New Aromatic Azapentalenes: 3*H*- and 2*H*-Imidazo[1,2-*d*]tetrazoles

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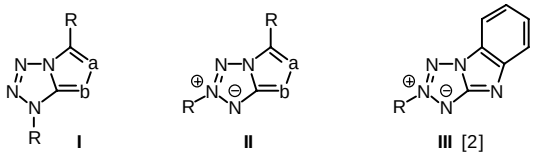
Abstract. A number of title compounds (**3a**,**c**, **4a**–**c**) were prepared by cyclization of 5-aminotetrazolium salts having ketonic substituents (**1**, **2**). The following procedures were applied: a) for **3a**, **4a**,**b**: heating of **1a**, **2a**,**b** with acetic anhydride/base; b) for **3c**, **4c**: heating of **1b**, **2b** in a buffer solution of pH 6.5 (Tschitschibabin reaction). The proclivity for ring closure was more pronounced with the salts **2**. The 6-unsubstituted representatives **3c** and **4c** underwent S_E-reactions, the 2*H*-isomer **4c** being slightly more reactive; this was confirmed by AM1 calculations. The nitroso product **4g** exists predominantly as the valence-isomeric nitrile oxide **6**.

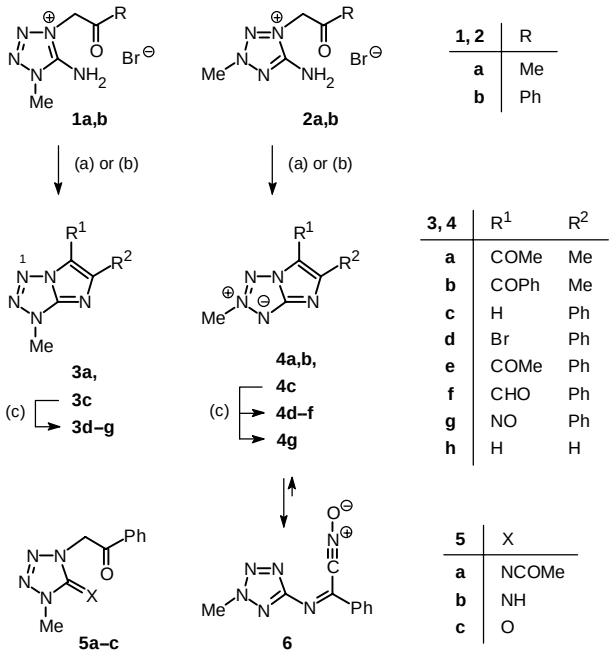
In contrast to imidazotetrazoles of type **IA** and **IIA** [1], the isomeric systems **IB** and **IIB** are still unknown; only a tricyclic congener of **IIB**, the tetrazolobenzimidazole **III**, has been described [2]. Earlier attempts to obtain representatives of **IB** and/or **IIB** include cyclization of 1,4-diphenacyl-1*H*-tetrazol-5(4*H*)-imine (**5b**: CH_2COPh in place of Me) [3] as well as methylation of the imidazo[1,2-*d*]tetrazolide anion [4]; these efforts remained unrewarded, the latter since alkylation occurred exclusively at the imidazolic half-ring. A previously claimed *N*-unsubstituted derivative of **IB** [5] has been shown to be in fact the respective 1-phenacylated 5-aminotetrazole [3]. In this note we report on the first examples of the title classes **IB** and **IIB**.



I **II** **III** [2]

A: a = N, b = CR [1]
B: a = CR, b = N

When the tetrazolium salts **1a** and **2a** were treated with acetic anhydride in the presence of triethylamine, *i.e*. under the conditions formerly applied to 1-acetonyl-4,5-dimethyltetrazolium bromide [6a], the imidazotetrazoles **3a** and **4a** were formed in reasonable to excellent yield (Table 2). Extension of this experiment to the salts **1b** and **2b** only gave the derivative of the **IIB** series, *viz*. **4b** (along with **4a**; *cf*. our observations with pyrrolotetrazoles [6a,b]), whereas the reaction with **1b** stopped at the open-chain stage **5a**. Attempts to convert **5a** into the target compound **3b** resulted in deacetylation (→ **5b**). This points to an enhanced proclivity for ring closure with the synthons of type **2**. Regarding cyclization of **1** and **2** *without* an external reagent for C(5) (Tschitschibabin reaction), we found that **3c** was formed on heating **1b** in a buffer solution showing pH 6.5 [7]. However, the



