# ON THE STEREOSELECTIVITY OF THE (–)-DIMENTHYL MALONATE ADDITION TO α,β-UNSATURATED KETONES

Lubomir SEBO[a], Juraj ALFOLDI[b], Grety RIHS[c] and Stefan TOMA[a1,*]

[a] *Department of Organic Chemistry, Comenius University, 842 15 Bratislava, Slovak Republic; e-mail: [1] toma@fns.uniba.sk*

[b] *Institute of Chemistry, Slovak Academy of Sciences, 842 15 Bratislava, Slovak Republic; e-mail: chempati@savba.sk*

[c] *CIBA-GEIGY Co., CH-4002 Basel, Switzerland*

Received March 18, 1996
Accepted September 23, 1996

The Michael addition of (–)-dimenthyl malonate to eight α, β-unsaturated ketones has been studied. The ratio of diastereomers was calculated on the basis of the $^1$H NMR spectra of the crude reaction products. The diastereomer excess varied from 10 to 50%, depending on the structure of the starting enone. The pure diastereomer produced by addition of (–)-dimenthyl malonate to 2-benzylidene-1,4-indandione was isolated by repeated crystallization. X-ray analysis has shown that the isomer is (–)-dimenthyl (*R*)-2-[1-(1,3-dioxoindan-2-yl)-1-phenylmethyl]malonate (**5a**). The predominating diastereomers of (–)-dimenthyl(3-ferrocenyl-3-oxophenylpropyl)malonate (**1a**) and (–)-dimenthyl-2-(1-(1,3-dioxo[3]ferrocenophan-2-yl)-1-phenyl malonate (**6a**) were also isolated in pure state by careful crystallization.
**Key words:** Michael addition; (–)-Dimenthyl malonate; Enones.

In our previous communications[1,2] we have described the stereoselective Michael addition of achiral methylene active compounds (e.g. dimethyl malonate and malononitrile) to chiral tricarbonylchromium complexes of chalcones. One report[3] describes an unsuccessful attempt to perform the Michael addition of (–)-dimenthyl malonate to 3-methyl-2-octen-1-one.

In the present study we examine diastereoselectivity of the (–)-dimenthyl malonate** addition to some reactive enones.

## RESULTS AND DISCUSSION

Our study of Michael addition of (–)-dimenthyl malonate started with ferrocenyl enones **1** and **2** as we supposed that the resulting (coloured) diastereomers should be

* The author to whom correspondence should be addressed.

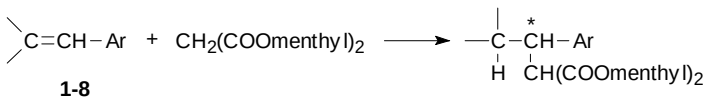
**(–)-Menthyl instead of (1*R*,2*S*,5*R*)-(–)-menthyl is used throughout.

easily separable by chromatography. For the *p*-methoxyphenyl derivative **2** it was assumed that the diastereomers could be distinguished by different chemical shifts of the methoxy group. The attempted chromatographic separation, however, failed and in all experiments the diastereomer excess (d.e.) was determined using the $^1$H NMR spectra.

As seen from Table I, the Michael addition of (–)-dimenthyl malonate to the ferrocenyl analogue **1** was satisfactory. The diastereomer ratio was determined from chemical shifts of the unsubstituted cyclopentadienyl (Cp) rings (singlets) in the diastereomers. Unfortunately, the methoxy derivative of chalcone **2** was unreactive and no product was detected by TLC even when the reaction was carried out at elevated temperature, with sodium methoxide or piperidine as catalysts.

In our further experiments we replaced the ferrocenyl moiety by $\eta^6$-phenyltricarbonylchromium which is a strong acceptor[4] and should activate the enones **3** and **4** in the addition. Both the complexes **3** and **4** gave the desired Michael adducts (Table I) in high yields. Unfortunately, the 300 MHz $^1$H NMR spectra of the products were rather complex and no well separated signals of their $CH(COO)_2$, CHPh or CHO protons were obtained. For this reason, the diastereomer excess of **4a** was estimated (50%) from the $OCH_3$ chemical shifts.

