Intramolecular Hydrogen Bonding in Imidazole-4(5)-alkoxycarbonyl-5(4)-carboxamide Derivatives

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The ir spectrum of imidazole derivatives, which have an alkoxycarbonyl group and a carboxamide group at the 4- and 5-positions of the imidazole ring respectively, exhibits the shift of the ester carbonyl band to a lower wave number. This phenomenon was investigated by spectroscopic measurements of a group of relevant compounds. The results indicate that the shift is caused by the intramolecular hydrogen bonds between the hydrogen atom of the amide and the carbonyl oxygen of the ester which is enhanced by the resonance stabilization of the imidazole ring.

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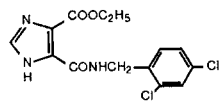
As described in a preceding paper [1], an imidazole derivative substituted with an alkoxycarbonyl group and a carboxamide group at the 4- and 5-positions, respectively, shows the ester carbonyl band at unusually lower wave number in its ir spectrum. For example, compound **1** shows ν C=O of the ester group at 1690 cm^{-1} in potassium bromide discs. In order to confirm whether this is a general trend, an analogous compound **2** was prepared from the diimidazopyrazine derivative **4a** and *n*-propylamine by a procedure similar to that used for compound **1** [1]. Compound **2** shows ν C=O of the ester group at 1682 cm^{-1}.

4(5)-Ethoxycarbonylimidazole (**3**), which was prepared from diimidazopiperazine-2,5-dione (**4b**) and ethanol according to the reported method [2], exhibits ν C=O at 1717 cm^{-1}, the usual wave number. The low-frequency shift of the ester carbonyl band, therefore, seems to be due to the influence of a neighboring carboxamide group. This influence has been examined in detail here.



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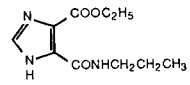

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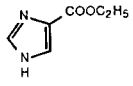

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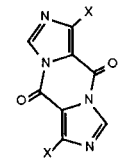
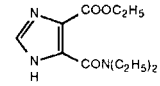


4a, X = -COOC$_2$H$_5$
b X = -H

As relevant compounds for the present subject, several analogs of **1** and **2** were prepared, and subjected to our spectroscopic measurements. The spectral data are summarized in Table 1.

In order to examine the influence of an amide hydrogen of the carboxamide, 4(5)-diethylaminocarbonyl-5(4)-ethoxycarbonylimidazole (**5**) was prepared by a similar procedure to the method described in the preceding paper [1].



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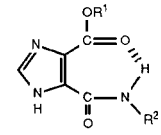
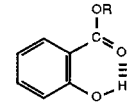
The ir spectrum of **5**, which has no amide hydrogen, does not show any shift of the ester carbonyl band to a lower wave number. It exhibits ν C=O of ester group at 1717 cm^{-1}, which corresponds to a normal position of an ester. Consequently, the low C=O frequency is presumed to be due to the hydrogen bond shown below.



As an example of the molecule with similar intramolecular hydrogen bonds, *ortho*-hydroxy- or *ortho*-aminobenzoic acid ester **6** and **7** are well known [3]. Its ester carbonyl band has actually been observed at a lower wave number compared with the corresponding compound without a hydrogen bond.



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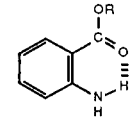

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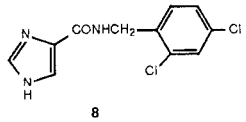
In order to confirm the presence of an intramolecular hydrogen bond in the imidazole derivatives, now in ques-

tion, their ir spectra were investigated in dilute carbon tetrachloride solution (about 0.01*M*). The ir spectra of compound **1** and **2** in solution gave ν C=O of the ester group at the same wave number as those in potassium bromide discs. If the above shifts were due to an intermolecular hydrogen bond, it should disappear at lower concentrations, *e.g.* those less than 0.01*M* in nonpolar solvents [4]. Thus, the presence of an intramolecular hydrogen bond may now be reasonably assumed in **1** and **2**.

