Phase-Transfer-Catalyzed Reaction of Tricarbonyl[η^6-2-chloro-1-(trifluoromethyl)benzene]chromium with Phenylacetonitrile

Sofía Varela Calafat, Edgardo N. Durantini, Juana J. Silber, and Stella M. Chiacchiera*

Departamento de Química y Física, Universidad Nacional de Río Cuarto, Agencia Postal # 3, 5800 Río Cuarto, Argentina

Received December 15, 1998

Summary: The reaction of tricarbonyl[η^6-2-chloro-1-(trifluoromethyl)benzene]chromium with in situ generated phenylacetonitrile anion affords two diastereomeric products, which yield α-phenyl-α-[2-(trifluoromethyl)phenyl]-acetonitrile upon decomplexation. The S_NAr intrinsic rate constant was evaluated, and the activation of the tricarbonylchromium moiety was compared with that of the nitro group.

Introduction

Aromatic nucleophilic substitution (S_NAr) reactions of activated aryl halides with carbanionic nucleophiles involve C−C bond formation and are synthetically relevant. However, the synthetic potential of the S_NAr reactions are limited by the requirement that the aromatic substrate should be activated with suitable withdrawing groups. This requirement severely limits the synthetic potential of the S_NAr reactions.

The temporal activation of the aromatic substrate by metal transition complexation renders the ring more susceptible to nucleophilic attack.[1] Thus, tricarbonyl-(η^6-arene)chromium, for example, has found powerful applications in the field of organic synthesis.[2] The main problem with these reactions is finding a medium where both the neutral and anionic reagents are compatible. In systems involving in situ generated nucleophiles, by base deprotonation of a weak acid precursor, phase-transfer catalysis (PTC) conditions can be an useful approach. The nucleophile, extracted into the organic phase as a fully lipophilic ion pair with the PT catalyst, reacts with the aromatic substrate in the organic phase.[3]

The combination of PTC and $Cr(CO_3)$ complexation of haloarenes has been successfully employed in S_NAr reactions.[4−8] The substitution product can be freed from the complex via oxidative decomplexation with I_2.[8]

We previously reported studies of S_NAr reactions with activated substrates and different nucleophiles in both homogeneous[9] and PTC media.[10,11] This work reports the reaction between tricarbonyl[η^6-2-chloro-1-(trifluoromethyl)benzene]chromium and the in situ generated phenylacetonitrile anion under PTC conditions. The reaction was performed in toluene using tetrabuthylammonium bromide (TBAB) as the catalyst in the presence of 50% NaOH aqueous solution. Quantitative yields of two diastereoisomeric pairs of the *ipso*-chloro-substituted complexes were obtained. The products appear at different rates and, upon I_2 decomplexation or photodissociation, afford racemic phenyl[2-(trifluoromethyl)phenyl]acetonitrile.

The reaction under consideration is useful in the synthesis of substituted diphenylmethanes. These compounds have diverse and important application as comonomers in polymer production,[12] spacers in helicans synthesis,[13] antistaminics, and biologically active compounds.[14]

Experimental Section

General Considerations. The HPLC measurements were performed on a Varian 5000 liquid chromatograph, equipped with a UV−visible variable-wavelength detector (Varian 2550) operating at 250 nm. A Varian MicroPak SI-5 (150 mm × 4 mm i.d.) column was used with 1% 2-propanol in *n*-hexane as eluent. UV−visible spectra were recorded on a Hewlett-Packard HP 8452 spectrophotometer. NMR spectra were acquired with a 200 MHz Bruker spectrometer. IR spectra were recorded with a Nicolet Impact 400 FT-IR. Mass spectra were taken on a gas chromatograph (Hewlett-Packard 5890) with a mass detector (Hewlett-Packard 5972). The melting point was taken in a Büchi apparatus.