1, 2	R
a	Me
b	Ph

3, 4	R^1	R^2
a	COMe	Me
b	COPh	Me
c	H	Ph
d	Br	Ph
e	COMe	Ph
f	CHO	Ph
g	NO	Ph
h	H	H

5	X
a	NCOMe
b	NH
c	O

(a) = Ac_2O/Et_3N (**1a**/**2a,b** → **3a**/**4a,b**) (b) = buffer pH 6.5 (**1b**/**2b** → **3c**/**4c**)

(c) = Br_2 (**3d**/**4d**), Ac_2O/NaOAc (**3e**/**4e**), HCOOAc (**3f**/**4f**), $NaNO_2$/AcOH (**3g**/**4g**,**6**)

Scheme 1

desired product **3c**, in agreement with the foregoing, was accompanied by substantial amounts of the tetrazolone **5c**. Again, formation of the 2*H*-isomer was facilitated (see Table 2 for yield of **4c**), evidently because the amino group of **2b** is more nucleophilic (*cf*. [9]) and, second, because the competing hydrolysis to give the mesoionic analogue of **5c** is a considerably slower process (*cf*. [10]). Attempts to cyclize **1a** and **2a** in like manner failed; additional efforts to cause ring closure of 5-aminotetrazolium salts having propargyl substitu-

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ents – an alternate principle for making *C*-methylazapentalenes [8a] – were also ineffectual [11].

The new bicycles **3** and **4** are well crystallized, generally stable compounds [12]. Spectroscopically, they exhibit the features of 10 π aromatic azapentalenes, including the details typical of mesoionic (*i.e.* non-classical) representatives [13]. Thus, we observed with **4**: a) in the UV/Vis spectra a bathochromic shift of the longest wavelength (except for the acyl derivatives **4a**,**e**,**f**, *i.e.* according to analogous pyrrolotetrazoles [6b]); b) in the NMR spectra the common downfield absorption of the bridgehead carbon atom (*e.g.* **4c**/**3c**: δ_C = 156.3/150.4 ppm) along with the deshielding of C and H of the *N*-methyl group (**4c**/**3c**: δ_C = 42.4/33.9, δ_H = 4.41/4.12 ppm); c) in the mass spectra a more intense molecular ion and, with the acetyl derivatives **4a**,**e**, a prominent M–15 peak (*cf.* the same behaviour of 2*H*-pyrrolotetrazoles [6b]).

As expected from related imidazoazoles [8a], **3c** and **4c** are susceptible to S_E-reactions, exemplified by the products **3d**–**g** and **4d**–**g** of Scheme 1. The nitroso derivative **3g**, quite different from its 1*H*-pyrrolotetrazole congener (*i.e.* CH in place of N) [6c], is stable with respect to imidazole ring opening. This can be rationalized as follows: the pyridine-like N(4) atom exerts an electron-withdrawing influence comparable to acyl groups. Indeed, if such functions are attached to C(7) of 5-nitroso-1*H*-pyrrolotetrazoles, the derivatives, under ordinary conditions, retain their bicyclic form, too [6c]! In the case of **4g**, however, the stabilizing acceptor effect is offset by the less nucleophilic N(4) atom of a (monocyclic) 2*H*-tetrazole, so that the nitroso compound exists predominantly as the open-chain valence isomer **6**. We found in dichloromethane solution the following proportions (%/°C): 96.2/25, 94.8/0, 94.3/–20, 93.3/–40 (values determined by ^{1}H NMR).

