101. *New Intermediates and Dyes. Part X.* Preparation and Reactions of* 2-n-*Alkylquinizarins.*

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2-Methylquinizarin was prepared by hydrolysis of 4-chloro-1-hydroxy-2-methylanthraquinone, or better, from 1,4-diamine-2-methylanthraquinone and aqueous alkaline dithionite. 2-Propyl-, 2-butyl-, 2-hexyl-, 2-heptyl-, and 2-octyl-quinizarin were derived by the interaction of leucoquinizarin and the appropriate aliphatic aldehyde; this reaction appeared to be limited, as the use of decyl- and dodecyl-aldehyde gave quinizarin only.

Inhibiting effects of the 2-n-alkyl groups in reactions with amines were examined. Thus, 2-methyl-, propyl-, and butyl-quinizarin and aqueous ammonia gave some disubstitution of the hydoxy-groups, but with derivatives of longer alkyl chain, only monosubstitution occurred; methylamine afforded yellow fluorescent products, probably formed by loss of water from 2-alkyl-1,4-bismethylaminoanthraquinones.

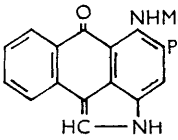
Whereas cyclohexylamine gave excellent yields of 2-alkyl-1,4-biscyclohexylaminoanthraquinones, disubstitution was inhibited in reactions with aniline, which gave monoanilino-derivatives.

2-Methylquinizarin (1,4-dihydroxy-2-methylanthraquinone) [1,2] is most conveniently prepared by heating 1,4-diamino-2-methylanthraquinone (ref. 3 and Part IX) with alkaline sodium dithionite at 80—85° in presence of nitrogen, followed by aeration.

2-Propylquinizarin was obtained in 61·3% yield by heating leucoquinizarin with propionaldehyde in alkaline dithionite solution in presence of nitrogen at 90—95°, followed by aeration; this novel reaction was recorded by Marschalk, Koenig, and Ourousoff.[4] Peters and Peters [5] obtained 81% of 2-butylquinizarin similarly, and also obtained it from 1,4-diamino-2-butylanthraquinone and alkaline dithionite.

Other new 2-n-alkylquinizarins, *viz.*, 2-n-hexyl-(92·6% yield), 2-n-heptyl-(91·2%), and 2-n-octylquinizarin (96·2%), were similarly derived from leucoquinizarin and the appropriate aldehyde; but the use of decyl- and dodecyl-aldehyde gave only quinizarin, even after 3 hours at 130° in a sealed tube.

2-Methylquinizarin and aqueous ethanolic ammonia when heated in the presence of sodium dithionite in a sealed tube (most of the air displaced by nitrogen) at 150—160° for 10 hours gave 1,4-diamino-2-methylanthraquinone and some impure monoamino-monohydroxy-analogue; 2-propyl- and 2-butyl-quinizarin behaved similarly; with 2-hexyl-, 2-heptyl-, and 2-octyl-quinizarin, no disubstitution was noted, and strongly-adsorbed chromatograph bands yielded resinous products only.



(I)

2-Methylquinizarin and 33% ethanolic methylamine, with sodium dithionite at 120° for 7 hours, gave small amounts of 2-methyl-1,4-bismethylaminoanthraquinone and impure monohydroxy-monomethylamino 1-analogue. 2-Propylquinizarin and methylamine yielded a mixture, from which was isolated a brown crystalline product, giving a strong yellowish-green fluorescence in organic solvents; this compound was probably derived by loss of water from 1,4-bismethylamino-2-propylanthraquinone, and could be (I) or its isomer.

With methylamine, 2-butyl- and 2-hexyl-quinizarin also gave similarly yellowish-brown

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* Part IX, *J.*, 1962, 3373.

[1] Nietzki, *Ber.*, 1877, **10**, 2011.
[2] Ullmann and Schmidt, *Ber.*, 1919, **52**, 2098.
[3] Ruggli and Merz, *Helv. Chim. Acta*, 1929, **12**, 71.
[4] Marschalk, Koenig, and Ourousoff, *Bull. Soc. chim. France*, 1936, 1545.
[5] Peters and Peters, *J.*, 1960, 1125.

solids with a strong greenish-yellow fluorescence in organic solvents, analogous to the above. 2-Heptyl- and 2-octyl-quinizarin gave fluorescent yellow resinous products.