(1) (a) Schellhaas, K.; Schmalz, H.-G.; Bats, J. W. *Chem. Eur. J.* **1998**, *4*, 57. (b) Fretzen, A.; Ripa, A.; Liu, R.; Bernardelli, G.; Kundig, E. P. *Chem. Eur. J.* **1998**, *4*, 251. (c) Pearson, A. J.; Gontcharov, A. *J. Org. Chem.* **1998**, *63*, 152.

(2) (a) Semmelhack, M. F. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, U.K., 1995; Vol. 12, pp 979−1015. (b) Davies, S. G.; McCarthy, T. D. In ref 2a, pp 1039−1070.

(3) Dehmlow, E. V.; Dehmlow, S. S. *Phase Transfer Catalysis*, 3rd ed.; Verlag Chemie: Weinheim, Germany, and New York, 1993.

(4) Alemagna, A.; Baldoli, C.; Del Buttero, P.; Licandro, E.; Maiorana, S. *Gazz. Chim. Ital.* **1995**, *115*, 555.

(5) Alemagna, A.; Del Buttero, P.; Licandro, E.; Maiorana, S. *J. Org. Chem.* **1983**, *48*, 605.

(6) Alemagna, A.; Cremonesi, P.; Del Buttero, P.; Licandro, E.; Maiorana, S. *J. Org. Chem.* **1983**, *48*, 3114.

(7) Brunelle, D. J. *J. Org. Chem.* **1984**, *49*, 1309.

(8) Baldoli, C.; Del Buttero, P.; Licandro, E.; Maiorana, S. *Gazz. Chim. Ital.* **1988**, *118*, 409.

(9) (a) Chiacchiera, S. M.; Singh, J. O.; Anunziata, J. D.; Silber, J. J., *J. Chem. Soc., Perkin Trans. 2* **1987**, 987. (b) Chiacchiera, S. M.; Singh, J. O.; Anunziata, J. D.; Silber, J. J., *J. Chem. Soc., Perkin Trans. 2* **1988**, 1585. (c) Chiacchiera, S. M.; Cattana, R. I.; Singh, J. O.; Anunziata, J. D.; Silber, J. J., *J. Phys. Org. Chem.* **1989**, *2*, 631. (d) Durantini, E. N.; Zingaretti, L.; Anunziata, J. D.; Silber, J. J. *J. Phys. Org. Chem.* **1992**, *2*, 557.

(10) Durantini, E. N.; Chiacchiera, S. M.; Silber, J. J. *Synth. Commun.* **1996**, *26*, 3849.

(11) Durantini, E. N.; Chiacchiera, S. M.; Silber, J. J. *J. Org. Chem.* **1993**, *58*, 7115.

(12) (a) Stevens, M. P. *Polymer Chemistry−An Introduction*, 2nd ed.; Oxford University Press: Oxford, U.K., 1990. (b) Bruno, J. G.; Chang, M. N.; Choisledeski, Y. M.; Green, D. M.; McGarry, D. G.; Regan, J. R.; Volz, F. A. *J. Org. Chem.* **1997**, *62*, 5174. (c) Tao, X. T.; Suzuki, H.; Watanabe, T.; Lee, S. H.; Miyata, S.; Sasabe, H. *Appl. Phys. Lett.* **1997**, *70*, 1503. (d) Kultys, A. *J. Polym. Sci., Part A: Polym. Chem.* **1997**, 35, 547. (e) Hulubei, C.; Cojocariu, C.; Pecincu, S.; Popescu, F. *J. Macromol. Sci., Pure Appl. Chem.* **1997**, *A34*, 1085.

(13) Constable, E. C.; Rees, D. G. F. *New J. Chem.* **1997**, *21*, 369.

(14) (a) Seno, H.; Hattori, H.; Kumazawa, T.; Suzuki, O. *Forensic Sci. Int.* **1993**, *62*, 187. (b) Yamato, T.; Sakaue, N.; Shinoda, N.; Matsuo, K.; *J. Chem. Soc., Perkin Trans. 1* **1997**, 1193.

