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1,3-Oxazines and Related Compounds. V.[1] *N*-Acylacetylation of Carboxamides with the Diketene-Halotrimethylsilane System or Acyl Meldrum's Acids[2]

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Various aliphatic and aromatic carboxamides smoothly underwent *N*-acetoacetylation by means of the diketene–iodotrimethylsilane system to give the corresponding *N*-acetoacetyl derivatives. The diketene–bromotrimethylsilane system was found to be very efficient for *N*-acetoacetylation of unsaturated carboxamides such as acrylamide and methacrylamide. In addition, acyl Meldrum's acids proved effective for *N*-acylacetylation of carboxamides, especially heterocyclic carboxamides such as picolinamides.

Keywords——carboxamide; acylacetylation; diketene; iodotrimethylsilane; bromotrimethylsilane; acyl Meldrum's acid

In the previous paper,[3] *N*-acetoacetylcarboxamides have been shown to be potentially useful as precursors of 1,3-oxazines and 1,3-thiazines. In the course of our continuing studies in this series, we required *N*-acylacetyl derivatives of a variety of carboxamides. We wish to report herein a general and facile procedure for *N*-acylacetylation of carboxamides using diketene–halotrimethylsilanes or acyl Meldrum's acids.

N-Acetoacetylation by Means of the Diketene-Halotrimethylsilane System (Methods A, B, and C)

Perekalin and Lerner[4] had reported that various carboxamides reacted directly with diketene to give the corresponding *N*-acetoacetyl derivatives. Kato and Kubota[5] reinvestigated this work and found that the reactions were not always successful. On the other hand, halotrimethylsilanes such as iodo- and bromotrimethylsilanes have recently been well investigated, especially as dealkylating reagents.[6] We were thus interested in the application of the reagents to *N*-acetoacetylation of carboxamides (**1**) with diketene (**2**).

It was found that aromatic and saturated aliphatic amides (**1a—k**) easily underwent *N*-acetoacetylation with **2** in the presence of iodotrimethylsilane (**3a**) (Method A). For instance, acetamide (**1a**) was treated with **2** in acetonitrile in the presence of **3a** [generated *in situ* from chlorotrimethylsilane (**3c**) and sodium iodide by the literature procedure][7] to afford *N*-acetoacetylacetamide (**4a**). Similarly, *N*-acetoacetylation of the other carboxamides (**1b—k**) proceeded smoothly giving the corresponding *N*-acetoacetyl derivatives (**4b—k**) in good yields.

Method A was also found to be effective for the *N*-acetoacetylation of unsaturated carboxamides such as crotonamide (**1n**) and cinnamamide (**1o**). However, similar treatment of acrylamide (**1l**) and methacrylamide (**1m**) exclusively gave rise to the corresponding *N*-acetoacetylated iodo derivatives (**5a, b**). The iodo derivatives (**5a, b**) were identical with the respective authentic samples which were synthesized from iodo carboxamides (**1t, u**) and **2** by the method described above. These results evidently suggest that addition of hydrogen iodide (produced in the reaction system) took place simultaneously with the *N*-acetoacetylation.

In the reactions of **1l, m**, removal of the hydrogen iodide[8] by continuously bringing nitrogen into the reaction mixture (Method B) led to an increase in the yields of the corresponding **4l** and **4m**, respectively. Furthermore, bromotrimethylsilane (**3b**), which was prepared *in situ* from **3c** and lithium bromide according to the method given in the literature,[9] was found to be particularly efficient for the reaction of **1l, m**, leading to isolation of the *N*-acetoacetylated

derivatives (**4l, m**) as sole products (Method C). The results of Method C together with those of Methods A and B are summarized in Table I.

A probable pathway for the *N*-acetoacetylation can be formulated as shown in Chart 1, involving the formation of the *O*-trimethylsilylated intermediate (**6a** and/or **6b**) from **2** and **3a**.

