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Reductive Carbonylation of *gem*-Dihalogenocyclopropanes by Pentacarbonyliron(0) in the Presence of Sodium Methoxide

Françoise Reyne, Bernard Waegell, and Pierre Brun[*,†]

Laboratoire de Stéréochimie, LASCO, URA 1409, Faculté des Sciences et Techniques de Saint Jerôme, Avenue Escadrille Normandie-Niemen, F-13397, Marseille Cédex 13, France

†Laboratoire de Synthèse Organique Sélective, GCOBO, URA 1320, Faculté des Sciences de Luminy, 163 Avenue de Luminy, F-13288, Marseille Cédex 9, France

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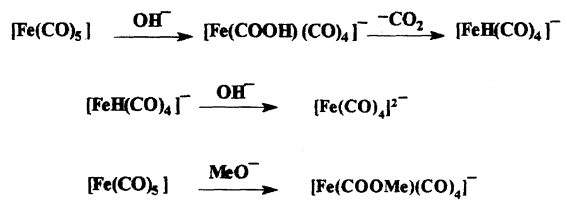
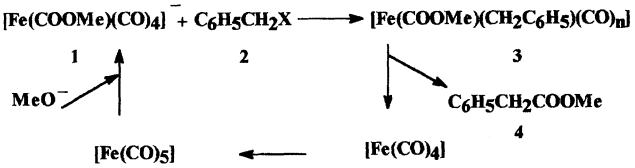
The reaction of *gem*-dihalogenocyclopropanes derivatives with (tetracarbonyl)(methoxycarbonylato) ferrate(I−) has been investigated; *gem*-dibromocyclopropanes and *gem*-chlorobromocyclopropane derivatives are reduced and carbonylated. It could be shown that a bromo ester such as methyl 1-bromo-2-phenylcyclopropanecarboxylate is an intermediate in the transformation of 1,1-dibromo-2-phenylcyclopropane into methyl *cis*- and *trans*-2-phenylcyclopropanecarboxylates and dimethyl 2-phenyl-1,1-cyclopropanedicarboxylate.

Metal carbonyl mediated carbonylation of organic halides is an area of continuing investigations.[1—6] In order to use the readily available and inexpensive [Fe(CO)$_5$] as a carbonylation reagent, it is necessary to remove a CO ligand to generate a coordinative insaturation site, or to generate an anionic iron complex such as [FeH(CO)$_4$]$^-$, [Fe(CO)$_4$]$^{2-}$, or [Fe(COOR)(CO)$_4$]$^-$. These complexes are obtained by reacting basic nucleophiles such as OH$^-$ or MeO$^-$ with pentacarbonyliron (Scheme 1).[3,7—11] Although such complexes are generally not isolated, it is now recognized that they are involved in the carbonylation of organic halides.[3,12] These will react more easily if they are prone to undergo a facile nucleophilic substitution, as it is the case with alkyl or benzyl halides. Phase transfer conditions are particularly suitable for such reactions (Scheme 2).[12]

However, several questions arise about the processes involved in the sequences described in Scheme 2. For instance, one might wonder if intermediate **3** is the result of a nucleophilic substitution on **2** or if it is the result of an oxidative addition with loss of X$^-$.[13] Furthermore, it can be seen that **4** will form readily if the reductive elimination on **3** proceeds easily and spontaneously under the reaction conditions. To achieve a catalytic process, it is also necessary that the tetracarbonyliron thus formed will be readily carbonylated into pentacarbonyliron and further transformed into the active species **1**.



Scheme 1.