10.1021/om981018+ CCC: $18.00
Publication on Web 06/15/1999

Starting Materials. 2-Chloro-1-(trifluoromethyl)benzene (CTB), 2-chloro-5-nitro-1-(trifluoromethyl)benzene (CNT), and phenylacetonitrile (HNu) from Aldrich and tetrabutylammonium bromide (TBAB) and sodium hydroxide from Fluka were used without further purification. Toluene, *n*-hexane, and dichloromethane from Sintorgan (HPLC quality) were used as received. Tetrahydrofuran (Sintorgan) and dibutyl ether (Aldrich) were distilled from acetophenone/sodium, collected over molecular sieves, and used immediately after purification.

Synthesis of Tricarbonyl[η^6-2-chloro-1-(trifluoromethyl)benzene]chromium (CTB-TCC). The tricarbonyl complex was synthesized using the apparatus described by Toma et al.[15] The synthesis of the complex was performed by following the procedure suggested for a related compound.[16] Thus, 2-chloro-1-(trifluoromethyl)benzene (107 mmol) in a dry argon-purged mixture of tetrahydrofuran (3.5 mL) and dibutyl ether (37.5 mL) was reacted with $Cr(CO)_6$ at 140−145 °C for 12 h. The reaction mixture was filtered over Celite and evaporated at reduced pressure to dryness. The pure complex was obtained by sublimation of the solid residue at reduced pressure. Mp: 71 °C. Yield: 80%. The pure compound shows the spectroscopic properties reported in the literature.[17]

Synthesis of Tricarbonyl[η^6-α-phenyl-α-(2-(trifluoromethyl)phenyl)acetonitrile]chromium. CTB-TCC (0.14 mmol), HNu (8.55 mmol), and TBAB (0.014 mmol) in 4 mL of toluene were placed in a three-necked flask equipped with an efficient mechanic stirrer and a gas inlet tube. After 10 min of stirring under an argon atmosphere, 4 mL of a 50.0% NaOH aqueous solution was added. The mixture was kept at room temperature for 1.5 h. The reaction mixture was neutralized with hydrochloric acid, washed with water, and extracted with dichloromethane. The organic phase was dried with $MgSO_4$ and the excess of the nucleophile and the solvent removed under reduced pressure. Flash chromatography (silica gel, Merck, 60 mesh, eluent 2:1 petroleum ether−dichloromethane) afforded the pure diastereomeric products (**1** and **2**) as determined by HPLC and GC-MS. The first eluted fraction presented the following spectral characteristics: ^{1}H NMR (200.13 MHz, $DCCl_3$, TMS) δ (ppm) 5.34 (d, 1H, J = 6 Hz, Ar H), 5.37 (dd, 1H, J = 0.6 and 6 Hz, Ar H), 5.44 (d, 1H, J = 6 Hz, Ar H), 5.62 (s, 1H, −CH), 5.63 (dd, 1H, J = 6 and 6 Hz, Ar H), 7.30−7.50 (m, 5H, C_6H_5); ^{13}C NMR (50.32 MHz, $DCCl_3$, TMS) δ (ppm) 38.0 (−CH), 86.8, 88.1, 88.4, 89.4, 90.1, 92.8, 117.5 (−CN), 123.0 ($-CF_3$), 128.6 (2-CH, C_6H_5), 129.5 (1-CH, C_6H_5), 129.9 (2-CH, C_6H_5), 134.3 (1-C, C_6H_5), 228.9 (3-CO); MS (m/z) 397 (M^+, 15, 397 calculated for $C_{18}H_{10}CrF_3NO_3$), 313 (46), 261 (31), 222 (82), 203 (22), 196 (100), 176 (26).[18] Anal. Calcd: C, 54.42; H, 2.54; N, 3.53. Found: C, 54.48; H, 2.47; N, 3.59.