Table 1 AM1 atomic charges for **3h** and **4h**

	3h		**4h**	
	total	π	total	π
N(1)	0.033	1.171	–0.010	1.319
N(2)	0.019	1.131	–0.073	1.445
N(3)	–0.182	1.658	–0.046	1.291
C(3a)	0.005	1.051	–0.048	1.059
N(4)	–0.121	1.259	–0.123	1.267
C(5)	–0.145	1.043	–0.089	0.979
C(6)	–0.121	1.143	–0.209	1.235
N(7)	–0.160	1.535	–0.081	1.409

During the experiments affording the two series of products **e**–**g**, the substrate **4c** proved more reactive than **3c**. This was borne out by AM1 calculations on the models **3h** and **4h** which indicate a higher electron density at C(6) of the 2*H*-isomer (Table 1) [14]. Compared to the exceptional ease observed with S_E-reactions of the analogous 1*H*- and 2*H*-pyrrolotetrazoles [6b], the imidazotetrazoles react less readily; for example, acetylation of **3c** and **4c** could be accomplished only after addition of sodium acetate (*cf.* [15]).

Experimental

M.p.: Kofler microscope. – IR: Philips PU-9800 FTIR. – UV/Vis: Philips PU-8730. – MS: Finnigan MAT 8430. – NMR: Bruker AM-400 (400.1 and 100.6 MHz for ^{1}H and ^{13}C, resp.). – Microanalyses (C, H, N): satisfactory figures obtained for all compounds (save **2a** and **3g**). – AM1 calculations: HyperChem 4.5 (optimization of geometries of **3h**/**4h**: Polak Ribiere optimizer, RMS gradient $\leq 10^{-1}$ kcal Å^{-1}mol^{-1}, convergence limit $\leq 10^{-5}$ kcal mol^{-1}).

1,4-/1,3-Substituted 5-Aminotetrazolium Bromides **1a,b/2a,b**

1a: Dimethyl sulfate (6.30 g, 50 mmol) was added to a solution of 1-acetonyl-5-aminotetrazole (1.41 g, 10 mmol) [16] in the minimum amount of nitromethane and the mixture held at room temperature for 48 h. After evaporation of the solvent, the oily residue was extracted with ether, dissolved in water, neutralized with aqueous $NaHCO_3$ and allowed to pass a column packed with anion exchange resin containing bromide ion. The resultant solution was concentrated and the residue crystallized from ethanol/ether at 0 °C. – Yield 0.33 g (14%); *m.p.* 240 °C (dec.). – IR (KBr): ν_{max}/cm^{-1} = 1742, 1689. – ^{1}H NMR (DMSO-d$_6$): δ/ppm = 2.28 (s, 3H), 3.95 (s, 3H), 5.61 (s, 2H), 9.42 (s, 2H). – ^{13}C NMR (DMSO-d$_6$): δ/ppm = 26.8 (q), 34.4 (q), 56.3 (t), 148.4 (s), 198.6 (s).

2a: Bromoacetone (1.51 g, 11 mmol) was added to a solution of 5-amino-2-methyltetrazole (0.99 g, 10 mmol) [9a, 17] in nitromethane (20 ml) and the mixture heated at 60 °C for 5 d. After evaporation of the solvent the product was crystallized from ethanol/ether. – Yield 1.06 g (45%); *m.p.* 140–170 °C (no improvement on recrystallization). – ^{1}H NMR (TFA): δ/ppm = 2.93 (s, 3H), 4.82 (s, 3H), 6.09 (s, 2H), 7.02 (s, 2H). – ^{13}C NMR (TFA): δ/ppm = 26.3 (q), 42.7 (q), 57.0 (t), 159.2 (s), 202.3 (s).

1b, **2b**: A solution of phenacylbromide (3.00 g, ca. 15 mmol) and 5-amino-1-/2-methyltetrazole (0.99 g, 10 mmol) [9a, 17] in nitromethane (100 ml) was held at 90 °C for 8 h (**1b**) and for 70 h (**2b**), respectively. Work-up as detailed below.