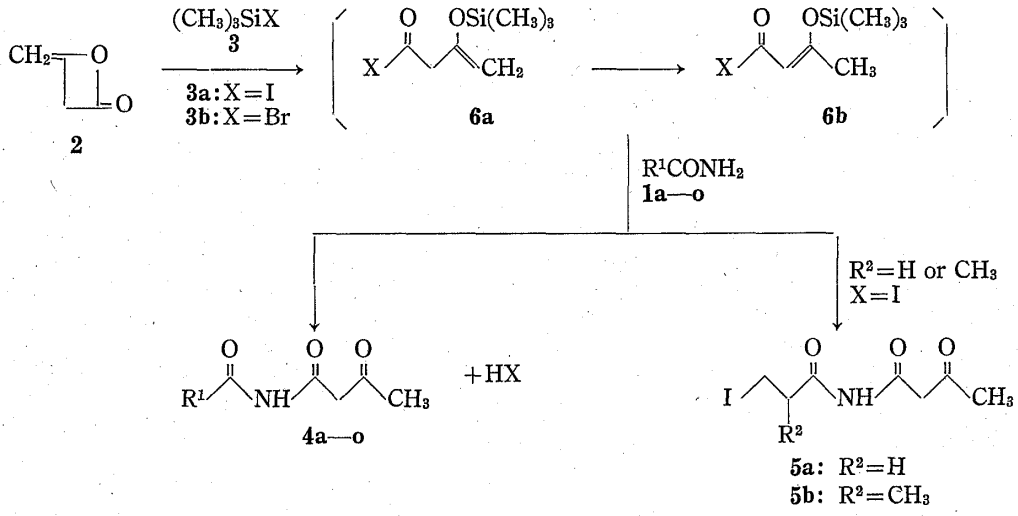


Chart 1

TABLE I. Preparation of *N*-Acetoacetylcarboxamides (**4a—o, 5a, b**)

Compd. No.	R^1	Yield (%) (Method)	Compd. No.	R^1	Yield (%) (Method)
4a	CH_3	62 (A) 64 (C)	**4i**	4-Cl-C_6H_4	88 (A)
4b	C_2H_5	77 (A)	**4k**	4-NO_2-C_6H_4	86 (A)
4c	*n*-C_3H_7	70 (A)	**4l**	CH_2=CH	29 (B) 77.5 (C)
4d	iso-C_3H_7	64 (A)	**4m**	CH_2=C(CH$_3$)	49 (B) 82 (C)
4e	*tert*-C_4H_9	81 (A)	**4n**	CH_3CH=CH	77 (A)
4f	$C_6H_5CH_2$	82 (A)	**4o**	C_6H_5CH=CH	80 (A)
4g	C_6H_5	86 (A) 76.5 (C)	**5a**	ICH_2CH_2	68 (A) 29 (B)
4h	4-CH_3-C_6H_4	83 (A)	**5b**	ICH_2CH(CH$_3$)	71 (A) 12 (B)
4i	4-CH_3O-C_6H_4	89.5 (A)			

N-Acylacetylation using Acyl Meldrum's Acids (Method D)

Acyl Meldrum's acid (5-acyl-2,2-dimethyl-1,3-dioxane-4,6-dione) has been demonstrated by Yonemitsu *et al.*[10] to be a synthetic equivalent of mixed diketenes. Application of acyl Meldrum's acid in the *N*-acylacetylation of carboxamides would offer considerable advantages as an additional methodology. Thus, the reactions of a variety of carboxamides with acyl Meldrum's acids were carried out.

Acyl Meldrum's acids used in this paper were prepared by a procedure similar to that described in the literature.[10] The acyl groups were acetyl, propionyl, isobutyryl, phenylacetyl, bromoacetyl, and benzoyl.

N-Acylacetylation of carboxamides with acyl Meldrum's acid was simply carried out: thus, heating a solution of benzamide (**1g**) and propionyl Meldrum's acid (**7b**) in benzene under reflux afforded *N*-propionylacetylbenzamide (**8a**) in a good yield. In a similar manner, various *N*-acylacetylcarboxamides (**8b—j**) were synthesized in satisfactory yields (Table II).

The structural assignments of **8a—j** were accomplished on the basis of spectroscopic (IR and ^{1}H-NMR) and analytical evidence.

