A New type of Dimroth Rearrangement: Formation of 1,2-Dihydro-3Hquinazolone 4-Oximes from 4-Amino-1,2-dihydroquinazoline 3-Oxides

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Contrary to earlier claims the primary product of the reaction of aldehydes and *o*-aminobenzamide oxime is, irrespective of the aldehyde, always a 4-amino-1,2-dihydroquinazoline 3-oxide. Thermolysis of 1-unsubstituted 2-substituted quinazoline 3-oxides (5) in solution or in melt gives rise, by a new type of Dimroth rearrangement, to the isomeric 1,2-dihydro-4-quinazolone oximes (6), while the 1-benzyl 2-unsubstituted analogue (9j) yields, presumably by an addition-elimination ring transformation coupled with oxidation, a quinoidal quinazolone 4-oxime (17).

Recently we described a novel thermal isomerization of 4aminopyrimidine 3-oxides (1) which gave rise by ring contraction to the oxadiazolines (2) (Scheme 1).¹



In order to explore the possibility of extending this transformation to benzo analogues of (1) the 4-amino-1,2-dihydroquinazoline 3-oxides (5) and (9) were now prepared and their behaviour studied.

The synthesis of 4-alkyl- and 4-aryl-1,2-dihydroquinazoline 3-oxides by allowing *o*-aminophenyl ketoximes and carbonyl compounds to react has already been described.² It has been reported, however, that extension of the method to the reaction of *o*-aminobenzamide oxime (3) with aldehydes (4) gives rise, depending on the nature and quantity of the aldehyde, to three different products: reaction of anisaldehyde (4c) and cinnamaldehyde (4g) with (3) in a molar ratio of 1:1 gave the cyclic oximes (6c,g), while with a 2:1 ratio the oxadiazolo[4,3-*c*]quinazolines (7c,g). With other aldehydes, *e.g.* (4a,d,e,f,i), the products were, independent of the molar ratio,³ the *N*-oxides (5).

In our studies, dependence of the reaction on the constitution of the aldehyde could not be confirmed. Instead we found that the primary product in the reaction of (3) and aldehydes were always quinazoline 3-oxides (5), compounds which, when heated, gave the semicyclic amidoximes.

Thus, having repeated the experiment in the literature,^{3a} we heated a 1:2 mixture of (3) and benzaldehyde on a steam-bath, to give a separable mixture of (5a), (6a), and (7a). In the literature only the formation of (5a) was mentioned with no indication of the yield ^{3a} (Scheme 2). When the reaction was repeated in ethanol at 20 °C, the pure N-oxide (5a) was obtained in good yield.

Compound (5a) (m.p. 190—192 °C) is a bright yellow substance and when heated in a solvent (toluene, xylene, butanol, or ethanol) or on brief melting, gave a colourless isomeric product of m.p. 179—181 °C to which the cyclic oxime structure (6a) was assigned. This isomerization is thus basically different from that of the monocyclic *N*-oxide analogues (1) which involved ring contraction.¹ Compound (6a) can be obtained



directly in excellent yield when an ethanolic solution of a 1:1 mixture of the components was heated in a sealed tube at 95 °C for 10 h. Reaction of the oxime (6a) with an additional mole equiv. of benzaldehyde yielded, in turn, the tricyclic oxadiazolo[4,3-c]quinazoline (7a), which explains the concurrent formation of (5a), (6a), and (7a) when (3) was treated with an excess of benzaldehyde.

As a literature analogue of the isomerization $(5a) \rightarrow (6a)$ the transformation of 4-aminopyrimidine 3-oxides to 4-pyrimidone oximes can be quoted, but these differ from our reaction in a way that the substrate contains a double bond between C-1 and N-2 and that the former are always assisted by some reagent.⁴ The transformations proceed by an addition-elimination mechanism in the presence of some acidic or basic catalyst,⁵ or an acylating agent.⁶

In contrast, in our isomerization no catalyst was needed and in the case of (5a), where the reaction was performed in different solvents, no solvent effect was observed. Thus, the half-life of the reaction (5a) \rightarrow (6a) at 140 °C was the same in butanol and dry



Scheme 3.

toluene (ca. 75 min). In the melt the reaction was complete within $1-2 \min at 190$ °C.