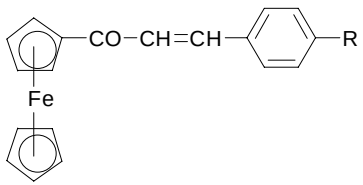
TABLE I
Results of Michael addition of (–)-dimenthyl malonate to enones **1–8**



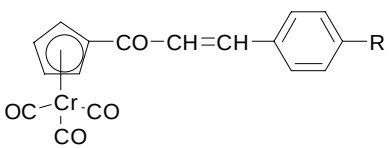

| Enone | *T*, °C | Time | Product | Yield, % | d.e., % |
|---|---|---|---|---|---|
| **1** | 20 | 5.5 d | **1a** | 61 | 25 |
| **2** | 60 | 4 h | **2a** | 0 | – |
| **3** | 20 | 3.5 h | **3a** | 46 | [a] |
| **3** | –20 | 13 h | **3a** | 85 | [a] |
| **4** | 20 | 26 h | **4a** | 98 | 50 |
| **5** | 20 | 5 h | **5a** | 97 | 34 |
| **5** | –20 | 5 d | **5a** | 95 | 49 |
| **6** | 20 | 18 h | **6a** | 84 | 20 |
| **7** | 80 | 4 h | **7a** | 72 | 10 |
| **8** | 20 | 18 h | **8a** | 74 | 50 |

[a] The ratio of diastereomers could not be determined on the basis of 300 MHz $^1$H NMR spectra.

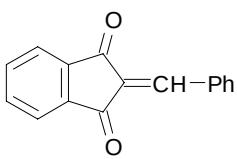
We decided to examine the reaction of enones derived from cyclic 1,3-dicarbonyl compounds, i.e. derivatives of 1,3-indandione **5** and [3]ferrocenophane-1,3-dione **6**. Both reacted easily and the products were isolated in good yields. In both cases, the diastereomers were distinguished by well separated doublets of the $CH(COO)_2$ and $CH(CO)_2$ groups: the reaction of the ferrocenophane derivative **6a** resulted in 20% d.e. and that of the 1,3-indandione derivative **5a** in 34% d.e. To achieve higher d.e., compound **5** was reacted with (–)-dimenthyl malonate at –20 °C. This experiment gave 49% d.e. and crystallization of the product (**5a**) enriched the crystals in the major diastereomer. The $^1$H NMR spectrum exhibited doublets at 3.74 and 4.79 ppm (minor isomer) and at 3.66 and 4.75 ppm (major isomer) due to the $CH(COO)_2$ and $CH(CO)_2$ groups, respectively. Three crystallizations from ethyl acetate–isohexane produced pure major diastereomer **5a**.



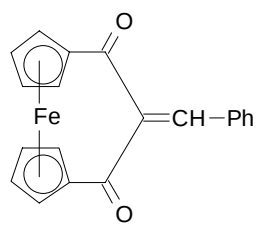

| | R |
|---|---|
| **1** | H |
| **2** | $OCH_3$ |




| | R |
|---|---|
| **3** | H |
| **4** | $OCH_3$ |




**5**




**6**

X-Ray analysis of the diastereomer **5a** allowed us to assign the absolute configuration *R* at the newly formed asymmetric carbon atom (see Fig. 1). The key crystallographic parameters are given in Tables II–IV.

Similar diastereoselectivity has been described recently[5] for the Michael addition of (–)-menthyl cyanoacetate to 2-cyano-1,3-diphenyl-2-propen-1-one.

Some reactions of tricarbonylchromium complexes are more selective than the same reactions on the corresponding free ligands[6,7]. We therefore prepared tricarbonylchro-

TABLE II
Crystal data and parameters for compound **5a**

| | |
|---|---|
| Crystal size, mm | 0.51 × 0.19 × 0.08 |
| Crystal system | orthorhombic |
| Space group | $P2_12_12_1$ |
| *a*, *b*, *c*, Å | 8.828(1); 19.057(3); 21.913(3) |
| *V*, Å$^3$ | 3686(1) |
| *Z* | 4 |
| $D_{calc}$, g/cm$^3$ | 1.108 |
| Radiation, Å | 1.5418(CuKα) |
| Temperature, °C | 23 |
| θ range for data collection | 3–75 |
| Number of variables | 406 |
| Number of reflections measured | 4 080 |
| Number of reflexions with $I > 3\sigma(I)$ | 1 870 |
| *R*, *wR* | 0.040, 0.040 |
| Weighting scheme | $w = 1/\sigma^2(\lvert F_o \rvert)$ |

