COMMUNICATIONS

LETTERS

# Reactions of π-(Halobenzene)chromium Tricarbonyl with Alkoxides by Solid-Liquid Phase Transfer Catalysis

**Bong Rae Cho† and Sang Woo Kim**

*Department of Chemistry, Korea University, 1-Anam Dong, Seoul 132, Korea* *(Received February 15, 1984)*

Electrophilic substitution on the aromatic ring provides an important method for attachment of carbon or other functional groups to the ring[1]. In contrast, the reaction with reverse polarity, that is, the nucleophilic aromatic substitution, is seldom used in orgainc synthesis. One of the problems associated with this reaction is that it usually requires a severe reaction condition.

The problem may be surmounted by using the chromium tricarbonyl unit as an activating group[2]. The $Cr(CO)_3$ group is strongly electron withdrawing and promotes nucleophilic addition to the arene ring in arene-$Cr(CO)_3$ complex[3]. Another way of facilitating the reaction may be to increase the reactivity of the attacking nucleophile. Recently, we found that the nucleophilicity of oxyanion was greatly enhanced under solid-liquid phase transfer catalytic condition.[4] Therefore, we decided to combine these two techniques to achieve a facile nucleophilic aromatic substitution reaction.

In this communication, we wish to report our preliminary studies on the reactions of π-(halobenzene)chromium tricarbonyl complexes with alkoxides by solid-liquid phase transfer catalysis (Eq. 1).

$$\underset{\mathbf{1}}{(C_6H_5X)Cr(CO)_3} + RONa \xrightarrow{PTC} \underset{\mathbf{2}}{(C_6H_5OR)Cr(CO)_3} \xrightarrow{I_2} \underset{\mathbf{3}}{C_6H_5OR} \quad (1)$$

X=F(a), Cl(b)

The overall process we have observed is as follows. The alkoxide was generated *in situ* from alcohol and NaH in $CH_3CN$. The π-(halobenzene)chromium tricarbonyl (**1a** or **1b**)[5] and $Bu_4\overset{+}{N}\overset{-}{Br}$ was added to the slurry of alkoxide in $CN_3CN$. The mixture was stirred at room temperature or refluxed. When the reaction was completed, the solvent was evaporated and ether was added to the product mixture. For the reaction of **1a** and EtONa, π-(ethoxybenzene) chromium tricarbonyl (**2'**) was isolated by washing the etheral solution with water and removing the solvent. The ether layer contained **2'** in high purity (81 % yield). Sublimation at 120°C (1.5 torr) afforded a pure sample of mp 71°C (*lit.*[6] mp 65–67°C). Removal of the $Cr(CO)_3$ group was quantitative.[7,8] The GC–mass spectrum of the decomposed product showed $m/e$=122($M^+$), 94 ($M-C_2H_4$), and 77 (M–OEt). In all other examples reported here, the intermediate complex **2** was not isolated; the crude product was oxidized with exess iodine in ether to give **3**. In each case, the product was identified by comparision of the GC retention time and GC–mass spec trum with those of authentic sample.

The results are summarized in Table 1. As may be seen, most of the reactions proceed readily under mild condition. The remakable activating effect of the $Cr(CO)_3$ group is apparent in the rapid conversion of **1a** to anisole (entry 1), compared to no reaction between uncomplexed fluorobenzene and MeONa after refluxing for 5 hours (entry 7). The low reactivity exhibited by *t*-BuONa (entries 6 and 13) seems to be due to its steric effect. The steric effect of *i*-$PrO^-$

**TABLE 1: Reactions of π-(Halobenzene)chromium Tricarbonyl (1a and 1b) with RONa by Solid-Liquid Phase Transfer Catalysis**

| Entry | Complex | RONa | Temp. | Time(hr) | Yield(%)[a] |
|---|---|---|---|---|---|
| 1 | **1a** | MeONa | *RT* | 1.0 | 92.0 |
| 2 | **1a** | EtONa | *RT* | 1.0 | 92.0(81.0)[b] |
| 3 | **1a** | *n*-PrON | *RT* | 1.0 | 94.1 |
| 4 | **1a** | *i*-PrONa | *RT* | 1.0 | 97.3 |
| 5 | **1a** | *n*-BuONa | *RT* | 1.0 | 90.2 |
| 6 | **1a** | *t*-BuONa | *RT* | 1.0 | 2.6 |
| 5 | $C_6H_5F$ | MeONa | Reflux | 5.0 | 0.0 |
| 8 | **1b** | MeONa | Reflux | 3.0 | 100.0 |
| 9 | **1b** | EtONa | Reflux | 3.0 | 95.0 |
| 10 | **1b** | *n*-PrONa | Reflux | 3.0 | 93.3 |
| 11 | **1b** | *i*-PrONa | Reflux | 3.0 | 14.3 |
| 12 | **1b** | *n*-BuONa | Reflux | 3.0 | 94.0 |
| 13 | **1b** | *t*-BuONa | Reflux | 3.0 | 1.0 |
| 14 | $C_6H_5Cl$ | MeONa | Reflux | 10.0 | 0.0 |

[a] Yields of $C_6H_5OR$ were determined by GLC using an appropriate internal standard; [b] Isolated yield of $(C_6H_5OC_2H_5)Cr(CO)_3$.

$Na^+$ is also observed in reaction with less reactive complex (**1b**, entry 11). The dependence of reactivity on leaving group for **1a** and **1b** is similiar to that observed in classical nucleophilic aromatic substitution[9] (entries 1 and 8).

*Acknowledgment.* The authors are grateful to the Korea Science and Engineering Foundation for support of this work.

