Condensation of 3-Methylbenzoxazolinone with α,β-Unsaturated Acids

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The reaction between 3-methylbenzoxazolinone and some unsaturated acids in PPA leads to mixtures of compounds, depending on the acid: 6-crotonyl- (or cinnamoyl)-3-methylbenzoxazolinones, 2,3-dihydro-2,5-(or 2,7)dioxo-3-methylcyclopenta[*f*]benzoxazoles and 6-(3-oxo-indanyl)-3-methylbenzoxazolinones. The structure of the products was established by ^{13}C and ^{1}H nmr spectroscopy and (or) by independent synthesis. Possible mechanisms of the reaction are discussed; when competition is possible as in the last step of the cyclization, the benzene ring shows a higher reactivity than the aromatic nucleus of the benzoxazolinone; the contrary is observed when the benzene ring is *p*-chloro-substituted.

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The cyclopenta-annelation of aromatic compounds by reaction between aromatic derivatives and α,β-unsaturated acids has been the subject of only a few investigations (1-4). Among substitutions on the aromatic nucleus of 3-methylbenzoxazolinone, acylation has recently been performed by action of organic acids with polyphosphoric acid as solvent and catalyst (5). It was of interest to study the condensation of 3-methylbenzoxazolinone with α,β-unsaturated acids in order to obtain compounds which might be starting materials for potential drugs synthesis. Moreover, these reactions could inform us about respective reactivities of the aromatic ring of benzoxazolinone.

The (*E*)-α,β-unsaturated acid **2** was added to an equimolecular solution of 3-methylbenzoxazolinone **1** in an excess of PPA at the appropriate temperature of reaction (see Table 1). Different compounds were obtained and the main product depends on the substituent of **2** (Scheme 1). Yields were probably lowered by polymerization reactions but it was not possible to isolate poly-condensed compounds.

Compounds **3, 4, 6b** and the unsubstituted indanone **5d** were prepared by independent synthesis (Scheme 2). The ketones **3b,c** were obtained by crotonisation of suitable benzaldehydes with 6-acetyl-3-methylbenzoxazolinone **7a**; the ketone **3a** was synthesized by bromination-dehydrobromination of 6-butyryl-3-methylbenzoxazolinone **7e**; ketones **3** were cyclized with PPA to give the corresponding indanones **4**. Compound **6b** was obtained by cyclization of 3-(3-methyl-6-benzoxazolinonyl)acrylophenone **9** synthesized by two different routes, and **5d** by cyclization of 3-(3-methyl-6-benzoxazolinonyl)propionic acid **12d** (6). The 3-(3-methyl-6-benzoxazolinonyl)-3-