Little inhibiting effect was noted in reactions of the 2-n-alkylquinizarins with cyclohexylamine. Refluxing 2-methylquinizarin with cyclohexylamine for 18 hours gave mainly the 1,4-biscyclohexylamino-2-methylanthraquinone with small amounts of, probably, 4-cyclohexylamino-1-hydroxy-2-methylanthraquinone; similarly formed were 1,4-biscyclohexylamino-2-propylanthraquinone and -2-butylanthraquinone. Even with longer alkyl chains in the 2-position, disubstitution was the main reaction. Thus, 2-hexyl-, 2-heptyl-, and 2-octyl-quinizarin and cyclohexylamine afforded 1,4-biscyclohexylamino-2-hexyl-, -2-heptyl- and -2-octyl-anthraquinone, respectively. The melting point of these disubstituted derivatives became progressively lower with increase in length of the 2-n-alkyl chain, and the 2-octyl-analogue was crystallised only with great difficulty.

When 2-methylquinizarin was heated on the steam bath with excess of aniline in the presence of aqueous ethanolic hydrochloric acid and a little boric acid and zinc dust for 4 hours, the purple 4-anilino-1-hydroxy-2-methylanthraquinone was obtained; this dyed cellulose acetate rayon a violet shade. In similar manner, only one of the two hydroxyl groups in 2-propyl-, 2-butyl-, 2-hexyl-, 2-heptyl-, and 2-octyl-quinizarin was replaced by the anilino-group, and only traces of dianilino-derivatives were noted; the 2-n-alkyl group inhibited replacement of both hydroxyl groups.

EXPERIMENTAL

1,4-Dihydroxy-2-methylanthraquinone (*2-Methylquinizarin*).—1,4-Diamino-2-methylanthraquinone (4 g.), 30% aqueous sodium hydroxide solution (3 ml.), and sodium dithionite (10 g.) in water (300 ml.) were stirred under nitrogen for 15 min. at 80—85°; More sodium dithionite (2 g.) and 30% aqueous sodium hydroxide (3 ml.) were added, and the mixture was stirred for a further 30 min. and then filtered hot. Water (2 l.) was added to the filtrate which was then aerated at room temperature for 4 hr. and finally acidified with acetic acid. The orange-brown solid (2·3 g.) was extracted with benzene (charcoal) to give, after recrystallisation from benzene–ethanol, orange-red needles, m. p. 176—177° (Found: C, 71·4; H, 4·3. Calc. for $C_{15}H_{10}O_4$: C, 70·9; H, 3·95%), of 2-methylquinizarin. This method was more convenient than the hydrolysis of 4-chloro-1-hydroxy-2-methylanthraquinone (10 g.) with sulphuric acid (100 ml.) and boric acid (20 g.) at 155° for 3 hr., which gave 2-methylquinizarin (1·5 g.)

2-Propylquinizarin.—Quinizarin (10 g.) was added to 1·5% aqueous sodium hydroxide solution (1 l.), followed by sodium dithionite (20 g.); a stream of nitrogen was passed through the apparatus, stirring being continued until reduction to the brown leuco-compound was completed (at 30°). Propionaldehyde (5·3 g.) was then added and the temperature of the stirred mixture raised to 90—95° and maintained there for 1·5 hr.; the nitrogen stream was stopped and the mixture allowed to cool, then aerated for 2 hr., and set aside overnight. The solid was extracted with benzene (charcoal) to give orange granules (7·2 g., 61·3%), m. p. 135·5—136·5° (Found: C, 72·35; H, 4·9. $C_{17}H_{14}O_4$ requires C, 72·35; H, 5·0%), of *2-propylquinizarin*. Chromatographic procedure confirmed its homogeneity and yielded crystals of the same m. p.

