a granular solid, 0.62 g, 38.7%, separated. Recrystallization from a mixture of ethyl acetate and acetonitrile gave colorless needles: mp 229–230°; ir ($CHCl_3$) 3030, 1705 (C=O), 1430 and 960 cm^{-1}; nmr (CH_3COCH_3) δ 7.2–7.8. *Anal.* Calcd for $(C_9H_7NO)_2$: C, 74.46; H, 4.86; mol wt, 290.4. Found: C, 74.25; H, 4.91; mol wt, 325 (osmometric).

In contrast the dimer **5a**, mp 167–168°, on heating in pyridine for 1 hr was transformed into isocarbostyril; its ir (pyridine) absorption was identical with a spectrum for authentic material in pyridine.

Registry No.—**2a**, 33066-17-0; **2b**, 33066-18-1; **2c**, 32528-95-3; **3a**, 33066-20-5; **3b**, 33066-21-6; **3c**, 33066-22-7; **4a**, 491-30-5; **4b**, 7114-80-9; **4c**, 7115-13-1; **5a**, 33041-36-0.

The Reaction of Acyl Cyanides with Grignard Reagents

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The reaction of benzoyl cyanide (**1**) with Grignard reagents occurs *via* addition to the carbonyl group to give the corresponding phenyl ketones **2** in good yield. Acetyl cyanide (**3**), however, reacts with aliphatic Grignard reagents predominantly by reduction of the carbonyl group and subsequent acylation by **3** to give cyano ester **5**. Carbonyl cyanide (**6**) is attacked by isopropylmagnesium bromide at carbonyl to give isobutyryl cyanide, which is further reduced and acylated to give isobutyraldehyde cyanohydrin and its isobutyl ester. Finally, **6** reacts with phenylmagnesium bromide by attack at both the carbonyl and cyano groups to give benzil, benzophenone, and minor amounts of benzonitrile and benzoyl cyanide. These variations in reaction selectivity are discussed in light of the mechanisms postulated, and INDO calculations of electron density and infrared stretching frequencies are brought to bear on the reactivity of these compounds.

Part A

The reaction of Grignard reagents with carboxylic acid derivatives has been extensively investigated;[2] one apparent exception to this is the acyl cyanide derivative. Some time ago we began an investigation of acyl cyanide and carbonyl cyanide reactions with Grignard reagents in order to answer the following questions. (1) Would these compounds react as "deactivated" acid chlorides; *i.e.*, would the cyano group act exclusively as a carbonyl activating group, or would it compete with the organometallic reagent? (2) Would the intermediate cyanohydrin magnesium salt (I or IV in eq 1 or 2) have sufficient stability to block further addition to the carbonyl group, thus permitting the synthesis of ketones, or would it compete with the carbonyl group in reaction with the organometallic reagent? (3) Could sequential addition to carbonyl cyanide be controlled to permit synthesis of unsymmetrical ketones?[3] The answers to these questions constitute the subject of this two-part paper.

We began by investigating the reactions of benzoyl cyanide (**1**) and acetyl cyanide (**3**) to determine the selectivity of carbonyl addition. Reaction of **1** with a variety of Grignard reagents proceeded as expected; the corresponding phenyl ketones **2a–c** were obtained in 65–84% yield when **1** was treated with 1 equiv of the organomagnesium compound in ether at −40°. Gas chromatographic analyses of the crude products showed <5% of the tertiary alcohol and no trace of product derived from addition to the cyano group of **1**. Similarly, reaction of **3** with phenylmagnesium bromide at −70° resulted in a 70% yield of **2a**. When **3** was allowed to react with isopropyl-, *n*-amyl-, or cyclohexylmagnesium bromide, however, a new product **5** was isolated in 58–77% yield in addition to minor amounts of the expected ketone. The structure of **5** was confirmed by nmr and by synthesis of an authentic sample; its mode of formation is postulated in eq 1 (R = R′ = CH_3). It is apparent that, in the case of **3**, reduction of the carbonyl group *via* hydride transfer predominates over addition. There was no evidence of addition or reduction at the cyano group of **3**.