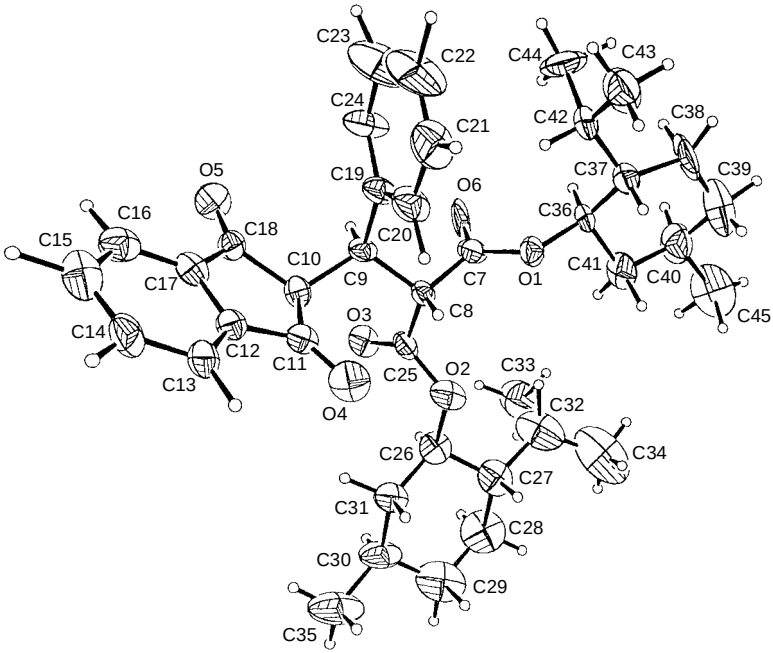
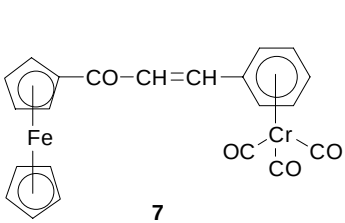
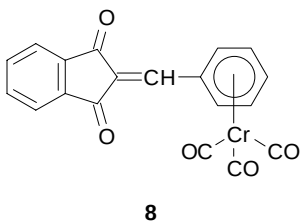



FIG. 1
ORTEP plot of the molecule **5a**

mium analogues of enones **1** and **5**, i.e., complexes **7** and **8**, and examined their reactivity. Interestingly, 50% d.e. was achieved for the addition of (–)-dimenthyl malonate to **8** (Table I) even when the reaction was carried out at 20 °C (34% d.e. was found for the addition to the free ligand **5**). We conclude that one side of the enone is flanked by the large $Cr(CO)_3$ moiety whereas the other is easily accessible to the attack of the bulky nucleophile. The reaction of **7** with (–)-dimenthyl malonate was sluggish and an elevated temperature (80 °C) was required to achieve a reasonable yield. The low facial selectivity (10% d.e.) might be explained by dissonant interaction of both the bulky $Cr(CO)_3$ and FeCp groups. This explanation also accounts for the low reactivity of the enone **7**.




**7**




**8**

## EXPERIMENTAL

$^1$H NMR spectra of solutions in deuteriochloroform were measured using TESLA BS 487 80 MHz, Bruker AM 300 MHz or Bruker AMX 500 MHz instruments. Tetramethylsilane was used as the internal standard. Melting points were determined on a Kofler hot stage and are uncorrected. The starting enones were prepared using described procedures, **1** and **2** (ref.[8]), **3** and **4** (ref.[9]), **5** (ref.[10]) and **6** (ref.[11]). The C=C double bond in enones **1–4** and **7** has the *E* configuration. (–)-Dimenthyl malonate was prepared as described in ref.[3].

1-Ferrocenyl-3-($\eta^6$-phenyltricarbonylchromium)propenone (**7**)

Acetylferrocene (360 mg, 1.75 mmol) and $\eta^6$-benzenetricarbonylchromium (423 mg, 1.75 mmol) were dissolved in methanol (5 ml). Sodium hydroxide (50% aqueous solution, 0.5 ml) was added and the reaction mixture was left to stand overnight at room temperature. The violet crystals of the product (468 mg, 66%) were separated and crystallized from ethyl acetate, m.p. 182–184 °C. For $C_{22}H_{16}CrFeO_4$ (452.2) calculated: 58.43% C, 3.57% H; found: 58.74% C, 3.48% H. $^1$H NMR spectrum (80 MHz): 4.23 s, 5 H (Cp); 4.62 t, 2 H ($H_\beta$-Cp); 4.89 t, 2 H ($H_\alpha$-Cp); 5.42 m, 3 H ($C_6H_5Cr(CO)_3$); 5.68 m, 2 H ($C_6H_5Cr(CO)_3$); 6.90 d, 1 H, $J$ = 15.6 Hz (CH); 7.37 d, 1 H, $J$ = 15.6 Hz (CH).

