506. *The Reaction of Ethyl 2-Oxocyclopentanecarboxylate with Arylamines. Part II.* The Preparation of 2,3-Dihydro-β-quinindones (2,3,4,9-Tetrahydro-9-oxo-1H-cyclopenta[b]quinolines).*

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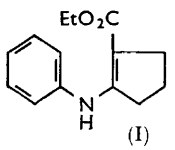
Substituted 2,3-dihydro-β-quinindones have been prepared by cyclisation of the corresponding ethyl 2-anilinocyclopent-1-enecarboxylates at 245°. The required starting materials were obtained by condensation of arylamines with ethyl 2-oxocyclopentanecarboxylate at room temperature.

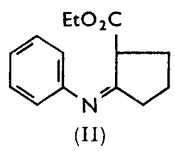
The reaction described in Part I * has been extended by the condensation of ethyl 2-oxocyclopentanecarboxylate with arylamines at low temperatures and the cyclisation of the products to derivatives of 2,3-dihydro-β-quinindone (2,3,4,9-tetrahydro-9-oxo-1*H*-cyclopenta[*b*]quinoline). In contrast to the high-temperature condensation (Part I), which gave moderate yields of the 2-oxocyclopentanecarboxyanilides and 2-anilinocyclopent-1-enecarboxyanilides, the room-temperature condensation now described gave nearly quantitative yields of the ethyl 2-anilinocyclopent-1-enecarboxylates.

Blount, Perkin, and Plant [1] condensed ethyl 2-oxocyclopentanecarboxylate with aniline at room temperature, and obtained ethyl 2-anilinocyclopent-1-enecarboxylate (I) as an oil which cyclised to 2,3-dihydro-β-quinindone (III) at 260° within a few minutes. Linstead and Bao Lang-Wang [2] repeated the preparation and claimed to have isolated the anilino-ester (I) crystalline.

In the present work, we found ethyl 2-anilinocyclopent-1-enecarboxylate to be a very pale yellow oil which resisted all attempts at crystallisation, in agreement with Blount *et al.* Examination of the infrared absorption spectrum of the condensation product of aniline with ethyl 2-oxocyclopentanecarboxylate showed that the compound was ethyl 2-anilinocyclopent-1-enecarboxylate (I) and not the tautomeric ethyl 2-phenyliminocyclopentanecarboxylate (II).



(I)



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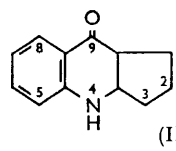

(III)

With few exceptions, substituted arylamines condensed smoothly with ethyl 2-oxocyclopentanecarboxylate at room temperature in the presence of a trace of acetic acid as

* Part I, Brown, Carver, and Hollingsworth, *J.*, 1961, 4295.

[1] Blount, Perkin, and Plant, *J.*, 1929, 1983.
[2] Linstead and Bao Lang-Wang, *J.*, 1937, 807.