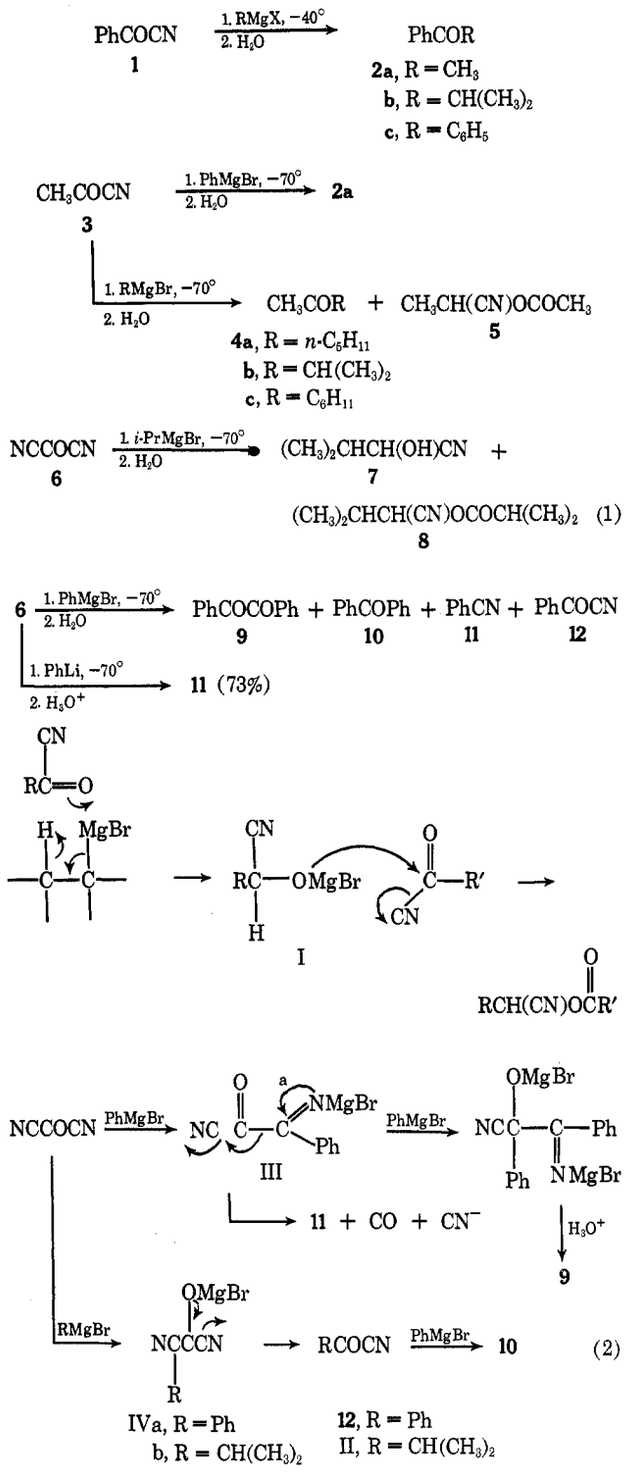
Reaction of carbonyl cyanide **6** with Grignard reagents also occurred by distinct pathways depending on the nature of the organomagnesium reagent. It should of course be noted that products resulting from reduction of **6** would be sufficiently volatile to escape detection under the reaction conditions. When **6** was treated with 1 equiv of isopropylmagnesium bromide in ether at −70°, **7** and **8** were isolated in 51 and 21% yield, respectively. The initial step in both cases involves addition at carbonyl and subsequent elimination of cyanide to give isobutyryl cyanide II as an intermediate. Reduction of II as in the case of **3** followed by trapping of the cyanohydrin magnesium salt I by **6** or II leads to the cyanohydrin esters (for R′ = CN, eq 2, the cyanoformate hydrolyses in water to give the cyanohydrin **7**).

