was evaporated at reduced pressure, and the remaining solution was acidified and extracted with ether. The crude product (0.3 g) was treated in ether solution with diazomethane. Separation on silica gel (20 g; elution with ether–hexane, 3:1) yielded **13** (120 mg, 39%) and 3,5-dimethyl-2-(methylthio)-4*H*-pyran-4-one[1] (60 mg, 22%).

Powdered **2** (310 mg) was stirred at 70 °C in 22 mL of the above NaHS solution for 3.5 h. The crude product was treated in ethyl acetate solution with a slight excess of benzylamine, yielding 440 mg (79%) of **11**, mp 180–183 °C. Acidification, extraction, and methylation of an aliquot from this salt yielded pure **13** (^{1}H NMR).

3,5-Dimethyl-2-(methylthio)-4*H*-thiopyran-4-one (13). Treatment of **9** in ether solution with a slight excess of diazomethane in ether, evaporation of the solvent and recrystallization from hexane yielded **13**: mp 78–79 °C; δ 2.17 (Me), 2.27 (Me), 2.54 (S-Me), 7.50 (vinylic H); ν_{max} 3010 (w), 2920 (w), 1585, 1570, 1555 (all s), 1505 (s), 1435, 1393, 1368, 1278, 1190, 1030, 992, 953 (all m) cm^{-1}; λ_{max} 243 nm (ε 13 600), 262 (7300), 308 (14 000); *m/e* 186 (M$^+$), 171, 153, 143, 140, 99, 71.

Anal. Calcd for $C_8H_{10}OS_2$: C, 51.58; H, 5.41. Found: C, 51.65; H, 5.45.

Acetylation of 9. Compounds 14 and 15. A solution of **9** (0.60 g) in pyridine (3 mL) was treated with acetic anhydride (1 mL) at room temperature for 6 h. The usual workup gave a mixture of two compounds that were separated by chromatography on silica gel (30 g).

4-Acetoxy-3,5-dimethyl-2*H*-thiopyran-2-thione (15): 0.11 g (15%, eluted with dichloromethane); mp 100–101 °C (hexane); δ 2.12 (Me), 2.27 (Me), 2.37 (Me), 7.37 (vinylic H); ν_{max} 1760 (s), 1580 (m), 1500 (m), 1365 (m), 1200 (s), 1190 (s), 1170 (s), 1160 (m), 1030 (m), 1015 (m), 1000 (s), 955 (m), 900 (m), 825 (m) cm^{-1}; λ_{max} 251 nm (ε 12 600), 314 (7800), 437 (5400); *m/e* 214 (M$^+$), 172, 139, 128, 101, 99.

Anal. Calcd for $C_9H_{10}O_2S_2$: C, 50.44; H, 4.70. Found: C, 50.65; H, 4.96.

2-(Acetylthio)-3,5-dimethyl-4*H*-thiopyran-4-one (14): 0.56 g (75%, eluted with dichloromethane–ethyl acetate, 1:1); mp 89–90 °C (hexane); δ 2.17 (Me), 2.25 (Me), 2.47 (Me), 7.60 (vinylic H); ν_{max} 1705 (s), 1580 (s), 1430 (m), 1370 (m), 1255 (m), 1118 (m), 1025 (m), 970 (m), 938 (m), 870 (m) cm^{-1}; λ_{max} 242 nm (ε 8100), 304 (11 400); *m/e* 214 (M$^+$), 197, 181, 162, 139, 128, 101, 99, 71.

Anal. Calcd for $C_9H_{10}O_2S_2$: C, 50.44; H, 4.70. Found: C, 50.63; H, 4.89.

Reaction of 14 with Benzylamine. Benzylamine (183 mg) dissolved in ethyl acetate (1 mL) was added to a solution of **14** (170 mg) in the same solvent (2 mL). Immediate reaction occurred with warming and precipitation of an oil which solidified on scratching. The solid was filtered and identified as **11** (125 mg). The solution was evaporated to dryness to give 220 mg of solid *N*-benzylacetamide, identical with an authentic sample (^{1}H NMR and melting point).

1-Benzyl-3,5-dimethyl-2-mercapto-4(1*H*)-pyridone (5b). Salt **12** (150 mg) was treated with 5% HCl and extracted with ethyl acetate. The crude product was filtered on 10 g of silica gel with ethyl acetate-hexane (7:3), yielding solid **5b** (90 mg). Recrystallization from ether-hexane yielded the pure compound: mp 89–90 °C; δ 2.05 (Me), 2.25 (Me), 3.57 (br, 1 H, exchanged with D_2O), 5.14 (CH_2), 7.02 (vinylic H), 7.37 (Ph); ν_{max} 2520 (m, br), 1640 (s), 1590 (s), 1575 (s), 1500 (m), 1453 (m), 1432 (m), 1363 (m), 1333 (m), 1328 (m), 996 (m), 928 (m), 765 (m), 730 (m) cm^{-1}; δ_{max} 229 nm (ε 20 500), 244 (sh, 8900), 304 (8900); *m/e* 245 (M$^+$), 154, 91.

Anal. Calcd for $C_{14}H_{15}NOS$: C, 68.54; H, 6.16; N, 5.71. Found: C, 68.39; H, 6.16; N, 5.81.

Methylation of **5b** in ether solution, as described above for **13**, yielded 1-benzyl-3,5-dimethyl-2-(methylthio)-4(1*H*)-pyridone (**7b**) as a distillable liquid: bp 160–170 °C (bath temperature; 0.01 torr); δ 2.15 (Me), 2.27 (Me), 2.42 (Me), 5.10 (CH_2), 7.01 (vinylic H), 7.32 (Ph); ν_{max} ($CHCl_3$) 1635 (s), 1578 (s), 1315 (m), 1120 (m), 1000 (m), 980 (m) cm^{-1}; λ_{max} 210 nm (ε 31 300), 238 (sh, 7200), 298 (sh, 5800), 319 (6100); *m/e* 259 (M$^+$), 226, 168, 149, 115, 113, 91.

