MECHANISM OF ACID CATALYZED CONDENSATION OF TRICARBONIL-CHROMIUM COMPLEXED BENZYLIC ACETATES WITH REACTIVE ARENES

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Results concerning the mechanism of acid catalyzed coupling reaction of η^6-(acetoxymethylenebenzene)tricarbonylchromium and η^6-(1,4-bisacetoxymethylene benzene)tricarbonilchromium complexes with various arenes are reported. Introduction of alkyl or alcoxy substituents in the structure of the arene significantly increases the reactivity. The sequence of constitutional motifs derived from chromium complex, (C) and arene, (A) in the product of an initial phase of the polycondensation process proved to depend on the structure of the arene being of type A-C-A for 1,3-dimethoxybenzene and C-A-C for 1,2,4,5-tetramethylbenzene. This is rationalized in terms of an assistance originated at chromium-ligand bond and transmitted via homoconjugation.

Keywords: η^6-(arene)tricarbonylchromium complexes; benzylic carbenium ions; carbon-carbon coupling reactions; metallated diarylmethanes

1. Introduction

Exceptional behavior of η^6-arene-tricarbonyl-chromium complexes to stabilize both electron rich and electron deficient intermediates opened a large field for applications in organic synthesis (see [1,2] and selected valuable reviews [3-9]). In this respect high stability of η^6-complexed benzylic carbenium ions [10-17]) provided new routes of synthesis based on the capture of the carbocationic intermediates with various nucleophiles including alcohols [18] amines [19] tiols

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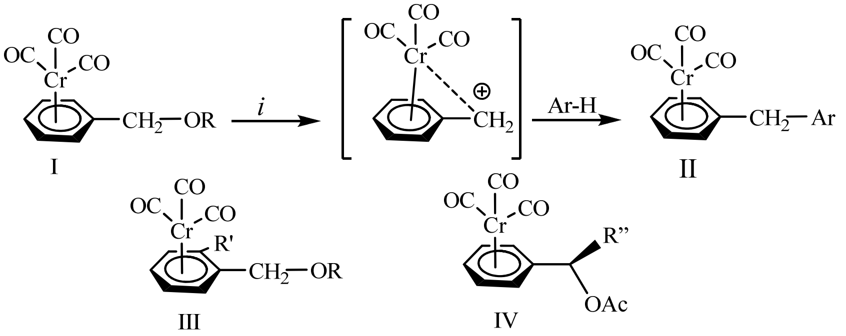
[20], Grignard reagents [21], silyl-enol-ethers [22] as well as by alkylation, acylation [23], Et3SiH-reduction [24] or fluorination [25] reactions.

On this research line we previously reported the reaction of η^6-complexed benzylic carbenium ions (generated under acid catalysis from benzylic alcohols, acetates or ethers) with arenes (*Scheme 1*) [26-29].



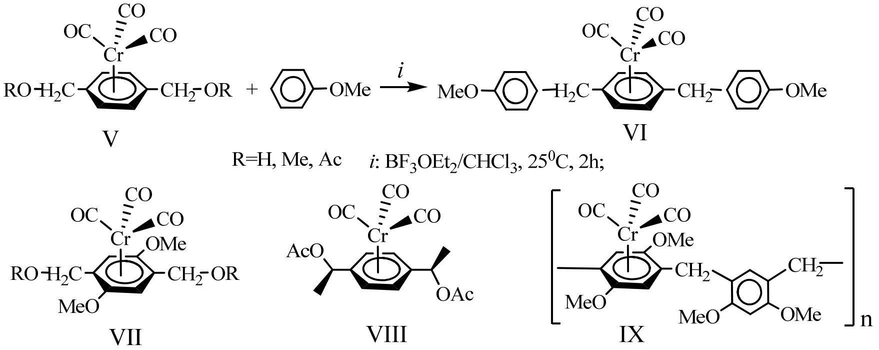
R= H, Me, Ac R'= Me, OMe R"=Me

i: BF_3OEt_2 or CF_3COOH; $CHCl_3$; r.t.; 2 hrs

Ar-H: Highly nucleophilic arenes

Scheme 1

The reaction is performed under mild conditions (r.t., few hours) affording a large variety of diarylmethanes in very good yields. The scope of this new carbon-carbon coupling reaction is enlarged by: (*i*)-the possibility to use difunctional complexed reagents (*V*, *VII*, *VIII*, *Scheme 2*) and (*ii*)-the access to enantiomerically pure products when a planar chiral (*VII*) reagent [27] or a η^6-complexed precursor bearing benzylic stereocenteres (*VIII*) [28] is used; (for this last type of starting reagent we have previously showed that coupling reaction takes place stereospecifically with retention of configuration as a result of a drastic restriction of C1-Cα rotation [26, 28].



