After venting the noncondensible gases the recovered solution was analyzed by gas–liquid chromatography. For reactions using *tert*-butylethylene, the volatile products (acetone, *tert*-butyl alcohol, and *tert*-butylethylene oxide) were analyzed on a 6-ft 15% FFAP column on Chromosorb P at 80 °C using methylcyclohexane as the internal standard. The products of the oxidation of norbornylene were analyzed on a 6-ft 15% TCEP column on Chromosorb W at 110 °C using *tert*-butylbenzene as the internal standard. The products of dineopentylethylene oxidation were analyzed using a 6-ft 15% TCEP column on Chromosorb W at 125 °C using *n*-tetradecane as the internal standard. GLC on a 6-ft SE-30 column at 200 °C showed that components boiling higher than the epoxides were not present.

A portion of the solution was titrated iodometrically for active oxygen following the procedure of Wibaut.[12]

The nonvolatile polymeric products were not analyzed in detail. Only the oxidation of norbornylene gave significant amounts of polymeric oxygenated products. The cobalt residues were separated from the solution by filtration, washed with organic solvents, and dried in vacuo. The volatile epoxides were separated by preparative GLC and identified by comparison of spectral properties with authentic samples prepared by peracid oxidation of the appropriate olefins.

Acknowledgment. We wish to thank the National Science Foundation for partial financial support of this work.

Registry No.—1, 141-70-8; 2, 4737-48-8; 3, 558-37-2; 4, 2245-30-9; *m*-chloroperbenzoic acid, 937-14-4; norbornylene oxide, 3146-39-2; norbornylene, 498-66-8; triisobutylene, 7756-94-7; 1-*tert*-butyl-2-neopentylpropene, 123-48-8; 2-*tert*-butyl-1-neopentylethylene oxide, 58191-06-3; 1-*tert*-butyl-2-neopentylpropylene oxide, 58191-07-4; Co(acac)$_3$, 21679-46-9; Co(acac)$_2$, 14020-48-7; Co(II)oct, 136-52-7; Co(OAc)$_2$, 71-48-7; Co(OAc)$_3$, 917-69-1; Co(II) nd, 32276-75-8.

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Copper-Catalyzed Oxidation of *o*-Phenylenediamines to *cis,cis*-Mucononitriles

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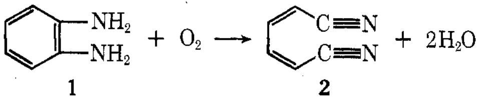
Oxidation of *o*-phenylenediamine (1) with molecular oxygen in the presence of CuCl in pyridine to give *cis,cis*-mucononitrile [(*Z,Z*)-2,4-hexadienedinitrile] was achieved in a high yield by selecting suitable reaction conditions. The molar ratio of 1 to CuCl in the reaction medium should be maintained below 0.5 in order to prevent intermolecular coupling of 1. *o*-Phenylenediamines substituted by electron-donating groups on the benzene ring gave the corresponding *cis,cis*-mucononitriles such as 3-methylmucononitrile, 3,4-dimethylmucononitrile, 3-methoxymucononitrile, and 3-chloromucononitrile, while no mucononitrile was obtained when electron-withdrawing groups were present. From 1,2-naphthalenediamine *o*-cyano-*cis*-cinnamonitrile was obtained. The structures of the products and the reaction mechanism are discussed.

Oxidation of organic compounds, especially phenols and aromatic amines, with molecular oxygen activated by metal salts is a well-established reaction. Oxidative coupling of aniline with oxygen catalyzed by CuCl gives azobenzene.[2] Also *o*-phenylenediamine (1) is oxidized in the presence of ferric chloride[3] to afford 2,3-diaminophenazine or 2-amino-3-oxophenazine in low yields. We have found that the oxidation of 1 can take a course completely different from the above ones by selecting proper reaction conditions; namely the ring cleavage reaction to give *cis,cis*-mucononitrile [(*Z,Z*)-2,4-hexadienedinitrile, 2] in a high yield proceeded smoothly at room temperature and under atmospheric pressure in the presence of CuCl in pyridine. Although 1



1 2

was oxidized to 2 by using a stoichiometric amount of nickel peroxide[4] or lead tetraacetate,[5] the yields were low and the metal salts cannot be reused. In contrast, the oxidation with CuCl gives an excellent yield of 2 and CuCl can be reused. This ring cleavage reaction resembles an enzymatic reaction of an oxygenase in regard to mild reaction conditions and participation of redox metals such as copper or iron.[6] The ring cleavage of pyrocatechol to *cis,cis*-muconic acid with pyrocatecase is a typical example.[7] A preliminary