Anal. Calcd for $C_{15}H_{17}NOS$: C, 69.46; H, 6.61; N, 5.40. Found: C, 69.06; H, 6.63; N, 5.37.

Acetylation of **5b** (0.25 g) with acetic anhydride in pyridine yielded after chromatography (15 g of silica gel; ethyl acetate–dichloromethane, 1:4) 0.18 g (61%) of 2-(acetylthio)-1-benzyl-3,5-dimethyl-4-(1*H*)-pyridone (**17**): mp 99–100 °C (hexane); δ 2.00 (Me), 2.28 (Me), 2.43 (Me), 5.13 (CH_2), 7.05 (vinylic H), 7.33 (Ph); ν_{max} 1702 (s), 1640 (s), 1582 (s), 1527 (m), 1498 (m), 1454 (m), 1437 (m), 1370 (m), 1135 (m), 1118 (m) cm^{-1}; λ_{max} 219 nm (ε 24 400), 329 (6000); *m/e* 287 (M$^+$), 245, 244, 212, 154, 91.

Anal. Calcd for $C_{16}H_{17}NO_2S$: C, 66.87; H, 5.96; N, 4.87. Found: C, 67.13; H, 6.09; N, 5.05.

Registry No. **1**, 61170-10-3; **2**, 61170-12-5; **4**, 75347-29-4; **5a**, 75347-30-7; **5b**, 75347-31-8; **6a**, 75347-32-9; **7a**, 75347-33-0; **7b**, 75347-34-1; **8a**, 75347-35-2; **8b**, 75347-36-3; **9** (isomer 1), 75347-37-4; **9** (isomer 2), 75347-38-5; **10**, 75347-39-6; **11**, 75347-41-0; **11** pyrrolidinium salt, 75347-42-1; **11** morpholinium salt, 75347-43-2; **12**, 75347-45-4; **13**, 75347-46-5; **14**, 75347-47-6; **15**, 75347-48-7; **16**, 75347-49-8; **17**, 75347-50-1; 3,5-dimethyl-2-(methylthio)-4*H*-pyran-4-one, 67844-82-0; methylamine, 74-89-5; benzylamine, 100-46-9.

N-Alkylation of Nitriles Using Chromium Tricarbonyl Complexes of Benzyl Alcohol and Its Derivatives: New Perspectives for the Ritter Reaction

Siden Top and Gérard Jaouen*

Stéréochimie des Elements de Transition, Laboratoire de Chimie des Organométalliques, Université de Rennes, 35042 Rennes, Cedex, France

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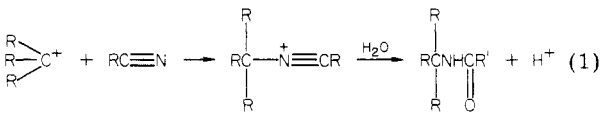
The Ritter reaction, which involves the reaction of nitrile on a carbenium ion, giving rise to an amide, can be considerably improved by using carbenium ion intermediates stabilized by a transition-metal moiety (e.g., $Cr(CO)_3$). However, an excessive stabilization can inhibit the reactivity. In complexed systems the reaction takes place with total stereochemical control.

The conversion of nitriles to amides by reaction with alcohols or alkenes in the presence of sulfuric acid is the Ritter reaction.[1] Acidification of the appropriate alcohol or alkene generates a carbenium ion which reacts with the nitrile as shown in eq 1.



(1)

While the successful course of the reaction certainly depends on the reactivity of the nitrile, a major factor is the stability and reactivity of the carbocationic intermediates. While tertiary alcohols generally give good yields, secondary and primary alcohols give only mediocre results;[2a] this is a reflection of the instability of the primary

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Table I. Data for *N*-Benzyl Amide Complexes 2 ($R^1 = R^2 = R^3 = H$) Obtained from 1

R^4	mp, °C	yield, %	R^4	mp, °C	yield, %
Me	94	99	CH_2=CH	93	98
Ph	132	78	$PhCH_2$	138	78
$ClCH_2$	108	98	*o*-MeC_6H_4	159	83
n-Pr	97	96			

and secondary carbenium ions in the purely organic series.

This paper shows that this important limitation can sometimes be overcome by use of organometallic intermediates which directly influence the stability of the carbenium ions. A preliminary communication has already appeared.[3]

Results and Discussion

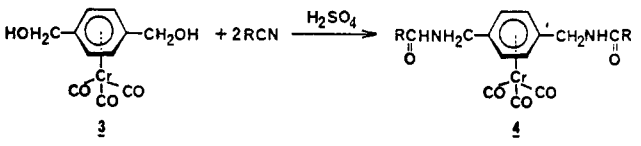
The remarkable stabilization of α-carbenium ions of organometallic complexes of transition metals is the most constant characteristic of these series.[4] While several studies have been devoted to the fundamental problem of elucidating the nature of this stabilization, the exploitation of this property in organic synthesis has scarcely been touched upon.[5] Although several organometallic series, for example, the ferrocenyl system, have been shown to allow ready accessibility of the α-carbenium ions, the intrinsic interest of the ultimate products to the synthetic organic chemists is not very compelling. However, in other series such as the benchrotrenes, the interest is much greater since each arene can theoretically be compared to its complexed analogue. Furthermore, the regeneration of the purely organic products presents no difficulties. Nevertheless, this latter series is characterized by the difficult accessibility of their stable carbenium ions, and this has militated against their strategic use in synthesis. Indeed, the first attempt[6] at isolation of an α-carbenium ion in the arene chromium tricarbonyl series, viz., $(OC)_3CrC_6H_5CH_2^+$, was unsuccessful. For a long time this initial problem could not be surmounted, and it was only recently that Seyferth et al.[5c] showed that the carbenium ion is sufficiently stable to be isolated only when two arene rings are complexed as in $(OC)_3CrC_6H_5C^+HC_6H_5Cr(CO)_3$. Concurrently, our work on the α-carbenium ions of arenechromium tricarbonyls[5b] has shown that even when they cannot be isolated they can be turned to synthetic advantage. By performing in situ reactions under adequate conditions, one can use these α-carbenium complexes despite their relatively short lifetimes. Indeed, the action of methanol or an amine on primary, secondary, or tertiary carbocations readily leads to the formation of ethers or amines. This approach is also applicable to the Ritter reaction, as shown in eq 2.

