

# New Carbon-carbon Bonds Formation Mediated by Chromium Hexacarbonyl

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We report here the reaction of various benzylic halides with hexacarbonylchromium(0) in boiling diglyme, providing – instead of  $\eta^6$ -arene-tricarbonyl-chromium complexes – products of reductive coupling: corresponding bibenzyls (from monohalides), alkenes or cyclopropanes (from dihalides). This is the first report concerning the one-pot synthesis in good yield of a cyclopropane derivative starting from easily accessible benzylic dichlorides. The experimental information concerning the formation of new carbon-carbon  $\sigma$ - and  $\pi$ -bonds in the above mentioned reactions is consisting with a mechanism comprising consecutive steps of oxidative-addition of reactive organic halide to chromium(0) followed by nucleophilic substitution or  $\beta$ -elimination reactions.

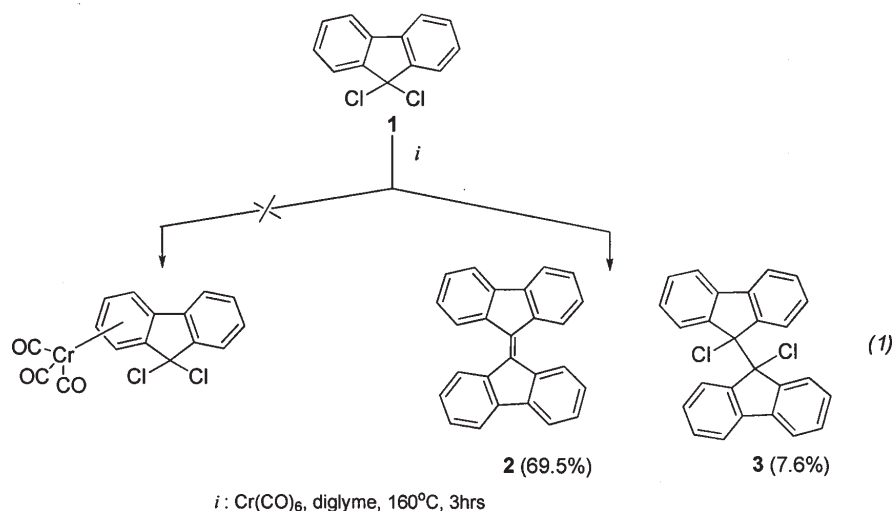
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The arene-tricarbonyl-chromium (0) complexes have been known since few decades to serve as valuable tools in various organic syntheses including enantioselective reactions, natural products synthesis or catalysis (see, for example, recent reviews [1-6] and an encyclopedic survey [7-9]).

The widest used route of access to  $\eta^6$ -complexes of this type consists in thermal reaction of arenes with hexacarbonylchromium(0) [10]. Including modern improvements concerning solvent composition of the reacting mixture [10-13], microwave heating [14,15] or replacement of Cr(CO)<sub>6</sub> by more reactive chromium derivatives (e.g. (NH<sub>3</sub>)<sub>3</sub>Cr(CO)<sub>3</sub> [16-18]) direct complexation of arenes provides, usually, excellent yields of  $\eta^6$ -arene-tricarbonyl-chromium(0) complexes.

Our attempt to use the above mentioned reaction – otherwise frequently successfully employed in our laboratory (see, for example [19-23]) – in tricarbonyl-chromium complexation of 9,9-dichlorofluorene, **1**, failed: reaction of **1**, in equimolar ratio, with hexacarbonylchromium(0), in boiling diglyme, provided instead of the  $\eta^6$ -arene-tricarbonyl-chromium(0) complex, the compound **2**, a product of reductive carbon-carbon coupling, in a good (69.5%) yield (scheme 1).

