hexoic acid being mainly obtained. This ketone has been obtained by carrying out the reaction with 0.1 mole of the anhydride in an equal volume of ethylene chloride. The mixture (saturated with boron fluoride) was stirred for four hours while cooled in a salt-ice slush, and then treated with sodium acetate. The solvent was distilled and the residue fractionated. However, when this modified procedure was used with 0.25 mole of the anhydride, the yield of ketone was very low, 2-ethylhexoic acid being mainly obtained.

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Bromo Derivatives of 1-Methyl-3-carbethoxy-4-piperidone

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The bromination of 1-methyl-3-carbethoxy-4-piperidone (I) in carbon tetrachloride with one equivalent of bromine yields the hydrobromide of 1-methyl-3-carbethoxy-3-bromo-4-piperidone (II); with one-half an equivalent of bromine a mixture of the hydrobromides of I and II are precipitated and some of the free base (II) remains in solution. The position of the bromo substituent in II is shown by its reaction as a positive bromine with phenylmagnesium bromide to give bromobenzene.

The bromination of the hydrobromide of I in glacial acetic acid with two equivalents of bromine produces the hydrobromide of 1-methyl-3-carbethoxy-3,5-dibromo-4-piperidone (III).[1] The further addition of bromine in this reaction yields only a perbromide of the salt of III.

When the hydrobromides of II and III are titrated with silver nitrate by the Volhard procedure only the ionic bromine of these salts react. However, titration by the Mohr procedure produces reaction with all of the bromine present in each of these salts. Inasmuch as α-bromo ketones such as the phenacyl bromides do not show any appreciable reaction with silver nitrate in the Mohr titration, it would appear that the reaction of the 5-bromo substituent of III in this titration is *via* an ethyleneimonium bromide of the type postulated to explain a similar behavior of 1-methyl-3-bromo-4-phenyl-1,2,3,6-tetrahydropyridine.[2]

Experimental

1-Methyl-3-bromo-3-carbethoxy-4-piperidone (II) Hydrobromide.—In a 250-ml. 3-necked round-bottom flask equipped with a reflux condenser, glass stirrer and dropping funnel, a solution of 18.5 g. (0.10 mole) of 1-methyl-3-carbethoxy-4-piperidone[3] in 200 ml. of carbon tetrachloride was heated to reflux and 16.0 g. (0.10 mole) of bromine added over a period of twenty minutes. The reaction mixture was heated for an additional fifteen minutes and then allowed to cool. The carbon tetrachloride was decanted and the usual residual oil treated with acetone to cause crystallization of 20.5 g. (58%) of the hydrobromide of II, m. p. 143–145° (dec.).

Anal. Calcd. for $C_9H_{15}Br_2NO_3$: C, 31.33; H, 4.38; Br (1), 23.1; Br (2), 46.2. Found: C, 30.95; H, 4.45; Br (Volhard), 22.7; (Mohr), 46.3.

Bromination of 11.1 g. (0.06 mole) of I in carbon tetrachloride at 0–5° with 4.8 g. (0.03 mole) of bromine yielded 9.2 g. of a precipitate, m. p. 142–146°, which was a mixture of the hydrobromides of I and II (halogen analysis). The filtrate was diluted with an equal volume of ether, and anhydrous hydrogen bromide added to precipitate 7.8 g. of a yellow-orange, hygroscopic solid; after crystallization from acetone, 5.0 g. (48%) of the hydrobromide of II, m. p. 141–143° (dec.), was obtained.

Reaction of 1-Methyl-3-bromo-3-carbethoxy-4-piperidone with Phenylmagnesium Bromide.—A solution of 47.1 g. (0.25 mole) of 1-methyl-3-carbethoxy-4-piperidone (I) in 350 ml. of anhydrous ether was placed in a 500-ml. round-bottom flask equipped with a stirrer and dropping funnel. To this solution was added over a period of fifteen minutes 20.4 g. (0.13 mole) of bromine. The precipitated solid was removed by filtration and the filtrate placed under nitrogen in a 1-l. round-bottom flask equipped with a mercury-seal Hershberg stirrer, reflux condenser and dropping funnel. A solution of 0.13 mole of phenylmagnesium bromide in 150 ml. of ether then was added; the resulting solution was refluxed for eight hours, and then stirred for an additional twelve hours. The reaction mixture was hydrolyzed and neutralized by the slow addition of 145 ml. of 1.04 *N* hydrochloric acid. The aqueous layer was separated and extracted with twenty 50-ml. portions of ether; the ether extracts were combined, dried over anhydrous sodium sulfate and the ether distilled on a steam-bath. The residue was fractionally distilled under reduced pressure to give (a) 9.2 g. bromobenzene, (b) 2.5 g. of I, b. p. 71–75° (1.4 mm.), (c) a residue of 3.7 g.

1-Methyl-3,5-dibromo-3-carbethoxy-4-piperidone (III) Hydrobromide.—In a three-necked 250-ml. round-bottom flask was placed a solution of 10.7 g. (0.04 mole) of 1-methyl-3-carbethoxy-4-piperidone hydrobromide in 100 ml. of glacial acetic acid. The flask was heated in an oil-bath to 65° and 12.8 g. (0.08 mole) of bromine in 15 ml. of glacial acetic acid added over a period of fifteen minutes, after which the heating was continued for one hour. The glacial acetic acid was removed under reduced pressure and the oily residue treated with acetone to precipitate 11 g. (62%) of 1-methyl-3,5-dibromo-3-carbethoxy-4-piperidone hydrobromide, m. p. 153–154° (dec.).

Anal. Calcd. for $C_9H_{14}Br_3NO_3$: C, 25.50; H, 3.33; Br (1), 18.9; Br (3), 56.6. Found: C, 25.54; H, 3.53; Br (Volhard), 18.7; (Mohr), 55.7.

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[1] *Cf.* the bromination of acetoacetic ester, Kharasch, *et al.*, THIS JOURNAL, **59**, 1655 (1937).

[2] McElvain and Safranski, *ibid.*, **72**, 3134 (1950).

[3] McElvain and Rorig, *ibid.*, **70**, 1820 (1948).

Colorimetric Study of Reaction of Siliceous Sodium Silicates with Sodium Hydroxide

BY R. C. MERRILL AND R. W. SPENCER

Changes in the absorption spectrum of the dye pinacyanol chloride in sodium silicate solutions[1,2] have been used to follow their reaction with ammonium sulfate and sulfuric acid.[3] This note shows that color changes of the dye during reactions of the silicates with other substances can be followed by means of an ordinary photoelectric colorimeter equipped with a suitable filter. The data to be presented show differences in silicates of the same composition and concentration but different history, and demonstrate that the re-

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[1] R. C. Merrill, R. W. Spencer and R. Getty, THIS JOURNAL, **70**, 2460 (1948).

[2] R. C. Merrill and R. W. Spencer, *ibid.*, **70**, 3583 (1948).

[3] R. C. Merrill and R. W. Spencer, *ibid.*, **72**, 2894 (1950).