at 760 mm.); $n^{20}D$ 1.4530. The infrared absorption spectrum[5] of this product was identical with that of II (Fig. 1).

1,1-Dichloro-3-methyl-1-butene (III).—The infrared spectrum of this compound was identical with that of the product obtained by the dehydrochlorination of 1,1,2-trichloro-3-methylbutane, the condensation product of isopropyl chloride and *cis*-dichloroethylene[4] (Fig. 2). The dehydrochlorination of 17 g. (0.10 mole) of the trichloride by the procedure described above for the dehydrochlorination of 1,1,2-trichloro-3,3-dimethylbutane yielded 6 g. (0.08 mole) of potassium chloride and 6.5 g. (0.05 mole) of product boiling at 115–116° at atmospheric pressure; $n^{20}D$ 1.4460.

1,1-Dichloro-2-cyclohexylethylene (IV).—Hydrolysis of 10 g. of this compound by heating with 100 g. of water at 275° for four hours yielded 5 g. of an organic acid boiling at 244–247° and melting at 28–29°. It yielded an amide melting at 166–167°. The reported[6] properties of cyclohexaneacetic acid are: b. p. 245–247°; m. p. ranging from 27 to 32–33°; amide, m. p. 168°, 171–172° (cor.).

Acknowledgment.—The author wishes to thank Mr. J. P. West for assistance in this work.

Summary

The condensation of *t*-butyl chloride with vinylidene chloride in the presence of ferric chloride yields a mixture of 1,1,1-trichloro-3,3-dimethylbutane and 1,1-dichloro-3,3-dimethyl-1-butene, the relative amounts of the two products depending chiefly on the reaction temperature.

The aluminum chloride catalyzed condensation of the secondary chlorides, isopropyl chloride and cyclohexyl chloride, with vinylidene chloride yields as major products the unsaturated dichlorides, 1,1-dichloro-3-methyl-1-butene and 1,1-dichloro-2-cyclohexylethylene respectively. 1,1,1-Trichloroethane, formed by the hydrochlorination of vinylidene chloride is a by-product in both cases.

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[5] The author is indebted to Dr. W. S. Gallaway, Physics Department, Universal Oil Products Company, for the infrared absorption analyses reported in this paper. For a description of the procedure used, see THIS JOURNAL, **69**, 1124 (1947).

[6] Beilstein, 4th ed., Vol. IX, p. 14.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF ST. VINCENT COLLEGE]

Furfuryl and Thenylalkylamines from Schiff Bases[1,2]

BY BERTIN L. EMLING, J. E. BEATTY AND J. R. STEVENS

A number of secondary amines have been prepared[3] by the action of organomagnesium halides on Schiff bases. However, since none of the furfurylideneamines or thenylideneamines have as yet been utilized in this type of reaction, it was decided to investigate their behavior. Six isomeric alkylfurfurylamines have been prepared as represented by the equations

$$C_4H_3OCHO + H_2N—R' \xrightarrow{(-H_2O)}$$

$$C_4H_3O—CH{=}N—R' + RMgBr \xrightarrow{\text{(hydrolysis)}} C_4H_3OCH(R)—NHR' \quad (1)$$

One thenylamine, $C_4H_3S—CH(C_2H_5)—NH(C_4H_9)$, was also prepared from thenylidenebutylamine and ethylmagnesium bromide. The Schiff bases prepared and used in the syntheses are listed in Table I. The methyl- and ethylfurfurylideneamines were prepared by Schwabbauer[4] who lists only their boiling points. The remaining Schiff bases are not described in the literature. Table II lists the furfurylamines, synthesized from the Schiff bases, and their α-naphthylurea derivatives. The ureas were prepared from the amines and α-naphthyl isocyanate.

