dialkylaminostilbazole methiodides, which reduce to colorless products, persisted during the hydrogenation until the hydrogen uptake was practically complete. This was taken to mean that some of the unreacted material was still present right up to the end. From this it was inferred that once reduction of a particular molecule had started it was carried to completion before another of the colored molecules was attacked. For if either the pyridine ring alone *or* the ethylenic side chain alone had been saturated the resulting molecule would be colorless. If either all pyridine rings or all side chains were preferentially hydrogenated then the reaction mixture should become practically colorless by the time three-fourths of the total hydrogen uptake had been accomplished in the first case or by the time one-fourth had been done in the second. As high color persisted significantly beyond the three quarters point both of these latter possibilities seem to be eliminated. In contrast, the ethylenic side chain of 2- or 4-stilbazole hydrochloride was reduced preferentially, under the same conditions, and the reduction could be stopped conveniently at that stage to yield the 2- or 4-phenethylpyridines.[3]

Experimental

Hydrogenation of the Stilbazole Methiodides.—The pure stilbazole methiodide (0.02–0.05 *M*) was dissolved or suspended in absolute methanol (50–100 cc.), approximately 0.2 g. of Adams catalyst was added, and the hydrogenation was carried out in a Burgess–Parr catalytic hydrogenation apparatus with shaking at two to three atmospheres overpressure of hydrogen. Hydrogen uptake proceeded rapidly (usually complete in one to two hours) and came to a stop at or near the calculated value. Platinum was removed by filtration, washed with methanol, and the methanol filtrates were evaporated to dryness. The residue stirred up with ether gave usually a white crystalline product, which was recrystallized from combinations of alcohol, ethyl acetate and ether. For details see Table I.

Acknowledgment.—The author wishes to thank Mr. Samuel W. Blackman for the microanalytical results included here.

(3) Phillips, *J. Org. Chem.*, **13**, 622 (1948).

WELLCOME RESEARCH LABORATORIES
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The Alpha Phase of Sodium Dodecyl Sulfate

BY FLOYD RAWLINGS, JR.,[1] AND E. C. LINGAFELTER

We have thought it of interest to compare the solid phases of the sodium alkyl sulfates with those of the sodium alkane sulfonates which have been under investigation in this Laboratory for some time.[1a,2,3,4] We have accordingly started an X-ray crystallographic investigation of the series, sodium hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tetradecyl, hexadecyl and octadecyl sulfates.

(1) Procter and Gamble Research Fellow, 1949–1950.
(1a) Jensen and Lingafelter, THIS JOURNAL, **66**, 1946 (1944).
(2) Jensen and Lingafelter, *ibid.*, **68**, 1729, 2730 (1946).
(3) Lingafelter and Jensen, *Am. Mineral.*, **32**, 691 (1947).
(4) Wilcox and Lingafelter, to be published.

From a solution of sodium dodecyl sulfate in 95% ethanol, slow evaporation at room temperature yielded a crop of well-formed crystals, some of which were used for X-ray investigation. The crystals are very similar in habit to the alpha phase of the sodium alkane sulfonates.[1a] They are quite thin, tabular on (001), and elongated parallel to the *a* axis. In most cases the tablet is outlined by (01*l*) and (11*l*).

X-Ray diffraction data were obtained from rotation, Weissenberg, and precession photographs using copper radiation. Table I contains the constants of the monoclinic unit cell, and the data for two sodium 1-alkane sulfonates for comparison.

TABLE I

	a_0, Å.	b_0, Å.	c_0, Å.	β
$C_{12}H_{25}SO_4Na \cdot xH_2O$	16.47	10.35	77.70	93° 18′
$C_{13}H_{27}SO_3Na \cdot {}^1/_8H_2O$[4]	16.76	10.04	78.21	91° 40′
$C_{12}H_{25}SO_3Na \cdot {}^1/_8H_2O$[1a]	16.80	10.14	76.07	92° 3′

The space group (Aa or A2/a) and the number of molecules in the unit cell (32) is the same for all three of the substances. The amount of hydration of the sodium dodecyl sulfate has not yet been determined. However, the assumption of $^1/_8$ H_2O gives a calculated density of 1.166 g./cc. (observed by flotation method, 1.165 g./cc.).

