J. prakt. Chem. 339 (1997) 261–265

Journal für praktische Chemie
Chemiker-Zeitung

Synthesis of 2-Substituted 2-Arylmalonates *via* Tricarbonylchromium Complexes

J. Deutsch, M. Bartoszek, M. Schneider, V. Zabel and H.-J. Niclas

Berlin, Institut für Angewandte Chemie Berlin-Adlershof e. V.

Received October 2nd, 1996, respectively November 24th, 1996

Dedicated to Prof. Dr. Hans Schick on the Occasion of his 60th Birthday

Abstract. Tricarbonylchromium complexes **1** react with monosubstituted malonic acid esters **2** in DMSO at room temperature in the presence of KOtBu to give the complexes **3**. After oxidative demetalation, the appropriate aryl derivatives **4** are obtained in moderate to good overall yields. Diastereoselective arylations of chirally modified malonates such as **5a–c** were studied. The stereoselectivity was highest for the products **6c/6c'** (80:20) with (–)-8-phenylmenthol as alcohol component in the malonate **5**.

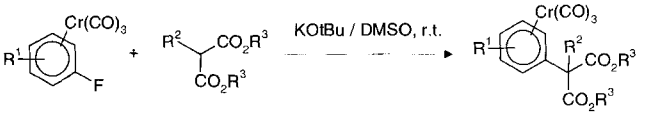
Aryl malonic acid derivatives are important synthons for the preparation of biologically active compounds. Thus, arylmalonic acid esters are used for the synthesis of nonsteroidal antiinflammatory agents and barbiturates [1–4]. Therefore, much attention has been focussed on the synthesis of arylated malonates and their application as intermediates. A literature search showed that the arylation methods most often used for carbanions are nucleophilic displacement reactions, arylations with aryllead triacetate, the use of pentavalent bismuth reagents, arylations with aryl iodonium salts (cf. reviews [5–7]), and arylations via arene complexation with cyclopentadienyliron [8].

Up to now, arylations by means of chromiumtricarbonyl complexes of chloro- and fluorobenzene have been limited to unsubstituted malonates [9, 10]. Reactions of stabilized carbanions of that type (pK_a<18) proceed exclusively as *ipso*-substitution of the haloatom [11].

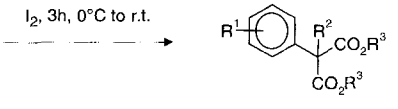
During the course of our studies on the chemistry of nitroactivated aromatics and related compounds, we could show that O/C arylations of cyclic β-diketones succeed with nitroactivated fluoroarenes [12]. In extension of this work, recently we described the arylation of methyl 2-oxo-cycloalkanecarboxylates [13]. We now report the arylation of monosubstituted dialkylmalonates **2** using tricarbonylchromium complexes of fluorobenzene and fluorotoluenes **1** to give compounds **4** *via* **3**.

Results and Discussion

Tricarbonyl(η^6-fluoroarene)chromium(0) complexes **1**, prepared from fluoroarenes and hexacarbonylchromium, were added to **2** under basic conditions. The reaction is carried out in DMSO at room temperature using equimolar amounts of potassium *tert*-butoxide. After 2 hours to 30 days compounds **3a–k** can be isolated (Table 1).



1 **2** **3a - k**



4a - k

3, 4	a	b	c	d	e
R^1	H	2-Me	3-Me	4-Me	H
R^2	Me	Me	Me	Me	i-Pr
R^3	Et	Et	Et	Et	Et

3, 4	f	g	h	i	k
R^1	H	3-Me	H	4-Me	H
R^2	NHCOMe	NHCOMe	OMe	OMe	F
R^3	Et	Et	Me	Me	Et

Table 1 Selected Physical and Spectroscopic Data of Tricarbonyl(η^6-arene)chromium(0) Complexes (**3a–k**)

