oxazolidine and Schiff base structures on the basis of their molecular refractivities was unsuccessful.

### Experimental[5]

**N-Butyl-*o*-hydroxybenzalamine (I).**—Azeotropic distillation of a mixture of 91.6 g. of salicylaldehyde, 54.7 g. of butylamine and an excess of benzene for two hours gave the theoretical quantity of water in the distillate. The benzene was removed under reduced pressure and the residue was distilled. The fraction, b. p. 84° at 0.1 mm., was yellow and weighed 127 g., $n^{25}\mathrm{D}$ 1.5442; $d^{25}{}_4$ 0.9919; $MR_{\mathrm{D}}$ (calcd.) 53.76; $MR_{\mathrm{D}}$ (obsd.) 56.43.

*Anal.* Calcd. for $C_{11}H_{15}NO$: C, 74.55; H, 8.51; N, 7.91. Found: C, 74.70; H, 8.48; N, 7.92.

**N-(2-Hydroxyethyl)-2-hydroxybenzalamine (II).**—Method (a): A mixture of 61 g. of salicylaldehyde, 30.5 g. of ethanolamine and 200 ml. of benzene was refluxed using a water-trap (9 ml. of water was collected in two hours). The residue was distilled and the fraction b. p. 110–120° at 0.2 mm. was yellow and weighed 74 g.; $n^{25}\mathrm{D}$ 1.6052; $d^{25}{}_4$ 1.1608; $MR_{\mathrm{D}}$ (calcd.) 46.04; $MR_{\mathrm{D}}$ (obsd.) 49.02.

*Anal.* Calcd. for $C_9H_{11}NO_2$: N, 8.48. Found: N, 8.48.

Method (b): To a solution of 30.5 g. of salicylaldehyde in 68 ml. of reagent grade *n*-butanol was added 15.2 g. of ethanolamine. An exothermic reaction caused the temperature to rise from 28 to 63°. The clear deep-yellow solution was boiled for four hours and then distilled. During the early part of the distillation a water layer was visible under the butanol. The fraction b. p. 110–115° at 0.2 mm. weighed 36 g.; $n^{25}\mathrm{D}$ 1.6050; $d^{25}{}_4$ 1.1608.

*Anal.* Calcd. for $C_9H_{11}NO_2$: C, 65.44; H, 6.71; N, 8.48. Found: C, 65.31; H, 6.80; N, 8.46.

**2-Phenyloxazolidine (III).**—This compound, prepared by the method of Knorr and Matthes,[3] was colorless, b. p. 86–88° at 0.1 mm.; $n^{25}\mathrm{D}$ 1.5729; $d^{25}{}_4$ 1.0707; $MR_{\mathrm{D}}$ (calcd.) 43.36; $MR_{\mathrm{D}}$ (obsd.) 45.93.

**2-*o*-Chlorophenyloxazolidine (IV).**—A mixture of 70.3 g. of *o*-chlorobenzaldehyde, 30.5 g. of ethanolamine and 200 ml. of benzene (exothermic on mixing) was refluxed for two hours using a water-trap (9 ml. of water collected). The material was distilled and the fraction b. p. 102–104° at 0.2 mm., weighed 82 g. After redistillation it was a colorless oil weighing 78 g.; $n^{25}\mathrm{D}$ 1.5793; $d^{25}{}_4$ 1.2073; $MR_{\mathrm{D}}$ (calcd.) 47.22; $MR_{\mathrm{D}}$ (obsd.) 50.57.

*Anal.* Calcd. for $C_9H_{10}ClNO$: C, 58.86; H, 5.49; N, 7.63. Found: C, 58.82; H, 5.46; N, 7.66.

**Ultraviolet Absorption Spectra.**—The data given in Fig. 1 were obtained using a Beckman quartz spectrophotometer with the hydrogen discharge lamp and quartz cells with a light path of 1 cm. A solution of 2.45 mg. of compound (I) in 100 ml. of absolute alcohol showed maxima at 255 mμ, $\epsilon$ = 95,500 and 315 mμ, $\epsilon$ = 30,000 (Curve A). A solution of 2.28 mg. of compound (II) in 100 ml. of absolute alcohol showed maxima at 252.5 mμ, $\epsilon$ = 100,000 and at 315 mμ, $\epsilon$ = 34,100 (Curve B). A solution of 2.53 mg. of compound (III) in 100 ml. of abs. alcohol showed maxima at 247.5 mμ, $\epsilon$ = 127,400 and 290 mμ, $\epsilon$ = 14,480 (Curve C). A solution of 2.28 mg. of compound (IV) in 100 ml. of abs. alcohol showed a maximum at 245 mμ, $\epsilon$ = 127,600 (Curve D).

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[5] Nitrogen analyses done by semi-micro Kjeldahl procedure. Carbon and hydrogen analyses by Micro-Tech Laboratories of Skokie, Ill.

