

in air and even purified without decomposition by silica gel column or thin layer chromatography. For comparison, Fe(TPP)(CO)(pyridine) or Fe<sup>II</sup>(TPP) complexes known for their relative stability toward oxidation, like Fe(TPP)(CCl<sub>2</sub>)<sup>4</sup> and Fe(TPP)(*i*-PrNO)(pyridine),<sup>13</sup> are oxidized irreversibly to the iron(III) state in aerated solvents (respective half-lives in benzene: 5 min, 4 h, and 5 h) and are destroyed during column or thin-layer chromatography.

The particular strength of the TPP Fe<sup>II</sup>-CS bond is also emphasized by the stability of complex **3** in the presence of excess pyridine. After 24 h, <5% complex **3**, initially  $6 \times 10^{-5}$  M in benzene in the presence of 1 M pyridine at 25 °C, is transformed into Fe(TPP)(pyridine)<sub>2</sub>, whereas Fe(TPP)(CCl<sub>2</sub>) and Fe(TPP)(*i*-PrNO)(pyridine) are half-transformed into Fe(TPP)(pyridine)<sub>2</sub>, respectively, within 1.5 and 6 h, under the same conditions. The differences between the strength of the TPP-Fe<sup>II</sup> bonds with CS and CO are in agreement with the better  $\sigma$ -donor and  $\pi$ -acceptor ability of CS, previously reported for thiocarbonyl complexes in general.<sup>2</sup>

Thiocarbonyl complexes analogous to **1** are obtained from various iron(II) porphyrins like octaethylporphyrin, deuteroporphyrin dimethyl ester and protoporphyrin IX.<sup>14</sup>

We are currently trying to obtain thiocarbonyl complexes of hemoproteins and studying the chemical properties of CS bound to iron(II) porphyrins.

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## References and Notes

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- TPP is used for the dianion of *meso*-tetraphenylporphyrin, DMF for dimethylformamide.
- The reaction can be performed without (CH<sub>3</sub>)<sub>2</sub>S and leads also to complex **1**, but with lower yields (15%). This can be related to the demetalation of the iron porphyrin observed in this case.
- Actually, the crystals were found to retain CH<sub>2</sub>Cl<sub>2</sub> (0.12 mol/mol of complex **1**, from <sup>1</sup>H NMR) even after 10-h heating at 50 °C under vacuum (10<sup>-6</sup> mmHg). Anal. Calcd for TPPFe(CS)(EtOH)(1/6CH<sub>2</sub>Cl<sub>2</sub>): C, 73.57; H, 4.49; Cl, 1.15; N, 7.28; S, 4.17. Found: C, 73.25; H, 4.47; Cl, 1.41; N, 7.24; S, 4.10.
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- NOTE ADDED IN PROOF. After acceptance of this communication, Professor J. W. Buchler told us that he independently obtained porphyrin iron(II) and osmium (II)(CS) complexes (paper in preparation), confirming the high stability of the Fe-CS bond in such complexes.

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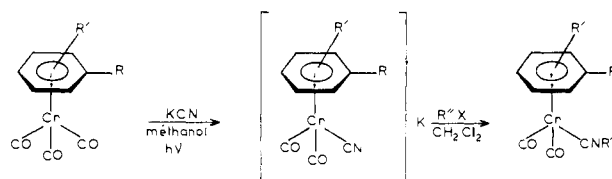
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## Structural and Chemical Aspects of Metal Stabilized *N*-Acyl Isocyanide Groups (MCNCOR)

Sir:

As extensively exemplified in metal-carbene chemistry, very reactive intermediates that are incapable of existence or iso-

Scheme I



lation in the free state may be studied and utilized after syntheses on a protecting metal.<sup>1</sup> Similar behavior might be anticipated for the potentially highly reactive *N*-acyl isocyanides series (:CNCOR).<sup>2</sup> Since alkylation of cyanide complexes has been used to synthesize alkyl or aryl isocyanides<sup>3</sup> on a metal atom, we considered the possible formation of *N*- $\alpha$ -functionalized isocyanides via electrophilic attack of acyl halides on metal cyanide ions. We report here the synthesis and the structural and chemical properties of arenechromium dicarbonyl *N*-benzoyl isocyanide derivatives prepared in this manner.