Table I. Oxidation of 1 to 2 with CuCl in Various Amines[a]

Amine	Yield, %
Pyridine	96
α-Pycoline	57
2,2′-Bipyridyl[b]	29
1,4-Diazabicyclo[2.2.2]octane[b]	38
Triethylamine	5
Quinoline, N,N-dimethylbenzylamine,[b] N,N-dimethylaniline, tri-n-butylamine, morpholine, or 2-hydroxyethylamine	0
Pyridine containing 2% H_2O	96
Pyridine containing 10% H_2O	94
Pyridine containing 20% H_2O	35

[a] 0.01 mol of 1 in 20 ml of amine or acetonitrile was added dropwise in 30 min to 50 ml of amine or acetonitrile solution[b] containing 0.02 mol of CuCl with continuous bubbling of air. [b] 10 g of amine was dissolved in 45 ml of acetonitrile.

Table II. Effect of Diluent in the Oxidation of 1 to 2 with CuCl in Pyridine[a]

Diluent	Yield, %
Acetonitrile	96
Benzene	45
Tetrahydrofuran	20

[a] In 70 ml of diluent 0.06 mol of pyridine and 0.03 mol of CuCl were dissolved and 0.01 mol of 1 in 15 ml of the same solvent as diluent was slowly added with continuous bubbling of air.

account has been reported[8] and details of the reaction are presented in this paper.

Results and Discussion

Cuprous chloride is slightly soluble in pyridine under an inert atmosphere at room temperature, but a mixture of CuCl and pyridine absorbs oxygen with stirring under oxygen atmosphere to give a deep green solution. Exactly 1 mol of oxygen is absorbed per four atoms of copper. From this solution an oxygen complex was precipitated by addition of ethyl ether and its elemental analysis supported a composition of $(CuCl)_4(C_5H_5N)_4O_2$. When a pyridine solution of 1 (0.5 molar equiv to CuCl) was added slowly to a pyridine solution of CuCl pretreated with oxygen, further absorption of oxygen was observed showing that the oxidation took place. The amount of oxygen absorbed during the oxidation was equimolar to 1 added, and after the usual work-up 2 was obtained nearly quantitatively. During the oxidation reaction the solution was purple, but it changed to deep green after the reaction suggesting the regeneration of the oxygen complex. The complex was isolated from the solution.

In addition to CuCl, CuBr showed the same activity, but other uni- and bivalent copper salts such as CuI, $[CuIP(C_4H_9)_3]_4$, Cu_2O, CuOAc, CuOH, $CuCl_2$, and $CuSO_4$ were inactive. Furthermore, FeO, $CoCl_2$, $NiCl_2$, $SnCl_2$, and $VOCl_3$ were useless.

Table III. Oxidation of 1 to 2 in the Presence of a Small Amount of Pyridine in Acetonitrile with CuCl[a]

Pyridine/CuCl (mol/mol)	O_2 absorption, mol/mol CuCl		Yield, %
	Before addition of 1	After addition of 1	
0.5	0.25	0.63	13.0
1	0.25	0.85	74.8
3	0.25	0.99	83.5

[a] 0.01 mol of 1 in 15 ml of acetonitrile was added dropwise in 15 min with stirring under O_2 atmosphere to 55 ml of acetonitrile solution containing CuCl (0.02 mol) and pyridine (0.01, 0.02, or 0.06 mol) which was allowed to absorb O_2 in advance.

Table IV. Oxidation of 1 to 2 with CuCl at Different Initial 1/CuCl Ratio in the Reaction Medium[a]

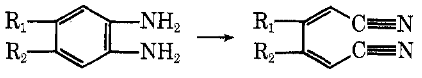
1/CuCl (mol/mol)	Yield, %	1/CuCl (mol/mol)	Yield, %
1/3	95	2/3	49
1/2	92	1/1	11

[a] Oxygen was introduced into 70 ml of pyridine containing 0.01 mol of 1 and 0.01, 0.015, 0.02, or 0.03 mol of CuCl.