TABLE I

N-ALKYLFURFURYLIDENEAMINES

Amine	B. p., °C.	Mm.	Yield, %	$n^{20}D$	d^{20}_4	N Analyses, % Calcd.	Found
Methyl	53	16	85	1.5269	1.025	12.8	12.6
Ethyl	67	18	86	1.5170	0.988	11.4	11.2
Propyl	87–88	21	90	1.5105	0.967	10.2	10.1
Butyl	90	13	90	1.5057	0.950	9.26	9.21
Amyl	104–105	10	85	1.5024	0.940	8.48	8.35
Butyl[a]	112–113	13	90	1.5459[b]	0.990[b]	12.0	11.9[c]

[a] Thenylideneamine. [b] $n^{25}D$ and d^{25}_4. [c] *Anal.* Calcd. for $C_9H_{13}S$: S, 19.2. Found: S, 19.1.

Gilman, Kirby and Kinney[3c] reported a case of 1,4-addition to benzophenone anil under reaction conditions involving high temperature and a long period of heating. While we were of the opinion that 1,2-addition to the carbon–nitrogen structure took place under the mild conditions used in our reactions we desired to prove this. For this purpose one of the furfurylamines was synthesized from furan

$$C_4H_4O + (C_2H_5CO)_2O \xrightarrow{ZnCl_2}$$

$$C_4H_3O—COC_2H_5 \xrightarrow{NH_2OH}$$

$$C_4H_3O—C(NOH)C_2H_5 \xrightarrow[C_2H_5OH]{Na}$$

$$C_4H_3O—CH(NH_2)C_2H_5 + C_4H_9I \xrightarrow{\text{xylene}} C_4H_3O—C(H)(NHC_4H_9)(CH_2CH_3) \quad (I)$$

The amine, I, was not isolated but reacted in ligroin with α-naphthyl isocyanate to give the corresponding urea, 1-butyl-1-(α-ethylfuryl)-3-(α-naphthyl)-urea.

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[1] Presented before the Organic Division at the 114th meeting of the American Chemical Society, Washington, D. C., Aug. 30–Sept. 3, 1948.

[2] The authors wish to acknowledge the assistance of John Heid, Harvey Patterson, Glenn Johnson, Ernest Goral, Thomas Solomon and Walter Hubis in some of the experimental work.

[3] (a) Campbell, *et al.*, THIS JOURNAL, **70**, 3868 (1948); (b) Moffett and Hoehn, *ibid.*, **69**, 1792 (1947); (c) Gilman, Kirby and Kinney, *ibid*, **51**, 2252 (1929).

[4] Schwabbauer, *Ber.*, **35**, 410–415 (1902).

TABLE II

N-ALKYL-(α-ALKYLFURFURYL)-AMINES, $C_4H_3O—CH(R)—NHR'$

Amine		B. p.	Yield,[a]				N Analyses, %		α-Naphthyl ureas[b]		
									M. p.,[c]	N Analyses, %	
R	R'	°C.	Mm.	%	n^{20}_D	d^{20}_4	Calcd.	Found	°C.	Calcd.	Found
CH_3	n-C_5H_{11}	102–103	15	36	1.4681	0.913	7.73	7.74	83	8.00	7.98
C_2H_5	n-C_4H_9	108–109	25	60	1.4635	.907	7.73	7.58	76–77	8.00	7.99
n-C_3H_7	n-C_3H_7	107–108	24	47	1.4634	.904	7.73	7.72	87	8.00	7.94
n-C_4H_9	C_2H_5	105.5–106.5	23	47	1.4636	.909	7.73	7.80	119–119.5	8.00	8.05
n-C_5H_{11}	CH_3	75–76	3	52	1.4649	.913	7.73	7.77	121	8.00	8.07
iso-C_5H_{11}	CH_3	67.5–68.5	4	55	1.4644	.913	7.73	7.66	149	8.00	7.97
C_2H_5	n-C_4H_9[d]	84	3	60	1.5172[e]	.961[e]	7.14	7.07[f]			

[a] Based on Schiff base. [b] Yields based on the isocyanate were all about 90%. [c] All melting points are corrected. [d] Thenylamine, $C_4H_3SCH(C_2H_5)NH(C_4H_9)$. [e] n^{25}_D and d^{25}_4. [f] *Anal.* Calcd. for $C_{11}H_{19}NS$: S, 16.25. Found: S, 16.18.