Next, as a reference compound 4(5)-(2,4-dichlorobenzylaminocarbonyl)imidazole (**8**), which has no ester group, was prepared by the reaction of **4b** with 2,4-dichlorobenzylamine.

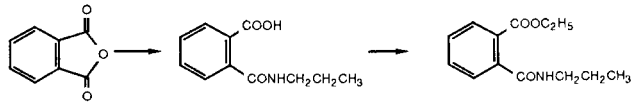


8

The spectroscopic data of **8** were compared with those of **1**. In ir spectrum, compound **8** shows ν NH at 3406 cm^{-1}, which is the normal position for a free NH absorption of secondary amides [4,5]. However, compounds **1** and **2** do not show NH absorption near 3400 cm^{-1}. They are probably shifted at 3280-3100 cm^{-1} and overlapped with the absorption of ν NH of imidazole [6].

In general, the hydrogen atom taking part in hydrogen bond is known to exhibit a down field shift in the proton nmr spectrum [7]. The nmr spectrum of **8** shows a triplet at δ 7.70 ppm due to the hydrogen atom of the CONH group in deuteriochloroform solution, whereas the corresponding signals of **1** and **2** are observed at δ 10.74 ppm and 10.30 ppm, respectively. These results are taken as supporting evidence for the presence of an intramolecular hydrogen bond.

If this hydrogen bond is ascribed only to the existence of an adjacent ester group and an amide group, this phenomenon should be observed also for the benzene derivatives. To study this point, the following compound **9** was examined, which was prepared by the following scheme.



9

The ir spectrum of **9** shows ν C=O of ester group at 1728 cm^{-1} in carbon tetrachloride solution. Since ethyl benzoate shows the absorption due to ester group at 1724 cm^{-1}, no hydrogen bond can be assumed to exist in compound **9**. This result suggests the role of the imidazole ring for the hydrogen bonds now in question. It may be

Table 1

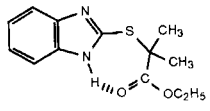
Spectral Data of Imidazole Derivatives and Benzene Analogs

Compound	FT-IR λ max cm^{-1} ν CO of ester		3500-2900 cm^{-1} region [c]	NMR δ, ppm amide proton	UV λ max, nm longer wave length than 230 nm
	Carbon tetrachloride solution	Potassium bromide disc	Carbon tetrachloride solution	Deuteriochlorform solution	Acetonitrile solution
1	1690	1690	3217, 3183, 3140, 3071	10.74	263 (11,200)
2	1684	1682	3159, 3098, 2957, 2940	10.30	262 (9,400)
3	1713 [a]	1717	3449, 3021, 2986 [a]	—	234 (11,400)
5	1721	1717	2982, 2936	—	243 (10,300)
8	—	—	3406*, 3164, 3215, 3071	7.70	[d]
9	1728	1720 [b]	3449*, 2967, 2936	5.88	not measured
11	1690	1680 [b]	3275, 3236, 3113, 3063, 2986, 2963	10.66	264 (9,400)
12	1713	1705 [b]	3422*, 2982, 2963, 2936, 2907	8.10	242 (shoulder) (9,400)
13	1270	1715 [b]	2986	—	249 (7,700)
14	—	—	3399*, 3021	8.06 and 11.06	263 (13,700)

[a] Chloroform solution. [b] Nujol (not ft-ir). [c] Absorption signals with asterisk(*) are assigned to free NH absorption. [d] Only λ max 227 nm (ε = 19,600) is observed.

pointed out here that the proposed intramolecular hydrogen bond forms a seven-membered ring, condensed with the five-membered ring (imidazole). It is probable that such a seven-membered ring is not stable if it is condensed with a six-membered ring (benzene ring).

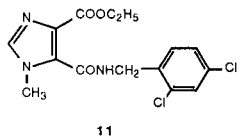
Another intramolecular hydrogen bond, related to the NH of imidazole has been reported for compound **10** [8]. The ir spectrum of **10** exhibits ν C=O absorption at 1710



10

cm^{-1}, which is located at a lower wave number in comparison with ν C=O of ethyl pivalate (1724 cm^{-1}) [8]. Thus **10** also has a seven-membered hydrogen bond ring condensed with a five-membered ring.