This result was not entirely unexpected: previous reports related to direct  $\pi$ -complexation of arenes noticed the failure of the reaction for the benzylic halides, even in cases where very reactive (NH<sub>3</sub>)<sub>3</sub>Cr(CO)<sub>3</sub>, (CH<sub>3</sub>CN)<sub>3</sub>Cr(CO)<sub>3</sub> complexing synthons were used [24]. In compensation,

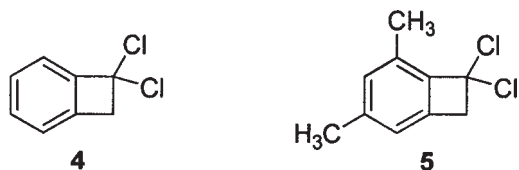


Scheme 1

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indirect synthesis of benzylic halides- complexes starting from corresponding benzylic alcohols is conceivable [25-27]. Despite the fact that reactions of benzylic halides with transition metals [28] or transition metal compounds [29-32] (other than chromium) are carefully studied, in the case of the reaction with hexacarbonylchromium(0) only little information remains available; most reports mentioning usually the formation of "complex unresolved mixtures". The only existing paper reporting reductive coupling by chromium(0) compounds refers to the reaction of benzylic halides with triamino-tricarbonyl-chromium(0) leading to 1,2-diarilmethanes, ethenes, and ethyne [24].

However the convenient yield obtained in the preliminary experiment shown in scheme 1 stands for a realist expectation to use one-pot reaction of benzylic halides with a less elaborated reagent ( $\text{Cr}(\text{CO})_6$ ) as valuable preparative tool. In this respect, taking into account our interest in chemistry of  $\pi$ -complexed benzocyclobutene system [33], the benzylic dichlorides **4** and **5** appeared to be suitable candidates



### Experimental part

$^1\text{H-NMR}$  spectra were recorded on a Bruker Avance DRX 400 spectrometer. Approximately 0.2 M (for  $^1\text{H-NMR}$  spectra) solution in  $\text{CDCl}_3$  and TMS as internal standard were used. Reported data refer to chemical shifts (ppm, TMS), multiplicity, intensity of the signal and attribution. 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 ion trap. Elemental analyses were performed on a Carlo Erba equipment mod. 1106. Melting points were determined using a Boetius type microscope with electric plate and are uncorrected. Solvents were purified according to procedures described in literature and kept on 4Å molecular sieves.

**9,9-Dichlorofluorene, 1**, was prepared by reaction of fluorenone with phosphorous pentachloride. From 9.0 g (0.05 mol) fluorenone and 12.5 g (0.06 mol)  $\text{PCl}_5$ , 2 h, 180°C, 9.5 g (81%) product **1**, b.p. = 98°C/5mm Hg was obtained.  $^1\text{H-NMR}$ : 7.59, dd, 2H ( $\text{H}^1, \text{H}^8$ ); 7.36, dt, 2H ( $\text{H}^2, \text{H}^7$ ); 7.44, dt, 2H ( $\text{H}^3, \text{H}^6$ ); 7.81, dd, 2H, ( $\text{H}^4, \text{H}^5$ ).  $^{13}\text{C-NMR}$ : 129.06 ( $\text{C}^1, \text{C}^8$ ); 125.48 ( $\text{C}^2, \text{C}^7$ ); 124.67 ( $\text{C}^3, \text{C}^6$ ); 136.53 ( $\text{aC}^1, \text{aC}^8$ ); 146.77 ( $\text{aC}^4, \text{aC}^5$ ). GC-MS:  $M_r = 234/236/238$ ; 98 % content of **1**.

**9,9'- Bisfluorenylidene, 2** and **1,1'-dichloro-1,1'-bi-9-fluorenyl, 3**. 2.35 g (10 mmol) **1**, 2.20 g (10 mmol)  $\text{Cr}(\text{CO})_6$  in 10 mL diglyme, heated under reflux 3h, then diglyme evaporated under reduced pressure (5mm Hg), reaction mixture decomposed in water, organic products extracted with diethylether, washed, dried and solvent evaporated. The residue was chromatographed on alumina (elution with petroleum ether- diethyl ether 2:1 and 1:1) afforded, after evaporation and recrystallization (EtOH), 1.14g (69.5%) compound **2**. *Elemental analysis*: C, 94.72%, H, 5.03%; Calc. for  $\text{C}_{26}\text{H}_{16}$ : C, 95.09%, H, 4.91%.  $^1\text{H-NMR}$ : 8.38, dd, 4H ( $\text{H}^1, \text{H}^8, \text{H}^{11}, \text{H}^8$ ); 7.21, dt, 4H ( $\text{H}^2, \text{H}^7, \text{H}^2, \text{H}^7$ ); 7.33, dt, 4H ( $\text{H}^3, \text{H}^6, \text{H}^3, \text{H}^6$ ); 7.70, dd, 4H ( $\text{H}^4, \text{H}^5, \text{H}^4, \text{H}^5$ ). The compound **3** identified by GC-MS in the crude reaction mixture in 7.6% yield.