This proof of the 1,2-addition was further substantiated by oxidizing two of the furfurylamines, *i. e.*, N-butyl-α-ethyl and N-n-amyl-α-methyl, with potassium ferricyanide[5] to 2-furoic acid. N-Butyl-(α-ethylthenyl)-amine was also oxidized with alkaline potassium permanganate to 2-thiophenecarboxylic acid.

Experimental

Reagents.—The chemicals used in all syntheses were reagent grade with the exception of furan which was kindly supplied by the Electrochemicals Department, E. I. du Pont de Nemours and Co.

Furfurylidenebutylamine.—All of the Schiff bases were prepared by essentially the same procedure.[6] The yields were uniformly 85% or better. Only the preparation of furfurylidenebutylamine will be outlined here. Freshly distilled furfural (96 g., 1 mole) was added dropwise with stirring to 88 g. (1.2 moles) of butylamine, kept at 15–20°, and the mixture was then stirred at room temperature for thirty minutes. Solid sodium hydroxide was added with cooling to saturate the aqueous layer, the mixture was extracted with ether and the ether extract dried over potassium hydroxide and distilled. The yield was 136 g., 90%.

N-Butyl-(α-ethylfurfuryl)-amine.—This procedure is typical. To the ethylmagnesium bromide obtained from 54.5 g. (0.5 mole) of ethyl bromide and 13 g. of magnesium turnings was added with cooling 68 g. (0.45 mole) of furfurylidenebutylamine dissolved in 70 ml. of ether. After refluxing for two hours the mixture was poured onto 300 g. of ice and then made acidic with hydrochloric acid. The ether layer was separated and the water layer after washing with an additional 75 ml. of ether was made basic with sodium hydroxide and steam distilled. The distillate was extracted with ether, dried over anhydrous magnesium sulfate and distilled; yield 49 g., 60%.

α-Naphthylureas.—These were prepared according to the procedure described by French and Wirtel[7] except that the amine was added to the α-naphthyl isocyanate in a 2:1 molar ratio. When no excess of amine was employed a glass resulted which was extremely difficult to crystallize. The urea of N-butyl-(α-ethylthenyl)-amine could not be crystallized. All of the ureas were recrystallized from ligroin.

Furyl Ethyl Ketone[8].—Eighty-eight grams (1.3 moles) of furan, 338 g. (2.6 moles) of propionic anhydride and about 5 g. of freshly fused zinc chloride were placed in a 1-liter 3-neck flask and stirred under anhydrous conditions for one hour and then at room temperature for two hours when 450 ml. of water was added. After stirring for an additional hour, potassium hydroxide was added with cooling until alkaline. The organic layer was extracted with ether, dried over anhydrous magnesium sulfate and distilled from a Claisen flask at 77–77.5° at 17 mm.; yield 84 g., 52%. The product crystallized on standing; m. p. 28°. The semicarbazone melted at 187–189° agreeing closely with the value reported by Asahina and Murayama.[9]

Furylethylketoxime.—This was prepared by a standard procedure[10]; yield, 68%; m. p. 46–48°.

Reduction of Furylethylketoxime.—Four hundred and fifty grams of absolute alcohol was placed in a 1-liter round-bottom flask provided with a wide mouth Liebig condenser. To this was added 32 g. of furylethylketoxime and then 80 g. of sodium in small pieces as rapidly as was consistent with the boiling of the alcohol. After one hour undissolved sodium was removed and the mixture cooled in an ice-bath and acidified with dilute sulfuric acid. Then 700 ml. of water was added. The alcohol was removed under vacuum. The residue was made alkaline with solid potassium hydroxide and then extracted with ether. The ether extract was dried over anhydrous magnesium sulfate and distilled; b. p. 63–65° at 7 mm.; yield, 10 g.; n^{25}_D, 1.4673. The picrate of the amine melted at 168–173° with decomposition. Erlenmeyer and Simon[11] report a melting point of 168° but do not mention decomposition.