Prod.	Reac. Time (h)	Molecular Formula[a]) (Mol. wt.)	*m.p.* (°C)	IR; ν (cm^{-1})	^1H NMR (DMSO-d_6) δ[b])	^{13}C NMR (DMSO-d_6); δ[c])	MS; *m/z* (%)
3a	2	$C_{17}H_{18}CrO_7$ (386.30)	yellow oil		5.46–5.52 (m, 2H), 5.84–5.96 (m, 3H)	56.46, 91.05, 96.92, 97.12, 107.10, 233.09 [M-3CO]$^{+\cdot}$	358 (9) [M-CO]$^{+\cdot}$, 302 (100) [M-3CO]$^{+\cdot}$
3b	720	$C_{18}H_{20}CrO_7$ (400.34)	84-86	1950, 1905, 1885 (CO), 1730, 1710 (CO ester)	5.60–5.85 (m, 3H), 5.98–6.04 (m, 1H)	57.30, 88.67, 93.75, 97.39, 98.17, 109.97, 113.09, 234.04	
3c	2	$C_{18}H_{20}CrO_7$ (400.34)	yellow oil	1960, 1875 (CO), 1720 (CO ester)	5.67–5.69 (m, 1H), 5.76–5.86 (m, 3H)	56.64, 92.81, 94.16, 96.54, 96.69, 107.91, 109.12, 233. 93	CI$^+$: 401 (100) [M+H]$^+$
3d	2	$C_{18}H_{20}CrO_7$ (400.34)	yellow oil	1955, 1880, (CO), 1715 (CO ester)	5.46 (d, 2H, J=6.40 Hz), 6.04 (d, 2H, J=6.40 Hz)	56.22, 91.73, 97.69, 104.83, 113.11, 233.87	CI$^+$: 401 (100) [M+H]$^+$
3e	12	$C_{19}H_{22}CrO_7$ (414.37)	yellow oil		5.49–5.93 (m, 5H)	57.91, 91.83, 95.11, 96.35, 107.88, 233.37	FAB$^+$, magic bullet: 415 (5) [M+H]$^+$,330 (100) [M-3CO]$^{+\cdot}$
3f	24	$C_{18}H_{19}CrNO_8$ (429.34)	140–142	3320 (NH), 1965, 1895, 1880 (CO), 1725 (CO ester), 1675 (CO amide)	5.52–5.56 (m, 2H), 5.91–5.98 (m, 3H)	67.18, 90.28, 97.77, 97.94, 103.05, 232.76	FAB$^+$: 430 (52) [M+H]$^+$, 345 (100)
3g	120	$C_{19}H_{21}CrNO_8$ (443.37)	yellow oil		5.25–6.00 (m, 4H)	67.20, 90.26, 91.46, 95.18, 97.63, 104.26, 106.40, 233.04	FAB$^+$, magic bullet: 444 (5) [M+H]$^+$, 387 (24) [M- 2 CO]$^{+\cdot}$ 359 (100) [M-3 CO]$^{+\cdot}$
3h	2	$C_{15}H_{14}CrO_8$ (374.26)	112–114	1960, 1900, 1880 (CO), 1740, 1710 (CO ester)	5.52.5.57 (m, 2H), 5.88–5.92 (m, 1H), 6.00–6.03 (m, 2H)	83.62, 90.62, 95.74, 97.29, 104.76, 232.70	CI$^+$: 392 (2) [M+NH_4]$^+$, 121 (100)
3i	3	$C_{16}H_{16}CrO_8$ (388.29)	106–109	1960, 1900 (CO), 1755, 1730 (CO ester)	5.46 (d, 2H, J=6.80 Hz), 6.08 (d, 2H, J=7.00 Hz)	83.55, 91.31, 96.43, 102.55, 113.22, 233.42	
3k	2	$C_{16}H_{15}CrFO_7$ (390.29)	yellow oil		5.48–5.64 (m, 2H), 5.94–6.37 (m, 3H)	90.94, 91.68 d (J_{FC}=205.0 Hz), 94.02 d (J_{FCCC}=8.2 Hz), 97.18, 100.77 d (J_{FCC}=23.0 Hz),232.27	FAB$^+$, magic bullet: 334 (100) [M-2 CO]$^{+\cdot}$

[a]) Satisfactory microanalyses: C ± 0.15, H ± 0.07, Cr ± 0.13. [b]) Selected values: $CH_{arom.}$. [c]) Selected values: $C_{arom.}$, $C_{quart.}$, $Cr(CO)_3$.

