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α,β-Unsaturated Carboxylic Acid Derivatives. IV. General Synthesis of Unsaturated Unsymmetric 3,6-Disubstituted-2,5-piperazinediones[1]

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A general synthetic route to unsymmetric 3,6-dialkylidene and 3-alkylidene-6-arylidene-2,5-piperazinediones is described. The condensation reaction of ethyl 2-oxocarboxylates with chloroacetamide in the presence of several acidic catalysts afforded *N*-chloroacetyldehydroamino acid esters. These compounds were cyclized in saturated ethanolic ammonia to give 3-monoalkylidene and benzylidene-2,5-piperazinediones (**2**). Compound **2** and 1-monoacetyl- or 1,4-diacetyl-3-alkylidene and benzylidene-2,5-piperazinediones, derived from a reaction of **2** with acetic anhydride, were condensed with alkyl and arylaldehyde in the presence of bases to afford **5**.

Many monocyclic or polycyclic 2,5-piperazinedione derivatives have recently been found in nature as antibiotics or alkaloids.[2–9]

One of the authors (C.S.) has investigated the syntheses and chemistry of several derivatives,[10–13] and succeeded in the synthesis of albonoursin,[11] 3-benzylidene-6-isobutylidene-2,5-piperazinedione, the first cyclic dehydrodipeptide isolated from the culture of *Streptomyces (St.) albus var. fungatus* and *St. noursei.*

It is well-known that the cyclization of two molecules of amino acids yields the saturated symmetric 3,6-disubstituted-2,5-piperazinedione[14] and the condensation reaction glycine anhydride with arylaldehyde gives unsaturated symmetric 3,6-disubstituted-2,5-piperazinedione.[15,16] However, natural 2,5-piperazinedione derivatives usually have an unsymmetric structure.

As unsymmetric derivatives, only a few 3-monoalkylidene-2,5-piperazinediones (**2**) have been reported. Bergmann *et al*[17] and others[18,19] have synthesized 3-methylidene derivative (**2a**) from glycylserine by halogenation and amination. One of the present authors (C.S.) succeeded in the preparation of isopropylidene derivative (**2d**) *via* ethyl 2-chloroacetamido-3-methyl-2-butenoate (**1d**) obtained by the reaction of dehydrovaline ethyl ester or the tautomeric imine with chloroacetyl chloride.[10,12,13] Similarly, 3-isobutylidene derivative (**2f**) was synthesized *via* ethyl 2-chloroacetamido-4-methyl-2-pentenoate (**1f**) derived by esterification of the free acid.[11] Recently, Dominy and Lawton reported the preparation of 3-benzylidene derivative (**2g**) by the reaction of *N*-acetyldehydrophenylalanylglycine with acetic anhydride.[20] Gallina and Liberatori reported another synthetic method for **2** from the reaction of 1,4-diacetyl-2,5-piperazinedione with alkyl or arylaldehyde.[21] Consequently,

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[1] The main subject of this series of papers was revised from "Studies on Nitro Carboxylic Acids" Part III: C. Shin, Y. Yonezawa, K. Katayama, and J. Yoshimura, This Bulletin, **46**, 1727 (1973). This work was presented at the 24th and 26th Annual Meetings of the Chemical Society of Japan, Osaka, April 3, 1971; Hiratsuka, April 2, 1972.

[2] A. S. Khokhlov and G. B. Lokshin, *Tetrahedron Lett.*, **1963**, 1881.

[3] M. Vondracek and Z. Vanek, *Chem. Ind.* (London.), **1968**, 1686.

[4] R. Brown, C. Kelly, and S. E. Wiberley, *J. Org. Chem.*, **30**, 277 (1965).

[5] A. J. Birch and J. J. Wright, *Chem. Commun.*, **1969**, 644.

[6] D. Brewer, R. Rahman, S. Safe, and A. Taylor, *ibid.*, **1968**, 1571.

[7] N. Neuss, R, Nagarajan, B. B. Molloy, and L. L. Huckstep *Tetrahedron Lett.*, **1968**, 4467.

[8] M. R. Bell, J. R. Johnstop, B. S. Wildi, and R. B. Woodward, *J. Amer. Chem. Soc.*, **80**, 1001 (1958).