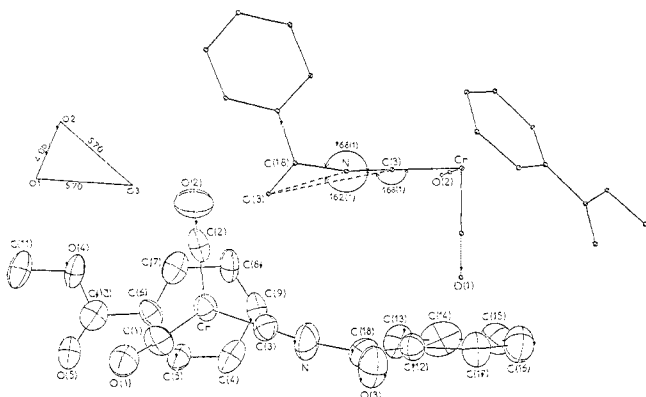
Scheme I outlines the general preparation of  $\eta^6$ -(arene)-Cr(CO)<sub>2</sub>CNR derivatives starting from the readily available  $\eta^6$ -(arene)Cr(CO)<sub>3</sub> complexes.<sup>4</sup> The air-sensitive monocyanide intermediates, generated by UV irradiation in presence of KCN, were treated with various electrophiles at room temperature. The overall yields, based on isolated products, were usually 65-80%.<sup>5</sup>

In a typical experiment 2 g of (methyl benzoate)Cr(CO)<sub>3</sub> ( $7.35 \times 10^{-3}$  M) and 1 g of KCN ( $1.54 \times 10^{-2}$  M) in 200 mL of deoxygenated methanol were irradiated (Lamp HANAU TQ 150) under nitrogen for 3 h. After vacuum evaporation of the solvent, the anion (C<sub>6</sub>H<sub>5</sub>CO<sub>2</sub>CH<sub>3</sub>)Cr(CO)<sub>2</sub>CN<sup>-</sup> (IR frequencies  $\nu_{CO}$  (CH<sub>2</sub>Cl<sub>2</sub>) 1910, 1830 cm<sup>-1</sup>; NMR (CD<sub>3</sub>COCD<sub>3</sub>)  $\delta_{C_6H_5Cr}$  5.82 (m, 2), 5.12 (m, 1), 4.84 (m, 2), and  $\delta_{OCH_3}$  3.47 (s, 3) ppm) was allowed to react with 1 g of C<sub>6</sub>H<sub>5</sub>COCl ( $7.1 \times 10^{-3}$  M) followed by immediate addition of 20 mL of CH<sub>2</sub>Cl<sub>2</sub>. After TLC purification (silica gel, eluent; ether-petroleum ether, 1:4), a 2.26-g sample of  $\eta^6$ -(C<sub>6</sub>H<sub>5</sub>CO<sub>2</sub>CH<sub>3</sub>)Cr(CO)<sub>2</sub>(CNCOC<sub>6</sub>H<sub>5</sub>) was isolated (yield 81%; mp 78 °C; NMR (CDCl<sub>3</sub>)  $\delta_{C_6H_5}$  8.45 (m, 2), 7.90 (m, 3),  $\delta_{C_6H_5Cr}$  6.45 (m, 2), 5.65 (m, 3), and  $\delta_{OCH_3}$  4.05 (s, 3); mass spectrum *m/e* 375.0200 (calcd 375.019879).

To prove the structure of (C<sub>6</sub>H<sub>5</sub>CO<sub>2</sub>CH<sub>3</sub>)Cr(CO)<sub>2</sub>(CNCOC<sub>6</sub>H<sub>5</sub>), an x-ray crystal structure analysis was carried out. Red crystals exhibiting two different morphologies were obtained by slow recrystallization from pentane. Although the poor diffractive properties of the crystals resulted in a low yield of data, it was possible to obtain, for both crystal forms, data of sufficiently high quality to allow a reasonably precise description of the solid-state structure.<sup>6</sup>

The structural analysis reveals that the stereochemistry of the molecular complex (Figures 1 and 2) is approximately the same in both crystal forms. Salient structural features include (i) a bent two-electron donating *N*- $\alpha$ -functionalized isocyanide ligand (C-N-C angle of 168 (1)°) coordinated in a linear fashion to the chromium atom (Cr-C(3)-N angle of 178.8 (9)°, average length of Cr-C(3) bond 1.85 (1) Å); (ii) a disparity in the Cr-C(arene) bonds arising in both forms from a significant lengthening of most of the Cr-C bonds (average length 2.24 (1) Å) compared with the short Cr-C(6) bonds in forms A and B plus the Cr-C(7) bond in form B (average length 2.20 (1) Å); (iii) an unusual staggered configuration of the C(1), C(2), and C(3) atoms of the Cr(CO)<sub>2</sub>CNCOC<sub>6</sub>H<sub>5</sub> which is tripod with respect to the C(5), C(7), and C(9) atoms of the arene ligand.<sup>7</sup>