The second eluted fraction was characterized by the following spectral data: ^{1}H NMR (200.13 MHz, $DCCl_3$, TMS) δ (ppm) 5.27 (dd, 1H, J = 0.6 and 6 Hz, Ar H), 5.28 (d, 1H, J = 6 Hz, Ar H), 5.43 (dd, 1H, J = 6 and 6 Hz, Ar H), 5.46 (d, 1H, J = 6 Hz, Ar H), 5.69 (s, 1H, −CH), 7.30−7.50 (m, 5H, C_6H_5); ^{13}C NMR (50.32 MHz, $DCCl_3$, TMS) δ (ppm) 39.2 (−CH), 87.5, 87.9, 88.5, 90.2, 90.9, 93.6, 117.1 (−CN), 123.2 ($-CF_3$), 128.7 (2-CH, C_6H_5), 129.4 (1-C, C_6H_5), 129.8, (2-CH, C_6H_5), 133.9 (1-C, C_6H_5), 225.2 (3-CO); MS (m/z) 397 (M^+, 27, 397 calculated for $C_{18}H_{10}CrF_3NO_3$), 313 (62), 261 (13), 222 (68), 203 (76), 196 (100), 176 (22).[18] Anal. Calcd: C, 54.42; H, 2.54; N, 3.53. Found: C, 54.37; H, 2.59; N, 3.56.

Kinetic Experiments. **Chromium Carbonyl Mediated Reactions**. The kinetic experiments were carried out as previously described.[10] In a typical run, CTB-TCC (0.31 mmol), HNu (17.45 mmol), and TBAB (0.02−0.04 mmol) were dissolved in toluene (5 mL) and transferred to the reactor cell. The organic solution was stirred at 1000 ± 50 rpm, and 4 mL of 50% NaOH was added. The reactor was kept at 40.0 ± 0.1 °C under an argon atmosphere. At given times, the stirring was stopped, the two phases were allowed to separate, and a 50 μL aliquot of the organic phase was withdrawn from the reactor. The extraction sample was quenched by dilution to 5 mL of hexane, stirred with 0.2 mL of hydrochloric acid (20% v/v), and analyzed by HPLC. The complexed products appear at 10.9 and 13.7 min in the HPLC chromatogram (column Varian MicroPak SI-5 (150 mm × 4 mm i.d., eluent 1% 2-propanol in *n*-hexane, flow rate 0.5 mL/min). A typical HPLC chromatogram of the reaction mixture is shown in Figure 1.

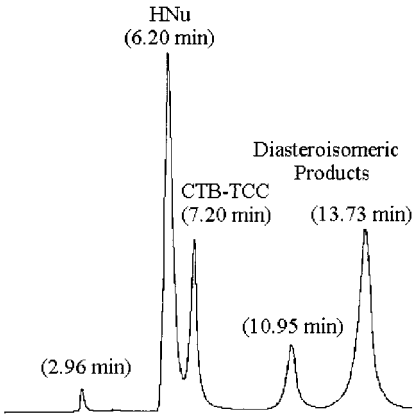


Figure 1. Typical HPLC chromatogram of the reaction mixture of CTB-TCC with phenylacetonitrile under PTC conditions.

The reaction mixture was protected from direct light exposure. The pseudo-first-order rate constants (k_{obs}) were calculated from a nonlinear least-squares fit of the plot of the experimental concentrations vs time values.

2-Chloro-5-nitro-1-(trifluoromethyl)benzene Reaction. The kinetic experiments were carried out as described above using equimolar amounts of CNTB and TBAB. Under this condition the *ipso*-chloro substitution product, phenyl[2-(trifluoromethyl)-4-nitrophenyl]acetonitrile, was obtained. Flash chromatography of the dry organic phase (silica gel, petroleum ether/dichloromethane gradient) afforded the pure product. Yield: 89%. ^{1}H NMR (200.13 MHz, $DCCl_3$, TMS): δ (ppm) 5.70 (s, 1H), 7.45 (m, 5H, C_6H_5), 7.76 (d, 1H, J = 8.5 Hz), 8.40 (dd, 1H, J = 2.3, 8.5 Hz), 8.59 (d, 1H, J = 2.4 Hz). ^{13}C NMR (50.32 MHz, $DCCl_3$, TMS): δ (ppm) 38.0, 117.4 (−CN), 121.9, 122.6 ($-CF_3$), 127.4, 128.8, 129.2, 129.8, 132.6, 133.4, 141.1, 147.3 (C−NO_2). MS (m/z): 306 (M^+) (306 calculated for $C_{15}H_9F_3N_2O_2$).