When **6** was treated with phenylmagnesium bromide in ether at −70°, however, four identifiable products were obtained as a result of addition at *both* the carbonyl and cyano groups: benzil (**9**), 49%; benzophenone (**10**), 19%; benzonitrile (**11**), 8%; and benzoyl cyanide (**12**), 5%. The formation of these products is postulated in eq 2; addition to the cyano group predominates over addition to carbonyl in **6** by 2.4 to 1. We have postulated the formation of **11** as occurring *via* intermediate III rather than IVa on the basis of the fact that IVb rapidly eliminates cyanide to give II (and ultimately **7** and **8**) under the reaction conditions. Thus, IVa would be expected to collapse to **12** before addition of a second phenyl group could occur. When phenyllithium was used as the organometallic reagent, **11** was the only detectable product,

(1) (a) Alfred P. Sloan Foundation Fellow; (b) taken in part from the Ph.D. thesis of S. R. L., University of Minnesota, 1971.

(2) M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Non-Metallic Substances," Prentice-Hall, New York, N. Y., 1954, pp 709–724.

(3) During the course of this work an excellent general method for unsymmetrical ketone synthesis was reported; for a review see D. Seebach, *Synthesis*, **1**, 17 (1969).



isolated in 73% yield. Presumably the more ionic nitrogen–lithium bond in III promotes more rapid collapse to **11**.

Part B

Experimental Section

Infrared (ir) spectra were measured on a Unicam SP-200 or a Perkin-Elmer 257 spectrophotometer. Nuclear magnetic resonance (nmr) spectra were obtained on Varian T-60 and A-60D instruments and are given in parts per million (δ) downfield from tetramethylsilane as an internal standard. Mass spectra were determined at 70 eV on a Hitachi RMU-6 instrument. Gas chromatographic (glpc) analyses were carried out on a Varian A90-P gas chromatograph using 0.25 in. × 10 ft columns with Chromosorb W as support. Microanalyses were determined by the Microanalytical Laboratory, University of Minnesota.

Benzoyl cyanide (1) was prepared by the method of Oakwood and Weisgerber[4] in 76% yield, mp 28–30°.

Reaction of Acyl Cyanides with Grignard Reagents. General Procedure.—A 50-ml three-neck flask was fitted with an air-tight mechanical stirrer and pressure-equalizing funnel and placed under an atmosphere of nitrogen. A solution of the acyl cyanide in 25 ml of anhydrous ether was added to the flask, and the resulting solution was cooled to the specified temperature. An equimolar quantity of the Grignard solution in ether was added dropwise over 1 hr; stirring was continued for the specified time. The mixture was removed from the cooling bath and poured into 200 ml of saturated aqueous ammonium chloride. The ether layer was separated, and the aqueous solution was extracted with three 25-ml portions of ether. The combined extracts were washed with water and dried ($MgSO_4$), and the solvent was removed by fractionation.

Grignard Reaction of 1. A. Methylmagnesium Iodide.—Benzoyl cyanide (0.66 g, 5.0 mmol) was treated with 3.7 ml (5.0 mmol) of 1.36 *M* methylmagnesium iodide at −40° for 8 hr. Work-up afforded 0.53 g of an oil which was 82% acetophenone (**2a**) (73% yield) and 18% unreacted **1** by glpc analysis.

B. Isopropylmagnesium Bromide.—A solution of 5.0 ml (5.0 mmol) of 1.0 *M* isopropylmagnesium bromide was added to 0.66 g (5.0 mmol) of benzoyl cyanide at −40° and stirred for 8 hr. Work-up afforded 0.64 g of an oil which was 98% isobutrophenone (**2b**) by glpc analysis (84% yield). A collected sample was identified by comparison of ir and nmr spectra with those of an authentic sample.