2-($\eta^6$-Phenyltricarbonylchromium)methylene-1,3-indandione (**8**)

1,3-Indandione (230 mg, 0.9 mmol) was dissolved in methanol (7 ml) and a solution of $\eta^6$-benzaldehydetricarbonylchromium (423 mg, 1 mmol) in methanol (3 ml) was added. A small amount of piperidine (0.2 ml) was added and the reaction mixture was left to stand for 1 h at room temperature and then overnight at –28 °C. The black crystals (340 mg) were filtered off and the filtrate was evaporated to dryness. Chromatography of the residue on an $SiO_2$ column in ethyl acetate–isohexane gave

TABLE III
Atomic coordinates for compound **5a**

| Atom | *x/a* | *y/b* | *z/c* | $U_{iso}$ |
|---|---|---|---|---|
| O1 | –0.133(1) | –0.5458(5) | –0.6446(4) | 0.0677 |
| O2 | 0.132(1) | –0.5240(6) | –0.5272(5) | 0.0746 |
| O3 | 0.325(1) | –0.5669(6) | –0.5819(5) | 0.0734 |
| O4 | 0.062(1) | –0.7185(7) | –0.4939(5) | 0.0990 |
| O5 | 0.364(1) | –0.7882(6) | –0.6607(5) | 0.0932 |
| O6 | 0.080(1) | –0.5432(9) | –0.6944(6) | 0.1061 |
| C7 | 0.011(2) | –0.563(1) | –0.6518(7) | 0.0728 |
| C8 | 0.072(1) | –0.6080(8) | –0.6020(6) | 0.0547 |
| C9 | 0.143(2) | –0.6752(9) | –0.6296(6) | 0.0579 |
| C10 | 0.223(2) | –0.7226(8) | –0.5839(7) | 0.627 |
| C11 | 0.139(2) | –0.751(1) | –0.5285(7) | 0.0661 |
| C12 | 0.174(2) | –0.827(1) | –0.5244(9) | 0.0622 |
| C13 | 0.128(2) | –0.875(1) | –0.4818(8) | 0.0772 |
| C14 | 0.173(2) | –0.942(1) | –0.487(1) | 0.0946 |
| C15 | 0.266(2) | –0.963(1) | –0.535(1) | 0.0972 |
| C16 | 0.311(2) | –0.913(1) | –0.5783(7) | 0.0885 |
| C17 | 0.262(2) | –0.846(1) | –0.5731(8) | 0.0623 |
| C18 | 0.294(2) | –0.787(1) | –0.6142(7) | 0.0641 |
| C19 | 0.010(2) | –0.7188(9) | –0.6615(8) | 0.0725 |
| C20 | –0.118(2) | –0.739(1) | –0.6306(7) | 0.0984 |
| C21 | –0.233(2) | –0.775(1) | –0.660(1) | 0.1261 |
| C22 | –0.208(4) | –0.790(2) | –0.722(2) | 0.1496 |
| C23 | –0.078(3) | –0.774(2) | –0.752(2) | 0.1649 |
| C24 | 0.029(2) | –0.735(1) | –0.721(1) | 0.1025 |
| C25 | 0.194(2) | –0.5660(9) | –0.5702(8) | 0.0669 |
| C26 | 0.233(2) | –0.485(1) | –0.4893(8) | 0.0765 |
| C27 | 0.158(2) | –0.419(1) | –0.486(1) | 0.1085 |
| C28 | 0.257(3) | –0.378(1) | –0.425(1) | 0.1264 |
| C29 | 0.308(3) | –0.422(2) | –0.372(1) | 0.1352 |
| C30 | 0.308(2) | –0.490(1) | –0.3907(9) | 0.1042 |

