alumina, in hexane at room temperature, affords sulfoxides in excellent yields (Table I). Only when the secondary bromo sulfoxide 1, (R = Ph, R′ = CH_3) was used as the substrate was the yield of 2 less than satisfactory (50%). In no case was any deoxygenated product isolated. A coupled, 1,4-disulfoxide (1:1 ratio of *dl*/meso) was obtained as a low-yield byproduct in the reaction of α-bromoethyl phenyl sulfoxide.

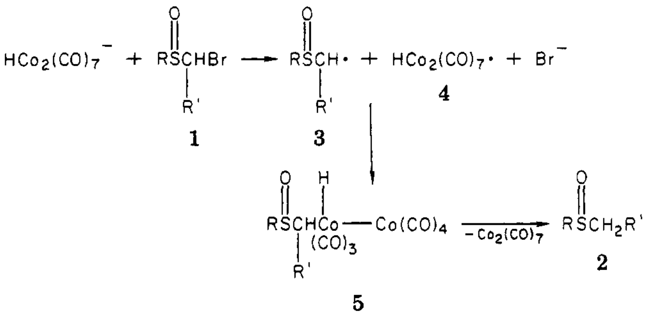
$$\underset{1}{R(O)SCH(R')Br} + Co_2(CO)_8/Al_2O_3 \xrightarrow[RT]{C_6H_{14}} R(O)SCH_2R'$$

Table I. Yields of Sulfoxides from the Reaction of 1 with $Co_2(CO)_8/Al_2O_3$

1, R =, R′ =	yield of 2,[a] %	mp/bp, (mmHg), °C	mp/bp (mmHg), lit., °C
Ph, H	80[b]	33-34	29.5[d]
p-ClC_6H_4, H	100	46-48	47-48[e]
$PhCH_2$, H	100	53-54	57-58[f]
p-$CH_3C_6H_4$, H	92	42-43	42-43[e]
β-naphthyl, H	100	102-104	104-105[g]
Ph, CH_3	50[c]	140 (15)	101-102 (0.01)[f]

[a] Products were identified by comparison of spectral data data (IR, NMR (^1H, ^{13}C), MS) with those for authentic materials. [b] $PhSOCH_2CH_2SOPh$ was isolated in 7% yield. [c] An unidentified byproduct was also formed. [d] Reference 10. [e] Reference 11. [f] Reference 12. [g] Reference 13.

Scheme I



Methyl phenyl sulfoxide was obtained from α-chloromethyl phenyl sulfoxide and $Co_2(CO)_8/Al_2O_3$ albeit in only 13% yield. The yield increased to 23% when the reaction was run in the presence of ultrasonic irradiation.[9] Still, at room temperature, this dehalogenation procedure is not useful for α-chloro sulfoxides.

A possible mechanism for the dehalogenation reaction is indicated in Scheme I. We previously proposed that $HCo_2(CO)_7^-Al(O^-)_x^+$ was generated by interaction of cobalt carbonyl with hydroxyl groups present on the alumina surface.[5] Electron-transfer reaction of the anionic cobalt hydride with 1 would give the radicals 3 and 4 and bromide ion. Coupling of 3 and 4 would give the cobalt hydride 5, which on reductive elimination affords the product 2. The formation of $PhSOCH_2CH_2SOPh$ as a low-yield byproduct (footnote b, Table I) may be due to self-coupling of 3 (R = Ph, R′ = H).

In conclusion, the dehalogenation of α-bromo sulfoxides can be attained, selectively and in fine yields, by $Co_2(CO)_8/Al_2O_3$.

Experimental Section

General Procedure. Alumina (20 g, Fisher adsorption, 80-200 mesh) was dried overnight at 150 °C and 3-6 mmHg pressure. The cooled adsorbent was then admixed with hexane (65-75 mL) containing $Co_2(CO)_8$ (3.0 mmol). The reaction mixture was stirred for 2 h during which time the alumina turned red. The α-halo sulfoxide (3.0 mmol) was then added, and the reaction mixture was stirred overnight at room temperature under a nitrogen atmosphere. The solution was filtered, the solid was washed with ether and ethyl acetate, and the washings were added to the filtrate. Rotary evaporation of the filtrate usually gave a pure product. In the event that the product was impure, it could be purified by either silica gel column chromatography (1:1 hexane-ether), preparative thin-layer chromatography (4:1 ether-hexane), or distillation.

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Registry No. 1 (R = Ph; R^1 = H), 31268-20-9; 1 (R = p-ClC_6H_4; R^1 = H), 38325-81-4; 1 (R = $PhCH_2$; R^1 = H), 26910-36-1; 1 (R = p-$CH_3C_6H_4$; R^1 = H), 26910-35-0; 1 (R = β-naphthyl; R^1 = H), 87174-67-2; 1 (R = Ph; R^1 = CH_3), 26910-34-9; $Co_2(CO)_8$, 10210-68-1; Al_2O_3, 1344-28-1; α-chloromethyl phenyl sulfoxide, 7205-94-9.