Scheme 1

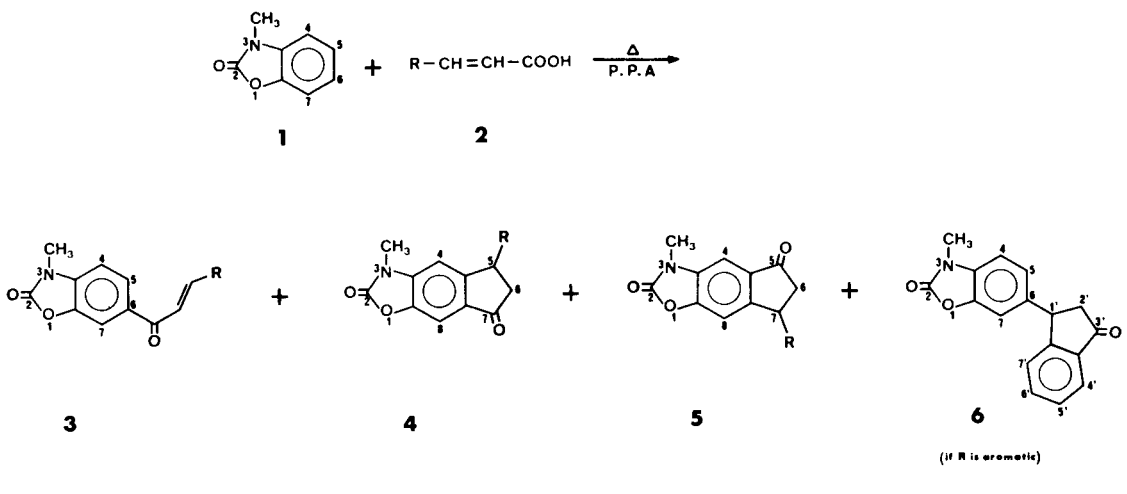

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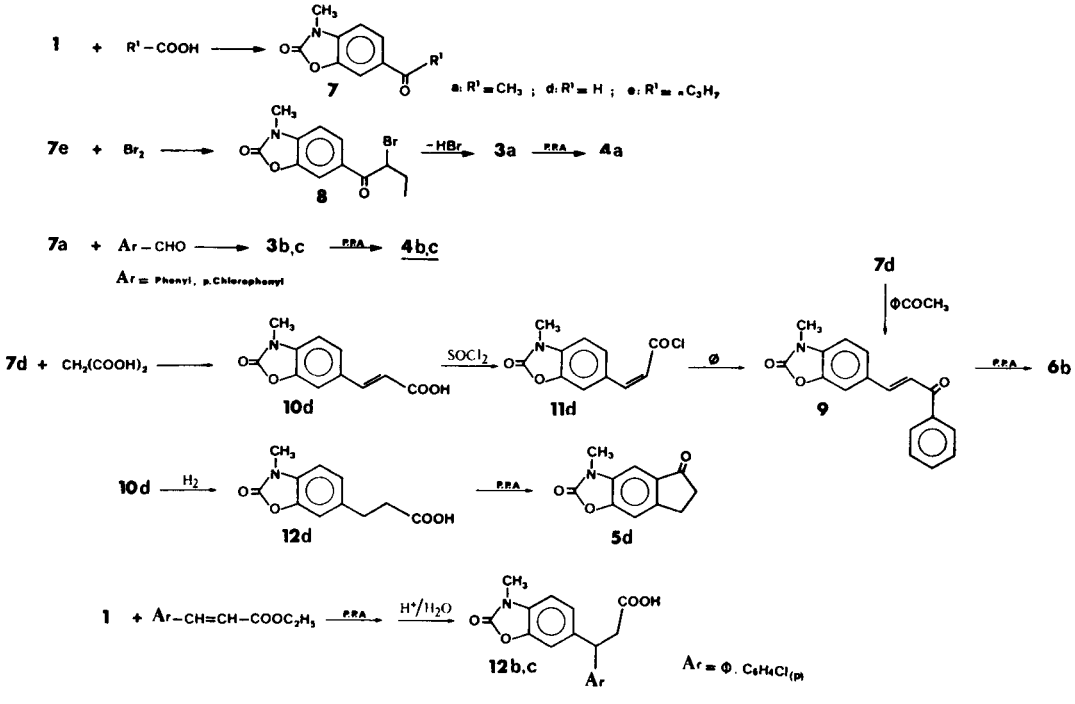
Table 1

Reaction Between 3-Methylbenzoxazolinone **1** and α,β-Unsaturated Acids **2** in PPA

	Δ °C	Time, Hours	Yields % (a)			
			3	**4**	**5**	**6**
1 + 2a	70	5	18	11	0	
	120	1/12	0	37	0	
1 + 2b	65	6	5	0	2	31
	65	7	0	0	2	35
1 + 2c	100	3	5	0	13	0
	120	2	2	0	29	0

(a) Isolated yields after recrystallization.

Scheme 2



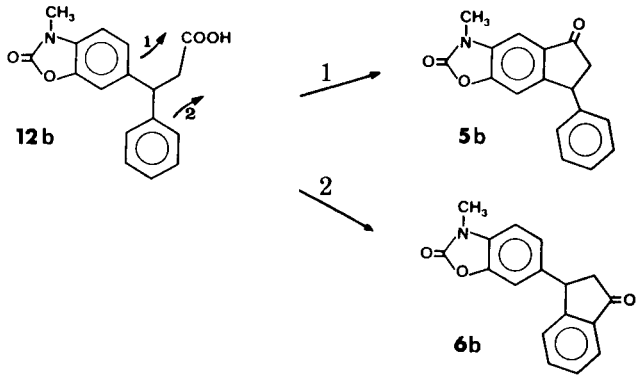
phenylpropionic acids **12b,c** were prepared by reaction of ethyl cinnamate (or its *p*-chloro derivative) with 3-methylbenzoxazolinone in PPA followed by hydrolysis of the ethyl ester of the acid.

