2-Methoxy-6-chloro-9-(dialkylaminoalkylamino)-acridines

By G. Bryant Bachman and D. E. Welton[1]

These compounds were prepared from 2-methoxy-6,9-dichloroacridine (I) and the appropriate dialkylaminoalkylamines by the general procedure of Magidson and Grigorovskii.[2] The products are listed in Table I.

Table I

2-Methoxy-6-chloro-9-(dialkylaminoalkylamino)-acridines

No.	Substituent, —R	Salt	M. p.,[a] °C.	Yield, % method	Crystallization solvent–diluent	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
1	$—CH_2C(CH_3)_2CH_2N(CH_3)_2$	2HCl	255–256	64	Water–dioxane	56.67	56.68 56.25	6.30	6.44 6.51
2	$—CH_2C(CH_3)_2CH_2N(C_2H_5)_2$	2HCl + $^1/_3H_2O^{b,c}$	243–245	29	Water–dioxane	57.66	57.63 57.75	6.89	7.84 7.01
3	$—CH_2C(CH_3)_2CH_2N(n\text{-}C_4H_9)$	2HCl	215–220	33	Water–dioxane	61.27	61.07 60.77	7.56	7.44 7.71
4	$—CHCH_3CH_2N(n\text{-}C_4H_9)_2$	2HCl + $^2/_3H_2O^{b,d}$	217–221	83	95% Ethanol–diethyl ether	58.30	58.39 58.37	7.33	7.45 7.65
5	$—(CH_2)_6N(CH_3)_2$	2HCl	281–282	64	Water–dioxane	57.55	57.41 57.37	6.58	6.72 6.73
6	$—CH[—CH_2N(CH_3)_2]_2{}^e$	3HCl + $·HOAc^f$	247–248	69	Acetic acid–none	49.62	49.49 49.63	6.14	6.08 6.38
7	$—CH[—CH_2N(n\text{-}C_3H_7)_2]_2{}^g$	3HCl	220–221	43	Methanol–diethyl ether	57.59	57.02 56.90	7.51	7.46 7.59

[a] Corrected; all melted with decomposition. [b] Dried to constant weight at 140° over phosphorus pentoxide. [c] Calcd.: N, 8.77. Found: N, 8.63. Ionizable Cl: Calcd., 14.83; found, 14.55. [d] % Ionizable Cl: Calcd., 13.85; found, 13.86. [e] Free base, m. p. 120–121°. %C: Calcd., 65.17; found, 65.19. %H: Calcd., 7.03; found, 7.13. [f] Dried to constant weight over calcium oxide at 100°. [g] Free base, m. p. 99–100°. %C: Calcd., 69.91; found, 69.77. %H: Calcd., 8.50; found, 8.64.

In spite of their general structural similarity, the products show considerable differences in ease of hydrolysis. Those in which the substituted ethylenediamine structure is present in the substituent group (Table I, nos. 4, 6 and 7) hydrolyze immediately in hot dilute hydrochloric acid solution to give a precipitate of 2-methoxy-6-chloroacridone, whereas those in which the amino groups are further separated are not affected under these conditions for at least one hour.

Only the 1,3-bis-(dialkylamino)-2-propylamine derivatives (Table I, nos. 6 and 7) form crystalline free bases, but all yield crystalline polyhydrochlorides which form hydrates of varying stabilities; the derivatives listed in Table I are the most nearly anhydrous materials obtainable in each case. Recrystallization of these salts from a mixture of solvents generally gives much more effective purification and recovery than a single solvent.

Pharmacological Testing.—All of the acridine derivatives listed in Table I were submitted for testing as antimalarial agents. The results of these tests will be reported in detail elsewhere. It may be noted, however, that compounds 1, 2, 3 and 5 showed activity against *P. lophurae* in ducks. Compounds 2, 3, 6 and 7 showed little or no trypanocidal activity. Compounds 3 and 7 were inactive toward *Streptococcus hemolyticus*, influenza-virus and Tetanus toxemia.

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[2] O. Y. Magidson and A. M. Grigorovskii, *Ber.*, **69B**, 396–412 (1936).

The Freezing Point of Pure Phthalic Anhydride

By D. E. Debeau

Phthalic anhydride is an article of great commercial importance and is sold on the basis of purity as determined by freezing point. Hence, it is important to know accurately the freezing point of this material with zero impurity. The values to be found in the literature vary from 130.84[1] to 131.60°.[2]

To reach a decision as to which of these values is the more reliable it was necessary to make the measurements reported below.

The phthalic anhydride used was supplied by the Oronite Chemical Company and was manufactured from *o*-xylene by air oxidation. Several methods of purification of the phthalic anhydride were tried. They were slow fractional crystallization, recrystallization from acetone, and sublimation at atmospheric pressure. Samples prepared by sublimation had the highest freezing points and gave the most reproducible results.

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[1] K. P. Monroe, *Ind. Eng. Chem.*, **11**, 1116 (1919).

[2] F. Burriel-Marti, *Bull. Soc. Chim. Belg.*, **39**, 590 (1930).

Recently Glasgow, Streiff and Rossini[3] have published a method for determining both the freezing point of a sample of a compound and the freezing point of the same compound with zero per cent. impurity from the same time-temperature cooling curve. We have applied this method to the determination of the freezing points of our phthalic anhydride samples.