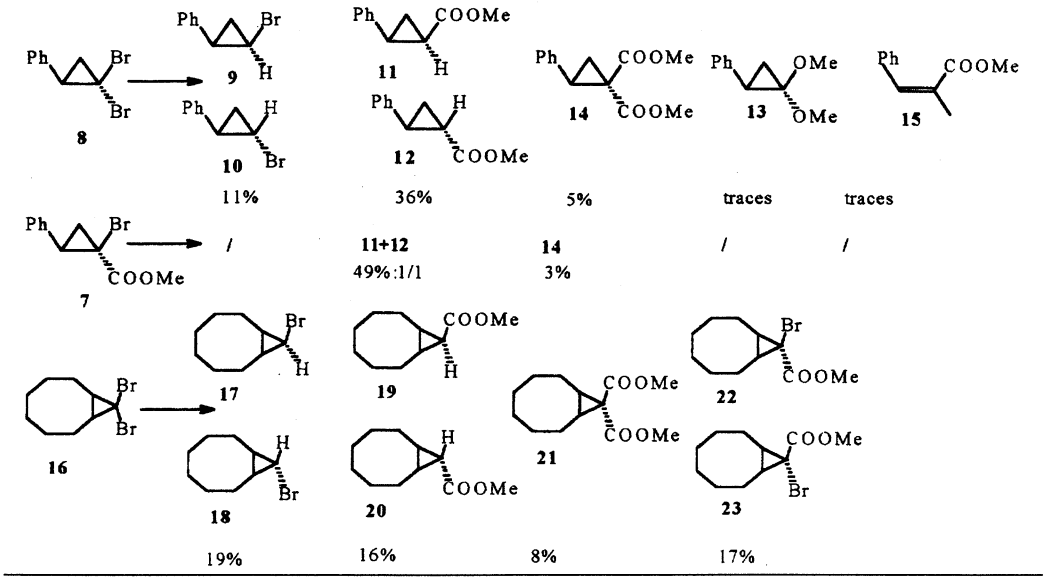
Scheme 2.

Cyclopropyl halides are of particular interest because i) they are versatile synthetic intermediates, ii) they are easily prepared by the addition of dihalogenocarbenes to olefinic compounds,[14] iii) they exhibit a peculiar reactivity of the carbon–halogen bond related with the hybridization of the cyclopropyl carbon–carbon bond.[14]

It is known that nucleophilic substitutions do not occur on cyclopropyl halides.[15] Therefore, the carbonylation of cyclopropyl halides with pentacarbonyliron presents an interesting challenge. But it has been reported that such carbonylation could be easily achieved with [Ni(CO)$_4$][4] under stoichiometric conditions, and catalytically with a combination of cobalt and metal salts under phase transfer conditions.[6]

Following our preliminary paper[16] we now report a full account of our work on the carbonylation of cyclopropyl halides derivatives with (tetracarbonyl)(methoxycarbonylato)ferrate(I−) anion **1**. Our aim was to gain a better understanding of the various intermedi-

Table 1. Carbonylation of Bromocyclopropane Derivatives with $[Fe(CO)_5]$/MeONa (5 molar amounts) in DMF (80 °C, 22 h)



ates involved. We wondered if an α-bromo ester such as **7** would be an intermediate when **1** is used as a carbonylating reagent. This derivative was initially proposed as an intermediate in the carbonylation of cyclopropyl halides with $[Ni(CO)_4]$, but later on rejected because of its lack of reactivity with an excess of $[Ni(CO)_4]$.[4] It was also of interest to know how pentacarbonyliron or the (tetracarbonyl)(methoxycarbonylato)ferrate(I−) (**1**) would interact with cyclopropyl halides which are unlikely to undergo a nucleophilic substitution.[15]

Results

Two sets of cyclopropyl halides were submitted to the carbonylation:

—the *gem*-dihalogenated (bromo or chloro) adducts obtained by dihalogenocarbene addition on styrene under phase transfer catalysis conditions.[14] These nonvolatile and relatively stable adducts, as well as the reduction and carbonylation products formed thereof, can be easily analyzed by ^1H and ^{13}C NMR.[17]

—the *gem*-dihalogenated adducts (chloro and bromo) obtained by dihalogenocarbene addition on cyclooctene under phase transfer conditions.[14]

The reduction of these *gem*-dihalogenated derivatives by zinc in acetic acid provided an entry into the corresponding monohalogenated products.[18] Stereochemically pure 2-phenylcyclopropanecarboxylic acid (**5**)[19] and 1-bromo-2-phenylcyclopropanecarboxylic acid (**6**)[20] were obtained by reaction of butyllithium respectively on the mixture of monobrominated derivatives **9** and **10** or on dibrominated adduct **8**, followed by carboxylation of the corresponding anion. The esters **7** and **11** have been obtained by treatment of the corresponding acids with diazomethane.