$$\underset{\mathbf{1}}{(\eta^6\text{-}R^1C_6H_4CR^2R^3OH)Cr(CO)_3} + R^4CN \xrightarrow[-15\ °C]{H_2SO_4} \underset{\mathbf{2}}{(\eta^6\text{-}R^1C_6H_4CR^2R^3NHCOR^4)Cr(CO)_3} \quad (2)$$

Table II. Data for Substituted *N*-Benzyl Amide Complexes 2 (R^4 = Me or Ph)

			R^4 = Me		R^4 = Ph	
R^1	R^2	R^3	mp, °C	yield, %	mp, °C	yield, %
p-Me	H	H	106	95	136	89
p-MeO	H	H	88	94	122	81
p-MeO	Me	H	138	99	125	84
H	Ph	H	170	82		0
H	Me	Me		0		0

Table III. Data for Diamides 4



R	mp, °C	yield, %
CH_3	160	70
Ph	213	73

The addition of concentrated sulfuric acid to a cooled (−15 °C), deoxygenated solution of alcohol 1 in an excess of the nitrile allows the in situ generation of the carbocation; this intermediate reacts immediately with the nitrile, and subsequent hydrolysis with water and extraction with ether give the product. The physical data for the amides 2 are summarized in Tables I and II.

A few general remarks can be made concerning this reaction. First, it is very rapid. The formation of the carbenium ion is almost instantaneous, and it reacts immediately with the nitrile. In contrast, the normal reaction is complete only after 20–40 h. As shown in Table I, good yields are obtained even with primary alcohols. This is a manifestation of the increased stability of the carbenium ions due to the attachment of the $Cr(CO)_3$ moiety. Indeed, the value of pK_{R^+} of $(PhCH_2^+)Cr(CO)_3$ is −11.8[7] while that of the noncomplexed benzyl cation is −17.3;[8] by way of comparison, purely organic carbenium ions such as Ph_3C^+ and Ph_2CH^+ have values of −6.6 and −13.4, respectively.[9] We note also that the conventional Ritter rection to produce *N*-benzyl, *N*-(*p*-methylbenzyl), and *N*-(*p*-methoxybenzyl) amides proceeds in modest yields (48%, 40%, and 60%, respectively) but only after two days.[10]

We see from Table II that benzhydrol does not react with PhCN and that 2-phenyl-2-propanol is inactive even with CH_3CN. These results indicate an excessive stabilization of the carbenium ion which completely inhibits its reactivity. Earlier studies on the diphenylalkylmethanols Ph_2RCOH [R = CH_3, C_2H_5, $CH(CH_3)_2$] have shown that these alcohols, which are precursors of very stable carbenium ions, are completely inactive.[11] Only the corresponding alkenes are isolated after the reaction. The reactivity of the benzhydrol complex toward CH_3CN but its inertness toward PhCN (as listed in Table II) does not fit in well with the reactivity sequence CH_2=CHCN > PhCN > CH_3CN previously observed for reactions with isobutene.[12]

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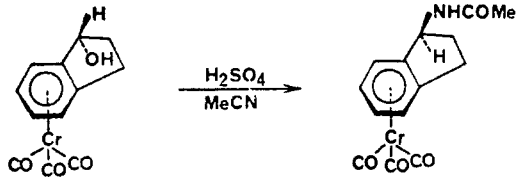
(12) G. Glikmans, B. Torch, M. Hellin, and F. Coussemant, *Bull. Soc. Chim. Fr.*, 1383 (1966).

Scheme I



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In a comparative study of the reactivities of different nitriles, Ritter[13] has shown that certain of them gave poor yields (e.g.: $ClCH_2CN$, 21%; *n*-PrCN, 50%; *o*-MeC_6H_4CN, 35%). With the complexed products we have not found (see Table I) any marked diminution of the yields in these cases. On the other hand, with solid nitriles, where one is obliged to use an auxiliary solvent, the yields are always poor. For example, stearonitrile leads to the amide $(OC)_3Cr(p\text{-}MeC_6H_4C(CH_3)HNHC(O)C_{17}H_{35}\text{-}n)$ which is obtained in only 18% yield (22% in the noncomplexed series).[13] Because of the short lifetime of the benchrotrene carbenium ions, all excessive dilution of the reacting species is to be avoided. However, even use of CH_2Cl_2 or acetic anhydride, in which the carbenium ions are quite stable, does not lead to amide formation. Acetic acid seems to be the only acceptable solvent for the complexes.

The presence of two alcohol functionalities in the same molecule only slightly affects the course of the reaction (see Table III), and reasonably good yields are obtained.[14]

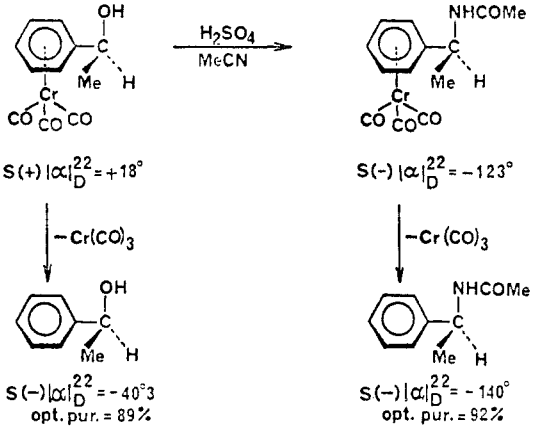
Several attempts to bring about a reaction with a dinitrile, NCRCN, were unsuccessful. This is probably attributable to the necessity of using an auxiliary solvent in this case, for, even with acetic acid, the yields are considerably reduced.

One should realize that in the organometallic series a number of interesting stereochemical features arise. It is known that the incorporation of a $Cr(CO)_3$ moiety imposes a three-dimensional structure on the molecule, and this can be profitably utilized in asymmetric transformations.