For the catalytic activity, the coordination of pyridine seems to be essential. In place of pyridine, other amines such as α-picoline, 2,2′-bipyridyl, and 1,4-diazabicyclo[2.2.2]octane were used, but found to be less effective (Table I). Pyridine plays roles of both ligand and solvent. Other solvents such as acetonitrile, benzene, and tetrahydrofuran can be used when mixed with pyridine (Table II). By using acetonitrile as the solvent, the influence of a ratio of pyridine to copper in the reaction medium was studied. Acetonitrile solutions of CuCl and pyridine were prepared with pyridine/copper ratios of 0.5, 1, and 3. Each solution absorbed about 1 mol of oxygen for four atoms of copper. Then 1 (0.5 molar equiv to CuCl) in acetonitrile was added slowly. The results of the oxidation in Table III show that the ratio of pyridine to copper higher than one seems to be essential for giving 2 in a high yield. Accumulation of certain amounts of water in the reaction medium showed no critical effect, but an unfavorable effect was observed in the presence of a larger amount of water (Table I). In these cases, even when the yield of 2 was low, almost no 1 was detected in the reaction mixture.

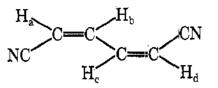
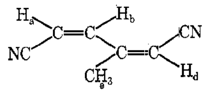
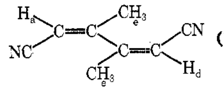
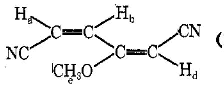
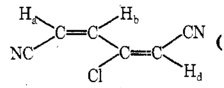
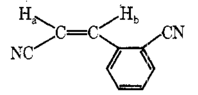
The ratio of 1 to copper in the reaction medium is the most important factor. Under argon atmosphere pyridine solutions of CuCl containing different amounts of 1 were prepared and then oxygen was introduced. The yields of 2 shown in Table IV were obtained. This result shows that it is necessary to keep the actual amount of 1 in the reaction medium below 0.5 molar equiv to CuCl in order to achieve a high yield of 2. This consideration clearly explains the fact that the oxidation of 1 in the presence of a so-called catalytic amount of CuCl in pyridine gave intractable polymer by the intermolecular reaction of 1. When the solution of 1 is added slowly to the pyridine solution of CuCl, 1 is oxidized rapidly to 2 as soon as it is added and the actual concentration of 1 in the reaction medium is always kept low and the active copper catalyst is regenerated. By this high dilution technique more than equimolar amounts of 1 can be oxidized to 2 nearly quantitatively. Also the oxidation reaction can be carried out successfully in a preparative scale.[9]

Following derivatives of 1 bearing an electron-donating group on the aromatic ring were oxidized similarly to give the corresponding muconontrile derivatives. In the pres-



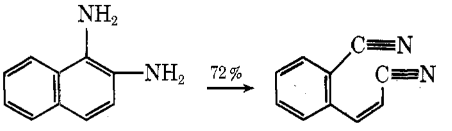
		yield
3, R_1 = Me; R_2 = H	9, R_1 = Me; R_2 = H	(62%)
4, R_1 = R_2 = Me	10, R_1 = R_2 = Me	(95%)
5, R_1 = MeO; R_2 = H	11, R_1 = MeO; R_2 = H	(75%)
6, R_1 = Cl; R_2 = H	12, R_1 = Cl; R_2 = H	(43%)
7, R_1 = Ac; R_2 = H		
8, R_1 = NO_2; R_2 = H		

Table V. Nuclear Magnetic Resonance Spectra Data of Mucononitriles and *o*-Cyanocinnamonitrile Obtained by the Oxidation with CuCl[a]

Compd		Chemical shifts, δ, ppm					Spin–spin coupling constants, Hz						
		H_a	H_d	H_c	H_b	H_e	J_{ab}	J_{ac}	J_{ad}	J_{bc}	J_{bd}	J_{cd}	J_{de}
	(2)	5.74 (8)		7.21 (8)			10.8	−1.1	1.4	11.5	−1.1	10.8	
	(9)	5.67 (4)	5.53 (m)		7.27 (2)	2.37 (2)	12.0		1.2		<0.5		2.0
	(10)	5.47 (4)				2.11 (2)			<0.1				1.7
	(11)	5.74 (4)	4.89		7.11 (2)	3.87	12.1		1.3		<0.5		
	(12)	5.90 (4)	5.96 (4)		7.25 (2)		12.2		1.4		0.7		
	(14)	5.84			7.62		12.1						

[a] Measured in $CDCl_3$ on a Varian A-60 except 2 which was measured on a Varian HA-100 (100 MHz) with Me_4Si as internal standard and the number in the parentheses shows multiplicity of the peak.

ence of an electron-withdrawing group on the aromatic ring the oxidation took place to give a polymeric product rather than the corresponding mucononitrile. Smooth ring cleavage was observed with 1,2-naphthalenediamine (**13**) giving *o*-cyano-*cis*-cinnamonitrile (**14**).



