

Synthesis of 1-(2-Furyl)-2-alkanones

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In connection with our interest in enolizable ketones (2), it was found of interest to synthesize a series of 1-(2-furyl)-2-alkanones. Previously three of these ketones were prepared by Hass, *et al.* (3) by the condensation of 2-furaldehyde and the requisite nitroalkane with subsequent reduction of the resulting nitroalkane to yield the ketone. This method lacks generality because of the difficulty in obtaining higher homologs of the nitroalkanes.

A convenient method of preparation of these ketones is the Darzens glycidic ester condensation and subsequent hydrolysis and decarboxylation of the glycidic ester to yield the requisite ketone. The ethyl 2-bromoesters were either purchased or prepared by the method of Schwenk and Papa (4). These ethyl 2-bromoesters were condensed with 2-furaldehyde essentially as described by Ruzicka and Ehmann (5). The resulting glycidic ester was not isolated, but rather saponified and decarboxylated in the usual manner to yield the 1-(2-furyl)-2-alkanone, usually in good yield. It should be noted that ethyl 2-bromo-3,3-dimethylbutanoate did not condense with 2-furaldehyde under the conditions employed. Several attempts were made but in every case no ketone was produced and an almost quanti-

tative yield of 2-bromo-3,3-dimethylbutanoic acid was recovered from the reaction mixture. It is suggested that this probably represents a practical steric limitation to the Darzens glycidic ester condensation. Hydantoin derivatives were prepared by the method of Henze and Speer (6).

EXPERIMENTAL

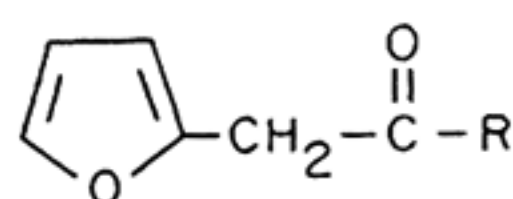
All melting points were taken on a Thomas-Hoover capillary melting point apparatus and were corrected. Elemental analyses were performed by Huffman Microanalytical Laboratories, Wheatridge, Colorado. Density determinations were determined using a pycnometer which held 1.5291 grams of water at 4°. Density and index of refraction determinations were made on samples purified by preparative gas chromatography using a 10 ft. x 3/8 in. column with 20% FFAP on 45/60 chromsorb W.

Preparation of 1-(2-Furyl)-2-alkanones.

A mixture of 29.8 g. (0.31 mole) 2-furaldehyde and 0.31 mole of the ethyl 2-bromoester were cooled to 5-10°. While maintaining this temperature and with stirring a solution of sodium ethoxide prepared from 13.8 g. (0.60 mole) sodium in 150 ml. of ethanol was slowly added to the aldehyde-ester mixture. The reaction mixture was stirred an additional 30 minutes at this temperature and then allowed to warm to room temperature with an additional