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## Preparation of Anhydrous Methyl Vinyl Ketone and Methyl Isopropenyl Ketone

BY HUGH J. HAGEMEYER, JR.

The preparation of methyl isopropenyl ketone by the aldol condensation of methyl ethyl ketone with formaldehyde and an evaluation of the method was reported by Landau and Irany.[1] In both the liquid phase aldol condensation and in the catalytic vapor phase condensation of formalin with methyl ketone[2,3] considerable difficulty is encountered in drying the unsaturated ketone and in removing traces of formaldehyde.

An alternate method of preparing methyl vinyl ketone and methyl isopropenyl ketone has now been evolved using the Mannich Reaction.[4,5,6,7] The Mannich base is prepared by treating a ketone with a secondary amine hydrochloride and formalin or paraformaldehyde. With acetone, diethylamine hydrochloride and formalin the reaction can be represented by the equation

$$CH_3COCH_3 + CH_2O + (C_2H_5)_2NH\cdot HCl \longrightarrow CH_3COCH_2CH_2N(C_2H_5)_2\cdot HCl + H_2O$$

The tertiary base is separated from the reaction mixture by treating the reaction product with 50% caustic. After drying and distillation it is suspended in an inert medium such as Dowtherm and an equivalent of anhydrous hydrogen chloride is added. The tertiary amine salt is then deaminated by heating to temperatures of 145–160°

$$CH_3COCH_2CH_2N(C_2H_5)_2\cdot HCl \longrightarrow CH_3COCH{=}CH_2 + (C_2H_5)_2NH\cdot HCl$$

The secondary amine hydrochloride can be recovered from the inert medium by filtration or extraction with water and reused in a subsequent batch. In practice it is preferred to add the tertiary amine hydrochloride gradually to the deaminating flask and the unsaturated ketone is distilled off continuously.

It is significant that with methyl ethyl ketone only methyl isopropenyl ketone was formed and there was no evidence for the formation of ethyl vinyl ketone. This indicates the mono-tertiary amine formed to be exclusively $\alpha$-methyl-$\beta$-dimethylaminoethyl methyl ketone.

$$CH_3COCH_2CH_3 + CH_2O + (CH_3)_2NH\cdot HCl \longrightarrow CH_3COCH(CH_3)CH_2N(CH_3)_2HCl + H_2O$$

The methyl isopropenyl ketone prepared by deamination of this tertiary amine hydrochloride had the same constants as those reported for pure methyl isopropenyl ketone by Brant.[8]

### Experimental

**General Procedure.**—A mixture of ketone, dialkylamine hydrochloride and formaldehyde is refluxed for eight to twelve hours. A large excess of ketone is preferred in order to minimize the formation of di-tertiary amine products. In some instances the addition of a small amount of ethanol or isopropyl alcohol is advantageous in order to give a homogeneous mixture. At the end of the reaction excess ketone is removed by distillation. An excess

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[1] Landau and Irany, *J. Org. Chem.*, **12**, 422 (1946).

[2] Brant, U. S. Patent 2,245,567.

[3] McMahon, Roper, Utermohlen, Hasek, Harris and Brandt, THIS JOURNAL, **70**, 2971 (1948).

[4] Defeu, McQuillan and Robinson, *J. Chem. Soc.*, 3089 (1931).

[5] Mannich, *Arch. Pharm.*, **255**, 261 (1917).

[6] Mannich and Salzmann, *Ber.*, **72**, 506 (1949).

[7] Mannich and Haf, *Arch. Pharm.*, **265**, 589 (1927).

[8] Brant, THIS JOURNAL, **64**, 2224 (1942).

of 50% alkali hydroxide is added slowly with cooling and the tertiary amine layer is separated, dried and distilled. It is desirable to concentrate the water solution in order to complete the separation of the tertiary amine.

By varying the conditions and the mole ratios of the reactants yields of 80–90% of the mono-tertiary amine can be realized. The tertiary amine is diluted with a suitable inert solvent and treated with an equivalent of anhydrous hydrogen chloride. The amine hydrochloride is suspended in Dowtherm and is deaminated by heating to 145–165°. Care should be exercised in the deaminating reaction so that no decomposition of the secondary amine hydrochloride takes place.

**Methyl Vinyl Ketone.**—Acetone (700 g., 12 moles) and diethylamine hydrochloride (6 moles) in 30% aqueous solution are mixed together. To this are added paraformaldehyde (240 g., 8 moles) and 150 cc. of isopropyl alcohol. The mixture is refluxed for six hours and then concentrated at reduced pressure from a water-bath. Five hundred grams of a 50% alkali hydroxide solution was added gradually with cooling. The tertiary amine layer is separated off and dried by distillation. The anhydrous amine distils at 74–75° at 15 mm. and titrates the theoretical equivalent weight of 143. The yield is 690 g. or 80.5%.