The oxidative demetalation of compounds **3a–k** to give the 2-substituted dialkyl 2-arylmalonates **4a–k** proceeds at 0 to 20 °C in the presence of iodine. The yields of isolated products **4** were strongly influenced by the substituents R^1 in compounds **1** as well as by the substituents R^2 of the malonate **2** (Table 2).

Thus, compared with the tricarbonyl(η^6-3(or 4)-fluorotoluene)chromium(0) complexes, the arylation of diethyl 2-methylmalonate by the appropriate complex of 2-fluorotoluene is delayed due to steric hindrance. Within the 2-substituted malonates, diethyl 2-acetylamino- and diethyl 2-*i*-propylmalonate showed reduced reactivity. Under the same reaction conditions, the arylation of diethyl 2-*tert*-butylmalonate does not succeed.

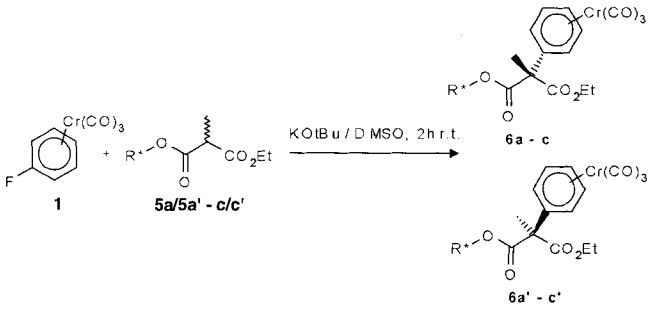
Furthermore, we have studied the diastereoselectivity of the arylation of chirally modified malonates by tricarbonyl(η^6-fluorobenzene)chromium(0) (Table 3). Using ethyl (*R*)-1-phenylethyl 2-methylmalonate **5a**, the diastereomer ratio is not affected. Ethyl (1*R*, 2*S*, 5*R*)-2-*i*-propyl-5-methyl-cyclohexyl 2-methylmalonate **5b** leads only to 10% *d.e.*, followed by **5c** affording the arylated products **6c/6c'** in 60% *d.e.* The structural assignment of the major diastereomers remains uncertain, but it is based on analogous assumptions. Thus, comparable results were obtained when methyl (1*R*, 2*S*, 5*R*)-5-methyl-2-(1-methyl-1-phenyl-ethyl)cyclohexyl 2-methylmalonate is fluorinated with 1-fluoro-2,4,6-trimethylpyridiniumtriflate (58% *d.e.*) [22].

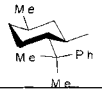
The structures of the reaction products **3** and **4** were established by mass spectra, IR, ^1H and ^{13}C NMR spectra. The molecular structure of compound **3f** (Figure 1) is in good agreement with the spectroscopic data.

Table 2 2-Substituted Dialkyl 2-Arylmalonates (Compounds **4a–k**)