**1,1-Dichlorobenzocyclobutene, 4** was prepared by reaction of benzyne (generated *in situ*) and vinylidene dichloride. From 13.7 g (0.01 mol) anthranilic acid and

21.8 g (0.186 mol) butylnitrite in 125 mL diethylether at 0°C, 17 g (92%) 2-carboxybenzenediazonium chloride was obtained and then this product reacted with 44.9 g (0.46 mol) vinylidene dichloride and 7.5 g (0.13 mol) propylene oxide in 175 mL  $\text{CH}_2\text{Cl}_2$ , to afford 7.8 g (50%) product **4**, colorless liquid, b.p. 86°C/10 mmHg.  $^1\text{H-NMR}$ : 4.11, s, 2H ( $\text{H}^2$ ); 7.17, dd, 1H ( $\text{H}^3$ ); 7.34, dt, 1H ( $\text{H}^4$ ); 7.40, dt, 1H ( $\text{H}^5$ ); 7.37, dd, 1H ( $\text{H}^6$ ).  $^{13}\text{C-NMR}$ : 78.98 ( $\text{C}^1$ ); 57.32 (HETCOR,  $\text{C}^2$ ); 123.95 ( $\text{C}^3$ ); 120.44 ( $\text{C}^4$ ); 131.92 ( $\text{C}^5$ ); 129.01 ( $\text{C}^6$ ); 137.41 ( $\text{aC}^1$ ); 148.31 ( $\text{aC}^2$ ).

**1,1-Dichloro-4,6-dimethylbenzocyclobutene, 5** was prepared by dehydrochlorination of compound **6** by heating at 170°C, for 6 h, under reduced pressure. From 21 g (0.088 mol) trichloromethylmesitylene 14.5 g (82%) dichloride **5** was obtained as white crystals m.p. 55°C [35].  $^1\text{H-NMR}$ : 2.31, s, 3H ( $\text{CH}_3$ , psn. 4); 2.35, s, 3H, ( $\text{CH}_3$ , psn. 6); 4.00, s, 2H ( $\text{H}^2$ ); 6.92, d, 1H ( $\text{H}^3$ ); 6.77, d, 1H ( $\text{H}^5$ ).  $^{13}\text{C-NMR}$ : 15.18 ( $\text{CH}_3$ , psn. 4); 22.20 ( $\text{CH}_3$ , psn. 6); 79.07 ( $\text{C}^1$ ); 56.62 ( $\text{C}^2$ ); 128.56 ( $\text{C}^3$ ); 132.13 ( $\text{C}^4$ ); 121.08 ( $\text{C}^5$ ); 136.94 ( $\text{C}^6$ ); 142.43 ( $\text{aC}^1$ ); 143.11 ( $\text{aC}^2$ ).

**2-Trichloromethyl-1,3,5-trimethylbenzene (trichloromethylmesitylene), 6** was prepared by Friedel-Crafts alkylation. From 15 g (0.0125 mol) mesitylene, 34 g (0.25 mol)  $\text{AlCl}_3$  in 100 mL  $\text{CCl}_4$ , 3hrs. at 37-42°C, 21 g (71%) compound **6** resulted, as a colorless liquid, b.p. 140°C/ 10 mm Hg [36].  $^1\text{H-NMR}$ : 2.42, s, 3H ( $\text{CH}_3$ , psn. 1); 2.30, s, 3H ( $\text{CH}_3$ , psn. 3); 2.25, s, 3H ( $\text{CH}_3$ , psn. 5); 6.89, d, 1H ( $\text{H}^6$ ).  $^{13}\text{C-NMR}$ : 20.34 ( $\text{CH}_3$ , psn. 1); 21.17 ( $\text{CH}_3$ , psn. 5); 136.15 ( $\text{C}^1$ ); 140.08 ( $\text{C}^2$ ); 129.25 ( $\text{C}^4$ ); 132.25 ( $\text{C}^5$ ); 128.80 ( $\text{C}^6$ ); 175.19 ( $\text{CCl}_3$ ).

