Electrophilic Carboxylation of Alkenes

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Received August 10, 1987

In the presence of 1.2 equivalents of boron trichloride 2,2-dichloro-1,3-benzodioxol (2) reacts with alkenes 4 to form 1:1 addition products 6, which are converted into the unsaturated *tert*-butyl esters 7 on treatment with potassium *tert*-butoxide. In the presence of $ZnCl_2$, these reactions do not usually terminate at the 1:1-product stage, and 2,2-disubstituted 1,3-benzodioxols 5 are formed by reaction of 2 with two equivalents of 4a–f.

Elektrophile Carboxylierung von Alkenen

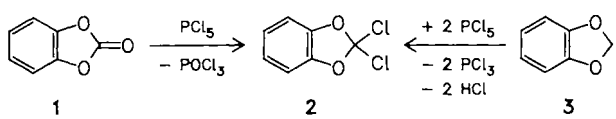
In Gegenwart von 1.2 Äquivalenten Bortrichlorid reagiert 2,2-Dichlor-1,3-benzodioxol (2) mit den Alkenen 4 unter Bildung von 1:1-Additionsprodukten 6, die durch Behandeln mit Kalium-*tert*-butoxid in die ungesättigten *tert*-Butylester 7 übergeführt werden. In Gegenwart von $ZnCl_2$ halten diese Reaktionen üblicherweise nicht auf der Stufe der 1:1-Produkte an, und bei der Umsetzung von 2 mit zwei Äquivalenten an 4a–f erhält man die 2,2-disubstituierten 1,3-Benzodioxole 5.

The substitution of vinylic hydrogens by carboxyl groups is usually achieved by multistep procedures, and only isolated cases of direct attack of $^{+}CO_2H$ equivalents at olefinic π bonds have been reported[1-4]. Phosgene, for example, reacts with enamines and enol ethers to give β-amino- and β-alkoxy-substituted α,β-unsaturated acid chlorides[1,2]. Various alkenes have been converted into β-chloro-substituted acid chlorides by treatment with phosgene and aluminium trichloride[1,2]. Furthermore, formal phosgene addition products have been obtained from the reactions of 1,1-diphenylethylene and cyclohexene with oxalyl halides[2]. Whereas phosgeniminium ions react with enamines and enol ethers to give the corresponding carboxamides[3], unactivated alkenes have not yet been observed to react with these weak electrophiles. In various cases, alkenes bearing electron donating substitutents can also be converted into *N*-substituted carboxamides by the reaction with isocyanates[4].

2,2-Dichloro-1,3-benzodioxol (**2**), an alternative $^{+}CO_2H$ equivalent, has been used for the carboxylation of electron-rich aromatic and heteroaromatic compounds by Gross and co-workers[5]. We describe now the Lewis acid-catalysed reactions of **2** with alkenes and related nonaromatic compounds.

Results

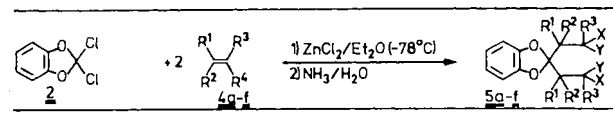
2,2-Dichloro-1,3-benzodioxol (**2**) has been prepared by Gross et al. by heating **1** and PCl_5 with simultaneous distillative removal of $POCl_3$[5,6]. Since the preparation of **1** requires the use of phosgene[7], we preferred to generate **2** from commercially available 1,3-benzodioxol (**3**) and PCl_5 as initially reported by Barger[8] and later modified by Yagupol'skii et al.[9]. Our attempts to prepare **1** from catechol and ethyl chloroformate instead of phosgene gave only 31% of the cyclic carbonate **1**.



1 2 3

When **2** was treated with 2 equivalents of the compounds **4a–f** in the presence of $ZnCl_2-Et_2O$[10], good yields of the 2:1 products **5a–f** have been obtained (Tab. 1). The NMR spectra (Tab. 4 and 5) show that the structures of **5a–f** are those expected from the results of other electrophilic alkylations: Markovnikov addition products are formed with the ordinary alkenes **4a, b**[11], and isoprene is attacked at the higher substituted double bond to give a 1,4-adduct, predominantly with (*E*)-configuration[11]. The well known S_E2' reaction takes place with allylsilane **4d**[12], and the (trimethylsiloxy)alkenes **4e, f** are converted into the corresponding

Table 1. Zinc chloride-catalyzed reactions of 2,2-dichloro-1,3-benzodioxol (**2**) with 2 equivalents of alkenes



R^1	R^2	R^3	R^4		Time		
H	H	CH_3	CH_3	4a	4.5 h	5a	(86%)
H	H	Ph	H	4b	22 h	5b	(70%)
H	H	CH_3	$CH=CH_2$	4c	4 h	5c	(67%)[a]
H	H	H	CH_2–$Si(CH_3)_3$	4d	7 h	5d	(73%)
H	H	C_6H_5	$OSi(CH_3)_3$	4e	3.5 h	5e	(59%)
CH_3	CH_3	OCH_3	$OSi(CH_3)_3$	4f	6 h	5f	(98%)

[a] With traces of a stereoisomer.

