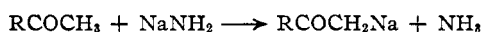


TABLE I
 ACYL-2-FUROYLMETHANES

Ketone	Ethyl ester	Product	Yield, %	B. p. °C.	Mm.	Copper salt, m. p. °C.
Acetone	2-Furoate	Acetyl-2-furoyl-methane ^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 <i>n</i> -amyl	2-Furoate	Caproyl-2-furoyl-methane ^c	79.1	143-146	7	97-101
2-Acetylfuran	Caproate		1.9			
Acetophenone	2-Furoate	Benzoyl-2-furoyl-methane ^d	86.7	165-169	3	245-248
2-Acetylfuran	Benzoate		5.4	68-68.5 (m. p.)		
2-Acetylthiophene	2-Furoate	2-Furoyl-2-thenoyl-methane ^d	74.5	192-195	6	272-274
				54.5-55.5 (m. p.)		

^a See ref. 3. ^b *Anal.* Calcd. for C₁₁H₁₄O₃: C, 68.02; H, 7.27. Found: C, 68.11; H, 7.32. ^c *Anal.* Calcd. for C₁₂H₁₆O₃: C, 69.20; H, 7.75. Found: C, 69.12; H, 7.75. ^d *Anal.* Calcd. for C₁₁H₈O₃S: 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.



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, C₆H₉O₂N 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.

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

DEPARTMENT OF CHEMISTRY
 UNIVERSITY OF PITTSBURGH
 PITTSBURGH 13, PA.

RECEIVED OCTOBER 27, 1948

Maleimide as a Dienophile

BY STEWART C. HARVEY¹

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

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

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

ethanol, 5% sodium hydroxide; slightly soluble in water, cold ethanol, cold acetic acid, diluted hydrochloric acid; insoluble ether. The adduct decomposed at temperatures above the melting point to give the original reagents; the addition was also somewhat reversible in cold sodium hydroxide solutions.

Anal. Calcd. for $C_9H_9O_2N$: N, 8.58. Found: N, 8.51.

3,6-Endomethylene-1,2,3,6-tetrahydro-*o*-phthalic Acid.

—Two-tenths gram of 3,6-endomethylene-1,2,3,6-tetrahydro-*o*-phthalimide were placed on a steam-bath with 5 ml. of 10% potassium hydroxide and heated for three hours, at the end of which time no ammonia was detectable in the vapors above the flask. Concentrated hydrochloric acid was added in excess, and the mixture was then evaporated to dryness. The residue was then triturated in 20 ml. of ether to remove the maleic acid formed by the alkali-catalyzed reversal of the addition. The remaining organic constituents were taken up in 10 ml. of boiling acetone, and petroleum ether was added to the solution until it became cloudy, whereupon the mixture was left at 0° to crystallize. After one recrystallization from alcohol-ether (1:2) the melting point was observed to be 177°, which was not lowered by 3,6-endomethylene-1,2,3,6-tetrahydro-*o*-phthalic acid from another source.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF COLORADO
BOULDER, COLORADO

RECEIVED NOVEMBER 4, 1948

N,N-Dimethyl-N'-(2-pyridyl)-N'-(2-furfuryl)-ethylenediamine

BY L. P. KYRIDES AND M. F. ZIENTY

In a recent publication Vaughan and Anderson¹ described the preparation of N,N-dimethyl-N'-(2-pyridyl)-N'-(2-furfuryl)-ethylenediamine (I) originally synthesized by Viaud.²

These authors reported that (I) is very unstable at temperatures even as low as -80° and that they were unable to prepare its mineral acid salts.³

Prior to the disclosure of Vaughan, *et al.*, the monohydrochloride of (I) had been prepared in this Laboratory for pharmacological evaluation. Since our findings do not support the observations reported, we are prompted to record our results.

Furfuryl alcohol was converted to the chloride in 75% yield by a modification of a synthesis described by Kirner,⁴ with thionyl chloride in ether solution in the presence of pyridine at -15-20°. Distilled furfuryl chloride⁵ was then treated with the lithium salt of N,N-dimethyl-N'-(2-pyridyl)-ethylenediamine in benzene solution at room

temperature. After removal of the solvent and unreacted N,N-dimethyl-N'-(2-pyridyl)-ethylenediamine the desired product distilled as a yellow oil, stable at room temperature.