**1,1'-bis-(4,6-Dimethylbenzocyclobutylidene), 7** was obtained in reaction of **5** with  $\text{Cr}(\text{CO})_6$ . From 1 g (5 mmol) **5** and 1.1 g (5mmol)  $\text{Cr}(\text{CO})_6$  in 10 mL diglyme, under argon, 3 hrs. at 160°C, 0.36 g (55%) hydrocarbon **7**, as white crystals, m.p. 189° [34].

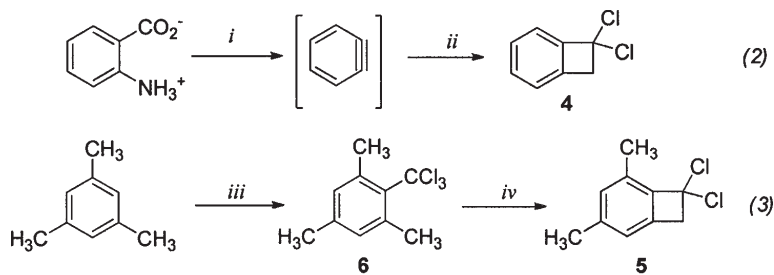
**1,1,2,2,3,3-tris-Benzocyclobutylidene cyclopropane, 8** was obtained in reaction of **4** with  $\text{Cr}(\text{CO})_6$ . Following the procedure described for compound **7** from 0.87 g (5mmol) dichloride **4** and 1.1 g (5 mmol)  $\text{Cr}(\text{CO})_6$  in 10 mL diglyme, 3 h at 160°C yielded 0.46 g (60%) of **8** as white crystals, m.p. 170°C. Structure and stereochemistry of this compound are discussed in the next section.

Reactions (6)-(11) were performed by heating (170°C, 3h) corresponding halide with  $\text{Cr}(\text{CO})_6$  in the molar ratio mentioned in the scheme 4 (10: 10 mmol ratio when no otherwise mentioned) in 10 mL diglyme, in a sealed glass tube. After reaction time, the reaction mixture was decomposed with water, organic compounds extracted with diethyl ether, washed, solvent removed carefully at normal pressure and products identified and quantitatively measured by GC-MS and  $^1\text{H-NMR}$  analyses (identification by comparison with authentic samples). For reaction (12) arene-tricarbonyl-chromium complexes were isolated and analyzed by  $^1\text{H-NMR}$ .

### Results and discussion

The synthesis of starting benzylic halides **4** and **5** followed the reaction shown in the scheme 2: for 1,1-dichlorobenzocyclobutene **4** the cycloaddition reaction of benzyne (generated *in situ* from anthranilic acid and butyl nitrite) with vinylidenedichloride was performed while 1,1-dichloro-4,6-dimethyl-benzocyclobutene **5** was prepared starting from mesitylene by Friedel-Crafts alkylation with tetrachloromethane followed by thermal dehydrochlorination.

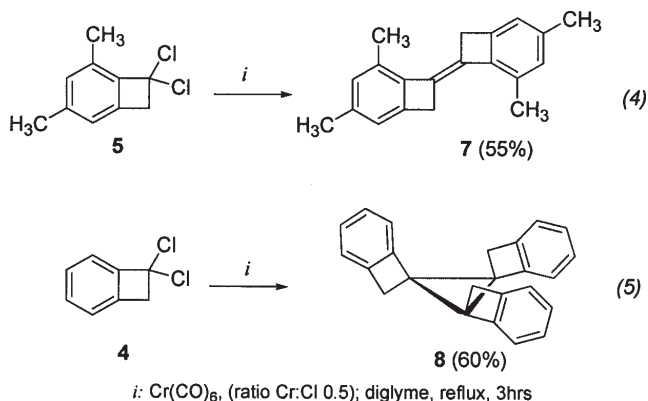
The reactions of benzylic dichlorides **4** and **5** with hexacarbonylchromium(0) are depicted in the scheme 3. From benzylic dichloride **5** the main reaction product is the



*i*: BuONO, CH<sub>2</sub>Cl<sub>2</sub>; *ii*: Cl<sub>2</sub>C=CH<sub>2</sub>; *iii*: CCl<sub>4</sub>, AlCl<sub>3</sub>; *iv*: 170°C

Scheme 2

alkene **7** (E configuration) but quite unexpectedly benzylic dichloride **4** afforded in relatively good yield the cyclopropane derivative **8**,



Scheme 3

The structures of the reaction products were established according to elemental analyses, <sup>1</sup>H- and <sup>13</sup>C-NMR and MS spectra.