[9] P. S. Steyn, *Tetrahedron*, **29**, 107 (1973).

[10] C. Shin, M. Masaki, and M. Ohta, This Bulletin, **39**, 858 (1966); *J. Org. Chem.*, **32**, 1860 (1967).

[11] C. Shin, Y. Chigira, M. Masaki, and M. Ohta, *Tetrahedron Lett.*, **1967**, 4601; This Bulletin, **42**, 191 (1969).

[12] M. Masaki, C. Shin, H. Kurita, and M. Ohta, *Chem. Commun.*, **1968**, 1447.

[13] C. Shin, M. Masaki, and M. Ohta, This Bulletin, **44**, 1657 (1971).

[14] E. Fischer, *Ber.*, **34**, 433 (1901).

[15] a) T. Sasaki, *Ber.*, **54**, 163 (1921); b) T. Sasaki and T. Hashimoto, *ibid.*, **54**, 168 (1921).

[16] M. Augustin, *J. Prakt. Chem.*, **32**, 158 (1966).

[17] M. Bergmann, A. Miekely, and E. Kann, *Ann. Chem.*, **445**, 17 (1925).

[18] E. Fischer and L. Prizont, *Rev. Asoc. Med. Argentina*, **69**, 21 (1955); *ibid.*, **70**, 30 (1956).

[19] M. Kland and W. M. Garrison, *Nature*, **197**, 859 (1963).

[20] B. Dominy and R. G. Lawton, *J. Org. Chem.*, **34**, 2013 (1969).

[21] C. Gallina and A. Liberatori, *Tetrahedron Lett.*, **1973**, 1135.

N-chloroacetyldehydroamino acid esters (**1**) seem to be a suitable intermediate for obtaining 3-monoalkylidene and benzylidene derivatives (**2**).

In a previous communication we reported briefly a general synthesis of **2** by the reaction of **1**, derived from ethyl 2-oxocarboxylates and chloroacetamide, with ammonia.[22]

This paper deals with the synthesis of **1** in detail under several experimental conditions and syntheses of unsymmetric 3,6-dialkylidene and 3-alkylidene-6-arylidene-2,5-piperazinediones (**5**) by the condensation of **2** or a mixture of 1-acetyl (**3**)- and 1,4-diacetyl-3-alkylidene-2,5-piperazinediones (**4**) with alkyl or arylaldehyde in the presence of bases.

Results and Discussion

3-Alkylidene-2,5-piperazinediones. Various acidic catalysts were examined in the synthesis of ethyl 2-chloroacetamido-2-pentenoate (**1c**) by the condensation of an equimolar amount of ethyl 2-oxopentanoate and chloroacetamide in refluxed dry benzene. Concentrated sulfuric acid and phosphorylchloride were found to be the most effective.[22]