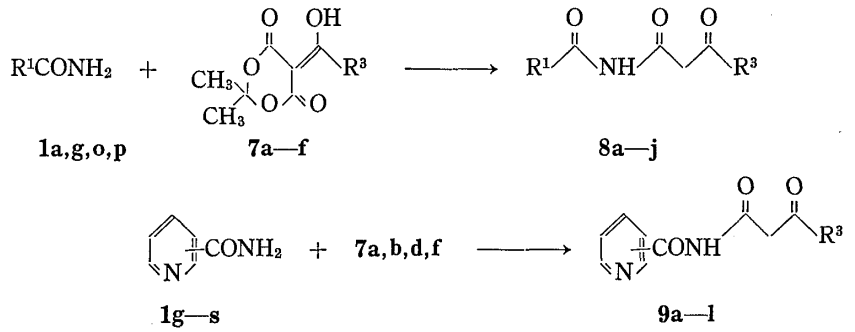


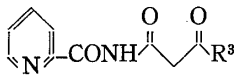
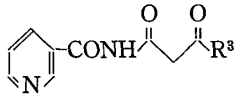
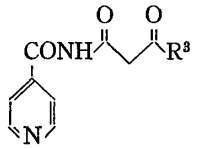
Chart 2

TABLE II. Preparation of *N*-Acylacetylcarboxamides (**8a—j**)

Compd. No.	R^1	R^3	Yield (%)	Compd. No.	R^1	R^3	Yield (%)
8a	C_6H_5	C_2H_5	81.5	**8f**	CH_3	C_2H_5	70
8b	C_6H_5	iso-C_3H_7	70	**8g**	CH_3	iso-C_3H_7	74
8c	C_6H_5	$C_6H_5CH_2$	69	**8h**	CH_3	$C_6H_5CH_2$	68.5
8d	C_6H_5	$BrCH_2$	62	**8i**	H	C_2H_5	59
8e	C_6H_5	C_6H_5	63	**8j**	$C_6H_5CH=CH$	C_2H_5	70

Attempts to prepare *N*-acylacetyl derivatives of **1l, m** by Method D resulted in polymerization of the starting material (**1l, m**). Meanwhile, it is significant that Method D proved effective for the *N*-acylacetylation of heterocyclic carboxamides such as α-picolinamide (**1g**), nicotinamide (**1r**), and isonicotinamide (**1s**), because Methods A, B, and C were unable to furnish the *N*-acylacetyl derivatives of such heterocyclic carboxamides, giving resinous substances without any isolable product in any case. In a typical case, a solution of **1g** and **7b** in benzene was heated for 30 min under reflux to provide *N*-propionylacetyl-α-picolinamide (**9d**). Nicotinamide (**1r**) and isonicotinamide (**1s**) analogously reacted to yield the corresponding *N*-acylacetyl derivatives (Table III).

TABLE III. Preparation of *N*-Acylacetyl Heterocyclic Carboxamides (**9a—l**)

	Compd. No.	R^3	Yield (%)	Compd. No.	R^3	Yield (%)	Compd. No.	R^3	Yield (%)	Compd. No.	R^3	Yield (%)
	**9a**	CH_3	70	**9d**	C_2H_5	68	**9g**	$C_6H_5CH_2$	74	**9j**	C_6H_5	64
	**9d**	CH_3	62	**9e**	C_2H_5	72	**9h**	$C_6H_5CH_2$	61	**9k**	C_6H_5	65
	**9c**	CH_3	64	**9f**	C_2H_5	64	**9i**	$C_6H_5CH_2$	70	**9l**	C_6H_5	60

Experimental

Melting points were obtained in a Mel-Temp melting point apparatus with an open capillary tube, and are uncorrected. Infrared (IR) spectra were taken on a Shimadzu IR-400 or IR-430 spectrometer. ^{1}H-Nuclear magnetic resonance (^{1}H-NMR) spectra were measured on a JEOL PMX 60 or Hitachi R-24B instrument. Chemical shifts are reported in δ values downfield relative to internal tetramethylsilane. The following abbreviations are used: s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet, br=broad and dd=double doublet.