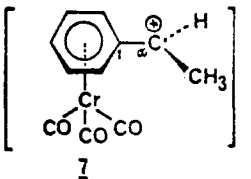
For example (Scheme I), the (*endo*-1-hydroxyindan)-chromium tricarbonyl **5** [racemic, mp 105 °C; optically pure (1*R*), mp 110 °C, $[\alpha]^{22}_D$ +60° (*c* 2.07, $CHCl_3$[15])] reacts with CH_3CN to give exclusively the exo amide **6** (racemic, mp 142 °C, yield 89%; optically pure (1*S*), mp 155 °C, $[\alpha]^{22}_D$ +143° (*c* 1.88, $CHCl_3$)]. There is thus a *total inversion* of the configuration at the chiral 1-position in the course of the reaction. The endo or exo nature of the product **6** was determined by decomplexation of the racemic mixture and then recomplexation of the liberated amide with $Cr(CO)_6$ (racemic endo, mp 206 °C).

Even in the open series (Scheme II), one observes a remarkable stereospecificity of reaction; thus (*S*)-(+)-(1-phenyl-1-hydroxyethyl)chromium tricarbonyl [$[\alpha]^{22}_D$ +18° (*c* 2.1, $CHCl_3$)] of optical purity 89% (calculated after decomplexation by using the values previously reported[16a]) reacts with CH_3CN, leading to the corresponding amide *S*-(−) compound [$[\alpha]^{22}_D$ −123° (*c* 1, $CHCl_3$)] of optical purity 92% (calculated by using the literature data[17]). Hence, the reaction proceeds with practically 100% *retention* of configuration.

Scheme II



This interesting result shows that the extent of asymmetric induction can be remarkably high even in the open series while using carbenium ions. This augurs well for later applications in the phenylethanol series where numerous studies have apparently suffered up to now because of large losses of optical activity during chemical transformations.[18] There is then reason to question the complete change in stereochemistry observed when one examines the rigid series (indanol, inversion) and the open series (phenylethanol, retention). To our minds there is no contradiction between these facts. In the indanol **5** the hydroxyl is essentially fixed in the endo position, and the generation of the carbenium ion can only occur upon departure of this moiety, giving unequivocally a structure which could only lead to the amide **6** by a stereospecifically exo attack; this type of attack normally occurs in this series,[19] as shown in Scheme I. A different situation obtains in the open series where the OH group could adopt either an endo or exo position. Even if the endo conformation is favored in solution, it is clear that, by virtue of either the steric protection or the anchimeric assistance afforded by the $Cr(CO)_3$ group,[4b,20] the rate of formation of the carbenium ion is very greatly accelerated when the OH is exo, thus preferentially generating the carbenium ion **7**. A rapid stereospecific exo attack by the nitrile, in



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a manner identical with the preceding case, now leads to the isolated product. We note also that for an ion such as **7** the difficulty of rotation about the C_1–C_α bond has recently been analyzed by NMR spectroscopy.[21] The observed exo attack by nitriles on the carbenium ion–$Cr(CO)_3$ complexes may be rationalized in the following way. In an α-ferrocenylcarbenium ion the α-carbon bends out of the plane of the Cp to which it is connected toward the Fe.[4c] The Fe and unsubstituted Cp also move toward the α-carbon. If we reasonably suppose the same structural distortion occurs in the benzene–$Cr(CO)_3$ complexes, then

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(18) See for example: (a) H. Hart and H. S. Eleuterio, *J. Am. Chem. Soc.*, **76**, 516 (1954). (b) H. Hart and H. S. Eleuterio, *ibid.*, **76**, 1379 (1954).
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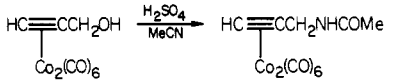
(21) M. Acampora, A. Ceccon, M. Dalfarra, G. Giacometti, and G. Rigatti, *J. Chem. Soc., Perkin Trans 2*, 483 (1977).

Scheme III



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endo attack is sterically congested, and exo attack will be the favored mode. This is rather like a tight ion pair with the $Cr(CO)_3$ group representing X^-, and back side attack is favored.

Proof of the ready accessibility of the carbenium ion by departure of the exo OH group was obtained in the following manner. An equimolar mixture of (*exo*- and *endo*-1-hydroxyindan)chromium tricarbonyls in acetonitrile solution was treated with concentrated sulfuric acid in a dropwise manner. The course of the reaction was followed very carefully by thin-layer chromatography and revealed the total disappearance of the exo alcohol, giving amide **6**, while the endo epimer remained largely unchanged in the medium.

This method of temporary complexation of reaction intermediates can also be extended to other organometallic systems of synthetic interest, e.g., (propargyl alcohol)dicobalt hexacarbonyl. In cases where the activating group $Co_2(CO)_6$ can be introduced[22] or eliminated[23] under mild conditions, these complexes seem to be ideal for eventual utilization as electrophilic propynyl synthons. The primary alcohol **8** (Scheme III) reacts with CH_3CN to give the amide **9** (mp 97 °C) in an identical manner with that in the $Cr(CO)_3$ series; the yield is 35%.

The low yield obtained is a result of the partial decomposition of the starting alcohol under our conditions. There is no doubt that optimizing the conditions would greatly improve the yield. The results depicted in Scheme III raise one's hopes of avoiding the extremely troublesome acid-catalyzed rearrangements so prevalent with noncomplexed propynyl alcohols.[24]

Conclusions

These experiments indicate that the use of organometallic intermediates in the Ritter reaction complements the classic uses of this reaction. Thus, the normally unstable primary carbenium ions are markedly stabilized, rendering their reactions facile and able to proceed in high yields. The selectivity of the substrates is now different. The limitations to this approach are inherent in its principle. In effect, a carbenium ion which is highly stabilized due to temporary complexation will become ipso facto inert. In such cases, however, the free ligand will be reactive and so can be used. A novelty offered in the complexed systems is the potential for stereochemical control, since we have shown that the reaction is stereospecific both in the cyclic series (which lead to inversion) and in the acyclic series (which show retention of configuration).