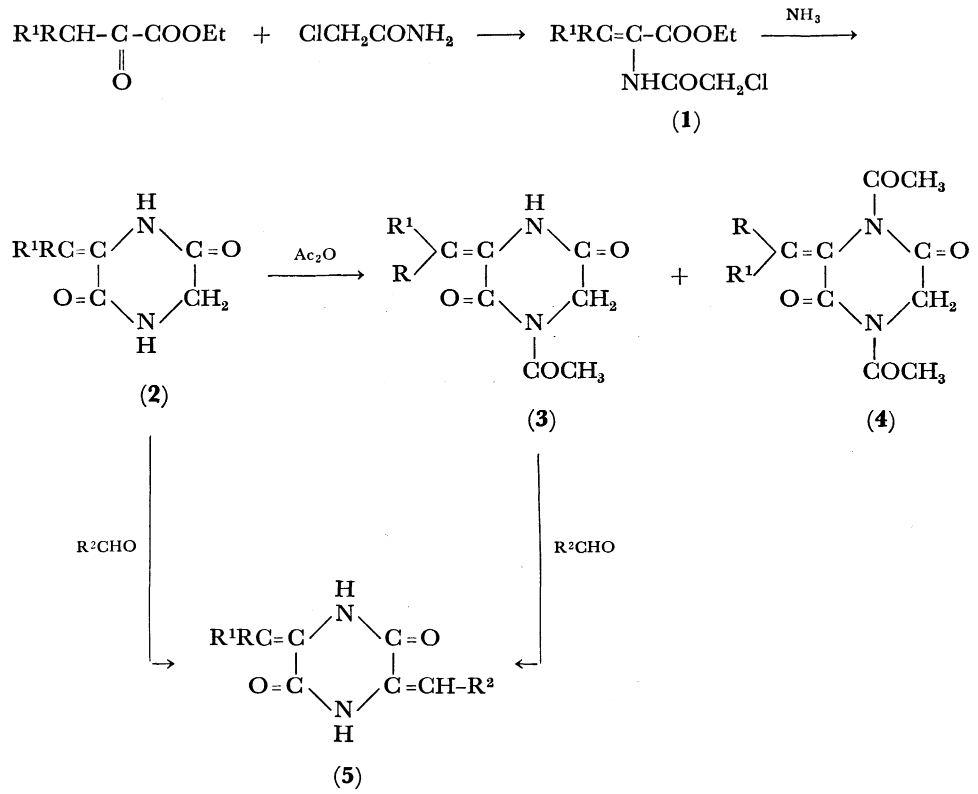
The effect of the molar ratio of chloroacetamide to ethyl 2-oxopentanoate and the reaction time in the presence of phosphorylchloride were also examined. When the reaction was continued for 8 hr, the yield of **1c** gradually increased as the molar ratio increased to 1.5 : 1 and reached a maximum 44.2% yield. At molar ratio of 1.5 : 1, the yield increased until the reaction time of 12 hr, and reached a 51.0% yield. It was found that the yield of **1c** was best at the molar ratio of 1.5 : 1 and reaction time 12 hr.

The structure of **1** obtained under the same conditions as for **1c** was confirmed by elementary analysis and IR spectrum. It is very similar to that of **1d** and **1f** prepared from a different synthetic route.[10,11]

When a cooled ethanol solution of **1** was saturated with dry ammonia and then allowed to stand at room temperature at least for one day, cyclization reaction occurred gradually to deposit colorless crystals. The crystals were recrystallized from boiling water to afford **2** in pure state as colorless amorphous.[22]

The structure of **2** was confirmed by elementary analysis as well as IR and UV spectrum, the pattern being essentially similar to those of **2d** and **2f** derived in the independent preparation.[10,11]

Acetylation and Condensation Reaction. When **2** was heated with acetic anhydride at 120—130 °C for half an hour, two kinds of crystals which were confirmed to be 1-acetyl (**3**)- and 1,4-diacetyl (**4**) derivatives of **2** were obtained in a ratio of *ca.* 3 : 7. Recent studies on the photoisomerization of carbon-carbon double bond of 3-benzylidene-2,5-piperazinediones by Sammes and co-workers[23,24] and a novel



a; $R^1=R=H$, b; $R^1=CH_3$, $R=H$, c; $R^1=C_2H_5$, $R=H$, d; $R^1=R=CH_3$, e; $R^1=n\text{-}C_3H_7$, $R=H$, f; $R^1=i\text{-}C_3H_7$, $R=H$, g; $R^1=C_6H_5$, $R=H$, R^2=several alkyl or aryl groups

Scheme.

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[22] C. Shin, M. Fujii, and J. Yoshimura, *ibid.*, **1971**, 2499.

[23] K. W. Blake and P. G. Sammes, *J. Chem. Soc., C.* **1970**, 980.

[24] A. E. A. Porter and P. G. Sammes, *ibid.*, **1970**, 2530.

preparative method for **3**[21] stimulated us to find a simple method for the isolation and determination of these isomers. The two compounds were separated by chromatography on silica-gel column by elution with a mixture of benzene and acetone (20 : 1). The melting points of **3** approximately agreed with those of the products obtained by Gallina and Liberatori.[21] From the results and the spectroscopic data (Table 1), it was assumed that compound **4** is *E*-conformer and **3** is *Z*-conformer with respect to carbon-carbon double bond. It was deduced that, in the case of *Z*-conformer, the steric hindrance of alkyl group hindered acetylation at 4-position of **2**.[24]

Since the isolation of **3** and **4** was tedious and time-consuming, the following method was adopted for the subsequent condensation reaction. On treatment of the mixture of **3** and **4** with arylaldehyde in the presence of triethylamine at 120—130 °C for about 3 hr, the expected 3-alkylidene-6-arylidene-2,5-piperazinedione (**5**) was obtained (Procedure A). On the other hand, **5** was also obtained by direct condensation of **2** with aralkyl or alkylaldehyde in acetic anhydride in the presence of sodium acetate at 120—130 °C for about 5 hr (Procedure B).

