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Synthesis of Dimethyl 2-(2-Alkyl-1,3-diaryl-3-oxopropyl)malonates and Their Reactions with Amines

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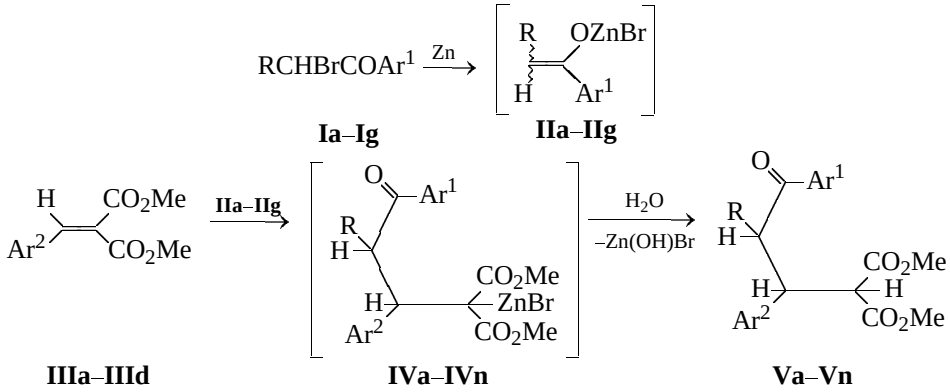
Abstract—Zinc enolates generated from 1-aryl-2-bromoalkanones and zinc react with dimethyl 2-(1-arylmethylene)malonate to form dimethyl 2-(2-alkyl-1,3-diaryl-3-oxopropyl)malonates. The latter react with benzylamine or cyclohexylamine to form the corresponding disubstituted amides, while the reactions with piperidine, morpholine, and *p*-methoxyaniline provide monosubstituted amides of the corresponding target derivatives.

A number of syntheses of dialkyl malonates containing a 3-oxopropyl fragment in the α position have been reported [1–7]. The first group of procedures is based on condensation of dialkyl α-benzylidenemalonates with carbonyl compounds in the presence of bases [6]. The second group involves the Michael reaction of anions derived from β-dicarbonyl compounds and their analogs with α,β-unsaturated carbonyl compounds [1–5, 7]. However, in the cited works we found no syntheses of alkyl 2-(2-alkyl-1,3-diaryl-3-oxopropyl)malonates. Therefore, we set ourselves the task to develop methods for preparing the latter compounds on the basis of the Reformatsky reaction. We reacted α-bromoketones **Ia**–**Ig**, zinc, and dimethyl 2-(1-arylmethylene)malonates **IIIa**–**IIId** in diethyl ether–ethyl acetate (1 : 3 v/v) under conditions of the Reformatsky reaction. It was shown that the reaction occurs by the following scheme.



I, II, R = Me, Ar^1 = 4-MeC_6H_4 (**a**), 2,4-$Me_2C_6H_3$ (**b**), 4-FC_6H_4 (**c**), 4-BrC_6H_4 (**d**); R = Et, Ar^1 = Ph (**e**), 4-BrC_6H_4 (**f**), 4-ClC_6H_4 (**g**); **III**, Ar^2 = Ph (**a**), 4-BrC_6H_4 (**b**), 4-ClC_6H_4 (**c**), 3,4-$(MeO)_2C_6H_3$ (**d**); **IV, V**, R = Me, Ar^1 = 4-MeC_6H_4, 4-ClC_6H_4 (**a**), 4-BrC_6H_4 (**b**); Ar^1 = 4-FC_6H_4, Ar^2 = 4-BrC_6H_4 (**c**); Ar^1 = 4-BrC_6H_4, Ar^2 = 4-ClC_6H_4 (**d**), 4-BrC_6H_4 (**e**), Ar^1 = 2,4-$(Me)_2C_6H_3$, Ar^2 = 4-ClC_6H_4 (**f**), 4-BrC_6H_4 (**g**), 3,4-$(MeO)_2C_6H_3$ (**h**); R = Et, Ar^1 = Ar^2 = Ph (**i**), Ar^1 = 4-ClC_6H_4, Ar^2 = 4-ClC_6H_4 (**j**), 4-BrC_6H_4 (**k**), 3,4-$(MeO)_2C_6H_3$ (**l**), Ar^1 = 4-BrC_6H_4, Ar^2 = 4-ClC_6H_4 (**m**), 4-BrC_6H_4 (**n**).

