133. Direct Clay-Catalyzed *Friedel-Crafts* Arylation and Chlorination of the Hydrocarbon Adamantane

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Multiple chlorinations and arylations at the tertiary positions of adamantane are promoted by $FeCl_3$-doped K10 montmorillonite in CCl_4 or in aromatic solvents. The process, remarkably easy to implement, can be tailored to selective formation of monosubstituted 1-adamantyl derivatives or 1,3-disubstituted adamantanes. The process achieves alkylation at the *meta-* and *para-*positions of toluene leading to a purely statistical distribution and displays no substrate specificity in competition experiments between toluene and benzene.

1. Introduction. – *'Paraffins are synonymous with chemical inertness':* much recent research has attempted to circumvent this proposition, with the dual ambition at advancement of chemical knowledge and at functionalization of hydrocarbons from fossil fuels [1]. In these applications, heterogeneous catalysts have up to now suffered from poor selectivity and have required drastic conditions [2]. Hence, the option to use homogeneous catalysis which, in the hands of a few groups, has led to some outstanding results. Organometallic complexes involved have been those of Pt [3], Ir [4], Re [5], Lu and Y [6], Pd [7], and Rh [8]. Yet another tactic has been to build systems mimicking oxygenation by cytochrome P-450 [9].

Our goals here and elsewhere [10] [11] are to devise new synthetic methods that are highly selective under mild conditions. We attempted to overcome the reluctance of saturated hydrocarbons towards substitution by means of clay-supported Fe(III), and we selected adamantane (**1**) as the trial substrate.

We elected to use the acidic K10 clay in association with the Fe(III) cation from consideration of previous results: Fe(III) salts, deposited on or doping this support, have given rise to an extraordinarily broad spectrum of chemical reactivity, manifestly linked to dehydrating conditions [11–13].

2. Results and Discussion. – First, the K10/Fe(III) catalyst was activated by dehydration, using $FeCl_3 \cdot 6H_2O$ mixed with K10 clay, dessication being carried out by azeotropic distillation with CCl_4 in a reverse *Dean-Stark* trap. Vigourous evolution of HCl followed the end of dehydration. *Scheme 1* provides a plausible description of the sequence of events.

When adamantane (**1**) was admixed to the catalyst and submitted to the above conditions of activation for 40 h, we observed formation *(Scheme 2)* of 1-chloro- and 1,3-dichloroadamantane (**2** and **3**, resp.) in appreciable amounts (see *Exper. Part*). Relative proportions depended on the amount of catalyst *(Table 1)*. Such results suggest the intermediacy of a tertiary 1-adamantyl cation as postulated in *Scheme 3*.

Scheme 1[a]

$$\mathrm{MMT}^{p-}\mathrm{H}_p^+\cdot n\mathrm{H_2O} \xrightarrow{\mathrm{b)}} \mathrm{MMT}^{p-}\mathrm{H}_p^+ + n\mathrm{H_2O}\nearrow \qquad (1)$$

$$\mathrm{FeCl_3\cdot 6H_2O} \xrightarrow{\mathrm{b)}} \mathrm{FeCl_3} + \mathrm{6H_2O}\nearrow \qquad (2)$$

$$\mathrm{MMT}^{p-}\mathrm{H}_p^+ + \mathrm{FeCl_3} \longrightarrow \mathrm{MMT}^{p-}\mathrm{H}_{p-i}^+ + (\mathrm{FeCl}_{3-i})^{i+} + i\mathrm{HCl}\nearrow \qquad (3)$$

[a] MMT^{p-}: montmorillonite polyanionic aluminosilicate sheet.
[b] Azeotropic distillation.