General Procedure for *N*-Acetoacetylation of Carboxamides 1——Method A: A solution of chlorotrimethylsilane (1.41 g, 13 mmol) in dry acetonitrile (10 ml) was added dropwise with stirring to an ice-bath cooled solution of **1** (10 mmol), sodium iodide (1.95 g, 13 mmol) and **2** (1.09 g, 13 mmol) in dry acetonitrile (30 ml). After completion of the addition, the cooling bath was removed and stirring was continued at room temperature for 2 h. The mixture was concentrated under an aspirator vacuum, followed by extraction with chloroform (3×20 ml). The chloroform layer was washed successively with 10% sodium thiosulfate solution (20 ml) and water (20 ml), then dried over anhydrous magnesium sulfate. Concentration of the chloroform layer gave the crude product **4**, which was purified by recrystallization from the solvent indicated in Table IV.

Method B: A solution of chlorotrimethylsilane (1.09 g, 10 mmol) in dry acetonitrile (10 ml) and a solution of 10 mmol of **1l** or **1m** in dry acetonitrile (20 ml) were successively added dropwise to a stirred solution of sodium iodide (1.5 g, 10 mmol) and **2** (0.84 g, 10 mmol) in dry acetonitrile (20 ml) under cooling with an ice-bath. During the addition of **1l** or **1m**, nitrogen was passed into the reaction mixture. Cooling,

Table IV. Melting Points and Analytical Data of *N*-Acetoacetylcarboxamides (**4a—o, 5a, b**)

Compd. No.	mp (°C) (Solvent)	Formula or lit. mp (°C)	Analysis (%) Calcd (Found) C	H	N
4a	86—86.5 (ether)	88—89[11]		——	
4b	116—117 (EtOH)	116—117[11]		——	
4c	95—95.5 (ether–P.E.)[a]	$C_8H_{13}NO_3$	56.12 (56.15	7.65 7.75	8.18 8.22)
4d	83—84 (ether–P.E.)[a]	81—82[11]		——	
4e	110—111 (ether)	$C_9H_{15}NO_3$	58.36 (58.14	8.16 8.14	7.56 7.40)
4f	146—147 (EtOH)	147—148[12]		——	
4g	120—121 (C_6H_6)	123—124[5]		——	
4h	144—145 (C_6H_6)	$C_{12}H_{13}NO_3$	65.74 (65.81	5.98 5.99	6.39 6.16)
4i	136.5—138 (C_6H_6)	$C_{12}H_{13}NO_4$	61.27 (60.97	5.57 5.45	5.96 6.03)
4j	148—149 (C_6H_6)	$C_{11}H_{10}ClNO_3$	55.13 (55.17	4.21 4.26	5.84 5.64)
4k	149—150 (MeOH)	$C_{11}H_{10}N_2O_5$	52.80 (52.80	4.03 3.96	11.20 11.08)
4l	125—126.5 (hexane)	$C_7H_9NO_3$	54.19 (53.90	5.85 5.88	9.03 8.84)
4m	52—52.5 (ether)	$C_8H_{11}NO_3$	56.79 (56.62	6.55 6.50	8.28 7.99)
4n	108—109 (ether)	$C_8H_{11}NO_3$	56.79 (57.00	6.55 6.67	8.28 8.31)
4o	114—115 (C_6H_6)	$C_{13}H_{13}NO_3$	67.52 (67.35	5.67 5.57	6.06 5.84)
5a	134—135 (EtOH)	$C_7H_{10}INO_3$	29.70 (29.58	3.56 3.43	4.95 4.73)
5b	98—99.5 (ether–P.E.)[a]	$C_8H_{12}INO_3$	32.34 (32.29	4.07 4.10	4.71 4.53)

a) P.E.=petroleum ether.

stirring, and passage of nitrogen were continued for a further 10 h. The resultant mixture was concentrated under an aspirator vacuum, followed by extraction with chloroform (3×20 ml). The chloroform layer was washed successively with 10% sodium thiosulfate solution (20 ml) and water (20 ml), then dried over anhydrous magnesium sulfate. Concentration of the chloroform layer gave a mixture of **4l** and **5a**, or of **4m** and **5b**, which were separated and purified by fractional recrystallization.