Zinc enolates **IIIa**–**IIId** formed in the first stage add as nucleophilic reagents to the double bond of electrophilic substrates **IIIa**–**IIId** to form intermediates **IVa**–**IVn** whose hydrolysis gives rise to target products **Va**–**Vn** (Table 1). The reaction successfully proceeds with zinc enolates containing various aryl groups, except for the zinc enolate derived from 2-bromo-1-mesityl-1-butanone, which is

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Table 1. Yields, melting points, IR spectra, ^{1}H NMR spectra, and elemental analyses of dimethyl 2-(2-alkyl-1,3-diaryl-3-oxopropyl)malonates **Va**–**Vn**

Comp. no.	Yield, %	mp, °C	IR spectrum, ν, cm^{-1}		^{1}H NMR spectrum, δ, ppm	Found, %		Formula	Calculated, %	
			CO (ester)	CO (ketone)		C	H		C	H
Va	42	93–96	1750	1675	0.82 d (3H, CH*Me*, *J* 7 Hz), 2.42 s (3H, *Me*C$_6$H$_4$), 3.37 s, 3.55 s (6H, COOMe, COOMe), 3.85 m (1H, 4-ClC$_6$H$_4$CH), 4.05 m (1H, C*H*Me), 4.08 d [1H, CH(COOMe)$_2$, *J* 10 Hz], 7.18 d, 7.38 d (4H, 4-ClC$_6$*H*$_4$, *J* 8 Hz), 7.32 d, 7.90 d (4H, 4-MeC$_6$*H*$_4$, *J* 8 Hz)	65.63	5.69	$C_{22}H_{23}ClO_5$	65.59	5.75
Vb	45	111–112	1750	1675	0.82 d (3H, CH*Me*, *J* 7 Hz), 2.42 s (3H, *Me*C$_6$H$_4$), 3.37 s, 3.55 s (6H, COOMe, COOMe), 3.83 m (1H, 4-BrC$_6$H$_4$C*H*), 4.05 m (1H, C*H*Me), 4.08 d [1H, C*H*(COOMe)$_2$, *J* 10 Hz], 7.12 d, 7.45 d (4H, 4-BrC$_6$H$_4$, *J* 8 Hz), 7.37 d, 7.90 d (4H, 4-MeC$_6$*H*$_4$, *J* 8 Hz)	59.12	5.14	$C_{22}H_{23}BrO_5$	59.07	5.18
Vc	38	105–107	1750	1675	0.83 d (3H, CH*Me*, *J* 7 Hz), 3.37 s, 3.55 s (6H, COOMe, COOMe), 3.83 m (1H, 4-BrC$_6$H$_4$C*H*), 4.08 d [1H, C*H*(COOMe)$_2$, *J* 10 Hz], 4.10 m (1H, C*H*Me), 7.15 d, 7.45 d (4H, 4-BrC$_6$H$_4$, *J* 8 Hz), 7.40 d.d, 8.10 d (4H, 4-FC$_6$H$_4$, *J* 8 Hz)	55.79	4.53	$C_{21}H_{20}BrFO_5$	55.89	4.47
Vd	43	121–123	1720–1750	1675	0.82 d (3H, CH*Me*, *J* 7 Hz), 3.37 s, 3.55 s (6H, COOMe, COOMe), 3.84 m (1H, 4-ClC$_6$H$_4$C*H*), 4.07 m (1H, C*H*Me), 4.09 d [1H, C*H*(COOMe)$_2$, *J* 10 Hz], 7.20 d, 7.33 d (4H, 4-ClC$_6$H$_4$, *J* 8 Hz), 7.80 d, 7.94 d (4H, 4-BrC$_6$H$_4$, *J* 8 Hz)	53.92	4.29	$C_{21}H_{20}BrClO_5$	53.93	4.31
Ve	40	126–128	1725	1675	0.82 d (3H, CH*Me*, *J* 7 Hz), 3.37 s, 3.55 s (6H, COOMe, COOMe), 3.82 m (1H, 4-BrC$_6$H$_4$C*H*), 4.07 m (1H, C*H*Me), 4.09 d [1H, C*H*(COOMe)$_2$, *J* 10 Hz], 7.12 d, 7.45 d (4H, 4-BrC$_6$H$_4$, *J* 8 Hz), 7.80 d, 7.93 d (4H, 4-BrC$_6$H$_4$, *J* 8 Hz)	49.23	3.97	$C_{21}H_{20}Br_2O_5$	49.25	3.94
Vf	67	101–103	1755	1675	0.83 d (3H, CH*Me*, *J* 7 Hz), 2.25 s, 2.35 s (6H, *Me*$_2$C$_6$H$_3$), 3.37 s, 3.61 s (6H, COOMe, COOMe), 3.82 m (1H, 4-ClC$_6$H$_4$C*H*), 3.92 m (1H, C*H*Me), 4.11 d [1H, C*H*(COOMe)$_2$, *J* 10 Hz], 7.13 d, 7.30 d (4H, 4-ClC$_6$H$_4$, *J* 8 Hz), 7.15 s, 7.20 d, 7.78 d [3H, 2,4-(Me)$_2$C$_6$*H*$_3$, *J* 8 Hz]	66.18	6.14	$C_{23}H_{25}ClO_5$	66.26	6.04