R=H, Me, Ac *i*: $BF_3OEt_2/CHCl_3$, 25^0C, 2h;

Scheme 2

The objectives of the present work are concerned with the coupling of difunctional benzylic reagents of type *V* (*VII*, *VIII*) with arenes bearing at least two reactive sites (e.g. 1,3-dimethoxybenzene or 1,2,4,5-tetramethylbenzene). In this case, the coupling reaction takes the course of a polycondensation process leading to potentially valuable materials, *IX* exhibiting a total control of the configuration.

In order to perform an efficient tailoring of such products (structure, configuration, polycondensation degree, reaction rates, two aspects of the polycondensation process appeared to be of preliminary interest: (*i*)-quantitative measurements of the reactivity for various arenes in the coupling reaction with η^6-complexed benzylic acetates (*ii*)-detailed ”step by step” mechanism of the polycondensation process.

2. Experimental

^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker Advance DRX spectrometer operating at 9.40 Tesla corresponding to resonance frequencies of 400.13 MHz for ^{1}H-NMR and 100.61 MHz for ^{13}C- nuclei. Approximately 0.2M (for ^{1}H-NMR spectra) solutions in $CDCl_3$ and TMS as internal standard were used. Reported data refer to chemical shifts (ppm, TMS) multiplicity; intensity of the signal (^{1}H-NMR) and attributions. *IR spectra* were recorded on FTIR Bruker Equinox 55 equipment in KBr. *GC-MS analyses* were performed using a Varian 3400 gas-chromatograph coupled with Saturn II mass spectrometer provided with in trap. *GC-analyses* were performed using a Carlo Erba HRGC 5300 equipment using capillary columns DB-1 and a FID device. *Melting points* were determined using a Böetius type microscope with electric plate and are uncorrected. Solvents were purified according to procedures described in literature and kept on sodium (diglyme, diethylether) or on 4□ molecular sieves.

Reactions involving *η^6-arene-tricarbonyl-chromium complexes* were performed under inert gas (argon) atmosphere.

η^6-(acetoxymethylenebenzene)tricarbonylchromium, **1** was prepared by direct complexation of benzyl acetate with chromium hexacarbonyl, following a procedure previously described. A mixture of 5g (10mmoles) benzyl acetate (sample existent in the laboratory collection, freshly distilled, purity checked by g.c.) and 2.2g (10mmoles) chromium hexacarbonyl in 10mL diglyme was heated at 160^{0}C under argon, for 3 hours. The solvent and unreacted $Cr(CO)_6$ were removed by distillation under reduced pressure (10mmHg); the residue was chromatographed on neutral alumina, products being eluted with petroleum ether (b.p. 30-40^{0}C) and ether. Evaporation of solvent afforded 1.95g (69%) of product **1**, yellow crystals, m.p. 93^{0}C (from *n*-heptane).

^{1}*H-NMR* (δ, ppm, $CDCl_3$): 2.11, s, 3H, (CH_3CO); 4.78, s, 2H, (CH_2); 5.31, d, 2H (H^2 and H^6); 5.32, t, H^4(1H); 5.38, t, 2H (H^3 and H^5).

^{13}*C-NMR* (δ, ppm, $CDCl_3$): 20.79 (CH_3); 64.42 (CH_2); 91.93 ($C^{3\ \mathrm{and}}\ C^5$); 90.03 ($C^{2\ \mathrm{and}}\ C^6$); 104.37(C^4); 112.3(C^1); 170.42 (CO); 232.09 (Cr*C*O)

IR (cm^{-1}, $CHCl_3$): 3087.7 ($\nu_{Car\text{-}H}$); 2968.9 (ν_{CH_3}); 1943.9 and 1856.2 ($\nu_{Cr\text{-}C\text{-}O}$); 1729.2$\nu_{C=O}$)

η^6-(1,4-Bisacetoxymethylenebenzene)tricarbonylchromium,2

Following the procedure described for **1**, from 2.22g (10mmoles) 1,4-bis-acetoxymethylene benzene (available in the laboratory collection of substances, freshly distilled and g.c. purity check) and 2.2g (10mmoles) $Cr(CO)_6$, after heating 4 hours at 160^{0}C, 2.04g (57%) of complex **2**, m.p. 123^{0}C (lit. 124^{0}C) were obtained.

