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The Alkylamination of Naphthazarin*

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ABSTRACT

*The alkylamination of naphthazarin (**1**) was investigated. TLC of the reaction product of **1** with* n*-butylamine under refluxing conditions showed the presence of at least 16 coloured spots. 2-Butylaminonaphthazarin (**2**) and leuco-5-butylamino-8-hydroxynaphthoquinone (**3**) in trace amounts and 4,8-bis(butylamino)-1,5-naphthoquinone (**4**, 9·9%) and 3,5-bis(butylamino)-8-hydroxynaphthoquinone (**5**, 25·6%) were isolated. The alkylamination largely depends on the reaction temperature and the molar ratio of the amine. At low temperature (0°C), **2** was obtained in 73·7% yield and the optimum conditions were using a 10–15 molar ratio of amine with respect to **1**. The reactivity of **2** with amines depends on the reaction temperature. Compound **5** was obtained in 82·3% yield by the reaction of **2** with the amine under refluxing conditions. A novel leuco-compound of **5** was synthesized and its structure was shown to be 3,5-bis(butylamino)-6,7-dihydro-1-hydroxy-naphthalene-4,8-dione. The amination mechanism is also discussed.*

1 INTRODUCTION

α-Aminosubstituted quinones from quinizarin[1] and naphthazarin[2] are currently produced by reaction with amines in the presence of reducing agents. Reduced species, leuco-compounds of the starting quinones, formed *in situ* have been believed to be key intermediates in the reactions, giving amino-substituted products in the reduced form. The materials obtained are reoxidized without isolation, usually by atmospheric oxygen in the presence of piperidine.

* Part IV in a series, 'Novel human hair dyes'.

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Whilst extensive work has been carried out on synthesis of amino-naphthoquinones,[3-9] studies on the reduced forms have received little attention, presumably because the leuco-compounds have long been regarded as unstable compounds.

We have recently found that leuco-naphthazarin is relatively stable even in an aerated solution and it dyes wool fibres[10] and human hair[11] effectively at room temperature from an aqueous solution under very mild conditions without any reducing agents and strong alkali in the dyebath. The colour development can be achieved without any oxidation.

Leuco-naphthazarin derivatives are thus expected to be potential dyestuffs for keratin fibres. From the viewpoint of colour variety and dyeability, substituted naphthoquinones and their leuco-derivatives are promising compounds. The stabilities of the substituted leuco-compounds are also important factors in designing the dyeing system.

We have reported the synthesis and structure determination of leuco-monoaminonaphthoquinone derivatives.[12,13]

Matsuoka *et al.* have reported that the reaction of naphthazarin with butylamine afforded many aminated compounds in quite low yield.[14] Klein[2] and Matsuoka *et al.*[15] have also reported that the reaction of leuco-naphthazarin with alkylamines gave 5,8-bis(alkylamino)-1,4-naphthoquinones. However, Bloom & Deduk have obtained the unsymmetrical 4,8-bis(alkylamino)-1,5-naphthoquinones in the same reaction.[16] These reactions of naphthazarin and its leuco-compound with amine are thus ambiguous.

Synthesis of the derivatives and the isolation of the leuco-compounds is very important in order to develop potential dyestuffs for keratin fibres. Attention should also be focused on structure determination of the leuco-compounds, since they exist in isomeric forms.[17-21]

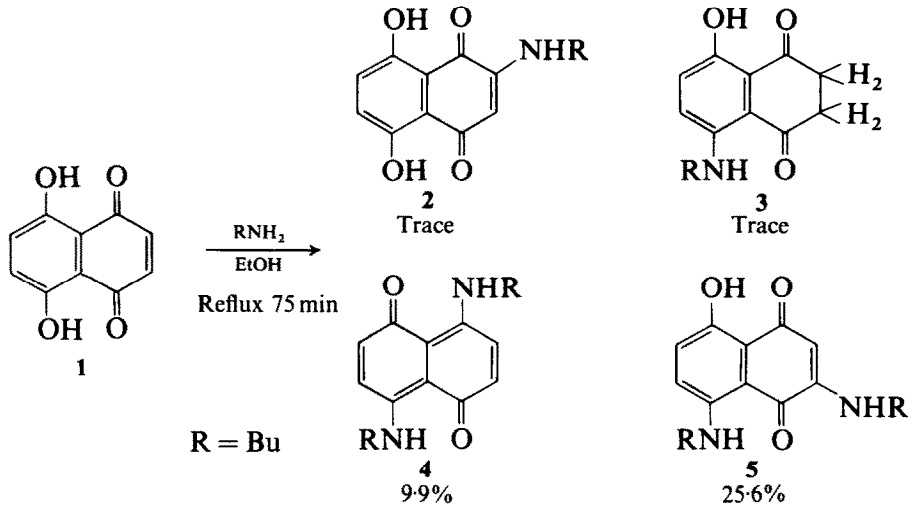
In this paper we report on studies on the alkylamination of naphthazarin.