TABLE III
(*Continued*)

| Atom | *x/a* | *y/b* | *z/c* | $U_{iso}$ |
|---|---|---|---|---|
| C31 | 0.285(2) | –0.528(1) | –0.4361(8) | 0.0888 |
| C32 | 0.088(4) | –0.377(1) | –0.520(2) | 0.1577 |
| C33 | 0.196(5) | –0.348(2) | –0.564(1) | 0.1990 |
| C34 | –0.009(4) | –0.316(2) | –0.502(2) | 0.2367 |
| C35 | 0.425(2) | –0.534(1) | –0.3371(9) | 0.1327 |
| C36 | –0.206(2) | –0.497(1) | –0.6874(7) | 0.0706 |
| C37 | –0.360(2) | –0.526(1) | –0.7040(8) | 0.0885 |
| C38 | –0.451(3) | –0.472(2) | –0.736(1) | 0.1177 |
| C39 | –0.459(4) | –0.404(2) | –0.707(2) | 0.1383 |
| C40 | –0.303(3) | –0.372(1) | –0.692(1) | 0.1351 |
| C41 | –0.215(2) | –0.426(1) | –0.6543(8) | 0.0935 |
| C42 | –0.347(2) | –0.597(1) | –0.7350(9) | 0.0930 |
| C43 | –0.495(2) | –0.639(1) | –0.7339(9) | 0.1362 |
| C44 | –0.289(2) | –0.598(1) | –0.8001(8) | 0.1327 |
| C45 | –0.326(3) | –0.305(1) | –0.659(1) | 0.1584 |

another portion (80 mg) of the product. Total yield 420 mg (67%) of the product **8**, m.p. >260 °C (decomp.). For $C_{19}H_{10}CrO_5$ (370.3) calculated: 61.68% C, 2.72% H; found: 61.94% C, 2.91% H. $^1$H NMR spectrum (80 MHz): 5.33 t, 2 H (*m*-$C_6H_5Cr(CO)_3$); 5.75 t, 1 H (*p*-$C_6H_5Cr(CO)_3$); 6.68 d, 2 H (*o*-$C_6H_5Cr(CO)_3$); 7.28 s, 1 H (CH); 7.76–8.07 m, 4 H ($C_6H_4$).

Addition of (–)-Dimenthyl Malonate to Enones **1–8**. General Procedure

(–)-Dimenthyl malonate (0.11 g, 0.3 mmol) and the enone (0.3 mmol) were dissolved in toluene (3 ml). Potassium carbonate (0.042 g, 3 mmol) and 18-crown-6 (0.12 g, 0.45 mmol) in toluene (2 ml) were added and the mixture was allowed to stand at the temperature specified in Table I. The course of the reaction was monitored by TLC. When the reaction was over, the reaction mixture was poured into ice water acidified with acetic acid, and the product was extracted with dichloromethane. The extract was washed with saturated NaCl solution and dried over anhydrous $MgSO_4$. The solution was filtered, the solvent evaporated and the residue chromatographed on an $SiO_2$ column in ethyl acetate–isohexane (9.5 : 0.5). The products (mixture of diastereomers) were eluted first and the ratio of diastereomers was determined by $^1$H NMR spectrum (300 MHz) of the products (vide infra).

In cases when attempts to separate the diastereomers by crystallization failed, a broad m.p. is given. The reaction conditions and results are given in Table I.

*(–)-Dimenthyl (3-ferrocenyl-3-oxo-1-phenylpropyl)malonate* (**1a**). For $C_{42}H_{56}FeO_5$ (696.7) calculated: 72.40% C, 8.10% H; found: 72.64% C, 8.18% H. Crystallization from ethyl acetate–isohexane

afforded pure major isomer, m.p. 159–160 °C. $^1$H NMR spectrum of the mixture of diastereomers: 0.50–2.00 m, 36 H (menthyl); 3.00–3.28 m, 2 H ($CH_2CO$); 3.85–3.90 dd, 1 H ($CH(COO)_2$); 4.12–4.25 m, 1 H (CHPh); 4.45–4.55 m, 1 H (CHO); 4.71–4.82 m, 1 H (CHO); 4.42 t, 2 H ($H_\beta$-Cp); 4.69 t, 2 H ($H_\alpha$-Cp); 7.15–7.40 m, 5 H ($C_6H_5$). Major isomer: 3.95 s, 3.2 H (Cp); minor isomer 3.90 s, 1.8 H (Cp).