Similarly prepared were: 2-butylquinizarin, from butyraldehyde (6·5 g.), giving an orange solid (11·2 g., 90·9%), and thence orange needles, m. p. 125°, from benzene. *2-Hexylquinizarin*, from hexaldehyde (9 g.), giving a reddish-brown solid (12·5 g., 92·6%), which crystallised from ethanol in orange needles, m. p. 101° (Found: C, 73·9; H, 6·1. $C_{20}H_{20}O_4$ requires C, 74·1; H, 6·2%). *2-Heptylquinizarin* (12·0 g., 91·2%), from n-heptaldehyde (10·3 g.), forming fine, orange needles, m. p. 91° [from light petroleum (b. p. 40—60°)] (Found: C, 74·45; H, 6·45. $C_{21}H_{22}O_4$ requires C, 74·6; H, 6·5%). [Only this compound was isolated when the total reaction product was chromatographed in benzene on alumina.] *2-Octylquinizarin*, from octaldehyde (11·6 g.), giving an orange-red solid (14·1 g., 96·2%), which crystallised from ethanol in lustrous orange plates, m. p. 95·5° (Found: C, 74·65; H, 6·6. $C_{22}H_{24}O_4$ requires C, 75·0; H, 6·8%).

Reactions of 2-Alkylquinizarins with Aqueous Ammonia.—2-Alkylquinizarin (2 g.), aqueous ammonia (*d* 0·88°, 20 ml.), ethanol (6 ml.), and sodium dithionite (1 g.) were heated in a sealed tube (swept out with nitrogen) at 150—160° for 10 hr.; the contents were added to water, the mixture aerated for 1 hr., and the deep violet solid collected, dried, and chromatographed in benzene on alumina. (i) Thus, 2-methylquinizarin gave a deep purple band, eluted with benzene, to yield deep violet needles (0·2 g.) with a coppery lustre (Found: C, 71·45; H, 4·6; N, 11·1. Calc. for $C_{15}H_{12}N_2O_2$: C, 71·4; H, 4·7; N, 11·1%), m. p. 247° not depressed on admixture with a synthetic sample, m. p. 248°, of 1,4-diamino-2-methylanthraquinone. A strongly-adsorbed zone suggested the presence of a monohydroxy-derivative, but no pure compound was isolated. 2-Propylquinizarin similarly gave an eluted band yielding bluish-violet needles (0·25 g.) (from benzene), m. p. 225—227° (Found: C, 73·4; H, 5·8; N, 9·1. $C_{17}H_{16}N_2O_2$ requires C, 72·9; H, 5·7; N, 10·0%), of 1,4-*diamino*-2-*propylanthraquinone*; another strongly adsorbed reddish-violet band suggested a hydroxy-derivative.

2-Butylquinizarin similarly afforded 1,4-diamino-2-butylanthraquinone,[5] but 2-hexyl-, 2-heptyl-, and 2-octyl-quinizarin gave no diamino-analogues, but only strongly adsorbed zones yielding intractable violet resins.

Reactions of 2-*Alkylquinizarins with Methylamine.*—2-Alkylquinizarin (2 g.), 33% ethanolic methylamine (30 ml.), and sodium dithionite (1 g.) were heated in a sealed tube, swept out with nitrogen, at 120° for 12 hr., and the diluted contents aerated, and the solid collected and purified by chromatography (trichlorobenzene–alumina).

2-Methylquinizarin yielded 2-methyl-1,4-bismethylaminoanthraquinone (1·4 g.), deep blue crystals (from ethanol), m. p. 196—200° (Found: N, 9·6. $C_{17}H_{16}N_2O_2$ requires N, 10·0%), not obtained pure, and a strongly adsorbed deep violet zone which on extraction with pyridine gave only a trace of violet solid, m. p. 40°.

2-Propylquinizarin yielded a product (1·5 g.), chromatographed to give a main yellowish-brown zone, which afforded brown lustrous needles (0·4 g.) (from ethanol), m. p. 145—146° (Found: C, 78·1; H, 6·4; N, 10·2. $C_{19}H_{18}N_2O$ requires C, 78·6; H, 6·2; N, 9·6%); this compound gave a strong yellowish-green fluorescence in organic solvents and was probably formed by elimination of water from 1,4-bismethylamino-2-propylanthraquinone.