^{1}*H-NMR*): 2.12, s, 6H, (CH_3CO); 4.77, s, 4H, (CH_2); 5.41, s, 4H (complexed ring).

^{13}*C-NMR*: 20.6 (CH_3); 64.12 (CH_2); 92.55 (C^2, C^3, C^5, C^6); 103.84 (C^1, C^4); 170.32 (CO); 231.44 (Cr-*C*O)

η^6-(2',3',5', 6'-Tetramethylenphenylmethylene)benzene)]tricarbonyl chromium, 3

A mixture of 286mg (1mmole) complex **1** and 670mg (5mmoles) 1,2,4,5-tetramethylbenzene in 5mL $CHCl_3$ was flushed with argon, 0.1mL (0.7mmoles) BF_3OEt_2 added and then kept for 4 hours at room temperature before to be poured into ice (5g). Organic layer was separated and aqueous layer was extracted with 2x5mL $CHCl_3$; Combined organic layers were washed with water, dried over $MgSO_4$ and evaporated. The residue was chromatographed on neutral alumina, products being eluted with petroleum ether (b.p. 30-40^0) and ether. Solvent evaporation of the lather fraction yield 306mg (85%) product **3**, m.p. 108^{0}C (from *n*-heptane)

^{1}*H-NMR*): 2.20 and 2.25 s, 12H, (CH_3 groups from positions 2', 6' and 3', 5' respectively); 3.95, s, 2H, (CH_2); 5.23-5.31, m, 5H (H^2-H^6); 6.94, s, 1H (H^4);

^{13}*C-NMR*: 16.51 and 20.95 (CH_3 groups, positions 2', 6' and 3', 5' respectively); 34.23 (CH_2); 92.07 (C^2, C^6); 94.31 (C^1, C^4); 111.90 (C^1); 130.97 (C^4); 133.35($C^{2'}$, $C^{6'}$); and 134.35 ($C^{3'}$, $C^{5'}$) respectively; 233.20 (Cr*C*O).

η^6-(2',4'-Dimethoxyphenylmethylene)benzene)]tricarbonyl chromium, 4

Following the procedure above described for **3**, from 335mg (0.5 mmoles) complex **1** and 345mg (2.5 mmoles) 1,3-dimethoxybenzene, 151mg (91%) complex **4**, m.p. 105^{0}C (lit. 104^{0}C) were obtained.

^{1}*H-NMR*): 3.63, s, 2H, (CH_2); 3.79, s, (OCH_3, psn 4$'$); 3.80, s, 3H, (OCH_3, psn 2$'$); 5.16, t, 1H, (H^4); 5.25, d, 2H (H^2,H^6); 5.33, t, 2H (H^3, H^5); 6.46, s, 1H ($H^{3'}$); 7.08, d, 1H (H^6).

^{13}*C-NMR*: 35.09 (CH_2); 55.53 and 55.65 (OCH_3 psn 2$'$ and 4$'$); 90.91 (C^4); 98.83 (C^2, C^6); 104,43 ($C^{3'}$), 108.83 ($C^{5'}$); 113.29 ($C^{1'}$); 119.66 ($C^{4'}$); 130.89 ($C^{6'}$); 158.22(C^4); 160.31 ($C^{2'}$); 233.34(Cr-*C*O).

η^6-[(1,4-Bis-(2$'$,4'-dimethoxyphennylmethylene)benzene]tricarbonyl chromium, 5

Following the procedure above described for **3**, starting from 176mg (0.5 mmoles) complex **2** and 828mg (6 mmoles) 1,3-dimethoxybenzene, 135mg (53%) **5**, as yellow crystals, m.p. 88^{0}C were obtained.