Calculation of Φ. To calculate Φ (eq 10), experiments were carried out as described above but without adding CTB-TCC. The amount of [TBA^+Nu^-] in the organic phase was spectrophotometrically determined by using the UV absorption band of Nu^- at λ_{max} 340 nm (log ϵ = 2.36). A calibration curve was constructed using solutions of TBA^+Nu^- of known concentrations. The Nu^- was quantitatively generated from the carbon acid through reaction with an excess of clean sodium metal under nitrogen, following a similar procedure as described for the quantitative generation of sodium methoxide.[19] TBAB was added to keep the anions in solution.

Results and Discussion

A kinetic study of the reaction of CTB-TCC with HNu was performed under PTC conditions. The organic reactants dissolved in toluene were stirred with 50% aqueous sodium hydroxide in the presence of different catalytic amounts of TBAB (Scheme 1).

(15) Hudecek, M.; Toma, S. *J. Organomet. Chem.* **1990**, *393*, 115.
(16) Rose-Munch, F.; Rose, E.; Semra, A.; Bois, C. *J. Organomet. Chem.* **1989**, *363*, 103.
(17) Rose-Munch, F.; Khourzom, R.; Djukic, J.-P.; Rose, E. *J. Organomet. Chem.* **1993**, *456*, C8.
(18) The complexed products almost completely decompose to the free substitution product at the injector temperature of the gas chromatograph.
(19) Crampton, M. R.; Stevens, J. A. *J. Chem. Soc., Perkin Trans 2* **1991**, 1715.

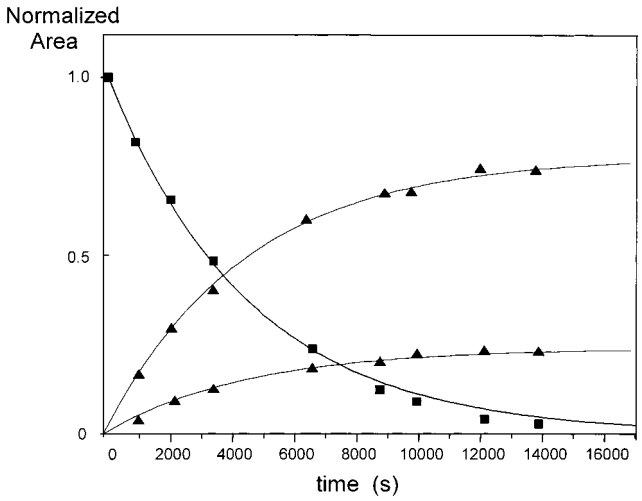
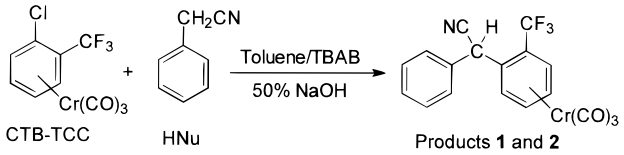


Figure 2. Kinetic profile for the reaction of CTB-TCC with phenylacetonitrile under PTC conditions: (■) substrate; (▲) complexed products.