In the case of **1b**, the mixture was cooled at 5 °C for 10 h and the precipitate filtered off; concentration of the filtrate to half its volume and standing at 5 °C gave a second crop. Both fractions were washed with ether and recrystallized from ethanol/ether. – Yield 2.70 g (88%; hemihydrate); *m.p.* 230 °C (dec.). – IR (KBr): ν_{max}/cm^{-1} = 1702, 1684. – ^{1}H NMR (DMSO-d$_6$): δ/ppm = 4.01 (s, 3H), 6.31 (s, 2H), 7.64–7.65 (m, 2H), 7.76–7.78 (m, 1H), 8.07–8.08 (m, 2H), 9.47 (s, 2H). – ^{13}C NMR (DMSO-d$_6$): δ/ppm = 34.6 (q), 54.4 (t), 128.6 [2C] (d), 129.0 [2C] (d), 133.4 (s), 134.7 (d), 148.9 (s), 189.8 (s).

In the case of **2b**, the mixture was concentrated and the residue washed with ether/dichloromethane (10 + 1). – Yield 1.84 g (60%; hemihydrate); *m.p.* 218 °C (dec.; from ethanol/ether). – IR (KBr): ν_{max}/cm^{-1} = 1702, 1656. – ^{1}H NMR (DMSO-d$_6$): δ/ppm = 4.49 (s, 3H), 6.42 (s, 2H), 7.63–7.67 (m, 2H), 7.77–7.81 (m, 1H), 8.07–8.09 (m, 2H), 8.59 (s, 2H). – ^{13}C NMR (DMSO-d$_6$): δ/ppm = 43.2 (q), 54.6 (t), 128.6 [2C] (d), 129.0 [2C] (d), 133.4 (s), 134.7 (d), 158.7 (s), 189.4 (s).

6-Acetyl-3,5-dimethyl-3H- (**3a**) and *6-Acetyl/Benzoyl-2,5-dimethyl-2H-imidazo[1,2-d]tetrazole* (**4a**,**b**)

To a stirred solution of **1a**, **2a** and **2b** (4 mmol), respectively,

in acetic anhydride (20–30 ml) was added triethylamine (1.5 ml, ca. 10 mmol) and the mixture heated at 110 °C for 0.5 h (**1a**), 1.5 h (**2a**) and 2h (**2b**). Then the unconsumed reagent was hydrolyzed with water (60 ml) at room temperature, the mixture neutralized with aqueous $NaHCO_3$ (10%) and the solution extracted with dichloromethane. The products were isolated by flash chromatography [silica gel 40–63 μm; chloroform/ethyl acetate (4 + 3)]; in the case of **2b**, elution gave as a first fraction **4b**, followed by **4a**. – For data, see Table 2 and 3.

Application of the above procedure to **1b** (110 °C, 0.5 h) gave 0.63 g (61%) **5a**; characterization data correspond to those of an authentic sample (see below).

3-Methyl-6-phenyl-3H- (**3c**) and *2-Methyl-6-phenyl-2H-imidazo[1,2-d]tetrazole* (**4c**)

A mixture of **1b** and **2b** (0.61 g, 2 mmol; hemihydrate), respectively, acetic acid (10.0 g, 167 mmol) and sodium acetate (4.00 g, 49 mmol) was adjusted to pH 6.5 by adding 9N

Table 2 Preparative and (in selection) IR, UV/Vis and MS data of **3a**,**c–g, 4a–f**, and **6**