The indanones **4** are likely formed by Friedel-Crafts acylation of the aromatic nucleus of benzoxazolinones to give the α,β-unsaturated ketones **3** with subsequent cyclization. The ketones **3** were observed in the reaction mixtures whatever the nature of the substituent of the acid **2**; these ketones are easily cyclized in PPA at 125° without traces of rearrangement (an acylation has been shown to be reversible in PPA (7)).

The indanones **5** are probably formed *via* the benzoxazolinonylpropionic acids which were not isolated from the mixtures of compounds **1** and **2** in PPA. Traces of 3-(2-methyl-5-thienyl)-2-methylpropionic acid have been noticed by Frejd and Karlsson in the reaction mixture of 2-methylthiophen with methacrylic acid in PPA (1). Frejd and Karlsson reported the cyclization of this thienylpropionic acid without rearrangement (though it had been noted by Palmer, *et al.*, (8)) in PPA and in the presence of methacrylic acid (but less than 1% without it). The 2,3-dihydro-2,5-dioxo-3-methylcyclopenta[*f*]benzoxazole **5d** is obtained by cyclisation of 3-(3-methyl-6-benzoxazolinonyl)propionic acid **12d** by heating at 125° in PPA without traces of rearrangement.

In PPA, the 3-(3-methyl-6-benzoxazolinonyl)-3-phenylpropionic acid **12b** is quantitatively cyclized to a mixture of **5b** and **6b** while in the same conditions, **12c** gave only **5c**. In the reaction of **1** with **2b**, the compounds **5b** and **6b**

Scheme 3



are more likely formed from **12b** (not isolated) by competitive acylation between the aromatic nucleus of benzoxazolinone and the benzene ring respectively (Scheme 3). In this case, the presence of a *p*-chloro substituent would deactivate the benzene ring and only path 1 is observed. Formation of **6b** could also be explained by alkylation of the benzoxazolinone by the 2-inden-1-one which could arise from the cyclisation of the cinnamic acid **2b** (it was in fact impossible to characterize this ketone by heating cinnamic acid in PPA, and furthermore transformation of (*E*)-cinnamic acid into its (*Z*)-isomer has been reported to occur at 80-95° in PPA (9)).

Atom 6-C of 3-methylbenzoxazolinone seems to be the more reactive site in this kind of reactions and this generalizes the previous observations of Lespagnol, *et al.*, (5).

^{13}C and ^{1}H nmr spectroscopy allows to distinguish indanones **4** and **5** (Table 2). (i) The 4-H and 8-H signals appear like singlets (W $\frac{1}{2} \sim 2$ Hz) which is characteristic of the coupling between *para* aromatic protons and excludes all other possibilities of cyclization. (ii) The ^{1}H nmr study of indanones of Kemp and Spanswick (3) shows that the aromatic proton in close proximity to the carbonyl group appears at lower field, and that a phenyl substituent at 3-C of indanone leads, with respect to a methyl group, to a shielding of indanone aromatic protons close to the substituent. In the lower field part of spectra of compounds **4** and **5**, the deshielded proton (except for **5d** where the shifts of 4-H and 8-H are very close) is less influenced by the aromatic substituent than the shielded proton. For steric considerations, the phenyl substituent is out of the plane of the cyclopenta[*f*]benzoxazole also, 4-H in **4b,c** and 8-H in **5b,c** are in the shielding zone of anisotropy of the benzene ring: the difference between the chemical shifts of 4-H in **4a** and **4b** (or **4c**) is close to that between the shifts of 8-H in **5d** and **5b** (or **5c**). A similar comparison can be observed on the difference between the shifts of 8-H in **4a** and **4b** (or **4c**) and that of 4-H in **5d** and **5b** (or **5c**). (iii) The experimental ^{13}C chemical shifts are in good agreement with the calculated ones and selective irradiations of 4-H and 8-H in compounds **4c** and **5c** result in sharpening of 4-C and 8-C respectively.