No.	Subst.†	Form	Solvent for crystn.*	M. p.	Yield (%)	Found (%) C	Found (%) H	Found (%) N	Formula	Required (%) C	Required (%) H	Required (%) N
			(A) *Substituted ethyl-2-anilinocyclopent-1-enecarboxylates* (I).									
1	2-Me	Plates	Me_2CO–H_2O	44—45°	90	73·3	7·9	5·8	$C_{15}H_{19}NO_2$	73·5	7·75	5·7
2	3-Me	Oil		*a*	80	73·5	7·9	5·4				
3	4-Me	Needles	Pet (a)	43—44	87	73·5	7·8	5·4				
4	2,4-Me_2	Needles	Pet (a)	47	92	74·5	8·2	5·5	$C_{16}H_{21}NO_2$	74·2	8·1	5·4
5	2,5-Me_2	Needles	Pet (a)	53—54	85	74·0	8·1	5·6				
6	2-MeO	Plates	Et_2O	83—84	90	68·8	7·4	5·1	$C_{15}H_{19}NO_3$	69·0	7·3	5·4
7	4-MeO	Needles	Pet (a)	54	80	68·9	7·4	5·7				
8	2,3-Benzo	Powder	Pet (a)	73—73·5	90	76·6	7·1	4·8	$C_{18}H_{19}NO_2$	76·9	6·8	5·0
9	2-Cl	Prisms	Pet (a)	54·5	90	63·1	6·2	5·6	$C_{14}H_{16}ClNO_2$	63·3	6·0	5·3
10	3-Cl	Oil		*b*	85	63·3	6·1	5·2				
11	4-Cl	Needles	EtOH–H_2O	40	65	63·5	6·2	5·3				
12	2,4-Cl_2	Needles	Et_2O	73	82	56·2	5·2	4·9	$C_{14}H_{15}Cl_2NO_2$	56·0	5·0	4·7
13	3-Cl-4-Me	Plates	EtOH–H_2O	53—54	90	64·2	6·7	4·9	$C_{15}H_{16}ClNO_2$	64·4	6·4	5·0
14	5-Cl-2-Me	Needles	Me_2CO–H_2O	62	95	64·2	6·8	5·0				
15	2-Br-4-Me	Needles	EtOH	101	95	55·6	5·8	4·5	$C_{15}H_{16}BrNO_2$	55·6	5·6	4·3
16	4-Br	Prisms	Pet (a)	62—63	95	54·2	5·5	4·5	$C_{14}H_{16}BrNO_2$	54·2	5·2	4·5
17	4-NHAc	Plates	EtOH–Pet (c)	155—156	95	66·4	7·1	9·8	$C_{16}H_{20}N_2O_3$	66·7	6·9	9·7
18	4-Ac	Pale yellow needles	Me_2CO–H_2O	74—75	90	70·1	7·0	5·1	$C_{16}H_{19}NO_3$	70·3	7·0	5·1
19	4-CO_2Et	Needles	Pet (b)	67	85	67·3	6·85	4·6	$C_{17}H_{21}NO_4$	67·3	6·9	4·6
20	2-NO_2	Orange-red prisms	Me_2CO–Pet (b)	71—72	80	60·7	6·0	10·1	$C_{14}H_{16}N_2O_4$	60·9	5·8	10·1
21	4-NO_2	Yellow needles	Me_2CO–Pet (b)	133—134	85	60·7	5·8	10·2				
22	2-Me-5-NO_2	Orange plates	Me_2CO–Pet (b)	138·5	90	62·1	6·4	9·4	$C_{15}H_{18}N_2O_4$	62·1	6·2	9·6
			(B) *Substituted* 2,3-*dihydro-β-quinindones* (III).									
1	5-Me	Needles	EtOH–H_2O		80	78·3	6·5	6·8	$C_{13}H_{13}NO$	78·4	6·6	7·0
2	6-Me	Needles	EtOH–H_2O		70	78·5	6·7	6·9				
3	7-Me	Needles	AcOH–H_2O		80	72·1	7·0	6·5	$C_{13}H_{13}NO,H_2O$ ‡	72·0	6·9	6·5
4	5,7-Me_2	Needles	EtOH–H_2O		80	78·5	7·3	6·5	$C_{14}H_{15}NO$	78·8	7·1	6·6
5	5,8-Me_2	Needles	EtOH–H_2O		85	73·0	7·7	6·0	$C_{14}H_{15}NO,H_2O$ ‡	72·8	7·4	6·1
6	5-MeO	Needles	EtOH		85	72·2	6·2	6·3	$C_{13}H_{13}NO_2$	72·5	6·1	6·5
7	7-MeO	Plates	MeOH–H_2O		65	72·2	6·2	6·45				
8	5,6-Benzo	Needles	AcOH–H_2O		70	75·7	6·1	5·7	$C_{16}H_{13}NO,H_2O$ ‡	75·9	6·0	5·5
9	5-Cl	Needles	EtOH		75	65·4	4·7	6·2	$C_{12}H_{10}ClNO$	65·6	4·6	6·4
10	6-Cl	Needles	EtOH–H_2O		70	65·5	4·9	6·3				
11	7-Cl	Needles	AcOH–H_2O		85	65·5	4·8	6·4				
12	5,7-Cl_2	Plates	Me_2CO–EtOH		65	56·5	3·6	5·3	$C_{12}H_9Cl_2NO$	56·7	3·6	5·5
13	6-Cl-7-Me	Needles	EtOH		80	66·6	5·4	5·8	$C_{13}H_{12}ClNO$	66·8	5·2	6·0
14	8-Cl-5-Me	Needles	EtOH–H_2O		85	66·6	5·4	5·9				
15	5-Br-7-Me	Prisms	EtOH		70	56·0	4·5	4·8	$C_{13}H_{12}BrNO$	56·1	4·4	5·0
16	7-Br	Needles	AcOH		65	54·4	4·1	5·4	$C_{12}H_{10}BrNO$	54·6	3·8	5·3
17	7-NHAc	Needles	AcOH		70	69·1	5·9	11·3	$C_{14}H_{14}N_2O_2$	69·4	5·8	11·6
18	7-Ac	Plates	AcOH–H_2O		65	74·2	5·8	6·1	$C_{14}H_{13}NO_2$	74·0	5·7	6·2
19	7-CO_2Et	Plates	AcOH–H_2O		45	70·1	6·0	5·5	$C_{15}H_{15}NO_3$	70·0	5·9	5·4