It is important to note that the N^1 -benzyl derivative (9a), prepared by allowing 2-benzylaminobenzamide oxime (8) and benzaldehyde to react, was completely resistant to thermolysis (Scheme 3); this indicated a crucial role for the labile hydrogen atom at N-1 in the isomerization.

In view of the above facts we propose for the transformation $(5a) \rightarrow (6a)$ the pathway shown in Scheme 3. The primary product is a Schiff-base (10), which is transformed at room temperature in a fast but reversible electrocyclic ring closure and proton migration to the nitrone (5a). At higher temperature the formation of the thermodynamically more stable semicyclic amidoxime (6a) is favoured. The process involves reversion to (10) by proton migration and cleavage of the C(2)-N(3) bond of the quinazoline ring, followed by rotation and recyclization.*

Transformation $(5a) \rightarrow (6a)$ is related to Dimroth rearrangements carried out without solvent or in an inert solvent,⁸ although formally it does not correspond in every respect to 'classical' examples of the Dimroth rearrangement.⁹

The key role of the hitherto unisolated Schiff-base intermediate (10) is strongly supported by the fact that the nitrile (11) gives, with hydroxylamine in ethanol at room temperature, the N-oxide (5a), while at 95 °C it gives rise to the oxime (6a) in excellent yield (Scheme 3). This interesting alternation between kinetic and thermodynamic control was also experienced in the reaction of (3) with the other aldehydes (4) too. Contrary to the literature³ the reaction of (3) and (4) gives first, independently of the constitution of the aldehyde, N-oxides of the type (5). Thus even in the case of (4c) and (4g) the N-oxides (5c) and (5g) can be readily isolated and can be then thermally isomerized to the cyclic oximes (6c) and (6g) respectively.

According to the literature types (5) and (6) can be distinguished by differences in the range of 3 600-3 300 cm⁻¹ of the solution i.r. spectra.^{3a} We found that an analysis of the spectra taken for KBr pellets in the range of 1 250-900 cm⁻¹ is simpler and provides more characteristic information. In compounds (5) a system of several bands characteristic of the N-O bond of non-aromatic nitrones (N-oxides) appears¹⁰ between 1 200 and 1 100 cm⁻¹, and the N-O band characteristic of oximes ^{10c,11} is absent in the range of 945-920 cm⁻¹; the latter band is very intensive with compounds (6) which makes identification very simple. It has to be mentioned here that from changes in the i.r. spectrum experienced on heating (5f) in bromoform, Goncalves and his co-workers postulated the transformation $(5f) \rightarrow (6f)$ but did not isolate (6f) and thus did not recognize the generality and preparative value of their observation.3a

The structure of our products were supported by ${}^{1}H$ and ${}^{13}C$ and in the case of (5a) and (6a) also by ${}^{15}N$ n.m.r. spectroscopy.

In the ¹⁵N n.m.r. spectrum of (**5a**) (Scheme 4) the most characteristic changes as compared with the spectrum of the parent compound (**3**) is the shift of the singlet at 283.3 p.p.m. to 205.6 p.p.m. This value is in good agreement with the shift of the *N*-oxide nitrogen in compound (**1a**) of established structure.¹ The doublet at 74.9 p.p.m. can be clearly assigned to the NH group and, further, the shift of the amino nitrogen at 67.7 p.p.m. is in good agreement with that recorded for (**1a**).

Transformation of (5a) to (6a) also involves significant changes in the ¹⁵N n.m.r. spectrum. The singlet signal appears at 281.9 p.p.m., virtually the same position as in (3), which indicates a similar chemical environment (amide oxime). At the same time the two triplets in the spectrum of (3) give way in (6a)to two doublets, as required by the presence of two NH groups in the cyclic structure.

In the ${}^{13}C$ n.m.r. spectra the shifts of C-2 have diagnostic value. Thus the signal is the only one which gives a doublet in the off-resonance spectrum and suffers an upfield shift *ca.* 10 p.p.m. on going from (**5a**) to (**6a**). This is in accordance with the

^{*} For a somewhat similar quinazoline N-oxide containing a double bond between N-1 and C-2, bond cleavage between C-2 and N-3 followed by recyclization on prolonged thermolysis was recently reported.⁷



fact that the electronegative oxygen atom is transposed from the nearby N-3 atom to a more distant nitrogen atom attached to position 4. A similar shift difference can be experienced for all pairs of compounds examined in this study. The shift of C-2 is, of course, subject to well known substituent effects (see Table 3).