Scheme 2

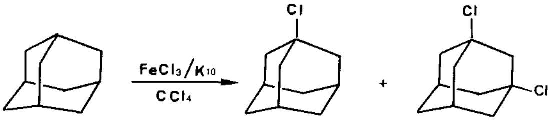

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Table 1. *Chlorination of Adamantane* (**1**) *by* CCl_4 *in the Presence of the K10/*$FeCl_3$ *Catalyst*

Run[a]	Unreacted **1** [%]	Monochloride **2** [%]	Dichloride **3** [%]
1	91.5	8.5	–
2	32.9	59.0	8.1
3	70.9	29.1	traces
4	49.0	51.0	traces
5	1.3	32.4	66.3
6	0.3	18.4	81.3
7	7.0	54.2	38.8
8	0.0	2.0	98.0

[a] Conditions: 2 g of **1** were submitted to reaction with: 6 g of K10 *(Run 1)*; 10 g of $FeCl_3$ *(Run 2)*; 5 g *(Run 3)*, 10 g *(Run 4)*, 20 g *(Run 5)*, and 25 g *(Run 6)* of Fe(III)-doped K10; 6 g of K10 together with 4 g of $FeCl_3$ *(Run 7)*; 12 g of K10 together with 8 g of $FeCl_3$ *(Run 8)*.

Scheme 3[a]

$$(\mathrm{FeCl}_{3-i})^{i+} + \mathrm{R{-}H} \longrightarrow (\mathrm{FeCl}_{3-i}\mathrm{H})^{(i-1)+} + \mathrm{R}^+ \qquad (4)$$

$$\mathrm{R}^+ + \mathrm{CCl_4} \longrightarrow \mathrm{R{-}Cl} + \mathrm{CCl}_3^+ \qquad (5)$$

$$\mathrm{CCl}_3^+ + (\mathrm{FeCl}_{3-i}\mathrm{H})^{(i-1)+} \longrightarrow \mathrm{CHCl_3} + (\mathrm{FeCl}_{3-i})^{i+} \qquad (6)$$

[a] R = adamantyl.

Consistent with this working hypothesis are the necessity of the use of CCl_4 as solvent (under similar conditions, no chlorination was observed in $CHCl_3$) and the production of $CHCl_3$ as the reaction proceeds. Moreover, *Mössbauer* analysis of the inorganic residue at the end of the process showed that all the iron is still in the oxydation state III. Analogy with earlier literature results also suggests an intermediate tertiary adamantyl carbocation. *Stetter* and coworkers obtained a mixture of 13% of monochloro- and 71% of dichloroadamantane when they submitted adamantane to reaction with $AlCl_3/CCl_4$ at room temperature [14] [15]. Aminoadamantanes have resulted likewise from use of $NCl_3/AlCl_3/CH_2Cl_2$ [16]. Such reactions are likely to proceed from the tertiary carbocation, generated when a *Lewis* acid (such as $AlCl_3$) abstracts a hydride ion from the hydrocarbon [17].

Generation of a 1-adamantyl cation in the presence of dehydrated Fe(III) deposited on K10 clay is thus quite plausible. An obvious test of this hypothesis was to engage adamantane together with the same solid catalyst in a *Friedel-Crafts* reaction [18], an arylation for example (our laboratory has continued interest in the molecular dynamics of such globular molecules [19], of which NMR relaxation rates can be measured (see [20])). This C-Ar condensation was easily performed by a slight adaptation of the chlorination procedure: dehydration of a mixture of the $K10/FeCl_3$ reagent and adamantane dispersed in benzene resulted indeed in fair to good yields of 1-phenyl- and 1,3-diphenyladamantane (**4** and **5**, resp.: *Scheme 4*). This result is noteworthy because the hydrocarbon **1**, not an already substituted derivative such as an acyl chloride or a halide [21] [22], gives directly the carbocation which is then quenched by the aromatic solvent. As observed in the chlorination reaction, the proportions of the reagent control the di/monosubstitution ratio *(Table 2)*.