2-Butylquinizarin gave a product (1·6 g.) and thence a royal blue zone eluted to yield bluish-violet needles (0·06 g.) (from ethanol), m. p. 164—165·5° (Found: C, 78·1; H, 7·2; N, 8·4%), of uncertain constitution, and a main greenish-yellow zone which gave yellowish-brown needles (0·3 g.) (from ethanol), m. p. 167—168° (Found: C, 78·45; H, 6·8; N, 9·35. $C_{20}H_{20}N_2O$ requires C, 78·9; H, 6·6; N, 9·2%), giving a strong greenish-yellow fluorescence in organic solvents, analogous to the above propyl derivative. A strongly-adsorbed violet zone was extracted with pyridine; crystallisation of the product from ethanol yielded purple needles (0·1 g.), m. p. 105·5—106·5° (Found: N, 4·7. Calc. for $C_{19}H_{19}NO_3$: N, 4·5%), probably a monohydroxy-derivative.

2-Hexylquinizarin afforded traces of violet and blue zones, and a main greenish-yellow zone yielding lustrous needles (0·3 g.), m. p. 61°, from a small amount of ethanol, left for 1 week in the ice-chest (Found: C, 78·2; H, 7·25; N, 7·8. $C_{22}H_{24}N_2O$ requires C, 79·5; H, 7·2; N, 8·4%). It had a strong yellowish-green fluorescence in solvents, and appears to be analogous to those described above from propyl- and butyl-quinizarin.

Heptyl- and octyl-quinizarin gave yellow fluorescent products, but these remained resinous, even after long storage in the ice-chest.

Reactions of 2-*Alkylquinizarins with Cyclohexylamine.*—2-Alkylquinizarin (2 g.) was refluxed with cyclohexylamine (25 ml.) and a trace of sodium dithionite for 18 hr., and the mixture added to dilute hydrochloric acid; the resulting solid was collected, dried, and chromatographed in benzene or toluene on alumina. Crystalline products were obtained and column separation was clear.

2-Methylquinizarin afforded a purple zone, eluted rapidly to yield a violet solid (1·4 g.), deep violet needles (from ethanol), m. p. 166°, of 1,4-*biscyclohexylamino*-2-*methylanthraquinone* (Found: C, 77·3; H, 7·4; N, 6·9. $C_{27}H_{32}N_2O_2$ requires C, 77·9; H, 7·7; N, 6·7%). A strongly adsorbed blue band was extracted with boiling pyridine, which gave violet needles (0·1 g.), m. p. 126—130°, from ethanol (Found: C, 74·0; H, 4·3. Calc. for $C_{21}H_{21}NO_3$: C, 75·2; H, 4·2%). This is probably impure 4-cyclohexylamino-1-hydroxy-2-methylanthraquinone.

2-Propylquinizarin yielded 1,4-*biscyclohexylamino*-2-n-*propylanthraquinone* (1·2 g.), lustrous violet plates (from ethanol), m. p. 131—132° (Found: C, 78·5; H, 7·8; N, 6·25. $C_{29}H_{36}N_2O_2$ requires C, 78·4; H, 8·1; N, 6·3%); traces only of strongly adsorbed violet-blue zones were obtained.

2-Butylquinizarin afforded similarly 1,4-*bis-cyclohexylamino*-2-n-*butylanthraquinone* (1·1 g.), glistening violet plates (from ethanol), m. p. 99·5—100° (Found: C, 78·8; H, 7·8; N, 6·5.

$C_{30}H_{38}N_2O_2$ requires C, 78·6; H, 8·3; N, 6·1%); a strongly adsorbed zone was extracted with ethanol and gave deep violet-blue prisms (0·2 g.) (from ethanol) m. p. 106—107°, probably of 4-*cyclohexylamino*-1-*hydroxy*-2-n-*butylanthraquinone* (Found: C, 75·8; H, 7·0; N, 3·7. $C_{24}H_{27}NO_3$ requires C, 76·4; H, 7·2; N, 3·7%).