2 RESULTS AND DISCUSSION

The reaction of naphthazarin (**1**) with *n*-butylamine was investigated. When **1** was reacted with an excess of *n*-butylamine in refluxing ethanol for 75 min, the product showed at least 16 coloured spots on TLC. The starting material was fully converted and four components, orange (**2**) and yellow (**3**) in trace amounts, and blue (**4**) and violet (**5**) in low yields, were isolated by careful column chromatography and PLC (Scheme 1).

The orange component **2** and yellow component **3** were shown to be 2-butylaminonaphthazarin and leuco-5-butylamino-8-hydroxynaphthoquinone, respectively, in comparison with authentic samples.[12]

The ^{1}H-NMR of the blue component **4** showed two amino protons at



Scheme 1

12·99 ppm, two types of aromatic protons as doublets at 7·25 and 7·03 ppm and two butyl protons. The structure of **4** was thus shown to be 4,8-bis(butylamino)-1,5-naphthoquinone, also supported by elemental analysis and the mass spectrum.

The ^{1}H-NMR spectrum of the violet component **5** showed two amino protons at 9·96 ppm, two types of aromatic protons as two doublets at 6·99 ($J = 9{\cdot}8$ Hz) and 7·17 ($J = 9{\cdot}8$ Hz) ppm, one hydroxyl proton at 14·58 ppm, one olefinic proton as a singlet at 5·64 ppm, and two types of butyl protons. The structure was thus concluded to be 2 (or 3),5-bis(butylamino)-8-hydroxynaphthoquinone, and this was also supported by elemental analysis and its mass spectrum. Compound (**5**) was also reported by Matsuoka *et al.*, but the positions of the butylamino groups have not been elucidated.[15,22] The positions of the butylamino groups were determined unequivocally to be 3 and 5 by the presence of $^3J_{C-9,10}H_{2,3}$ in the ^{13}C-NMR spectra. The structure determination of the components **4**, **5** will be discussed later.

At lower reaction temperatures (such as 0°C) 2-butylaminonaphthazarin (**2**) was obtained in relatively high yield (73·7%). An excess of amine was used to increase the solubility of naphthazarin in ethanol. The influence of the molar ratio of *n*-butylamine to **1** is summarized in Table 1.

The best conditions for the synthesis of the orange component 2-butylaminonaphthazarin (**2**) was with a 10–15 molar ratio of amine with respect to **1**.

The temperature dependence of the amination of 2-butylaminonaphthazarin (**2**) was also examined and is summarized in Table 2. When 2-butylaminonaphthazarin (**2**) was treated with *n*-butylamine in ethanol, only compound **5** was obtained.

TABLE 1
Effect of Molar Ratio of Butylamine on the 2-Butylamination of Naphthazarin (**1**)

Run	*Molar ratio* $[BuNH_2]/[1]$	*Temp* (°C)	*Time* (*h*)	*Yield* (%)[a]	
				2	**1**
1	5	0	4	67·1	Trace
2	10	0	4	73·7	1·7
3	15	0	4	73·0	6·0
4	25	0	4	56·6	9·0

Reaction conditions: [**1**] = 10 mmol, EtOH 40 ml.
[a] Yield isolated by column chromatography and PLC.