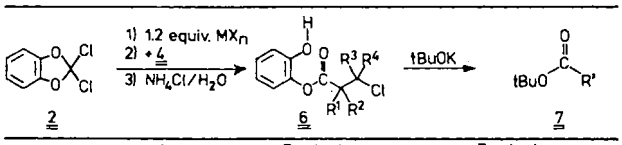
  0009–2940/88/0202–0339 $ 02.50/0

carbonyl compounds **5e, f**[13]. So far we have failed to selectively remove the ketal protecting group in **5a–f**, and therefore cannot yet use **2** as a building block in ketone synthesis.

When *one equivalent* of trimethylethylene (**4g**) or tetramethylethylene (**4h**) was added to a solution of **2** and $ZnCl_2-Et_2O$, the reaction terminated at the 1:1-product stage and the 1:1 products **6g, h** and **8** were obtained in fair yields (Tab. 2). Under the same conditions, isobutene (**4a**) and **2** gave a 5:1 mixture of the 2:1 product **5a** and the 1:1 product **6a**, and this ratio decreased to 3.5 when the reaction was run in CH_2Cl_2/CH_3NO_2 (2:1, v/v). When $ZnCl_2-Et_2O$ was replaced by BCl_3 (1.2 equivalents), this reaction also terminates at the 1:1-product stage, and compound **6a** was isolated in 61% yield.

Analogous conditions (1.2 equivalents of BCl_3) were then employed for the carboxylation of styrene (**4b**) and of the alkenes **4i–l**. Since the catechol esters **6** cannot easily be purified, the crude reaction mixtures were treated with KO*t*Bu in ether/*tert*-butyl alcohol or toluene to give the unsaturated *tert*-butyl esters **7** (Tab. 2).

Table 2. Formation of 1:1 products from 2,2-dichloro-1,3-dioxol (**2**) and alkenes **4**

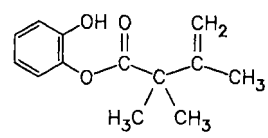


2 6 7

Alkene	MX_n	Product (Yield)	Product (Yield[d])
(4a)	$ZnCl_2$	5a : 6a = 5:1	
	BCl_3	6a (61%)	7a (37%)
(4b)	BCl_3	b)	7b (20%)
(4g)	$ZnCl_2$	6g (54%)	7g (52%)
	BCl_3	6g (64%)	
(4h)	$ZnCl_2$	6h (37%), 8 (21%)	7h (40%)
	BCl_3	6h (47%), 8 (28%)	
(4i)	BCl_3	b)	7i (39%)
(4j)	BCl_3	b)	7j (57%)
(4k)	BCl_3	b)	7k[c] (11%), 9 (20%)
(4l)	BCl_3	b)	7l[d] (75%)

[a] With respect to **2**. — [b] The intermediate product **6** was not characterized. — [c] *syn*:*anti* ≈ 1:1. — [d] (*E*):(*Z*) = 97:3.

The structural assignment of the compounds **7** can be based on their NMR spectra (Tab. 7, 8). Whereas usually α,β-unsaturated esters are formed, tetramethylethylene, which lacks an α-hydrogen, yields the β,γ-unsaturated ester **7h**. The major isomer obtained from camphene (**4l**) was assigned the (*E*)-configuration since the bridgehead 1-H (δ 3.92) was considerably deshielded with respect to 1-H of the minor isomer (δ 2.64).



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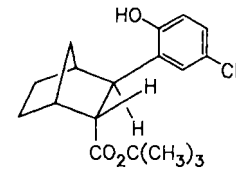


9

The formation of the norbornene-7-carboxylic esters **7k** can be explained similarly as the results of the electrophilic alkylations of norbornene[14], but the mechanism leading to compound **9**, which has structurally been assigned by a 2D-INADEQUATE experiment, is not yet known.

Discussion

The influence of the reaction conditions on the product distribution is rationalized on the basis of Scheme 1. Compound **2** will be more or less ionized, depending on the nature and concentration of the Lewis acid. The reaction with alkene **4** initially yields a 1:1 product **10** ⇌ **10**$^+$, which may react with a second alkene molecule to give the 2:1 product **5**. The relative reactivity of **2**/**2**$^+$ and **10**/**10**$^+$ towards the alkene **4** will determine, whether the reaction terminates at the 1:1-product stage.