C. Phenylmagnesium Bromide.—Benzoyl cyanide (1.00 g, 7.6 mmol) was treated with 9.7 ml (7.6 mmol) of 0.79 *M* phenylmagnesium bromide for 2 hr at −40°. Work-up afforded 1.31 g of crude product. A 1.23-g sample of this product was chromatographed on silica gel (30 g). Elution with 2:3 benzene–petroleum ether (bp 30–60°) gave 0.85 g (66%) of benzophenone (**2c**), 2,4-DNP mp 236–238°. Elution with 1:19 chloroform–benzene gave 0.06 g (3%) of triphenylcarbinol, identified by ir and tlc comparison with an authentic sample.

Grignard Reaction of 3. A. Phenylmagnesium Bromide.—Acetyl cyanide[5] (**3**) (0.98 g, 14.1 mmol) was treated with 13.0 ml (14.1 mmol) of 1.08 *M* phenylmagnesium bromide for 1.5 hr at −70°. Work-up afforded 1.43 g of yellow oil which was shown by glpc analysis to contain 83% acetophenone (**2a**) (70% yield), 2,4-DNP mp 246–248°.

B. *n*-Amylmagnesium bromide is representative of the "reducing" Grignard reagents. Acetyl cyanide (0.49 g, 7.1 mmol) was allowed to react with 8.3 ml (7.1 mmol) of 0.85 *M* *n*-amylmagnesium bromide for 5 hr at −70°. Work-up afforded 0.63 g of an oil which was shown to be 22% 2-heptanone (**4a**) and 49% α-cyanoethyl acetate (**5**) by glpc analysis. A collected sample of **5** was identified by ir and nmr comparison with an authentic sample prepared as described below: ir (CCl_4) 1760 cm^{-1}; nmr (CCl_4) δ 1.59 (d, 3, J = 7 Hz), 2.10 (s, 3), 5.32 (q, 1, J = 7 Hz). Yields of 2-heptanone and **5** based on acetyl cyanide were 22 and 77%, respectively.

α-Cyanoethyl Acetate (**5**).—To a mixture of 5.6 ml (0.10 mol) of a 20% aqueous solution of acetaldehyde and 10.2 g (0.10 mol) of acetic anhydride at 5° was added over 10 min with stirring a solution of sodium cyanide (4.90 g, 0.10 mol) in 25 ml of water. Stirring was continued for 30 min at 10–20°, and the reaction mixture was then extracted with three 25-ml portions of ether. The combined extracts were washed with aqueous sodium bicarbonate, dried ($MgSO_4$), and evaporated *in vacuo* to give 5.77 g of crude product. Distillation afforded one major fraction (3.8 g): bp 166–170°; ir (CCl_4) 1760 cm^{-1}; nmr (CCl_4) 1.61 (d, 3, J = 7 Hz), 2.10 (s, 3), 5.33 (q, 1, J = 7 Hz). An analytical sample was prepared by preparative glpc. *Anal.* Calcd for $C_5H_7NO_2$: C, 53.05; H, 6.23; N, 12.39. Found: C, 52.78; H, 6.15; N, 12.41.

Carbonyl cyanide (**6**) was prepared in 80% yield from tetracyanoethylene oxide according to the procedure of Linn, Webster, and Benson,[6] bp 64–66° (lit. bp 65–66°).

(4) T. S. Oakwood and C. A. Weisgerber, "Organic Syntheses," Collect Vol. III, Wiley, New York, N. Y., p 112.

(5) Available as pyruvonitrile from Aldrich Chemical Co., Milwaukee, Wis.

(6) W. Linn, O. W. Webster, and R. Benson, *J. Amer. Chem. Soc.*, **87**, 3651 (1965).