Scheme 1



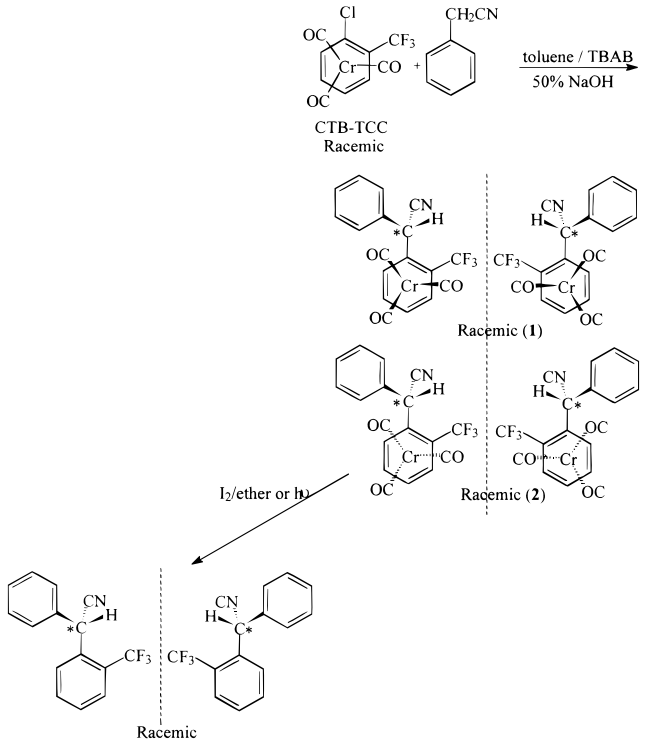
No reaction was observed either in the absence of catalyst or in aqueous sodium hydroxide. All the kinetic studies were performed using an excess of nucleophile precursor, HNu. Typical HPLC chromatograms of the reaction mixture at different times show a quantitative decrease in the CTB-TCC peak area (t_R = 7.2 min) and the appearance of two new peaks (Figure 1). The kinetic profiles show a complete conversion of the CTB-TCC at infinite time (Figure 2). Under the present experimental conditions no poisoning of the catalyst by the complexed product was observed.

Taking in consideration the racemic nature of the substrate (CTB-TCC), the reaction with the prochiral HNu yields almost quantitatively two diastereomeric *ipso*-chloro-substituted complexed pairs of enantiomers (racemic **1** and **2**) shown in Scheme 2. An exo addition of the nucleophile to CTB-TCC yields two intermediates with differing steric congestion. The most stable transition state, i.e., one bearing the bulkiest groups further apart, leads to the formation of **2**, which is produced in higher proportion.

Both products exhibit the characteristic MLCT absorption of (arene)tricarbonylchromium complexes at 320 nm.[20] From the kinetics data, the ratio **1**:**2** = 0.23:0.77 was obtained, assuming that the molar extinction coefficients for both products are the same. Irradiation of the reaction mixture at 320 nm produces bleaching of the solution. The only detected product was α-phenyl-α-[2-(trifluoromethyl)phenyl]acetonitrile, as shown by GC-MS analysis of the photolyzed solution. (MS *m*/*z* (relative intensity) 261 (M^+, 40), 242 (10), 221 (100), 192 (10), and 165 (24)).

The free organic product was also obtained by oxidative decomplexation of **1** and **2** with iodine (ether solution, room temp, 3 h).

Scheme 2



Effect of TBAB Concentration. The variation of the pseudo-first-order rate constant with the catalyst concentration, keeping other experimental conditions fixed, is shown in Figure 3. A linear dependence with k_{obs} was found with a slope of $(2.5 \pm 0.2) \times 10^{-2}$ M^{-1} s^{-1}. Such linear behavior is characteristic when the HNu deprotonation occurs at the interface and the rate-limiting step is the nucleophilic substitution.[21] The intercept of the plot in Figure 3 is negligible, showing that the uncatalyzed reaction does not occur.