The structures of **3**, **4** and **5** were confirmed by elementary analysis as well as IR, UV and NMR spectra. The IR spectrum of **5** showed the absorption bands of NH (3200—3160 and 3100—3020 regions), carbon-oxygen double bond (1690—1670 region) and carbon-carbon double bond (1640—1635 cm^{-1} region). The physical constants, yields and spectral data are given in Tables 1, 2 and 3.

Experimental

All melting points are uncorrected. The IR spectra were recorded with a Hitachi EPI-S2 Spectrometer. The UV spectra were recorded with a Shimadzu UV-50 Spectrometer. The NMR spectra were measured with a JNM-4H-100 Spectrometer (Japan Electron Optics Laboratory Co., Ltd.) using tetramethyl silane as an internal standard.

*N-Chloroacetyldehydroamino Acid Ethyl Esters (**1**).* In a 200 ml round-bottomed flask, fitted with water separater, were placed the appropriate ethyl 2-oxocarboxylate (0.1 mol), chloroacetamide (0.15 mol), phosphorylchloride (6 ml) and dry benzene (100 ml). The mixture was refluxed for about 12 hr until no water separated out. The reaction mixture was removed in a separating funnel and washed with water and then extracted with benzene. The benzene extract was washed with water, dried over anhydrous magnesium sulfate and then evaporated. The residual dark brown syrup was distilled under reduced pressure to give yellow oil.[22] In a similar manner, the condensation reaction of ethyl 2-oxophenylpropanoate with chloroacetamide was performed, and ethyl 2-chloroacetamide-3-phenyl-2-pentenoate (**1g**) was obtained as a yellow syrup, which gradually crystallized at room temperature. The crystalline product was collected and recrystallized from ethanol to give yellow needles (38.7%), bp 151—155 °C/1.5 mmHg (mp 103—104 °C). IR (KBr): 3270, 1720, 1680, 1520 cm^{-1}.

TABLE 1. 1-ACETYL (**3**)- AND 1,4-DIACETYL-3-ALKYLIDENE(BENZYLIDENE)-2,5-PIPERAZINEDIONES(**4**)

Compound	Yield (%)	Mp (°C)	Formula	Found (Calcd), % C	H	N	IR Spectrum[a)] cm^{-1}, in KBr	^{1}H(τ) NMR Spectrum -NH-	-CH=C- (J_{Hz})	-CH$_2$-	-COCH$_3$
3b[21]	28	180—182	$C_8H_{10}N_2O_3$	52.48 (52.74	5.51 5.53	15.09 15.38)	3190, 3080, 1710, 1695, 1650	0.26	3.65 q (7.5)	5.46	7.40
3c[21]	28	152—154	$C_9H_{12}N_2O_3$	55.11 (55.09	6.06 6.17	14.39 14.28)	3195, 3080, 1710, 1690, 1635	0.25	3.65 t (7.5)	5.47	7.41
3e[21]	29	138—139	$C_{10}H_{14}N_2O_3$	56.98 (57.13	5.77 6.71	13.29 13.33)	3190, 3070, 1710, 1685, 1640	0.25	3.64 t (8.0)	5.46	7.39
3f[21]	32	151—152	$C_{10}H_{14}N_2O_3$	57.10 (57.13	6.52 6.71	13.58 13.33)	3190, 3075, 1710, 1690, 1640	0.68	3.68 d (9.5)	5.55	7.36
3g[21]	31	201—202	$C_{13}H_{12}N_2O_3$	64.12 (63.92	5.05 4.95	11.46 11.47)	3190, 3100, 1710, 1695, 1620	1.87	2.84 s	5.39	7.55
4b	61	164—165	$C_{10}H_{12}N_2O_4$	53.61 (53.57	5.43 5.39	12.33 12.50)	1740, 1710, 1655		3.25 q (7.5)	5.56	7.41 7.45
4c	59	144—145	$C_{11}H_{14}N_2O_4$	55.23 (55.45	6.08 5.92	11.79 11.76)	1740, 1705, 1650		3.26 t (7.5)	5.58	7.40 7.44
4e	68	112—113	$C_{12}H_{16}N_2O_4$	57.12 (57.13	6.57 6.39	11.08 11.11)	1740, 1710, 1650		3.26 t (8.0)	5.57	7.39 7.45
4f	64	115—116	$C_{12}H_{16}N_2O_4$	56.89 (57.13	6.51 6.39	11.32 11.11)	1740, 1710, 1630		3.46 d (9.5)	5.50	7.40 7.44
4g	69	152—153	$C_{15}H_{14}N_2O_4$	63.07 (63.92	4.92 4.95	10.12 11.47)	1740, 1705, 1630		2.75 s	5.55	7.40 7.45