In order to understand the following discussion, it is necessary to take into account the results obtained in preliminary assays: Monochlorinated, monobrominated as well as *gem*-dichlorinated cyclopropyl derivatives are completely inert towards catalytic or stoichiometric amounts of pentacarbonyliron, whether one operates under phase transfer conditions (CH_2Cl_2, H_2O, $[Bu_4N]HSO_4$, 24 h) or under homogeneous conditions (in DMF, in absence or in presence of sodium methoxide). However, under phase transfer conditions, 1,1-dibromocyclopropane derivative **8** is converted (20%) into the corresponding monobrominated derivatives as a mixture of stereoisomers **9** and **10**. The same mixture is obtained with poor yield (6%) with a fivefold excess of $[Fe(CO)_5]$ alone, after 22 h of reaction, under homogeneous conditions (DMF, 80 °C). This yield of the transformation of **8** into **9** and **10** can be increased to 80% by using five molar amounts of $[Fe_2(CO)_9]$ or 2 molar amounts of $Na_2[Fe(CO)_4]$ prepared independently. For all these reactions performed in DMF, a final hydrolysis and decomplexation step with Ce^{IV} is required prior the isolation of the products.[21]

When a mixture of $[Fe(CO)_5]$ and MeONa is used to generate complex **1**[9] (the formation of **1** in the reaction medium was ascertained by IR spectroscopy; $\nu_{C=O}$: 2010, 1895, and 1640 cm^{-1}), carbonylation is observed (see Table 1). But, as previously mentioned, a final decomplexation of the reaction mixture with cerium^{IV} nitrate is necessary to isolate the organic products of the reaction and to observe reproducible results.[21] The carbonylation results are reported in Table 1. All the yields reported correspond to isolated and purified products.

It can immediately be seen that the carbonylation reaction proceeds simultaneously with reduction (formation of **11**+**12** from **8**, and of **19** and **20** from **16**). Furthermore, in the case of **8**, we observe the

Table 2. Influence of the Experimental Conditions on the Reductive Carbonylation of **8**

Entry[a]	$[Fe(CO)_5]$ molar amounts	MeONa molar amounts	Time	**8**[c]	**9+10**	**11+12**	**14**	**13**	**15**
1	5	5	22 h	—	11%	36%	5%	Traces	Traces
2	5	5	72 h	—	11%	36%	3%	Traces	Traces
3	5	5	7 d	—	8%	23%	Traces		
4	1	5	22 h	—	27%	37%	6%	Traces	Traces
5	5	1	22 h	—	25%	16%	10%	Traces	Traces
6	1	1	22 h	50%	7%	12%			
7	5	10	22 h	—				15%	
8	0	10	22 h	—				81%	
9[b]	2	1	22 h	—	17%	4%			15%

a) The reactions were carried out at 80 °C in DMF. b) One tenth molar amount of PPh_3 is added to the reaction mixture. The yields reported correspond to isolated and purified products obtained after decomplexation with Ce^{IV}. c) Recovered from the reaction mixture.

formation of significant amounts (11%) of noncarbonylated monohalogeno derivatives **9** and **10**, while the analogous monobromo derivatives **17** and **18** are the major products formed from **16**. With both dibromo derivatives, small amounts of dicarbonylated compounds (—respectively **14** (5%) and **21** (8%)—) are observed.

The major observation is that independently prepared α-bromocarboxylic ester **7** —which is postulated as an intermediate in the carbonylation of **8** (see discussion below)— yields a mixture of **11** and **12** as well as small amounts of **14** (3%) when submitted to the same reaction conditions as **8**. This reactivity had not be observed with $[Ni(CO)_4]$ in the presence of a nucleophile.[4] Furthermore, no cyclopropene derivatives could be isolated from the interaction of **7** with MeONa in the presence of $[Fe(CO)_5]$.[22] Compounds **22** and **23** with the same bromocyclopropanecarboxylic ester structure are formed from **16** with 17% yield and can be isolated from the reaction mixture. This quite surprising stability of **22** and **23** under the reductive carbonylation conditions clearly shows that the overall reaction must be very sensitive to the structural features of the *gem*-dibromocyclopropane starting material. The influence of the experimental conditions on the outcome of the reductive carbonylation of **8** has been studied. The results are reported in Table 2.