Scheme 4

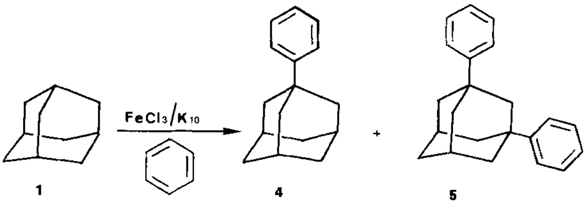


Table 2. *Distribution of the Products Formed from Adamantane* (**1**) *by Reaction with Benzene, $FeCl_3$, and K10*

Run[a])	**1** [mmol]	K10 [g]	$FeCl_3$ [mmol]	*t* [h]	**4** [%][b])	**5** [%][b])
1	7.3	6	0	24	5	0
2[c])	7.3	0	15	24	10	0
3[c])	7.3	6	15	24	52	7
4[c])	14.6	24	90	16	56	25
5	14.6	24	90	16	48	47
6	14.6	24	90	5	51	47
7[a])	14.6	24	90	5	65	5
8[d])	14.6	40	146	5	17	83

[a]) 200 ml of benzene were used, except in *Run 7* where the volume was 800 ml.

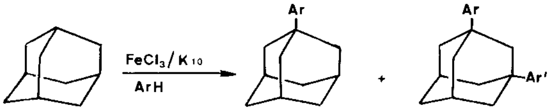
[b]) % of conversion by GC analysis; in all cases, **1** was the remaining compound.

[c]) With $FeCl_3 \cdot 6H_2O$, the optimum yield was obtained in *Run 4*. All further experiments were carried out using anhydrous $FeCl_3$.

[d]) Traces of the dimer of **4**.

This is, to our knowledge, *the first reported example of direct arylation of adamantane*. Its simplicity of implementation and its ease of workup are extremely advantageous with respect to previous literature methods [22–29]. However, while the method could be

Scheme 5



1	**6** Ar=3–$CH_3C_6H_4$	**8** Ar=Ar'=3–$CH_3C_6H_4$
	7 Ar=4–$CH_3C_6H_4$	**9** Ar=4–$CH_3C_6H_4$, Ar'=3–$CH_3C_6H_4$
		10 Ar=Ar'=4–$CH_3C_6H_4$
	11 Ar=3,5–$(CH_3)_2C_6H_3$	**12** Ar=Ar'=3,5–$(CH_3)_2C_6H_3$
	13 Ar=3,4–$(CH_3)_2C_6H_3$	
	14 Ar=4–ClC_6H_4	**16** Ar=Ar'=4–ClC_6H_4
	15 Ar=3–ClC_6H_4	**17** Ar=Ar'=3–ClC_6H_4
		18 Ar=4–ClC_6H_4, Ar'=3–ClC_6H_4
		19 Ar=Ar'=4–BrC_6H_4
		20 Ar=3–BrC_6H_4, Ar'=4–BrC_6H_4
		21 Ar=Ar'=3–BrC_6H_4
		22 Ar=C_6H_5, Ar'=3–$CH_3C_6H_4$
		23 Ar=C_6H_5, Ar'=4–$CH_3C_6H_2$

Table 3. *Distribution of Products in the Reaction of Adamantane* (**1**) *with Various Aromatic Compounds, Following the Typical Procedure.* See *Scheme 5.*

Ar(Ar')	Monosubstituted	Disubstituted
$CH_3C_6H_4$	53% of **6** + **7**	16.9% of **8** + **9** + **10**
3,5-$(CH_3)_2C_6H_3$	36% of **11**	2.9% of **12**
3,4-$(CH_3)_2C_6H_3$	17% of **13**	–
ClC_6H_4	13.5% of **14** + **15**	35.4% of **16** + **17** + **18**
BrC_6H_4	–	56.8% of **19** + **20** + **21**

extended to other aromatic compounds (*Table 3*), it is unfortunately not altogether general: aromatic substrates bearing highly electron-donating or -withdrawing substituents either are unreactive or react by various other pathways.

When toluene was the aromatic-solvent partner, five products were obtained: the monosubstituted (*meta*- and *para*-tolyl)adamantanes **6** and **7**, respectively, and the disubstituted di(*meta*-tolyl)-, (*meta*-tolyl)(*para*-tolyl)-, and di(*para*-tolyl)adamantanes **8**, **9**, and **10**, respectively. Equiprobability of aromatic electrophilic substitution at the *meta* and *para* positions was conspicuous from the statistical product ratio **6**/**7** of almost exactly 2 (34.6% and 18%, resp.). The disubstituted products were likewise distributed according to statistics, with percentages (13% of **8**, 13.3% of **9**, and 3.4% of **10**) matching exactly the calculated values of 12.9, 13.4, and 3.5%, respectively.