One might suspect that the NH of imidazole is involved in the intramolecular hydrogen bonding now in question. In order to examine this point, an *N*-methylated compound at the imidazole nitrogen of **1** was prepared. Methylation of **1** at the imidazole NH group with methyl iodide by a reported procedure [9] afforded a chromatographically separable mixture of the isomeric *N*-methyl derivatives **11** and **12** in a 1:5 ratio.



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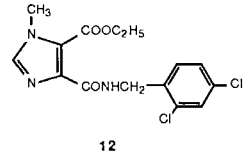

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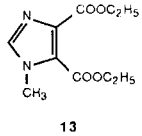
Identification of each isomer was carried out by comparing the chemical shift of the *N*-methyl protons with those of model compounds in the proton nmr spectrum. As model compounds, 1-methyl-4,5-diethoxycarbonylimidazole (**13**) and 1-methyl-4,5-di(2,4-dichlorobenzylamino-carbonyl)imidazole (**14**) were prepared, respectively, by the reaction of 1-methylimidazole-4,5-dicarbonyl dichloride [10] with ethanol and 2,4-dichlorobenzylamine.



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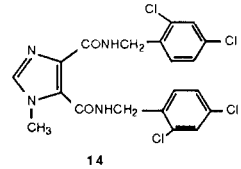


14

The chemical shift of *N*-methyl protons of imidazole has been known to be influenced by the electronegativity of a substituent at the 5-position of imidazole [11]. The chemical shift of the *N*-methyl protons of **13** is δ 3.79 ppm and that of **14** is δ 3.94 ppm. These results suggest that 2,4-dichlorobenzylaminocarbonyl group has a stronger electronic effect than the ethoxycarbonyl group. While, the chemical shift of the 1-methyl protons of the isomer (**11** or **12**) having the higher Rf value is δ 4.02 ppm and that of the isomer (**11** or **12**) having the lower Rf value is δ 3.84. Therefore, the former is identified as **11** and the latter as **12**.

In their ir spectra, compound **11** exhibits a lower wave number shift of the ester band, whereas compound **12** does not exhibit the shift. In addition, compound **11** shows a down field shift amide hydrogen in the nmr spectrum and does not show ν NH in the 3400 cm^{-1} region in the ir spectrum, similar to compound **1** and **2**. Consequently, the presence of the NH of imidazole is not necessarily essential for the occurrence of the intramolecular hydrogen bond now in question.

Finally, all the experimental results described above may be interpreted by postulating the following resonance structure. Here, the intramolecular hydrogen bond in the

seven-membered ring is favored by the resonance stabilization of the imidazole ring.

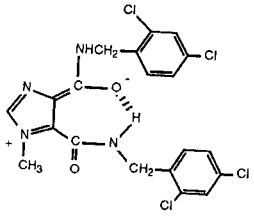
An example to show that the C-C bond between position 4 carbon of an imidazole ring and a carbonyl carbon is apt to take a double bond nature is given below. Here, imidazole-4(5)-formaldehyde (**15**) is supposed to be in the tautomeric hydroxymethylene form [12].

15

The reason why the ester carbonyl band of **12** does not show the lower wave number shift can be described as follows. For the occurrence of the resonance stabilization, the ester group, in question, has to lie in the same plane of the imidazole ring. While, in compound **12**, the ester group is not considered to achieve such co-planarity because of steric hindrance due to the adjacent *N*-methyl group. Consequently, compound **12** does not have a contribution of resonance stabilization, while **11** does. Such a torsion of the ester group by a neighboring group has already been assumed in the case of *ortho*-substituted benzoic acid esters [13].

In the nmr spectrum of **14**, one of the amide hydrogen atoms is observed at δ 8.06 ppm, which is near to that of **8**. However another one exhibits a downfield shift at δ 11.60 ppm. This result suggests that the latter amide proton

takes part in the hydrogen bonding. In a similar manner to that in compound **11**, the amide hydrogen of the carboxamide at 5-position in **14** is considered to form a hydrogen bond with the amide oxygen of the carboxamide group at the 4-position.