—The ratio of carbonylated compounds relatively to reduced products is the best when a fivefold excess of **1** (equimolar amount of $[Fe(CO)_5]$ and MeONa) was reacted for 22 h with **8** (Entry 1). However the yield of both reduced (**9+10**) and carbonylated products (**11+12+14**) can be increased when an excess of MeONa relative to $[Fe(CO)_5]$ is used (Entry 4).

—The lengthening of the reaction time to 72 h (Entry 2) improves neither the overall yield nor the ratio of carbonylated compounds. The yield is even lowered if the reaction time is extended to a week (Entry 3).

—An excess of the $[Fe(CO)_5]$/MeONa reagent is required in order to convert all the starting material (compare Entries 1 and 6).

—Increase of the ratio of MeONa, relatively to $[Fe(CO)_5]$ (Entry 4), results into the formation of larger amounts of monobromides **9** and **10**. When the reverse is done (Entry 5) it is the amount of reduced carbonylated derivatives **11** and **12** which is decreased; under these conditions, slightly more dicarbonylated derivative **14** (10%) is formed.

—An excess of base (Entry 7) renders the reaction mixture messy; compound **13** is the only product which can be isolated. The latter obviously results from the reaction of sodium methoxide alone and does not require the presence of $[Fe(CO)_5]$ (compare Entries 7 and 8). We did not isolated any traces of a cyclopropene derivative. Methyl cinnamate (**15**), which is always observed in small amounts, becomes noticeable when triphenylphosphine is added to the reaction mixture (Entry 9).

More generally, the overall examination of the table shows that it is the excess of complex **1** formed by the interaction of $[Fe(CO)_5]$ and MeONa which is responsible for the formation of esters **11**, **12**, and **14**. However $[Fe(CO)_5]$ alone could be responsible for the formation of small amounts of **9** and **10** (see preliminary assays).

Discussion

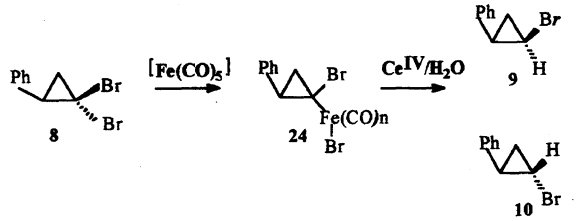
The experimental results show that two geminated bromines are necessary to observe either the reductive carbonylation or the reduction. It is therefore reasonable to assume that one of the carbon–halogen bond activates the second one, or stabilises a reactive intermediate produced by the cleavage of the second carbon–bromine bond. An anionic or a radical intermediate is more likely than a carbocation, which would immediately rearrange.[14,19]

As monohalides **9** and **10** can be formed from the interaction of **8** with $[Fe(CO)_5]$ alone (that is without added methanol), an oxidative addition of the latter is likely to occur on one of the carbon–bromine bonds

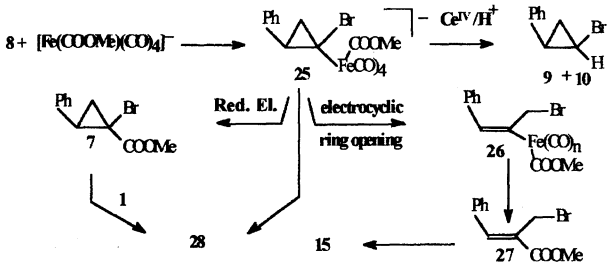
of **8** to yield complex **24**. The latter will be hydrolyzed during the decomplexation procedure (Scheme 3). The need for a decomplexation step before the isolation procedure is an indication that this kind of intermediate complex does not spontaneously decompose under the reaction conditions used.