Table 2

Chemical Shifts of Protons and Carbons in Positions 4 and 8 in Compounds **4** and **5** in Deuteriochloroform, Relative to Tetramethylsilane

Compound	4-H	8-H	4-C	8-C
4a	7.03	7.45	104.2 (a) (105.9) (b)	103.9 (a) (104.2)
4b	6.76	7.54	105.3	104.1
4c	6.72	7.54	105.1	104.2
5b	7.35	7.03	101.9	107.9
5c	7.36	7.00	102.0	107.8
5d	7.27	7.31	102.4 (103.0) (b)	107.7 (108.0)

(a) Shifts can be exchanged. (b) Values in brackets are the calculated ones; for **5d** from the shifts of 3-methylbenzoxazolinone and indan-1-one; for **4a** from the shifts of 3-methylbenzoxazolinone and increments arising from **5d**.

The low field ^{1}H spectrum of **6b** is more complex to study because the systems are more strongly coupled; the observed ^{13}C chemical shifts of this compound are close to the calculated ones. The nmr of the chalcones **3b,c** are in good agreement with the results of Solcaniova, *et al.*, (10,11).

EXPERIMENTAL

Infrared spectra were recorded with a Perkin-Elmer 297 spectrometer. ^{13}C and ^{1}H nmr spectra were recorded with a Bruker WP 80 pulsed Fourier transform spectrometer; tetramethylsilane was used as the internal reference of chemical shifts. Compounds **7a** and **7d** (5), **10d**, **11d** and **12d** (6) were previously described.

Reaction of 3-Methybenzoxazolinone with α,β-Unsaturated Acids. General Method.

The acid (0.02 mole) was added portionwise to a stirred solution of 3-methylbenzoxazolinone (2.98 g, 0.02 mole) in polyphosphoric acid (45 g) heated at a suitable temperature (Table 1). The mixture was stirred at this temperature for the prescribed time, cooled and hydrolysed with ice-water (10 volumes). The resulting precipitate was collected by filtration, washed with water and aqueous sodium carbonate, dried and recrystallized from ethanol (which does not dissolve the ketones **3b** and **3c**). Compounds **5b** and **6b** were separated by fractionnal recrystallization from ethanol-water (50:50), compounds **3a** and **4a** from ethanol.

6-Crotonyl-3-methylbenzoxazolinone (**3a**).

This compound had mp 206°; ir (potassium bromide): 1760 (N-CO-O), 1660 (C=O), 1615 and 1600 (ethylenic and aromatic C=C), 975 cm^{-1} (*trans* CH=CH); nmr (deuteriochloroform): 2.01 (3H, d, J = 5.6, C*H*$_3$-CH=), 3.45 (3H, s, N-C*H*$_3$), 6.91 (1H, d, J = 15.1, =C*H*-CO), 7.02 (1H, d, J = 8.1, 4-H), 7.11 (1H, m, =C*H*-CH$_3$), 7.80 (1H, d, J = 1.5, 7-H), 7.89 (1H, dd, 5-H).

Anal. Calcd. for $C_{13}H_{11}NO_3$: C, 66.35; H, 5.10; N, 6.45. Found: C, 66.36; H. 4.94; N, 6.55.

6-Cinnamoyl-3-methylbenzoxazolinone (**3b**).

This compound had mp 204°; ir (potassium bromide): 1780 (N-CO-O), 1640 (C=O), 1600 and 1580 (ethylenic and aromatic C=C), 980 cm^{-1} (*trans* CH=CH); nmr (deuteriochloroform): 3.47 (3H, s, N-CH_3), 7.05 (1H, d, 4-H), 7.38-7.78 (5H, m, phenyl), 7.53 (1H, d, J = 15.5, =C*H*-CO), 7.85 (1H, d, C*H*=CH-CO), 7.92 (1H, bs, 7-H), 8.00 (1H, dd, J_{ortho} = 8.3 and J_{meta} = 1.7, 5-H).

Anal. Calcd. for $C_{17}H_{13}NO_3$: C, 73.07; H, 4.65; N, 5.01. Found: C, 72.69; H, 4.61; N, 4.99.

6-(*p*-Chloro-cinnamoyl)-3-methylbenzoxazolinone (**3c**).