The alkene **7** was isolated in 55% yield as a white crystalline product with m.p. 189°C (from *n*-heptane). The elemental analysis and the mass spectrum are consistent with the molecular formula C<sub>20</sub>H<sub>20</sub>. The <sup>1</sup>H-NMR spectrum (CDCl<sub>3</sub>) shows three singlet signals at δ 2.35 ppm (12H), 3.80 ppm (4H) and 6.85 ppm (4H). The compound was previously described in literature [34]. The previously reported synthesis [34] involved the thermal decomposition of the *p*-toluenesulphonylhydrazone of 4,6-dimethylbenzocyclobutene-1-one. The cyclopropane derivative **8** was isolated in a 60% yield as crystalline colorless product with m.p. 170°C. The compound **8** was not described previously, and its structure was assigned to 1,1,2,2,3,3-tris-benzocyclobutylidene cyclopropane in the *cis-trans* configuration. The assignment of the structure and configuration for compound **8** is described below.

The molecular formula C<sub>24</sub>H<sub>18</sub> was deduced based on the elemental analysis (calculated C 94.08%, H 5.92%, found C 93.1%, H 5.82%) and mass spectrometry (M<sup>+</sup> = 306).

The <sup>1</sup>H-NMR spectrum (CDCl<sub>3</sub>) shows two signals for the CH<sub>2</sub> group belonging to the cyclobutane ring (fig.1).

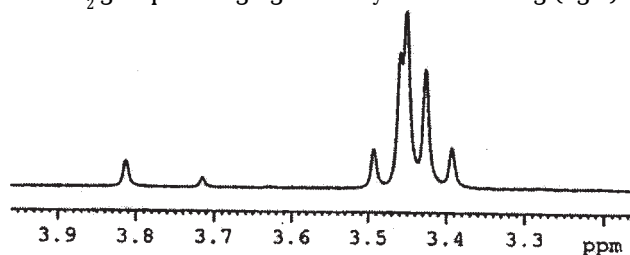


Fig. 1. The <sup>1</sup>H-NMR spectrum for the CH<sub>2</sub> region belonging to the cyclobutane ring of compound **8**

Thus there is one singlet at 3.45 ppm (2H) and two doublets with a AB pattern centered at 3.41 ppm and 3.47 ppm with ac coupling constant J<sub>AB</sub> of 10.2 Hz. This NMR pattern is consistent with a *cis-trans* configuration for the substituents in the positions 1, 2 and 3 of the cyclopropane ring of the compound **8** (fig. 2).

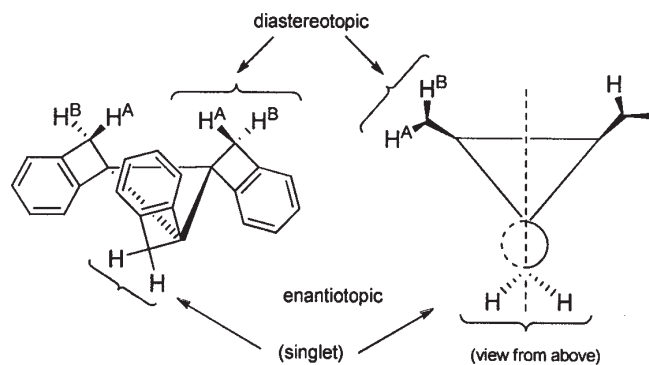


Fig. 2. The configuration of the compound **8**

The assigned structure for compound **8** is further confirmed by the <sup>13</sup>C-NMR spectrum (CDCl<sub>3</sub>). The cyclopropane structure is supported by the two signals at 44.43 and 44.20 ppm which are consistent with chemical shifts for benzylic quaternary carbon atoms and not with sp<sup>2</sup> carbon atoms. The *cis-trans* configuration is supported by the existence of a pair of signals in the ratio 1:2 corresponding to the two types of benzocyclobutylidene substituents (fig. 3).