	Yield (%)	*m.p.* (°C)	recrystallized from	FTIR [a] ν (cm^{-1})	UV/Vis [b] λ_{max} (lg ε)	EIMS [c] *m/z* (%)
3a	51	124–125	Et_2O	1657	279 (4.13), 222 (3.92)	179 (M^+, 24), 109 (50), 108 (100)
4a	86	129–130	Et_2O	1631	279 (4.16), 240 (3.99), 231 (4.01)	179 (M^+, 76), 164 (100)
4b	16 [d]	153–155	CH_2Cl_2/Et_2O	1663		
3c	11 [e]	118–119	CH_2Cl_2/Et_2O	3109	289 (3.94), 252 (4.18), 224 (4.01), 217 (4.08)	199 (M^+, 18), 171 (32), 144 (20), 103 (100)
4c	57	198–200	CH_2Cl_2/p.e. [f]	3135	328 (3.98), 271 (4.10), 224 (4.16)	199 (M^+, 100), 103 (38)
3d	86	149 dec.	CH_2Cl_2/p.e.		296 (3.84), 248 (4.14)	
4d	93	150–151	CH_2Cl_2/p.e.		334 (3.88), 267 (4.08), 225 (4.11)	
3e	66	113–114	Et_2O	1656	289 (4.06), 249 (4.17), 223 (4.09)	241 (M^+, 18), 170 (100), 103 (18)
4e	58	152–154	CH_2Cl_2/p.e.	1663	280 (4.08), 254 (4.27), 222 (4.02)	241 (M^+, 100), 226 (98), 129 (22), 103 (6)
3f	62	150–152	CH_2Cl_2/Et_2O [g]	1650	298 (4.19), 254 (4.27), 227 (4.16)	
4f	69	229–231	CH_2Cl_2/p.e.	1642	294 (4.17), 259 (4.60), 220 (4.03)	
3g	44	149–150	CH_2Cl_2/p.e.		357 (4.27), 273 (4.05), 237 (4.02)	
6	58	105–107	CH_2Cl_2/p.e.	2283	309 (4.11), 286 (4.15), 226 (3.95)	

[a]) In KBr; $CH_{imidazole}$, C=O and C≡NO, respectively. [b]) In MeOH. [c]) 70 eV; ion source temperature (°C): **3a**, 25; **3c**, 25; **3e**, 25; **4a**, 55; **4c**, 50; **4e**, 75. [d]) Besides 77% **4a**. [e]) Besides 89% **5c** (based on ^1H NMR). [f]) Petroleum ether. [g]) With addition of petroleum ether.

Table 3 ^1H and ^{13}C NMR data of **3a**,**c–g, 4a–f**, and **6**

	^1H NMR [a] δ (ppm)	^{13}C NMR [a] δ (ppm)
3a	2.575 (3H), 2.578 (3H), 4.10 (3H)	17.2 (q), 29.4 (q), 33.9 (q), 121.1, 145.1, 157.7, 185.7
4a	2.62 (3H), 2.77 (3H), 4.53 (3H)	18.0 (q), 28.9 (q), 42.5 (q), 118.4, 156.3, 159.4, 184.6
4b	2.33 (3H), 4.57 (3H), 7.49–7.51 (m, 3H), 7.73–7.76 (m, 2H)	28.6 (q), 42.6 (q), 118.4, 128.2 [2C] (d), 129.76 (d), 129.83 [2C] (d), 133.9, 156.5, 159.8, 185.0
3c	4.12 (3H), 7.30–7.35 (m, 1H), 7.39–7.43 (m, 2H), 7.79 (1H), 7.79–7.84 (m, 2H)	33.9 (q), 101.9 (d), 125.7 [2C] (d), 128.3 (d), 128.7 [2C] (d), 133.7, 145.3, 150.4
4c	4.41 (3H), 7.33–7.37 (m, 1H), 7.42–7.45 (m, 2H), 7.80 (1H), 7.93–7.95 (m, 2H)	42.4 (q), 99.2 (d), 125.7 [2C] (d), 128.3 (d), 128.7 [2C] (d), 134.0, 151.4, 156.3
3d	4.13 (3H), 7.38–7.48 (m, 3H), 7.99–8.01 (m, 2H)	34.0 (q), 84.1, 127.4 [2C] (d), 128.5 [2C] (d), 128.6 (d), 132.7, 144.3, 146.8
4d	4.45 (3H), 7.39–7.49 (m, 3H), 8.09–8.11 (m, 2H)	42.5 (q), 79.8, 127.8 [2C] (d), 128.5 [2C] (d), 128.8 (d), 132.9, 149.6, 155.0
3e	2.52 (3H), 4.19 (3H), 7.46–7.48 (m, 3H), 7.79–7.82 (m, 2H)	29.4 (q), 34.1 (q), 120.8, 128.2 [2C] (d), 129.8 [2C] (d), 129.9 (d), 133.4, 145.4, 157.5, 185.4
4e	2.33 (3H), 4.57 (3H), 7.49–7.50 (m, 3H), 7.72–7.75 (m, 2H)	28.6 (q), 42.7 (q), 118.4, 128.2 [2C] (d), 129.78 (d), 129.83 [2C] (d), 133.9, 156.4, 159.8, 185.1
3f	4.23 (3H), 7.51–7.53 (m, 3H), 7.80–7.82 (m, 2H), 9.95 (1H)	34.2 (q), 120.8, 129.0 [2C] (d), 129.3 [2C] (d), 130.5 (d), 132.1, 146.9, 161.3, 176.7 (d)
4f	4.60 (3H), 7.55–7.58 (m, 3H), 7.95–7.97 (m, 2H), 9.89 (1H)	42.8 (q), 117.4, 128.9 [2C] (d), 129.2 [2C] (d), 130.2 (d), 132.3, 157.4, 160.6, 175.8 (d)
3g	4.19 (3H), 7.63–7.71 (m, 3H), 8.59–8.61 (m, 2H)	34.1 (q), 129.2 [2C] (d), 129.9 [2C] (d), 131.4, 132.3 (d), 148.3, 154.1, 161.5
6	4.42 (3H), 7.52–7.59 (m, 2H), 7.61–7.65 (m, 1H), 8.01–8.19 (m, 2H) [**4g**: 4.55 (integral < 5% of s at 4.42)]	40.1 (q), 128.9 [2C] (d), 129.0 [2C] (d), 133.6 (d), 134.7, 144.1, 167.3; C of CNO group not observed [b])