1-Butyl-1-(α-ethylfurfuryl)-3-α-naphthylurea.—In a 200-ml. round-bottom flask 20 ml. of technical xylene, 1.6 g. (0.013 mole) of (α-ethylfurfuryl)-amine and 4.2 g. (0.023 mole) of butyl iodide was refluxed gently for four hours. After cooling the xylene was extracted with 25 ml. of water. The water solution was made basic with sodium hydroxide and extracted with 6 ml. of ligroin. The ligroin solution was dried over sodium hydroxide and reacted with 2 ml. of α-naphthyl isocyanate dissolved in 2 ml. of ligroin. An oil precipitated. The ligroin was decanted and about 6 ml. more of ligroin was added to the oil and the mixture stirred. After the oil had separated the second ligroin solution was decanted. The residual oil solidified to a glass but could not be crystallized. Four drops of α-naphthyl isocyanate was now added to each of the decanted ligroin solutions and a precipitate formed in each. After combining the two precipitates and recrystallizing three times from ligroin the small quantity of crystals obtained melted at 76–77° (cor.) on a Fisher–Johns apparatus. Mixed m. p. with the urea prepared by means of the Grignard method was 76–77° (cor.). This was the only successful attempt at isolation of the pure urea. Other attempts under what appeared to be the same conditions failed.

Oxidation of N-Butyl-(α-ethylfurfuryl)-amine.—Two grams of the amine, 50 g. of potassium ferricyanide and 20 g. of potassium hydroxide were dissolved in 300 ml. of water and refluxed for two hours when 25 g. more of po-

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(5) Brown, *Iowa State College J. Sci.*, **11**, 227–229 (1937).

(6) Campbell, Sommers and Campbell, THIS JOURNAL, **66**, 82–84 (1944).

(7) French and Wirtel, *ibid.*, **48**, 1736–1739 (1926).

(8) Hartough and Kosak, *ibid.*, **69**, 1012–1013 (1947).

(9) Asahina and Murayama, *Archiv. Pharm.*, **252**, 455 (1914); "Beilstein," 1st supplement, **17**, 157.

(10) Samuel M. McElvain, "The Characterization of Organic Compounds," The Macmillan Co., New York, N. Y., 1946, p. 198.

(11) Erlenmeyer and Simon, *Helv. Chim. Acta*, **24**, 1210–1213 (1941).

tassium ferricyanide and 10 g. of potassium hydroxide were added and reflux continued for two more hours. Iron oxide was removed by filtering the hot mixture. The solution was then evaporated under 15 mm. pressure to one-half its original volume, cooled and filtered, made acidic with hydrochloric acid and extracted with ether. The ether was evaporated and the residue recrystallized from ligroin giving 0.02 g. of a solid; m. p. 130°; mixed m. p. with Eastman Kodak Co. white label furoic acid, 130°.

Oxidation of N-Butyl-(α-ethylthenyl)-amine.—To a solution of 8 g. of sodium hydroxide and 8.8 g. of potassium permanganate in 500 ml. of water was added slowly with stirring 1 g. of N-butyl-(α-ethylthenyl)-amine. After six hours the solution was filtered, evaporated to about 100 ml. and again filtered. The filtrate was washed with ether, made acidic with dilute hydrochloric acid and extracted with ether. Evaporation of the ether gave 0.55 g. of crystals; m. p. 126–126.5° after two recrystallizations from water.

Neutral equivalent: calcd. for 2-thiophenecarboxylic acid, 128.1; found, 128.8.