Also of interest is the possibility of the occurrence of an intramolecular interaction considering (a) the geometry of the Cr-CN-CO- group in which N...O(3) distance is only 2.26 (1)

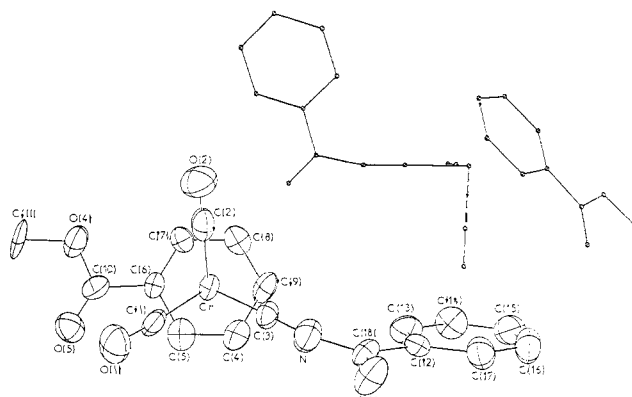


**Figure 1.** Monoclinic form of  $\text{CrC}_{18}\text{O}_5\text{NH}_{13}$ ; top, geometry of the Cr-CN-CO group looking along the normal to C(3)-N-C(18) plane; bottom, a view of the molecule looking along the normal to the complex arene ring. The hydrogen atoms are removed for clarity and thermal ellipsoids correspond to 50% probability. Note the relative orientation of the phenyl groups resulting in a dihedral angle of  $20^\circ$  between the O(1)-O(2)-O(3) and C(4)-C(5)-C(6)-C(7)-C(8)-C(9) planes.

$\text{\AA}$  (the corresponding sum of van der Waals radii is  $2.85 \text{ \AA}$ ) and the Cr-C(3)-O(3) and C(3)-N-O(3) angles of  $168 (1)$  and  $163 (1)^\circ$  respectively; (b) the orientation of the nearly planar CrCNCOC<sub>6</sub>H<sub>5</sub> system leading to existence of a plane of the oxygen atoms O(1), O(2), and O(3) of the same nature as that with the tripod Cr(CO)<sub>3</sub>.

The following experiment suggests a possible effect of the above features on the chemical reactivity.  $(\eta^6\text{-C}_6\text{H}_5\text{CO}_2\text{CH}_3)\text{Cr}(\text{CO})_2(\text{CNCOC}_6\text{H}_5)$ , treated in acetone for 3 h at  $85^\circ\text{C}$  under CO pressure (110 atm), gave rise to  $(\text{CO})_5\text{Cr}(\text{CNCOC}_6\text{H}_5)_2$  (mp  $86^\circ\text{C}$ ; mass spectrum  $m/e$  322.9521 (calcd 322.952195)) and  $(\text{C}_6\text{H}_5\text{CO}_2\text{CH}_3)\text{Cr}(\text{CO})_3$  in 80:20 proportion, while 40% of the starting material was recovered unchanged. Since the source of the (arene)Cr(CO)<sub>3</sub> derivative could not be ascribed unambiguously to a new kind of intramolecular arrangement on this basis alone, we feel this point deserves further study.<sup>8</sup> Therefore we focused our attention on the major reaction involving labilization of the six-electron ligand. We found that a slight modification of the arene ring greatly favored the above transformation which proceeded to completion in <3 h.  $(\eta^6\text{-1-CO}_2\text{CH}_3\text{-2-CH}_3\text{C}_6\text{H}_4)\text{Cr}(\text{CO})_2\text{CNCOC}_6\text{H}_5$  (mp  $54^\circ\text{C}$ ; NMR ( $\text{CDCl}_3$ )  $\delta_{\text{C}_6\text{H}_5}$  8.4 (m, 2), 7.85 (m, 3),  $\delta_{\text{C}_6\text{H}_4\text{Cr}}$  6.5 (m, 1), 5.9 (m, 1), 5.4 (m, 2), and  $\delta_{\text{OCH}_3}$  2.6 (s, 3)) or  $(\eta^6\text{-1-CO}_2\text{CH}_3\text{-3-CH}_3\text{C}_6\text{H}_4)\text{Cr}(\text{CO})_2\text{CNCOC}_6\text{H}_5$  (mp  $61^\circ\text{C}$ ; NMR ( $\text{CDCl}_3$ )  $\delta_{\text{C}_6\text{H}_5}$  8.3 (m, 2), 7.85 (m, 3),  $\delta_{\text{C}_6\text{H}_4\text{Cr}}$  6.25 (m, 2), 5.7 (m, 2),  $\delta_{\text{OCH}_3}$  4 (s, 3), and  $\delta_{\text{CH}_3}$  ( $\text{CDCl}_3$ ) 2.3 (s, 3)), when allowed to react with CO (110 atm) at  $85^\circ\text{C}$  for 3 h, led to  $(\text{CO})_5\text{-CrCNCOC}_6\text{H}_5$  (yield based on isolated products, 65–69%) while no significant amount of (arene)Cr(CO)<sub>3</sub> could be detected. The additional substitution on the arene ring appears to have increased the disparity in the Cr-arene bonds which are already perturbed by the CNCOC<sub>6</sub>H<sub>5</sub> ligand in the way revealed by the x-ray structure.