Prod. [Lit.]	Overall Yield [a] (%)	Molecular Formula [b] (Mol. wt.)	*b.p.*/mbar δ [c]) (°C) [c]) or *m.p.* (°C)	^{1}H NMR (DMSO-d_6); δ [e])	^{13}C NMR (DMSO-d_6); δ [f])	MS; *m/z* (%)
4a [14]	84	$C_{14}H_{18}O_4$ (250.28)	80–90/0.15	7.27 (m, 5H)	58.31, 127.26, 127.38, 128.02, 138.28	250 (11) $[M]^{+\cdot}$, 103 (100)
4b [15]	58	$C_{15}H_{20}O_4$ (264.31)	115–125/0.19	7.09–7.12 (m, 3H), 7.21–7.26 (m, 1H)	58.96, 125.92, 126.79, 127.47, 132.03, 136.65, 137.90	264 (1) $[M]^{+\cdot}$, 117 (100)
4c	88	$C_{15}H_{20}O_4$ (264.31)	90–110/0.15	7.09–7.13 (m, 3H), 7.22–7.27 (m, 1H)	58.28, 124.58, 127.90, 128.06, 128.18, 137.28, 138.44	264 (7) $[M]^{+\cdot}$, 117 (100)
4d [8]	84	$C_{15}H_{20}O_4$ (264.31)	95–115/0.17	7.14–7.22 (m, 4H)	57.98, 127.31, 128.73, 135.48, 136.79	264 (9) $[M]^{+\cdot}$, 117 (100)
4e [16]	45	$C_{16}H_{22}O_4$ (278.34)	95–105/0.08	7.26–7.38 (m, 5H)	66.38, 127.24, 127.81, 128.54, 135.99	278 (3) $[M]^{+\cdot}$, 91 (100)
4f [17,18]	55	$C_{15}H_{19}NO_5$ (293.31)	68–71 [d])	7.33–7.39 (m, 3H), 7.45–7.49 (m, 2H)	68.56, 127.40, 127.83, 128.14, 134.99	FAB$^+$, magic bullet: 294 (100) $[M+H]^+$
4g	51	$C_{16}H_{21}NO_5$ (307.34)	86–89 [d])	7.15–7.17 (m, 1H), 7.24–7.27 (m, 3H)	68.50, 124.49, 127.75, 127.86, 128.76, 135.01, 136.87	307 (100) $[M]^{+\cdot}$
4h [19]	83	$C_{12}H_{14}O_5$ (238.23)	115–125/0.37	7.37–7.43 (m, 5H)	85.91, 127.00, 128.15, 128.71, 134.98	238 (1) $[M]^{+\cdot}$ 179 (100)
4i	79	$C_{13}H_{16}O_5$ (252.26)	[d])	7.20 (d, 2H; *J*=8.2 Hz), 7.33 (d, 2H; *J*=8.4 Hz)	85.88, 127.12, 128.86, 132.21, 138.33	252 (1) $[M]^{+\cdot}$, 119 (100)
4k [20, 21]	79	$C_{13}H_{15}FO_4$ (254.25)	120-140/1	7.44–7.47 (m, 5H)	94.00 (d, J_{FC}=197.1 Hz), 125.64, 128.55, 129.71, 132.95 (d, J_{FCC}=21.8 Hz)	FAB$^+$, magic bullet: 255(100) $[M+H]^+$

[a]) Overall yields of pure, isolated products; purity confirmed by ^{1}H NMR. [b]) Satisfactory microanalyses: C±0.21, H±0.13.
[c]) B. p. were determined using an air-bath. [d]) After flash-chromatography, toluene/ ethyl acetate 10:1.
[e]) Selected values: $CH_{arom.}$. [f]) Selected values: $C_{quart.}$, $C_{arom.}$



5,6	R*	Diastereomeric Ratio of **6**
a/a'		50 : 50
b/b'		55 : 45
c/c'		80 : 20

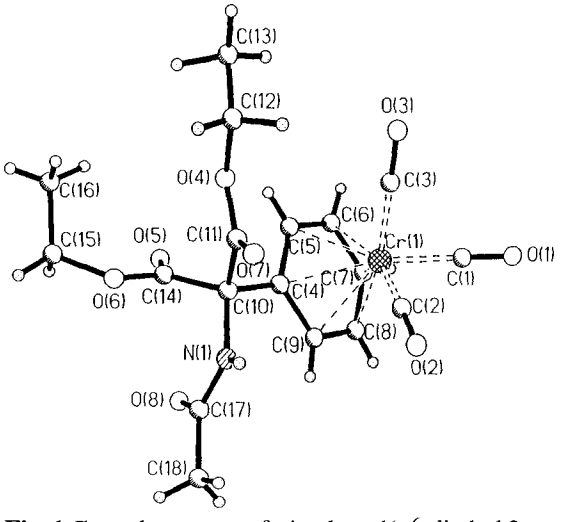


Fig. 1 Crystal structure of tricarbonyl(η^6-diethyl 2-acetamido-2-phenylmalonate) chromium(0) **3f**

This work was supported by the Federal Ministry of Education, Science, Research and Technology of the FRG and the Berlin Senate Department for Science, Research and Culture (Project: 03C 3005). Furthermore, we thank Dr. B. Costisella for NMR spectra and Dr. A. Kunath for HPLC investigations.