We have recently reported that the relative electrophilicity of two competing partially ionized compounds R^1-Cl and R^2-Cl can be influenced by the Lewis acid concentration[15]. If more than one equivalent of a completely ionizing Lewis acid is employed, the less stabilized carbenium ion was found to be more reactive, while the relative reactivities turned out to be opposite in the presence of catalytic amounts of Lewis acids. In the latter case, the compound, which is ionized to a greater extent, i.e. the compound which forms the better stabilized carbenium ions, reacts faster.

Precipitates formed when **2** was treated with BCl_3 in CH_2Cl_2 indicating the generation of **2**$^+$. The NMR spectroscopic investigation of the homogeneous mixture of **2** and BCl_3 (1:1.4) in CD_2Cl_2/CD_3NO_2 (3:1, v/v) showed that **2** was ionized to approximately 35% under these conditions. When one equivalent of isobutene (**4a**) was added to this solution, **10a**$^+$ was formed, and unionized **10a** was not detectable in the NMR (Table 3). The corresponding experiments with $ZnCl_2 \cdot Et_2O$ in CD_2Cl_2/CD_3NO_2 showed that compound **2** is covalent under these conditions while the 1:1 product **10a** is also ionized by $ZnCl_2/Et_2O$ in CD_2Cl_2/CD_3NO_2.

Both experiments show that **10a**$^+$ is a better stabilized carbenium ion than **2**$^+$ and, in accord with previous conclusions[15], the 1:1 products **10**$^+$ are formed selectively,

Scheme 1

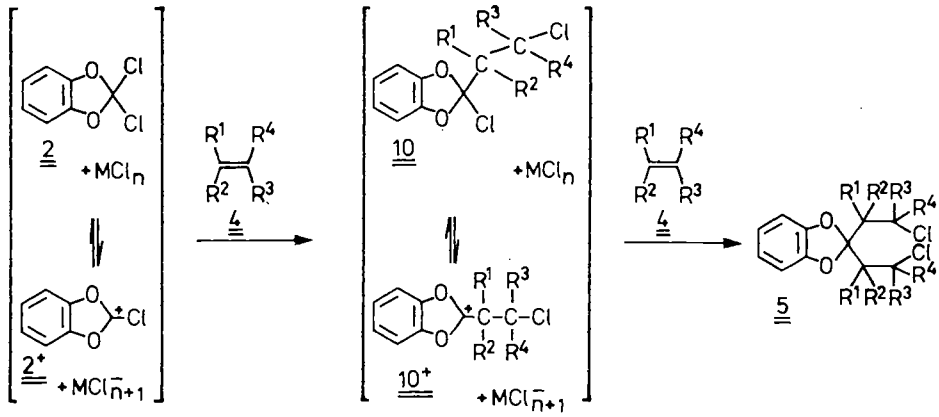
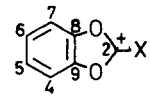


Table 3. ^1H and ^{13}C NMR chemical shifts of 1,3-benzodioxolium ions



X	Solvent	^1H NMR		^{13}C NMR				
		Aryl-H	X	C-2	C-4,7	C-5,6	C-8,9	ref.
H	FSO_3H/SO_2	8.1 (s), 8.2 (s)	10.4 (s)	170.4	114.8	132.3	144.4	16, 17)
OH	$FSO_3H/SbF_5/SO_2ClF$	8.0 (s)	13.2 (s)	165.1	113.6	130.2	143.7	16)
Cl ($\underline{2}^+$)	$SbCl_5/SO_2$	8.26 (br. s)						17)
Cl ($\underline{2}^+$)	$BCl_3/CD_2Cl_2/CD_3NO_2$	7.90 (m), 8.03 (m)		a)	114.02	131.40	146.31	b)
$-CH_2-C(CH_3)_2Cl$ ($\underline{10a}^+$)	$BCl_3/CD_2Cl_2/CD_3NO_2$	7.89 - 7.94 (m) 8.08 - 8.13 (m)	1.88 (s) 4.25 (s)	182.18	114.25	131.29	144.89 c)	b)

[a] Not observed. — [b] This work. — [c] Further ^{13}C NMR chemical shifts 32.30, 44.81, 64.82.

when more than 1 equivalent of the strong Lewis acid BCl_3 is employed (rule A in ref.[15]). In the presence of the weaker Lewis acid $ZnCl_2-Et_2O$ the 1:1 product **10a**/**10a**$^+$ is more reactive than **2**/**2**$^+$, and the reaction of **2** with 1 equivalent of isobutene (**4a**) yields the 2:1 products predominantly. The reactivity difference of **10a**/**10a**$^+$ and **2**/**2**$^+$ cannot be very great, however, since the steric hindrance in the trimethylethylene adduct **10g**$^+$ is already sufficient to prevent its reaction with a second molecule of **4g**. The experiments with isobutene (**4a**) clearly show, however, that in the absence of strong steric effects carboxylations with **2** require the presence of equimolar amounts of strong Lewis acids.