Method C: A solution of chlorotrimethylsilane (2.17 g, 20 mmol) in acetonitrile (10 ml) was added dropwise with stirring to an ice-bath cooled solution of **1** (10 mmol), lithium bromide (1.74 g, 20 mmol) and **2** (1.26 g, 15 mmol) in acetonitrile (40 ml). The mixture was stirred at 50°C (bath temp.) in an oil bath for 3 h, and then concentrated under an aspirator vacuum, followed by extraction with chloroform (3×30 ml). The chloroform layer was washed with water (20 ml) and dried over anhydrous magnesium sulfate. Concentration of the chloroform layer gave the crude product **4**, which was purified by recrystallization from the solvent indicated in Table IV. Table IV also shows the analytical data and melting points of *N*-acetoacetylcarboxamides (**4** and **5**) prepared. Spectral data for **4** and **5** are summarized in Table V.

Table V. *N*-Acetoacetylcarboxamides (**4a—o, 5a, b**)

Compd. No.	IR^{KBr}_{max} cm^{-1}	Ratio keto: enol	PMR (60 MHz, $CDCl_3$) δ [ppm]						
					keto		enol		
			R^1	NH	R^3	CH_2	R^3	$-CH=$	OH
4a	1740 1700(sh)	5:1	2.23(3H,s)	9.60	2.33(s, CH_3)	3.83	2.07(s, CH_3)	5.90	13.40
4b	1730 1700(sh)	4:1	1.16(3H, t, J=8 Hz) 2.35(2H, q, J=8 Hz)	9.40	2.33(s, CH_3)	3.83	2.03(s, CH_3)	6.00	13.43
4c	1740 1700(sh)	5:1	0.93(3H, t, J=6 Hz) 1.8(2H, m), 2.24(2H, t, J=6 Hz)	9.43	2.33(s, CH_3)	3.86	2.00(s, CH_3)	6.07	13.40
4d	1720 1700(sh)	4:1	1.17(6H, d, J=8 Hz) 2.7(1H, m)	9.10	2.30(s, CH_3)	3.90	2.03(s, CH_3)	6.23	13.60
4e	1720 1690	7:1	1.23(9H, s)	8.93	2.27(s, CH_3)	3.93	2.00(s, CH_3)	6.40	13.66
4f	1740 1720	4:1	3.83(2H, s) 7.37(5H, s)	9.67	2.43(s, CH_3)	4.00	2.13(s, CH_3)	6.27	—[a]
4g	1710 1680	7:3	7.4—8.2(5H, m)	9.70	2.34(s, CH_3)	4.07	2.10(s, CH_3)	6.63	13.65
4h	1720(sh) 1700	5:1	2.40(3H, s) 7.2—7.8(4H, m)	9.23	2.32(s, CH_3)	4.00	2.07(s, CH_3)	6.53	13.63
4i	1720 1700 1680	6:1	3.93(3H, s) 6.9—8.0(4H, m)	—[a]	2.43(s, CH_3)	4.17	2.17(s, CH_3)	6.53	—[a]
4j	1720 1700 1680	7:1	6.9—8.0(4H, m)	—[a]	2.47(s, CH_3)	4.15	2.17(s, CH_3)	6.50	—[a]
4k	1710 1680	6:1	8.0—8.6(4H, m)	—[a]	2.50(s, CH_3)	4.53	2.20(s, CH_3)	6.60	—[a]
4l	1720 1700(sh) 1630	10:3	5.7—6.6(3H, m)	9.57	2.33(s, CH_3)	3.97	2.05(s, CH_3)	6.20	13.50
4m	1720 1710(sh) 1675	7:2	2.00(3H, s) 5.47(1H, s) 5.90(1H, s)	9.00	2.30(s, CH_3)	3.97	2.08(s, CH_3)	6.37	13.73
4n	1715 1640	2:1	1.97(3H, dd, J=2, 7 Hz); 6.17(1H, dd, J=2, 15 Hz); 7.05(1H, dq, J=7, 15 Hz)	9.70	2.30(s, CH_3)	4.00	2.10(s, CH_3)	6.10	13.60
4o	1720 1670 1630	5:2	6.80(1H, d, J=14 Hz) 7.2—7.6(5H, m) 7.60(1H, d, J=14 Hz)	9.73	2.37(s, CH_3)	3.93	2.00(s, CH_3)	6.13	13.60
5a	1740 1720 1700(sh)	5:1	3.3(4H, m)	9.80	2.40(s, CH_3)	4.00	2.10(s, CH_3)	6.00	—[a]
5b	1740(sh) 1720	3:1	1.30(3H, d, J=7 Hz) 2.7—3.4(3H, m)	9.23	2.30(s, CH_3)	3.87	2.05(s, CH_3)	6.10	13.43

a) In 10:1 $CDCl_3/CF_3COOH$ solution.