Table I

1-(2-Furyl)-2-alkanones

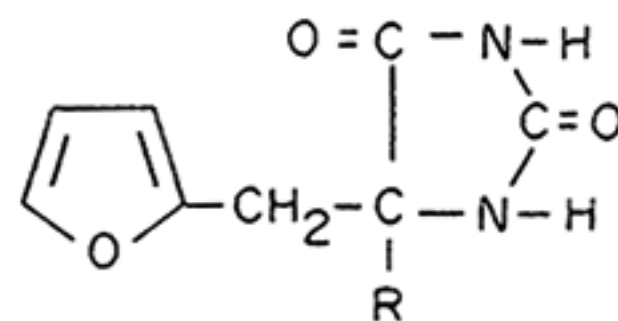


-R	B.P. °C/mm	n _D ²⁰	d ₄ ²⁰	Yield %	Formula	Analysis			
						Calcd. C	H	Found C	H
CH ₃	46/0.4	1.4798	1.061	37	C ₇ H ₈ O ₂ (a)				
C ₂ H ₅	51/0.4	1.4711	1.051	48	C ₈ H ₁₀ O ₂ (b)				
<i>n</i> -C ₃ H ₇	61/0.5	1.4675	1.019	64	C ₉ H ₁₂ O ₂ (c)				
<i>iso</i> -C ₃ H ₇	54/0.4	1.4672	1.016	46	C ₉ H ₁₂ O ₂	71.05	7.89	70.88	7.77
<i>n</i> -C ₄ H ₉	55/0.3	1.4660	0.995	29	C ₁₀ H ₁₄ O ₂	72.29	8.43	71.97	8.18
<i>iso</i> -C ₄ H ₉	56/0.3	1.4644	0.991	46	C ₁₀ H ₁₄ O ₂	72.29	8.43	72.33	8.48
<i>sec</i> -C ₄ H ₉	52/0.2	1.4652	1.005	43	C ₁₀ H ₁₄ O ₂	72.29	8.43	71.99	8.53
<i>n</i> -C ₅ H ₁₁	68/0.3	1.4674	0.982	58	C ₁₁ H ₁₆ O ₂	73.33	8.89	73.29	8.72

(a) Reported B.P. 179-180° (3). (b) Reported B.P. 76°/11-12 mm, n_D²⁵ 1.4680, sp. gr. 25°/25° 1.032, (3). (c) Reported B.P. 95°/15 mm, n_D²⁵ 1.4629, sp. gr. 25°/25° 0.999 (3).

Table II

5-Alkyl-5-furfurylhydantoin



R	M.p., °C	Formula	C	Analysis					
				Calcd. H	N	C	Found H	N	
CH ₃	147-148	C ₉ H ₁₀ N ₂ O ₃	55.67	5.19	14.43	55.96	5.24	14.29	
C ₂ H ₅	165.5-167.5	C ₁₀ H ₁₂ N ₂ O ₃	57.68	5.81	13.45	57.74	5.94	13.33	
<i>n</i> -C ₃ H ₇	200.5-201.5	C ₁₁ H ₁₄ N ₂ O ₃	59.45	6.35	12.60	59.60	6.31	12.44	
<i>iso</i> -C ₃ H ₇	203.5-205.5	C ₁₁ H ₁₄ N ₂ O ₃	59.45	6.35	12.60	59.50	6.62	12.54	
<i>n</i> -C ₄ H ₉	160.5-162.5	C ₁₂ H ₁₆ N ₂ O ₃	61.00	6.83	11.86	61.01	6.89	11.76	
<i>iso</i> -C ₄ H ₉	193-194	C ₁₂ H ₁₆ N ₂ O ₃	61.00	6.83	11.86	60.96	6.94	11.81	
<i>sec</i> -C ₄ H ₉	184-185	C ₁₂ H ₁₆ N ₂ O ₃	61.00	6.83	11.86	60.75	6.88	11.81	
<i>n</i> -C ₅ H ₁₁	153-154	C ₁₃ H ₁₈ N ₂ O ₃	62.38	7.25	11.19	62.32	7.30	11.32	

2 hours of stirring. Approximately 30 ml. of water were added to the flask and the mixture stirred on a steam bath for 3 hours. The reaction mixture was cooled to room temperature and a sufficient quantity of dilute phosphoric acid was added to the solution to bring the pH in a range of 3-4. As the acid was added a large quantity of carbon dioxide was evolved. The ketone was extracted with ether, washed with 5% sodium bicarbonate solution, water and dried over anhydrous sodium sulfate. After removal of the ether by flash distillation the ketone was distilled through a Nester-Faust annular Teflon spinning-band column under reduced pressure. These ketones are shown in Table I.

Preparation of 5-Alkyl-5-furfurylhydantoin.

A mixture of 4.5 g. of ammonium carbonate, 1.3 g. of potassium cyanide, and 1.0 g. of 1-(2-furyl)-2-alkanone in 50 ml. of a 50% water-ethanol mixture was placed in a flask fitted with an air condenser. The flask was placed in a 70° water bath overnight, carefully acidified with concentrated hydrochloric acid to pH range 6-7, evaporated to one half volume and cooled. The hydantoin

precipitate was removed by filtration and recrystallized from water-ethanol mixture. The hydantoin is found in Table II.

Acknowledgement.

We gratefully acknowledge the financial support by the Robert A. Welch Foundation, (Grant No. AO-413).

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