The presence of the resonance structures described above must produce a change in the uv spectrum. With regard to compounds **5** and **12**, the absorption band is observed at 243-244 nm, near to that of **13** (λ max 249 nm). On the other hand, compounds **1**, **2** and **11**, which show a lower wave number shift in the ir spectrum, exhibit an absorption maximum at a longer wavelength than those of **5** and **12**. They have λ max 262-264 nm. Compound **14** also has λ max 263 nm. These results support postulating the resonance structure accompanied by the intramolecular hydrogen bond as described above.

EXPERIMENTAL

Infrared absorption spectra were measured on a Shimadzu IR-430 spectrophotometer or Digilab STS-15E spectrophotometer (ft-ir). Measurements in solutions were performed with 2-3 mg/ml of carbon tetrachloride solutions in a sodium chloride cell of 0.1 mm thickness. Proton nuclear magnetic resonance spectra were measured on a Varian EM-390 (90 MHz) spectrometer and JEOL GX-400 (400 MHz) using TMS as an internal reference. Ultraviolet absorption spectra were measured in an acetonitrile solution on a Shimadzu 624 spectrometer. Mass spectra were measured on a JEOL DX-300 mass spectrometer.

4(5)-Ethoxycarbonyl-5(4)-*n*-propylaminocarbonylimidazole (**2**).

To a solution of *n*-propylamine (1.48 g, 25 mmoles) in dichloromethane (100 ml), **4a** (1.66 g, 5 mmoles) was added and the mixture was stirred for 4 hours under reflux. After removal of an insoluble solid, the filtrate was concentrated. A residual solid was recrystallized from tetrahydrofuran, ethyl acetate and petroleum ether to give 1.86 g (83%) of **2**; ir (potassium bromide): ν max 1682 (-$COOC_2H_5$), 1659 cm^{-1} (-CONH-); nmr (deuteriochloroform): δ 0.99 (t, 3H, -$NHCH_2CH_2CH_3$), 1.42 (t, 3H, -$COOCH_2CH_3$), 1.68 (m, 2H, -$NHCH_2CH_2CH_3$), 3.42 (q, 2H, -$NHCH_2CH_2CH_3$), 4.42 (q, 2H, -$COOCH_2CH_3$), 7.72 (s, 1H, imidazole C_2-H), 10.30 (br s, 1H, -CONH-).

Anal. Calcd. for $C_{10}H_{15}N_3O_3$: C, 53.32; H, 6.71; N, 18.66. Found: C, 53.07; H, 6.67; N, 18.63.

4(5)-Ethoxycarbonylimidazole (**3**).

A suspension of **4b** (0.255 g, 1.36 mmoles), prepared by the reported method [1], in ethanol (50 ml) was stirred under reflux for 18 hours. The resulting solution was concentrated and a residual solid was crystallized from acetone to give 0.15 g (39%) of **3**; ir (potassium bromide): ν max 1717 cm^{-1} (-$COOC_2H_5$); nmr (DMSO-d_6): δ 1.28 (t, 3H, -$COOCH_2CH_3$), 4.18 (q, 2H, -$COOCH_2CH_3$), 7.74 (s, 2H, imidazole ring protons); fd-ms: $(M+H)^+$ at m/z 141 (mol wt. 140).

Anal. Calcd. for $C_6H_8N_2O_2$: C, 51.42; H, 5.75; N, 19.99. Found: C, 51.41; H, 5.77; N, 20.48.

4(5)-Diethylaminocarbonyl-5(4)-ethoxycarbonylimidazole (**5**).