General Procedure for *N*-Acylacetylation of Carboxamide 1 using Acyl Meldrum's Acid (Method D)——A solution of **1** (10 mmol) and acyl Meldrum's acid **7** (13 mmol) in benzene (30 ml) was heated under reflux for 30 min then concentrated under an aspirator vacuum. The residue was purified by recrystallization or distillation to give *N*-acylacetylated carboxamide (**8** and **9**). In the case of *N*-acetylacetylation of **1r** or **1s**

Table VI. Melting Points and Analytical Data of *N*-Acylacetylcarboxamides (**8a—j**)

Compd. No.	mp (°C) (Solvent) or bp (Torr)	Formula	Analysis (%) Calcd (Found) C	H	N
8a	125—126.5 (C_6H_6)	$C_{12}H_{13}NO_3$	65.74 (65.98	5.98 5.99	6.39 6.35)
8b	115—116 (ether)	$C_{13}H_{15}NO_3$	66.93 (67.14	6.48 6.39	6.01 5.83)
8c	138—140 (C_6H_6–ether)	$C_{17}H_{15}NO_3$	72.58 (72.46	5.37 5.18	4.98 4.82)
8d	126—127 (C_6H_6)	$C_{11}H_{10}BrNO_3$	46.50 (46.65	3.55 3.42	4.93 4.83)
8e	178—179 (acetone)	$C_{16}H_{13}NO_3$	71.90 (71.66	4.90 4.64	5.24 5.08)
8f	88—89.5 (EtOH)	$C_7H_{11}NO_3$	53.49 (53.19	7.05 6.97	8.91 8.75)
8g	113—115 (1.7)	$C_8H_{13}NO_3$	56.12 (55.88	7.65 7.45	8.18 8.04)
8h	124—125 (C_6H_6)	$C_{12}H_{13}NO_3$	65.74 (65.90	5.98 6.07	6.39 6.40)
8i	57—59 (ether)	$C_6H_9NO_3$	50.34 (50.52	6.34 6.24	9.79 9.64)
8j	127—128 (C_6H_6)	$C_{14}H_{15}NO_3$	68.55 (68.30	6.16 6.18	5.71 5.58)

Table VII. Melting Points and Analytical Data of *N*-Acylacetyl Heterocyclic Carboxamides (**9a—l**)

Compd. No.	mp (°C) (Solvent)	Formula	Analysis (%) Calcd (Found) C	H	N
9a	111—112 (C_6H_6)	$C_{10}H_{10}N_2O_3$	58.25 (58.21	4.89 4.71	13.58 13.47)
9b	122—124 (dec.) (C_6H_6)	$C_{10}H_{10}N_2O_3$	58.25 (58.49	4.89 4.71	13.58 13.45)
9c	95.5—97 (ether)	$C_{10}H_{10}N_2O_3$	58.25 (57.98	4.89 4.63	13.58 13.30)
9d	56—59 (ether–P.E.)	$C_{11}H_{12}N_2O_3$	59.99 (60.12	5.49 5.50	12.72 12.94)
9e	111.5—112 (dec.) (C_6H_6)	$C_{11}H_{12}N_2O_3$	59.99 (60.23	5.49 5.43	12.72 12.97)
9f	100—101 (C_6H_6–ether)	$C_{11}H_{12}N_2O_3$	59.99 (59.90	5.49 5.51	12.72 12.85)
9g	93—94 (ether)	$C_{16}H_{14}N_2O_3$	68.07 (67.99	5.00 5.02	9.92 9.94)
9h	103—104 (dec.) (EtOH)	$C_{16}H_{14}N_2O_3$	68.07 (68.26	5.00 4.97	9.92 9.89)
9i	129—130 (C_6H_6)	$C_{16}H_{14}N_2O_3$	68.07 (68.29	5.00 5.04	9.92 10.01)
9j	118—120 (C_6H_6)	$C_{15}H_{12}N_2O_3$	67.15 (67.30	4.51 4.56	10.44 10.73)
9k	145—148 (dec.) (EtOH)	$C_{15}H_{12}N_2O_3$	67.15 (67.17	4.51 4.49	10.44 10.42)
9l	147—149 (C_6H_6)	$C_{15}H_{12}N_2O_3$	67.15 (66.86	4.51 4.56	10.44 10.31)