The sodium dodecyl sulfate differs from the sodium tridecane sulfonate by the substitution of an oxygen atom for a methylene group. Taking the covalent radii to be 0.66 and 0.77 Å., respectively,[5] and assuming the angle of tilt of the chains from the normal to (001), one calculates an expected decrease in d_{001} of 0.68 Å. compared with the observed decrease of 0.51 Å. There is also a small, but real, decrease in a_0 and increase in b_0.

Two other solid phases of sodium dodecyl sulfate have been found, one from 95% alcohol at 25–26° and one from water at 25–26°, both of which are also similar in habit to known phases of the sodium alkane sulfonates. We are continuing the investigation of these phases and others which may be discovered for the long-chain sodium alkyl sulfates.

(5) Pauling, "The Nature of the Chemical Bond," 2nd edition, Cornell University Press, Ithaca, N. Y., 1948, p. 164.

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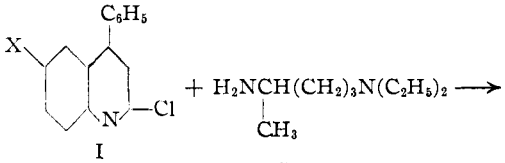
Synthesis of 2-(4′-Diethylamino-1′-methylbutylamino)-4-phenylquinoline and a 6-Chloro Derivative

BY GEORGE A. REYNOLDS AND CHARLES R. HAUSER

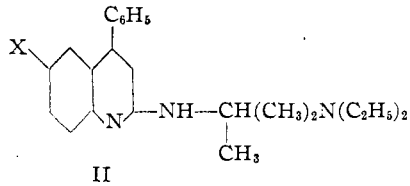
The recent synthesis of 4-phenyl-2-chloroquinoline (I, X = H)[1] from aniline and ethyl benzoylacetate followed by treatment with phosphorous oxychloride has made possible the convenient

(1) Hauser and Reynolds, THIS JOURNAL, **70**, 2402 (1948).

preparation of compound (II, X = H), which is structurally similar to certain antimalarial and other drugs. The side chain was attached to the heterocyclic nucleus by coupling the halogen compound with 1-diethylamino-4-aminopentane (Noval diamine). The coupled product formed solid salts with hydrochloric, hydroiodic, and meconic acids, but these salts were very hygroscopic and attempts to isolate them in the pure condition failed.



I



II

In a similar manner, the 6-chloro derivative (II, X = Cl) was synthesized by coupling Noval diamine with the 2,6-dichloro compound (I, X = Cl), which was prepared from *p*-chloroaniline and ethyl benzoylacetate followed by treatment with phosphorus oxychloride. Cyclization of the intermediate anilide was unusually difficult to effect, overnight heating apparently being required. An attempt to isolate the pure hydrochloride salt of the coupled product was unsuccessful.

Experimental

2-(4'-Diethylamino-1'-methylbutylamino)-4-phenylquinoline.—A mixture of 20 g. (0.09 mole) of 4-phenyl-2-chloroquinoline,[1] 70 ml. of Noval diamine and 0.8 g. of copper powder was heated in a sealed tube at 180° for five hours.[2] After cooling, the contents of the tube were poured onto about 200 ml. of water and the aqueous solution extracted several times with ether. The ether extracts were dried over Drierite and the solvent distilled. The residue was distilled *in vacuo* until the temperature reached 200° at 5 mm., the distillate being discarded. The material remaining in the flask was transferred to a 10 ml. insulated Claisen flask and distilled by means of a mercury diffusion pump. There was obtained 15 g. (46%) of coupled product boiling at 160–165° at 0.01 mm.