a) Measured in CDCl$_3$.

Found: C, 58.44; H, 5.12; N, 5.61%. Calcd for $C_{13}H_{14}NO_3Cl$: C, 58.32; H, 5.23; N, 5.23%.

*3-Alkylidene- and Benzylidene-2,5-piperazinediones (**2**).* A solution of **1** (0.1 mol) in ethanol (100 ml) was saturated with dry gaseous ammonia under cooling. When the solution was allowed to stand at room temperature for one day, crystalline substance precipitated. Ethanol was evaporated under reduced pressure and the residual crystals were collected and washed successively with cold water, ethanol, and then ether. Recrystallization from boiling water afforded colorless amorphous.[22]

In a similar manner, cyclization reaction of **1g** with ammonia was performed, and 3-benzylidene-2,5-piperazinedione (**2g**) was obtained as pale yellow prisms (58.8%), mp 279—280 °C(decomp.).[20] IR(KBr): 3200, 3050, 1690, 1620 cm^{-1}.

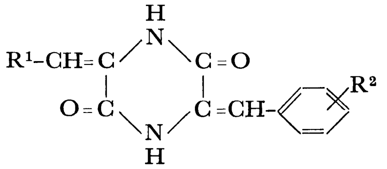
Found: C, 65.31; H, 4.86; N, 13.81%. Calcd for $C_{11}H_{10}N_2O_2$: C, 65.35; H, 4.95; N, 13.86%.

*Acetylation of **2**.* A suspension of **2** (0.01 mol) in acetic anhydride (6 ml) was heated at 120—130 °C for half an hour, and the resulting solution was allowed to stand at room temperature for 1 hr. The reaction solution was concentrated under reduced pressure to dryness giving a crystalline residue. The crystalline product was collected and recrystallized from ethanol to afford two kinds of crystals, which were separated by chromatography on a silica-gel column by elution with a mixture of benzene and acetone (20 : 1) to give **3** and **4**. The results are summarized in Table 1.

*Unsymmetric Unsaturated 3,6-Disubstituted-2,5-piperazinediones (**5**). a) Condensation of Mixture of **3** and **4** with Arylaldehyde in the Presence of Triethylamine (Procedure A).* A mixture of **3** and **4**(*ca.* 3 : 7 ratio, *ca.* 2.4× 10^{-3} mol) and the appropriate arylaldehyde (2.4× 10^{-3} mol) was heated in the presence of triethylamine (0.12 g) at 120—130 °C for 3 hr. The resulting reddish solid mass was treated with ethanol and filtered. The collected crystals were recrystallized from glacial acetic acid to give the expected condensation product. The results are summarized in Table 2.

*b) Condensation of **2** with Aralkyl- or Alkylaldehyde in the Presence of Sodium Acetate (Procedure B).* A mixture of **2** (6× 10^{-3} mol), the appropriate aldehyde (16× 10^{-3} mol), and anhydrous sodium acetate (2.5 g) in acetic anhydride (4 ml) was heated at 120—130 °C for 5 hr and then allowed to stand overnight at room temperature. The mixture was treated with a small quantity of water and ether and filtered. The crystalline product was washed successively with ether and ethanol. Recrystallization from glacial acetic acid afforded the expected condensation product. The results are summarized in Table 3.