To a solution of diethylamine (1.83 g, 25 mmoles) in dichloromethane (100 ml), **4a** (1.66 g, 5 mmoles) was added and the mixture was stirred for 4 hours under reflux. After removal of an insoluble solid, the filtrate was concentrated. A residual solid was recrystallized from a mixture of ethyl acetate, diethyl ether and petroleum ether to give 0.98 g (41%) of **5**. Recrystallization from ethyl acetate and petroleum ether gave analytically pure **5**; ir (potassium bromide): ν max 1717 (-$COOC_2H_5$), 1643 cm^{-1} (-CON<); nmr (DMSO-d_6): δ 0.97, 1.14 (two sets of triplets, each 3H, -$CON(CH_2CH_3)_2$), 1.23 (t, 3H, -$COOCH_2CH_3$), 3.08, 3.40 (two sets of quartets, each 2H, -$CON(CH_2CH_3)_2$), 4.17 (q, 2H, -$COOCH_2CH_3$), 7.77 (s, 1H, imidazole C_2-H); fd-ms: M^+ at m/z 239 (mol wt 239).

Anal. Calcd. for $C_{11}H_{17}N_3O_3 \cdot 0.5H_2O$: C, 53.20; H, 7.32; N, 16.93. Found: C, 53.38; H, 7.33; N, 17.18.

4(5)-(2,4-Dichlorobenzylaminocarbonyl)imidazole (**8**).

To a solution of 2,4-dichlorobenzylamine (1.4 g, 8 mmoles) in dichloromethane (30 ml), **4b** (0.3 g, 1.6 mmoles) was added and the mixture was stirred for 19 hours under reflux. After concentration, a residue was dissolved in ethyl acetate (50 ml) and extracted with two 25 ml portions of 5% hydrochloric acid. The combined extracts were concentrated, and a precipitate generated was collected by filtration. The solid thus obtained was dissolved in a mixture of water (20 ml) and ethyl acetate (30 ml). The aqueous layer was brought to *p*H 8 with 2*N* aqueous sodium hydroxide under stirring and the organic layer was separated. The aqueous layer was extracted with ethyl acetate (30 ml). The combined extracts were dried and evaporated. Addition of petroleum ether to the residue gave a precipitate. The solid thus obtained was isolated by filtration, and recrystallization from ethyl acetate and petroleum ether gave 0.22 g (25%) of **8**; ir (potassium bromide): ν max 1632 cm^{-1} (-CONH-); nmr (deuteriochloroform): δ 4.63 (d, 2H, -$NHCH_2$-), 7.11-7.38 (m, 3H, -Ph-2,4 Cl), 7.52 (s, 2H, imidazole ring protons), 7.70 (br t, 1H, -CONH-).

Anal. Calcd. for $C_{11}H_9Cl_2N_3O$: C, 48.91; H, 3.37; N, 15.56. Found: C, 48.78; H, 3.63; N, 15.20.

1-Ethoxycarbonyl-2-*n*-propylaminocarbonylbenzene (**9**).

To a solution of *n*-propylamine (7.1 g, 120 mmoles) in dichloromethane (50 ml), phthalic anhydride (6.0 g, 40 mmoles) was added and the mixture was stirred for 4 hours under reflux. After concentration, a residue was dissolved in water (100 ml) and washed with ethyl acetate. To the aqueous layer ethyl acetate (100 ml) was added and the aqueous layer was brought to *p*H 2 with 6% hydrochloric acid. After the organic layer was separated, the aqueous layer was extracted with ethyl acetate (100 ml). The combined extracts were dried and concentrated. An addition of petroleum ether to the residue gave a precipitate, which was recovered and dried to give 6.33 g (76%) of 1-carboxy-2-*n*-propylaminocarbonylbenzene; nmr (DMSO-d_6 + deuteriochloroform): δ 0.90 (t, 3H, -$NHCH_2CH_2CH_3$), 1.53 (m, 2H, -$NHCH_2CH_2CH_3$), 3.16 (q, 2H, -$NHCH_2CH_2CH_3$), 7.17-7.80 (m, 4H, aromatic protons), 8.07 (br s, 1H, -CONH-).