^{1}*H-NMR*): 3.60, s, 4H, (CH_2); 3.75, s, 6H and 3.78, s, 6H (OCH_3 psn 2$'$ and 4$'$); 5.15, m, 4H (complexed arene ring); 6.47, s, 2H ($H^{3'}$); 6.49, d, 2H ($H^{5'}$); 7.14, d, 2H ($H^{6'}$).

1,4-[Bis-(4'-acetoxymethylenebenzene)tricarbonylchromium-methylene]-2,3,5,6-tetramethylbenzene, 6

Following the procedure described for **3**, starting from 358mg (1 mmole) complex **2** and 22mg (0.17 mmoles) 1,2,4,5-tetramethylbenzene, 62mg (17% with respect to complex **2**) of complex **6**, purified by t.l.c., was obtained.

^{1}*H-NMR*): 2.08, s, 6H, (CH_3CO); 2.10, s, and 2.14, s, 6H (CH_3 groups from psn 2,3,5,6); 3.68, s, 4H (CH_2 psns 1 and 4); 4.77, s, 4H (CH_2OCO'); 5.43, m, 8H (complexed arene ring).

Relative rates in the condensation of the complex 1 with various arenes

A mixture of arenes was prepared by disolving 558.3mg (4.01 mmoles) of 1,3-dimethoxybenzene, 2259.0mg (16.84 mmoles)1,2,4,5-tetramethylbenzene, 4047.4mg (33.67mmoles) 1,3,5-trimethylbenzene and 2548.9mg (23.57 mmoles) methoxybenzene in 50mL $CHCl_3$. A sample of 100mg (0.337 mmoles) of complex **1** was dissolved in 5mL of above solution, the solution deaerated by flushing with argon and, after addition of 0.15mL BF_3Et_2O, the mixture was left to react for 24 hrs at room temperature and at the dark. Reacted mixture was then poured and conc. HCl solution was added until the color turned to green. The organic layer was separated washed, dried over $MgSO_4$, concentrated under normal pressure and analyzed by GC-MS to identify condensation products, **7** with 1,2,4,5-tetramethylbenzene (M=224.8, **7a**); 1,3,5-trimethylbenzene (M=210.8, **7b**); methoxybenzene (M=198.8, *para* posn, **7c**); methoxybenzene (M=198.8, *ortho* posn, **7d**); 1,3-dimethoxybenzene (M=212.9, posn 4, **7e**); 1,3-

dimethoxybenzene (M=212.9, posn.2, **7f**). GC-analysis provided quantitative composition.

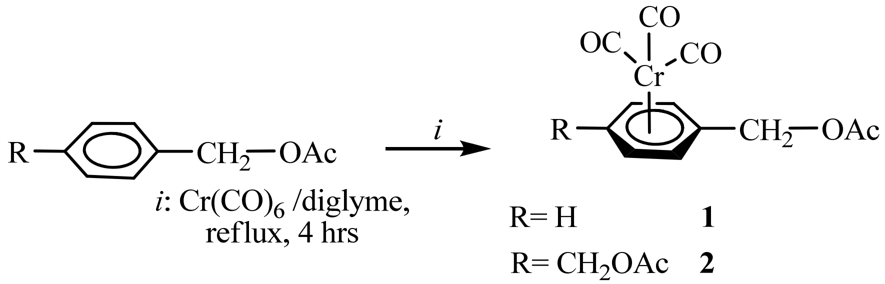
Relative ratios of products in the condensation of the complex 2 with various arenes

Following the procedure above described for the condensation with complex 1 and starting from a mixture consisting of complex 2, 1,3-dimethoxybenzene and 1,3,5-trimethylbenzene in a molar ratio of 1:1.5:12 the products **8a-8g** were identified by GC-MS as follows: M=282, **8a**; M=300, **8b**; M=342, **8c**; M=360, **8d**; M=360, **8e**; M=378, **8f**; M=378, **8g** (sec *Scheme 6*)