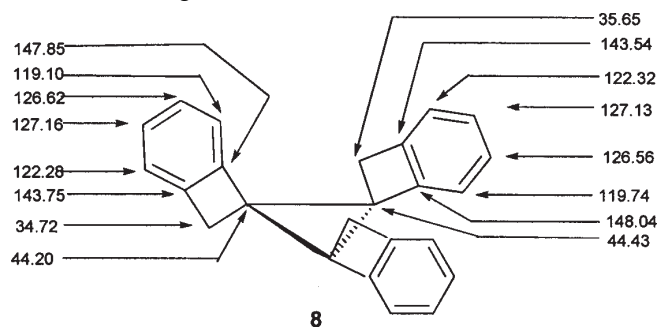
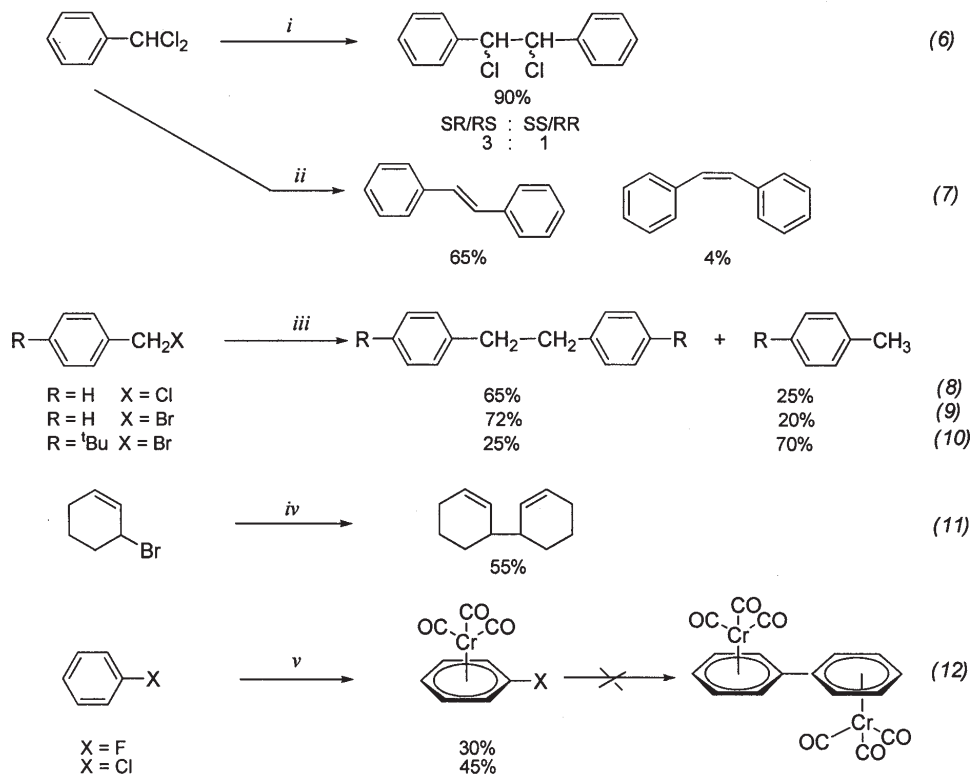


Fig. 3. The assignment of the signals in the <sup>13</sup>C-NMR spectrum (CDCl<sub>3</sub>) for compound **8**

Other performed reactions are depicted in Scheme 4. The main information resulted from these reactions refers to sequential coupling of benzylidene dichloride with isolation of 1,1'-dichloro-bibenbenzyl derivative (**6**), formation of by-products of reduction (**8**)-(10), high reactivity in coupling of alkyl halides (**11**) and the lack of any tendency for carbon-carbon coupling in the cases of both aryl halides or their tricarbonyl-chromium(0) complexes (**12**).