In most *Friedel-Crafts* reactions, competition between toluene and benzene favors the former: $k_{\text{toluene}}/k_{\text{benzene}} = 1.60–15.6$, depending on the system [30]. A benzene/toluene competition (benzene/toluene 22.8:27.2 (v/v)) also gave a purely statistical distribution of products (*Table 4*), indicative of equivalent reactivities of benzene and toluene towards the bulky adamantyl moiety. *Ortho* attack was not observed with toluene, presumably due to steric hindrance. Benzene and toluene have six and three (two *meta* and one *para*) equiprobable sites of attack, respectively; hence ratios **4**/**6**/**7** of 6:2:1 are expected, and values of 5.8:1.9:1 were indeed found (*Table 4*). Interpretation of the *ortho*/*meta*/*para*

Table 4. *Distribution of the Products Formed from Adamantane* (**1**) *with an Equimolar Mixture of Benzene and Toluene as Solvent*

Hydrocarbon	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**22**	**23**
Found [%]	44.1	11.8	14.7	7.6	1.6	1.7	0.5	7.9	4.4
Calc.[a]) [%]	45.6	12.3	15.2	(7.6)[b])	1.3	1.4	0.4	8.2	4.2

[a]) On the basis of simple statistics.

[b]) Assumed.

selectivity in aromatic *Friedel-Crafts* reactions as well as of substrate selectivity such as $k_{\text{toluene}}/k_{\text{benzene}}$ is a debated topic.

Could we be dealing here with a radical rather than an aromatic electrophilic substitution mechanism? The observed lack of selectivity is not sufficient to argue in favor of a radical pathway (see [18] for a fine recent discussion). Furthermore, if the K10/$FeCl_3$-catalyzed reaction went through radical intermediates, one would expect formation of 2-aryl-substituted adamantanes [31]. None could be found.

Clearly, an interesting mechanism is operative here; presumably, a carbocation is generated from adamantane in a 'hot' enough state that it will attack indiscriminately *any* aromatic neighboring molecule, at *any* position except at the sterically excluded *ortho* position.

The most noteworthy features of these experiments are the very high reactivities achieved, such that adamantane can be directly arylated. This bypasses the usual need for a 1-substituted adamantyl derivative as precursor to the 1-adamantyl carbocation [21].

Experimental Part

1. General. Melting points (m.p.): uncorrected; *Laboratory Devices, Melt-Temp apparatus.* IR spectra: *Perkin-Elmer-1320-IR spectrophotometer.* ^{13}C- and ^{1}H-NMR spectra: *Bruker AM 300 WB.* Mass spectra: *Micromass 7070 F.*

All IR, ^{1}H-NMR and MS of previously described compounds are in agreement with the proposed structure.

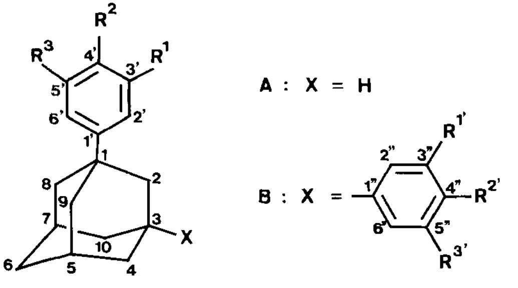
2. Chlorination of Adamantane (**1**). To a mixture of a few g's (*Table 1*) of K10 bentonite (*Süd Chemie*), either doped with Fe(III) [32] or commixed with $FeCl_3 \cdot 6H_2O$, and 2 g of **1**, 150 ml of CCl_4 (stored on $KHCO_3$) are added. The reaction is run at reflux for 40 h under azeotropic dehydration conditions using a water estimator (reverse Dean-Stark). The inorg. materials are filtered off. Solvent evaporation yields **1**–**3**, separated by column chromatography and identified by their consenting IR, ^{1}H- and ^{13}C-NMR and m.p. Typical runs in the presence of clay-supported reagents afford 2 to 2.8 g of crude isolated materials. The relative amounts are measured by capillary GC.