13 **14**

This unique oxidation method with CuCl in pyridine was extended to the oxidation of dihydrazones of α-diketones to acetylenes[10] and that of catechol to *cis,cis*-muconate.[11]

Geometrical Configuration of the Products. The mucononitriles obtained by the oxidation of *o*-phenylenediamines were found to have the cis,cis configuration of the 1,3-butadiene system as described below. It is reported that spin–spin coupling constants of vinyl protons in nuclear magnetic resonance spectra are 6–15 Hz for J_{cis} and 15–22 Hz for J_{trans}.[12] Long-range coupling constants of protons in 1,3-butadiene systems were reported to be 1.3–1.9 Hz in cis,cis isomers and 0.5–0.8 Hz in cis,trans isomers.[13] The nuclear magnetic resonance spectrum of mucononitrile obtained showed an A_2B_2 pattern and its chemical shifts and spin–spin coupling constants were calculated by the least-squares method of five Newton iterations to a root mean square error of 0.070 with the aid of a computer.[14] The calculated coupling constants are in good agreement with values reported by Elvidge and Ralph[15] for cis,cis isomer except J_{ad}. The latter is 1.4 Hz in the present analysis, while 1.7 Hz was given by them, and Hall and Patterson[16] reported 0.6 Hz. The observed data of **9**, **11**, and **12** are in good agreement with those reported for cis,cis isomers,[16] where each J_{ad} is between 1.2 and 1.4 Hz suggesting cis,cis configuration. No nuclear magnetic resonance spectrum of **10** was reported and the geometrical configuration of **10** can not be determined from data shown in Table V. It is considered to be cis,cis isomer by analogy with other products. The negligibly small value of J_{ad} of **10** suggests that **10** exists in a nonplanar conformation.[13] The data of *o*-cyanocinnamonitrile are also in agreement with those reported for the cis configuration.[16]

Table VI. Ultraviolet[a] and Infrared Absorption Spectra Data of Mucononitriles and *o*-Cyanocinnamonitrile Obtained by the Oxidation with CuCl

	Ultraviolet spectra		
Compd	λ_{max}, nm	ϵ_{max}	Infrared spectra in KBr, selected bands, cm^{-1}
2	260 270 s 252	27800 20600 22200	2219 (s), 1764 (w), 1701 (w), 1555 (m), 1349 (m), 1201 (s), 940 (m), 756 (vs)
9	264.5 274 s 254	22370 18000 18900	2200 (s), 1754 (w), 1570 (m), 1435 (m), 1409 (w), 1380 (m), 1330 (w), 1184 (w), 1053 (m), 1032 (m), 788 (s), 777 (s)
10	204 s 222	13000 7420	2200 (s), 1622 (s), 1443 (s), 1382 (s), 1060 (m), 1037 (s), 1024 (m), 842 (s), 825 (s)
11	235 256 287 s 248	11900 7000 9400 8400	2200 (s), 1767 (w), 1630 (m), 1568 (vs), 1464 (s), 1438 (m), 1404 (s), 1325 (m), 1266 (s), 1209 (s), 1030 (s), 934 (m), 797 (s), 778 (s)
12	267 s 274 s 259	19400 18300 16800	1190 (s), 1745 (w), 1669 (w), 1552 (s), 1404 (w), 1305 (w), 1110 (s), 1009 (m), 954 (w), 912 (m), 838 (s), 778 (s), 709 (s)
14	271 230 223 s 237 s 315	14300 15500 15700 11600 680	2210 (m), 1585 (m), 1473 (m), 1447 (m), 1240 (m), 968 (w), 940 (m), 780 (vs), 715 (m)

[a] Measured in ethanol.