Table 1. (Contd.)

Comp. no.	Yield, %	mp, °C	IR spectrum, ν, cm^{-1}		^{1}H NMR spectrum, δ, ppm	Found, %		Formula	Calculated, %	
			CO (ester)	CO (ketone)		C	H		C	H
Vg	62	101–102	1755	1675	0.83 d (3H, CH*Me*, *J* 7 Hz), 2.25 s, 2.35 s (6H, $Me_2C_6H_3$), 3.37 s, 3.60 s (6H, COOMe, COOMe), 3.80 m (1H, 4-BrC_6H_4CH), 3.90 m (1H, C*H*Me), 4.12 d [1H, C*H*$(COOMe)_2$, *J* 10 Hz], 7.07 d, 7.45 d (4H, 4-BrC_6H_4, *J* 8 Hz), 7.15 s, 7.20 d, 7.77 d [3H, 2,4-$(Me)_2C_6H_3$, *J* 8 Hz]	59.80	5.49	$C_{23}H_{25}BrO_5$	59.88	5.46
Vh	60	106–108	1755	1675	0.87 d (3H, CH*Me*, *J* 7 Hz), 2.23 s, 2.35 s (6H, $Me_2C_6H_3$), 3.37 s, 3.60 s (6H, COOMe, COOMe), 3.68 s, 3.72 s [6H, 3,4-$(MeO)_2C_6H_3$], 3.76 m (1H, C*H*Me), 3.88 m [1H, 3,4-$(MeO)_2C_6 \cdot H_3CH$], 4.08 d [1H, C*H*$(COOMe)_2$, *J* 10 Hz], 6.60 d, 6.65 s, 6.80 d [3H, 3,4-$(MeO)_2C_6H_3$, *J* 8 Hz], 7.15 s, 7.20 d, 7.77 d [3H, 2,4-$(Me)_2C_6H_3$, *J* 8 Hz]	67.87	6.81	$C_{25}H_{30}O_7$	67.86	6.83
Vi	38	114–115	1750	1675	0.75 t (3H, CH_2Me, *J* 7 Hz), 1.62 m (2H, CH_2Me), 3.35 s, 3.65 s (6H, COOMe, COOMe), 3.80 m (1H, C_6H_5CH), 3.98 d [1H, C*H*$(COOMe)_2$, *J* 10 Hz], 4.15 m (1H, C*H*Et), 7.05–7.20 m (5H, CHC_6H_5), 7.45–7.76 m (5H, COC_6H_5)	71.68	6.52	$C_{22}H_{24}O_5$	71.72	6.57
Vj	85	131–134	1750	1675	0.55 t (3H, CH_2Me, *J* 7 Hz), 1.34 m, 1.42 m (2H, CH_2Me), 3.37 s, 3.52 s (6H, COOMe, COOMe), 3.80 m (1H, 4-ClC_6H_4CH), 4.01 d [1H, C*H*$(COOMe)_2$, *J* 10 Hz], 4.05 m (1H, C*H*Et), 7.25 d, 7.34 d (4H, 4-$ClC_6H_4 \cdot CH$, *J* 10 Hz), 7.65 d, 8.05 d (4H, 4-ClC_6H_4CO, *J* 8 Hz)	60.49	5.12	$C_{22}H_{22}Cl_2O_5$	60.42	5.07
Vk	70	135–136	1740	1675	0.55 t (3H, CH_2Me, *J* 7 Hz), 1.33 m, 1.40 m (2H, CH_2Me), 3.37 s, 3.52 s (6H, COOMe, COOMe), 3.78 m (1H, 4-BrC_6H_4CH), 4.01 d [1H, C*H*$\cdot (COOMe)_2$, *J* 10 Hz], 4.05 m (1H, C*H*Et), 7.20 d, 7.45 d (4H, BrC_6H_4, *J* 8 Hz), 7.65 d, 8.05 d (4H, ClC_6H_4, *J* 8 Hz)	54.76	4.68	$C_{22}H_{22}BrClO_5$	54.85	4.60