To a cooled ethanol (10 ml), thionyl chloride (2.5 ml) was added dropwise at -10°. To this solution 1-carboxy-2-*n*-propylaminocarbonylbenzene (2 g, 9.6 mmoles), without further purification, was added, and the mixture was stirred for 2 days at room temperature. After concentration, a residue was dissolved in ethyl acetate (50 ml) and washed with 5% aqueous sodium bicarbonate. The organic layer was dried and concentrated to give 1.6 g of a residual oil. The residue was purified by column chromatography on a silica gel (80 g) using 50:1 (v/v) chloroform-methanol. The fraction containing the desired product was collected and concentrated to give 0.69 g (31%) of **9** as a residual oil, which was solidified on cooling in a refrigerator; ir (nujol): ν max 1720 (-$COOC_2H_5$), 1635 cm^{-1} (-CONH-); nmr (deuteriochloroform): δ 0.98 (t, 3H, -$NHCH_2CH_2CH_3$), 1.35 (t, 3H, -$COOCH_2CH_3$), 1.65 (m, 2H, -$NHCH_2CH_2CH_3$), 3.37 (q, 2H, -$NHCH_2CH_2CH_3$), 4.30 (q, 2H, -$COOCH_2CH_3$), 5.88 (br s, 1H, -CONH-), 7.25-7.91 (m, 4H, aromatic protons).

Anal. Calcd. for $C_{13}H_{17}NO_3$: C, 66.26; H, 7.28; N, 5.95. Found: C, 66.08; H, 7.27; N, 5.82.

1-Methyl-4-ethoxycarbonyl-5-(2,4-dichlorobenzylaminocarbonyl)imidazole and 1-Methyl-5-ethoxycarbonyl-4-(2,4-dichlorobenzylaminocarbonyl)imidazole (**11** and **12**).

To a solution of **1** (1.71 g, 5 mmoles) in ethanol (50 ml) containing sodium ethoxide (0.41 g, 6 mmoles), methyl iodide (1.42 g, 10 mmoles) was added, and the mixture was stirred for 7 hours at 50°. After removal of an insoluble solid by filtration, the filtrate was concentrated and a residue was dissolved in ethyl acetate (50 ml). The solution was washed with water and water saturated with sodium bicarbonate. The organic layer was dried and concentrated to give 1.23 g (69%) of a mixture of *ca* 11% and *ca* 58% as determined by nmr; Rf 0.80 for **11** and 0.37 for **12** (silica gel using 10:1 (v/v) chloroform-methanol). The isomers **11** and **12** were separated by column chromatography on a silica gel (70 g) using the same solvent as tlc. For analytical samples, **11** and **12** were recrystallized from benzene-petroleum ether and benzene-chloroform respectively. Compound **11**; ir (nujol): ν max 1680 (-$COOC_2H_5$), 1660 cm^{-1} (-CONH-); nmr (deuteriochloroform): δ 1.45 (t, 3 H, -$COOCH_2CH_3$), 4.02 (s, 3H, imidazole N-CH_3), 4.44 (q, 2H, -$COOCH_2CH_3$), 4.66 (d, 2H, -$CONHCH_2$-), 7.21-7.41 (m, 3H, -Ph-2,4 Cl), 7.51 (s, 1H, imidazole C_2-H), 10.67 (br s, 1H, -CONH-); compound **12**; ir (nujol): ν max 1705 (-$COOC_2H_5$), 1655 cm^{-1} (-CONH-); nmr (deuteriochloroform): δ 1.40 (t, 3H, -$COOCH_2CH_3$), 3.84 (s, 3H, imidazole N-CH_3), 4.42 (q, 2H, -$COOCH_2CH_3$), 4.66 (d, 2H, -$CONHCH_2$-), 7.21-7.41 (m, 3H, -Ph-2,4 Cl), 7.46 (s, 1H, imidazole C_2-H), 8.09 (br s, 1H, -CONH-).

Anal. Calcd. for $C_{15}H_{15}Cl_2N_3O_3$: C, 50.57; H, 4.25; N, 11.80. Found for **11**: C, 50.94; H, 4.46; N, 11.45. Found for **12**: C, 50.17; H, 4.26; N, 11.54.

1-Methyl-4,5-diethyoxycarbonylimidazole (**13**).