Assuming that nucleophile precursor deprotonation takes place at the interface, the following mechanism can be proposed:[3]

$$HNu_{int} + HO^-_{int} \overset{K}{\rightleftharpoons} Nu^-_{int} + H_2O_{int} \quad (1)$$

$$TBA^+X^-_{org} + Nu^-_{int} \overset{K_s}{\rightleftharpoons} TBA^+Nu^-_{org} + X^-_{int} \quad (2)$$

$$CTB\text{-}TCC_{org} + TBA^+Nu^-_{org} \xrightarrow{k} products_{org} + TBA^+X^-_{org} \quad (3)$$

where the subscripts int and org indicate the interface and the organic phase, respectively. k is the overall second-order rate coefficient for the reaction of CTB-TCC with $TBA^+Nu^-_{org}$. K represents the acid−base equilibrium constant at the phase boundary defined as

$$K = \frac{[Nu^-]_{int}[H_2O]_{int}}{[HNu]_{int}[OH^-]_{int}} \quad (4)$$

The Na^+ salt of the interface generated carbanion can migrate neither into the organic phase nor into the highly saline aqueous phase.[22] K_s is the selectivity

(20) Geoffroy, G. L.; Wrighton, M. S. *Organometallic Photochemistry*; Academic Press: New York, 1979.

(21) Solaro, R.; D'Antone, S.; Chiellini, E. *J. Org. Chem.* **1980**, *45*, 4179.

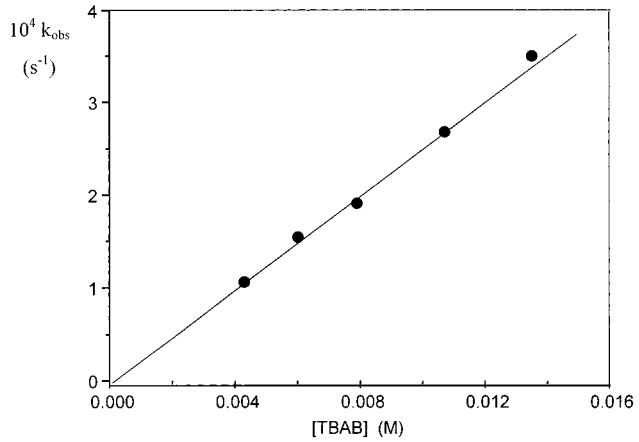


Figure 3. Dependence of k_{obs} on catalyst concentration [TBAB] for the reaction of CTB-TCC with phenylacetonitrile under PTC. Experimental conditions: 0.3 mmol of CTB-TCC, 17.5 mmol of HNu, TBAB in 5 mL of toluene, and 4 mL of 50% aqueous NaOH, $T = 40.0 \pm 0.5$ °C.

constant[3] for the extraction of HNu^- with respect to that of X^-, defined as

$$K_s = \frac{[TBA^+Nu^-]_{org}[X^-]_{int}}{[TBA^+X^-]_{org}[Nu^-]_{int}} \quad (5)$$

Since the two parallel reactions that lead to the diastereomeric products are of the same kinetic order, the following rate (r) expression can be written:

$$r = -d[CTB - TCC]/dt = k[TBA^+Nu^-]_{org}[CTB-TCC] \quad (6)$$

where k involves the sum of the two individual rate constants for product formation. When both HNu and base are in great excess over the catalyst, it can be assumed that $[TBA^+ Nu^-]_{org}$ remains constant throughout the reaction and eq 7 can be written

$$r = k_{obs}[CTB\text{-}TCC] \quad (7)$$

by application of the preequilibrium approximation to this mechanism and taking into account that $[TBAB^0] = [TBA^+X^-]_{org} + [TBA^+Nu^-]_{org}$ (eq 8) can be obtained:

$$k_{obs} = \frac{kKK_s[TBAB^0][HNu]_{int}[OH^-]_{int}}{[X^-]_{int}[H_2O]_{int} + KK_s[HNu]_{int}[OH^-]_{int}} \quad (8)$$