In addition to establishing that the liberation of the arene occurs under conditions where the CNCOC<sub>6</sub>H<sub>5</sub> ligand preserves its identity, this facile substitution reaction by three carbonyl groups furnishes a new synthetic route to Cr(CO)<sub>5</sub>-CN(CO)R complexes in reasonable yields. It may also be imagined that a coordinatively unsaturated moiety resulting from the likely stepwise liberation of the arene would lead, under different conditions, not to stable species but to an intermediate that may have catalytic potential. The following experiment confirms this idea. Thus 2.5 g ( $2.27 \cdot 10^{-2}$  M) of *cis*-cyclooctene, heated for 15 h at  $60^\circ\text{C}$  in 15 mL of  $\text{CCl}_4/\text{THF}$  (1:1) in presence of  $\eta^6\text{-1-CO}_2\text{CH}_3\text{-2-CH}_3\text{C}_6\text{H}_4\text{Cr}(\text{CO})_2\text{CNCOC}_6\text{H}_5$  ( $0.1 \text{ g}$ ,  $2.6 \cdot 10^{-4}$  M) un-



**Figure 2.** Corresponding views of the triclinic form of  $\text{CrC}_{18}\text{O}_5\text{NH}_{13}$ .

derwent addition of  $\text{CCl}_3$  and Cl units to the olefin. A 3.6-g sample ( $1.36 \cdot 10^{-2}$  M, conversion yield 60%) of 1-trichloromethyl-2-chlorocyclooctane was isolated from the reaction mixture. No such reaction involving addition of a functional group onto an olefin substrate occurred with the use of the corresponding tricarbonyl benzenechromium precursors.<sup>9</sup> Further experiments are underway to delineate the scope and limitation of this reaction and to search for new catalytic reactions utilizing the strong labilizing effect of these promising ligands.