Reactions of Carbonyl Cyanide. A. Isopropylmagnesium Bromide.—Carbonyl cyanide (1.74 g, 21.8 mmol) was treated with 25.6 ml (21.8 mmol) of 0.85 *M* isopropylmagnesium bromide for 4 hr at −70°. Work-up afforded 1.23 g of dark oil, which was shown by glpc analysis to contain 45% α-hydroxyisovaleronitrile (**7**) [ir (CCl_4) 3620 cm^{-1}; nmr (CCl_4) δ 1.09 (d, 6), 1.96 (m, 1), 3.61 (s, 1), and 4.20 (d, 1); mass spectrum *m/e* (rel intensity) 72 (11), 43 (32), 27 (37)] and 32% α-cyanoisobutyl isobutyrate (**8**) [ir (CCl_4) 1760 cm^{-1}; nmr (CCl_4) δ 1.06 (m, 12), 2.16 (m, 2), 5.14 (d, 1)].

Anal. Calcd for $C_9H_{15}NO_2$: C, 63.98; H, 8.95. Found: C, 63.95; H, 9.20.

Yields of **7** and **8** based on isopropylmagnesium bromide were 51 and 21% respectively.

B. Phenylmagnesium Bromide.—Carbonyl cyanide (0.54 g, 6.8 mmol) was treated with 6.3 ml (6.8 mmol) of 1.08 *M* phenylmagnesium bromide for 4 hr at −70°. Following work-up with 1 *N* hydrochloric acid, removal of ether gave 0.66 g of yellow oil which contained (glpc) benzil (**9**), 49%; benzophenone (**10**), 19%; benzonitrile (**11**), 8%; and benzoyl cyanide (**12**), 5%. Collected samples were identified by comparison of their ir spectra and glpc retention times with those of authentic samples.

C. Phenyllithium.—Carbonyl cyanide (0.75 g, 9.3 mmol) was allowed to react with 9.0 ml (9.3 mmol) of 1.04 *M* phenyllithium in ether for 3 hr at −70°. Work-up afforded 0.99 g of oil which contained 69% benzonitrile by glpc analysis. Benzil and benzophenone were completely absent from the reaction mixture (glpc). The yield of benzonitrile was 73% based on carbonyl cyanide.

Discussion

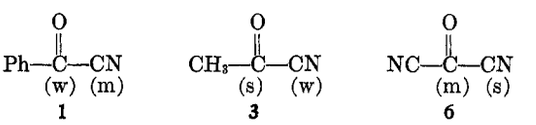
Infrared Spectra and Electron Density Calculations.—In order to gain insight into the detailed structure of the acyl cyanides and thus explain the apparent inconsistencies in the results, we calculated electron densities on **1**, **3**, and **6** *via* SCF calculations in INDO approximation.[7] These results together with the corresponding infrared stretching frequencies are reported in Table I. The most surprising result was the

TABLE I
INFRARED ABSORPTION FREQUENCIES AND INDO II ELECTRON DENSITY CALCULATIONS FOR THE C=O AND C≡N GROUPS IN ACYL CYANIDES

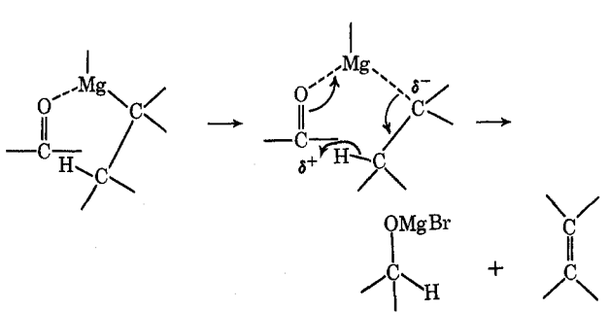
Compd	$\nu_{max}^{C=O}$, cm^{-1}	$\nu_{max}^{C\equiv N}$, cm^{-1}	$q_c^{C=O}$	$q_O^{C=O}$	$\lvert q_O q_C\rvert$	$q_c^{C\equiv N}$
PhCOCN	1680	2225	+0.297	−0.307	0.091	+0.059
CH_3COCN	1730	2220	+0.366	−0.331	0.121	+0.049
NCCOCN	1710	2240	+0.326	−0.243	0.079	+0.070