[a]) In $CDCl_3$ (except for ^1H of **3a**, ^{13}C of **4c** and ^1H / ^{13}C of **3g** which were measured in DMSO-d_6); unspecified signals are singlets. [b]) *Cf.* [19].

NH_3 and heated at 105–110 °C for 3.5 h (**1b**) and at 100 °C for 2 h (**2b**). The cooled solution was made weakly alkaline with aqueous $NaHCO_3$ (10%) and the products were extracted with dichloromethane. For isolation of **3c**, the concentrated extract showing 11% **3c** and 89% **5c** (based on ^{1}H NMR; data below) was dissolved in ethanol and, after addition of ethanolic picric acid, briefly heated at reflux. On cooling at 0 °C crystals of the *picrate* of **3c** precipitated (*m.p.* 156–157 °C; from ethanol) which were suspended in dichloromethane and repeatedly shaken with aqueous $NaHCO_3$ (10%) to give 0.036 g (9%) of the free base **3c**. – For data, see Table 2 and 3.

6-Bromo-3-methyl-5-phenyl-3H- (**3d**) and *6-Bromo-2-methyl-5-phenyl-2H-imidazo[1,2-d]tetrazole* (**4d**)

To a stirred solution of **3c** and **4c** (0.40 g, 2 mmol), respectively, in chloroform (5 ml) was dropwise added bromine (0.34 g, 2.1 mmol) in the same solvent (2 ml) at 0 °C. After 0.5 h the suspension formed was treated with aqueous NaH–CO_3 (10%) until the solid had dissolved; the mixture was diluted with chloroform (25 ml) and the product isolated from the organic layer. – For data, see Table 2 and 3.

6-Acetyl-3-methyl-5-phenyl-3H- (**3e**) and *6-Acetyl-2-methyl-5-phenyl-2H-imidazo[1,2-d]tetrazole* (**4e**)*; 3-Methyl-5-phenyl-3H-* (**3f**) and *2-Methyl-5-phenyl-2H-imidazo[1,2-d]tetrazole-6-carbaldehyde* (**4f**)

A mixture of **3c** and **4c** (0.40 g, 2 mmol), respectively, and a) acetic anhydride (5.00 g, 49 mmol) and sodium acetate (0.70 g, 8.5 mmol) or b) acetic formic anhydride (15 ml) [18] was heated as detailed below: a) 130–140 °C/25 h (**3c**) and 120–130 °C/3 h (**4c**); b) with stirring 85 °C/2.5 h (**3c**) and 85 °C/1.5 h (**4c**). After cooling the excess reagent was hydrolyzed with water (30–40 ml), the solution was made alkaline (pH 8–9) by adding Na_2CO_3 and the product extracted with dichloromethane. – For data, see Table 2 and 3.