One hundred and forty-three grams (1 mole) of the tertiary amine is suspended in Dowtherm (1000 cc.) and anhydrous hydrogen chloride (35 g.) is added to form the amine hydrochloride. The suspension is added gradually to 500 cc. of Dowtherm in a 3-liter flask heated to 150° and equipped with a sweep stirrer and a short Vigreux column (45 cm.). Pure anhydrous methyl vinyl ketone distils off at 81° (734 mm.). The deamination is quantitative and the diethylamine hydrochloride is separated from the Dowtherm by washing with water.

**Methyl Isopropenyl Ketone.**—Methyl ethyl ketone (12 moles), dimethylamine hydrochloride (6 moles) and paraformaldehyde (8 moles) together with 300 cc. of isopropyl alcohol are mixed and refluxed for eight hours. The solution is concentrated, treated with excess 50% alkali hydroxide and the α-methyl-β-dimethylaminomethyl ethyl ketone is separated off and distils at 58° and 15 mm. Yield is 695 g. or 89%.

One mole (165 g.) of the tertiary amine hydrochloride is suspended in Dowtherm and deaminated at 160°. A 92% yield of anhydrous methyl isopropenyl ketone distilling at 96–97° at 734 mm. is obtained.

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## Surface Tension of Chloroform

BY M. CONSILIA HANNAN AND M. CLARE MARKHAM

Recently R. Fanelli[1] has discussed the values of surface tension of chloroform determined by many investigators using various methods. Since no values were determined by the pendant-drop method, it was interesting to use apparatus already constructed in this Laboratory in connection with other work, to determine values of surface tension of chloroform.

This apparatus was similar to that of Hauser and his associates[2] and the techniques and method of calculation used, have been developed by Hauser. The chloroform was prepared from C. P. analyzed grade by washing with water, drying over calcium chloride and fractionally distilling. The portion boiling at 61° was used.

The surface tension values obtained at 25.00° were: 26.6, 26.6, 26.5, 26.5, 26.4, 26.5; average 26.5 dynes per cm.

Fanelli reports average values of 26.53 dynes per cm. obtained at 25.0° by the maximum bubble pressure, Sugden's double capillary method, using dried nitrogen; and average 26.46 dynes per cm. using nitrogen saturated with chloroform. The values obtained as noted above by the pendant-drop method check very closely those of Fanelli.

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RECEIVED NOVEMBER 22, 1948

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[1] R. Fanelli, THIS JOURNAL, **70**, 1792 (1948).

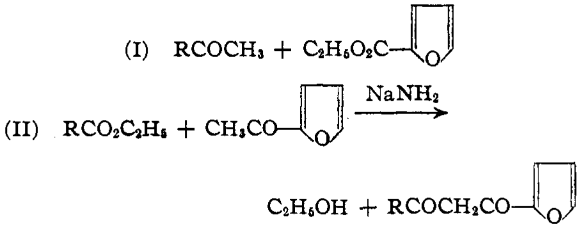
[2] J. M. Andreas, E. A. Hauser and W. B. Tucker, *J. Phys. Chem.*, **42**, 1001 (1938).

## The Synthesis of Certain β-Diketones Containing a Furan Nucleus[1]

BY SAMUEL R. HARRIS[2] AND ROBERT LEVINE

The synthesis of a number of β-diketones by the acylation of 2-acetylthiophene with a series of esters has been reported in a recent communication from this Laboratory.[1] In the present investigation, several β-diketones containing a furan ring have been prepared. Two of these compounds have been prepared previously by other investigators.[3,4] Thus, acetyl-2-furoylmethane was prepared by acylating acetone with ethyl furoate using sodium ethoxide as the condensing agent[3] and benzoyl-2-furoylmethane has been synthesized by acylating acetophenone with ethyl furoate in the presence of sodium ethoxide[3] or metallic sodium.[4]

In the present work, two methods were used to prepare the β-diketones. The following equations, in which R represents an alkyl, aryl, or 2-thienyl group, indicate the reactions which take place.



The method of acylation used consists of allowing an ethereal suspension of two equivalents of sodium amide to react with two equivalents of the methyl ketone. The sodio derivative of the ketone thus formed is then acylated with an equivalent of the appropriate ester and the reaction mixture stirred and refluxed for two hours. This procedure is essentially that reported previously from this[1] and other laboratories.[5]

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[1] Paper III in the series, Condensation Effected by the Alkali Amides. For Paper II, see THIS JOURNAL, **70**, 3360 (1948).

[2] Present address: Department of Chemistry, Howard University, Washington, D. C.

[3] Sprague, Beckham and Adkins, THIS JOURNAL, **56**, 2665 (1934).

[4] Semmler and Ascher, *Ber.*, **42**, 2355 (1909).

[5] Levine, Conroy, Adams and Hauser, THIS JOURNAL, **67**, 1510 (1945).