3. Results and discussion

Synthesis of (arene)tricarbonylchromium complexes and coupling reactions

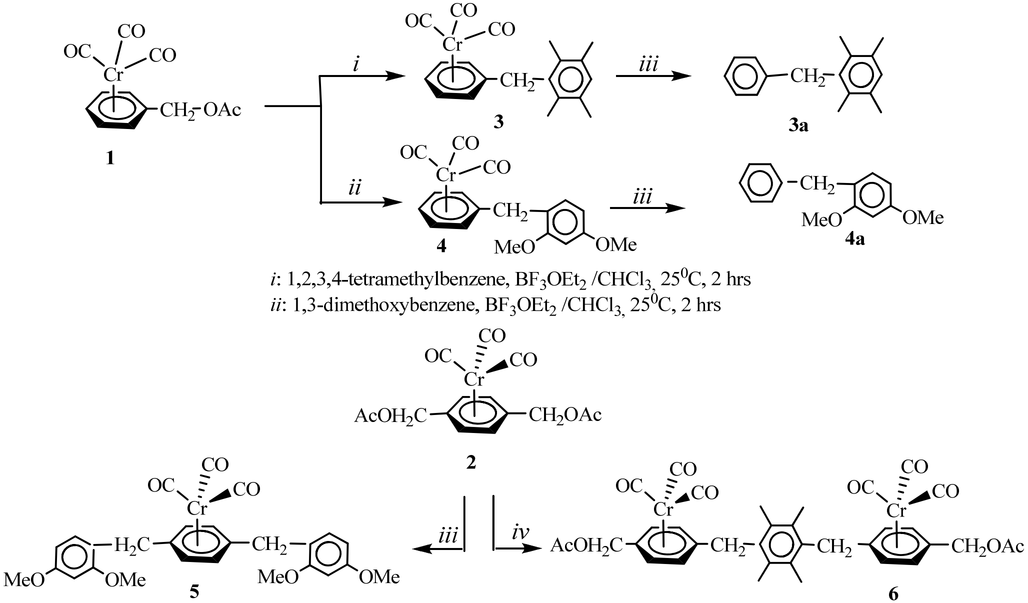
The title experimental task is aiming to provide a model method and substances for measurement of relative coupling rates and for disclosing details of ”step by step” of polycondensation type coupling process. In this aspect, two η^6-(arene)tricarbonylchromium complexes bearing one (**1**) and two reactive benzylic functions (**2**) were synthesized by direct complexation previously described [26,27]. (*Scheme 3*).



Scheme 3

Coupling reactions were performed as described in *Scheme 4*: starting from monofunctional complex **1** coupled products, were obtained in reactions with 1,2,4,5-tetramethylbenzene (**3**) and 1,3-dimethoxybenzene, (**4)** respectively. After structural characterization products were subjected to decomplexation (mild oxidation with $NaNO_2$/HCl) and the free ligands (**3a**, **4a**) were analyzed by GC-

MS thus validating a method suitable for quantitative analysis of a multicomponent mixture of coupling products.



i: 1,2,3,4-tetramethylbenzene, BF_3OEt_2 /$CHCl_3$, 25^{0}C, 2 hrs
ii: 1,3-dimethoxybenzene, BF_3OEt_2 /$CHCl_3$, 25^{0}C, 2 hrs

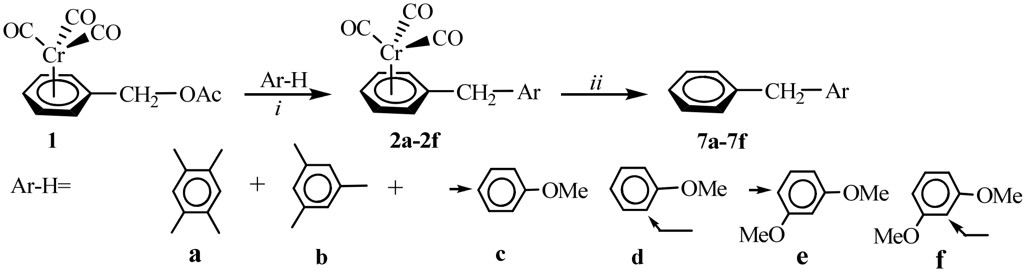
iii: 1,3-dimethoxybenzene, mol. rat. 10:1, BF_3OEt_2 /$CHCl_3$, 25^{0}C, 2 hrs
iv: 1,2,4,5-tetramethylbenzene, mol. rat. 0.1:1, BF_3OEt_2 /$CHCl_3$, 25^{0}C, 2 hrs

Scheme 4

On the other hand, starting from difunctional complex, **2** the coupling with an excess of 1,3-dimethoxybenzene afforded the bis-coupled product **5** for which the structure A-C-A (arene-complex-arene) was assigned while the coupling with the 1,2,4,5-tetramethylbenzene (this time using a large excess of complex) led to coupled product **6** exhibiting a structure of sequence C-A-C (*Scheme 4*). ^{1}H-NMR pattern of above described of a polycondensation process.