Table 3 Chirally Modified Compounds **5a/a'–c/c'** and Diastereomeric Mixtures of the Arylation Products **6a/a'–c/c'**

Prod.	Yield (%)	Molecular Formula (Mol. Wt.)	^{1}H NMR (DMSO-d_6) [c]; δ [d]	^{13}C NMR (DMSO-d_6); δ [d][e]	MS (LSIMS, magic bullet); *m/z* (%)
5a/5a'	79 [a]	$C_{14}H_{18}O_4$ (250.28)	1.12/1,16 (t/t, 3H, $\underline{CH_3}CH_2O$, *J*=7.04/7.10 Hz), 1.28 (d, 3H, $\underline{CH_3}CH(CO)CO$, *J*=7.12 Hz), 3.60/3.61 (q/q, 1H, $CH_3\underline{CH}(CO)CO$, *J*=7.19/7.17 Hz), 4.10/4.12, (q/q, 2H, $CH_3\underline{CH_2}O$, *J*=7.14, 7.13 Hz)	168.84/168.95 (CO), 169.55/169.60 (CO)	251 (100) $[M+H]^+$
5b/5b'	83 [a]	$C_{16}H_{28}O_4$ (284.38)	1.17/1.18 (t/t, 3H, $\underline{CH_3}CH_2O$, *J*=7.15/7.05 Hz), 1.25/1.26 (d/d, 3H, $\underline{CH_3}CH(CO)CO$ *J*=7.10/7.10 Hz), 3.51/3.53 (q/q, 1H, $CH_3\underline{CH}(CO)CO$, *J*=7.17/7.13 Hz), 4.02–4.16 (m, 2H, $CH_3\underline{CH_2}O$)	169.13/169.18 (CO), 169.53/169.56 (CO)	285 (100) $[M+H]^+$
5c/5c'	92 [a]	$C_{22}H_{32}O_4$ (360.48)	1.08/1.09 (d/d, 3H, $\underline{CH_3}CH(CO)CO$, *J*=7.11/7.11 Hz), 1.12/1.19 (t/t, 3H, $\underline{CH_3}CH_2O$, *J*=7.10/7.10 Hz),2.59/3.13 (q/q, 1H, $CH_3\underline{CH}(CO)CO$, *J*=7.11/7.10 Hz), 3.99–4.13 (m, 2H, $CH_3\underline{CH_2}O$)	168.35/168.96 (CO) 69.29/169.49 (CO)	361 (26) $[M+H]^+$
6a/6a'	91[b]	$C_{23}H_{22}CrO_7$ (462.41)	4.10–4.20 (m, 2H, $CH_3\underline{CH_2}O$), 5.53–6.01 (m, 5H, C_6H_5-$Cr(CO)_3$)	57.67/57.81 ($C_{quart.}$), 92.44/92.52, 97.52/97.77, 98.20/98.30, 108.48/108.60 ($C_{arom.}$), 234.36 ($Cr(CO)_3$)	378 (46) $[M-3CO]^{+\cdot}$
6b/6b'	88 [b]	$C_{25}H_{32}CrO_7$ (496.51)	4.15/4.21 (q/q, 2H, $CH_3\underline{CH_2}O$), 5.54–5.98 (m, 5H, C_6H_5-$Cr(CO)_3$)	56.47/56.59 ($C_{quart.}$), 91.42/91.47, 95.78/95.95, 96.55, 96.64/96.83, 107.70/107.86 ($C_{arom.}$), 233.09/233.15 ($Cr(CO)_3$)	412 (100) $[M-3CO]^{+\cdot}$
6c/6c'	68	$C_{31}H_{36}CrO_7$ (572.60)	1.18/1.20 (t/t, 3H, $\underline{CH_3}CH_2O$), 4.10/4.16 (q/q, 2H, $CH_3\underline{CH_2}O$), 5.48–5.56 (m, 2H,C_6H_5-$Cr(CO)_3$), 5.84–5.95 (m, 3H, C_6H_5-$Cr(CO)_3$) [d]	56.55/56.71 ($C_{quart.}$), 91.14/91.28,95.81,96.16/ 96.78, 97.41/97.56, 107.31/107.65 ($C_{arom.}$), 233.11/233.16 ($Cr(CO)_3$)	488 (22) $[M-3\ CO]^{+\cdot}$

[a] Yields are related to the alcoholysis of methylmalonic acid ethyl ester chloride. [b] Crude products. [c] Compounds **6a/6a'–6c/6c'**: signals are broadened; bad resolution. [d] Selected values. [e] The δ-values of the major diastereomer are underlined.