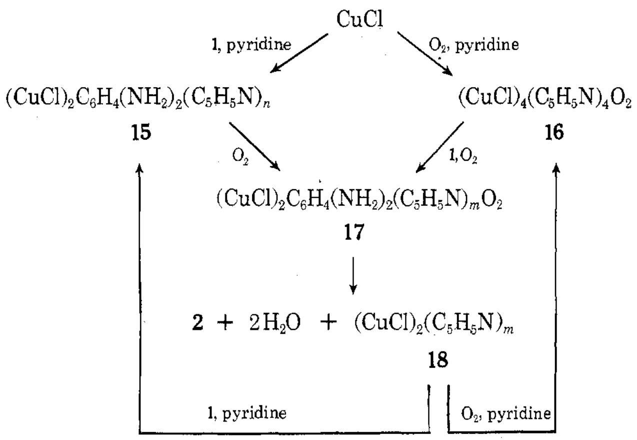
The infrared absorption spectra of the dinitriles are shown in Table VI. Precise data of cis,cis, cis,trans, and trans,trans isomers have been reported and the observed spectra of **2** are in good agreement with those of the cis,cis isomer.[15] The presence of a set of cis hydrogens in **9**, **11**, **12**, and **14** is suggested from their absorption spectra in the range of 778–788 cm^{-1}.

The ultraviolet spectra of the dinitriles are shown in Table VI. The main absorption band of **2** was observed at

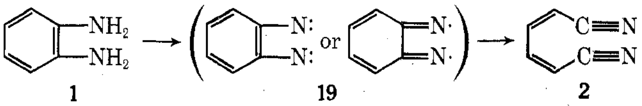
260 nm and its shifts induced by monosubstitution of β carbon with methyl, chloro, and methoxy groups are +4.5, +7, and +27 nm, respectively. The effect of substitution is similar to those reported by Woodward on 1,3-butadienes.[17] The main absorption band of **10** was observed at 204 nm, a lower wavelength absorption like that of acrylonitrile (200 nm), indicating that two double bonds are not in conjugation with each other but in conjugation with the respective triple bond of the cyano group. It is quite interesting that conjugation of the double bonds is forbidden by introduction of another methyl group at β′ position of **9** in which steric hindrance by both the methyl and cyano groups should be considered.

Reaction Mechanism. For this stereospecific and catalytic reaction, the following reaction mechanism (Scheme I) can be proposed.

Scheme I



Cuprous chloride and **1** in pyridine form in the absence of oxygen a yellow complex **15** which is converted into an oxygen complex **17** by introducing oxygen. The complex **17** is also formed by the addition of **1** to O_2–pyridine–CuCl complex **16** in pyridine. In the coordination sphere of the complex **17** electron transfer from the nitrogen to the oxidized form of copper takes place leading to species **2**, possibly via species **19**. Once **19** is formed, the ring cleavage proceeds smoothly to give **2**. Thus the cis,cis configuration of protons on the aromatic ring is retained during the reaction and only the cis,cis isomer of muconronitrile is formed selectively. When **1** of more than 0.5 molar equiv to CuCl is present in the reaction system, some pyridine molecules coordinated to copper in the complex **17** are replaced with another molecule of **1** and polymer of **1** is formed by an intermolecular coulpling reaction by radical species which are derived from **1**. Thus, it is important to control the ratio of **1** to copper in the reaction mixture to give **2** in a high yield. The complexes **15** or **16** can be regenerated via complex **18** and recycled as a catalyst.



1 19 2

Experimental Section

Melting points are uncorrected. Infrared spectra were recorded on a Shimazu Model IR-27 infrared spectrophotometer, ultraviolet spectra on a Varian-Cary 14M spectrometer, and nuclear magnetic resonance spectra on a Varian HA-100 (100 MHz) and a Varian A-60 (60 MHz) using tetramethylsilane as internal standard in $CDCl_3$. All metal salts and diamines were obtained commercially.

General Procedure of Oxidation. A. Procedure I. Cuprous chloride and pyridine were added in a glass flask immersed in a water bath under argon atmosphere with vigorous stirring and then the atmosphere was replaced with oxygen. After the absorption of oxygen ceased, the diamine in pyridine was added slowly with further absorption of oxygen. The amount of oxygen absorbed was measured with a gas buret. Pyridine was distilled off under reduced pressure after the reaction, and the residue was extracted with ether to give a crude product which was recrystallized from ether or other solvents. More conveniently the reaction was carried out by bubbling air in the reaction mixture.