However complex **25** (formed from the interaction of **1** with **8**)[23] can also be an intermediate for the formation of **9** and **10** (Scheme 4).

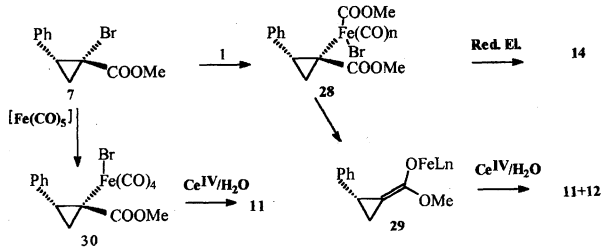
With bromine acting as a leaving group, complex **25** is able to undergo an electrocyclic ring opening, giving rise to **26**, which yields **27** by reductive elimination. The transformation of the latter into **15** in presence of $[Fe(CO)_5]$ is a known process.[23] Traces of compound **15** are observed except when triphenylphosphine is added to the reaction mixture (see Table 2, Entry 9). Therefore it is likely that either **25** or **26** are stabilized by the added ligand. But the major process occurring on **25** is a reductive elimination which yields the bromo ester **7**. As the latter compound could not be isolated under the reaction conditions used, it is possible to consider a direct conversion of **25** into **28**; this would require a reaction of **25** with **1**, followed by a reductive elimination step. However, derivatives **22** and **23** analogous to **7** are formed from **16**, and can be isolated from the reaction mixture (see Table 1). Furthermore, when **7** is prepared independently (bromine cis with the phenyl group) and reacted with **1**, a mixture of **11**, **12**, and **14** is obtained (Scheme 5). The structure of these products provides an indication of the occurrence of an intermediate such as **28** resulting from the interaction of **7** with **1**. Diester **14** results from a reductive elimination occurring on **28**; as a consequence no decomplexation is required in the process. This is not anymore the case when **28** is transformed into the enolic form **29**.[4,24] This process requires a decomplexation step followed by hydrolysis to yield the mixture of **11** and **12**. A single stereoisomer



Scheme 3.



Scheme 4.



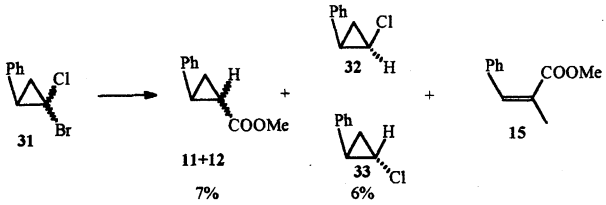
Scheme 5.

11, can also be obtained with retention of configuration via **30** by the interaction of **7** with $[Fe(CO)_5]$, followed by decomplexation and hydrolysis.

As nucleophilic substitutions do not occur on halogenocyclopropanes, the most likely intermediate is a carbanion. It is known from previous work that the latter are able to retain their configuration, at least better than the corresponding radicals.[14,19]

gem-Dichlorocyclopropanes do not undergo reductive carbonylations nor reductions in presence of complex **1**; the carbon–chlorine bond is not reactive enough to undergo the first step of the reaction, which is the oxidative addition process. Chlorobromocyclopropane **31** should nevertheless exhibit some reactivity especially for the carbon–bromine bond. As shown in Scheme 6, the reductive carbonylation (formation of **11** and **12**) and the reduction (formation of **32** and **33**) are indeed observed, as well as some electrocyclic ring opening (formation of **15**).

The conclusions of our investigations are the following: complex $[Fe(COOMe)(CO)_4]^-$ (**1**) formed in situ, by the interaction of pentacarbonyliron with sodium methoxide, in DMF, reductively carbonylates *gem*-dibromo and *gem*-bromochlorocyclopropane derivatives **8**, **16**, and **31**. With 9,9-dibromobicyclo[6.1.0]nonane (**16**) the intermediate bromo esters **22** and **23** can be isolated from the reaction medium, whereas this is not anymore the case with 1,1-dibromo-2-phenylcyclopropane (**8**). However, when methyl 1-bromo-2-phenylcyclopropane-1-carboxylate (**7**), prepared independently, is submitted to the action of **1**, a mixture of methyl 2-phenylcyclopropanecarboxylates **11** and **12** and dimethyl 2-phenylcyclopropane-1,1-dicarboxylate (**14**) are obtained. Consequently a bromo ester is a reactive intermediate of the reductive carbonylation of *gem*-dibromocyclopropanes with $[Fe(COOMe)(CO)_4]^-$ (**1**), contrary to the observations made with the corresponding nickel complexes. As some reactive pathways require decomplexation and



