STEREOSELECTIVITY OF MICHAEL ADDITION TO 3-PHENYL-1-(η^6-*o*-TOLYLTRICARBONYLCHROMIUM)PROPENONE

Lubomir SEBO[a], Jan SRAGA[a], Grety RIHS[b] and Stefan TOMA[a,*]

[a] *Department of Organic Chemistry, Comenius University, 842 15 Bratislava, The Slovak Republic*
[b] *CIBA-GEIGY Co., 4002 Basel, Switzerland*

Received September 13, 1994
Accepted October 15, 1994

Dedicated to Professor Milan Kratochvil on the occasion of his 70th birthday.

The stereoselectivity of the Michael addition of several *C*-nucleophiles to 3-phenyl-1-(η^6-*o*-tolyltricarbonylchromium)propenone has been studied. The ratio of diastereoisomers formed varied from 65 : 35 (malonodinitrile), 72 : 28 (methyl cyanoacetate) and 78 : 22 (nitromethane) and to 90 : 10 (dimethyl malonate). The ratio of diastereoisomers 63 : 37 was found even when addition of dimethyl malonate was carried out at 75 °C in methanol using piperidine as the catalyst. The (*S*,*R*) or (*R*,*S*) configuration of the main pair of isomers was proved by the X-ray analysis of the dimethyl malonate adduct.

It is well documented[1–3] that nucleophilic attack to a carbonyl group directly attached to a complexed *o*-substituted benzene ring usually leads to high diastereoselectivity. The same was found to be valid in the case of Michael addition of dimethyl malonate to tricarbonylchromium complexes of chalcones in which the coordinated aromatic ring is bonded to the C=C double bond, that is when the attack of the nucleophile takes place again at the α-position with respect to the complexed benzene ring[4]. Solladie-Cavallo[5] described stereoselective attack of Grignard reagents at the β-position with respect to the complexed aromatic ring in Schiff bases derived from benzaldehydes and η^6-(*ortho*-substituted aniline)tricarbonylchromium complexes. Recently two papers[6,7] appeared describing stereoselective attack at the γ-position of the complexed arene moiety. The first paper deals with face differentiation during addition of organocopper reagents to the (*o*-substituted phenyl-α,β-unsaturated ketone)tricarbonylchromium complexes and a stereoselectivity up to 92 : 8 was obtained. The second one[8] describes

* The author to whom correspondence should be addressed.

the stereoselective addition of nitromethane to 2-arylidene-1-tetralones complexed with $Cr(CO)_3$ (d.e. 78 – 90%).

The main goal of this work was to study the effect of the nucleophile, the solvent, the base and the temperature on the stereoselectivity obtained during Michael addition at the γ-position to the complexed benzene ring of a flexible system 3-phenyl-1-(η^6-*o*-tolyltricarbonylchromium)propenone.

RESULTS AND DISCUSSION

The tricarbonylchromium moiety is a powerful electron withdrawing group which caused some difficulties in the synthesis of 3-phenyl-1-(η^6-*o*-tolyltricarbonylchromium)propenone (*I*). Direct condensation of η^6-(*o*-methylacetophenone)tricarbonylchromium with benzaldehyde in alkaline media proceeded rapidly but the product was contamined with the product of subsequent Michael addition of the second molecule of complexed acetophenone. Isolation of the desired product needed rapidly chromatography on silica gel column and the yields were rather low. However, changing the molar ratio of the reactants η^6-(*o*-methylacetophenone)tricarbonylchromium–benzaldehyde from 1 : 1 to 1 : 5, as well as the way of the addition (η^6-(*o*-methylacetophenone)-tricarbonylchromium was portionwise added to alkaline solution of benzaldehyde) gave high yield of the product. The pure (*E*)-isomer of chalcone was formed as was found from its ^{1}H NMR spectrum (J(CH=CH) = 16 Hz).