Relative rates of coupling with various arenes

Previously reported data [26] showed that the conversions and yields in coupling reactions of complexed benzylic acetates with arenes are significantly dependent on the nucleophilicity of arenes. In order to obtain accurate quantitative information concerning this topic (essential for the design of further efficient couplings and polycouplings) measurements of relative rates were performed following the procedure summarized in *Scheme 5*: a mixture of 4 different arenes possessing a total number of 6 reactive sites (**a-f**) was left to react, under typical coupling conditions, with a limited amount of complex **1**. The crude mixture of complexed products was subjected to decomplexation ($NaNO_2$/HCl) and then analyzed by GC-MS.



R= H, Me, Ac R'= Me, OMe

i: $BF_3OEt_2/CHCl_3$; r.t.; 24 hrs; *ii*: $NaNO_2$+ HCl

Scheme 5

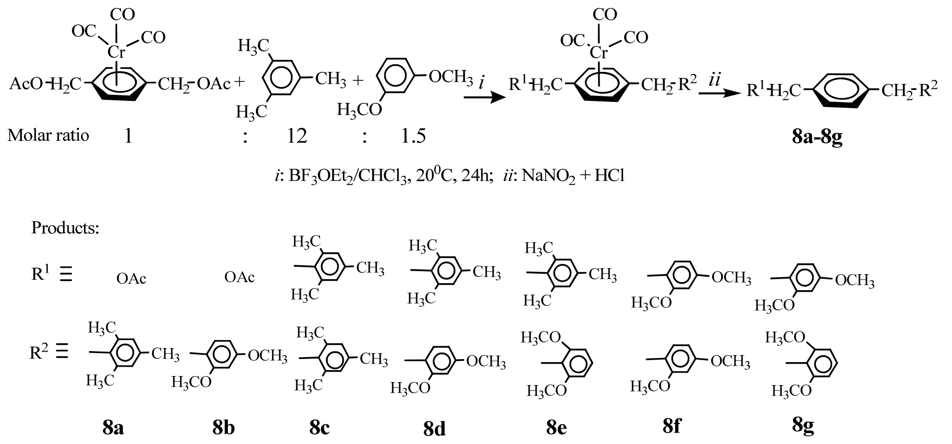
Table 1

Relative rates of condensation with η^6-(benzylacetate)tricarbonyl chromium of some activated arenes (encording to the *Scheme 5*)

Product structure	**7a**	**7b**	**7c**	**+ 7d**	**7e**	**+7f**
Initial molar ratio for arenes	5	10	7		1.2	
Conc. in product mixture **7** (mol%)	1.08	32.08	5.07	1.72	51.3	8.03
Relative rate	1	10.1	6.70	1.14	198	62.0

Results reported in *Table 1* clearly show a strong enhancement of reactivity by accumulation of electron-releasing substituents in the structure of arene: in agreement with substituent $\sigma_{Hammett}$ parameters, reactivities follow the order methoxy > methyl (compare **7b** vs **7e**) and relative position *p* > *o* > *m* (compare e.g. **7a** vs **7b** and **7c** vs **7d**). As a whole, Table 1 date are in agreement with main lines of an aromatic electrophilic mechanism involving intervention of a σ type complex as intermediate in the rate determining step.

Above results were confirmed by experiments of coupling with difunctional complex, **2**. In a typical experiment of this type outlined in *Scheme 6* a mixture of two activated arenes was reacted with a limited amount of the complex **2** providing a number of 7 products (**8a-8g**). Relative abundance of different coupling products finely reflects the influence of both relative reactivities and molar ratios of the arene reagent (*Scheme 6*)