**Acknowledgment.** We thank Professor Jack Lewis for helpful discussions.

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- (4) To our knowledge, the easiest way to prepare these Cr(CO)<sub>3</sub> complexes in excellent yields (equal or superior to 90%) has been reported by C. A. L. Mahaffy and P. L. Pauson, *Inorg. Syn.*, in press.
- (5) The herein described procedure has been applied to complexes bearing on the  $\pi$ -compound ring either electron-donating groups ( $\text{R} = \text{CH}_3$ ,  $\text{CH}(\text{CH}_3)_2$ ,  $\text{C}(\text{CH}_3)_3$ ,  $\text{OCH}_3$ ) or electron-withdrawing substituents ( $\text{R} = \text{CO}_2\text{Me}$ ,  $\text{COMe}$ ) ( $\text{R}' = \text{H}$ ,  $\text{CH}_3$ , or  $\text{CO}_2\text{Me}$ ), while the following substituents were fixed on the para position of the *N*-benzoyl group ( $\text{H}$ ,  $\text{Cl}$ ,  $\text{CH}_3$ ,  $\text{NO}_2$ ). Whereas the preparation of the (arene)Cr(CO)<sub>2</sub>(CNCOC<sub>6</sub>H<sub>5</sub>) complex failed, several other new families of functional isocyanides have been fully characterized by usual spectroscopic methods and elemental analysis (e.g., :CNCOC<sub>6</sub>H<sub>5</sub>, :CNCOC<sub>6</sub>H<sub>4</sub>, :CNCOC<sub>6</sub>H<sub>3</sub>, :CNCOC<sub>6</sub>H<sub>2</sub>, :CNCOC<sub>6</sub>H, :CNCOC<sub>5</sub>H<sub>4</sub>, :CNCOC<sub>5</sub>H<sub>3</sub>, :CNCOC<sub>5</sub>H<sub>2</sub>, :CNCOC<sub>5</sub>H, :CNCOC<sub>4</sub>H<sub>3</sub>, :CNCOC<sub>4</sub>H<sub>2</sub>, :CNCOC<sub>4</sub>H, :CNCOC<sub>3</sub>H<sub>2</sub>, :CNCOC<sub>3</sub>H, :CNCOC<sub>2</sub>H<sub>2</sub>, :CNCOC<sub>2</sub>H, :CNCOC<sub>2</sub>, :CNCOC<sub>1</sub>H, :CNCOC<sub>1</sub>).
- (6) Crystal data and refinement results are as follows.  $\text{CrC}_{18}\text{O}_5\text{NH}_{13}$ , parallelepiped, form A: triclinic;  $a = 6.766 (8)$ ,  $b = 10.101 (8)$ ,  $c = 13.465 (7) \text{ \AA}$ ;  $\alpha = 92.05 (6)$ ,  $\beta = 111.34 (6)$ ,  $\gamma = 105.94 (10)^\circ$ ;  $\rho_{\text{calcd}} = 1.53$ ,  $\rho_{\text{obsd}} = 1.58 \text{ g cm}^{-3}$ ;  $Z = 2$ ; space group  $P\bar{1}$ . Hexagonal platelike form B: monoclinic;  $a = 6.836 (3)$ ,  $b = 19.086 (8)$ ,  $c = 12.670 (8) \text{ \AA}$ ;  $\beta = 98.42 (5)^\circ$ ;  $\rho_{\text{calcd}} = 1.53$ ,  $\rho_{\text{obsd}} = 1.58 \text{ g cm}^{-3}$ ;  $Z = 4$ ; space group  $P2_1/C$ . Three dimensional x-ray diffraction data were collected on a computer-controlled four-circle Nonius CAD4 autodiffractometer using graphite-monochromated Mo K $\alpha$  radiation and  $\omega$ - $2\theta$  scans. For both structures, atoms were located through direct methods (MULTAN) and standard difference Fourier techniques and the resulting structural parameters have been refined to convergence (form A,  $R = 0.080$  and  $R_w = 0.079$  for 1035 independent reflexions having  $\theta < 30^\circ$  and  $I > 2\sigma(I)$ ; form B,  $R = 0.099$  and  $R_w = 0.101$  for 1614 independent reflexions having  $\theta < 25^\circ$  and  $I > 2\sigma(I)$ ) using unit-weighted full-matrix least-squares techniques with anisotropic thermal parameters for all nonhydrogen atoms.
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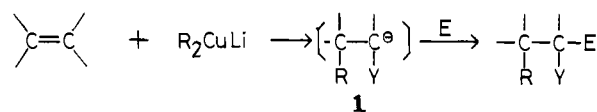
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### Zinc-Promoted One-Step Joining Reaction of Alkyl Halides, Activated Olefins, and Carbonyl Compounds

*Sir:*

Conjugate addition of organocopper reagents has been accepted as a versatile tool to introduce an alkyl group into the

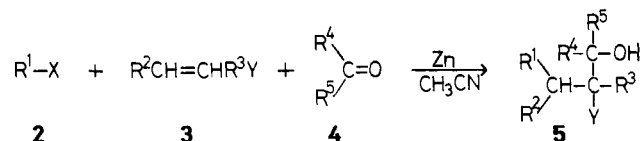


Y: electron-withdrawing group


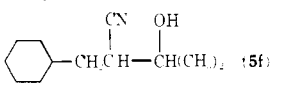

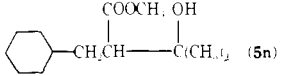
E: electrophile

$\beta$ -position of  $\alpha,\beta$ -conjugated olefinic systems.<sup>1</sup> The trapping of the anionic intermediate **1** with electrophiles<sup>2</sup> other than alkylating agents<sup>3</sup> has also been shown in some syntheses. The organocopper reagents, however, are not necessarily simple in their preparation and operation.