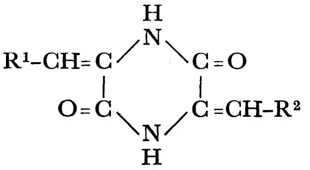
TABLE 2. 3-ALKYLIDENE-6-ARYLIDENE-2,5-PIPERAZINEDIONES (**5**) (Procedure A)



Substituents		Yield (%)	Mp °C[a)]	Formula	Found, %			Calcd, %		
R¹	R²				C	H	N	C	H	N
CH_3	H	67	294—296[b)]	$C_{13}H_{12}N_2O_2$	68.33	5.52	11.98	68.41	5.30	12.27
CH_3	*o*-Cl	46	283—285[b)]	$C_{13}H_{11}N_2O_2Cl$	59.59	4.21	10.37	59.43	4.19	10.69
CH_3	*p*-Cl	42	300—302[b)]	$C_{13}H_{11}N_2O_2Cl$	59.41	4.28	10.58	59.43	4.19	10.69
CH_3	*m*-CH_3COO	58	250—251[c)]	$C_{15}H_{14}N_2O_4$	62.84	4.66	10.02	62.93	4.93	9.79
CH_3	*p*-CH_3O	49	267—269[d)]	$C_{14}H_{14}N_2O_3$	65.33	5.38	10.75	65.10	5.46	10.85
CH_3	*p*-CH_3	45	279—281[b)]	$C_{14}H_{14}N_2O_2$	69.67	5.46	11.47	69.40	5.83	11.47
CH_3	*p*-NO_2	62	275—277[d)]	$C_{13}H_{11}N_3O_4$	56.98	4.11	15.42	57.14	4.06	15.38
C_2H_5	H	61	268—280[b)]	$C_{14}H_{14}N_2O_2$	69.58	5.71	11.45	69.40	5.83	11.56
C_2H_5	*o*-Cl	68	286—287[c)]	$C_{14}H_{13}N_2O_2Cl$	60.58	4.71	10.04	60.76	4.70	10.13
C_2H_5	*p*-Cl	44	235—238[c)]	$C_{14}H_{13}N_2O_2Cl$	60.51	4.89	10.23	60.76	4.70	10.13
C_2H_5	*m*-CH_3COO	41	237—238[c)]	$C_{16}H_{16}N_2O_4$	64.12	5.26	9.48	63.99	5.39	9.33
C_2H_5	*p*-CH_3O	43	263—265[b)]	$C_{15}H_{16}N_2O_3$	65.98	6.02	10.12	66.16	5.92	10.29
C_2H_5	*p*-CH_3	58	273—274[b)]	$C_{15}H_{16}N_2O_2$	70.36	6.28	10.81	70.29	6.29	10.93
C_2H_5	*p*-NO_2	54	282—283[d)]	$C_{14}H_{13}N_3O_4$	58.39	4.78	14.62	58.53	4.56	14.63
n-C_3H_7	H	42	276—278[b)]	$C_{15}H_{16}N_2O_2$	70.29	6.30	10.78	70.29	6.29	10.93
n-C_3H_7	*o*-Cl	56	278—280[b)]	$C_{15}H_{15}N_2O_2Cl$	62.11	5.28	9.31	61.97	5.19	9.64
n-C_3H_7	*m*-CH_3COO	53	269—270[b)]	$C_{17}H_{18}N_2O_4$	65.08	5.67	9.10	64.95	5.77	8.91
n-C_3H_7	*p*-CH_3O	52	279—281[b)]	$C_{16}H_{18}N_2O_3$	66.99	6.43	9.68	67.11	6.34	9.78
n-C_3H_7	*p*-CH_3	45	284—285[b)]	$C_{16}H_{18}N_2O_2$	70.91	6.88	10.29	71.09	6.71	10.36
n-C_3H_7	*m*-NO_2	48	268—269[b)]	$C_{15}H_{15}N_3O_4$	59.78	5.11	14.21	59.79	5.02	13.95
n-C_3H_7	*p*-NO_2	51	290—291[b)]	$C_{15}H_{15}N_3O_4$	60.01	4.98	13.78	59.79	5.02	13.95
i-C_3H_7	*o*-Cl	52	267—268[b)]	$C_{15}H_{15}N_2O_2Cl$	62.15	5.08	9.55	61.97	5.19	9.64
i-C_3H_7	*p*-Cl	53	241—243[b)]	$C_{15}H_{15}N_2O_2Cl$	61.89	5.21	9.77	61.97	5.19	9.64
i-C_3H_7	*m*-CH_3COO	49	245—246[b)]	$C_{17}H_{18}N_2O_4$	65.03	5.91	8.76	64.95	5.77	8.91
i-C_3H_7	*p*-CH_3	46	269—271[b)]	$C_{16}H_{18}N_2O_2$	70.96	6.77	10.29	71.09	6.71	10.36
i-C_3H_7	*m*-NO_2	63	292—293[b)]	$C_{15}H_{15}N_3O_4$	59.98	4.96	14.28	59.79	5.02	13.95
i-C_3H_7	*p*-NO_2	58	280—281[b)]	$C_{15}H_{15}N_3O_4$	60.01	4.89	13.91	59.79	5.02	13.95