Experimental

Melting points were determined with a Boëtius apparatus and are corrected. ^{1}H NMR spectra were measured at 300 MHz on a Varian Unity 300 or at 500 MHz on a Varian Unity 500 in DMSO-d_6 with TMS as internal standard. ^{13}C NMR spectra were obtained on a Varian Gemini 300 spectrometer in DMSO-d_6; internal standard: HMDS (δ: 1.9ppm). Mass spectra were carried out on an Autospec (Fisons). IR spectra were recorded on a Specord 75 (Carl Zeiss, Jena). Elemental analyses were performed on a Elemental Analyzer 1106 (Carlo Erba); chromium was determined by means of ICP-OES using an Optima 3000 XL (Perkin-Elmer). Flash-chromatography was carried out using silica gel (Kieselgel 60 (Merck), 230–400 mesh).

The fluoroarenes and the 2-substituted dialkylmalonates were purchased from Aldrich and used without further purification. Compounds **1** were prepared according to [23–25], and compound **2e** according to [26]. The preparation of the chirally modified malonates **5a–c** was carried out as described for the synthesis of ethyl *tert*-butyl 2-methylmalonate from diethyl 2-methylmalonate [27]. The products obtained were purified by flash-chromatography (eluent: toluene/ethyl acetate 5/1). Compounds **5a–c** were isolated as diastereomeric mixtures (colourless liquids, 50:50; determined by ^{1}H NMR spectroscopy).

Dialkyl Arylmalonates (4a–k); General Procedure:

Arylation Steps (**1+2 → 3**) *and* (**1+5→6**)

To a solution of potassium *tert*-butoxide (1.12 g, 0.01 mol) in abs. DMSO (4 mL), 0.01 mol of compound **2** is added dropwise. After 15 min 0.01 mol of the appropriate tricarbonyl(η^6-fluoroarene)chromium(0) is added, the mixture stirred at *r.t.* in a closed flask under exclusion of light (reaction

times are given in Table 1). The beginning of reaction is indicated by the precipitation of KF.

After completion (monitored by TLC), ethyl acetate (75 mL) is added, the organic layer is washed with brine (3×75 mL), dried over Na_2SO_4, filtrated, and the solvent removed under reduced pressure to afford the crude products **3.** Compounds **3b, 3f, 3h,** and **3i** are recrystallized from diethyl ether, compound **3e** is subjected to flash-chromatography (eluent: toluene). Due to easy oxidation by air, the liquid complexes **3a**, **3c**, **3d**, **3e**, **3g**, and **3k** are characterized as crude products. The diastereomeric mixtures **6a/6a'** and **6b/6b'** are also characterized as crude products. **6c/6c'** is purified by flash-chromatography as described for **3e**. Compounds **6** are viscous yellow oils.

Decomplexation Step (**3** → **4**)
Under vigorous stirring and cooling with ice-water, a solution of iodine (3.8 g, 0.015 mol) in diethyl ether (25 mL) is added to the the ethyl acetate reaction mixture from the arylation step within 30 min and stirring continued for 2.5 h at *r.t.*. Compound **3e,** purified by flash-chromatography, is dissolved in 75 mL of ethyl acetate and demetalated with an equimolar amount of iodine as described above.

Then the organic layer is washed successively with water (1×100 mL, 2×50 mL), aqueous sodium bisulfite (5%, 2×25 mL), and again with water (2×25 mL). The organic phase is then dried over Na_2SO_4 and concentrated *in vacuo* to give the crude products **4** which are purified by Kugelrohr distillation (compounds **4a–e**, **4h, 4k**) or by flash-chromatography (**4f**, **4g, 4i**).

X-Ray Structure Determination of Tricarbonyl(η^6-diethyl 2-acetamido-2-phenylmalonate)chromium(0) (3f) [1)]

The structure was investigated on an ENRAF-NONIUS CAD4 diffractometer at room temperature employing graphite-monochromatized MoKα radiation (λ = 0.71073 Å) and $\omega/2\theta$ scans. The data were corrected for Lorentz and polarization effects. The structure was solved with direct methods (SHELX-86 [28]) and anisotropic refinement (SHELX-93 [29]) of the non-hydrogen atoms.

[1)] Lists of structure factors, anisotropic thermal parameters, atom coordinates and table of bond distances and angles may be obtained through Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany, referring to CSD#ld, the authors, and the bibliographical data.