Anal.[3] Calcd. for $C_{24}H_{31}N_3$: C, 79.74; H, 8.63; N, 11.61. Found: C, 79.74; H, 8.59; N, 11.37.

2-(4'-Diethylamino-1'-methylbutylamino)-4-phenyl-6-chloroquinoline.—A mixture of 0.25 mole of ethyl benzoylacetate and *p*-chloroaniline was refluxed for fifteen minutes, allowed to cool and the solid anilide suction filtered. Additional anilide was obtained by refluxing the filtrate and cooling the mixture, the process being repeated once again. The total amount of anilide (m. p. 156–157°) obtained was 50 g. (74%). A solution of 50 g. of the anilide in 100 g. of concentrated sulfuric acid was heated on the steam-bath for twelve hours. After cooling to about 60°, the solution was poured onto a large excess of water. The precipitate was filtered, dried and recrystallized from ethanol and water. There was obtained 29 g. (62%) of 4-phenyl-6-chloro-2-hydroxyquinoline (m. p. 253–254°). This product was converted by phosphorus oxychloride to 2,6-dichloro-4-phenylquinoline (m. p. 114–115°) in 92% (28 g.) yield.

Anal.[3] Calcd. for $C_{15}H_9NCl_2$: C, 65.70; H, 3.01; N, 5.11. Found: C, 65.75; H, 3.42; N, 4.98.

This 2,6-dichloro compound (8 g., 0.029 mole) was heated with 32 ml. of Noval diamine essentially as described above for the 2-chloro derivative, the coupled product, b. p. 295–300° at 1 mm., being obtained in 40% (4.4 g.) yield.

Anal.[3] Calcd. for $C_{24}H_{30}N_3Cl$: C, 72.79; H, 7.63. Found: C, 73.19; H, 7.22.

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(2) See Bergstrom, Strutz and Tracey, *J. Org. Chem.*, **11**, 239 (1946).

(3) Analysis by Clark Microanalytical Laboratory, Urbana, Illinois.

The Conversion of Monosubstituted Malonic Esters to Malondiamides

BY PETER B. RUSSELL

During the course of some synthetic studies, at present being carried out in this laboratory, it became necessary to prepare several monosubstituted malondiamides. Compounds of this type have previously been prepared by the reaction of the corresponding dimethyl or diethyl esters with ammonium hydroxide solution or with alcoholic ammonia under a variety of conditions of time and temperature.[1,2,3,4] In the experience of these previous investigators and also in our own experience these methods are unsatisfactory. They leave much to be desired in the way to yield and also the product often contains considerable quantities of the ester-amide.

It is known that methyl esters react more readily with ammonia than do ethyl esters.[5,6] In addition it has been shown that the reaction of methyl phenylacetate with ammonia is retarded by ammonium salts and accelerated by sodium methylate.[7,8] Consequently it was considered possible that the reaction of an ethyl alkylmalonate with ammonia in methanol containing sodium methylate would result in a satisfactory yield of the diamide partly through the base catalyzed conversion of the ethyl to the methyl ester (*Umesterung*)[9] and partly to catalytic action of the sodium methylate on the reaction of the methyl and/or ethyl ester with ammonia. This view proved to be correct and treatment at room temperature of a monosubstituted ethylmalonate dissolved in methanol with a saturated solution of ammonia in methanol containing a catalytic amount of sodium methylate gave excellent (85–100%) yields of pure diamide in 20–100 hours.

(1) Freund and Goldsmith, *Ber.*, **21**, 1245 (1888).
(2) Meyer, *Monatsh.*, **27**, 1092 (1906).
(3) Fischer and Dilthey, *Ber.*, **35**, 849 (1902).
(4) Bischoff and Siebert, *Ann.*, **239**, 96 (1887).
(5) Baltzly, Berger and Rothstein, to be published.
(6) Gordon, Miller and Day, THIS JOURNAL, **70**, 1946 (1948).
(7) Betts and Hammett, *ibid.*, **59**, 1568 (1937).
(8) Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 359.
(9) Ref. 8, p. 356.