Dimethyl malonate (*IIa*), malononitrile (*IIb*), methyl cyanoacetate (*IIc*) and nitromethane (*IId*) were chosen as the reactants to study the effect of temperature, base and the solvent on the stereoselectivity of the Michael addition to 3-phenyl-1-(η^6-*o*-tolyltricarbonylchromium)propenone (*I*, Scheme 1). The diastereoisomer ratios were determined using the toluene moiety methyl group signals which differ by 0.08 – 0.17 ppm (Table I) in the two diastereoisomers *III*, *IV*. In most cases the results were checked by the chromatographic separation of diastereoisomers. The results are summarized in Table II.

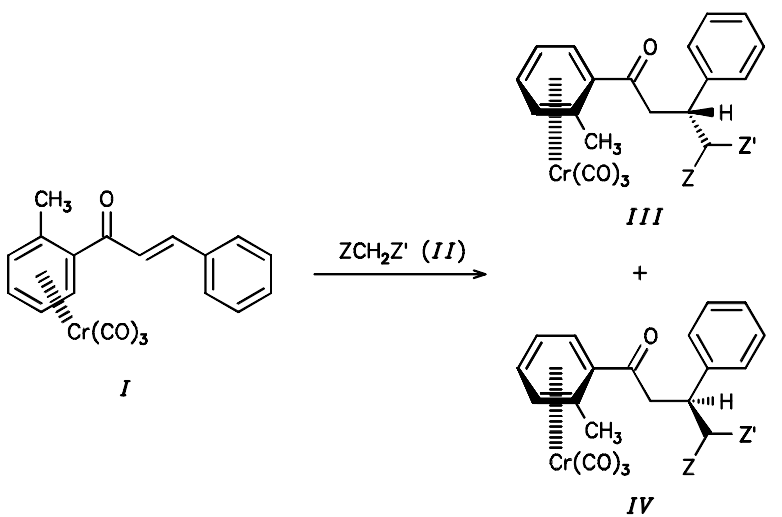
TABLE I

The melting points and ^{1}H NMR (δ, ppm) chemical shifts (80 MHz, $CDCl_3$) of the toluene moiety methyl group of the compounds *III*, *IV*

Compound	M.p., °C		^{1}H NMR	
	III	*IV*	*III*	*IV*
a	118 – 119	91 – 92	2.27	2.10
b	151 – 152	138 – 139	2.39	2.30
c	124 – 125	132 – 134	2.22	2.32
d	109 – 111	121.5 – 124	2.30	2.22

It seems that the temperature has dominant effect on the stereoselectivity of Michael addition only with dimethyl malonate (*IIa*). The diastereoselectivity changes slightly with the change of the solvent and the base. A lower ratio (55 : 45) was found when Laszlo's base[9] (*tert*-BuOK on xonotlite) was used in ether. The ratio of diastereoisomers upon addition of dimethyl malonate reached 81 : 19 when the reaction was carried out at 0 °C and 90 : 10 at –20 °C. It is surprising that the ratio 63 : 37 was found even if the reaction temperature was 75 °C.

In all attempts at the Michael addition of malononitrile (*IIb*) the ratio of diastereoisomers close to 65 : 35 was found. This can be explained by very small differences between the $\Delta G^{\#}$ values of the transition state leading to the different isomers due to the small size of the nucleophile and its high reactivity. The high reactivity of malonodinitrile was proved indirectly by the fact that the addition proceeded (experiment No. 9) also without the addition of an external base. Nitromethane (*IId*) was chosen as a reagent to compare the stereoselectivity of addition to the rigid and flexible α,β-unsaturated ketone. The stereoselectivity observed was reasonable (d.e. up to 56%), but as expected not as high as that described for the rigid system[7] (72 – 92%). The addition product of ethyl cyanoacetate (*IIc*) possesses 3 centres of chirality and therefore 4 pairs of diastereoisomers should be formed. To our surprise only two products could be detected by TLC and 80 MHz ^{1}H NMR spectroscopy and isolated in the ratio 68 : 32. The



In formulae *II* – *IV* : ***a***, Z = Z' = $COOCH_3$; ***b***, Z = Z' = CN; ***c***, Z = CN; Z' = $COOCH_3$; ***d***, Z = H; Z' = NO_2

SCHEME 1

400 MHz ^{1}H NMR spectra of the main product *IVc* revealed that it is a mixture of two isomers in the ratio 88 : 12. This determination was also based on the chemical shifts of the toluene moiety methyl group. The predominant isomer has (in C_6D_6) the chemical shift at 2.04 ppm, while the minor isomer at 1.95 ppm. The analogous spectra of the minor product *IIIc* revealed that it is only one isomer ($\delta(CH_3\text{-Ar})$ = 2.09 ppm). These results show that either only three pairs of diastereomers are formed (which is less probable) or that the fourth one is formed in a negligible quantity.