The monohydrochloride was prepared as well as the dihydrogen citrate salt.

The synthesis of (I) is described in detail.

Experimental⁶

N,N-Dimethyl-N'-(2-pyridyl)-N'-(furfuryl)-ethylenediamine.—To a suspension of 8.3 g. (0.36 mole) of lithium amide in 500 cc. of dry benzene was added 59.4 g. (0.36 mole) of N,N-dimethyl-N'-(2-pyridyl)-ethylenediamine,^{7,8} and the mixture refluxed for three hours with stirring. The reaction was cooled to 25° and maintained at this temperature while a solution of 42 g. (0.36 mole) of furfuryl chloride in 200 cc. of dry benzene was added dropwise during one hour, then refluxed for one hour. On cooling, the solid material was removed by suction filtration and the solvent distilled under reduced pressure. After a forerun of 17.7 g. (28.7% recovery) of the starting ethylenediamine (b. p. 100-105° (0.4 mm.)), 45.9 g. (52%) of the desired tertiary amine was collected as a light yellow oil, b. p. 117.5-118° (0.2 mm.). The dihydrogen citrate was prepared in 88% yield by treating a methanol solution of 4.9 g. (0.026 mole) anhydrous citric acid with a methanol solution of 10 g. (0.04 mole) of (I) and precipitation with dry ether. Recrystallization of this salt from methanol-ether gave colorless crystals, m. p. 95-97°.^{1a}

The monohydrochloride was prepared by treating an ethyl acetate solution of 36.2 g. (0.14 mole) (I) with 5 g. (0.14 mole) dry hydrochloric acid in methanol. On cooling, 37.8 g. (92%) of monohydrochloride was obtained. Recrystallization from ethyl acetate yielded colorless needles, m. p. 117-119°.

Anal. Calcd. for $C_{14}H_{19}N_3O \cdot HCl$: Cl, 12.61. Found: Cl, 12.80.

(6) All melting points are corrected.

(7) Whitmore, Goldsmith and Rytina, *THIS JOURNAL*, **67**, 393 (1945).

(8) Huttner, Djerassi, Beeers, Mayer and Scholz, *ibid.*, **68**, 1999 (1946).

RESEARCH LABORATORIES OF
SUMNER CHEMICAL COMPANY, INC.
ELKHART, INDIANA

RECEIVED OCTOBER 20, 1948

The Influence of Crystal Face in the Catalytic Deposition of Cobalt on a Single Crystal of Copper¹

BY HENRY LEIDHEISER, JR., AND RICHARD MEELHEIM

It has previously been shown in two different cases^{2,3} that the rate of gaseous, catalytic reactions on the surface of a metal differs with the crystal face exposed at the surface. It has also been shown by Beeck, Smith and Wheeler⁴ that the rate of the reaction of hydrogen and ethylene on a nickel film with a (110) orientation parallel to the surface is greater than that on an unoriented film. Results reported herein show that the rate of another type of catalytic reaction, the

(1) This work was supported by a grant from the Research Corporation.

(2) Reaction of hydrogen and oxygen on copper: Leidheiser and Gwathmey, *THIS JOURNAL*, **70**, 1200 (1948).

(3) Decomposition of carbon monoxide on nickel: Leidheiser and Gwathmey, *ibid.*, **70**, 1206 (1948).

(4) Beeck, Smith and Wheeler, *Proc. Roy. Soc. (London)*, **A177**, 62 (1940).

(1) Vaughan and Anderson, *THIS JOURNAL*, **70**, 2807 (1948), reported m. p. 95-97°.

(2) Viaud, *Technologie Produits Pharmaceutiques*, **2**, 53 (1947).

(3) In a personal communication, Dr. Anderson, after receiving the manuscript of this article, has written us as follows: "We today converted a sample of our stable citrate to the base and then to the hydrochloride in solution. In contrast to our previous experience, the solution remained colorless. Our only explanation is that an impurity in the original base caused its instability to temperature and mineral acids, and in the process of preparing the citrate this impurity was removed. We found also that the 5-bromofurfuryl analog hydrochloride appears to be stable when made from the citrate," and authorizes us to publish this statement as a footnote.

(4) Kirner, *THIS JOURNAL*, **50**, 1958 (1928).

(5) Gilman and Vernon, *ibid.*, **46**, 2576 (1924), reported furfuryl chloride as extremely unstable.