3. Reaction between Adamantane (**1**) *and Aromatic Compounds* (see *Table 3*). *3.1. Typical Procedure.* A soln. of **1** (15 mmol, 2.04 g) in the arylating reagent (200 ml), together with 50 ml of cyclohexane (except for the benzene and the toluene cases, where no cyclohexane was used), 24 g of K10 clay, and 14.6 g (90 mmol) of anh. $FeCl_3$, is refluxed for 5 h through a *Dean-Stark* trap under vigourous stirring. The clay material is filtered off, and the filtrate is washed with H_2O and dried. The components of the residual oil are separated by chromatography on a silica-gel column and the compounds obtained recrystallised.

3.2. Arylations with Benzene. Chromatography on silica gel using hexane/CH_2Cl_2 9:1. Yields; see *Table 2*. *1-Phenyltricyclo[3.3.1.1^{3,7}]decane* (**4**): m.p. 80° (from MeOH). Anal. calc. for $C_{16}H_{20}$ (212.33): C 90.51, H 9.49; found: C 90.10, H 9.39.

1,3-Diphenyltricyclo[3.3.1.1^{3,7}]decane (**5**): m.p. 98–9° (from MeOH). Anal. calc. for $C_{22}H_{24}$ (288.43): C 91.61, H 8.39; found: C 91.94, H 8.47.

Table 5a. *^{13}C-NMR Chemical Shifts ($CDCl_3$) of Products of Monoarylation of Adamantane.* Experimental (top) and calculated (bottom) values in ppm relative to TMS.



No	Compounds			C-Atoms[a]										
	R^1	R^2	R^3	C(1)	C(2)	C(3)	C(4)	C(1′)	C(2′)	C(3′)	C(4′)	C(5′)	C(6′)	Me
4	H	H	H	36.24	43.27	29.08	36.92	131.30	124.83	128.12	125.51	124.83	128.12	
6	Me	H	H	36.09	43.25	29.06	36.90	151.32	125.65	137.40	126.29	128.03	121.88	21.72
								151.30	125.60	137.40	126.30	128.10	121.90	
7	H	Me	H	35.85	43.31	29.06	36.90	148.46	124.72	128.83	134.85	124.72	128.83	20.87
								148.40	124.80	128.90	134.80	124.80	128.90	
11	Me	H	Me	35.85	43.20	28.99	36.83	151.31	122.59	137.24	127.09	122.59	137.24	21.43
								151.30	122.73	137.42	127.11	122.73	137.42	
13	Me	Me	H	35.69	43.25	28.99	36.82	148.95	126.11	135.87	133.46	129.33	122.09	19.90
														19.05
								148.40	125.63	138.22	135.61	128.98	121.93	
14	H	Cl	H	36.07	43.22	28.97	36.78	149.92	126.40	128.20	131.25	126.40	128.20	
								149.40	126.10	128.50	131.70	126.10	128.50	
15	Cl	H	H	36.46	43.14	28.97	36.78	153.59	125.50	134.20	125.69	129.37	123.13	
								152.60	125.20	134.30	125.90	129.40	122.90	

[a] Numbering according to *Formula* **A**.

Table 5b. *^{13}C-NMR Chemical Shifts ($CDCl_3$) of Products of Diarylation of Adamantane.* Experimental (top) and calculated (bottom) values in ppm relative to TMS.