The reaction did not proceed at all below room temperature and **2** was almost fully recovered at room temperature (runs 1 and 2). Although it has been reported that the reaction of **2** with *n*-butylamine did not proceed at all,[22] the reaction gave the diaminated compound **5** above 52–55°C, this arising by replacement of a hydroxyl group by an amino group. In refluxing conditions for 2h, the reaction proceeded easily and the diaminated component **5** was obtained in 82·9% yield with recovery of the starting material **2** in 3·8% yield (run 4).

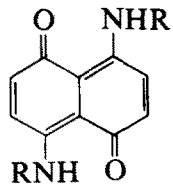
The alkylamination of leuco-naphthazarin (**6**) was also examined. Klein has reported that leuco-naphthazarin (**6**) reacts with alkylamine to give 5,8-bis(alkylamino)naphthoquinone (**4b**), followed by oxidation.[2] Bloom & Deduk have reported that 4,8-bis(alkylamino)-1,5-naphthoquinone (**4a**) is the only isolable component in this reaction.[16]

Matsuoka *et al.* have reported that leuco-naphthazarin, formed *in situ*, reacts with *n*-butylamine to give 5,8-bis(butylamino)naphthoquinone (**4b**, R = Bu).[15]

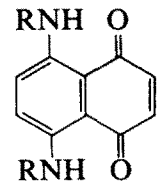
TABLE 2
Temperature Dependence of the Amination of 2-Butylaminonaphthazarin (**2**)

Run	*Temp.* (°C)	*Time* (*h*)	*Yield* (%)[a]	
			5	**2**
1	0	4	0	99·2
2	23–25	4	0	94·7
3	52–55	4	13·0	79·3
4	Reflux	2	82·9	3·8

Reaction conditions [**2**] = 1 mmol, $[BuNH_2]/[2]$ = 20, EtOH 8 ml.
[a] Yield isolated by column chromatography and PLC.



4a

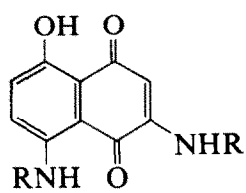


4b

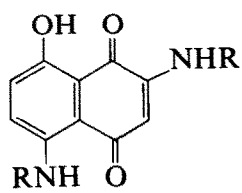
We have reinvestigated the reaction of leuco-naphthazarin (**6**) with *n*-butylamine. A mixture of **6** and *n*-butylamine in ethanol was stirred under reflux conditions under argon. By flash column chromatography and PLC, a yellow component having λ_{max} at 466 nm with yellow fluorescence and a blue component having λ_{max} 606 nm and 660 nm were obtained as isolable compounds. The yellow component (6·6% yield) was leuco-5-butylamino-8-hydroxynaphthoquinone (**3**), whose structure has been already elucidated as 5-butylamino-2,3-dihydro-8-hydroxynaphthalene-1,4-dione.[12] The blue component (12·0% yield) was found to be 4,8-bis(butylamino)-1,5-naphthoquinone (**4a**, R = Bu) in accord with Bloom's report.[16] Its ^{1}H-NMR pattern [two types of aromatic protons as doublets at 7·25 ppm (J = 10·4 Hz) and 7·03 ppm (J = 9·8 Hz)] was the same as that of the blue component obtained in the reaction of naphthazarin with *n*-butylamine under refluxing conditions.

If this component was 5,8-bis(butylamino)naphthoquinone (**4b**, R = Bu), its ^{1}H-NMR data should give two aromatic protons and two olefinic protons as singlets respectively.

The structure of the violet component **5** is either **5a** or **5b** by ^{1}H-NMR, mass spectroscopy and elemental analysis.