Equation 8 can be rewritten in the form of eq 9:

$$k_{obs} = \frac{k[TBAB^0][HNu]_{int}}{\Phi^{-1} + [HNu]_{int}} \quad (9)$$

The evaluation of Φ under the experimental conditions can be carried out with the KK_s product expression and the amount of TBA^+Nu^- in the organic phase, as shown in eq 10:

$$\Phi = \frac{KK_s[OH^-]_{int}}{[X^-]_{int}[H_2O]_{int}} = \frac{[TBA^+ + Nu^-]_{org}}{([TBAB^0] - [TBA^+ + Nu^-]_{org})[HNu]_{int}} \quad (10)$$

A Φ value of 0.124 M^{-1} was obtained for 50% NaOH aqueous phase, as described in the Experimental Section. The overall second-order rate coefficient k (eq 3), for the intrinsic S_NAr reactions in the organic phase, can be evaluated from the slope of the k_{obs} vs $[TBAB^0]$ plot according to eq 9 (Figure 3). The introduction of the calculated Φ value in eq 9, with the assumption that $[HNu]_{int}$ equals $[HNu]_{org}$, provides the value $k = (8.0 \pm 0.4) \times 10^{-2}$ M^{-1} s^{-1}.

The activation process either by tricarbonyl complexation or nitro group substitution has been the subject of theoretical studies, but no direct theoretical comparison between the relative *ipso* activation could be performed.[23] To evaluate the degree of the activation effect exerted by the tricarbonyl moiety, a study was carried out using 2-chloro-5-nitro-1-(trifluoromethyl)benzene (CNTB) as substrate.[24] The reaction was performed at [CNTB]/[TBAB] = 0.1, but the other experimental conditions were kept the same as with CTB-TCC. Under these conditions no poisoning of the catalyst by the product occurs and the *ipso*-chloro substitution product is obtained in quantitative yield. For CNTB a value of 0.76 s^{-1} M^{-1} was obtained for the intrinsic second-order rate constant of the S_NAr reaction (k_{CNTB}). The results show a rate constant relationship for the nitro-activated substrate relative to the one activated by the tricarbonyl moiety (k_{CNTB}/k) ≅ 10. The finding agrees with the previously reported reactivity order for electron-deficient arenes.[2a]

Conclusion

Tricarbonyl[η^6-2-chloro-1-(trifluoromethyl)benzene]-chromium reacts with phenylacetonitrile under PTC conditions to yield the *ipso*-chloro substitution product as two racemic mixtures of diastereoisomers. The free product, racemic phenyl[2-(trifluoromethyl)phenyl]acetonitrile, can be obtained by either photolysis or oxidative decomplexation with I_2.

A general mechanism that includes the interfacial deprotonation of the phenylacetonitrile has been proposed and the intrinsic second-order rate constant for the S_NAr reaction evaluated. The activation power of the chromium tricarbonyl moiety is 10 times smaller than that exerted by a *p*-nitro group.

The combination of PTC methodology with the stoichiometric activation of aromatic substrates by chromium carbonyl complexation is an interesting approach to the synthesis of diphenylacetonitrile derivatives.

Acknowledgment. Financial support from the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), the Consejo de Investigaciones Científicas y Tecnológicas de la Provincia de Córdoba (CONICOR), and Universidad Nacional de Río Cuarto is gratefully acknowledged. S.V.C. thanks CONICOR for a research fellowship.
OM981018+

(22) Makosza, M.; Fedorynski, M. *Advances in Catalysis;* Eley, D. D., Pines, H., Weisz, P. B., Eds.; Academic Press: London, 1987; Vol. 35, p 375.
(23) Morgantini, P. Y.; Fluekiger, P.; Weber, J. *J. Chim. Phys. Phys-Chim. Biol.* **1992**, *89*, 301.
(24) Chiacchiera, S. M.; Durantini, E. N.; Varela Calafat, S.; Silber, J. J. η^6-(2-Chlorotrifluoromethylbenzene)Tricarbonyl Chromium In The Synthesis Of Phenyl-2-Trifluoro Methylphenylacetonitrile Under Phase Transfer Catalysis. Abstracts, 32nd International Conference on Coordination Chemistry, Santiago de Chile, Chile, Aug 1997; Issue 117, p 112.