(10 mmol), two equivalents of acyl Meldrum's acid and 150 ml of benzene as a solvent were employed, and the reaction mixture was refluxed for 60 min. Analytical results and melting points of *N*-acylacetylcarboxamides (**8** and **9**) are listed in Table VI and VII, and spectral data are summarized in Table VIII.

TABLE VIII. *N*-Acylacetylcarboxamides (**8a—j, 9a—l**)

Compd. No.	IR ν_{max}^{KBr} cm^{-1}	Ratio keto: enol	PMR (60 MHz, $CDCl_3$) δ[ppm]						
			keto				enol		
			R^1	NH	R^3	CH_2	R^3	-CH=	OH
8a	1730(sh) 1710 1680	3:1	7.3—7.9 (5H, m)	9.30	1.10 (t, J=7 Hz, CH_2-CH_3); 2.60 (q, J=7 Hz, CH_2CH_3)	4.00	1.17 (t, J=7 Hz, CH_2CH_3); 2.33 (q, J=7 Hz, CH_2-CH_3)	6.50	14.00
8b	1730(sh) 1715 1685	1:0	7.4—7.9 (5H, m)	9.30	3.19 (d, J=8 Hz, CH-$(CH_3)_2$); 2.5—3.0 (m, $CH(CH_3)_2$)	4.07			
8c	1725 1710 1680	3:1	7.2—7.9 (5H, m)	9.06	3.87 (s, $C_6H_5CH_2$) 7.2—7.9 (m, arom H)	3.97	3.60 (s, $C_6H_5CH_2$) 7.2—7.9 (m, arom H)	6.50	13.73
8d	1740 1715 1685	2:1	7.4—8.0 (5H, m)	9.26	4.13 (s, $BrCH_2$)	4.23	3.93 (s, $BrCH_2$)	6.83	13.55
8e	1710 1690 1680	5:3	7.2—8.1 (10H, m)	10.33 (0.37H) 10.83 (0.63H)		4.53		7.10	14.50
8f	1740 1720 1700	9:2	2.20 (2.45H, s) 2.26 (0.55H, s)	9.56	1.06 (t, J=7 Hz, CH_2-CH_3); 2.58 (q, J=7 Hz, CH_2CH_3)	3.73	1.13 (t, J=7 Hz, CH_2CH_3); 2.58 (q, J=7 Hz, CH_2-CH_3)	5.80	13.50
8g	1735[a] 1720 1690	5:2	2.23 (2.14H, s) 2.30 (0.86H, s)	9.60	1.13 (d, J=7 Hz, CH-$(CH_3)_2$); 2.4—3.0 (m, $CH(CH_3)_2$)	3.83	1.13 (d, J=7 Hz, $CH(CH_3)_2$); 2.4—3.0 (m, $CH(CH_3)_2$)	5.83	13.55
8h	1735 1720 1695	4:1	2.18 (2.4H, s) 2.25 (0.6H, s)	8.90 (0.2H) 9.50 (0.8H)	3.73 (s, $C_6H_5CH_2$) 7.26 (s, arom H)	3.83	3.55 (s, $C_6H_5CH_2$) 7.26 (s, arom H)	5.78	13.46
8i	1750 1710 1680	9:4	8.97 (0.31H) 9.13 (0.69H)	9.20 (0.69H) 9.80 (0.31H)	1.10 (t, J=7 Hz, CH_2-CH_3); 2.63 (q, J=7 Hz, CH_2CH_3)	3.60	1.16 (t, J=7 Hz, CH_2CH_3); 2.33) (q, J=7 Hz, CH_2-CH_3)	5.11	13.20
8j	1720 1705 1680	4:1	6.75 (1H, d, J=15 Hz) 7.2—7.6 (5H, m) 7.78 (1H, d, J=15 Hz)	9.57	1.00 (t, J=7 Hz, CH_2-CH_3); 2.53 (q, J=7 Hz, CH_2CH_3)	3.83	1.07 (t, J=7 Hz, CH_2CH_3); 2.23 (q, J=7 Hz, CH_2-CH_3)	6.10	13.70
9a	1715 1640(sh) 1610	2:1	7.3—8.7 (4H, m)	10.16 (0.33H) 10.57 (0.66H)	2.33 (s, CH_3)	4.10	2.07 (s, CH_3)	6.50	13.97
9b	1740(sh) 1705 1680	3:1	7.3—9.1 (4H, m)	10.13	2.37 (s, CH_3)	4.07	2.10 (s, CH_3)	6.50	13.60
9c	1720(sh) 1710 1680	10:3	7.6—7.7 (2H, m) 8.7—8.8 (2H, m)	9.63 (0.23H) 10.43 (0.77H)	2.33 (s, CH_3)	4.07	2.10 (s, CH_3)	6.47	13.57
9d	1715 1620(sh)	2:1	7.3—8.7 (4H, m)	10.76	1.10 (t, J=7 Hz, CH_2-CH_3); 2.63 (q, J=7 Hz, CH_2CH_3)	4.06	1.20 (t, J=7 Hz, CH_2CH_3); 2.37 (q, J=7 Hz, CH_2 CH_3)	6.50	14.00
9e	1730(sh) 1715 1685	4:1	7.3—9.1 (4H, m)	10.20	1.10 (t, J=7 Hz, CH_2-CH_3); 2.63 (q, J=7 Hz, CH_2CH_3)	4.03	1.20 (t, 7 Hz, CH_2-CH_3); 2.37 (q, J=7 Hz, CH_2-CH_3)	6.50	13.60