The reaction mechanism has to rationalize the formation of different products (alkene **7** and cyclopropane derivative **8**) from halides of apparently similar structure (**4** and **5**). The reaction of 1,1-dichloro-4,6-dimethylbenzocyclobutene with hexacarbonylchromium(0) led to 1,1'-



Scheme 4

i:  $\text{Cr}(\text{CO})_6$  (ratio Cr : Cl 0.25), diglyme,  $180^\circ\text{C}$ , 3hrs, ii-v:  $\text{Cr}(\text{CO})_6$  (ratio Cr : Cl 0.5), diglyme,  $180^\circ\text{C}$ , 3hrs

bis-(4,6-dimethylbenzocyclobutylidene), **7** (E configuration). The same compound **7** (E configuration) was previously obtained by another route consisting in the photolysis of the sodium salt of 4,6-dimethylbenzocyclobutenone tosyl hydrazone, this latter reaction being rationalized in terms of dimerization of the corresponding carbene.

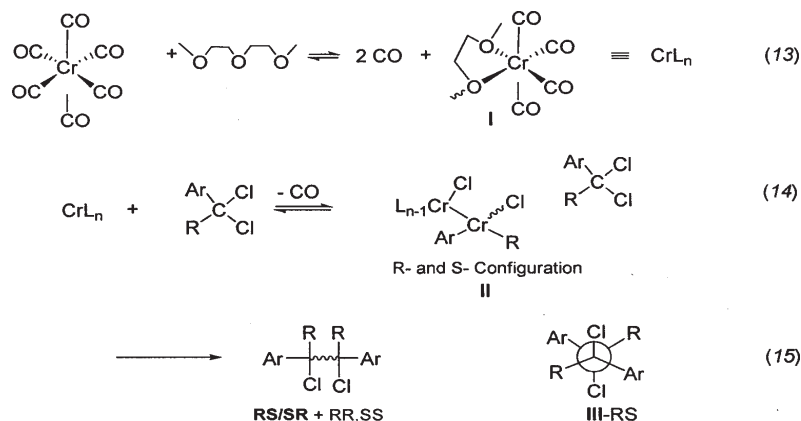
Based on the structural and configurational similarity of the products for the two reactions the first temptation is to assign the same type of mechanism and, consequently, to suspect a singlet type carbene as main unstable intermediate. According to this idea the dimerization of carbene would lead to E-alkene and further, the formation of the cyclopropane ring observed in the reaction (5) would undergo as a 2+1 cycloaddition.

However the above mechanistic path is not consistent with other experimental facts: in the reaction (6) of benzylidene dichloride with an insufficient amount of  $\text{Cr}(\text{CO})_6$  the main product was 1,2-dichloro-1,2-diphenyl-

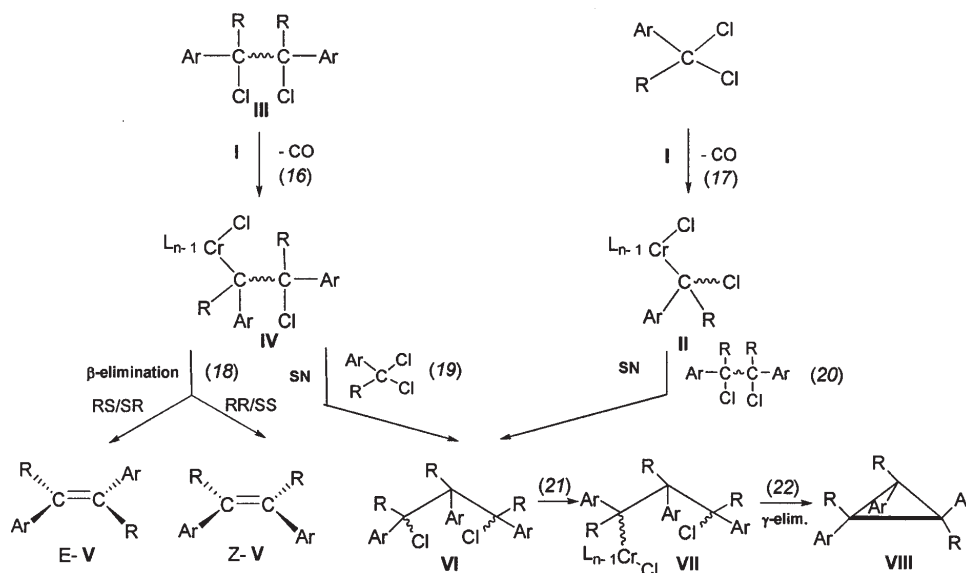
ethane (*mezo-racemic*) while in an excess of  $\text{Cr}(\text{CO})_6$ , reaction (7), the product was the expected alkene (E-stilbene). This clearly shows that the intermediate is not a *carbene* but a monocoupling product with a structure of vicinal dihalide. The benzylidene dichloride is not singular in this behavior: similarly products of monocoupling have been also noticed in the case of 9,9-dichlorofluorene (the product **3** identified by GC-MS) and 1,1-dichloro-1,2-dihydrocyclobutabenzene (monocoupling product inferred by  $^1\text{H-NMR}$  analysis of the crude reaction product).