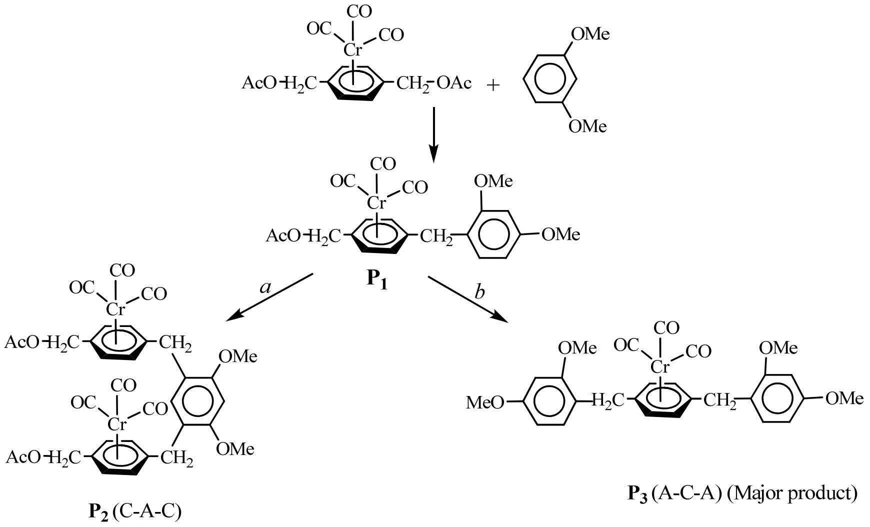


	8a	8b	8c	8d	8e	8f	8g
Content (mol %)	7.2	1.0	11.1	44.9	5.3	29.1	1.4

Scheme 6

"Step by step" mechanism of polycondensation

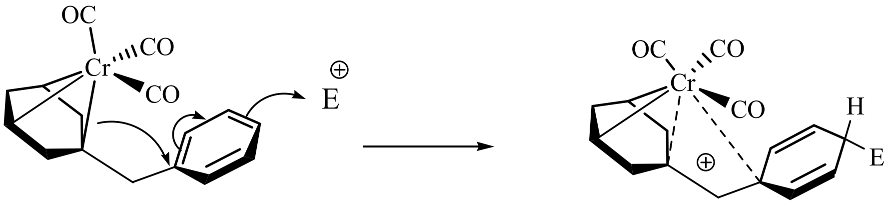
The problem discussed here is outlined in *Scheme 7*



	Ratio in P_2	Ratio in P_3	
OMe+CH_2/Ar-H	10/10 = 1.0	16/10 = 1.6	Exp = **1.51**
Ac-O-CH_2/Ar-H	10/10 = 1.0	0/10 = 0	Exp ~ **0**

Scheme 7

In the coupling reaction of the difunctional compound **2** with an arene exhibiting two equivalent reactive sites (1,3-dimethoxybenzene) first coupling process leads compulsory to product P_1; for next step the reaction can take two different routes: either a reaction with a new molecule of complex thus affording the product P_2 of structure C-A-C, on a reaction with a new molecule of arene thus providing the product P_3 of A-C-A. P_2 or P_3 are easily identified by ^{1}H-NMR pattern (e.g. ratio of intensities for OMe+CH_2/Ar-H signals which is 10/10 = 1.0 for product P_2 or 16/10 = 1.6 for product P_3). The experimental value (recorded for short reaction time when low molecular mass products are prevailing) was found to be 1.51 indicating the structure A-C-A for main product. Quite interesting in the condensation of complex **2** with 1,2,4,5-tetramethylbenzene: an opposite result was obtained, the reaction following, this time, a C-A-C sequence. This unexpected difference could be rationalized in terms of stabilization of the intermediate generated by the electrophilic attack on arene (*Scheme 8*)



Scheme 8

It is reasonable to admit that a certain contribution to this stabilization is supplied by metal-carbon bond *via* a *homoconjugation effect*. This effect, able to activate *para* position, is valid for tetramethyl- substituted arene, but is inoperative in the case of 1,3-dimethyl-substituted system where further substitution takes place on in a *meta* position.

4. Conclusions

1. Acid catalyzed coupling reaction of tricarbonylchromium complexed benzylic acetates with arenes exhibits characteristics of an aromatic electrophilic substitution involving a σ type intermediate.
2. Relative coupled rates show the following order of reactivities for substituted benzenes: 1,2,4,5-tetramethyl < *o*-methoxy < *p*-methoxy < 2,4,6-trimethyl < 2,6-dimethoxy < 2,4-dimethoxy substituents.
3. Step by step mechanism of a polycondensation type coupling showed preferred sequences A-C-A or C-A-C depending on the structure of the arene (relative *meta* or *para* position of the reactive sites).

R E F E R E N C E S

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