We thank *R. Lammers* for experimental assistance, *R. Koschinsky* and Dr. *E. Bäuml* for discussions, the *Deutsche Forschungsgemeinschaft* and the *Fonds der Chemischen Industrie* for financial support.

Experimental

NMR: XL 200 (Varian), internal standard TMS. — Mass spectra: 70–250 (VG-Instruments). — IR: IR-435 (Shimadzu). — Separations by middle pressure liquid chromatography (MPLC) were carried out in 30 × 2.5 cm glass columns. — Compounds **4e**[18] and **4f**[19] were prepared according to literature procedures, all other olefinic substrates **4** were commercially available.

2,2-Dichloro-1,3-benzodioxol (**2**)[9]: 1,3-Benzodioxol (**3**) (24.4 g, 200 mmol) and PCl_5 (83.3 g, 400 mmol) were mixed in a 100-ml round bottom flask under nitrogen and heated at 120°C. The orange mixture became homogeneous and was then heated at reflux for 2 additional hours. PCl_3 was removed by distillation to give 29.7–33.6 g (78–88%) of **2** with b.p. 83–86°C/20 mbar (ref.[9] 100°C/26 mbar). — IR (neat): 1642 cm^{-1}, 1478, 1352, 1238, 1055, 850, 736. — ^1H NMR (CCl_4): δ = 6.97 (s). — ^{13}C NMR ($CDCl_3$): δ = 109.71 (d), 123.82 (d), 129.60 (s), 144.11 (s). — MS (70 eV): *m/z* (%) = 194, 192, 190 (2, 12, 19, M^+), 157 (31), 155 (100).

2,2-Disubstituted 1,3-Benzodioxols **5a–f**

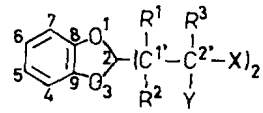
General Procedure: A solution of $ZnCl_2$ (1.6 g, 12 mmol) in 1.9 ml of ether and 3.8 ml of CH_2Cl_2[10] was added to a precooled (−78°C) solution of **2** (1.91 g, 10 mmol) in 10 ml of CH_2Cl_2. Solutions of the compounds **4a–f** (22 mmol) in 20 ml of CH_2Cl_2 were added dropwise within 45 min. The solution was stirred for 4 to 22 h (see Table 1). The cold solutions were then washed with 30 ml of conc. aqueous ammonia, and the aqueous layers were extracted twice with 10 ml of ether. After drying with $CaCl_2$, the solvents were evaporated to give compounds **5a–f** as crystalline materials or viscous oils. Reaction times and yields: Table 1. Physical and spectroscopic data: Tables 4 and 5.