1-Methyl-4,5-imidazoledicarbonyl dichloride (2.07 g, 10 mmoles), prepared by the reported method [10], was dissolved in carbon tetrachloride (30 ml), and ethanol (20 ml) was added thereto. The mixture was stirred for 4 hours under reflux. After concentration, the residue was dissolved in a mixture of chloroform (50 ml) and 5% aqueous sodium bicarbonate (50 ml). The organic layer was separated, washed with water and dried. Concentration of the organic layer gave 1.87 g (81%) of **13** as a residual oil; nmr (deuteriochloroform): δ 1.36 (t, 6H, -$COOCH_2CH_3$), 3.79 (s, 3H, imidazole N-CH_3), 4.29 (q, 4H, -$COOCH_2CH_3$), 7.39 (s, 1H, imidazole C_2-H); fd-ms: M^+ at m/z 226 (mol wt. 226).

Anal. Calcd. for $C_{10}H_{14}N_2O_4 \cdot 0.2H_2O$: C, 52.24; H, 6.31; N, 12.20. Found: C, 52.43; H, 6.31; N, 12.23.

1-Methyl-4,5-(2,4-dichlorobenzylaminocarbonyl)imidazole (**14**).

To a solution of 1-methyl-4,5-imidazoledicarbonyl dichloride (2.07 g, 10 mmoles) in carbon tetrachloride (50 ml), dichlorobenzylamine (10.5 g, 60 mmoles) was added and the mixture was stirred for 4 hours under reflux. After removal of an insoluble solid, a filtrate was washed with 1*N* hydrochloric acid, 5% aqueous sodium bicarbonate and water. The organic layer was dried and concentrated. Recrystalization of a residual solid from ethyl acetate and petroleum ether gave 2.64 g (54%) of **14**; nmr (deuteriochloroform): δ 3.94 (s, 3H, imidazole N-CH_3), 4.57 (d, 4H, -$CONHCH_2$), 7.02-7.35 (m, 6H, -Ph-2,4Cl), 7.28 (s, 1H, imidazole C_2-H); 8.02 (br t, 1H, -CONH-).

Anal. Calcd. for $C_{20}H_{16}Cl_4N_4O_2$: C, 49.40; H, 3.32; N, 11.53. Found: C, 49.52; H, 3.60; N, 11.59.

REFERENCES AND NOTES

[1] N. Yasuda, *J. Heterocyclic Chem.*, **22**, 413 (1985).

[2] S. Kasina and J. Nematollahi, *Synthesis*, 162 (1975).

[3] R. S. Rasmussen and R. R. Brattain, *J. Am. Chem. Soc.*, **71**, 1073 (1949).

[4] R. M. Silverstein, G. C. Bassler and T. C. Morrill, "Spectrometric Identification of Organic Compounds", 4th Edition, John Wiley and Sons, New York, 1981, p 95.

[5] L. J. Bellamy, "The Infra-red Spectra of Complex Molecules", John Wiley and Sons, New York, 1958, p 203.

[6] M. R. Grimmett, "Comprehensive Heterocyclic Chemistry", Vol 5, "Five-membered Rings with Two or More Nitrogen Atoms", K. T. Potts, ed, Pergamon Press, Oxford, 1984, p 357.

[7] Ref [4] p 181.

[8] J. Elguero, G. Llouquet and C. Mazin, *Tetrahedron Letters*, 4085 (1975).

[9] L. Bauer, C. N. V. Nambury and D. Dhaman, *J. Heterocyclic Chem.*, **1**, 275 (1964).

[10] K. Takahashi, K. Suzuki, H. Ishiguro, T. Zaima and K. Mitsuhashi, *Nippon Kagaku Kaishi*, 801 (1974).

[11]E. Chans, S. R. Putt and H. D. H. Showalter, *J. Org. Chem.*, **47**, 3257 (1982).

[12] W. Huffall and F. L. Pyman, *J. Chem. Soc.*, 21 (1928).

[13] M. Yamaguchi, *Nippon Kagaku Zasshi*, **80**, 155 (1959).