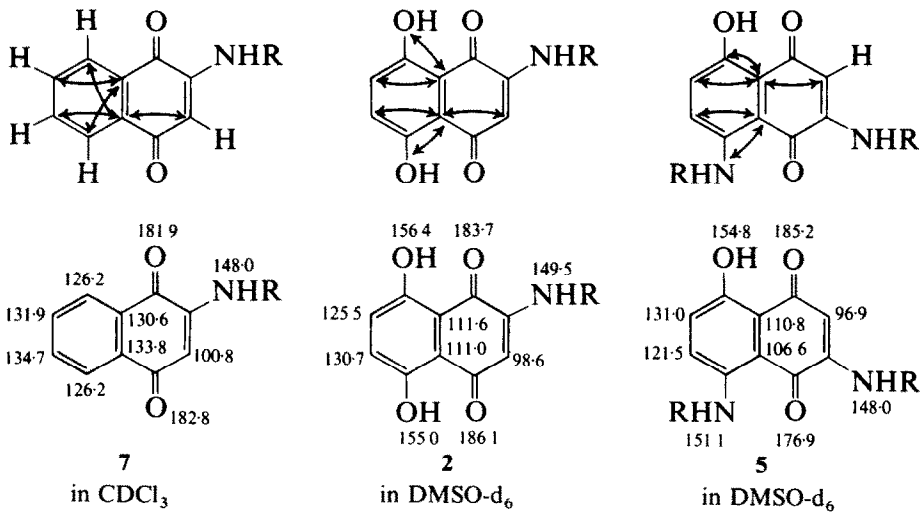
5a



5b

The structure was determined by the observation of ^{13}C, ^{1}H long-range coupling and each carbon was assigned.

Although the assignment of carbons of 2-morpholinonaphthoquinone has been reported by Höfle,[23] inner carbons (C-9,10) could not be assigned. A definite assignment of the inner carbons would be most important in elucidating the position (C-2,3) of the butylamino group by the observation of $^3J_{\text{C-2 (or 3), H-9 (or 10)}}$. We have attempted the assignment of carbons in 2-butylaminonaphthoquinone (7) by ^{1}H, ^{13}C-NMR and LSPD (long-range selective proton decoupling). As a result, the assignment of the inner carbons



7 in $CDCl_3$ **2** in DMSO-d_6 **5** in DMSO-d_6

Fig. 1. The ^{13}C, ^{1}H coupling patterns of naphthoquinones **2**, **5** and **7** and their assignments.

was achieved by observation of $^{3}J_{C\text{-}9,H\text{-}7}$, $^{3}J_{C\text{-}9,H\text{-}5}$ for C-9 and $^{3}J_{C\text{-}10,H\text{-}6}$, $^{3}J_{C\text{-}10,H\text{-}8}$, $^{3}J_{C\text{-}10,H\text{-}3}$ for C-10.

^{13}C, ^{1}H coupling patterns of naphthoquinones (**2**, **5**, **7**) and their assignments of carbons are shown in Fig. 1.

Accordingly, in 2-butylaminonaphthazarin **2**, the coupling observed to these inner carbons include $^{3}J_{C\text{-}9,8\text{-}OH}$, $^{3}J_{C\text{-}9,H\text{-}7}$ for C-9 and $^{3}J_{C\text{-}10,H\text{-}6}$, $^{3}J_{C\text{-}10,H\text{-}3}$ for C-10. The inner carbons were definitely assigned by the LSPD of the olefinic proton at C-3. The assignment of the violet component **5** is as follows. The assignment of carbons (C-5, 6, 7, 8, 9, 10) was readily achieved. The inner carbons include $^{3}J_{C\text{-}9,H\text{-}7}$, $^{3}J_{C\text{-}9,8\text{-}OH}$, $^{3}J_{C\text{-}10,H\text{-}6}$, $^{3}J_{C\text{-}10,5\text{-}NH}$, and $^{3}J_{C\text{-}9\,(or\ 10),H\text{-}2\,(or\ 3)}$. LSPD of the olefinic proton at C-2 (or 3) induced the decoupled signal pattern only on the C-9, while the C-10 was not affected at all as shown in Fig. 2. Therefore the positions of the butylamino groups are 3 and 5.

The alkylamination of leuco-2-butylaminonaphthazarin (**8**) was also examined. The structure of **8** has been shown to be 6-butylamino-2,3-dihydro-5,8-dihydroxynaphthalene-1,4-dione.[12] The reaction of **8** with *n*-butylamine at 0°C for 4 h gave 3,5-bis(butylamino)-8-hydroxynaphthoquinone (**5**, 24·0% yield) as diaminated compound and 2-butylaminonaphthazarin (**2**, 12·2% yield) as parent quinone. With refluxing conditions for 2 h, compound **5** was obtained as the only isolable component in 51·7% yield.