It would be of interest to determine the relative configuration of the products to see if the main product was formed via *exo*-attack of the nucleophile. From the comparison of the ^{1}H NMR spectra of all isolated pairs of diastereoisomers can be stated only that the chemical shifts of CH_3-Ar group of the main product is always at the lower ppm value (2.10 – 2.32) than that of the minor product (2.22 – 2.39). The relative configuration of the main isomer was proved by X-ray analysis of the dimethyl malonate adduct *IVa*. The structure is given in the Fig. 1. The main crystallographic parameters are

TABLE II
Results of Michael adition of the compounds *II* to the compound *I*

No.	Reagent	Reaction conditions				Yield, %	Ratio *IV*/*III*[a]
		solvent	catalyst	temp., °C	time		
1	*IIa*	methanol	piperidine	0	7 d	87	81 : 19
2	*IIa*	methanol	piperidine	20	2 d	91	77 : 23
3	*IIa*	methanol	piperidine	75	20 h	86	63 : 37
4	*IIa*	ether	K_2CO_3/18-crown-6	–20	3 d	92	90 : 10
5	*IIa*	ether	K_2CO_3/18-crown-6	20	20 h	93	69 : 31
6	*IIa*	ether	*tert*-BuOK/xonotlite	20	3 d	74	55 : 45
7	*IIb*	ether	K_2CO_3/18-crown-6	–20	3 d	78	65 : 35
8	*IIb*	ether	K_2CO_3/18-crown-6	20	3 h	82	67 : 33
9	*IIb*	methanol	–	20	1 d	84	61 : 39
10	*IIb*	methanol	piperidine	–20	30 min	90	66 : 34
11	*IIb*	methanol	piperidine	20	15 min	84	63 : 37
12	*IIc*	methanol	piperidine	–20	20 h	75	72 : 28
13	*IId*	–	KF/18-crown-6	–20	6 d	83	78 : 22
14	*IId*	–	KF/18-crown-6	20	2 h	87	68 : 32

[a] The ratio of diastereoisomers determined from the ^{1}H NMR spectrum.

given in Tables III – V. It is evident that the main product of this addition was formed via *exo*-attack of the nucleophile and it is a racemate having (*S*,*R*) and (*R*,*S*) relative configuration on both chiral centers.

Chiral arenetricarbonylchromium moiety was shown to be good chiral auxiliary even in the case when the reaction centre is in γ-position to this moiety. We believe that even higher stereoselectivity can be observed if either less reactive or bulkier reagent would be used.

EXPERIMENTAL

^{1}H NMR spectra (δ, ppm; *J*, Hz) were measured in $CDCl_3$ (unless stated otherwise) at TESLA BS 487 (80 MHz) instrument. Flash chromatography was carried out on silica gel column (2.2 × 13 cm) using isohexane–acetate (3 : 1) mixture as the eluent. η^6-(*o*-Methylacetophenone)tricarbonylchromium was prepared in 94% yield by the method described in the literature[9].

3-Phenyl-1-(η^6-*o*-tolyltricarbonylchromium)propenone (*I*)

η^6-(*o*-Methylacetophenone)tricarbonylchromium (0.759 g, 2.81 mmol) was added portionwise over 3 h to a stirred solution of benzaldehyde (1.49 g, 14.04 mmol) in methanol (6.8 ml) and 10% NaOH solution (1.3 ml). The reaction mixture was stirred at room temperature for 18 h. Then ether (50 ml) was added and the mixture was washed with a 5% acetic acid solution (20 ml). The combined aqueous phases were extracted with ether (2 × 15 ml). The combined organic phases were dried over