This compound had mp 260°; ir (potassium bromide): 1770 (N-CO-O), 1650 (C=O), 1605 and 1585 (ethylenic and aromatic C=C), 985 cm^{-1} (*trans* CH=CH); nmr (deuteriochloroform): 3.47 (3H, s, N-CH_3), 7.05 (1H, d, 4-H), 7.34-7.65 (4H, AA'BB', J = 8.6, chlorophenyl), 7.50 (1H, d, J = 16.1, =C*H*-CO), 7.80 (1H, d, C*H*=CH-CO), 7.91 (1H, bs, 7-H), 7.98 (1H, dd, J_{ortho} = 7.8 and J_{meta} = 1.5, 5-H).

Anal. Calcd. for $C_{17}H_{12}ClNO_3$: C, 65.08; H, 3.85; Cl, 11.30; N, 4.46. Found: C, 65.00; H, 3.76; Cl, 11.15; N, 4.53.

2,3-Dihydro-3,5-dimethyl-2,7-dioxo-cyclopenta[*f*]benzoxazole (**4a**).

This compound had mp 190°; ir (potassium bromide): 1770 (N-CO-O), 1695 (C=O), 1610 cm^{-1} (aromatic); nmr (deuteriochloroform): 1.44 (3H, d, J = 6.8, CH_3), 2.32 (1H, *A*BX, J_{gem} = 18.8 and J_{vic} = 3.2, 6-H *cis*), 2.97 (1H, A*B*X, J_{vic} = 7.5, 6-H *trans*), 3.25-3.62 (1H, m, 5-H), 3.47 (3H, s, N-CH_3), 7.03 (1H, s, 4-H), 7.45 (1H, s, 8-H).

Anal. Calcd. for $C_{12}H_{11}NO_3$: C, 66.35; H, 5.10; N, 6.45. Found: C, 66.32; H, 5.13; N, 6.48.

2,3-Dihydro-2,5-dioxo-3-methyl-7-phenylcyclopenta[*f*]benzoxazole (**5b**).

This compound had mp 228°; ir (potassium bromide): 1770 (N-CO-O), 1680 (C=O), 1600 cm^{-1} (aromatic); nmr (deuteriochloroform): 2.73 (1H, *A*BX, J_{gem} = 19.2 and J_{vic} = 3.5, 6-H *cis*), 3.27 (1H, A*B*X, J_{vic} = 7.9, 6-H *trans*), 3.45 (3H, s, N-CH_3), 4.59 (1H, AB*X*, 7-H), 7.03 (1H, s, 8-H), 7.06-7.60 (5H, m, phenyl), 7.35 (1H, s, 4-H).

Anal. Calcd. for $C_{17}H_{13}NO_3$: C, 73.07; H, 4.65; N, 5.01; O, 17.19. Found: C, 73.10; H, 4.69; N, 4.96; O, 17.45.

2,3-Dihydro-2,5-dioxo-3-methyl-7-(*p*-chlorophenyl)-cyclopenta[*f*]benzoxazole (**5c**).

This compound had mp 206°; ir (potassium bromide): 1780 (N-CO-O), 1695 (C=O), 1610 cm^{-1} (aromatic); nmr (deuteriochloroform): 2.66 (1H, *A*BX, J_{gem} = 19.2 and J_{vic} = 3.6, 6-H *cis*), 3.26 (1H, A*B*X, J_{vic} = 7.8, 6-H *trans*), 3.46 (3H, s, N-CH_3), 4.59 (1H, AB*X*, 7-H), 7.00 (1H, s, 8-H), 7.00-7.36 (4H, AA'BB', J = 8.5, chlorophenyl), 7.36 (1H, s, 4-H).

Anal. Calcd. for $C_{17}H_{12}ClNO_3$: C, 65.08; H, 3.85; Cl, 11.30; N, 4.46; O, 15.30. Found: C, 65.22; H, 3.86; Cl, 11.11; N, 4.41; O, 15.44.

6-(3-Oxo-indanyl)-3-methylbenzoxazolinone (**6b**).