The structures of the leuco-compounds of the bis(alkylamino)naphthoquinones (**4**, **5**) were examined. The structure of the leuco-compound of 4,8-bis(alkylamino)-1,5-naphthoquinone has already been elucidated by Bloom

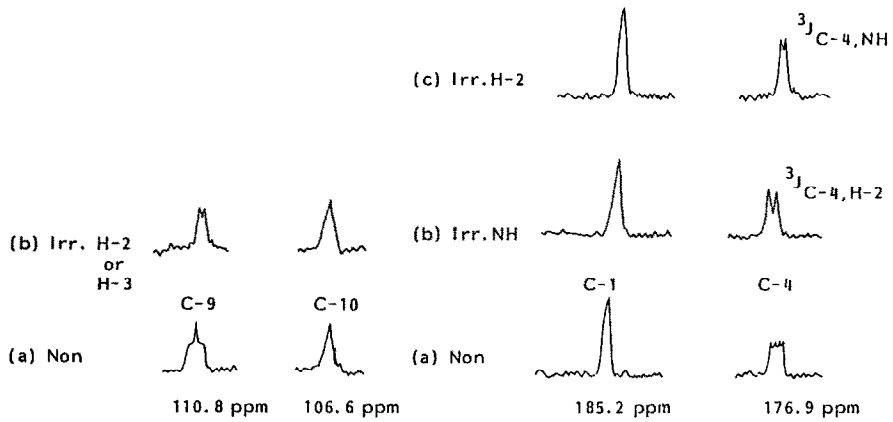
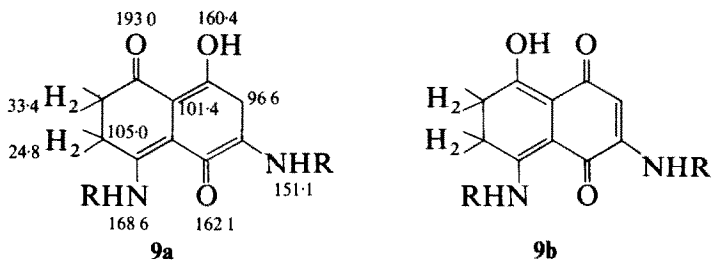


Fig. 2. The $^{13}C,^1H$ coupling pattern of compound **5**. Non, non-decoupling; Irr, irradiation.

& Deduk.[16] Reduction of 3,5-bis(butylamino)-8-hydroxynaphthoquinone (**5**) with sodium dithionite and sodium carbonate in 50% ethanol solution was carried out under argon. The leuco-compound (**9**) was carefully isolated by preparative TLC in 31·9% yield. Its ^{1}H-NMR spectrum had one hydroxyl proton at 13·85 ppm, two types of amino protons at 15·10 and 6·10 ppm, respectively, one aromatic proton at 5·95 ppm as a singlet, and two types of methylene protons at 2·97 and 2·74 ppm as triplets, respectively. The structure was considered to be either **9a** or **9b**.