2-Hexylquinizarin gave, on elution, 1,4-*biscyclohexylamino*-2-n-*hexylanthraquinone* (1·1 g.), lustrous, deep violet prismatic needles (from ethanol), m. p. 97—98° (Found: C, 79·4; H, 8·3; N, 5·8. $C_{32}H_{42}N_2O_2$ requires C, 79·0; H, 8·6; N, 5·8%); a strongly adsorbed product crystallised from ethanol in lustrous violet plates (0·06 g.), m. p. 102—103°, probably of 4-cyclohexylamino-1-hydroxy-2-n-hexylanthraquinone (Found: N, 3·7. $C_{26}H_{31}NO_3$ requires N, 3·5%).

2-Heptylquinizarin gave 1,4-*biscyclohexylamino*-2-*heptylanthraquinone* (1·25 g.) deep violet plates (from ethanol), m. p. 84° (Found: C, 79·6; H, 8·6; N, 5·7. $C_{33}H_{44}N_2O_2$ requires C, 79·2; H, 8·8; N, 5·6%); two minute blue bands were noted also.

Similarly formed was 1,4-*biscyclohexylamino*-2-*octylanthraquinone* (0·9 g.), which separated from light petroleum, after storage in the ice-chest, in deep violet plates, m. p. 55—56° (Found: C, 79·5; H, 8·8; N, 5·6. $C_{34}H_{46}N_2O_2$ requires C, 79·4; H, 9·0; N, 5·45%).

Reactions of Alkylquinizarins with Aniline.—2-Alkylquinizarin (2 g.) was heated on the water-bath with aniline (11 ml.), hydrochloric acid (4 ml.), water (1 ml.), ethanol (12 ml.), boric acid (0·25 g.), and zinc dust (0·25 g.) for 4 hr.; the mixture was distilled with steam and the dried residue extracted with benzene or toluene and chromatographed.

Thus, 2-methylquinizarin yielded a main strongly adsorbed blue zone, which after extraction with boiling pyridine and concentration, crystallisation from ethanol gave long, violet prismatic needles (1·2 g.), m. p. 171—172°, of 4-*anilino*-1-*hydroxy*-2-*methylanthraquinone* (Found: C, 77·0; H, 4·7; N, 4·6. $C_{21}H_{15}NO_3$ requires C, 76·6; H, 4·6; N, 4·3%).

Similarly obtained from the appropriate alkylquinizarin were 4-*anilino*-1-*hydroxy*-2-*propyl*- (1·2 g.), fine, deep violet needles (from ethanol), m. p. 131—132° (Found: C, 77·6; H, 5·35; N, 4·0. $C_{23}H_{19}NO_3$ requires C, 77·3; H, 5·3; N, 3·9%); -2-*butyl*- (0·75 g.), violet needles (from ethanol), m. p. 110° (Found: C, 77·55; H, 5·6; N, 3·9. $C_{24}H_{21}NO_3$ requires C, 77·6; H, 5·7; N, 3·8%); -2-*hexyl*- (0·9 g.), reddish-violet feathery needles (from ethanol), m. p. 94° (Found: C, 78·2; H, 6·0; N, 3·5. $C_{26}H_{25}NO_3$ requires C, 78·2; H, 6·3; N, 3·5%); -2-*heptyl*- (1·3 g.), lustrous violet leaflets (from ethanol), m. p. 96—97° (Found: C, 78·7; H, 6·5; N, 3·4. $C_{27}H_{27}NO_3$ requires C, 78·45; H, 6·5; N, 3·4%); and -2-*octyl-anthraquinone* (1·2 g.), deep violet needles (from ethanol), m. p. 107° (Found: C, 79·2; H, 7·25; N, 3·1. $C_{28}H_{29}NO_3$ requires C, 78·7; H, 6·8; N, 3·3%), respectively. In the experiment with 2-hexylquinizarin, a small bluish-violet zone was extracted with pyridine to give violet needles, m. p. 82—84° (from ethanol) (Found: C, 76·4; H, 6·1; N, 4·0%), probably impure 1-anilino-4-hydroxy-2-hexylanthraquinone; it depressed the m. p. of the isomeric derivative. Similarly, a small amount of the 2-heptyl-analogue was isolated as reddish-violet needles (from ethanol), m. p. 72—74° (Found: N, 3·9%).

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