Table 1. (Contd.)

Comp. no.	Yield, %	mp, °C	IR spectrum, ν, cm^{-1}		^{1}H NMR spectrum, δ, ppm	Found, %		Formula	Calculated, %	
			CO (ester)	CO (ketone)		C	H		C	H
Vl	45	99–102	1750	1675	0.55 t (3H, CH_2*Me*, *J* 7 Hz), 1.40 m (2H, C*H*$_2$Me), 3.37 s, 3.51 s (6H, COOMe, COOMe), 3.73 s [6H, (*Me*O)$_2$C$_6$H$_3$], 3.75 m [1H, 3,4-(MeO)$_2$C$_6$H$_3$C*H*], 3.98 d [1H, C*H*·(COOMe)$_2$, *J* 10 Hz], 4.00 m (1H, C*H*Et), 6.70 d, 6.78 s, 6.83 d [3H, 3,4-(MeO)$_2$C$_6$*H*$_3$, *J* 8 Hz], 7.65 d, 8.05 d (4H, 4-ClC6H4, *J* 8 Hz)	62.31	5.83	$C_{24}H_{27}ClO_7$	62.27	5.88
Vm	66	120–122	1755	1685	0.55 t (3H, CH_2*Me*, *J* 7 Hz), 1.34 m, 1.41 m (2H, C*H*$_2$Me), 3.37 s, 3.52 s (6H, COOMe, COOMe), 3.79 m (1H, 4-ClC$_6$H$_4$C*H*), 4.01 d [1H, C*H*·(COOMe)$_2$, *J* 10 Hz], 4.04 m (1H, C*H*Et), 7.25 d, 7.33 d (4H, 4-ClC$_6$H$_4$, *J* 8 Hz), 7.75 d, 7.96 d (4H, 4-BrC$_6$H$_4$, *J* 8 Hz)	54.71	4.65	$C_{22}H_{22}BrClO_5$	54.85	4.60
Vn	58	127–	1755	1685	0.55 t (3H, CH_2*Me*, *J* 7 Hz), 1.33 m, 1.40 m (2H, C*H*$_2$Me), 3.37 s, 3.52 s (6H, COOMe, COOMe), 3.78 m (1H, 4-BrC$_6$H$_4$C*H*), 4.02 d [1H, C*H*·(COOMe)$_2$, *J* 10 Hz], 4.04 m (1H, C*H*Et), 7.20 d, 7.45 d (4H, 4-BrC$_6$*H*$_4$·CH, *J* 8 Hz), 7.80 d, 7.95 d (4H, 4-BrC6H4CO, *J* 8 Hz)	50.29	4.41	$C_{22}H_{22}Br_2O_5$	50.21	4.21