3-Methyl-6-nitroso-5-phenyl-3H-imidazo[1,2-d]tetrazole (**3g**) and *[(2-Methyltetrazol-5-yl)imino]-phenylacetonitrile oxide* (**6**)

To a stirred solution of **3c** and **4c** (0.40 g, 2 mmol), respectively, in acetic acid (10.0 g) was added $NaNO_2$ (0.28 g, 4 mmol) in water (1 ml) at 0 °C. After 45 min (**3c**) or 15 min (**4c**) the mixture was made weakly alkaline by adding 9N NH_3 and the product extracted with dichloromethane. – For data, see Table 2 and 3.

5-Functionalized 4,5-Dihydro-1-methyl-4-phenacyl-1H-tetrazoles **5a**–**c** *(Authentic Samples)*

5a: To a solution of **5b** (0.35 g, 1.6 mmol) in dichloromethane (30 ml) was added acetyl chloride (0.14 g, 1.8 mmol) in the same solvent at 0–5 °C. After 5 min the mixture was treated with aqueous $NaHCO_3$ (10%) until the solid had dissolved and the product isolated from the organic layer. – Yield 0.41 g (99%); *m.p.* 124–126 °C (from dichloromethane/petroleum ether). – IR (KBr): ν_{max}/cm^{-1} = 1699, 1631. – ^{1}H NMR ($CDCl_3$): δ/ppm = 2.05 (s, 3H), 3.85 (s, 3H), 5.94 (s, 2H), 7.51–7.54 (m, 2H), 7.64–7.67 (m, 1H), 7.96–7.98 (m, 2H). – ^{13}C NMR ($CDCl_3$): δ/ppm = 26.6 (q), 34.4 (q), 55.0 (t), 128.1 [2C] (d), 129.0 [2C] (d), 133.6 (s), 134.4 (d), 149.3 (s), 178.2 (s), 189.1 (s).

5b: To an aqueous solution of **1b** (3.07 g, 10 mmol; hemihydrate) was dropwise added 9N NH_3, whereupon the mixture was extracted with dichloromethane to afford the product. – Yield 2.06 g (95%); *m.p.* 143–145 °C (dec.; from dichloromethane/petroleum ether). – IR (KBr): ν_{max}/cm^{-1} = 3338, 1700, 1658. – ^{1}H NMR ($CDCl_3$): δ/ppm = 3.58 (s, 3H), 4.09 (s, 1H), 5.39 (s, 2H), 7.49–7.53 (m, 2H), 7.62–7.66 (m, 1H), 7.97–7.99 (m, 2H). – ^{13}C NMR ($CDCl_3$): δ/ppm = 32.0 (q), 50.9 (t), 128.2 [2C] (d), 129.0 [2C] (d), 134.1 (s), 134.3 (d), 150.1 (s), 190.3 (s). – The same material was isolated after heating **5a** in acetic acid (reflux, 30 min).

5c: The product was obtained by heating **1b** in 6N NaOH at 100 °C for 1 h and extraction of the reaction mixture with dichloromethane. – Yield quantitative; *m.p.* 122–124 °C (from dichloromethane/petroleum ether). – IR (KBr): ν_{max}/cm^{-1} = 1735, 1716, 1697. – ^{1}H NMR ($CDCl_3$): δ/ppm = 3.67 (s, 3H), 5.41 (s, 2H), 7.51–7.55 (m, 2H), 7.64–7.68 (m, 1H), 7.96–7.99 (m, 2H). – ^{13}C NMR ($CDCl_3$): δ/ppm = 31.5 (q), 50.4 (t), 128.1 [2C] (d), 129.1 [2C] (d), 133.9 (s), 134.5 (d), 151.3 (s), 189.8 (s).

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