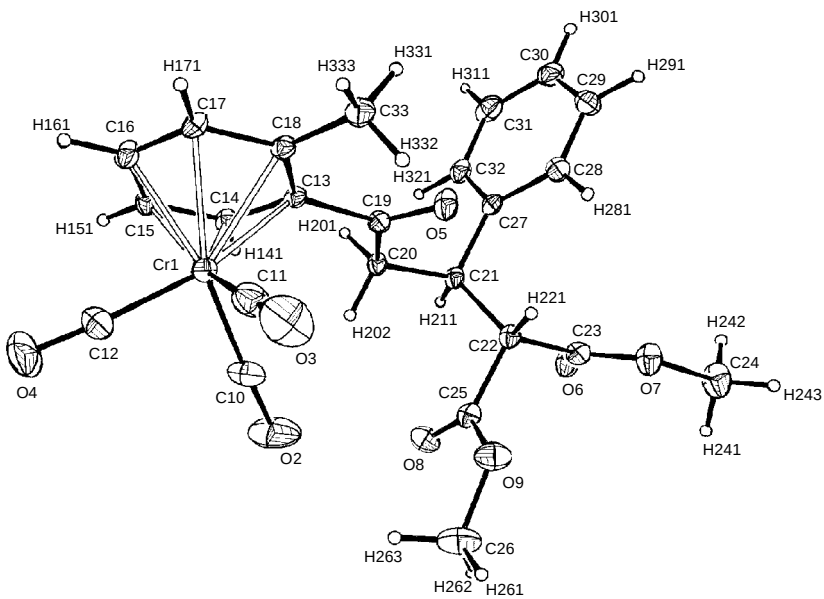


FIG. 1
ORTEP drawing of one enantiomer of the compound *IVa* (the main product of the Michael addition)

anhydrous $MgSO_4$. After filtration the solvent was evaporated and the residual oil was purified by flash chromatography. Benzaldehyde was eluted with first 500 ml of the eluent. The residue left after evaporation of the eluate was dissolved in the minimum amount of ether, isohexane was added and the product was left in the freezer for crystallization. Red crystals of the compound *I* (935 mg; 93%), m.p. 84 – 86 °C, were isolated. $C_{19}H_{14}CrO_4$ (358.3) calculated: 63.68% C, 3.94% H; found: 63.59% C, 3.91% H. ^{1}H NMR spectrum: 2.39 s, 3 H (CH_3-Ar); 5.11 d, 1 H, *J* = 6 (H-3′); 5.20 t, 1 H, *J* = 6 (H-4′); 5.64 t, 1 H, *J* = 6 (H-5′); 5.92 d, 1 H *J* = 6 (H-6′); 7.22 d, 1 H, *J* = 16 (CH=); 7.43 t, 2 H (*o*,*p*-Ph); 7.68 dd, 2 H, (*m*-Ph); 7.80 d, 1 H, *J* = 16 (CH=).

Michael Addition of Dimethyl Malonate (*IIa*)

A. The experiments 1 – 3. To the stirred solution of *I* (180 mg, 0.5 mmol) in dry methanol (3 ml) were added dimethyl malonate *IIa* (0.55 mmol) and piperidine (2 drops) at appropriate temperature. After the reaction was finished (TLC), the solvent was evaporated and the residue was chromato-

TABLE III
Data collection and refinement parameters for the compound *IVa*

Crystal system	triclinic
Space group	*P*-1
a, Å	10.511(1)
b, Å	10.970(1)
c, Å	11.089(1)
α, °	104.37(1)
β, °	108.13(1)
γ,°	99.75(1)
V, Å^3	1 134.1 (4)
Z	2
D_{calc}, g cm^{-3}	1.436
Crystal size, mm	0.70 × 0.36 × 0.12
Diffractometer	Philips PW1100
Radiation	graphite monochromated MoKα
Wavelength, Å	0.70926
Scan mode	ω/2θ
μ, cm^{-1}	5.4
F(000)	508
Scan range, 2θ	6 – 56
Number of measured reflection	5 778
Number of observed reflection, $I > 2\sigma(I)$	3 451
Refinement method	full matrix
No. of parameters	381
Value of *R* and *wR*	0.046, 0.051
Weighting scheme	$1/\sigma^2(F)$
Max. and min. density in final Δρ map	0.632, –0.593 e Å^{-3}