## Refernces

(1) (a) G.A. Olah, Ed., "Friedel–Craft and Related Reactions," Vols 1–4, Wiley, New York, 1963–1965. (b) R. O. C. Norman and R. Taylor, "Electrophilic Substitution in Benzenoid Compounds" Elsevier, Amsterdam, 1965

(2) For recent review, see (a) M.T. Semmlhack, *J. Organomet Chem. Libr.*, **1**, 361 (1976); (b) J. P. Collman and L. S. Hegedus, "Principles and Application of Organotransition Metal Chemistry," University Science Press, Mill Valley, CA, 1980, Chapter 14.

(3) M.F. Semmelhack, H. T. Hall, Jr., R. Farina, M. Yoshifuji, G. Clark, T. Barger, and K Hirotsu, *J. Amer. Chem. Soc.*, 101, 3535 (1979).

(4) B. R. Cho and S. D. Park, *Bull. Korean. Chem.Soc.***5**, 126 (1984).

(5) C. A. L. Mahaffy and P. L. Pauson, *Inorg., Syn.* **19**, 154 (1979)

(6) A. C. Knipe, S. J. McGuinness and W.E. Watts, *J.C.S. Perkin* II, 193 (1981)

(7) Control experiment showed that **2'** was oxidized by $I_2$ in ether within 20 minutes at room temperature, affording the ethoxybenzene quantitatively.

(8) The stoichiometry of the oxidtion reaction[2b] is $(C_6H_5OR)Cr(CO)_3 \xrightarrow{I_2} C_6H_5OR + Cr(III) + 3\,CO$.

(9) J. F. Bunnett, *Quart. Rev.*, **12**, 1 (1958)

# Unusual Rearrangements of 3a, 7a-Dihydroindole Esters

**Chang Kiu Lee† and Nan Sook Lee**

*Department of Chemistry, Kangweon National University, Chuncheon 200, Korea* (*Received May 15, 1984*)

Tetramethyl 3a,7a–dihydro–1–methylindole–2,3,3a,4–tetracarboxylate (**2b**), the 1:2 adduct from the reaction of 1–methylpyrrole (**1b**) with dimethyl acetylenedicarboxylate (DMAD), underwent quite unusual rearrangement upon reflux with sodium methoxide in methanol for 24 h to give indole–2,3,4,5–tetraester (**4b**).[1] The base–catalyzed rearrangement did not occur if there was no substituent on the nitrogen atom of the adduct (*e.g.* **2a**). Instead, loss of the $C_{3a}$–ester group and eventual aromatization resulted to give **5a**. When the compound **2b** was heated to reflux in xylene, another type of rearrangement took place to give indoline derivative **3b**. On the other hand, the unsubstituted analong **2a** did not give any rearrangement under the same reaction conditions. The contrary results from the reactions of **2a** and **2b** led us to investigate the scope of the reactions and their mechanisms, and we report our preliminary results in the present paper.

At first, we attempted to prepare a series of N–substituted derivatives of **2** in order to examine the steric and electronic effect on the rearrangement. However, our persistent efforts to prepare the compounds of type **2** having bulky alkyl groups (*e.g. tert-butyl, sec*–butyl) or aryl groups (*e.g.* phenyl, *p*–methoxy–phenyl, *p*–nitrophenyl) have not been successful. Therefore, we decided to prepare a series of substituted benzyl derivatives (**2c–g**) which are sterically bulky and effectively electron-withdrawing or –donating through inductive effect.

Benzylpyrroles (**1c–g**) were prepared by a typical method using 2,5–diethoxytetrahydrofuran and substituted benzylamines.[2] By refluxing pyrroles (**1c–g**) with DMAD in anhydrous ether were prepared the 1:2 adducts (**2c–g**). The yields and melting points of them are listed in the Table 1. Spectroscopic data are consistent with the structures.[3] The yields of benzyl derivatives **2c–g** were good but substantially lower than that of methyl compound **2b**, indicating that the steric effect played a role. Approach of the dienophile seemed to be hindered by N–benzyl group. With pyrrole itself (**1a**) the observed lowest yield seems to be due to the predominant aromatic character which makes the conjugated double bonds poor diene system.[1]

One of the spectroscopic characteristics of the 1:2 adducts (**2c–g**) was the appearance of an AB pattern in NMR spectra ($CDCl_3$) for benzylic $CH_2$ group at around $\delta$ 4.8 with $J$ = 15–18 Hz.[4] Free rotation of phenyl ring seems to be very much restricted and its spatial arrangement may be one of the critical factors in the reaction described below.

The rearrangements of **2b–g** to indolines (**3b–g**) were found

**TABLE 1 Yields, Boiling Points or Melting Points of 1 and 2**

| R | 1 | | 2 | |
|---|---|---|---|---|
| | bp, °C (mm) | % yield | mp, °C | % yield |
| *a* H | [a] | | 162–165[b] | 10 |
| *b* $CH_3$ | [a] | | 146[c] | 90[c] |
| *c* $CH_2$–$C_6H_5$ | 129 (10) | 65 | 135[c] | 70[c] |
| *d* $CH_2$–$C_6H_4$–$CH_3$–*p* | 99–105 (2.5) | 78 | 141–142.5 | 71 |
| *e* $CH_2$–$C_6H_4$–$OCH_3$–*p* | 109 (0.3) | 57 | 104–107 | 79 |
| *f* $CH_2$–$C_6H_4$–Cl–*p* | 104 (0.8) | 46 | 154–155 | 49 |
| *g* $CH_2$–$C_6H_4$–$OCH_3$–*m* | 85 (1.0) | 90 | 60.5–61 | 20 |

[a] Commercially available. [b] See reference 1. [c] See reference 5.