This compound had mp 183°; ir (potassium bromide): 1770 (N-*CO*-O), 1690 (C=O), 1600 cm^{-1} (aromatic); nmr (deuteriochloroform): 2.65 (1H, *A*BX, J_{gem} = 19.1 and J_{vic} = 3.8, 2'-H *cis*), 3.26 (1H, A*B*X, J_{vic} = 8.1, 2'-H *trans*), 3.40 (3H, s, N-CH_3), 4.63 (1H, AB*X*, 1'-H), 6.97-7.20 (7H, m, 4-H, 5-H, 7-H, 4'-H, 5'-H, 6'-H, 7'-H).

Anal. Calcd. for $C_{17}H_{13}NO_3$: C, 73.07; H, 4.65; N, 5.01. Found: C, 73.04; H, 4.91; N, 5.29.

Synthesis of 6-Crotonyl (or Cinnamoyl)-3-methylbenzoxazolinones (**3**).

6-Butyryl-3-methylbenzoxazolinone (**7e**).

3-Methylbenzoxazolinone (8.94 g, 0.06 mole) was dissolved in PPA (150 g) at 100° and butyric acid (5.51 ml, 0.06 mole) was added. The mixture was stirred at this temperature for 1.5 hours and hydrolysed with ice-water (1 liter). The resulting precipitate was collected by filtration, washed with water until neutrality, with cold acetone and recrystallized from acetone or ethanol, yield, 82%, mp 160°; ir (potassium bromide): 1765 (N-CO-O), 1660 (C=O), 1600 cm^{-1} (aromatic); nmr (deuterochloroform): 1.01 (3H, t, J = 7.0, CH_2-CH_3), 1.78 (2H, m, CH_2-CH_3), 2.94 (2H, t, J = 7.0, CH_2-CO), 3.45 (3H, s, N-CH_3), 7.01 (1H, d, 4-H), 7.82 (1H, bs, 7-H), 7.90 (1H, dd, J_{ortho} = 8.0 and J_{meta} = 1.5, 5-H).

Anal. Calcd. for $C_{12}H_{13}NO_3$: C, 65.74; H, 5.98; N, 6.39; O, 21.89. Found: C, 65.71; H, 6.03; N, 6.37; O, 22.06.

6-(2-Bromobutyryl)-3-methylbenzoxazolinone (**8**).

Bromine (3.35 ml, 0.065 mole) in dry chloroform (50 ml) was added to a solution of 6-butyryl-3-methylbenzoxazolinone (14.25 g, 0.065 mole) in dry chloroform (100 ml) and the mixture was stirred for 1 hour at room temperature. The solvent was evaporated and the solid residue recrystallized from ethanol, yield, 90%, mp 112°; ir (potassium bromide): 1760 (N-CO-O), 1670 (C=O), 1605 cm^{-1} (aromatic); nmr (deuteriochloroform): 1.09 (3H, t, J = 7.0, CH_2-CH_3), 2.20 (2H, m, CH_2-CH_3), 3.46 (3H, s, N-CH_3), 5.02 (1H, t, J = 7.0, C*H*Br-CO), 7.04 (1H, d, 4-H), 7.88 (1H, bs, 7-H), 7.96 (1H, dd, J_{ortho} = 8.0 and J_{meta} = 1.5, 5-H).

Anal. Calcd. for $C_{12}H_{12}BrNO_3$: C, 48.34; H, 4.05; Br, 26.80; N, 4.70; O, 16.10. Found: C, 48.57; H, 4.03; Br, 26.65; N, 4.68; O, 15.88.

6-Crotonyl-3-methylbenzoxazolinone (**3a**).

A solution of 6-(2-bromobutyryl)-3-methylbenzoxazolinone (2.98 g, 0.01 mole) in dimethylsulfoxide (10 ml) and triethylamine (1.4 ml, 0.01 mole) was stirred for 3 hours at 150°. The mixture was cooled, poured into cold water (100 ml) and acidified with 1N hydrochloric acid. The resulting precipitate was collected by filtration, washed with water until neutrality, dried and recrystallized from ethanol, yield, 44%.

6-Cinnamoyl (or *p*-Chlorocinnamoyl)-3-methylbenzoxazolinone (**3b** or **3c**).

The suitable benzaldehyde (0.025 mole) was added to a solution of 6-acetyl-3-methylbenzoxazolinone **7a** (4.78 g, 0.025 mole) in ethanol (350 ml) saturated with dry hydrogen chloride. The mixture was stirred for 2 hours at room temperature. After filtration, the precipitate was washed with water until neutrality and purified by washing with hot ethanol, yield, 85%.