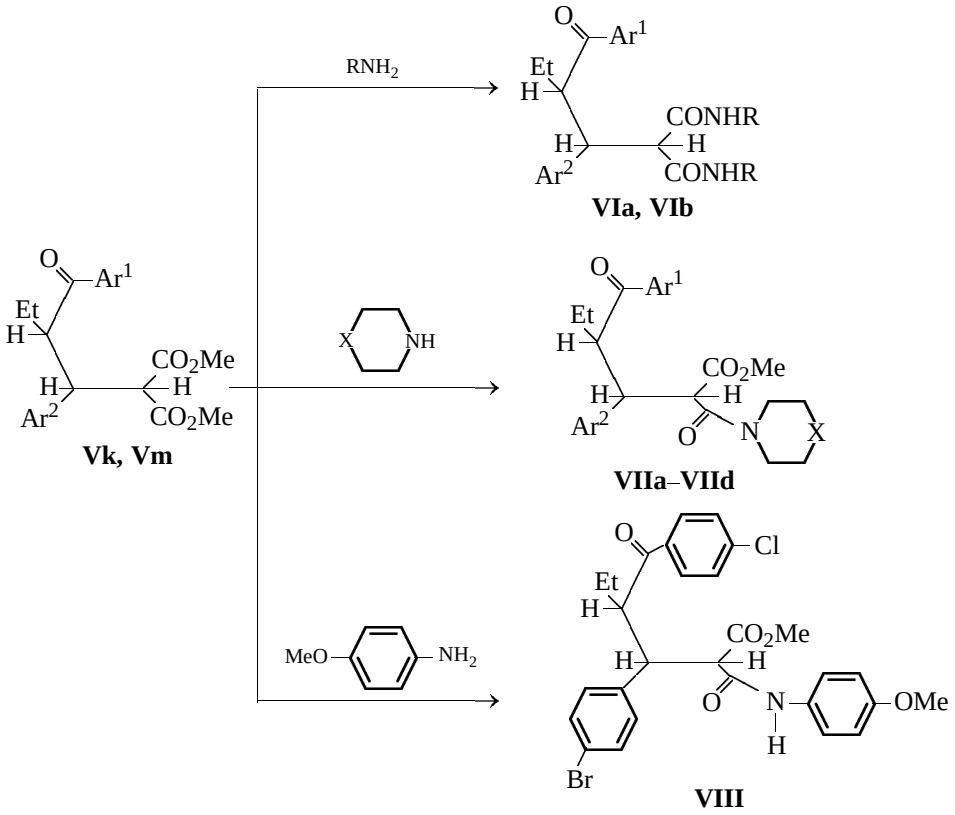
explained by the steric effect of the mesityl group. The composition and structure of compounds **Va**–**Vn** were proved by the elemental analyses and ^{1}H NMR and IR spectra (Table 1).

The IR spectra of compounds **Va**–**Vn** contain ketone and ester carbonyl absorption bands at 1675–1685 and 1720–1755 cm^{-1}, respectively. The ^{1}H NMR spectra, too, provide evidence to show that the reaction occurs stereoselectively to form as the major diastereomer an isomer whose CH(CO$_2$Me)$_2$ methine proton gives a doublet signal with *J* 10 Hz. The fraction of the minor diastereomer (*J* < 2 Hz) is sometimes 10%, but in most cases tends to zero. With the spectral evidence in hand we are unable to make rigorous diastereomeric assessment of the major and minor components.

Further we reacted the resulting dimethyl 2-(2-ethyl-1,3-diaryl-3-oxopropyl)malonates with N-nucleophiles, specifically amines (see scheme below).

Compounds **Va**–**Vn** contain three electrophilic carbonyl-containing groups: one ketone and two ester, and, therefore, the reaction can occur by tree electrophilic centers, i.e. the carbon atoms of these three groups. Therefore, we used a threefold excess on boiling in *o*-xylene one substrate molecule reacts with two primary amine (benzylamine and cyclohexylamine) molecules; therewith, reacting are the ester groups. As a result, disubstituted amides, N^1-R-N^2-R-2-(1-aryl-2-aroylbutyl)malonamides **VIa** and **VIb** are formed. The ketone group is not touched in these conditions, probably because it is less sterically accessible than the alkoxycarbonyl groups.