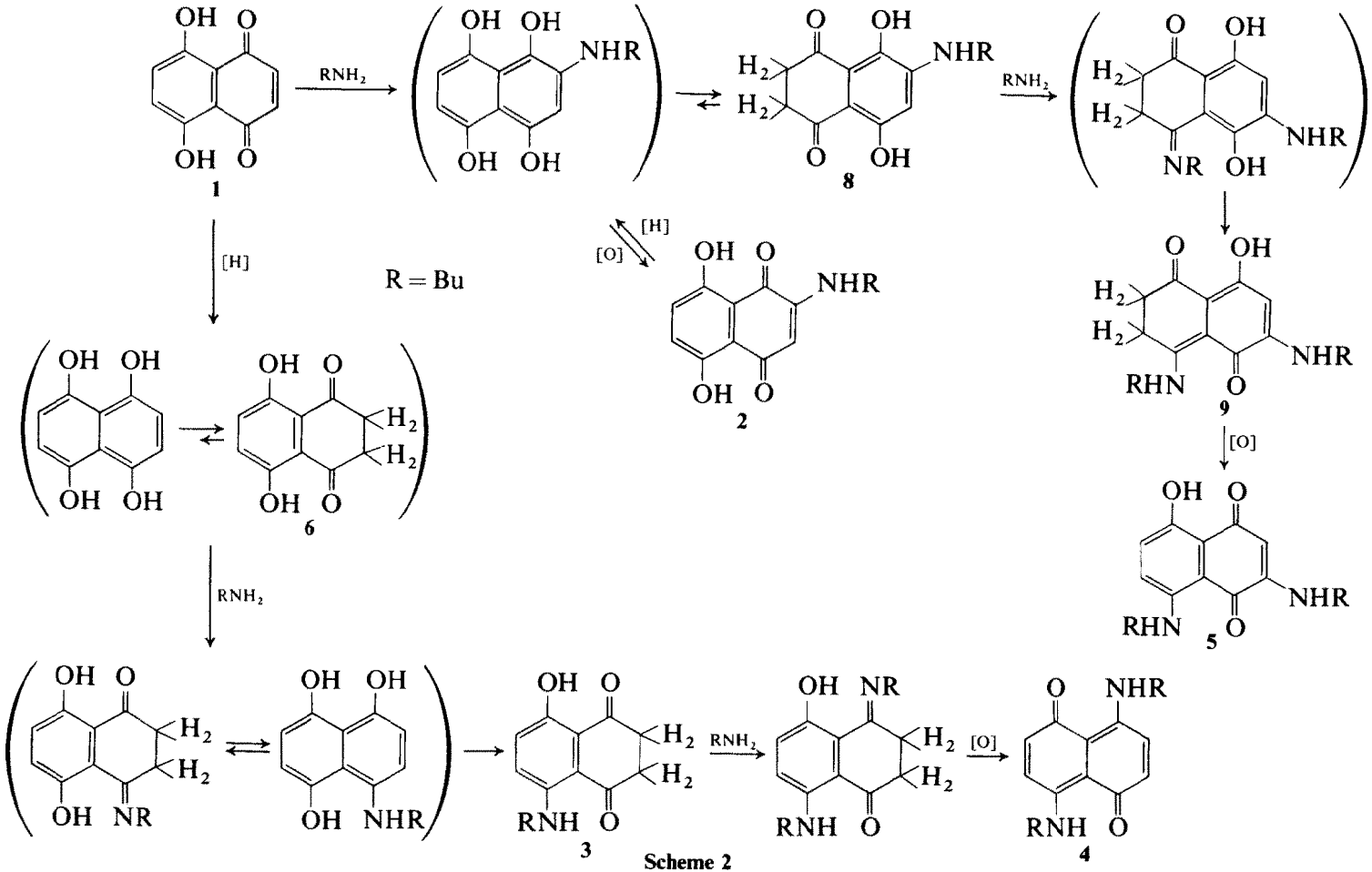


9a **9b**

The ^{13}C-NMR spectrum definitely showed the existence of one carbonyl carbon at 193·0 ppm adjacent to a methylene group and each carbon was assigned successfully by LSPD. Thus the structure of the leuco-compound **9** was shown to be 3,5-bis(butylamino)-6,7-dihydro-1-hydroxynaphthalene-4,8-dione (**9a**). This leuco-derivative is new and is a relatively stable yellow compound in aerated solution with yellow fluorescence.

Although the amination mechanism is still ambiguous, it could be summarized as shown in Scheme 2.

At low temperatures the butylamination of naphthazarin (**1**) affords 2-butylaminonaphthazarin (**2**) via 1,4-addition and oxidation. However, under refluxing conditions **2** is presumably reduced to the unstable leuco-compound, tetrahydroxynaphthalene, which is easily isomerized to the



Scheme 2

stable diketo form **8** which reacts with amine to give 3,5-bis(butylamino)-8-hydroxynaphthoquinone (**5**) via 1,2-addition and oxidation. These conclusions are supported by the facts that (a) the aminations of **2** and its leuco-compound **8** afforded **5** and that (b) the leuco-compound **9** was oxidized to the parent quinone, **5**.

At low temperature naphthazarin **1**, is not reduced to leuco-naphthazarin **6**, but under refluxing conditions **1** is easily reduced and **6** reacts with amine to give leuco-5-butylamino-8-hydroxynaphthalene-1,4-dione (**3**) via 1,2-addition. The 4,8-bis(butylamino)-1,5-naphthoquinone **4** is obtained by reaction of **3** with amine via 1,4-addition and subsequent oxidation.