*(–)-Dimenthyl (3-oxo-1-phenyl-3-(η$^6$-phenyltricarbonylchromium)propyl)malonate* (**3a**). For $C_{41}H_{52}CrO_8$ (724.8) calculated: 67.94% C, 7.23% H; found: 68.11% C, 7.12% H. M.p. 138–155 °C. $^1$H NMR spectrum of mixture of diastereomers: 0.40–2.00 m, 36 H (menthyl); 3.20–3.30 m, 2 H ($CH_2CO$); 3.79–3.82 dd, 1 H ($CH(COO)_2$); 4.05–4.17 m, 1 H (CHPh); 4.45–4.57 m, 1 H (CHO);

TABLE IV
Bond lengths for compound **5a**

| Atoms | Distances | Atoms | Distances |
|---|---|---|---|
| O1–C7 | 1.32(2) | C20–C21 | 1.39(2) |
| O1–C36 | 1.48(2) | C21–C22 | 1.39(3) |
| O2–C25 | 1.35(2) | C22–C23 | 1.35(4) |
| O2–C26 | 1.43(2) | C23–C24 | 1.38(3) |
| O3–C25 | 1.19(2) | C26–C27 | 1.49(2) |
| O4–C11 | 1.19(1) | C26–C31 | 1.50(2) |
| O5–C18 | 1.20(1) | C27–C28 | 1.51(2) |
| O6–C7 | 1.18(2) | C27–C32 | 1.51(3) |
| C7–C8 | 1.49(2) | C28–C29 | 1.51(3) |
| C8–C9 | 1.52(2) | C29–C30 | 1.50(3) |
| C8–C25 | 1.51(2) | C30–C31 | 1.49(2) |
| C9–C10 | 1.56(2) | C30–C35 | 1.50(3) |
| C9–C19 | 1.55(2) | C32–C33 | 1.47(3) |
| C10–C11 | 1.52(2) | C32–C34 | 1.51(3) |
| C10–C18 | 1.52(2) | C36–C37 | 1.51(2) |
| C11–C12 | 1.49(2) | C36–C41 | 1.54(2) |
| C12–C13 | 1.36(2) | C37–C38 | 1.48(3) |
| C12–C17 | 1.37(2) | C37–C42 | 1.51(2) |
| C13–C14 | 1.36(2) | C38–C39 | 1.45(4) |
| C14–C15 | 1.39(2) | C39–C40 | 1.53(4) |
| C15–C16 | 1.39(2) | C40–C41 | 1.53(2) |
| C16–C17 | 1.36(2) | C40–C45 | 1.48(3) |
| C17–C18 | 1.47(2) | C42–C43 | 1.54(3) |
| C19–C20 | 1.37(2) | C42–C44 | 1.52(2) |
| C19–C24 | 1.35(2) | | |

4.75–4.85 m, 1 H (CHO); 5.19–5.25 m, 2 H (*m*-$C_6H_5Cr(CO)_3$); 5.63 t, 1 H (*p*-$C_6H_5Cr(CO)_3$); 6.03 t, 1 H (*o*-$C_6H_5Cr(CO)_3$); 6.12–6.18 t, 1 H (*o*-$C_6H_5Cr(CO)_3$); 7.15–7.40 m, 5 H ($C_6H_5$).

*(–)-Dimenthyl (1-(4-methoxyphenyl)-3-oxo-3-(η⁶-phenyltricarbonylchromium)-3-propyl)malonate* (**4a**). For $C_{42}H_{54}CrO_9$ (754.9) calculated: 66.83% C, 7.21% H; found: 68.64% C, 7.58% H. M.p. 128–141 °C. $^1$H NMR spectrum of mixture of diastereomers: 0.40–2.00 m, 36 H (menthyl); 3.06–3.33 bt, 2 H ($CH_2CO$); 3.73–3.76 dd, 1 H ($CH(COO)_2$); 3.97–4.09 m, 1 H (CHPh); 4.46–4.55 m, 1 H (CHO); 4.69–4.82 m, 1 H (CHO); 5.20 t, 2 H (*m*-$C_6H_5Cr(CO)_3$); 5.61 t, 1 H (*p*-$C_6H_5Cr(CO)_3$); 6.05 t, 2 H (*o*-$C_6H_5Cr(CO)_3$); 6.77 d, 2 H, $J$ = 8 Hz ($C_6H_4$); 7.16 d, 2 H, $J$ = 8 Hz ($C_6H_4$). Major isomer: 3.73 s, 2.4 H ($OCH_3$); minor isomer 3.75 s, 0.6 H ($OCH_3$).