Temperatures were measured with a Bureau of Standards calibrated platinum resistance thermometer used in conjunction with a White Double Potentiometer. The resistance of the thermometer was checked at the ice-point before and after the work on phthalic anhydride.

The highest freezing point of any sample obtained was 130.97° with several samples freezing at 130.95°. Our average value for the freezing point of phthalic anhydride with zero impurity is 130.95 ± 0.03°. This value is the average of those found for nine different samples of phthalic anhydride.

Our value for the freezing point of pure phthalic anhydride is in much better agreement with the value given by Monroe (130.84°) than with that given by Burriel-Marti (131.60°).

Monroe has also published data for the system phthalic anhydride–phthalic acid. Our value for the freezing point (129.80°), and composition (1.65 mole per cent. phthalic acid), of the eutectic is in fair agreement with the values published by Monroe (129.74° and 1.75 mole per cent. phthalic acid).

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[3] A. R. Glasgow, Jr., A. J. Streiff and F. D. Rossini, *J. Research Nat. Bur. Standards*, **35**, 355 (1945).

CALIFORNIA RESEARCH CORPORATION
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The Variation of Composition of 40:60 Isoprene–Styrene Copolymers with Conversion[1]

BY ELIZABETH DYER AND DOROTHY LEVIS MUNROE[2]

There is little published work dealing with the emulsion copolymerization of isoprene and styrene.[3,4] In ascertaining the effect of varying conditions on the emulsion copolymerization of a 40:60 mixture of isoprene and styrene, an approximately equimolecular mixture, it was observed that the initially formed copolymer contained about 80% of styrene. As the reaction was continued to maximum conversion, the styrene content decreased to approximately 60%. These results show that at this monomer ratio styrene enters the copolymer faster than does isoprene. This behavior is similar to that of styrene when copolymerized with acrylonitrile and with vinylidene chloride.[5] The evidence also indicates that the copolymer is not homogeneous with respect to composition.

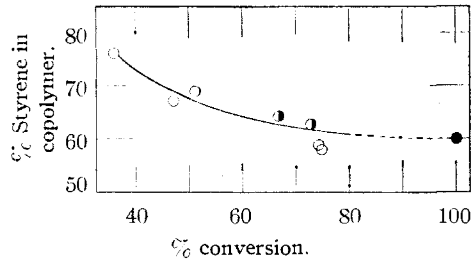

Fig. 1.—Variation of styrene content with degree of conversion: ○, run 20; ◑, run 21; ●, theoretical point.

Procedure.—The most satisfactory polymerization recipe in parts by weight was: isoprene, 40; styrene, 60; water, 200; potassium persulfate, 0.30; sodium oleate, 20; dodecyl mercaptan, 0.25. The experiments were carried out with 10 g. of monomers in 50-ml. test-tubes[6] which had been cleaned with concentrated nitric acid and which were seated on a rotating shaft and turned end over end in an insulated water-bath at 40°.

After agitation for the specified time, the latex was steam distilled to remove unchanged monomers and the polymer was coagulated with 0.6 *M* hydrochloric acid. The tough, rubbery coagulum was cut into small pieces to facilitate removal of acid, then dissolved in benzene containing phenyl-β-naphthylamine in an amount equal to 2% by weight of the polymer. The benzene solution was dried with calcium chloride, and the polymer further purified by several reprecipitations from benzene and methanol. The removal of most of the solvent prior to analysis was done by the frozen benzene technique.[7] The samples were finally dried to constant weight at 56° and a pressure of about 2 mm.

The conversion was measured by drying a known portion of the acid coagulum to constant weight at 80°.

The composition of the polymer samples in terms of percentage of styrene was determined from their iodine numbers according to the method of Kemp and Peters[8] in which $\%$ styrene $= 100 - (100 \times \text{iodine value}/372.6)$. Results from two runs are shown in Fig. 1. The data of Run 20 were obtained from samples taken after reaction periods of three, eight, thirteen, twenty-one, and twenty-four hours, respectively, while those of Run 21 were from ten and sixteen hour samples.

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[1] From the Master's Thesis of Dorothy Levis Munroe, University of Delaware, 1946.

[2] Armstrong Cork Company Research Fellow.

[3] Copolymers of styrene and isoprene were described by Fryling at the Atlantic City Meeting of the American Chemical Society, which was held after the completion of this thesis.

[4] Soday, U. S. 2,317,857, April 27, 1943.

[5] Lewis, Mayo and Hulse, THIS JOURNAL, **67**, 1704 (1945).

[6] Fryling, *Ind. Eng. Chem., Anal. Ed.*, **16**, 2 (1944).

[7] Lewis and Mayo, *Ind. Eng. Chem., Anal. Ed.*, **17**, 135 (1945).

[8] Kemp and Peters, *Ind. Eng. Chem., Anal. Ed.*, **15**, 455 (1943).

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Ionization Constants of Some Weak Acids in Aqueous Tertiary Butyl Alcohol

BY WILLIAM H. FLETCHER[1]

The objective of the work reported in this paper was to obtain reasonably accurate information regarding the ionization constants of certain mercaptans and alkyl substituted phenols. A review of the literature failed to show any recorded work on the ionization constants of aliphatic mercaptans, although thiophenol and a number of its derivatives have been investigated by Schwarzenbach and Egli,[2] using cells with liquid junctions in 49 and 95% (by vol.) ethanol.

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[2] Schwarzenbach and Egli, *Helv. Chim. Acta*, **22**, 360 (1939); **17**, 1176 (1934).