The 1,4-addition of a nucleophile such as an amine with naphthoquinone is well known and 1,2-addition for leuco-compounds is most probable, since the carbonyl groups have the character of an aliphatic ketone in leuco-naphthazarin, which has a 2,3-dihydro-5,8-dihydroxynaphthalene-1,4-dione structure. Leuco-quinizarin (2,3-dihydro-9,10-dihydroxyanthracene-1,4-dione) is known to undergo similar 1,2-addition of a nucleophile in the carbonyl group.[24]

3 EXPERIMENTAL

3.1 General

^{1}H, ^{13}C-NMR spectra were recorded on a JEOL JNM-GX 400 FT NMR spectrometer using TMS as internal standard. The assignment of each carbon was achieved by the observation of $^{13}C,^{1}H$ long-range selective proton decoupling (LSPD). GC–Mass spectra were measured on a Hitachi RMU-6M spectrometer using a ZT column. Glass plates coated with 2-mm silica gel (Merck 5745) were used for PLC. Column chromatography was carried out on silica gel (Wako C-300) using benzene or chloroform as eluent.

3.2 Reaction of naphthazarin (1) with *n*-butylamine

A mixture of naphthazarin (**1**, 10 mmol) and *n*-butylamine (20 mmol) in ethanol (40 ml) was stirred under reflux for 75 min. The reaction mixture was poured into an aqueous hydrochloric acid and the product was filtered, washed with water, and dried *in vacuo*. TLC of the product showed at least 16 coloured spots. A trace of 2-butylaminonaphthazarin (2) and leuco-5-butylamino-8-hydroxynaphthoquinone (3) as orange and yellow components respectively, 4,8-bis(butylamino)-1,5-naphthoquinone (**4**, 9·9% yield) as blue component and 3,5-bis(butylamino)-8-hydroxynaphthoquinone (**5**, 25·6% yield) as violet component were isolated by column chromatography

and PLC on silica gel using chloroform as eluent. 2-Butylaminonaphthazarin (**2**) and leuco-5-butylamino-8-hydroxynaphthoquinone (**3**) were identified by comparison with authentic samples.[12] Other compounds could not be isolated.

Compound ***4***
M.p. 102·5–103·0°C
UV: λ_{max} (benzene) 660 nm (ε 26 250), 606 nm (ε 12 360).
Mass spectrum: M^+ 300 ($C_{18}H_{24}O_2N_2 = 300{\cdot}399\,8$).
Elemental analysis: Found: C, 71·9; H, 8·1; N, 9·3. Calcd: C, 72·0; H, 8·05; N, 9·3%.

^{1}H-NMR ($CDCl_3$): 12·99 (2H, NH, bro.), 7·25 [2H, arom., d (J = 10·4 Hz)], 7·03 [2H, arom., d (J = 9·8 Hz)], 3·54 (4H, $NHCH_2 \times 2$, q), 1·75 (4H, $NHCH_2CH_2 \times 2$, m), 1·51 (4H, $CH_2CH_3 \times 2$, m), 0·98 (6H, $CH_3 \times 2$, t).

Compound ***5***
M.p. 77·0–78·0°C
UV: λ_{max} (benzene) 600 nm (ε 11 060), 557 nm (ε 11 970), 525 nm (ε 7650), 492 nm (ε 5280).
Mass spectrum: M^+ 316 ($C_{18}H_{24}O_3N_2 = 316{\cdot}3992$).
Elemental analysis: Found: C, 68·4; H, 7·7; N, 8·8. Calcd: C, 68·3; H, 7·65; N, 8·85%.

^{1}H-NMR ($CDCl_3$): 14·58 (1H, OH, s), 9·96 (1H, NH, bro.), 7·17 [1H, arom., d (J = 9·8 Hz)], 6·99 [1H, arom., d (J = 9·8 Hz)], 6·29 (1H, NH, bro.), 5·64 (1H, H-2, s), 3·37 (2H, $NHCH_2$, q), 3·19 (2H, $NHCH_2$, q), 1·69 (4H, $NHCH_2CH_2 \times 2$, m), 1·47 (4H, $CH_2CH_3 \times 2$, m), 0·98 (6H, CH_3, q).