a) Decomposition. b) Yellow powder. c) Pale yellow powder. d) Brown powder.

TABLE 3. UNSYMMETRIC 3,6-DIALKYLIDENE AND 3-ALKYLIDENE-6-BENZYLIDENE-2,5-PIPERAZINEDIONES (**5**) (Procedure B)



Substituents		Yield (%)	Mp °C$^{a)}$	Formula	Found (Calcd), %			UV Spectrum nm, in EtOH ($\varepsilon \times 10^3$)
R¹	R²				C	H	N	
CH_3	$CH_3CH=CH$	36	305—306$^{b)}$	$C_{10}H_{12}N_2O_2$	62.32	6.48	14.71	321(30.0)
					(62.48	6.29	14.58)	
CH_3	$C_6H_5CH=CH$	46	322—325$^{b)}$	$C_{15}H_{14}N_2O_2$	70.98	5.23	10.91	365(27.7)
					(70.85	5.55	11.02)	
C_2H_5	$CH_3CH=CH$	18	311—312$^{c)}$	$C_{11}H_{14}N_2O_2$	63.85	6.81	13.66	
					(64.04	6.84	13.58)	
C_2H_5	$C_6H_5CH=CH$	68	304—306$^{b)}$	$C_{16}H_{16}N_2O_2$	71.57	6.21	10.62	365(40.0)
					(71.62	6.01	10.44)	
n-C_3H_7	$CH_3CH=CH$	19	310—311$^{d)}$	$C_{12}H_{16}N_2O_2$	65.32	7.44	12.69	325(30.9)
					(65.43	7.32	12.72)	
n-C_3H_7	$C_6H_5CH=CH$	65	307—309$^{b)}$	$C_{17}H_{18}N_2O_2$	72.33	6.58	9.78	365(43.9)
					(72.32	6.43	9.92)	
i-C_3H_7	$CH_3CH=CH$	17	285—287$^{c)}$	$C_{12}H_{16}N_2O_2$	65.61	7.41	13.01	
					(65.43	7.32	12.72)	
i-C_3H_7	$C_6H_5CH=CH$	63	311—312$^{b)}$	$C_{17}H_{18}N_2O_2$	72.55	6.28	9.77	366(42.4)
					(72.32	6.43	9.92)	
C_6H_5	$CH_3CH=CH$	18	286—288$^{b)}$	$C_{15}H_{14}N_2O_2$	71.01	5.32	10.98	345(34.9)
					(70.85	5.55	11.02)	
C_6H_5	$C_6H_5CH=CH$	54	309—311$^{b)}$	$C_{20}H_{16}N_2O_2$	75.85	5.23	8.85	383(51.7)
					(75.93	5.10	8.86)	
C_6H_5	$CH_3(CH_2)_5CH_2$	8	286—287$^{c)}$	$C_{18}H_{22}N_2O_2$	72.50	7.44	9.58	344(37.0)
					(72.45	7.43	9.39)	

a) Decomposition. b) Yellow powder or needles. c) Pale yellow powder. d) Brown powder.