trum of the higher melting racemate. We assigned the downfield doublet to the proton on C_1 and the central multiplet to the overlapping resonances of the two neighboring protons on C_2 and C_3. These selections were based on a comparison with the nmr spectrum of 1,1,2,3,3-pentaphenyl-1-propanol, which shows only two absorptions apart from the phenyl multiplets. The hydroxyl proton of the latter was identified by deuterium exchange, leaving the C_2 and C_3 protons with overlapping resonances.

The 132°C melting compound reported by earlier workers (*1, 4*) is undoubtedly a mixture of diastereomers. The acetonate of Kohler, mp 160–161°C, is the acetonate of our higher melting racemate. The available data do not permit the assignment of absolute configurations.

Acknowledgment

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Alkyl 4-Pyridylmethyl Ketones and Derivatives

John L. Bond, David L. Krottinger, Rodney M. Schumacher, Eldon H. Sund,[1] and Timothy J. Weaver
Department of Chemistry, Midwestern University, Wichita Falls, Tex. 76308

Nine alkyl 4-pyridylmethyl ketones were prepared by the interaction of 4-picolylsodium and the requisite methyl ester. Physical properties were determined, and hydantoin and picrate derivatives of these ketones were prepared.

Recently, we had need of some alkyl 4-pyridylmethyl ketones. A careful perusal of the literature revealed that some of the required ketones had been prepared, but physical properties as well as derivatives were sparse or lacking completely. Therefore, as the ketones were prepared, some of their physical constants were determined, and derivatives prepared.

The synthesis of these ketones was patterned after the method of Raynolds and Levine (*4*) in which 4-picolylsodium was interacted with the requisite methyl ester. Typical carbonyl derivatives, i.e., oximes, semicarbazones, and 2,4-dinitrophenylhydrazones, proved to be difficult to prepare and recrystallize from these ketones. Thus, hydantoin derivatives, which could be prepared with relative ease, were chosen. The hydantoin derivatives were prepared by the method of Henze and Speer (*1*).

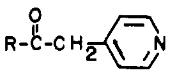
Table I lists the yields of the alkyl 4-pyridylmethyl ketones as well as some of their physical constants. Table II lists the data on the hydantoin and picrate derivatives.

Experimental

Reactants were obtained commercially and used without further purification. Elemental analyses were performed by Huffman Microanalytical Laboratories, Wheatridge, Colo. Melting points were determined on a Thomas-Hoover melting-point apparatus and were corrected. Density determinations were determined with a pycnometer which held 1.5291 grams of water at 4.0°C (*5*). The following examples illustrate the syntheses of the alkyl 4-pyridylmethyl ketones and the 5-alkyl-5-(4-pyridylmethyl) hydantoins.

1-(4-Pyridyl)-3-methyl-2-pentanone. A sodium dispersion was prepared from 53 grams (2.3 moles) of sodium in 68 ml of decane with approximately 0.5 ml oleic acid as the dispersion agent. To this sodium dispersion was added 750 ml of anhydrous benzene, and the temperature adjusted to 55 ± 5°C. Approximately 10 ml of a solution of 112 grams (1.0 mole) of chlorobenzene in 102 ml of benzene was added all at once to the rapidly stirred mixture. After 2–10 min the reaction mixture changed from grey to black and the temperature rose, indicating the formation of the phenylsodium. The temperature could be easily controlled by means of an ice bath, and the remainder of the chlorobenzene–benzene solution was added at such a rate to keep the requisite temperature. After all the chlorobenzene–benzene solution had been added, the mixture was stirred for an additional 2 hr at 55 ± 5°C.

Table I. Alkyl 4-Pyridylmethyl Ketones



R	Yield, %	Bp, °C/mm	$n^{20}D$	$d^{20}4$
CH_3	18	81/0.7[a]	1.5208	1.069
C_2H_5	20	88/0.5[b]	1.5130	1.048
n-C_3H_7[c]	35	97/0.55	1.5063	1.023
iso-C_3H_7	40	87/0.65[d]	1.5064	1.022
n-C_4H_9[c]	39	106/0.5	1.5051	1.005
iso-C_4H_9[c]	26	98/0.7	1.5017	0.999
sec-C_4H_9[c]	33	100/1.0	1.5048	1.006
tert-C_4H_9	9	92/0.75[e]	1.5038	1.005
n-C_5H_{11}[c]	13	115/0.7	1.5024	0.994

[a] Reported bp, 75.5°C/0.1 mm (**2**). [b] Reported bp, 86–88.5°C/1.0 mm (**3**). [c] Elemental analyses (C, H, and N) in agreement with theoretical values have been obtained and submitted for review. [d] Reported bp, 95–97°C/1.0 mm (**3**). [e] Reported bp, 98–102°C/1.0 mm (**3**).