Experimental Section

All the arene tricarbonylchromium alcohols were prepared by the direct complexation of aromatic precursors with $Cr(CO)_6$.[25] The cobalt complex of 2-propynol was prepared from the alkyne by direct reaction with $Co_2(CO)_8$ in ether.[26] Nitriles were purchased from Aldrich and used without purification. RP Normapur sulfuric acid was purchased from Prolabo. The solvents are indicated as follows: E = ether, He = hexane, Ac = acetone, Hep = heptane. ^1H NMR spectra were recorded on either a Varian EM 360 or a JEOL MH 100. Chemical shifts are reported in δ units downfield from internal tetramethylsilane (s = singlet, d = doublet, t = triplet, m = multiplet). Infrared spectra were obtained by using a Unicam SP 1100 infrared spectrophotometer in either $CHCl_3$ or CH_2Cl_2 solution or in KBr or Nujol. Specific rotations were obtained on a Perkin-Elmer 241 MC polarimeter using a 1-dm cell thermostated at 22 °C.

General Method for the Preparation of Amides. A complexed alcohol was dissolved in an excess of nitrile under N_2. The mixture was cooled at −15 °C in a salt–ice bath, and then concentrated sulfuric acid, thoroughly purged with nitrogen before use, was slowly added. The mixture was allowed to stir for 1 min, poured into ice–water, and extracted with ether. In general, the amide was obtained in nearly pure form, and it was then purified by recrystallization. But in certain cases, the crude product should be purified either by column chromatography or by preparative TLC over Merck silica gel to eliminate an excess of high boiling point nitrile and secondary products.

$(C_6H_5CH_2NHCOCH_3)Cr(CO)_3$. From $(C_6H_5CH_2OH)Cr(CO)_3$ (1.22 g, 5×10^{-3} mol), CH_3CN (30 mL), and H_2SO_4 (5 mL) was obtained 1.4 g (99%) of amide after evaporation of ether: mp 94 °C (Ac/He); yellow; NMR ($CDCl_3$) δ 5.53 (s, complex aromatic), 4.39 (d, CH_2), 2.13 (s, CH_3); IR ($CHCl_3$) ν_{CO} = 1689 cm^{-1}, ν_{NH} = 3465 cm^{-1}. Anal. Calcd for $C_{12}H_{11}O_4CrN$: C, 50.53; H, 3.89; N, 4.91. Found: C, 51.05; H, 4.08; N, 4.58.

$(C_6H_5CH_2NHCOPh)Cr(CO)_3$ was obtained from $(C_6H_5CH_2OH)Cr(CO)_3$ (0.50 g, 2×10^{-3} mol), PhCN (10 mL), and H_2SO_4 (5 mL). The crude product was purified by column chromatography with Ac/He (1/1) as eluent to give 0.55 g of amide (78%): mp 132 °C (Ac/Hep); yellow; NMR (CD_3COCD_3) δ 4.81 (m, complex aromatic), 4.50 (d, CH_2), 7.79 and 8.25 (m, Ph); IR ($CHCl_3$) ν_{CO} = 1678 cm^{-1}, ν_{NH} = 3480 cm^{-1}. Anal. Calcd for $C_{17}H_{13}O_4CrN$: C, 58.79; H, 3.77; N, 4.03. Found: C, 59.17; H, 3.78; N, 4.02.

$(C_6H_5CH_2NHCOCH_2Cl)Cr(CO)_3$. From $(C_6H_5CH_2OH)Cr(CO)_3$ (0.50 g, 2×10^{-3} mol), $ClCH_2CN$ (10 mL), and H_2SO_4 (5 mL) was obtained 0.63 g of amide (98%): mp 108 °C (Ac/Hep); yellow; NMR (CD_3COCD_3) δ 5.85 (s, complex aromatic), 4.40 (d, CH_2), 4.31 (s, CH_2Cl); IR ($CHCl_3$) ν_{CO} = 1690 cm^{-1}, ν_NH = 3450 cm^{-1}. Anal. Calcd for $C_{12}H_{10}O_4CrNCl$: C, 45.08; H, 3.15; N, 4.38; Cl, 11.09. Found: C, 45.09; H, 3.29; N, 4.60; Cl, 11.23.

$(C_6H_5CH_2CHCO\text{-}n\text{-}C_3H_7)Cr(CO)_3$. From $(C_6H_5CH_2OH)Cr(CO)_3$ (0.50 g, 2×10^{-3} mol), *n*-C_3H_7CN (10 mL), and H_2SO_4 (5 mL) was obtained 0.61 g of amide (97%): mp 97 °C (Ac/Hep); yellow; NMR (CD_3COCD_3) δ 5.85 (s, complex aromatic), 4.33 (d, CH_2), 2.32 (t, $COCH_2$), 0.95 (t, CH_3); IR ($CHCl_3$) ν_{CO} = 1685 cm^{-1}, ν_{NH} = 3475 cm^{-1}. Anal. Calcd for $C_{14}H_{15}O_4CrN$: C, 53.67; H, 4.82; N, 4.47. Found: C, 53.79; H, 4.90; N, 4.31.

$(C_6H_5CH_2NHCOCH{=}CH_2)Cr(CO)_3$. From $(C_6H_5CH_2OH)Cr(CO)_3$ (0.50 g, 2×10^{-3} mol), $CH_2{=}CHCN$ (10 mL), and H_2SO_4 (5 mL) was obtained 0.58 g of amide (98%): mp 93 °C; yellow; NMR ($CDCl_3$) δ 5.56 (s, complex aromatic), 4.48 (d, CH_2); IR ($CHCl_3$) ν_{CO} = 1687 cm^{-1}, ν_{NH} = 3460 cm^{-1}. Anal. Calcd for $C_{13}H_{11}O_4CrN$: C, 52.53; H, 3.73; N, 4.71. Found: C, 52.60; H, 3.75; N, 4.68.