B. Procedure II. Under argon atmosphere, CuCl, pyridine, and diamine were mixed in a flask stirred magnetically and then the atmosphere was replaced with oxygen. After the absorption of oxygen ceased, the reaction mixture was treated by the same method as in procedure I (see Table IV).

***cis,cis*-Muconronitrile (2).** *o*-Phenylenediamine (**1**, 1.08 g) in 20 ml of pyridine was treated by procedure I with CuCl (1.98 g) in 50 ml of pyridine to give **2** (0.98 g), mp 128–129 °C.

Anal. Calcd for $C_6H_4N_2$: C, 69.22; H, 3.87; N, 26.91. Found: C, 69.16; H, 3.85; N, 26.96.

3-Methyl-*cis,cis*-muconronitrile (9). 4-Methyl-*o*-phenylenediamine (**3**, 1.22 g) in 20 ml of pyridine was treated by procedure I with CuCl (1.98 g) in 50 ml of pyridine to give **9** (0.73 g), mp 53–54 °C.

Anal. Calcd for $C_7H_4N_2$: C, 71.16; H, 5.12; N, 23.72. Found: C, 71.35; H, 4.98; N, 23.92.

3,4-Dimethyl-*cis,cis*-muconronitrile (10). 4,5-Dimethyl-*o*-phenylenediamine (**4**, 1.36 g) in 20 ml of pyridine was treated by procedure I with CuCl (1.98 g) in 50 ml of pyridine to give **10** (1.25 g), mp 95 °C.

Anal. Calcd for $C_8H_8N_2$: C, 72.70; H, 6.10; N, 21.20. Found: C, 72.48; H, 6.20; N, 21.02.

3-Methoxy-*cis,cis*-muconronitrile (11). 4-Methoxy-*o*-phenylenediamine (**5**, 1.38 g) in 20 ml of pyridine was treated by procedure I with CuCl (1.98 g) in 50 ml of pyridine to give **11** (1.01 g), mp 115–117 °C.

Anal. Calcd for $C_7H_6N_2O$: C, 60.85; H, 7.30; N, 20.28. Found: C, 60.56; H, 7.33; N, 20.50.

3-Chloro-*cis,cis*-muconronitrile (12). 4-Chloro-*o*-phenylenediamine (**6**, 1.43 g) in 20 ml of pyridine was treated by procedure I with CuCl (3.37 g) in 50 ml of pyridine to give **12** (0.6 g) (recrystallized from *n*-hexane), mp 85–86 °C.

Anal. Calcd for $C_6H_7ClN_2$: C, 52.00; H, 2.19; Cl, 25.60; N, 20.21. Found: C, 52.02; H, 2.23; Cl, 25.90; N, 20.30.

***o*-Cyano-*cis*-cinnamonitrile (14).** 1,2-Naphthalenediamine (**13**, 9.0 g) in 100 ml of pyridine was treated by procedure I with CuCl (15 g) in 400 ml of pyridine to give **14** (6.6 g) (recrystallized from *n*-hexane–CCl_4), mp 68–69 °C.

Anal. Calcd for $C_{10}H_6N_2$: C, 77.90; H, 3.92; N, 18.17. Found: C, 77.90; H, 3.93; N, 17.95.

O_2–pyridine–CuCl Complex (16). An oxygen complex of CuCl was isolated by adding a large amount of ether to a pyridine solution of CuCl pretreated with oxygen (Complex **16a**). Another complex was isolated from the reaction mixture of the oxidation of **1** by procedure I as a residue of extraction with ether (complex **16b**). Both complexes showed the same infrared spectra.

Anal. Calcd for $C_{20}H_{20}Cl_4Cu_4N_4O_2[(CuCl)_4(C_5H_5N)_4O_2]$: C, 32.27; H, 2.71; Cl, 19.05; N, 7.53. Found for complex **16a**: C, 30.38; H, 3.22; Cl, 19.53; N, 7.03. Found for complex **16b**: C, 31.45; H, 2.57; Cl, 20.8; N, 6.64.