Similar changes can be observed in the chemical shifts of the hydrogen atom attached to C-2.

Further characteristic differences between structures (5) and (6) can be recognized in the shifts of atoms C-4, C-4a, and C-8a (see Table 3).

The 2-alkylquinazoline 3-oxides (**5h**) and (**5i**) isomerize much slower than the 2-phenyl and 2-styryl analogues (**5a**—g) and yields are lower too. Since with Dimroth rearrangements, it is known that electron attracting substituents promote isomerization,⁹ the different electronic effects of alkyl and aryl substitution noted in our work are not surprising. Thus, compound (**5h**) can only be transformed to the oxime (**6h**) in moderate yield by prolonged (21 h) heating in butanol; also detected in the reaction mixture were starting material and compounds (**3**), (**12h**), and (**13h**) (detected both by ¹³C n.m.r. spectroscopy and preparative methods). Results with (**5i**) were similar (Scheme 5).



In (12h,i) and (13h,i), in agreement with their aromatic structure, the C-2 signal appears in the range 154-167 p.p.m. As with the 1,2-dihydro derivatives, in (13h,i) the signal of C-2 is shifted upfield by 9-10 p.p.m. as a result of the effect of the oxygen atom attached to the adjacent N-3 atom. The chemical shift of the other neighbouring atom, C-4, also decreases to a value corresponding to an N-oxide, while the shifts of the more remote atoms C-4a and C-8a change only slightly (see Table 3).



The 4-aminoquinazoline 3-oxides (13h,i) were formed, presumably during the prolonged heating by dehydrogenation of the dihydro compound (5). Oxidation of (5i) to (13i) was also possible with potassium permanganate. When compounds (5h,i) were heated in butanol in the absence of air, (13h,i) did not form. The 4-aminoquinazolines (12h,i) may have been formed by dehydration both from (5h,i) and (6h,i). Since under the conditions of the ring transformation (12h,i) could not be obtained from the cyclic oximes (6h,i), the former probably arise from the nitrones (5h,i). Considering previous proposals for the dehydration of related partially saturated cyclic nitrones 11,12 we suggest for our case the route shown in Scheme 6.

The N-oxide tautomer (5) transforms via the tautomer (14) by loss of water to the 1,4-dihydroquinazoline (15), which then gives rise to the more stable amine form (12).¹³ In the case of the acyl derivatives of (12) we have reported recently a similar tendency to aromatization.¹⁴ Under the given conditions, hydrolysis of both (5) and (6) may yield the benzamide oxime (3), the water needed being provided by the formation of (12) by dehydration.

Like the phenyl analogue (9a) compound (9h) prepared from (8) and acetaldehyde, was unchanged when heated, a result which supports our view that the transformation $(5) \rightarrow (6)$ requires a labile hydrogen at N-1 (Scheme 3).

Reaction of (3) with formaldehyde is somewhat different from that of other aldehydes. If (3) was treated in ethanol or diethyl ether with 1 mol equiv. of aqueous formaldehyde, only the 4-amino-1,2-dihydro-1-hydroxymethylquinazoline 3-oxide (16) and unchanged (3) was obtained. With 2 mol equiv. of formaldehyde the N-oxide (16) was isolated in good yield. The two-fold incorporation of formaldehyde into (3) is analogous to the reaction of o-aminobenzamide with formaldehyde, where a 1-hydroxymethyl derivative was formed too.¹⁵ Thus, the simplest representative of the quinazoline N-oxides (5), *i.e.* 4amino-1,2-dihydroquinazoline 3-oxide (5j), was prepared in moderate yield by treating (3) with paraformaldehyde in the presence of toluene-p-sulphonic acid (Scheme 7).

Since compounds (5j) and (16) decomposed when heated, they could not be subjected to isomerization experiments.

With the N-oxide (9j), readily obtainable from (8) and formaldehyde, a novel and interesting transformation is observed. In contrast to the stable 2-substituted analogues (9h,a), when heated in ethanol (9j) underwent oxidative ring transformation ('ring degenerate rearrangement') to give the quinoidal semicyclic amide oxime (17).* The structure of (17) was supported

^{*} Quinoidal 4-iminoquinazolines corresponding to (17) were described by us recently (ref. 14).



by i.r. bands at 950 and 975 cm⁻¹, characteristic for oximes, =NOH and =CH-¹H n.m.r. signals at δ 9.1 and 7.6 respectively, as well as the comparison of ¹³C n.m.r. signals [*e.g.* δ 148.4 (s, C-4) and 149.2 p.p.m. (d, C-2), (see Table 3)] with proper model compounds.