Scheme 6.

hydrolysis steps, reductive carbonylation of *gem*-dihalogenocyclopropanes with $[Fe(COOMe)(CO)_4]^-$ (**1**) under these conditions cannot become a catalytic process.

Experimental

IR spectra were recorded on a Perkin–Elmer 297 spectrometer in chloroform solutions. NMR spectra were obtained on Varian EM360 (60 MHz) and Varian XL200 (200 MHz) spectrometers in $CDCl_3$ solutions with tetramethylsilane as an internal standard. Most of the compounds described in the present work could be matched by their physical data to compounds previously synthesized and characterized as reported in the literature. However, as some NMR data had not been reported, we described the ^1H and ^{13}C NMR spectra of the compounds used in the present work.

***gem*-Dibromocyclopropanes:** **8**:[25] IR 3060—3015, 1620, 1510, 1110, 1080, 1040 cm^{-1}; ^1H NMR δ=1.9 (dd, 1H, J=8.4, 7.8 Hz), 2.1 (dd, 1H, J=10.6, 7.8 Hz), 2.9 (t, 1H, J=9 Hz), 7.0—7.42 (5H, m); ^{13}C NMR δ=26.9, 28.3, 35.6, 127.3, 128.0, 128.6, 135.6.

16:[26] IR 2900, 2850, 1460, 1440, 760 cm^{-1}; ^1H NMR δ=1—1.25 (1H, m), 1.25—1.7 (5H, m), 1.95—2.10 (1H, m); ^{13}C NMR δ=25.4, 26.4, 27.9, 33.3, 36.9.

***gem*-Bromochlorocyclopropanes:** **30a**:[27] IR 3090, 3060, 3030, 1610, 1500, 1225, 1110, 1080, 1045, 1025, 945, 930, 770, 740, 715, 695 cm^{-1}; ^1H NMR δ=1.9 (dd, 1H, J=8.4, 7.8 Hz), 2.0 (dd, 1H, J=10.6, 7.8 Hz), 2.8 (dd, 1H, J=10.6, 8.4 Hz), 6.8—7.0 (m, 5H); ^{13}C NMR δ=26.4, 36.0, 44.0, 127.5, 128.2, 128.8, 134.5.

30b: ^1H NMR δ=1.9 (dd, 1H, J=8.4, 7.8 Hz), 2.0 (dd, 1H, J=10.6, 7.8 Hz), 3.0 (1H, dd, J=10.6, 8.4 Hz), 6.8—7.0 (m, 5H); ^{13}C NMR δ=26.4, 35.4, 47.0, 127.5, 128.2, 128.8, 135.8.

Monohalogenocyclopropanes: **9**, **10**[28] *syn*/*anti*: 25/75. **9**: IR (**9**+**10**) 3090, 3070, 3030, 1610, 755, 685 cm^{-1}; ^1H NMR δ=1.38 (ddd, 1H, J=9.6, 7.8, 4.7 Hz), 1.7 (ddd, 1H, J=9.6, 7.6, 7.5 Hz), 2.4 (ddd, 1H, J=7.8, 7.8, 7.6 Hz), 3.4 (ddd, 1H, J=7.8, 7.5, 4.7 Hz), 7.0—7.4 (m, 5H); ^{13}C NMR δ=18.8, 21.5, 26.7, 125.8, 126.3, 128.3, 139.5.

10: ^1H NMR δ=1.4 (ddd, 1H, J=9.6, 5.0, 4.6 Hz), 1.57 (ddd, 1H, J=8.4, 6.5, 4.6 Hz), 2.3 (ddd, 1H, J=9.6, 6.5, 4.6 Hz), 3.3 (ddd, 1H, J=8.4, 5.0, 4.6 Hz), 7.2—7.4 (m, 5H); ^{13}C NMR δ=14.2, 22.1, 24.0, 126.8, 127.9, 129.2, 137.7.