TABLE IV
Bond distances (Å) for the compound *IVa*

Atoms	Distances	Atoms	Distances
Cr1–C10	1.818(5)	Cr1–C11	1.845(5)
Cr1–C12	1.841(5)	Cr1–C13	2.208(4)
Cr1–C14	2.183(4)	Cr1–C15	2.210(4)
Cr1–C16	2.201(4)	Cr1–C17	2.199(4)
Cr1–C18	2.219(4)	O2–C10	1.163(6)
O3–C11	1.145(5)	O4–C12	1.151(6)
O5–C19	1.206(4)	O6–C23	1.194(4)
O7–C23	1.314(5)	O7–C24	1.453(5)
O8–C25	1.197(5)	O9–C25	1.314(5)
O9–C26	1.450(7)	C13–C14	1.419(5)
C13–C18	1.438(5)	C13–C19	1.502(5)
C14–C15	1.387(5)	C14–H141	1.01(4)
C15–C16	1.403(5)	C15–H151	1.00(4)
C16–C17	1.385(6)	C16–H161	0.99(4)
C17–C18	1.419(5)	C17–H171	0.99(4)
C18–C33	1.492(6)	C19–C20	1.527(5)
C20–C21	1.542(5)	C20–H201	1.00(4)
C20–H202	1.02(4)	C21–C22	1.538(5)
C21–C27	1.523(5)	C21–H211	1.02(3)
C22–C23	1.532(5)	C22–C25	1.521(5)
C22–H221	1.01(4)	C24–H241	1.02(5)
C24–H242	0.98(5)	C24–H243	1.01(5)
C26–H261	0.99(5)	C26–H262	0.98(5)
C26–H263	1.02(5)	C27–C28	1.392(5)
C27–C32	1.386(6)	C28–C29	1.380(6)
C28–H281	1.01(4)	C29–C30	1.371(7)
C29–H291	1.00(4)	C30–C31	1.384(7)
C30–H301	1.00(4)	C31–C32	1.387(6)
C31–H311	1.01(4)	C32–H321	1.00(4)
C33–H331	0.98(4)	C33–H332	0.99(4)
C33–H333	0.85(4)		

TABLE V
Bond angles (°) for the compound *IVa*

Atoms	Angles	Atoms	Angles
C11–Cr1–C10	88.3(2)	C12–Cr1–C10	88.2(2)
C12–Cr1–C11	92.0(2)	C13–Cr1–C10	110.5(2)
C13–Cr1–C11	92.9(2)	C13–Cr1–C12	160.7(2)
C14–Cr1–C10	147.7(2)	C14–Cr1–C11	88.3(2)
C14–Cr1–C12	124.0(2)	C14–Cr1–C13	37.7(1)
C15–Cr1–C10	161.3(2)	C15–Cr1–C11	110.3(2)
C15–Cr1–C12	92.9(2)	C15–Cr1–C13	67.9(1)
C15–Cr1–C14	36.8(1)	C16–Cr1–C10	124.6(2)
C16–Cr1–C11	146.9(2)	C16–Cr1–C12	86.0(2)
C16–Cr1–C13	79.8(1)	C16–Cr1–C14	66.2(1)
C16–Cr1–C15	37.1(1)	C17–Cr1–C10	95.4(2)
C17–Cr1–C11	159.7(2)	C17–Cr1–C12	108.0(2)
C17–Cr1–C13	67.1(1)	C17–Cr1–C14	78.0(1)
C17–Cr1–C15	66.5(2)	C18–Cr1–C10	87.6(2)
C18–Cr1–C11	123.2(2)	C18–Cr1–C12	144.4(2)
C18–Cr1–C13	37.9(1)	C18–Cr1–C14	67.8(1)
C18–Cr1–C15	80.6(1)	C17–Cr1–C16	36.7(2)
C18–Cr1–C16	67.8(2)	C18–Cr1–C17	37.5(1)
C24–O7–C23	116.7(4)	C26–O9–C25	116.7(4)
O2–C10–Cr1	179.0(5)	O3–C11–Cr1	176.5(5)
O4–C12–Cr1	177.3(6)	C14–C13–Cr1	70.2(2)
C18–C13–Cr1	71.5(2)	C18–C13–C14	118.5(3)
C19–C13–Cr1	129.0(2)	C19–C13–C14	120.1(3)
C19–C13–C18	121.4(3)	C13–C14–Cr1	72.1(2)
C15–C14–Cr1	72.7(2)	C15–C14–C13	123.1(3)
H141–C14–Cr1	129.1(20)	H141–C14–C13	119.5(21)
H141–C14–C15	117.4(22)	C14–C15–Cr1	70.5(2)
C16–C15–Cr1	71.1(2)	C16–C15–C14	118.3(4)
H151–C15–Cr1	129.9(22)	H151–C15–C14	121.0(23)
H151–C15–C16	120.7(23)	C15–C16–Cr1	71.8(2)
C17–C16–Cr1	71.6(2)	C17–C16–C15	120.2(4)
H161–C16–Cr1	128.8(23)	H161–C16–C15	119.2(23)
H161–C16–C17	120.6(23)	C16–C17–Cr1	71.7(2)
C18–C17–Cr1	72.1(2)	C18–C17–C16	123.0(3)
H171–C17–Cr1	129.9(22)	H171–C17–C16	119.8(23)
H171–C17–C18	117.2(23)	C13–C18–Cr1	70.6(2)
C17–C18–Cr1	70.5(2)	C17–C18–C13	116.9(3)