Evidence for the importance of steric effects in the reaction in hand is provided by the reaction of the



VI, R = *cyclo*-C_6H_{11}, Ar^1 = 4-ClC_6H_4, Ar^2 = 4-BrC_6H_4 (**a**); R = Bn, Ar^1 = 4-BrC_6H_4, Ar^2 = 4-ClC_6H_4 (**b**); **VII**, X = CH_2, Ar^1 = 4-ClC_6H_4, Ar^2 = 4-BrC_6H_4 (**a**), Ar^1 = 4-BrC_6H_4, Ar^2 = 4-ClC_6H_4 (**b**); X = O, Ar^1 = 4-ClC_6H_4, Ar^2 = 4-BrC_6H_4 (**c**), Ar^1 = 4-BrC_6H_4, Ar^2 = 4-ClC_6H_4 (**d**).

same substrate with secondary amines (piperidine and morpholine). Increased steric bulk of such amines results in that only one alkoxycarbonyl groups can exhibit activity, and these reactions yield monoamides, methyl 3-aryl-4-aroyl-2-(piperidinocarbonyl)- and -(morpholinocarbonyl)hexanoates **VIIa**–**VIId**.

On the other hand, electronic effects in amines, too, are of importance for the above reactions. Thus, no target amides could be prepared with weakly basic aromatic amines, such as *p*-toluidine. At the same time, the electron-donor methoxy substituent in the benzene ring of an aromatic amine renders the latter more basic; as a result, a monoamide, methyl 3-(4-bromophenyl)-4-(4-chlorobenzoyl)-2-(4-methoxyphenylcarbamoyl)hexanoate (**VIII**) could be prepared.

The composition and structure of compounds **VIa**, **VIb**, **VIIa**–**VIId**, and **VIII** are proved by the elemental analyses and ^{1}H NMR and IR spectra.

The IR spectra of diamides **VIa** and **VIb** contain absorption bands of amide and ketone carbonyl and NH groups at 1650–1680, 1650–1680, and 3300 cm^{-1}, respectively. In the IR spectra of monoamides **VIIa**–**VIId**, there are bands of amide, ketone, and ester carbonyl groups at 1640–1645, 1675–1685, and 1720–1730 cm^{-1}, respectively. The IR spectrum of compound **VIII** displays amide, ketone, and ester carbonyl bands at 1655–1670, 1720, and 3320 cm^{-1}, respectively. The ^{1}H NMR spectra of compounds **VIa** and **VIb** are given in Experimental, and of **VIIa**–**VIId** and **VIII**, in Table 2.

EXPERIMENTAL

The IR spectra were measured on a UR-20 instrument in mineral oil. The ^{1}H NMR spectra were recorded for DMSO-d_6 solutions on a Bruker-DRX instrument (500 MHz), internal reference TMS.

Dimethyl 2-(2-alkyl-1-,3-diaryl-3-oxopropyl)-malonates Va–**Vn.** To 2 g of fine zinc turnings in 7 ml of diethyl ether and 7 ml of ethyl acetate, 0.08 mol of dimethyl 2-(4-arylmethylene)malonate **IIIa**–**IIId** and 0.015 mol of 1-aryl-2-bromoalkanone **Ia**–**Ig** were added. The mixture was heated to initiate reaction, after which spontaneous reaction was observed. After the reaction was complete, the mixture

Table 2. Yields, melting points, IR spectra, ^{1}H NMR spectra, and elemental analyses of methyl 3-aryl-4-aroyl-2-(piperidinocarbonyl)-, -(morpholinocarbonyl)-, and -(4-methoxyphenylcarbamoyl)hexanoates **VIIa**–**VIId** and **VIII**