18, 19:[29] **18**: IR 2930, 2860, 1470, 1165, cm^{-1}; ^1H NMR δ=0.8—0.99 (m, 2H), 1.23—1.90 (m, 12H), 2.35 (t, 1H, J=3.5 Hz); ^{13}C NMR δ=24.2, 25.6, 26.3, 26.9, 28.9.

19: ^1H NMR δ=0.8—0.99 (m, 2H), 1.23—1.90 (m, 12H), 3.22 (t, 1H, J=7.5, 7.5 Hz); ^{13}C NMR δ=19.1, 24.3, 25.6, 26.3, 26.7, 28.8, 30.6.

Reference Compounds: **5**:[30] IR 3500—2500, 2910, 1795, 1620, 1290, 1220, 955 cm^{-1}; ^1H NMR δ=1.0—2.25 (m, 3H), 2.25—2.75 (m, 1H), 7.0—7.3 (m, 5H); ^{13}C NMR δ=9.6, 20.3, 24.1, 125.2, 126.6, 128.2, 135.9, 170.2.

6:[20] IR 3500—2500, 1717, 1620, 1510, 1460, 1440, 1310 cm^{-1}; ^1H NMR δ=1.7 (dd, 1H, J=4.8, 4.8 Hz), 2.2 (dd, 1H, J=5.2, 4.8 Hz), 3.07 (dd, 1H, J=5.2, 5.2 Hz), 7.0—7.2 (m, 5H), 8.7 (s, 1H); ^{13}C NMR δ=23.1, 30.6, 38.2, 127.5, 128.2, 128.8, 133.6, 173.2.

12:[31] IR 3100, 3075, 3040, 3020, 2960, 1740, 1610, 1290, 1200, 925, 915, 845 cm^{-1}; ^1H NMR δ=1.3 (ddd, 1H, J=8.4, 6.5, 4.6 Hz), 1.6 (ddd, 1H, J=9.3, 5.0, 4.6 Hz), 1.9 (ddd, 1H, J=8.4, 5.0, 4.6 Hz), 2.52 (ddd, 1H, J=9.3, 6.5, 4.6 Hz), 3.7 (s, 3H), 7—7.3 (m, 5H); ^{13}C NMR δ=11.4, 21.7, 25.6, 51.3, 126.7, 127.9, 129.2, 136.4, 171.4.

7:[14,19] IR 3105, 3080, 3050, 3070, 1740, 1610, 1225, 1205, 1185, 1125, 1090, 1075, 925, 800 cm^{-1}; ^1H NMR δ=1.8 (dd, 1H, J=4.8, 4.8 Hz), 2.38 (dd, 1H, J=5.2, 4.8 Hz), 3.1 (dd, 1H, J=5.2, 5.2 Hz), 3.45 (s, 3H), 7.0—7.35 (m, 5H); ^{13}C NMR δ=22.1, 31.3, 36.7, 52.8, 127.4, 128.1, 128.2, 128.6, 134.3, 167.3; MS 254/256 (M^+ 32%), 223/225 ($M^+ - OCH_3$ 2%), 116 (100%).

Carbonylation Reactions: All the reactions were performed in a Schlenck tube. Methanol or sodium methoxyde (0 to 10 molar amounts) are added to 20 ml of freshly dried DMF under nitrogen atmosphere. After addition of freshly distillated $[Fe(CO)_5]$ (0 to 5 molar amounts), the reaction medium is stirred for 30 min at room temperature. The IR spectrum of complex **1** thus formed is identical to the one reported in the literature.[9] One molar amount of the halogenocyclopropane is then added and the temperature is raised to 75 °C for 24 h to one week. At the end of the reaction, the crude reaction mixture is decomplexed and the different compounds are isolated by column chromatography on silica gel 70—230 mesh. Solvents must be carefully dried. Decomplexation, which is essential in order to observe reproducible yields, is done as follows: for 25 mmoles of $[Fe(CO)_5]$ used, 25 g of ammoniacal cerium^{IV} nitrate dissolved in 50 ml of water are slowly added to the stirred reaction mixture. The reaction is exothermic and CO is evolved. After 12 h, the aqueous phase is acidified (pH 1) and extracted with ether (5×50 mol).