Summary

1. Five furfurylideneamines, three of which are new, and one new thenylideneamine have been prepared.

2. Six new furfurylamines and one new thenylamine have been synthesized.

3. The structures of the furfurylamines and of the thenylamines have been shown to be most probably those which result from 1,2-addition of the alkylmagnesium halides to the carbon–nitrogen double bond of the Schiff bases.

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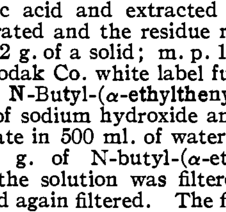
[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Leucenol. VI. A Total Synthesis

BY ROGER ADAMS AND J. L. JOHNSON[1]

Leucenol, from *Leucaena glauca Bentham*, has been shown through degradation studies to have formula I.[2] During the investigation of leucenol in this Laboratory, a variation in the melting point and rotation was frequently observed, which appeared to be dependent on the method of extraction and purification. Experiments have now been completed which permit a clarification of this variability. As obtained directly from the extract by the procedure used originally in this Laboratory or by the method of Kostermans,[3] leucenol had a rotation of −21° in water and a melting point of 228–229°. One recrystallization from water does not cause any essential change in these constants. Mascré[4] and Adams, *et al.*,[2a] reported optical inactivity for leucenol, Bickel and Wibaut[2c] reported −9°, while still others[2e,3,5] gave values of −21° or −22°. The rotation in 1% hydrochloric acid was found to be +10° as compared with Bickel and Wibaut's[2c] value of +6.7°. Mascré[4] and Adams, *et al.*,[2a] observed melting point values of 283–287° and 291°, the latter authors specifying a Maquenne block, but in open tubes previous investigators have given values of 226–227°,[2c] 228°,[5] and 231°.[5]



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An explanation of these variations is found in the following observations. Samples of leucenol, after two or three crystallizations from water, were found to have rotations of −16 to −18°, although the melting points were about the same as before recrystallization. By boiling in water for forty-eight hours, the optical activity completely disappeared. The product had obviously racemized. When the racemic modification crystallized from a boiling aqueous solution as the water was evaporated to a volume below that of saturation of the compound, the product had a melting point of 235–236°. On the other hand, if a cold aqueous solution was permitted to evaporate, the product which was obtained had a melting point of 227–228°. By analysis, the former was shown to be anhydrous and the latter hydrated with one-half molecule of water. The anhydrous and hydrated forms are interconvertible by the treatment described. The hydrate does not lose its water even at 150°, and at 180° it decomposes. These two products have quite different infrared absorption spectra (Fig. 1). It is noteworthy that 3,4-dihydroxypyridine (3-hydroxy-4-pyridone) and α-amino-β-(N-4-pyridone)-propionic acid, of which leucenol is a derivative, hydrate and the infrared absorption spectra of the anhydrous and hydrated forms differ.[2b] Optically active leucenol does not form a hydrate under the conditions used for preparing the hydrated racemic modification. The facile

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(1) From a thesis presented by J. L. Johnson to the Graduate College of the University of Illinois in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1949.

(2) (a) Adams, Cristol, Anderson and Albert, THIS JOURNAL, **67**, 89 (1945); Adams and Jones, *ibid.*, **69**, 1803 (1947); Adams and Govindachari, *ibid.*, **69**, 1806 (1947); (b) Adams, Jones and Johnson, *ibid.*, **69**, 1810 (1947); (c) Bickel and Wibaut, *Rec. trav. chim.*, **65**, 65 (1946); Wibaut and Kleipool, *ibid.*, **66**, 24 (1947); Wibaut, *Helv. Chim. Acta*, **29**, 1669 (1946); (d) Bickel, THIS JOURNAL, **69**, 1801, 1805 (1947); (e) **70**, 326, 328 (1948).

(3) Kostermans, *Rec. trav. chim.*, **65**, 319 (1946).

(4) Mascré, *Compt. rend.*, **204**, 890 (1937).

(5) Renz, *Z. physiol. Chem.*, **244**, 153 (1936); Nienburg and Tauböck, *ibid.*, **250**, 80 (1937).