Table 4. 2,2-Disubstituted 1,3-benzodioxols **5a–f**

Compound	mp/°C (solvent)	IR/cm^{-1}	^{1}H NMR ($CDCl_3$)	MS (70 eV) m/z (relative int.)	Formula	Analysis	Calcd.	Found
5a	44 – 46 (ether/pentane)	neat: 3063, 2934, 1485, 1239, 738	1.68 (s, 12 H), 2.66 (s, 4 H), 6.81 (mc, 4 H)	306, 304, 302 (1, 4, 6%, M^+), 213 (33), 211 (99), 175 (100)	$C_{15}H_{20}Cl_2O_2$ (303.2)	C H	59.42 6.65	59.46 6.57
5b [a]	oil	neat: 3065, 3063, 1482, 1455, 1258, 1236, 1119, 734, 695	2.65 – 2.95 (m, 4 H), 5.05 – 5.15 (m, 2 H), 6.30 – 6.80 (m, 4 H), 7.23 (mc, 10 H)	402, 400, 398 (3, 14, 22%, M^+) 261 (22), 259 (67), 127 (36), 125 (100)	$C_{23}H_{20}Cl_2O_2$ (399.3)	C H	69.18 5.05	70.16 5.12
5c [b]	oil	neat: 1485, 1238, 737	1.80 (d, J = 1.3 Hz, 6 H), 2.63 (s, 4 H), 4.02 (d, J = 7.8 Hz, 4 H), 5.60 (mc, 2 H), 6.74 (mc, 4 H)	330, 328, 326 (0.1, 0.6, 1%, M^+), 225 (19), 223 (58), 187 (100), 151 (45)				
5d	bp 49 – 51/ 0.01 mbar	neat: 3078, 2942, 1643, 1484, 1236, 921, 736	2.67 (dt, J = 7.0, 1.2 Hz, 4 H), 5.12 – 5.24 (m, 4 H), 5.74 – 5.96 (m, 2 H), 6.76 (mc, 4 H)	202 (23%, M^+), 162 (35), 161 (100)	$C_{13}H_{14}O_2$ (202.3)	C H	77.20 6.98	77.09 7.01
5e	144 – 147 (CH_2Cl_2)	KBr: 1688, 1594, 1484, 1361, 1237, 752	4.10 (s, 4 H), 6.81 (s, 4 H), 7.45 – 7.57 (m, 6 H), 7.94 – 7.99 (m, 4 H)	358 (19%, M^+), 249 (15), 105 (100), 77 (52)	$C_{22}H_{18}O_4$ (358.4)	C H	77.08 5.06	76.97 5.05
5f	74 – 75 (ether)	KBr: 1730, 1720, 1489, 1273, 1243, 1151, 1073, 736	1.34 (s, 12 H), 3.63 (s, 6 H), 6.73 – 6.87 (m, 4 H)	322 (37%, M^+), 222 (79), 221 (100), 162 (40), 161 (42), 152 (25), 151 (100), 147 (48), 121 (35)	$C_{17}H_{22}O_6$ (322.4)	C H	63.34 6.88	63.37 6.70

[a] Mixture of stereoisomers. – [b] Predominantly (*E,E*) with traces of a second stereoisomer.

Table 5. ^{13}C NMR chemical shifts of 2,2-disubstituted 1,3-benzodioxols **5a–f**



	C-2	C-4,7	C-5,6	C-8,9	C-1'	C-2'	R^1-R^3, X, Y
5a	118.05	108.83	121.70	146.55	52.15	67.76	33.59 (q)
5b [a]	116.91	109.23	122.30	147.40	48.66	57.81	127.69 (d), 129.09 (d), 125.25 (d), 142.12 (s)
	116.91	109.34	122.35	147.47	48.76	57.81	127.71 (d), 129.12 (d), 129.28 (d), 142.15 (s)
5c	118.68	108.14	121.13	147.46	40.38	135.91	17.51 (q), 47.00 (t), 126.50 (d)
5d	118.16	108.21	121.09	147.60	41.91	130.74	119.70 (t)
5e	115.87	109.02	121.72	146.46	44.71	195.63	128.22 (d), 128.56 (d), 133.43 (d), 136.89 (s)
5f	120.18	107.28	121.16	149.06	52.75	174.34	22.21 (q), 52.09 (q)

[a] 1:1 mixture of diastereomers.

Preparation of the 1:1 Products **6** *and* **7**

1. *Reactions of* **2** *with one Equivalent of* **4**: A 1 M solution of BCl_3 in CH_2Cl_2 (60 ml) was added dropwise to a precooled solution of **2** (9.55 g, 50.0 mmol) in 50 ml of CH_2Cl_2 to give a suspension of $\mathbf{2}^+$ BCl_4^-. Solutions of the alkenes **4** (55 mmol) in 40 ml of CH_2Cl_2 were added within 45 min. After 4–7 h stirring at –78°C, the mixture was poured onto 150 ml of 25% aqueous NH_4Cl solution. The aqueous layer was washed with ether (2 · 50 ml), and the combined organic layers were dried with $CaCl_2$. After evaporation of the solvents, eventually formed catechol carbonate **1** was removed by sublimation (80 – 100°C (bath)/1 mbar) to give the crude catechol esters **6** (Tab. 2).

Catechol 3-Chloro-3-methylbutyrate (**6a**): The crude product (9.00 g) which contained 7.00 g (61%) of **6a** according to NMR was purified by MPLC (stationary phase: RP18, eluent: CH_3OH/H_2O = 92:8, flow: 12.5 ml/min, R_t = 8.6 min). The eluent containing **6a** was diluted with water, and **6a** was extracted with CH_2Cl_2. Drying with $CaCl_2$ and evaporation of the solvent gave 5.08 g (44%) of **6a**. – IR (neat): 3414 cm^{-1}, 2977, 1741, 1598, 1509, 1500, 1226, 751. – ^{1}H NMR ($CDCl_3$): δ = 1.82 (s, 6H, CH_3), 3.08 (s, 2H, CH_2),