TABLE V
(*Continued*)

Atoms	Angles	Atoms	Angles
C33–C18–Cr1	130.5(3)	C33–C18–C13	124.4(3)
C33–C18–C17	118.7(3)	C13–C19–O5	123.1(3)
C20–C19–O5	121.1(3)	C20–C19–C13	115.7(3)
C21–C20–C19	116.6(3)	H201–C20–C19	109.0(21)
H201–C20–C21	108.3(22)	H202–C20–C19	109.1(21)
H202–C20–C21	107.1(22)	H202–C20–H201	106.3(30)
C22–C21–C20	112.7(3)	C27–C21–C20	112.1(3)
C27–C21–C22	114.7(3)	H211–C21–C20	105.8(21)
H211–C21–C22	106.1(20)	H211–C21–C27	104.4(21)
C23–C22–C21	110.2(3)	C25–C22–C21	111.0(3)
C25–C22–C23	104.8(3)	H221–C22–C21	108.6(21)
H221–C22–C23	110.7(22)	H221–C22–C25	111.5(21)
O7–C23–O6	126.1(4)	C22–C23–O6	123.0(4)
C22–C23–O7	110.8(3)	H241–C24–O7	109.7(30)
H242–C24–O7	108.9(32)	H242–C24–H241	107.6(42)
H243–C24–O7	109.9(30)	H243–C24–H241	109.3(42)
H243–C24–H242	111.5(42)	O9–C25–O8	124.2(4)
C22–C25–O8	124.2(4)	C22–C25–O9	111.5(3)
H261–C26–O9	111.7(29)	H262–C26–O9	111.1(29)
H262–C26–H261	109.4(39)	H263–C26–O9	110.5(28)
H263–C26–H261	108.4(41)	H263–C26–H262	105.6(42)
C28–C27–C21	124.2(4)	C32–C27–C21	117.6(4)
C32–C27–C28	118.2(4)	C29–C28–C27	120.6(4)
H281–C28–C27	120.2(23)	H281–C28–C29	119.3(23)
C30–C29–C28	120.8(5)	H291–C29–C28	119.7(24)
H291–C29–C30	119.6(24)	C31–C30–C29	119.6(5)
H301–C30–C29	120.6(25)	H301–C30–C31	119.8(25)
C32–C31–C30	119.8(5)	H311–C31–C30	120.3(26)
H311–C31–C32	120.0(26)	C31–C32–C27	121.1(4)
H321–C32–C27	118.9(23)	H321–C32–C31	120.0(24)
H331–C33–C18	116.1(25)	H332–C33–C18	110.5(24)
H332–C33–H331	109.3(34)	H333–C33–C18	112.9(30)
H333–C33–H331	97.7(35)	H333–C33–H332	109.5(36)

graphed. A small amount of starting chalcone was eluted as the first fraction. The mixture of diastereoisomers *IIIa*, *IVa* (83 – 95%), was isolated as the second fraction. Repeated flash chromatography afforded pure diastereoisomers *IIIa*, *IVa*.