We wish to report a novel zinc-promoted joining reaction<sup>4,5</sup> of three components consisting of alkyl halides **2**, activated olefins **3**, and carbonyl compounds **4**. This one-step joining reaction is characterized by remarkable simplicity and high yield. The reaction may proceed through formation of an anionic species from **2** followed by addition of the anion to **3** and



**Table I.** One-Step Joining Reaction of Three Components **2**, **3**, and **4** in Acetonitrile<sup>a</sup>

Halide <b>2</b> , R <sup>1</sup> X	Activated Olefin <b>3</b>			Carbonyl Compound <b>4</b>		Product <b>5</b>	Yield, <sup>b</sup> %
	R <sup>2</sup>	R <sup>3</sup>	Y	R <sup>4</sup>	R <sup>5</sup>		
(CH <sub>3</sub> ) <sub>2</sub> CHI	H	H	CN	CH <sub>3</sub>	CH <sub>3</sub>	(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> CH(OH)C(CH <sub>3</sub> ) <sub>2</sub> ( <b>5a</b> <sup>f</sup> )	98
(CH <sub>3</sub> ) <sub>2</sub> CHI	H	H	CN	C <sub>6</sub> H <sub>5</sub>	H	(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> CH(OH)CHC <sub>6</sub> H <sub>5</sub> ( <b>5b</b> )	94
(CH <sub>3</sub> ) <sub>2</sub> CHI	H	H	CN	(CH <sub>2</sub> ) <sub>5</sub>		(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> CH(OH)C(CH <sub>2</sub> ) <sub>5</sub> ( <b>5c</b> )	99
(CH <sub>3</sub> ) <sub>2</sub> CHI	H	H	CN	(CH <sub>2</sub> ) <sub>4</sub>		(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> CH(OH)C(CH <sub>2</sub> ) <sub>4</sub> ( <b>5d</b> )	92
(CH <sub>3</sub> ) <sub>2</sub> CHI	H	H	CN	C <sub>2</sub> H <sub>5</sub>	H	(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> CH(OH)CHCH <sub>2</sub> CH <sub>3</sub> ( <b>5e</b> )	65
	H	H	CN	CH <sub>3</sub>	CH <sub>3</sub>	 ( <b>5f</b> )	95
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> I	H	H	CN	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH(OH)C(CH <sub>3</sub> ) <sub>2</sub> ( <b>5g</b> )	63
CH <sub>3</sub> I	H	H	CN	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH(OH)C(CH <sub>3</sub> ) <sub>2</sub> ( <b>5h</b> ) <sup>f</sup>	52
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br	H	H	CN	CH <sub>3</sub>	CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH <sub>2</sub> CH(OH)C(CH <sub>3</sub> ) <sub>2</sub> ( <b>5i</b> )	46
(CH <sub>3</sub> ) <sub>2</sub> CHI	CH <sub>3</sub>	H	CN	C <sub>6</sub> H <sub>5</sub>	H	(CH <sub>3</sub> ) <sub>2</sub> CHCH(CH <sub>3</sub> )CH(OH)CHC <sub>6</sub> H <sub>5</sub> ( <b>5j</b> )	95
(CH <sub>3</sub> ) <sub>2</sub> CHI	H	CH <sub>3</sub>	CN	C <sub>6</sub> H <sub>5</sub>	H	(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> C(CH <sub>3</sub> )CHC <sub>6</sub> H <sub>5</sub> ( <b>5k</b> )	73
(CH <sub>3</sub> ) <sub>2</sub> CHI	H	CH <sub>3</sub>	CN	CH <sub>3</sub>	CH <sub>3</sub>	(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> C(CH <sub>3</sub> )C(CH <sub>3</sub> ) <sub>2</sub> ( <b>5l</b> ) <sup>f</sup>	72
(CH <sub>3</sub> ) <sub>2</sub> CHI	H	H	COOCH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> CH(OH)C(CH <sub>3</sub> ) <sub>2</sub> ( <b>5m</b> )	57
	H	H	COOCH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	 ( <b>5n</b> )	52

<sup>a</sup> The molar ratios of **2**, **4**, and zinc to **3** were 3.0, 3.0, and 5.0, respectively. <sup>b</sup> Isolated yields. <sup>c</sup> Substitution of isopropyl iodide with isopropyl bromide resulted in the decrease in the yield (31%) of **5a**. <sup>d</sup> The molar ratio of **2** to **3** was 5.0. <sup>e</sup> Acetone was used as solvent. An unexpected product, (CH<sub>3</sub>)<sub>2</sub>CHCH<sub>2</sub>C(CN)(CH<sub>3</sub>)COCH<sub>3</sub> was obtained in acetonitrile, the yield being 42%.<sup>8</sup>