a) Neat.

Compd. No.	IR ν_{max}^{KBr} cm^{-1}	Ratio keto: enol	PMR (60 MHz, $CDCl_3$) δ[ppm]						
					keto		enol		
			R^1	NH	R^3	CH_2	R^3	-CH=	OH
9f	1730 1715 1690	5:1	7.7—7.8 (2H, m) 8.7—8.8 (2H, m)	8.80 (0.17H) 10.60 (0.83H)	1.08 (t, J=7 Hz, CH_2-CH_3); 2.67 (q, J=7 Hz, CH_2CH_3)	4.00	1.15 (t, J=7 Hz, CH_2CH_3); 2.37 (q, J=7 Hz, CH_2-CH_3)	6.50	13.67
9g	1720 1710 1690	2:1	7.3—8.6 (2H, m)	10.70	3.88 (s, $C_6H_5CH_2$) 7.32 (s, arom H)	4.00	3.58 (s, $C_6H_5CH_2$) 7.23 (s, arom H)	6.47	13.90
9h	1720 1715(sh) 1685	7:3	8.0—9.2 (4H, m)	9.87	3.90 (s, $C_6H_5CH_2$) 7.2 (s, arom H)	4.00	3.63 (s, $C_6H_5CH_2$) 7.30 (s, arom H)	6.50	13.60
9i	1720 1705 1685	5:2	7.6—7.8 (2H, m) 8.7—8.9 (2H, m)	9.60	3.87 (s, $C_6H_5CH_2$) 7.23 (s, arom H)	3.97	3.58 (s, $C_6H_5CH_2$) 7.23 (s, arom H)	6.50	13.70
9j	1720 1630	1:9	7.3—8.7 (9.90H, m)	10.40		4.67			14.50
9k	1715 1690 1670	4:3	7.3—9.4 (9.43H, m)	10.05		4.55			14.10
9l	1720 1685	5:2	7.4—9.0 (9.28H. m)	9.85		4.56			14.20

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