B. The experiments 4, 5. To the stirred solution of *I* (180 mg, 0.5 mmol) in dry ether (10 ml) were added dimethyl malonate *IIa* (0.55 mmol), K_2CO_3 (40 mg, 0.5 mmol) and 18-crown-6-ether (132 mg, 0.5 mmol) at the appropriate temperature. After the reaction was finished, the solution was filtered. The isolation procedure of pure diastereoisomers *IIIa*, *IVa* was the same as in the case *A*.

C. The experiment 6. To the stirred solution of *I* (50 mg, 0.14 mmol) in dry ether (3 ml) were added dimethyl malonate *IIa* (0.2 mmol) and *tert*-BuOK on xonotlite (100 mg) at room temperature. After the reaction was finished (TLC detection), the solution was filtered. The isolation procedure of pure diastereoisomers *IIIa*, *IVa* was the same as in the case *A*. For $C_{24}H_{22}CrO_8$ (490.4) calculated: 58.77% C, 4.52% H; found (*IIIa*): 58.42% C, 4.53% H; found (*IVa*): 58.56% C, 4.58% H. ^{1}H NMR spectrum: *IIIa*: 2.27 s, 3 H (CH_3-Ar); 3.20 and 3.36, 2 × 1 H, J = 17, J = 5 (CH_2); 3.53 s, 3 H (OCH_3); 3.76 s, 3 H (OCH_3); 3.83 d, 1 H, J = 8 (CH(COOR)$_2$; 4.12 dt, 1 H (CH); 4.98 d, 1 H, J = 6 (H-3′); 5.04 t, 1 H (H-4′); 5.55 t, 1 H (H-5′); 5.62 d, 1 H, J = 6 (H-6′); 7.28 m, 5 H (Ph). *IVa*: 2.105 s, 2 H (CH_3-Ar); 3.28 and 3.45 dd, 2 × 1 H, J = 17, J = 9 (CH_2); 3.52 s, 3 H (OCH_3); 3.74 s, 3 H (OCH_3); 3.80 d, 1 H, J = 8 (CH(COOR)$_2$; 4.08 m, 1 H (CH); 4.93 d, 1 H, J = 6 (H-3′); 5.10 t, 1 H (H-4′); 5.60 t, 1 H (H-5′); 5.98 d, 1 H, J = 6 (H-6′); 7.26 m, 5 H (Ph).

Michael Addition of Malonodinitrile (*IIb*)

Reactions were carried out as described above (see procedure *A*), malonodinitrile was used as the reagent. For $C_{22}H_{16}CrN_2O_4$ (424.4) calculated: 62.26% C, 3.77% H, 6.60% N; found (*IIIb*): 60.68% C, 3.71% H, 6.30% N; found (*IVb*): 61.95% C, 3.75% H, 6.50% N. ^{1}H NMR spectrum: *IIIb*: 2.39 s, 3 H (CH_3-Ar); 3.47 d, 2 H, J = 7 (CH_2); 3.90 q, 1 H (CH); 4.47 d, 1 H, J = 5 (CH(CN)$_2$); 5.05 d, 1 H, J = 6 (H-3′); 5.10 t, 1 H (H-4′); 5.65 t, 1 H (H-5′); 5.82 d, 1 H, J = 6 (H-6′); 7.43 m, 5 H (Ph). *IVb*: 2.30 s, 3 H (CH_3-Ar); 3.47 d, 2 H, J = 7 (CH_2); 3.90 q, 1 H (CH); 4.40 d, 1 H, J = 4 (CH(CN)$_2$; 5.00 d, 1 H, J = 6 (H-3′); 5.15 t, 1 H (H-4′); 5.67 t, 1 H (H-5′); 5.93 d, 1 H, J = 6 (H-6′); 7.42 m, 5 H (Ph).