$(CO)_3CrC_6H_5CH_2NHCOCH_2C_6H_5$ was obtained from $(C_6H_5CH_2OH)Cr(CO)_3$ (0.50 g, 2×10^{-3} mol), $C_6H_5CH_2CN$ (10 mL), and H_2SO_4 (3 mL). The crude product was purified by column chromatography with E/He (2/1) as eluent to give 0.55 g of amide (76%): mp 138 °C (Ac/Hep); NMR (CD_3COCD_3) δ 5.74 (s, complex aromatic), 4.28 (d, CH_2), 3.67 (s, $COCH_3$), 7.55 (s, C_6H_5); IR ($CHCl_3$) ν_{CO} = 1685 cm, ν_{NH} = 3450 cm^{-1}. Anal. Calcd for $C_{18}H_{15}O_4CrN$: C, 59.81; H, 4.18; N, 3.87. Found: C, 59.92; H, 4.41; N, 4.01.

$(CO)_3CrC_6H_5CH_2NHCO(o\text{-}MeC_6H_4)$ was obtained from $(C_6H_5CH_2OH)Cr(CO)_3$ (0.50 g, 2×10^{-3} mol), *o*-tolunitrile (10 mL), and H_2SO_4 (3 mL). The crude product was purified by column chromatography with E/He (1/1) as eluent, affording 0.60 g of amide (83%): mp 159 °C (Ac/Hep); yellow; NMR (CD_3COCD_3)

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δ 5.85 (m, complex aromatic), 4.46 (d, CH_2), 7.53 (m, C_6H_4), 2.46 (s, CH_3); IR ($CHCl_3$) ν_{CO} = 1676 cm^{-1}, ν_{NH} = 3455 cm^{-1}. Anal. Calcd for $C_{18}H_{15}O_4CrN$: C, 59.83; H, 4.18; N, 3.87. Found: C, 59.97; H, 4.16; N, 3.91.

(*p*-MeC$_6$H$_4$CH$_2$NHCOCH$_3$)Cr(CO)$_3$. From (*p*-MeC$_6$H$_4$CH$_2$OH)Cr(CO)$_3$ (1.02 g, 4 × 10^{-3} mol), CH_3CN (30 mL), and H_2SO_4 (8 mL) was obtained 1.14 g of amide (95%): mp 106 °C (Ac/Hep); yellow; NMR ($CDCl_3$) δ 5.41 and 5.68 (2 d, complex aromatic), 4.33 (d, CH_2), 2.27 (s, *p*-Me), 2.12 (s, CH_3); IR ($CHCl_3$) ν_{CO} = 1685 cm^{-1}, ν_{NH} = 3465 cm^{-1}. Anal. Calcd for $C_{13}H_{13}O_4CrN$: C, 52.18; H, 4.38; N, 4.68. Found: C, 52.38; H, 4.28; N, 4.75.

[(CO)$_3$Cr][*p*-MeC$_6$H$_4$CH$_2$NHCOPh]. From (*p*-MeC$_6$H$_4$CH$_2$OH)Cr(CO)$_3$ (0.50 g, 2 × 10^{-3} mol), PhCN (10 mL), and H_2SO_4 (5 mL) was obtained 0.55 g of amide (78%): mp 136 °C (Ac/Hep); yellow; NMR (CD_3COCD_3) δ 5.86 (m, complex aromatic), 4.51 (d, CH_2), 7.79 and 8.26 (m, Ph); IR ($CHCl_3$) ν_{CO} = 1675 cm^{-1}, ν_{NH} = 3475 cm^{-1}. Anal. Calcd for $C_{18}H_{15}O_4CrN$: C, 59.83; H, 4.18; N, 3.87. Found: C, 59.90; H, 4.16; N, 3.77.

[(CO)$_3$Cr][*p*-MeOC$_6$H$_4$CH$_2$NHCOCH$_3$]. From (*p*-MeOC$_6$H$_4$CH$_2$OH)Cr(CO)$_3$ (1.08 g, 4 × 10^{-3} mol), CH_3CN (30 mL), and H_2SO_4 (8 mL) was obtained 1.18 g of amide (94%): mp 88 °C (Ac/Hep); yellow; NMR ($CDCl_3$) δ 5.33 and 5.84 (2 d, complex aromatic), 4.21 (d, CH_2), 3.83 (s, MeO), 2.09 (s, CH_3); IR ($CHCl_3$) ν_{CO} = 1685 cm^{-1}, ν_{NH} = 3470 cm^{-1}. Anal. Calcd for $C_{13}H_{13}O_5CrN$: C, 49.51; H, 4.15; N, 4.44. Found: C, 49.94; H, 4.11; N, 4.32.

[(CO)$_3$Cr][*p*-MeOC$_6$H$_4$CH$_2$NHCOPh] was obtained from (*p*-MeC$_6$H$_4$CH$_2$OH)Cr(CO)$_3$ (0.56 g, 2 × 10^{-3} mol), PhCN (10 mL), and H_2SO_4 (5 mL). The crude product was purified by column chromatography with E/He (2/1) as eluent to give 0.61 g (81%) of amide: mp 122 °C (Ac/Hep); yellow; NMR (CD_3COCD_3) δ 5.61 and 6.18 (2 d, complex aromatic), 4.38 (d, CH_2), 3.88 (s, MeO), 7.80 and 8.25 (2 m, Ph); IR ($CHCl_3$) ν_{CO} = 1674 cm^{-1}, ν_{NH} = 3475 cm^{-1}. Anal. Calcd for $C_{18}H_{15}O_5CrN$: C, 57.29; H, 4.01; N, 3.71. Found: C, 57.23; H, 4.16; N, 3.92.

[(CO)$_3$Cr][*p*-MeOC$_6$H$_4$CHCH$_3$NHCOCH$_3$]. From (*p*-MeOC$_6$H$_4$CHOHCH$_3$)Cr(CO)$_3$ (0.86 g, 3 × 10^{-3} mol), CH_3CN (30 mL), and H_2SO_4 (5 mL) was obtained 0.98 g of amide (99%): mp 138 °C (Ac/Hep); yellow; NMR (CD_3COCD_3) δ 5.56 and 6.20 (d, m, complex aromatic), 4.96 (m, CH), 1.43 (d, CH_3), 3.86 (s, MeO), 1.93 (s, $COCH_3$); IR ($CHCl_3$) ν_{CO} = 1682 cm^{-1}, ν_{NH} = 3455 cm^{-1}. Anal. Calcd for $C_{14}H_{15}O_5CrN$: C, 51.06; H, 4.59; N, 4.25. Found: C, 51.43; H, 4.63; N, 3.99.

