Discussion

The method used for obtaining the dielectric constants is least accurate in the low mole fraction methanol region. Accordingly the results do not justify any conclusions about the polarizability of methanol which has been covered so ably elsewhere.[3,4,5] However, the figures obtained are useful in evaluating the relative contributions of association[6] and field interaction[7] to the anomalous behavior of the dielectric constant as a function of concentration.

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(5) J. D. Stranathan, *J. Chem. Phys.*, **6**, 395 (1938).

(6) W. H. Rodebush, D. R. Eddy and L. D. Eubank, *ibid.*, **8**, 899 (1940).

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Formation of Symmetrical Ketones from Self-condensations of Anhydrides by Boron Fluoride[1]

BY EUGENE H. MAN AND CHARLES R. HAUSER

Meerwein and Vossen[2] reported that, although acetylacetone is formed exclusively in the self-condensation of acetic anhydride by boron fluoride, the corresponding symmetrical mono-ketone is produced mainly with propionic or *n*-butyric anhydride and exclusively with isobutyric anhydride. Intermediate self-acylation products (coördinated with boron fluoride) such as I or II appear to be produced[2] and these, on hydrolysis and decarboxylation, yield the mono-ketone.

$(RCH_2COCHRCO)_2O \cdot 3BF_3$ (I) $(R_2CHCOCR_2CO)_2O \cdot 3BF_3$ (II)

TABLE I

KETONES FROM SELF-CONDENSATION OF ANHYDRIDES BY BORON FLUORIDE

Anhydride	Ketone	Yield, %	B. p. °C.	Mm.	Analyses, %[a] Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
Butyric	Di-*n*-propyl	60	144–145	atm.	...	...	...	...
Caproic	Di-*n*-amyl	64	124–125	35	77.58	77.62	13.03	12.72
2-Ethylbutyric	*sym*-Tetraethylacetone	57	103–104	30	77.58	77.76	13.03	13.13
2-Ethylhexoic	α,α'-Diethyl-di-*n*-amyl	32[b]	157–157.5	35	79.57	79.80	13.36	13.60

[a] Analyses by Clark Microanalytical Laboratories, Urbana, Illinois. [b] Obtained on a 0.1 mole scale by the modified procedure.

We have confirmed this result with *n*-butyric anhydride, avoiding the time-consuming steam distillation employed by the earlier workers, and have extended this convenient method to certain higher ketones (Table I). Various other symmetrical ketones could probably be prepared similarly in satisfactory yields. The method appears to be particularly attractive as a laboratory procedure for ketones of the type $(R_2CH)_2CO$ for which the convenient method involving the Claisen self-condensation of esters is not generally satisfactory.[3] However, our procedure has not been very satisfactory with 2-ethylhexoic anhydride. Unsuccessful attempts were made to produce mixed ketones from acetic anhydride with caproic, 2-ethylbutyric, and 2-ethylhexoic anhydrides.

Experimental[4]

Caproic, 2-ethylbutyric, and 2-ethylhexoic anhydrides were prepared by the acetic anhydride–acid exchange method.[5]

In a 1-liter round-bottomed distilling flask fitted with a 25-cm. Vigreux column and downward condenser, were placed 2.5 moles of the acid corresponding to the anhydride desired, 5 moles of acetic anhydride and 0.5% by weight of sulfuric acid. The flask was heated to distil first acetic acid, then the excess acetic anhydride. The residue was distilled twice *in vacuo*. The following anhydrides were prepared by this method: caproic anhydride, b. p. 138–140° at 15 mm; yield, 52%. 2-Ethylbutyric anhydride, b. p. 137–139° at 35 mm; yield, 54%. 2-Ethylhexoic anhydride, b. p. 154–157° at 10 mm; yield, 63%.

Ketones from Anhydrides (Table I).—In a 500-ml. three-necked flask was placed 0.25 mole of the anhydride, and an inlet tube for boron fluoride was inserted so that its tip was about two centimeters from the liquid surface. The flask was fitted with a sealed stirrer, low temperature thermometer and a calcium chloride tube serving as a gas outlet, and then immersed in an acetone-Dry Ice-bath until the temperature reached − 10°. Boron fluoride gas was added from a tank as rapidly as possible, with rapid stirring, keeping the temperature around 0°. In ten to twenty minutes excess boron fluoride began to escape from the calcium chloride tube, and the addition was continued fifteen or twenty minutes longer at a slower rate to ensure complete saturation. The addition tube was replaced by a water condenser. To the stirred reaction mixture was added cautiously through the condenser a solution of 102 g. of sodium acetate in 200 ml. of water, and the stirring continued while heating on the steam-bath for an hour. The oil which separated was extracted twice with ether, and the combined ether extracts washed with saturated sodium bicarbonate solution until no further evolution of carbon dioxide occurred. After washing with water, the ether solution was dried over Drierite and the solvent distilled. The residue was fractionated *in vacuo*.

The above procedure has failed to produce α,α'-diethyl di-*n*-amyl ketone from 2-ethylhexoic anhydride, 2-ethyl-

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[1] This work was carried out under Contract N7onr-455 with the Office of Naval Research.

[2] Meerwein and Vossen, *J. prakt. Chem.*, [2] **141**, 149 (1934).

[3] See Hauser and Hudson, "Organic Reactions," Vol. I, Chapter 9, John Wiley and Sons, Inc., New York, N. Y., 1942.

[4] Samples of caproic, 2-ethylbutyric and 2-ethylhexoic acids and of *n*-butyric, 2-ethylbutyric and 2-ethylhexoic anhydrides were kindly furnished by the Carbide and Carbon Chemicals Corporation.

[5] This method is based on procedures described in Hickenbottom, "Reactions of Organic Compounds," 2nd ed., Longmans, Green and Company, New York, N. Y., 1948, p. 227; see also Schulz, U. S. Patent 2,163,013, June 20, 1939, *C. A.*, **33**, 7821 (1939).

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

By S. M. McElvain and John C. Safranski, Jr.

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).