Direct Acylamination of Pyridine 1-Oxide with *N*-Phenylarenimidoyl Chlorides and Fluorides

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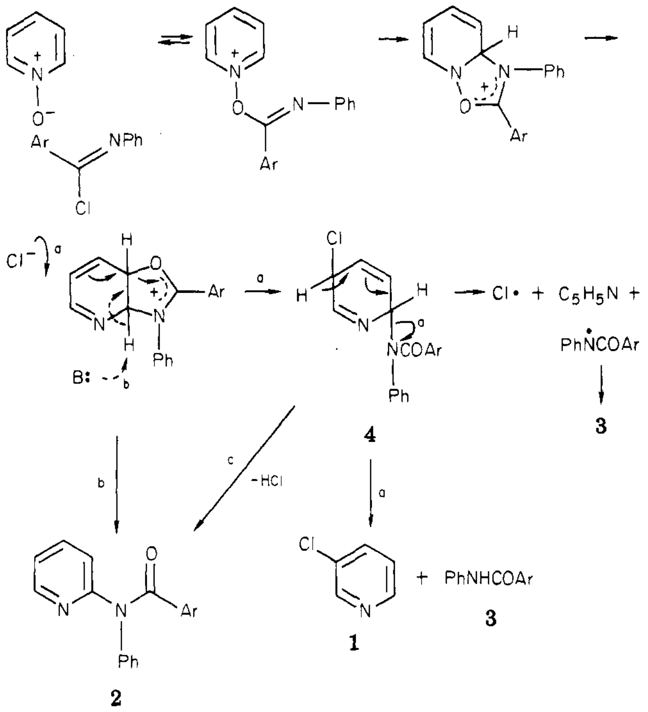
Pyridine 1-oxide reacts with *N*-phenylbenzimidoyl chloride to give 2-(*N*-benzoylanilino)pyridine (2) and 3-chloropyridine (1).[1] When substituted *N*-phenylbenzimidoyl chlorides are used, the yields of acylaminated pyridine and of 1 depend on the substituents present in both the anilide[1] and the acyl[2] moieties of the imidoyl chloride. Preliminary results[2] of the reaction of pyridine 1-oxide with some *N*-phenylarenimidoyl chlorides suggested that electron-donating substituents in the para position favored the formation of 2-(acylamino)pyridine and hindered that of 3-chloropyridine. Electron-accepting substituents suppressed both reactions.

A multistep pathway has been proposed for the reactions involved,[3] and the electrical properties of the substituents in the imidoyl chloride could influence each of these in different ways. This prompted us to study the influence of substituents in *N*-phenylarenimidoyl chlorides systematically in order to see if any regularities could be observed and to select the best reagent for the preparation of one of the two products in high yield. We also report the reaction with *N*-phenylbenzimidoyl fluoride, which was found not to produce any 3-fluoropyridine.

Results and Discussion

The products of the reactions of 16 *N*-phenylarenimidoyl chlorides with pyridine 1-oxide are summarized in Table I. It can be seen that, as anticipated, there appears to be no simple relationship between the electronic properties of the substituents and the yields of the 2-(acylanilino)pyridine 2 and 3-chloropyridine (1). The highest yields of 2 are obtained by using either the *o*- or *p*-toluenimidoyl chloride. The highest yield of 1 is achieved with *N*-phenyl-*m*-nitrobenzimidoyl chloride; in this reaction, and contrary to what is reported with the *p*-nitrobenzimidoyl chloride,[2] a significant amount of 2-[*N*-(*m*-nitrobenzoyl)anilino]pyridine is formed. Electron-withdrawing substituents in the imidoyl chloride should facilitate attack by the *N*-oxide but hinder both the departure of chloride ion and nucleophilic attack by nitrogen onto the pyridine ring. It appears that these processes are delicately balanced with ortho and particularly para substituents in the aroyl portion.

Scheme I



According to the proposed mechanism (Scheme I)[3] for the formation of 3-chloropyridine (1) and the corresponding *N*-aroyl anilide (ArCONHPh) (3), these should be formed simultaneously and, therefore, in equal yields. Table I indicates that 3 is invariably formed in higher yield than 1. Consequently, there must be an additional pathway to 3. By analogy with side-chain acylaminations,[4] we propose that homolysis of 4 may be taking place to give Cl· and $ArCO\dot{N}Ph$. The latter can abstract hydrogen from the solvent or from another substrate or react with Cl· to give ArCON(Cl)Ph which hydrolyzes to 3 on workup. The fate of the pyridine fragment has not been determined. In support of an origin of a least some of 3 from 4 is the fact that if a strong external base is added (e.g., Et_3N or DBU), no 1 or 3 is formed from pyridine 1-oxide and *N*-phenylbenzimidoyl chloride, and the yield of 2 increases appreciably.[5] In addition, the original adduct may also undergo homolysis (for a somewhat related homolysis, see ref 5) to give $ArCO\dot{N}Ph$ and a pyridinyl radical, the latter eventually leading to the tars invariably observed. Similarly, two pathways can lead to 2: base-catalyzed proton abstraction and ring opening of the 2,3-dihydropyridine derivative (path b, Scheme 1) or elimination of HCl from 4 (path c, Scheme I).

To determine whether or not 3-fluoropyridine could be prepared in this way, we studied the reaction of pyridine 1-oxides with *N*-phenylbenzimidoyl fluoride.[6] Pyridine 1-oxide gave 2-(*N*-benzoylanilino)pyridine (2, Ar = Ph, 40%), benzanilide (45%), and pyridine 1-oxide hydrofluoride (41%), but no 3-fluoropyridine. 3-Picoline 1-oxide

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