sequence observed for the carbonyl stretching frequencies. For the series benzoyl chloride–acetyl chloride–phosgene ($\nu_{max}^{C=O}$ 1773, 1790, and 1810 cm^{-1}, respectively), the carbonyl stretching frequency increases as a result of the progressively greater electron-withdrawing effect in going from methyl to phenyl to chlorine in increasing the force constant for the C=O bond. Based on both the σ_m values for -Cl and -CN[8a] and on the p*K* values for chloro- and cyanoacetic acids,[8b] one would expect the same order for the acyl cyanide C=O frequencies. However, carbonyl cyanide is intermediate between acetyl cyanide and benzoyl cyanide. The INDO results are in agreement with this result, the partial charge on the carbonyl carbon of **6** falling between that of **1** and **3**. Similarly, the nitrile stretching frequencies correlate with the partial charge on the nitrile carbon, the order being **6** > **1** > **3**. It is interesting to note that the infrared and INDO results are in excellent qualitative agreement and support the theory that electrostatic interactions make a major contribution in determining bond strength for two-electron (as apposed to one-electron) bonds.[9]

Thus the electronic character of the three acyl cyanides can be summarized as follows (s, m, w = strong, medium, and weakly electropositive). Delocalization of the carbonyl charge is clearly responsible for the electron distribution in **1**. In the case of acetyl cyanide, the inductive effect of the cyano group creates a sizable electron deficiency at the central carbon; the charge at the cyano carbon is presumably minimized as a result of charge repulsion. One might anticipate that the presence of two cyano groups bonded to carbonyl would increase this effect, as occurs for the acyl chlorides. Such an electron distribution would have a large repulsion energy, however, arising from three adjacent electropositive carbon atoms. Thus **6** achieves a more stable configuration by lengthening the C=O bond (relative to $COCl_2$) and shortening the C≡N bond (relative to **3**).



Addition *vs.* Reduction.—Having in hand a qualitative picture of the electron distribution in **1**, **3**, and **6**, we can attempt to correlate this data with the experimental results. It has been established[10] that carbonyl group reduction by Grignard reagents is enhanced by the presence of strong electron-withdrawing groups proximate to the carbonyl carbon, *i.e.*, is enhanced by increased bond polarization ($q_c q_o$ in Table I) in the carbonyl group. For example, acetaldehyde reacts with isopropylmagnesium bromide exclusively by addition, but trifluoroacetaldehyde reacts by reduction to give trifluoroethanol in 87% yield.[10] Thus our results concerning addition *vs.* reduction are consistent with the spectral and calculated data. Benzoyl and carbonyl cyanides, with their relatively stabilized carbonyl groups, undergo addition exclusively; acetyl and isobutyryl cyanides, however, react predominantly by reduction. We do not completely understand the reason for this correlation between carbonyl group polarization and reduction. A possible explanation lies in the fact that the complexing of an organomagnesium reagent will be



(7) J. A. Pople and D. L. Beveridge, (a) *J. Chem. Phys.*, **47**, 158 (1967); (b) "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N. Y., 1970, Chapter 3.

(8) (a) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Rinehart, and Winston, New York, N. Y., 1959, p 221; (b) p 201.

(9) R. Ferreira, *J. Phys. Chem.*, **75**, 3012 (1971).

(10) E. T. McBee, O. R. Pierce, and J. F. Higgins, *J. Amer. Chem. Soc.*, **74**, 1736 (1952).

much stronger in the case of a highly polarized carbonyl group, and thus the magnesium–carbon bond will be substantially weakened. This in turn would assist in the hydride transfer from the β carbon due to the increase in electron density on the carbon bonded to magnesium.