Table 6. *tert*-Butyl carboxylates **7** from 2,2-dichloro-1,3-benzodioxol (**2**) and Alkenes **4**

	Formation of **6**			Formation of **7**				
	Lewis acid	Time	Procedure	Yield	bp (°C/mbar)	Formula	Calcd.	Found
a	BCl_3	6.5 h	A	2.89 g (37%)	60 - 61/26	$C_9H_{16}O_2$	C 69.19	68.96
						(156.2)	H 10.32	10.44
b	BCl_3	5.5 h	A	2.04 g (20%)	80 - 81/ 0.4	$C_{13}H_{16}O_2$	C 76.44	77.00
						(204.3)	H 7.89	7.74
g	$ZnCl_2$	4.5 h	A	4.43 g (52%)	68 - 69/24	$C_{10}H_{18}O_2$	C 70.55	71.12
						(170.3)	H 10.66	11.06
h	$ZnCl_2$	7 h	B	3.68 g (40%)	65 - 67/28	$C_{11}H_{20}O_2$	C 71.70	71.70
						(184.3)	H 10.94	10.87
i	BCl_3	4 h	B	3.55 g (39%)	30 - 50 (bath)/ 0.1	$C_{11}H_{18}O_2$	C 72.49	72.37
						(182.3)	H 9.95	9.89
j	BCl_3	4 h	B	5.56 g (57%)	50 - 55 (bath)/ 0.2	$C_{12}H_{20}O_2$	C 73.43	73.36
						(196.3)	H 10.27	10.29
k	BCl_3	6 h	B	1.04 g (11%)[a]	90 -105 (bath)/22	$C_{12}H_{18}O_2$	C 74.19	73.91
						(194.3)	H 9.34	9.46
l	BCl_3	6 h	B	8.82 g (75%)[b]	74 - 79°C/ 0.25	$C_{15}H_{24}O_2$	C 76.23	75.84
						(236.4)	H 10.23	10.14

[a] With 3.23 g (20%) of **9**. — [b] Separation of the diastereomers by MPLC (Lichroprep Si 60 15–25 μ; *n*-hexane/ether 20:1; 12.5 ml/min, R_t (*Z*-isomer) = 9.4 min; R_t (*E*-isomer) = 11 min).

Table 7. ^{13}C NMR chemical shifts of the *tert*-butyl carboxylates **7**

	$(\underline{C}H_3)_3C$	$(CH_3)_3\underline{C}$	C-1	C-2	C-3	Other signals
7a	28.28	79.42	166.30	117.84	154.66	19.92 (q), 27.28 (q)
7b	28.19	80.45	166.29	120.14	143.53	127.92 (d) [a], 128.80 (d) [a], 129.94 (d), 134.62 (s)
7g	27.99	79.69	169.25	123.95	139.79	15.55 (q), 21.75 (q), 22.34 (q)
7h	27.86	79.97	175.76	48.25	148.27	20.00 (q), 24.63 (q), 109.93 (t)
7i	28.33	79.65	165.97	128.82	153.66	16.23 (q), 21.22 (t), 33.85 (t), 40.84 (t)
7j	28.18	79.70	168.73	125.88	143.08	21.65 (q), 22.31 (t) [a], 26.46 (t), 33.28 (t)
anti-7k [b]	27.97	79.68	171.00	62.20		22.59 (t), 43.15 (d), 135.75 (d)
syn- 7k [b]	28.04	79.68	171.80	63.69		24.76 (t), 44.23 (d), 133.21 (d)
(E)-7l	28.30	79.16	166.81	109.34	177.65	23.39 (t), 25.54 (q), 27.67 (t), 28.43 (q), 37.36 (t), 43.40 (d), 44.09 (s), 47.02 (d)
(Z)-7l	28.25	79.26	165.67	110.86	175.76	22.73 (q), 23.65 (t), 25.15 (q), 28.52 (t), 36.48 (t), 43.28 (s), 50.34 (d), 50.41 (d)

[a] Relative intensity 2. — [b] Spectrum taken of a *syn/anti* mixture; assignments to the different isomers are tentative (ref.[14]).

5.53 (s, 1H, OH), 7.18 (mc, 4H, aromatic H). — ^{13}C NMR ($CDCl_3$): δ = 32.74 (q), 49.84 (t), 66.51 (s), 117.39 (d), 120.75 (d), 122.47 (d), 127.26 (d), 137.90 (s), 147.10 (s), 167.74 (s). — Attempts to purify **6a** by distillation (130–145°C (bath)/0.9 mbar) led to partial decomposition of the material by HCl elimination.