*(–)-Dimenthyl 1-(1,3-dioxoindan-2-yl)-1-phenylmethylmalonate* (**5a**). For $C_{39}H_{50}O_4$ (582.8) calculated: 80.37% C, 8.64% H; found: 80.68% C, 8.74% H. Repeated crystallization from toluene afforded pure major isomer, m.p. 151–152 °C, $[\alpha]_D$ –90° (toluene). $^1$H NMR spectrum of mixture of diastereomers: 0.40–2.00 m, 36 H (menthyl); 4.35–4.45 m, 1 H (CHO); 4.69–4.77 m, 1 H (CHO); 7.00–7.90 m, 9 H ($C_6H_5$ + $C_6H_4$). Major isomer: 3.66 d, 0.67 H, $J$ = 3.8 Hz ($CH(COO)_2$); 4.37 t, 0.66 H, (CHPh); 4.75 d, 0.67 H, $J$ = 12.4 Hz ($CH(CO)_2$). Minor isomer: 3.74 d, 0.33 H, $J$ = 3.8 Hz ($CH(COO)_2$); 4.25 t, 0.33 H (CHPh); 4.79 d, 0.33 H, $J$ = 12.3 Hz ($CH(CO)_2$). $^1$H NMR spectrum (500 MHz) of pure major isomer: 0.24 d, 3 H, $J$ = 6.9 Hz ($CH_3$); 0.65 d, 3 H, $J$ = 7 Hz ($CH_3$); 0.70 d, 3 H, $J$ = 6.9 Hz ($CH_3$); 0.79 d, 3 H, $J$ = 6.6 Hz ($CH_3$); 0.85 d, 3 H, $J$ = 6.5 Hz ($CH_3$); 0.87 d, 3 H, $J$ = 6.9 Hz ($CH_3$); 0.67–0.88 m, 3 H (menthyl); 0.97–1.57 m, 10 H (menthyl); 1.62–1.69 m, 3 H (menthyl); 1.85–1.93 m, 2 H (menthyl); 3.64 d, 1 H, $J$ = 3.9 Hz ($CH(COO)_2$); 4.31–4.34 dd, 1 H, $J_1$ = 12.4 Hz, $J_2$ = 3.9 Hz (CHPh), 4.35–4.40 dt, 1 H, $J_1$ = 10.9 Hz, $J_2$ = 4.5 Hz (CHO); 4.68–4.74 m, 1 H (CHO); 4.72 d, 1 H, $J$ = 12.4 Hz ($CH(CO)_2$); 6.99–7.05 m, 3 H, (*o*- and *p*-$C_6H_5$); 7.14–7.16 m, 2 H (*m*-$C_6H_5$); 7.65–7.69 m, 2 H (*m*-$C_6H_4$); 7.73–7.75 ddd, 1 H, $J_1$ = 6.9 Hz, $J_2$ = 1.4 Hz, $J_3$ = 0.7 Hz (*o*-$C_6H_4$); 7.85–7.87 ddd, 1 H, $J_1$ = 7.5 Hz, $J_2$ = 1.4 Hz, $J_3$ = 0.7 Hz (*o*-$C_6H_4$).

*(–)-Dimenthyl 2-(1-(1,3-dioxo[3]ferrocenophan-2-yl)-1-phenyl)malonate* (**6a**). For $C_{46}H_{54}FeO_6$ (722.7) calculated: 71.46% C, 7.53% H; found: 71.99% C, 7.75% H. Crystallization from ethyl acetate–isohexane afforded pure major isomer, m.p. 218.5–220.5 °C. $^1$H NMR spectrum of mixture of diastereomers: 0.52–1.90 m, 36 H (menthyl); 4.21 m, 0.4 H ($H_\beta$-Cp); 4.41 m, 0.6 H ($H_\beta$-Cp); 4.41 m, 2 H ($H_\alpha$-Cp); 4.48–4.70 m, 6 H (3 × H-Cp, CHPh, 2 × CHO); 7.15–7.50 m, 5 H ($C_6H_5$). Major isomer: 4.18 d, 0.7 H, $J$ = 7.9 Hz ($CH(COO)_2$); 5.33 d, 0.7 H, $J$ = 9.7 Hz ($CH(CO)_2$); minor isomer: 4.04 d, 0.3 H, $J$ = 7.6 Hz ($CH(COO)_2$); 5.42 d, 0.3 H, $J$ = 9.2 Hz ($CH(CO)_2$).