Michael Addition of Methyl Cyanoacetate (*IIc*)

Reactions were carried out as described above (see procedure *A*), methyl cyanoacetate was used as the reagent. For $C_{23}H_{19}CrNO_6$ (457.4) calculated: 60.39% C, 4.19% H, 3.06% N; found (*IIIc*): 61.04% C, 4.22% H, 3.06% N; found (*IVc*): 60.34% C, 4.18% H, 2.94% N. ^{1}H NMR spectrum (C_6D_6): *IIIc*: 2.09 s, 3 H (CH_3-Ar); 2.99 and 3.17 dd, 2 × 1H, J = 18, J = 7 (CH_2); 3.04 s, 3 H (OCH_3); 3.69 d, 1 H, J = 6 (CH(CN)(COOR)); 4.02 d, 1 H, J = 7 (H-3′); 4.09 dt, 2 H (H-4′,CH); 4.63 t, 1 H (H-5′); 4.97 d, 1 H, J = 6 (H-6′); 7.03 t, 1 H (*p*-Ph); 7.11 t, (*m*-Ph); 7.44 d, 2 H, J = 6 (*o*-Ph). *IVc* (the major isomer): 2.04 s, 3 H (CH_3-Ar); 3.14 s, 3 H (OCH_3); 3.20 dd, 1 H, 3.87 d, 1 H, J = 6; 4.03 d, 1 H, J = 6 (H-3′); 4.11 m, 2 H (H-4′,CH); 4.65 t, 1 H (H-5′); 5.17 d, 1 H, J = 6 (H-6′); 7.04 t, 1 H (*p*-Ph); 7.20 t, 2 H (*m*-Ph); 7.40 d, 2 H (*o*-Ph). *IVc* (the minor isomer): 1.95 s, 3 H (CH_3-Ar); 3.14 s, 3 H (OCH_3); 3.30 dd, 1 H, 3.95 d, 1 H, J = 6; 3.91 d, 1 H, 3.97 d, 1 H (H-3′); 4.15 m, 2 H (H-4′,CH); 4.61 t, 1 H (H-5′); 5.26 d, 1 H (H-6′); 7.02 t, 1 H (*p*-Ph); 7.13 t, 2 H (*m*-Ph); 7.31 s, 2 H (*o*-Ph).

Michael Addition of Nitromethane (*IId*)

To the stirred solution of *I* (50 mg, 0.14 mmol) in nitromethane *IId* (5 ml) were added anhydrous KF (10 mg, 0.14 mmol) and 18-crown-6-ether (5 mg) at appropriate temperature. When the reaction was finished (TLC detection), the solution was filtered and the isolation procedure of pure diastereo-

isomers *IIId*, *IVd* was the same as above. For $C_{20}H_{17}CrNO_6$ (419.3) calculated: 57.28% C, 4.08% H, 3.34% N; found (*IIId*): 57.32% C, 4.05% H, 3.34% N; found (*IVd*): 57.58% C, 4.13% H, 3.33% N. ^{1}H NMR spectrum: *IIId*: 2.30 s, 3 H (CH_3-Ar); 3.22 d, 2 H, J = 7 (CH_2); 4.15 t, 1 H; 4.70 d, 2 H; 5.05 t, 2 H; 5.62 t, 2 H, 7.31 m, 5 H (Ph). *IVd*: 2.22 s, 3 H (CH_3-Ar), 3.29 d, 2 H, J = 7 (CH_2); 4.12 t, 1 H, 4.65 d, 2 H, 4.92 d, 1 H, J = 6 (H-3′); 5.07 t, 1 H (H-4′); 5.60 t, 1 H (H-5′); 5.85 d, 1 H, J = 6 (H-6′); 7.31 m, 5 H (Ph).

Our thanks are due to Drs E. Solcaniova and E. Greiplova and their staff for ^{1}H NMR spectra and elemental analyses, respectively, as well as Dr P. Romanes of Geneva University for 400 MHz NMR spectra. Financial support of the Swiss National Science Foundation and Slovak Ministry of Education (grant No. 0909) is gratefully acknowledged.

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