Other catechol esters **6** have not been isolated, but the crude reaction products obtained by the above procedure have been subjected to treatment with KO*t*Bu as described in the following section.

2. *tert-Butyl Carboxylates* **7**

Procedure A: A solution of crude **6** (obtained from 50 mmol of **2**) in 40 ml of ether was added dropwise within 0.5 h to a mixture of KO*t*Bu (19.6 g, 175 mmol), *tert*-butyl alcohol (5.56 g, 75.0 mmol), 18-crown-6 (1.06 g, 4.00 mmol), and 150 ml of dry ether. The mix-

Table 8. IR, ^{1}H NMR and MS data of the *tert*-butyl carboxylates **7**

Compound	IR (neat)/cm^{-1}	^{1}H NMR ($CDCl_3$)	MS (70 eV) m/z (rel. intensity)
7a	2973, 1711, 1655, 1239, 1139, 852	1.47 (s, 9 H), 1.85 (d, J = 1.3 Hz, 3 H), 2.13 (d, J = 1.3 Hz, 3 H), 5.60 (mc, 1 H)	156 (0.1%, M^+), 141 (0.5), 101 (40), 100 (66), 83 (94), 57 (100)
7b	2974, 1700, 1638, 1328, 1149, 979, 768	1.54 (s, 9 H), 6.36 (d, J = 16 Hz, 1 H), 7.44 (mc, 5 H), 7.58 (d, J = 16 Hz, 1 H)	204 (12%, M^+), 148 (100), 147 (69), 131 (77), 77 (34), 57 (76)
7g	2973, 1700, 1367, 1285, 1171, 1099	1.50 (s, 9 H), 1.76 (br. s, 3 H), 1.82 (mc, 3 H), 1.96 (mc, 3 H)	170 (1%, M^+), 114 (80), 97 (61), 57 (100)
7h	2968, 1719, 1642, 1453, 1367, 1252, 1160, 1129, 892, 849	1.27 (s, 6 H), 1.43 (s, 9 H), 1.74 (dd, J = 1.4, 0.7 Hz, 3 H), 4.83 (mc, 1 H), 4.86 (mc, 1 H)	128 (4%, $M^+-C_4H_8$), 83 (30), 57 (100)
7i	2963, 2925, 1701, 1645, 1365, 1169, 1119	1.50 (s, 9 H), 1.73 - 1.86 (m, 2 H), 2.06 (mc, 3 H), 2.40 - 2.63 (m, 4 H)	182 (1%, M^+), 127 (31), 126 (90), 109 (58), 81 (100), 57 (63)
7j	2966, 2926, 2858, 1705, 1365, 1278, 1244, 1163, 1141, 1075	1.50 (s, 9 H), 1.58 (mc, 4 H), 1.94 (mc, 3 H), 2.06 - 2.09 and 2.22 - 2.24 (m, 4 H)	196 (1%, M^+), 141 (10), 140 (100), 123 (39), 95 (74), 57 (93)
7k [a]	2869, 1724, 1367, 1165	0.94 - 1.19 (m, 4 H), 1.38 (s, $C(CH_3)_3$), 1.43 (s, $C(CH_3)_3$), 1.68 - 1.78 (m, 4 H), 2.31 (mc, CH-CO), 2.97 (mc, bridgeheads of anti-isomer), 3.10 (mc, bridgeheads of syn-isomer), 5.99 (mc, vinyl-H of syn-isomer), 6.03 (mc, vinyl-H of anti-isomer)	194 (1%, M^+), 166 (2), 138 (48), 121 (21), 110 (60), 57 (100)
(E)-7l	2948, 2872, 1702, 1649, 1389, 1362, 1289, 1254, 1236, 1207, 1167, 1161,	1.05 (s, 3 H), 1.06 (s, 3 H), 1.26 - 1.32 (m, 2 H, 5',6'-H_{endo}), 1.48 (s, 9 H), 1.50 - 1.79 (m, 4 H, 5',6'-H_{exo}, 7'-H), 1.92 (mc, 1 H, 4'-H), 3.92 (mc, 1 H, 1'-H), 5.37 (s, Vinyl-H)	181 (31%), 180 (83, $M^+-C_4H_8$), 163 (41), 139 (45), 112 (50), 57 (100)
(Z)-7l	2956, 2870, 1710, 1646, 1388, 1363, 1356, 1150,	1.21 - 1.34 (m, 2 H, 5',6'-H_{endo}), 1.29 (s, 3 H), 1.31 (s, 3 H), 1.47 (s, 9 H), 1.70 - 1.79 (m, 4 H, 5',6'-H_{exo}, 7'-H), 1.91 (mc, 1 H, 4'-H), 2.64 (mc, 1 H, 1'-H), 5.60 (s, 1 H, vinyl-H)	181 (23%), 180 (100, $M^+-C_4H_8$), 163 (27), 139 (64), 112 (47), 57 (38)

[a] *syn/anti* mixture.

ture was stirred for 2 h at ambient temperature and washed with 50 ml of water. The organic layer was dried with Na_2SO_4, the solvent evaporated, and the residue distilled.

