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.

CHEMICAL DEVELOPMENT LABORATORIES
TENNESSEE EASTMAN CORP.
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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.

SAINT JOSEPH COLLEGE
WEST HARTFORD, CONN. RECEIVED NOVEMBER 22, 1948

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

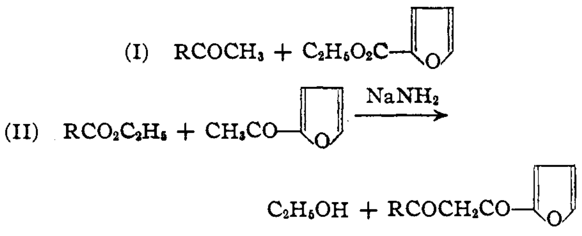
[2] J. M. Andreas, E. A. Hauser and W. B. Tucker, *J. Phys. Chem.*, **42**, 1001 (1938).

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]

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

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[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).

TABLE I

ACYL-2-FUROYLMETHANES

Ketone	Ethyl ester	Product	Yield, %	B. p. °C.	B. p. Mm.	Copper salt, m. p. °C.
Acetone	2-Furoate	Acetyl-2-furoylmethane[a]	43.3	107–110	10	219–222
2-Acetylfuran	Acetate		3.9			
Methyl isobutyl	2-Furoate	Isovaleryl-2-furoyl-methane[b]	73.4	119–121	4	93–97
2-Acetylfuran	Isovalerate		3.6			
Methyl *n*-amyl	2-Furoate	Caproyl-2-furoylmethane[c]	79.1	143–146	7	97–101
2-Acetylfuran	Caproate		1.9			
Acetophenone	2-Furoate	Benzoyl-2-furoylmethane[a]	86.7	165–169	3	245–248
2-Acetylfuran	Benzoate		5.4	68–68.5 (m. p.)		
2-Acetylthiophene	2-Furoate	2-Furoyl-2-thenoylmethane[d]	74.5	192–195 54.5–55.5 (m. p.)	6	272–274

[a] See ref. 3. [b] *Anal.* Calcd. for $C_{11}H_{14}O_3$: C, 68.02; H, 7.27. Found: C, 68.11; H, 7.32. [c] *Anal.* Calcd. for $C_{12}H_{16}O_3$: C, 69.20; H, 7.75. Found: C, 69.12; H, 7.75. [d] *Anal.* Calcd. for $C_{11}H_8O_3S$: S, 14.56. Found: S, 14.81.

The results of the present study are found in Table I. It may be seen that when the same β-diketone is prepared according to Schemes I and II above, the yield using ethyl 2-furoate as the acylating ester is invariably much higher than when an aliphatic or aromatic ester is used to acylate 2-acetylfuran. This large discrepancy in yield might have been difficult to explain if there had not been a visible side reaction occurring. It was observed that as soon as the first few drops of the 2-acetylfuran, which was being added from an addition funnel, came in contact with the ethereal suspension of sodium amide in the reaction flask, the residual 2-acetylfuran in the funnel became cloudy and as the addition was continued a fluid solid material formed in the funnel. It was felt that this solid was formed by the interaction of the ketone with ammonia. Ammonia is present in the reaction mixture either because some remains in solution when the sodium amide is suspended in ether or because of the following reaction which is the first step in the acylation of ketones with esters.

$$RCOCH_3 + NaNH_2 \longrightarrow RCOCH_2Na + NH_3$$

A sample of freshly distilled 2-acetylfuran was dissolved in absolute ether and the solution was then saturated with gaseous ammonia. An exothermic reaction took place and a brown solid material precipitated out of solution. This solid was water-soluble and unreactive toward 2,4-dinitrophenylhydrazine reagent, indicating that the carbonyl group was no longer free. An analysis of this solid (calcd. N, 11.02. Found: N, 11.11) suggested a molecular formula, $C_6H_9O_2N$ for the compound. It is probably a ketone ammonia and should therefore not be acylated by esters.

A detailed investigation of the reactions of 2-acetylfuran with ammonia and amines is now in progress in this Laboratory.

Experimental

Synthesis of Acyl-2-furoylmethanes.—The apparatus used in these reactions consisted of a 1000-ml. three-necked round-bottomed flask having ground-glass joints and equipped with a mercury-sealed stirrer, an addition funnel, and a condenser (protected from atmospheric moisture by a drying tube filled with Drierite). Four-tenths of a mole of sodium (9.2 g.) is converted to sodium amide and suspended in absolute ether as described previously.[6] To the rapidly stirred suspension of sodium amide in ether, 0.4 mole of the appropriate ketone dissolved in 50 ml. of absolute ether is added, followed after fifteen minutes by 0.2 mole of the acylating ester. The reaction mixture is refluxed for two hours on a water-bath and then worked up as described earlier.[1,6] The yields of the compounds prepared are found in Table I.

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(6) Adams and Hauser, THIS JOURNAL, **66**, 1220 (1944).

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Maleimide as a Dienophile

BY STEWART C. HARVEY[1]

Although maleic anhydride, maleic acid, and maleic esters have been used extensively as dienophiles in the Diels–Alder diene synthesis, the dienophilic character of maleimide has remained uninvestigated. In order to test its activity, maleimide was dissolved in ether with cyclopentadiene-1,3; the quantitative separation of a crystalline adduct, subsequently shown to be 3,6-endomethylene-1,2,3,6-tetrahydro-*o*-phthalimide, gave clear evidence of dienophilic activity. The structure of the adduct was confirmed by alkaline hydrolysis to give the known 3,6-endomethylene-1,2,3,6-tetrahydro-*o*-phthalic acid, which was identified by a mixed melting point procedure employing the same compound prepared in another manner.[2]

Experimental

3,6-Endomethylene-1,2,3,6-tetrahydro-*o*-phthalimide.—A mixture consisting of 1.1 g. (1.4 ml.) of cyclopentadiene-1,3 and 1.6 g. of maleimide in 40 ml. of anhydrous ether was allowed to stand at room temperature. Evidence of a reaction was the appearance of a faint yellow color a few minutes after the reagents were brought together. The following morning 2.5 g. of gleaming white needles had separated from the solution. Recrystallization from alcohol–ether (1:2) gave a product melting at 187°. It was found to be very soluble in acetone, hot

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(1) Present address: University of Texas School of Dentistry, Houston 4, Texas.

(2) O. Diels and K. Alder, *Ann.*, **460**, 98 (1928).