* Pet (a) = light petroleum (b. p. 40—60°). Pet (b) = light petroleum (b. p. 60—80°). Pet (c) = light petroleum (b. p. 80—100°).
† In aryl ring of (I). ‡ "Loss" was determined and supported the formula stated.
[a] B. p. 149°/0·7 mm., n_D^{20} 1·5954. [b] B. p. 157°/0·5 mm., n_D^{20} 1·6098.

catalyst to give the corresponding aryl-substituted ethyl 2-anilinocyclopent-1-enecarboxylates as crystalline compounds of rather low melting point. Cyclisation of these compounds proceeded smoothly under nitrogen at 245° in 30 minutes, to give the substituted 2,3-dihydro-β-quinindones in high yield. As was expected, attempts to cyclise the nitro-substituted anilino-esters proved unsuccessful.

Monosubstituted arylamines with the substituent in the *meta*-position gave anilino-esters which were oils at room temperature, but which crystallised readily at −5°. Cyclisation of these compounds could give rise to either the 6- or 8-substituted 2,3-dihydro-β-quinindones, but in each of the cases examined we have found only one compound in the cyclised product. We have been unable to assign the position of the substituent in these compounds with certainty, but have treated them provisionally as the 6-substituted 2,3-dihydro-β-quinindones. Further work is in hand in attempts to confirm this structural assignment.

All the 2,3-dihydro-β-quinindones described herein melted with decomposition at temperatures above 300°. They were markedly more soluble in organic solvents than the corresponding 2,3-dihydro-α-quinindones described in Part I.

Experimental

Yields quoted are isolated yields of purified compounds.

Ethyl 2-Anilinocyclopent-1-enecarboxylate.—Ethyl 2-oxocyclopentanecarboxylate,[3] b. p. 108—109°/13 mm., n_D^{20} 1·44765 (0·05 mole), aniline (0·05 mole), and acetic acid (0·1 ml.) were mixed in the cold and kept over sodium hydroxide pellets for 14 days. The resulting pale yellow oil (yield 85%) resisted all attempts at crystallisation and was purified by repeated distillation under reduced pressure. It had b. p. 142°/0·5 mm., n_D^{20} 1·5926 (Found: C, 72·6; H, 7·3; N, 6·2. Calc. for $C_{14}H_{17}NO_2$: C, 72·7; H, 7·4; N, 6·1%). Infrared spectra, determined in carbon tetrachloride solution on a Grubb–Parsons double-beam spectrometer model S3A, contained: (1) an NH band at 3333 cm.$^{-1}$; this did not shift on progressive dilution, showing intramolecular hydrogen bonding; (2) an aniline-type C–NH band at 1307 cm.$^{-1}$; (3) a carbonyl band at 1653 cm.$^{-1}$; this is too low for a non-conjugated system, but is compatible with the hydrogen bonded NH·C:C·CO system. The infrared spectrum is thus compatible with the structure ethyl 2-anilinocyclopent-1-enecarboxylate, but incompatible with the tautomeric ethyl 2-phenyliminocyclopentanecarboxylate.

The *compounds* in Table (A) were prepared similarly. Ethyl 2-oxocyclopentanecarboxylate failed to condense with *p*-aminobenzoic acid, anthranilic acid, 2-aminopyridine, or cyclohexylamine.

2,3-Dihydro-β-quinindone.—Ethyl 2-anilinocyclopent-1-enecarboxylate (10 g.) was heated in a vapour-bath under nitrogen at 245° for 30 min. Ethanol was slowly evolved, and in 25 min. the mixture solidified. The cooled solid was refluxed with benzene (100 ml.) for 30 min. to remove coloured impurities. The resulting 2,3-dihydro-β-quinindone recrystallised from ethanol as needles (80%), m. p. 325° (decomp.) (with previous coloration) (Found: C, 77·7, H, 6·1; N, 7·5. Calc. for $C_{12}H_{11}NO$: C, 77·8; H, 5·95; N, 7·6%). Blount, Perkin, and Plant give m. p. 327° (with previous blackening).

The *compounds* in Table (B) were prepared similarly. All melted at temperatures above 300°, with previous darkening, softening, and, ultimately, decomposition. The following notes apply:

Table (B). Nos. 3, 5, and 8. These hydrates were very stable; the water of crystallisation could only be removed by heating the compounds at 120°/1 mm. for 4 hr. On exposure to a moist atmosphere, the anhydrous materials were rehydrated in 6—8 hr.

Attempts to cyclise the nitro- and methyl-nitro-derivatives of ethyl 2-anilinocyclopent-1-enecarboxylate proved unsuccessful.

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Waltham Abbey, Essex. [*Received, December 15th*, 1961.]

[3] Dobson, Ferns, and Perkin, *J.*, 1909, **95**, 2015.