Addition at C=O *vs.* C≡N.—Addition of organomagnesium reagents occurs exclusively at carbonyl in both the aroyl and acyl cyanide systems. The nitrile functions only as an activating group and does not compete in electrophilic addition. Similarly, carbonyl cyanide suffers initial attack by isopropylmagnesium bromide exclusively at the carbonyl group. In contrast, however, phenylmagnesium bromide attacks predominantly (and phenyllithium exclusively) at the cyano group. These results can be explained as follows. The carbonyl group is undoubtedly the more electrophilic site in **6**, and in the absence of other factors addition occurs at this site. The generation of intermediate IVb (see eq 2) also removes the charge repulsion interactions present in **6**. In the case of phenyl Grignard addition, however, the stabilization of intermediate III renders addition at the cyano group competitive with addition at carbonyl, and both products are formed. This type of stabilization would be expected to be more important in the case of the more ionic lithium intermediate (III where MgBr is replaced by Li), and hence addition at the cyano group occurs exclusively.

It is apparent that these explanations do not provide complete support for the results described; other factors must be operating in the transition state complexes. It is interesting to note, however, that a consistent pattern emerges with spectral, experimental, and calculated data in agreement to support what we consider *a priori* to be surprising results.

Registry No.—**1**, 613-90-1; **2a** 2,4-DNP, 1677-87-8; **2c** 2,4-DNP, 1733-62-6; **3**, 631-57-2; **5**, 15657-96-2; **6**, 1115-12-4; **7**, 15344-34-0; **8**, 32861-42-0; methylmagnesium chloride, 676-58-4; isopropylmagnesium bromide, 920-39-8.

Formation of 1,1′-Oligomeric Ferrocenes from Mixed Ullmann Reactions of Haloferrocenes

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A series of 1,1′-oligomeric ferrocenes, including biferrocene, 1,1′-terferrocene, 1,1′-quaterferrocene, 1,1′-quinqueferrocene, and 1,1′-sexiferrocene, have been formed from a mixed Ullmann reaction between a haloferrocene and 1,1′-diiodoferrocene. Conditions were varied as to the haloferrocene, the ratio of haloferrocene to 1,1′-diiodoferrocene, and the type of copper used in order to ascertain the maximum yields of each oligomer. Mass spectra of all the 1,1′-oligomeric ferrocenes have been obtained.

Considerable interest has been focused recently on the thermal and conductivity properties of oligomeric ferrocenes;[1-4] yet the chemistry of ferrocene oligomers larger than biferrocene is virtually unknown. In the last 11 years, biferrocene (**1**) has been synthesized in many ways.[4-12] The most useful of these methods has utilized the Ullmann reaction.[7,12] Iodoferrocene is an extremely reactive compound in the Ullmann reaction, since a 97% yield of biferrocene can be obtained at temperatures as low as 60°.[12]

Nesmeyanov and coworkers[13] first isolated 1,1′-terferrocene (**2**) when they conducted a mixed Ullmann reaction with bromoferrocene (**7**) and 1,1′-dibromoferrocene to give a 57% yield of biferrocene, a 14% yield of 1,1′-terferrocene (**2**), and other higher oligomeric ferrocenes which were not separated. 1,1′-Terferrocene (**2**) has also been synthesized in an unequivocal manner from cyclopentadienylferrocene by Rinehart and coworkers.[14] More recently, Watanabe, *et al.*,[15] have described the formation of the 1,1′-oligomeric ferrocenes from biferrocene (**1**) to sexiferrocene (**5**), resulting from the treatment of a mixture of mono- and 1,1′-dilithioferrocenes with cobalt chloride. The yields were low and a number of butylated products, resulting from the excess *n*-butyllithium being present, were also isolated.

Results and Discussion

Based on our earlier successful studies on the Ullmann coupling of haloferrocenes,[12] and also on current interest in oligomeric ferrocenes, we decided to investigate in some detail the formation of this series of organometallic compounds *via* the Ullmann route. The mixed Ullmann reaction (eq 1) between a haloferrocene and 1,1′-diiodoferrocene (**9**) has indeed been found to give higher yields of the 1,1′-oligomeric ferrocenes than have the previous methods.[1,13,15,16] A reaction time of

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(15) N. Watanabe, I. Motoyama, and K. Hata, *Bull. Chem. Soc. Jap.*, **39**, 790 (1966).
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