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Silane Reductions in Acidic Media. VII. Aluminum Chloride Catalyzed Hydrogen–Halogen Exchange between Organosilanes and Alkyl Halides. An Efficient Hydrocarbon Synthesis[1a]

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Alkyl halides are conveniently reduced to hydrocarbons by organosilanes in good yields when a catalytic amount of aluminum chloride is used. Hydrogen–halogen exchange between organosilanes and tertiary, secondary, primary, or methyl halides is rapid, and no significant difference in reactivity between alkyl bromides and chlorides is observed. Reduction by triethylsilane is competitive with the rearrangement of bromocycloheptane to 1-bromo-1-methylcyclohexane and with Friedel–Crafts alkylation reactions. Deuterium transfer from triethyldeuteriosilane to the alkyl cation formed from 1-bromohexane or cyclohexylmethyl bromide and aluminum chloride gives 2-deuteriohexane or 1-deuterio-1-methylcyclohexane, demonstrating that rearrangement to a more stable carbenium ion precedes reduction in these cases. The scope and limitations in the use of organosilanes for aluminum chloride catalyzed alkyl halide reductions is discussed.

Alkanes have long been known to transfer hydrogen intermolecularly to carbenium ions formed from alkyl halides and catalytic amounts of aluminum chloride.[2] By comparison, Lewis acid catalyzed reductions of alkyl halides by organosilanes have received limited attention; and the synthetic potential of this process for hydrocarbon formation has not been examined. Whitmore, Pietrusza, and Sommer have shown that an aluminum chloride catalyzed hydrogen–halogen exchange of triethylsilane with primary alkyl chlorides can be used to trap carbenium ions but point out that the experimental method is beset by a relatively long "induction period" followed by an often violent exothermic reaction.[3] In a subsequent investigation Sommer, Citron, and Lyons described a palladium-catalyzed reaction between triorganosilicon hydrides and halocarbons that is reported to be superior to the Lewis acid catalyzed exchange reaction for silyl halide formation;[4] this method, however, is not satisfactory as a synthetic procedure for hydrocarbon formation owing to the often complex nature of the reduction products.[5]

We have found that alkyl halides are readily reduced to hydrocarbons by organosilanes in good yields when catalytic amounts of aluminum chloride are used, that there is no observable "induction period" when tertiary alkyl halides are involved, and that organosilanes are clearly superior to hydrocarbons in hydrogen transfer reactions with carbenium ions. In this paper we report the scope and limitations in the use of organosilanes for aluminum chloride catalyzed alkyl halide reductions.

Results and Discussion

Addition of anhydrous aluminum chloride (usually ≤5 mol %) to a solution of an alkyl halide and organosilane, cooled in an ice–water bath, produced a rapid exothermic reaction. A solvent, usually pentane, was required only when the alkyl halide and silane were not mutually soluble. Product analysis of the reaction mixture after heating at 40 °C for usually less than 1 h showed only alkane and silyl halide (eq 1).

$$RX + R'_3SiH \xrightarrow{AlCl_3} RH + R'_3SiX \qquad (1)$$

Results from organosilane reductions of representative alkyl halides are given in Table I. No major difference in product yields was observed when the alkyl halide was alternatively added to the cooled mixture of silane and aluminum chloride. The reaction temperature could, however, be more effectively controlled by the slow addition of the alkyl halides to the $AlCl_3$–silane mixture (method II) than by the addition of aluminum chloride to the alkyl halide–silane solution (method I).

Tertiary alkyl halides reacted smoothly with organosilanes in the presence of a catalytic amount of aluminum chloride and gave no evidence of an initial induction period. A short time period in which no apparent reaction occurred was usually observed with both secondary (≤1 min) and primary (2 min) alkyl halides when the aluminum chloride was added to the alkyl halide–organosilane solution or when the alkyl halide was added to the silane–aluminum chloride mixture. In no case, however, was a long induction period followed by a violent exothermic reaction, similar to that previously observed,[3] noted for the reactions reported in Table I. No significant difference in reactivity was observed in silane reductions of comparable alkyl chlorides and bromides.

The aluminum chloride catalyzed reaction of organosilanes with alkyl halides provides an alternative and potentially useful synthetic route to hydrocarbons. Compared to the organotin hydrides,[6] organosilicon hydrides are stable to air and to acids and bases. Reductions of alkyl chlorides and bromides by organosilanes occur under the same reaction conditions; toward organotin hydrides alkyl chlorides are much less reactive than are the corresponding alkyl bromides and require reaction temperatures in excess of 100 °C for reasonable reaction times.[6] In addition, the organosilane reduction method favors tertiary alkyl halides over primary or secondary substrates; reactions with primary or secondary alkyl halides are usually preferred in procedures employing nucleophilic reducing agents.[7,8] Hy-