The reaction leading to (17) is basically different from the transformation $(5) \rightarrow (6)$. While in the latter the solvent plays no important role, both solvent and the presence of air are decisive factors in the former. The reaction fails to take place in toluene or xylene and, when air is excluded, not even in alcohols. This encourages the suggestion that this reaction is related to addition-elimination type Dimroth rearrangements⁴ proceeding with the participation of the alcohol and described earlier for similar compounds.^{5,6} This mechanistic proposal, involving rotation of the open-chain intermediate (18) and oxidation of the recyclized intermediate (19) is shown in Scheme 7.

Compound (19) was only tentatively assigned as the intermediate undergoing oxidation, but since the reaction $(5h,i) \rightarrow$ (13h,i) takes place under similar conditions, it is probable that dehydrogenation occurs after recyclization.

Conclusion.—In view of results presented here and earlier,¹ reaction of aldehydes with β -amino carboxamide oximes involves, as the primary product, 4-amino-1,2-dihydropyrimidine 3-oxides, which then readily undergo thermal or thermal-solvolytic ring transformations to give cyclic amide oxime derivatives (2), (6), and (17).

Experimental

(12 pp.)].* Evaporations were carried out under reduced pressure; m.p.s are not corrected.

General Method for the Preparation of 2-Substituted 4-Amino-1,2-dihydroquinazoline 3-Oxides (5a-i).—(a) To a solution of 2-aminobenzamide oxime (3)¹⁶ (3.03 g, 20 mmol) in ethanol (15 ml) the aldehyde (4) (21 mmol) was added with stirring and cooling at 15 °C during 0.5 min. After being stirred for 30 min the mixture was diluted with diethyl ether (20 ml), stirred for a further 30 min, and then set aside in the refrigerator. Next day the yellow crystalline product was filtered off and washed with ethanol and ether. If necessary it was recrystallized from ethanol with brief heating.

(b) The aldehyde (4) (10 mmol) was added dropwise with stirring, and with the temperature being kept below $15 \,^{\circ}$ C with cooling, to finely powdered (3) (1.51 g, 10 mmol). After 2 h, the product was triturated with diethyl ether, set aside for 24 h in the refrigerator, and then filtered off, and washed with diethyl ether. If necessary it was recrystallized with brief heating from methanol or ethyl acetate.

(c) Compound (5a) was prepared by adding hydroxylamine hydrochloride (1.4 g, 20 mmol) to a solution of sodium (0.46 g, 0.02 mol) in ethanol (40 ml). After 2 h sodium chloride was filtered off and the solution added to a solution of (11) (2.06 g, 10 mmol) in ethanol (40 ml). After 3 days the solution was evaporated under 25 °C and the residue washed with water and recrystallized from methanol to give (5a) (2.1 g, 88%).

Elemental analyses, and i.r., ¹H n.m.r., and ¹³C n.m.r. data have been treated as a Supplementary publication [SUP. No. 56640

^{*} For details of the Supplementary Publications Scheme, see Instruction for Authors (1986), J. Chem. Soc., Perkin Trans. 1, 1986, Issue 1.

Table 1. Yields, methods, and m.p.s of the quinazolines (5).

	Yield		M.p.
Compd.	(%)	Method	(°C)
(5a)	88	а	192 <i>ª</i>
(5a)	77	b	192 <i>ª</i>
(5b)	73	а	196
(5 c)	92	а	118
(5 c)	37	b	118
(5d)	96	а	191 ^{<i>b</i>}
(5e)	67	а	182°
(5f)	65	а	213 ^d
(5g)	69	b	138
(5h)	52	а	198
(5 i)	61	a	196°
^a Lit., ^{3a} 192 °C. ^b Lit., ^{3a}	' 191 °C. ' Li	t ^{3a} 187 °C. ^d L	it ^{3a} 220 °C. ^e Lit ³
215 °C.			, ,

Methods for the preparation of (5a--i), yields, and m.p.s are shown in Table 1.