3.3 Amination of 2-butylaminonaphthazarin (2)

Reaction of 2-butylaminonaphthazarin (**2**, 1 mmol) with *n*-butylamine (20 mmol) in ethanol (8 ml) gave 3,5-bis(butylamino)-8-hydroxynaphthoquinone (**5**, 82·9% yield) after refluxing for 2 h, followed by column chromatography. The starting material (**2**) was recovered in 3·8% yield.

3.4 Reaction of leuco-2-butylaminonaphthazarin (8) with *n*-butylamine

Leuco-2-butylaminonaphthazarin (**8**) was obtained as previously reported.[12] A mixture of leuco-2-butylaminonaphthazarin (**8**, 1 mmol) and *n*-butylamine (20 mmol) in ethanol (8 ml) was stirred under reflux for 2 h. The reaction mixture was poured into aqueous hydrochloric acid and extracted with benzene. All starting material had reacted. The crude product was

purified by column chromatography on silica gel using benzene as eluent to give 3,5-bis(butylamino)-8-hydroxynaphthoquinone (**5**) in 51·7% yield as the only isolable component. At lower reaction temperature, such as 0°C for 4 h, all starting material was also converted and 3,5-bis(butylamino)-8-hydroxynaphthoquinone (**5**) in 24·0% yield and the parent quinone, 2-butylaminonaphthazarin (2) in 12·2% yield, were obtained as isolable components by column chromatography.

3.5 Reaction of leuco-naphthazarin (6) with *n*-butylamine

A mixture of leuco-naphthazarin (**6**, 5 mmol) and *n*-butylamine (2 ml) in ethanol (60 ml) was stirred under reflux for 2 h under argon. The mixture was dried *in vacuo* and purified by flash column chromatography and PLC on silica gel using benzene as eluent to give leuco-5-butylamino-8-hydroxy-naphthoquinone (**3**) in 6·5% yield and 4,8-bis(butylamino)-1,5-naphtho-quinone (**5**) in 12·0% yield as isolable components.

3.6 Reduction of 3,5-bis(butylamino)-8-hydroxynaphthoquinone (5)

A mixture of 3,5-bis(butylamino)-8-hydroxynaphthoquinone (**5**, 1·11 mmol), sodium carbonate (2·34 mmol), and sodium dithionite (6·39 mmol) in 50% ethanol solution (40 ml) was stirred at 80°C for 400 min under argon. The reaction mixture was evaporated until some crystals appeared and was then filtered and the product washed with water and dried *in vacuo*. All procedures were carried out under argon. The leuco-compound was isolated by PLC on silica gel using chloroform as eluent. The leuco-compound (**9**) was obtained in 31·9% yield; it had a yellow fluorescence and was susceptible to oxidation on the silica gel plate to give violet 3,5-bis(butylamino)-8-hydroxynaphthoquinone (**5**) as the parent quinone.

*Compound **9***
M.p. 119·3–121·0°C.
UV: λ_{max} (benzene) 474 nm (ε 8860), 454 nm (ε 8810), 376 nm (ε 9460), 338 nm (ε 5600).
Mass spectrum: M^+ 316 ($C_{18}H_{26}O_3N_2 = 318{\cdot}415$).
Elemental analysis: Found: C, 68·3; H, 8·2; N, 8·8. Calcd: C, 68·3; H, 8·2; N, 8·8%.

^{1}H-NMR ($CDCl_3$): 15·10 (1H, NH, bro.), 13·85 (1H, OH, s), 6·10 (1H, NH, bro.), 5·95 (1H, arom., s), 2·97 (2H, CH_2, t), 2·74 (2H, CH_2, t), 5-NHBu; 3·60 (2H, $NHCH_2$, t), 1·75 (2H, $NHCH_2CH_2$, m), 1·51 (2H, CH_2CH_3, m), 1·00 (3H, CH_3, t), 3-NHBu; 3·20 (2H, $NHCH_2$, q), 1·64 (2H, $NHCH_2CH_2$, m), 1·44 (2H, CH_2CH_3, m), 0·95 (3H, CH_3, t).

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