Comp. no.	Yield, %	mp, °C	IR spectrum, ν, cm^{-1}			^{1}H NMR spectrum, δ, ppm	Found, %		Formula	Calculated, %	
			CO (amide)	CO (ketone)	CO (ester)		C	H		C	H
VIIa	55	212–215	1640	1675	1720	0.63 t (3H, CH_2*Me*, *J* 7 Hz), 1.40–1.65 m, 3.50 m, 3.70 m (10H, $C_4H_{10}N$), 1.46 m (2H, C*H*$_2$Me), 3.32 s (3H, COOMe), 3.65 m (1H, C*H*Et), 3.86 d. d (1H, 4-BrC_6H_4C*H*, *J* 6, 10 Hz), 4.62 d (1H, C*H*COOMe, *J* 10 Hz), 7.00 d, 7.37 d (4H, 4-BrC_6H_4, *J* 8 Hz), 7.65 d, 8.08 d (4H, 4-ClC_6H_4, *J* 8 Hz)	58.40	5.49	$C_{26}H_{29}BrClNO_4$	58.38	5.46
VIIb	29	196–198	1640	1685	1725	0.64 t (3H, CH_2*Me*, *J* 7 Hz), 1.40–1.65 m, 3.50 m, 3.72 m (10H, $C_4H_{10}N$), 1.46 m (2H, C*H*$_2$Me), 3.32 s (3H, COOMe), 3.65 m (1H, C*H*Et), 3.88 d.d (1H, 4-ClC_6H_4C*H*, *J* 6, 10 Hz), 4.62 d (1H, C*H*COOMe, *J* 10 Hz), 7.06 d, 7.23 d (4H, ClC_6H_4, *J* 8 Hz), 7.80 d, 8.00 d (4H, 4-BrC_6H_4, *J* 8 Hz)	58.36	5.51	$C_{26}H_{29}BrClNO_4$	58.38	5.46
VIIc	37	186–188	1640	1675	1720	0.64 t (3H, CH_2*Me*, *J* 7 Hz), 1.46 m (2H, C*H*$_2$Me), 3.35 s (3H, COOMe), 3.45–3.85 m (8H, C_4H_8NO), 3.67 m (1H, C*H*Et), 3.89 d.d (1H, 4-BrC_6H_4C*H*, *J* 6, 10 Hz), 4.62 d (1H, CHCOOMe, *J* 10 Hz), 7.03 d, 7.39 d (4H, 4-BrC_6H_4, *J* 8 Hz), 7.65 d, 8.08 d (4H, 4-ClC_6H_4, *J* 8 Hz)	55.85	5.10	$C_{25}H_{27}BrClNO_5$	55.93	5.07
VIId	36	171–173	1645	1685	1730	0.64 t (3H, CH_2*Me*, *J* 7 Hz), 1.46 m (2H, C*H*$_2$Me), 3.35 s (3H, COOMe), 3.45–3.85 m (8H, C_4H_8NO), 3.66 m (1H, C*H*Et), 3.89 d. d (1H, 4-ClC_6H_4C*H*, *J* 6, 10 Hz), 4.63 d (1H, CHCOOMe, *J* 10 Hz), 7.07 d, 7.25 d (4H, 4-ClC_6H_4, *J* 8 Hz), 7.80 d, 8.00 d (4H, 4-BrC_6H_4, *J* 8 Hz)	55.90	5.11	$C_{25}H_{27}BrClNO_5$	55.93	5.07

Table 2. (Contd.)

Comp. no.	Yield, %	mp, °C	IR spectrum, ν, cm^{-1}			^{1}H NMR spectrum, δ, ppm	Found, %		Formula	Calculated, %	
			CO (amide)	CO (ketone)	CO (ester)		C	H		C	H
VIII[a]	35	178–180	1655–1670		1720	0.65 t (3H, CH_2*Me*, *J* 7 Hz), 1.45 m (2H, CH_2Me), 3.63 s, 3.69 s (6H, COOMe, 4-*Me*OC_6H_4), 3.85 m (2H, C*H*Et, 4-BrC_6H_4C*H*), 4.19 d (1H, C*H*COOMe, *J* 10 Hz), 6.75 d, 7.05 d (4H, 4-BrC_6H_4, *J* 8 Hz), 7.12 d, 7.47 d (4H, 4-MeOC_6H_4, *J* 8 Hz), 7.65 d, 8.05 d (4H, 4-ClC_6H_4, *J* 8 Hz), 9.85 s (1H, NH)	59.00	4.81	$C_{28}H_{27}BrClNO_5$	58.70	4.75