4-Amino-1,2-dihydroquinazoline 3-Oxide (5j).--To a solution of (3) (3.02 g, 20 mmol) in diethyl ether (100 ml) toluene-psulphonic acid (0.17 g, 1 mmol) and paraformaldehyde (0.6 g, 20 mmol) was added with stirring at 20 °C. After being stirred for 6 h the mixture was left for 1 day, and then the product, a mixture of (3) and (5j), was filtered off and chromatographed on a column of silica gel with methanol to give (3) (0.6 g) and (5j); the latter was crystallized by trituration with ether and then recrystallized from methanol (0.85 g, 26%), m.p. 154 °C.

4-Amino-1,2-dihydro-1-hydroxymethylenequinazoline 3-Oxide (16).-30% Aqueous formaldehyde (4.0 g, 40 mmol) was added to a solution of (3) (3.02 g, 20 mmol) in diethyl ether (60 ml). An oil was precipitated which crystallized on the addition of ethanol (5 ml); yield 3.1 g (80%), m.p. 152-153 °C (from ethanol--ethyl acetate).

1,2-Dihydro-2-phenyl-4(3H)-quinazolone Oxime (6a).--(a) A solution of (5a) (2.4 g, 10 mmol) in toluene (25 ml) was heated in a sealed vessel in an oil-bath of 140 °C for 4 h; the yellow colour of the solution faded gradually. 70% Of the solvent was evaporated off after which the mixture was kept in a refrigerator for 1 day. The product was filtered off and crystallized from ethanol to give (6a) (2.1 g, 87%), m.p. 181 °C. Reaction carried out in butanol or xylene at 140 °C for 4 h, or in ethanol at 95 °C for 10 h gave similar results.

(b) Compound (5a) (0.48 g, 2 mmol) was heated in a sealed tube at 195 °C for 2 min and the product crystallized from ethanol to give (**6a**) (0.31 g, 64%).

(c) Benzaldehyde (1.06 g, 10 mmol) was added with stirring to a solution of (3) (1.51 g, 10 mmol) in ethanol (10 ml) at 15 $^{\circ}$ C. After 10 min the mixture was stirred and heated, with the exclusion of air, for 10 h at 95 °C; it was then stored in a refrigerator for 2 days to give (6a) (2.0 g, 84%).

(d) To a solution of sodium (0.46 g, 0.02 mol) in ethanol (40 ml) finely powdered hydroxylamine hydrochloride (1.4 g, 10 mmol) was added. After the mixture had been stirred for 1 h, sodium chloride was filtered off and compound (11) (2.06 g, 10 mmol) and ethanol (40 ml) were added; the mixture was then kept in a sealed tube at 80 °C for 12 h. Evaporation, treatment with water, and crystallization of the residue from ethanol gave (6a) (1.95 g, 82%).

General Method for the Preparation of 2-Aryl- and 2-Styryl-4-amino-1,2-dihydro-4(3H)-quinazolone Oximes (6b-g).

Table 2. Times of isomerizatio	ns in toluene at 140 °	C, yields, m.p.s, and
recrystallization solvents (r.s.)	of the quinazolines	(6 bg)

Compd.	Time (h)	Yield (%)	М.р. (°С)	R .s.
(6b)	8	73	79	Hexane
(6c)	1	78	203 ª	MeOH
(6d)	6	64	69	Hexane
(6e)	4	71	208	EtOH
(6f)	16	80	169	EtOAc
(6 g)	1	72	160 <i>*</i>	MeOH-hexane (1:1)
^a Lit., ^{3a} 206—	-207 °C. ^b L	it., ^{3a} 166-	—168 °C.	

Method (a) (see above) proved to be the best. For details see Table 2.

5,6-Dihydro-3,5-diphenyl-3H-1,2,4-oxadiazolo[4,3-c]quinazoline (7a).-Compound (6a) (2.39 g, 10 mmol) and benzaldehyde (1.06 g, 10 mmol) were heated in ethanol (40 ml) in a sealed tube at 95 °C for 5 h. The product was separated and crystallized from methanol to give (7a) (2.1 g, 64%), m.p. 193-195 °C.