[(CO)$_3$Cr][*p*-MeOC$_6$H$_4$CHCH$_3$NHCOPh] was obtained from (*p*-MeOC$_6$H$_4$CHOHCH$_3$)Cr(CO)$_3$ (0.58 g, 2 × 10^{-3} mol), PhCN (10 mL), and H_2SO_4 (3 mL). The crude product was purified by column chromatography with E/He (2/1) as eluent, providing 0.65 g (84%) of amide: mp 125 °C (Ac/Hep); yellow; NMR (CD_3COCD_3) δ 5.58 and 6.30 (d, m, complex aromatic), 5.22 (m, CH), 1.63 (d, CH_3), 3.89 (s, MeO), 7.77 and 8.24 (2 m, Ph); IR ($CHCl_3$) ν_{CO} = 1670 cm^{-1}, ν_{NH} = 3455 cm^{-1}. Anal. Calcd for $C_{19}H_{17}O_5CrN$: C, 58.31; H, 4.38; N, 3.58. Found: C, 58.37; H, 4.54; N, 3.65.

[(CO)$_3$Cr][(C$_6$H$_5$)$_2$CHNHCOCH$_3$]. From ($C_6H_5CHOHC_6H_5$)Cr(CO)$_3$ (0.96 g, 3 × 10^{-3} mol), CH_3CN (30 mL), and H_2SO_4 (5 mL) was obtained 0.89 g of amide (82%): mp 170 °C (Ac/Hep); yellow; NMR (CD_3COCD_3) δ 5.76 and 6.11 (2 m, complex aromatic), 6.30 (d, CH), 7.69 (m, Ph), 2.04 (s, CH_3); IR ($CHCl_3$) ν_{CO} = 1690 cm^{-1}, ν_{NH} = 3460 cm^{-1}. Anal. Calcd for $C_{18}H_{15}O_4CrN$: C, 59.83; H, 4.18; N, 3.87. Found: C, 59.72; H, 4.08; N, 3.98.

[(CO)$_3$Cr][CH$_3$CONHCH$_2$C$_6$H$_4$CH$_2$NHCOCH$_3$]. From ($HOCH_2C_6H_4CH_2OH$)Cr(CO)$_3$ (0.55 g, 2 × 10^{-3} mol), CH_3CN (20 mL), and H_2SO_4 (3 mL) was obtained 0.50 g of amide (70%): mp 160 °C (Ac/Hep); yellow; NMR (CD_3COCD_3) δ 5.50 (s, complex aromatic), 3.98 (d, CH_2, 1.88 (s, CH_3); IR (CH_2Cl_2) ν_{CO} = 1692 cm^{-1}, ν_{NH} = 3470 cm^{-1}. Anal. Calcd for $C_{15}H_{16}O_5CrN_2$: C, 50.56; H, 4.53; N, 7.86. Found: C, 50.65; H, 4.57; N, 7.84.

[(CO)$_3$Cr][PhOCNHCH$_2$C$_6$H$_4$CH$_2$NHCOPh]. From ($HOCH_2C_6H_4CH_2OH$)Cr(CO)$_3$ (0.55 g, 2 × 10^{-3} mol), PhCN (15 mL), and H_2SO_4 (3 mL) was obtained 0.70 g of amide (73%): mp 213 °C (Ac/Hep); yellow; NMR (CD_3COCD_3) δ 5.30 (s, complex aromatic), 2.19 (d, CH_2), 7.24 and 7.70 (2 m, Ph); IR (Nujol) ν_{CO} = 1650 cm^{-1}, ν_{NH} = 3300 cm^{-1}. Anal. Calcd for $C_{25}H_{20}O_5CrN_2$: C, 62.49; H, 4.19; N, 5.83. Found: C, 62.54; H, 4.12; N, 5.75.

(*exo*-1-Acetamidoindan)tricarbonylchromium 6. Racemic Series. From (*endo*-1-hydroxyindan)tricarbonylchromium (0.41 g, 1.5 × 10^{-3} mol), CH_3CN (20 mL), and H_2SO_4 (3 mL) was obtained the amide **6**: 0.42 g (89 %); mp 142 °C (Ac/Hep); yellow; NMR ($CDCl_3$) δ 2.01 (s, CH_3); IR ($CHCl_3$) ν_{CO} = 1684 cm^{-1}, ν_{NH} = 3460 cm^{-1}. Anal. Calcd for $C_{14}H_{13}O_4CrN$: C, 54.02; H, 4.21; N, 4.50. Found: C, 54.13; H, 4.29; N, 4.61.

Optically Active Series. The product was obtained from (1*R*)-(*endo*-1-hydroxyindan)tricarbonylchromium ($[\alpha]^{22}_D$ +60° ($CHCl_3$), 0.30 g, 1.1 × 10^{-3} mol). The crude product was purified by TLC, with ether as eluent leading to 0.27 g (79%) of the amide **6**: mp 155 °C (Ac/Hep); yellow; $[\alpha]^{22}_D$ +143° (*c* 1.88, $CHCl_3$).

(*endo*-1-Acetamidoindan)tricarbonylchromium. The 1-acetamidoindan was obtained by decomplexation of the racemic *exo*-1-acetamidoindan complex, mp 142 °C. A 0.30-g sample of the decomplexed amide was recomplexed, according to the usual method,[24] with 1 g of $Cr(CO)_6$ in 80 mL of Bu_2O and 10 mL of THF. Recrystallization of the crude product, obtained after evaporation of the solvents, from Ac/He gave 0.3 g of the racemic endo amide: mp 206 °C; yellow; NMR (CD_3COCD_3) δ 1.94 (s, CH_3); IR (CH_2Cl_2) ν_{CO} = 1690 cm^{-1}, ν_{NH} = 3460 cm^{-1}. Anal. Calcd for $C_{14}H_{13}O_4CrN$: C, 54.02; H, 4.21. Found: C, 53.94; H, 4.23.