*(–)-Dimenthyl 3-ferrocenyl-3-oxo-1-(η⁶-phenyltricarbonylchromium)propylmalonate* (**7a**). For $C_{45}H_{56}CrFeO_8$ (832.8) calculated: 64.90% C, 6.78% H; found: 65.37% C, 6.27% H. M.p. 70–78 °C. $^1$H NMR spectrum of mixture of diastereomers: 0.40–2.00 m, 36 H (menthyl); 3.75 m, 1 H ($CHC_6H_5Cr(CO)_3$); 4.51 m, 2 H ($H_\beta$-Cp); 4.61–4.86 m, 5 H (2 × $H_\alpha$-Cp, 2 × CHO, $CH(CO)_2$); 5.16 m, 2 H (*m*-$C_6H_5Cr(CO)_3$); 5.40 m, 1 H (*p*-$C_6H_5Cr(CO)_3$); 5.76 d, 1 H (*o*-$C_6H_5Cr(CO)_3$); 5.79 d, 1 H (*o*-$C_6H_5Cr(CO)_3$). Major isomer: 4.21 s, 2.6 H ($C_5H_5$); 4.09 d, 0.55 H, $J$ = 5 Hz ($CH(COO)_2$); minor isomer: 4.22 s, 2.4 H ($C_5H_5$); 4.01 d, 0.45 H, $J$ = 5 Hz ($CH(COO)_2$).

*(–)-Dimenthyl 1-(1,3-dioxoindan-2-yl)-1-(η⁶-phenyltricarbonylchromium)methyl malonate* (**8a**). For $C_{42}H_{50}CrO_9$ (750.8) calculated: 67.18% C, 6.72% H; found: 66.81% C, 6.88% H. M.p. 74–82 °C. $^1$H NMR spectrum of mixture of diastereomers: 0.50–1.90 m, 36 H (menthyl); 3.70 bt, 1 H (CHPh); 3.94–4.01 m, 1 H (CHO); 4.01–4.18 m, 1 H (CHO); 5.14 m, 2 H (*m*-$C_6H_5Cr(CO)_3$); 4.75 m, 1 H (*p*-$C_6H_5Cr(CO)_3$); 5.22–5.29 m, 1 H (*o*-$C_6H_5Cr(CO)_3$); 5.37 m, 1 H (*o*-$C_6H_5Cr(CO)_3$) 7.77–8.07 m, 4 H ($C_6H_4$). Major diastereomer: 5.77 d, 0.66 H, $J$ = 6 Hz ($CH(COO)_2$); 6.13 d, 0.66 H, $J$ = 6 Hz ($CH(CO)_2$); minor diastereomer: 5.63 d, 0.33 H, $J$ = 4 Hz ($CH(COO)_2$); 5.97 d, 0.33 H, $J$ = 6 Hz ($CH(CO)_2$).

*Our thanks are due to Dr E. Greiplova and Dr E. Solcaniova for the microanalyses and 80 MHz NMR measurements, respectively. The financial support by Slovak Ministry of Education (Grant No. 1/1443/94) is acknowledged.*

**REFERENCES**

1. Gajda V., Widhalm M., Toma S.: Monatsh. Chem. *120*, 147 (1989).
2. Sebo L., Sraga J., Rihs G., Toma S.: Collect. Czech. Chem. Commun. *59*, 2621 (1994).
3. Hoeve W. T., Wynberg M.: J. Org. Chem. *45*, 2754 (1980).
4. Davies S. G., Coote S. J., Goodfellow C. L.: *Adv. Metal. Org. Chem.*, Vol. 2, p. 1. JAI Press, London 1991.
5. Solladie-Cavallo A., Suffert J., Farkhami D.: Ann. Chim. *9*, 683 (1984).
6. Albert J., Davies S. G.: Tetrahedron Lett. *30*, 5945 (1989).
7. Tirouflet J., Boichard J.: C. R. Acad. Sci. *250*, 1861 (1960).
8. Federic J., Toma S., Gautheron B.: J. Organomet. Chem. *338*, 211 (1988).
9. Radulescu D., Georgescu V.: Bull. Soc. Chim. Fr. *37*, 1969 (1925).
10. Salisova M., Toma S., Solcaniova E.: Collect. Czech. Chem. Commun. *45*, 1290 (1980).
11. Martin N., Martinez-Gran A., Seoane C.: Tetrahedron Asym. *5*, 1435 (1994).