4-Amino-1-benzyl-1,2-dihydro-2-phenylquinazoline 3-Oxide (9a).—Compound (8)¹⁷ (2.41 g, 10 mmol) and benzaldehyde (1.06 g, 10 mmol) were heated in ethanol (20 ml) in a sealed flask at 95 °C for 4 h. After evaporation the residue, a red oil, slowly crystallized under diethyl ether (30 ml) to give (9a) (2.20 g, 67%). m.p. 181-183 °C (from methanol).

4-Amino-1-benzyl-1,2-dihydro-2-methylquinazoline 3-Oxide (9h).—Compound (8) (2.41 g, 10 mmol)¹⁷ and acetaldehyde (0.44 g, 20 mmol) were kept at 20 °C in ethanol (20 ml) for 2 days. On dilution with diethyl ether (80 ml) and cooling (9h) was precipitated after 1 day. The product was filtered off and crystallized from acetone-methanol (1:1) to give (8) (2.52 g, 94%), m.p. 203-205 °C.

4-Amino-1-benzyl-1,2-dihydroguinazoline 3-Oxide (9j).--A mixture of (8) 2.41 g, 10 mmol),¹⁷ 30% formaldehyde (1.2 g, 12 ml) and ethanol (20 ml) were kept at 22 °C for 1 day. Evaporation of the mixture and crystallization of the residue afforded (9j) (2.1 g, 83%), m.p. 174-177 °C (decomp.).

2-Benzylideneaminobenzonitrile (11).--A solution of 2aminobenzonitrile (5.90 g, 50 mmol), benzaldehyde (5.30 g, 50 mmol), and 6 drops of pyridine in ethanol (100 ml) were boiled for 8 h. Evaporation and crystallization from ethanol gave (11) (8.6 g, 83%), m.p. 112-114 °C.

Thermolysis of (5h) in Butanol: Formation of 1,2-Dihydro-2methyl-4(3H)-quinazolone Oxime (6h), 4-Amino-2-methylquinazoline (12h), 4-Amino-2-methylquinazoline 3-Oxide (13h) and (3).—A solution of (5h) (1.77 g, 10 mmol) in butanol (25 ml) was stirred in an oil-bath of 140 °C for 21 h. Evaporation of the reaction mixture and trituration of the residue with ether (50 ml) afforded some (5h) and (13h) (0.21 g, 12%), m.p. 272-275 °C (lit.,¹⁶ m.p. 280 °C) identified by comparison with a sample prepared according to the literature (t.l.c., i.r. and ¹³C n.m.r.). Evaporation of the mother liquor and chromatography of the residue on silica gel (eluant chloroform-acetone, 1:1) gave (12h) (0.16 g, 10%), m.p. 224-225 °C (lit.,¹⁸ m.p. 228-229 °C, lit.,¹⁴ m.p. 225-227 °C), (3) 0.12 g (7.5%) and (6h) 0.7 g (39.5%), m.p. 56-59 °C (from hexane).

Thermolysis of (5i) in Butanol: Formation of 1,2-Dihydro-2propyl-4(3H)-quinazolone Oxime (6i), 4-Amino-2-propylquinazoline 3-Oxide (13i), and (3).—Treatment of (5i) (1.0 g, 5 mmol) in butanol (15 ml) as described for (5h) gave, on similar workup, some unchanged (5i), (13i) (0.08 g, 8%), (12i) (0.2 g, 20%), m.p. 212—213 °C (lit.,¹⁴ m.p. 214—216 °C), (3) (0.12 g, 12%), and (6i) (0.53 g, 53%), m.p. 130—133 °C (from ethanol).

Preparation of (13i) from (6i).—2% Aqueous potassium permanganate solution (30 ml, 3.8 mmol) was added dropwise at 20 °C to a suspension of (6i) (1.0 g, 5 mmol) in chloroform (80 ml). After being stirred for 1 h the mixture was filtered and extracted with chloroform. Evaporation gave (13i) (0.82 g, 82%), m.p. 192 °C (from ethyl acetate).

1-Benzyl-4(1H)-quinazolone Oxime (17).—A solution of (9j) (0.5 g, 2 mmol) in propanol (15 ml) was boiled for 9 h. Evaporation, crystallization of the residue from ethanol, and drying of the crystals at 110 °C gave (17) (0.41 g, 82%), m.p. 157—159 °C. Boiling (9j) in ethanol for 16 h gave a similar result. When air was excluded no change was observed in either solvent. When boiled in toluene or xylene (9j) was recovered unchanged.

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