[(*S*)-(+)-1-Phenyl-1-hydroxyethyl]tricarbonylchromium. The complex alcohol was resolved according to a slight modification of the Downer and Kenyon[27] method for the free ligand. The details of the resolution will be published elsewhere. The 1-phenylethanol complex was obtained: mp 27 °C; $[\alpha]^{22}_D$ +18° (*c* 2.1, $CHCl_3$). Decomplexation gave (*S*)-(−)-phenylethanol, $[\alpha]^{22}_D$ −40° (*c* 6.5, MeOH), optical purity 89% [lit.[16a] absolute specific rotation $[\alpha]^{23}_D$ −45° (*c* 4.91, MeOH)].

[(*S*)-(−)-*N*-(1-Phenylethyl)acetamido]tricarbonylchromium. From (1-phenyl-1-hydroxyethyl)tricarbonylchromium (0.43 g, 1.5 × 10^{-3} mol), CH_3CN (20 mL), and H_2SO_4 (5 mL) was obtained 0.43 g of amide: mp 142°; yellow; $[\alpha]^{22}_D$ −123° (*c* 1, $CHCl_3$); NMR (CD_3COCD_3) δ 1.40 (d, CH_3), 1.84 (s, $COCH_3$); IR ($CHCl_3$) ν_{CO} = 1683 cm^{-1}, ν_{NH} = 3460 cm^{-1}.

Decomplexation gave (*S*)-(−)-(1-phenylethyl)acetamide: mp 101 °C; $[\alpha]^{22}_D$ −140° (*c* 7.5, EtOH); optical purity 92% [lit.[17] mp 101 °C; $[\alpha]^{23}_D$ −152° (EtOH)].

(*N*-Propargylacetamido)hexacarbonyldicobalt 9 was obtained from ($HC{\equiv}CCH_2OH)Co_2(CO)_6$[5a] (0.51 g, 1.5 × 10^{-3} mol) CH_3CN (30 mL), and H_2SO_4 (5 mL). During the reaction considerable gas evolution was observed. A 0.20-g (35%) amount of amide **9** was obtained: mp 97 °C (E/He); red; NMR (CD_3COCD_3) δ 6.22 (s, HC≡), 4.27 (d, CH_2), 1.84 (s, CH_3); IR (KBr) ν_{CO} = 1657 cm^{-1}, ν_{NH} = 3280 cm^{-1}. Anal. Calcd for $C_{11}H_7O_7Co_2N$: C, 34.49; H, 1.84; N, 3.65; Co, 30.77. Found: C, 35.00; H, 2.17; N, 3.76; Co, 30.80.

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Registry No. ($C_6H_5CH_2NHCOCH_3$)Cr(CO)$_3$, 71744-42-8; ($C_6H_5CH_2NHCOPh$)Cr(CO)$_3$, 71744-43-9; ($C_6H_5CH_2NHCOCH_2Cl$)Cr(CO)$_3$, 71744-44-0; ($C_6H_5CH_2NHCO$-*n*-C_3H_7)Cr(CO)$_3$, 71744-45-1; ($C_6H_5CH_2NHCOCH{=}CH_2$)Cr(CO)$_3$, 71744-46-2; (CO)$_3$Cr$C_6H_5CH_2$-NHCO$CH_2C_6H_5$, 71744-47-3; (CO)$_3$Cr$C_6H_5CH_2NHCO$(*o*-MeC_6H_4), 75625-49-9; (*p*-$MeC_6H_4CH_2OH$)CrCO_3, 32914-20-8; [(CO)$_3$Cr][*p*-$MeC_6H_4CH_2NHCOPh$], 71744-53-1; [(CO)$_3$Cr][*p*-$MeOC_6H_4CH_2NHCOCH_3$], 71744-50-8; [(CO)$_3$Cr][*p*-$MeOC_6H_4CH_2NHCOPh$], 71771-22-7; [(CO)$_3$Cr][*p*-$MeOC_6H_4CHCH_3NHCOCH_3$], 71744-51-9; [(CO)$_3$Cr][*p*-$MeOC_6H_4CHCH_3NHCOPh$], 71744-37-1; [(CO)$_3$Cr][$(C_6H_5)_2CHNHCOCH_3$], 71744-52-0; [(CO)$_3$Cr][$CH_3CONHCH_2C_6H_4CH_2NHCOCH_3$], 75625-50-2; [(CO)$_3$Cr][$PhOCNHCH_2C_6H_4CH_2NHCOPh$], 75625-51-3; (*exo*-1-acetamidoindan)tricarbonylchromium, 71963-16-1; (*endo*-1-acetamidoindan)tricarbonylchromium, 75684-19-4; [(*S*)-(+)-1-phenyl-1-hydroxyethyl]tricarbonylchromium, 75625-52-4; [(*S*)-(−)-*N*-1-phenylethyl)acetamido]tricarbonylchromium, 73690-92-3; (*N*-propargylacetamido)hexacarbonyldicobalt, 71744-39-3; ($C_6H_5CH_2OH$)Cr(CO)$_3$, 12116-45-9; (*P*-$MeOC_6H_4CH_2OH$)Cr(CO)$_3$, 32914-19-5; (*P*-$MeOC_6H_4CHOHCH_3$)Cr(CO)$_3$, 67235-69-2; ($C_6H_5CHOHC_6H_5$)Cr(CO)$_3$, 12155-17-8; ($HOCH_2C_6H_4CH_2OH$)Cr(CO)$_3$, 69439-58-3; (*endo*-1-hydroxyindan)tricarbonylchromium, 55700-45-3; (*S*)-(−)-phenylethanol, 1445-91-6; ($HC{\equiv}CCH_2OH)Co_2(CO)$, 12264-12-9; (*S*)-(−)-*N*-(1-phenylethyl)acetamide, 19144-86-6; (*p*-$MeC_6H_4CH_2NHCOCH_3$)Cr(CO)$_3$, 71744-49-5; (*endo*-1-hydroxyindan)tricarbonylchromium, 57130-49-1.

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