[a] The ν(NH) band of compound **VIII** appears at 3320 cm^{-1}.

was heated under reflux for 15–20 min and then cooled, hydrolyzed with 10% HCl, treated with diethyl ether, the organic layer was separated, wshed to neutral with 10% sodium bicarbonate, dried with sodium sulfate, and the solvents were removed by distillation. The final products were purified by double crystallization from methanol.

***N,N*-R_2-2-(1-Aroyl-2-aroylbutyl)malonamides VIa and VIb.** To 2.1 mmol of dimethyl 2-(1-aryl-3-aryl-3-oxo-2-ethylpropyl)malonate **Vl** and **Vn**, dissolved in 10 ml of *o*-xylene, 6.3 mmol of amine (cyclohexylamine or benzylamine) was added. The mixture was heated for 6 h. The solvent was removed by distillation, and amide **VIa** or **VIb** that precipitated was doubly crystallized from methanol.

***N,N*'-Dicyclohexyl-2-[1-(4-bromophenyl)-2-(4-chlorobenzoyl)butyl]malonamide (VIa),** yield 42%, mp 220–221°C. IR spectrum, ν, cm^{-1}: 1655 (amide C=O), 1680 (ketone C=O), 3300 (N–H). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 0.64 t (3H, CH_2*Me*, *J* 7 Hz), 0.79–1.80 m (20H, 2 *cyclo*-C_6H_{11}), 1.43 m, 1.52 m (2H, CH_2Me), 3.64 m [3H, C*H*$(CONH)_2$, C*H*Et, NHC*H*], 3.77 m (2H, 4-BrC_6H_4C*H*, NHC*H*), 6.80 d, 7.36 d (4H, 4-BrC_6H_4, *J* 8 Hz), 7.39 br.s, 7.77 br.s (2H, NH, NH), 7.69 d, 8.05 d (4H, 4-ClC_6H_4, *J* 8 Hz). Found,%: C 62.45; H 6.50. $C_{32}H_{40}BrClN_2O_3$. Calculated, %: C 62.39; H 6.54.

***N,N*'-Dibenzyl-2-[1-(4-bromophenyl)-2-(4-chlorobenzoyl)butyl]malonamide (VIb),** yield 35%, mp 224–226°C. IR spectrum, ν, cm^{-1}: 1660–1675 (amide C=O), (ketone C=O), 3300 (N–H). ^{1}H NMR spectrum (DMCO-d_6), δ, ppm: 0.60 t (3H, CH_2*Me*, *J* 7 Hz), 1.46 m, 1.56 m (2H, CH_2Me) 3.56 m (1H, 4-ClC_6H_4·C*H*), 3.88 m (1H, C*H*Et), 3.99 d [1H, C*H*$(CONH)_2$, *J* 10 Hz], 4.00 d, 4.09 d, 4.35 d, 4.42 d (4H, 2NH·C$H_2C_6H_5$, *J* 8 Hz), 6.67 d, 6.85 d, 7.10 m, 7.25 m, 7.32 m (10H, $2C_6H_5$, *J* 8 Hz), 7.10 d, 7.24 d (4H, 4-ClC_6H_4, *J* 8 Hz), 7.75 d, 7.86 d (4H, 4-BrC_6H_4, *J* 8 Hz), 8.17 br.s, 8.57 br.s (2H, NH, NH). Found, %: C 64.59; H 5.22. $C_{34}H_{32}BrClN_2O_3$. Calculated, %: C 64.62; H 5.10.

Methyl 3-aryl-4-aroyl-2-(piperidinocarbonyl)-, -(morpholinocarbonyl)-, -(4-methoxyphenylcarbamoyl)hexanoates VIIa–VIId and VIII were prepared like **VIa** and **VIb**, but using piperidine, morpholine, and *p*-anisidine (Table 2).

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