Procedure B: A solution of crude **6** (obtained from 50 mmol of **2**) in 40 ml of toluene was added dropwise within 45 min to a boiling mixture of KO*t*Bu (19.6 g, 175 mmol), *tert*-butyl alcohol (5.56 g, 75.0 mmol), and 18-crown-6 (1.06 g, 4.00 mmol) in 150 ml of toluene. After 6 h stirring at reflux temperature, the mixture was worked up as in procedure A.

Yields, physical, and spectroscopic data of the compounds **7** are given in Tables 6–8. The reaction of **2** with norbornene (**4k**) and

successive treatment with KO*t*Bu according to procedure B gave 1.04 g (11%) of **7k**. Purification of the distillation residue by MPLC (Lichroprep Si 60 15–25 μ; *n*-hexane/ether 1:1; 12.5 ml/min; R_t = 10.8 min) yielded 3.23 g (20%) of *tert-butyl exo-3-(5-chloro-2-hydroxyphenyl)bicyclo[2.2.1]heptane-endo-2-carboxylate* (**9**): IR (neat): 3268 cm^{-1}, 2954, 1726, 1685, 1480, 1367, 1294, 1265, 1226, 1152, 1122, 851, 817, 651. – ^1H NMR ($CDCl_3$): δ = 1.32–1.89 (m; 6H, 5,6,7-H), 1.49 [s; 9H, $C(CH_3)_3$], 2.53–2.59 (m; 2H, 2,4-H), 2.67–2.70 (m; 1H, 1-H), 2.99 (br. d; *J* = 5.9 Hz; 1H, 3-H), 6.81 (d; *J* = 8.6 Hz, 1H, 3′-H), 7.05 (dd; *J* = 8.6; 2.6 Hz, 1H, 4′-H), 7.15 (d; *J* = 2.6 Hz, 1H, 6′-H), 8.51 (br. s; 1H, OH). – ^{13}C NMR ($CDCl_3$): δ = 24.36 (t; C-6), 28.02 [q; $C(CH_3)_3$], 30.71 (t; C-5), 38.96 (t; C-7), 40.39 (d; C-1), 42.11, 42.21 (2d; C-3,4), 58.59 (d; C-2), 82.71 [s; $C(CH_3)_3$], 118.25 (d; C-3′), 124.57 (s; C-5′), 125.73 (d; C-6′), 127.20 (d; C-4′), 132.70 (s; C-1′), 153.28 (s; C-2′), 177.26 (s; C=O). – MS (70 eV): *m/z* (%) = 324, 322 (4, 12, M^+), 268, 266 (13, 38), 251, 249 (8, 26), 250, 248 (35, 100).

CAS Registry Numbers

2: 2032-75-9 / **3**: 274-09-9 / **4a**: 115-11-7 / **4b**: 100-42-5 / **4c**: 78-79-5 / **4d**: 762-72-1 / **4e**: 13735-81-4 / **4f**: 31469-15-5 / **4g**: 513-35-9 / **4h**: 563-79-1 / **4i**: 693-89-0 / **4j**: 108-87-2 / **4k**: 498-66-8 / **4l**: 79-92-5 / **5a**: 110614-13-6 / **5b**: 110637-28-0 / **5c**: 110614-14-7 / **5d**: 110614-15-8 / **5e**: 110614-16-9 / **5f**: 110614-17-0 / **6a**: 110614-18-1 / **6b**: 110614-21-6 / **6g**: 110614-19-2 / **6h**: 110614-20-5 / **6i**: 110614-22-7 / **6j**: 110614-23-8 / **6k**: 110614-24-9 / **6l**: 110614-25-0 / **7a**: 22842-54-2 / **7b**: 14990-09-1 / **7g**: 110614-26-1 / **7h**: 110614-27-2 / **7i**: 110614-28-3 / **7j**: 110614-29-4 / (*syn*)-**7k**: 110614-30-7 / (*anti*)-**7k**: 110614-33-0 / (*E*)-**7l**: 110614-31-8 / (*Z*)-**7l**: 110614-34-1 / **8**: 110614-35-2 / **9**: 110614-32-9

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