References

[1] D. Lednicer, L. A. Mitcher: The Organic Chemistry of Drug Synthesis;Wiley: New York 1977; Vol. 1, p. 85; 1980, Vol. 2, p. 63

[2] R. Meyer, M. Rollet: Barbituric Acid and Barbiturates, in: Kirk-Othmer Encyclopedia of Chemical Technology, Wiley, New York 2nd Ed., 1964, p. 60

[3] D. R. Wesson, D. E. Smith: Barbiturates, Their Use, Misuse and Abuse, Human Science Press, New York 1977

[4] W. J. Doran: Barbituric Acid Hypnotics, in: Medicinal Chemistry, eds. F F. Blicke and H. Cox, Wiley, New York 1959, Vol. 4

[5] F. Terrier: Nucleophilic Aromatic Displacement: The Influence of the Nitro Group; VCH Publishers, Inc.: New York, Weinheim, Cambridge 1991

[6] J.–P. Finet, Chem. Rev. **89** (1989) 1487

[7] R. A. Abramovich, D. H. R. Barton, J.–P. Finet, Tetrahedron **44** (1988) 3039

[8] A. Piorko, A. S. Abd–El–Aziz, C. C. Lee. R. G. Sutherland, J. Chem. Soc., Perkin Trans. I **1989**, 469

[9] M. F. Semmelhack, H. T. Hall, J. Am. Chem. Soc. **96** (1974) 7091

[10] C. Baldoli, P. Del Buttero, E. Licandro, S. Maiorana, Gazz. Chim. Ital. **118** (1988) 409

[11] M. F. Semmelhack, in: Comprehensive Organic Syntheses, Vol. 4, Trost, B. M.; Fleming, I., Eds.; Pergamon Press: Oxford 1991, p. 517

[12] J. Deutsch, H.–J. Niclas, J. Prakt. Chem. **335** (1993) 69

[13] J. Deutsch, M. Bartoszek, M. Schneider, V. Zabel, H.–J. Niclas, J. Prakt. Chem. **339** (1997) 171

[14] J. M. Domagala, R. D. Bach, J. Org. Chem. **44** (1979) 2429

[15] S. Gosh, S. N. Pardo, R. G. Salomon, J. Org. Chem. **47** (1982) 4692

[16] J. H. Clark, J. M. Miller, J. Chem. Soc., Perkin Trans. I **1977**, 1743

[17] F. M. Beringer, P. S. Forgione, J. Org. Chem. **28** (1963) 714

[18] T. Sheradsky, Z. Nir, Tetrahedron Lett. **1969**, 77

[19] S. Lee, N. J. Cooper, J. Am. Chem. Soc. **112** (1990) 9419

[20] R. E. Banks, R. A. Du Boisson, W. D. Morton, E. Tsiliopoulos, J. Chem. Soc., Perkin Trans. I **1988**, 2805

[21] Z.–Q. Xu, D. D. DesMarteau, Y. Gotoh, J. Fluorine Chem. **58** (1992) 71

[22] M. Ihara, T. Kai, N. Taniguchi, F. Fukumoto, J. Chem. Soc., Perkin Trans. I **1990**, 2357

[23] F. Rose–Munch, E. Rose, A. Semra, L. Mignon, J. Garcia–Oricain, C. Knobler, J. Organomet. Chem. **363** (1989) 297

[24] C. A. L. Mahaffy, P. L Pauson, Inorg. Synth. **28** (1990) 136

[25] F. Rose–Munch, K. Aniss, E. Rose, J. Vaisserman, J. Organomet. Chem.**1991**, 415

[26] G. A. Holmberg, Acta Chem. Scand. **12** (1958) 229

[27] H. Aebli, C. A. Grob, Helv. Chim. Acta **40** (1957) 2185

[28] G. M. Sheldrick, SHELX-86, Program for Solution of Crystal Structures from Diffraction Data, Universität Göttingen 1986

[29] G. M. Sheldrick, SHELX-93, Program for Refinement of Crystal Structures, Universität Göttingen 1993

Address for correspondence:
Prof. Dr. Hans-Joachim Niclas
Institut für Angewandte Chemie Berlin-Adlershof e.V.
Rudower Chaussee 5
D-12484 Berlin