Synthesis of 2,3-Dihydro-2,7-dioxo-3-methylcyclopenta[*f*]benzoxazoles **4**.

General Method.

A mixture of the α,β-unsaturated ketone **3** (1 g) and PPA (15 g) was stirred at 125° for 20-35 minutes, cooled and hydrolysed by ice-water (10 volumes). The resulting precipitate was collected by filtration, washed with water, dried and recrystallized from ethanol.

2,3-Dihydro-3,5-dimethyl-2,7-dioxo-cyclopenta[*f*]benzoxazole (**4a**).

This compound was obtained in a yield of 58%.

2,3-Dihydro-2,7-dioxo-3-methyl-5-phenylcyclopenta[*f*]benzoxazole (**4b**).

This compound was obtained in a yield of 55%, mp 161°; ir (potassium bromide): 1780 (N-CO-O), 1680 (C=O), 1605 cm^{-1} (aromatic); nmr (deuteriochloroform): 2.71 (1H, *A*BX, J_{gem} = 19.0 and J_{vic} = 3.7, 6-H *cis*), 3.26 (1H, A*B*X, J_{vic} = 7.9, 6-H *trans*), 3.35 (3H, s, N-CH_3), 4.58 (1H, AB*X*, 5-H), 6.76 (1H, s, 4-H), 7.06-7.60 (5H, m, phenyl), 7.54 (1H, s, 8-H).

Anal. Calcd. for $C_{17}H_{13}NO_3$: C, 73.07; H, 4.65; N, 5.01. Found: C, 72.99; H, 4.75; N, 4.96.

2,3-Dihydro-2,7-dioxo-3-methyl-5-(*p*-chlorophenyl)-cyclopenta[*f*]benzoxazole (**4c**).

This compound was obtained in a yield of 67%, mp 190°; ir (potassium bromide): 1780 (N-CO-O), 1690 (C=O), 1610 cm^{-1} (aromatic); nmr (deuteriochloroform): 2.66 (1H, *A*BX, J_{gem} = 19.0 and J_{vic} = 3.8, 6-H *cis*), 3.26 (1H, A*B*X, J_{vic} = 8.0, 6-H *trans*), 3.37 (3H, s, N-CH_3), 4.57 (1H, AB*X*, 5-H), 6.72 (1H, s, 4-H), 7.01-7.37 (4H, AA'BB', J = 8.7, chlorophenyl), 7.54 (1H, s, 8-H).

Anal. Calcd. for $C_{17}H_{12}ClNO_3$: C, 65.08; H, 3.85; Cl, 11.30; N, 4.46; O, 15.30. Found: C, 65.05; H, 3.93; Cl, 11.29; N, 4.45; O, 15.36.

Synthesis of 2,3-Dihydro-2,5-dioxo-3-methylcyclopenta[*f*]benzoxazole (**5d**).

3-(3-Methyl-6-benzoxazolinonyl)propionic acid **12d** was cyclized by heating in PPA at 130° during 20 minutes. Work-up as for **4** afforded the compound **5d** in a yield of 86%, mp 202°; ir (potassium bromide): 1775 (N-CO-O), 1690 (C=O), 1605 cm^{-1} (aromatic); nmr (deuteriochloroform): 2.66-2.82 (2H, m, 6-H), 3.12-3.27 (2H, m, 7-H), 3.44 (3H, s, N-CH_3), 7.27 (1H, s, 4-H), 7.31 (1H, s, 8-H).

Anal. Calcd. for $C_{11}H_9NO_3$: C, 65.02; H, 4.46; N, 6.89; O, 23.62. Found: C, 64.96; H, 4.47; N, 6.94; O, 23.59.

Synthesis of 6-(3-Oxo-indanyl)-3-methylbenzoxazolinone (**6b**).

3-(3-Methyl-6-benzoxazolinonyl)acrylophenone (**9**).

Procedure 1.