Very likely the stepwise mechanism which is going to be outlined starts by an oxidative addition of the benzyl halide on  $\text{Cr}(\text{CO})_6$  compound (scheme 5 where an unsymmetrical benzylic dichloride is taken as example). The Cr(0) compound is hexacarbonylchromium(0) or, more likely, a derivative, **I**, formed by the intervention of donor solvent in the ligand exchange equilibrium (13).

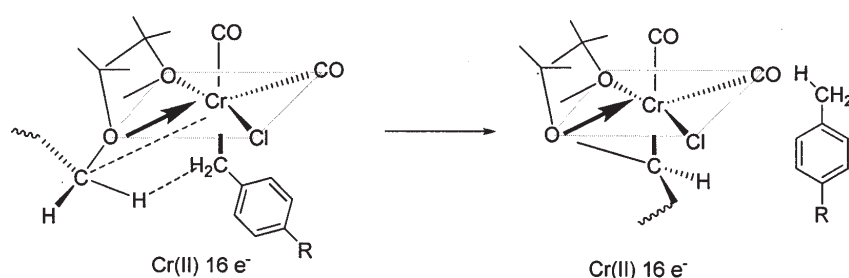
The product of oxidative addition, **II** (racemic) reacts then with a new molecule of dichloride (nucleophilic



Scheme 5



Scheme 6



Scheme 7

substitution) to provide a diastereomeric mixture of monocoupled product, **III**. Diastereomeric composition depends on steric requirements of R and Ar; the larger is steric difference between Ar and R the more favored will be *meso* configuration. From relatively stable product **III** final products are formed *via* a second oxidative addition (stepwise mechanism) as depicted in scheme 6. The intermediate of oxidative addition, **IV**, is responsible for alkene formation by a  $\beta$ -elimination reaction (out of anti periplanar conformation of the transition state an E-V alkene from RS/SR and Z-V from RR/SS configurations are conceivable).

The same intermediate **IV** is possibly involved in the formation of the cyclopropane derivative by the coupling of a new molecule of benzylic dichloride (compound **VI**) followed by the third oxidative addition (21) and finally a  $\gamma$ -elimination to cyclopropane **VIII**.

Reductive processes are often accompanying the coupling reactions. This is clearly showed in the reaction of benzylic halides (both chlorides and bromides, (8)-(10)). The source of hydrogen for the reduction reaction is most probably the solvent (diglyme, scheme 7). This is proved by an experiment in which decomposition of the reaction mixture was performed in a mixture of EtOD/D<sub>2</sub>O and the reduced product did not show any significant incorporation of deuterium (<sup>1</sup>H-NMR). On the other hand among by-products of the coupling/reduction reactions some heavy components suspected to be cross-coupling diglyme-benzylic derivative (<sup>1</sup>H-NMR, GC-MS) were notified, however without isolation in a pure form.

## Conclusions

The reaction of benzylic dichlorides (readily accessible from corresponding aryl-ketones) with hexacarbonylchromium(0) consists in carbon-carbon coupling sequence leading to new  $\sigma$ - and  $\pi$ -bonds.

In this respect we report here the first example of one-pot synthesis, in relatively good yield, of a cyclopropane derivative, starting from a benzylic dichloride.

Depending on the structure of the starting benzylic dichloride and the conditions of the reaction with Cr(CO)<sub>6</sub>, symmetrical 1,1-dichloro-bibenzyl or bi-benzylidene derivatives are also accessible for good yields.

According to our preliminary data the most likely reaction mechanism involves stepwise oxidative additions of benzylic halides to Cr(0) reagent followed by coupling *via* nucleophilic substitution and  $\beta$ - or  $\gamma$ -eliminations.

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