No	Compounds						C-Atoms[a]																			
	R^1	R^2	R^3	$R^{1'}$	$R^{2'}$	$R^{3'}$	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(8)	C(1′)	C(2′)	C(3′)	C(4′)	C(5′)	C(6′)	C(1″)	C(2″)	C(3″)	C(4″)	C(5″)	C(6″)	Me
5	H	H	H	H	H	H	37.32	49.01	37.32	42.35	29.67	35.87	42.35	150.66	124.94	128.24	125.77	128.24	124.94	150.66	124.94	128.24	125.77	128.24	124.94	
8	Me	H	H	Me	H	H	37.18	49.09	37.18	42.37	29.66	36.00	42.37	150.66	125.71	137.50	126.48	128.10	121.95	150.66	121.95	128.10	126.48	137.50	125.71	21.70
							36.40	48.26	36.40	41.91	29.37	35.56	41.91													
9	H	Me	H	Me	H	H	36.93	49.09	37.18	42.37	29.66	36.00	42.40	147.79	124.79	128.89	135.08	128.89	124.79	150.66	121.95	128.10	126.48	137.50	125.71	20.86
																										21.70
							36.16	48.32	36.40	41.91	29.37	35.56	41.97													
10	H	Me	H	H	Me	H	36.93	49.09	36.93	42.40	29.66	36.00	42.40	147.79	124.79	128.89	135.08	128.89	124.79	147.79	124.79	128.89	135.08	128.89	124.79	20.86
							36.16	48.38	36.16	41.97	29.37	35.56	41.97													
12	Me	H	Me	Me	H	Me	37.04	49.14	37.04	42.35	29.64	35.99	42.35	150.72	122.68	137.37	127.28	137.37	122.68	150.72	122.68	137.37	127.28	127.37	122.68	21.43
							36.16	48.16	36.16	41.79	29.23	35.42	41.79													
16	H	Cl	H	H	Cl	H	37.04	48.85	37.04	42.11	29.42	35.65	42.11	148.81	126.36	128.29	131.51	128.29	126.36	148.81	126.36	128.29	131.51	128.29	126.36	
							36.29	48.20	36.29	41.76	29.19	35.32	41.76													
17	Cl	H	H	Cl	H	H	37.43	48.74	37.43	42.03	29.42	35.65	42.03	152.50	125.44	134.26	125.96	129.48	123.11	152.50	123.11	129.48	125.96	134.26	125.44	
							36.68	48.04	36.68	41.68	29.19	35.32	41.68													
18	H	Cl	H	Cl	H	H	37.04	48.79	37.43	42.03	29.42	35.65	42.11	148.88	126.36	128.29	131.51	128.29	126.36	152.57	123.11	129.48	125.96	134.26	125.44	
							36.29	48.12	36.68	41.68	29.19	35.32	41.76													
19	H	Br	H	H	Br	H	37.03	48.62	37.03	41.95	29.37	35.53	41.95	149.28	126.67	131.16	119.53	131.16	126.67	149.28	126.67	131.16	119.53	131.16	126.67	
														149.70	126.53	131.52	120.01	131.52	126.53	149.70	126.53	131.52	120.01	131.52	126.53	
20	Br	H	H	H	Br	H	37.36	48.62	37.03	41.95	29.31	35.53	41.95	152.75	128.27	122.57	128.82	129.70	123.46	149.23	126.67	131.16	119.53	131.16	126.67	
								48.62		41.95	29.31	35.53	41.95	153.00	128.23	122.62	128.91	129.82	123.23	149.70	126.53	131.52	120.01	131.52	126.53	
21	Br	H	H	Br	H	H	37.36	48.62	37.36	41.95	29.31	35.53	41.95	152.68	128.27	122.57	128.82	129.70	123.46	152.68	128.27	122.57	128.82	129.70	123.46	
														153.00	128.23	122.62	128.91	129.82	123.23	153.00	128.23	122.62	128.91	129.82	123.23	

[a] All diaryladamantanes are numbered in the same way, according to formula **B** with the Ar substituent (primed C-atoms; R^1, R^2, R^3; see **A**) at C(1) and the Ar′ substituent (doubly primed C-atoms; $R^{1'}$, $R^{2'}$, $R^{3'}$) at C(3) of the adamantane skeleton (see *Scheme 5*). Systematic numbering in the *Exper. Part*.