Acetophenone (1.2 g, 0.01 mole) was added to a solution of 6-formyl-3-methylbenzoxazolinone (**7d**) (1.77 g, 0.01 mole) in ethanol (100 ml) saturated with dry hydrogen chloride. The mixture was then worked up as described for **3b** and **3c**, yield, 36%, mp 198°; ir (potassium bromide): 1760 (N-CO-O), 1650 (C=O), 1585 and 1570 (ethylenic and aromatic C=C), 975 cm^{-1} (*trans* CH=CH); nmr (deuteriochloroform): 3.44 (3H, s, N-CH_3), 7.00 (1H, d, J = 8.3, 4-H), 7.40-7.64 (5H, m, phenyl) 7.48 (1H, d, J = 15.6, C*H*=CH-CO), 7.81 (1H, d, =C*H*-CO), 7.95-8.10 (2H, m, 5-H, 7-H).

Anal. Calcd. for $C_{17}H_{13}NO_3$: C, 73.07; H, 4.65; N, 5.01; O, 17.19. Found: C, 73.05; H, 4.71; N, 4.97; O, 17.27.

Procedure 2.

Aluminium chloride (1.34 g, 0.01 mole) was added to a mixture of dry benzene (0.88 ml, 0.01 mole) and dry nitrobenzene (10 ml). 3-(3-Methyl-6-benzoxazolinonyl)acryloyl chloride **11d** (2.38 g, 0.01 mole) was added portionwise and the mixture was heated at 100° for 1 hour, cooled and acidified with cold 1*N* hydrochloric acid. The resulting precipitate was collected by filtration, washed with water, petroleum ether and recrystallized from benzene, yield, 29%.

6-(3-Oxo-indanyl)-3-methylbenzoxazolinone (**6b**).

3-(3-Methyl-6-benzoxazolinonyl)acrylophenone **9** was cyclized by heating in PPA at 160° during 30 minutes. Work up as for cyclization of **3** afforded the compound **6b** in a yield of 70%.

Synthesis of 3-(3-Methyl-6-benzoxazolinonyl)-3-phenylpropionic Acid **12b** and of its 3-(*p*-Chlorophenyl) Derivative **12c**.

General Method.

A mixture of the suitable ethyl cinnamate (0.05 mole), 3-methylbenzoxazolinone (7.45 g, 0.05 mole) and PPA (120 g) was stirred at 80° for 3 hours, cooled, hydrolysed by ice-water, extracted with chloroform and the solvent was evaporated. The residue was heated with 1*N* hydrochloric acid and extracted with chloroform. The extract was neutralized with sodium carbonate solution and the aqueous layer, after acidification, was extracted with chloroform and concentrated.

3-(3-Methyl-6-benzoxazolinonyl)-3-phenylpropionic Acid (**12b**).

This compound was separated from cinnamic acid by recrystallization from ethanol-water (50:50) in a yield of 46%, mp 194°; ir (potassium bromide): 1760 (N-CO-O), 1700 (acid C=O), 1610 cm^{-1} (aromatic); nmr (deuteriochloroform): 3.09 (2H, d, J = 7.9, CH_2), 3.36 (3H, s, N-CH_3), 4.56 (1H, t, CH), 6.80-7.30 (8H, m, 4-H, 5-H, 7-H with 4-H at 6.85 and J_{ortho} = 8.5, phenyl).

Anal. Calcd. for $C_{17}H_{15}NO_4$: C, 68.68; H, 5.08; N, 4.71; O, 21.52. Found: C, 68.49; H, 5.07; N, 4.63; O, 21.70.

3-(3-Methyl-6-benzoxazolinonyl)-3-(*p*-chlorophenyl)propionic Acid (**12c**).

This compound was separated from *p*-chlorocinnamic acid by recrystallization from cyclohexane-acetone (50:50) in a yield of 8%, mp 205-206°; ir (potassium bromide): 1755 (N-CO-O), 1700 (acid C=O), 1610 cm^{-1} (aromatic); nmr (deuteriochloroform): 3.07 (2H, d, J = 7.8, CH_2), 3.38 (3H, s, N-CH_3), 4.55 (1H, t, CH), 6.80-7.30 (7H, m, 4-H, 5-H, 7-H (with 4-H at 6.87 and J_{ortho} = 8.5), phenyl).

Anal. Calcd. for $C_{17}H_{14}ClNO_4$: C, 61.55; H, 4.25; N, 4.22. Found: C, 61.52; H, 4.21; N, 4.19.

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