11,12:[31] **11**: ^1H NMR δ=1.22 (m, 1H), 1.65 (m, 1H), 2 (m, 1H), 2.5 (m, 1H), 3.7 (s, 3H), 7.0—7.3 (m, 5H); ^{13}C NMR δ=17.0, 23.9, 26.3, 51.8, 126.2, 126.5, 128.5, 140.0, 173.8.

12 has been previously described (see above).

13:[32] IR 3100, 3070, 3015, 2970, 2950, 2845, 1720, 1640, 1610, 1285, 1170, 1050, 880, 840 cm^{-1}; ^1H NMR δ=1.27 (dd, 1H, J=8.0, 5.0 Hz), 1.4 (dd, 1H, J=10.0, 5.0 Hz), 2.4 (ddd, 1H, J=10.0, 8.0 Hz), 3.2 (s, 3H), 3.45 (s, 3H), 7.15—7.4 (m, 5H); ^{13}C NMR δ=19.1, 30.6, 53.4, 53.7, 93.4, 126.0, 127.6, 128.1, 137.3. Found: C, 67.38; H, 7.74; O, 17.9%. Calcd for $C_{11}H_{14}O_2$: C, 67.42; H, 7.87; O, 18.00%.

14:[33] IR 3500—2500, 1690, 1640, 1280 cm^{-1}; ^1H NMR δ=1.75 (dd, 1H, J=8.0, 5.0 Hz), 2.25 (dd, 1H, J=9.0, 5.0 Hz), 2.31 (m, 3H), 3.4 (s, 3H), 3.8 (s, 3H), 7.15—7.45 (m, 5H); ^{13}C NMR δ=19.1, 32.6, 37.2, 52.2, 128.2, 128.4, 128.5, 134.6, 167.0, 170.2.

15: IR 3050, 3040, 3005, 2980, 1715, 1265, 1120 cm^{-1}; ^1H NMR δ=2.13 (d, 3H, J=1.6 Hz), 3.85 (s, 3H), 7.1—7.45 (m, 5H), 7.7 (s, 1H); ^{13}C NMR δ=14.1, 51.9, 128.3, 128.4, 129.7, 135.9, 138.9, 169.0.

19+20:[34] **19**: IR 3020, 2950, 2880, 1745, 1645, 1270, 1205, 1175 cm^{-1}; ^1H NMR δ=1.0—2.0 (m, 15H), 3.45 (s, 3H); ^{13}C NMR δ=20.8, 24.8, 26.4, 29.2, 51.1, 172.9.

20: ^1H NMR δ=0.90—1.10 (m, 3H), 1.15—1.85 (m, 9H), 1.9—2.1 (m, 2H), 3.5 (s, 3H); ^{13}C NMR δ=25.7, 25.9, 26.5, 27.5, 29.1, 51.5, 173.9.

21:[35] IR 3020, 2950, 2880, 1740, 1270 cm^{-1}; ^1H NMR δ=1.2—2.0 (m, 8H), 3.55 (s, 3H), 3.60 (s, 3H); ^{13}C NMR δ=23.5, 26.3, 31.3, 36.3, 38.7, 52.1, 52.6, 167.7, 171.5.

22: IR (**22**+**23**) 3020, 2950, 1740, 1450 cm^{-1}; ^1H NMR

δ=1.35—2.20 (m, 7H), 3.5 (s, 3H); ^{13}C NMR δ=25.4, 27.2, 27.5, 30.5, 51.5, 176.0.

23: ^{13}C NMR δ=25.7, 26.2, 34.4, 38.6, 51.5, 173.4.

22+23: Found: C, 50.42; H, 6.50; O, 12.7%. Calcd for $C_{11}H_{17}O_2$ Br: C, 50.59; H, 6.56; O. 12.5%.

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