3.3. Arylation with Toluene (Standard Conditions). Chromatography on silica gel using hexane. *1-(m-Tolyl)-* and *1-(p-tolyl)tricyclo[3.3.1.1^{3,7}]decane* (**6** + **7**): 1.8 g (53%), m.p. 56–7° (from MeOH). Anal. calc. for $C_{17}H_{22}$ (226.36): C 90.20, H 9.80; found: C 90.67, H 10.09.

1,3-Di(m-tolyl)-, 1-(m-tolyl)-3-(p-tolyl)-, and *1,3-di(p-tolyl)tricyclo[3.3.1.1^{3,7}]decane* (**8** + **9** + **10**): 0.8 g (16.9%), m.p. 65–6° (from MeOH). Anal. calc. for $C_{24}H_{28}$ (316.49): C 91.08, H 8.92; found: C 90.90, H 9.08.

3.4. Isomer Distribution in the Products from Toluene and **1**. Adamantane (**1**) and toluene were reacted as described above, except that reflux was maintained for 16 h. Under these conditions, the overall conversion of **1** was 82.3%. The yield of each component was determined by gas chromatography. Statistics predictions are easily derived; *e.g.*: (% **9**) = 2 × {(% **6**)/[(% **6**) + (% **7**)]} × {(% **7**)/[(% **6**) + (% **7**)]} × [(% **8**) + (% **9**) + (% **10**)].

3.5. Arylation with meta-Xylene. Chromatography on silica gel using hexane. *1-(3,5-Xylyl)tricyclo[3.3.1.1^{3,7}]decane* (**11**): 1.3 g (36%), m.p. 151–2° (from MeOH/$CHCl_3$). Anal. calc. for $C_{18}H_{24}$ (240.39): C 89.94, H 10.06; found: C 89.82, H 10.36.

1,3-Di(3,5-xylyl)tricyclo[3.3.1.1^{3,7}]decane (**12**): 0.15 g (2.9%), m.p. 228–9° (from MeOH). Anal. calc. for $C_{26}H_{32}$ (344.54): C 90.64, H 9.36; found: C 90.16, H 9.45.

3.6. Arylation with ortho-Xylene. Chromatography on silica gel using pentane/CH_2Cl_2 9:1. *1-(3,4-Xylyl)tricyclo[3.3.1.1^{3,7}]decane* (**13**): 0.6 g (17%), m.p. 108–9° (from MeOH). Anal. calc. for $C_{18}H_{24}$ (240.39): C 89.94, H 10.06; found: C 89.65, H 10.27.

3.7. Arylation with Chlorobenzene. Chromatography on silica gel with pentane. *1-(4-Chlorophenyl)-* and *1-(3-chlorophenyl)tricyclo[3.3.1.1^{3,7}]decane* (**14** + **15**): 0.5 g (13.5%), m.p. 84–5° (from MeOH). Anal. calc. for $C_{16}H_{19}Cl$ (246.78): C 78.87, H 7.76; found: C 77.8, H 7.93.

1,3-Bis(4-chlorophenyl)-, 1,3-bis(3-chlorophenyl)-, and *1-(3-chlorophenyl)-3-(4-chlorophenyl)tricyclo[3.3.1.1^{3,7}]decane* (**16** + **17** + **18**): 1.9 g (35.4%), oil. Anal. calc. for $C_{22}H_{22}Cl_2$ (357.33): C 73.95, H 6.21; found: C 73.69, H 6.32.

3.8. Arylation with Bromobenzene. Chromatography on silica gel with pentane/CH_2Cl_2 4:1. *1,3-Bis(4-bromophenyl)-, 1-(3-bromophenyl)-3-(4-bromophenyl)-,* and *1,3-bis(3-bromophenyl)tricyclo[3.3.1.1^{3,7}]decane* (**19** + **20** + **21**): 3.8 g (56.8%), oil. Anal. calc. for $C_{22}H_{22}Br_2$ (446.22): C 59.22, H 4.97; found: C 58.57, H 4.88.

4. ^{13}C-NMR Spectra. Attributions were performed on the basis of an incremental additivity procedure, see *Table 5.*

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