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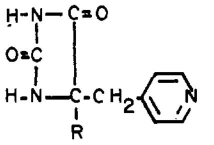
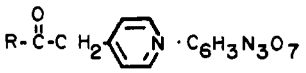
[1] To whom correspondence should be addressed.

Table II. Hydantoin[a] and Picrate[a] Derivatives of Alkyl 4-Pyridylmethyl Ketones





R	Mp, °C	Mp, °C
CH_3	259–60	156–7.5[b]
C_2H_5	211.5–3.5	163.5–5.5[c]
n-C_3H_7	219.5–20.5	137–8
iso-C_3H_7	241.5–2.5	119–21[d]
n-C_4H_9	217.5–8.5	97.5–9.5
iso-C_4H_9	287–8	138.5–9.5
sec-C_4H_9	217.5–9.5	142–3.5
tert-C_4H_9	220.5–1.5	158.5–9.5[e]
n-C_5H_{11}	223.5–4.5	93–3.5

[a] Elemental analyses (N) in agreement with theoretical values have been obtained and submitted for review. [b] Reported mp, 154°C (2). [c] Reported mp, 163.2–4°C (3). [d] Reported mp, 121–1.7°C (3). [e] Reported mp, 157.3–7.8°C (3).

The mixture was cooled to 0 ± 5°C, and 90 grams (0.9 mole) of diisopropylamine in 126 ml of benzene was added, after which the mixture was stirred for an additional hour at 0 ± 5°C. To the solution of sodium diisopropylamide was added 85 grams (0.9 mole) of 4-picoline in 89 ml of benzene, to give the 4-pyridylmethylsodium. The mixture was stirred for an additional 30 min at 0 ± 5°C, and 51 grams (0.45 mole) of methyl 2-methylbutyrate in 58 ml of benzene was added. After 1 additional hr of stirring at 0 ± 5°C, the mixture was poured onto ice and made strongly acidic with concentrated hydrochloric acid.

This mixture was extracted several times with benzene to remove unreacted ester, then made strongly alkaline with 20% sodium hydroxide, and extracted several times with ether. The ether extracts were dried over anhydrous sodium sulfate, the ether was removed by flash distillation, and the ketone distilled through a Nester-Faust annular Teflon spinning-band column under reduced pressure. There was obtained 30 grams (33%) of 1-(4-pyridyl)-3-methyl-2-pentanone, bp, 100/(1.0 mm), $n^{20}D$ 1.5048, $d^{20}4$ 1.006. A picrate was prepared by the method of Shriner et al. (*5*), mp, 142–3.5°C.

5-sec-Butyl-5-(4-pyridylmethyl) hydantoin. A mixture of 4.5 grams of ammonium carbonate, 1.3 grams of potassium cyanide, and 1.0 gram of 1-(4-pyridyl)-3-methyl-2-pentanone in 50 ml of water was placed in a flask fitted with an air condenser. The flask was placed in a 70°C water bath for 4 hr, carefully acidified with concentrated hydrochloric acid to pH 6–7, and cooled. The hydantoin precipitate was removed by filtration and recrystallized from water, mp, 217.5–9.5°C.

Acknowledgment

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Some New Cyclic Organopolysiloxanes

Tse C. Wu[1] and Philip J. Launer[2]
Silicone Products Department, General Electric Co., Waterford, N.Y. 12188

Eight new cyclosiloxanes containing five- and seven-membered rings, fused rings, spiro rings, and separated rings were prepared. Yields, melting points, and infrared spectra are given for these compounds.

Organic cyclotrisiloxanes and cyclotetrasiloxanes are well known as useful intermediates which can be rearranged into high-molecular-weight linear polysiloxanes. In a study of polysiloxanes with unconventional structures, several new cyclosiloxanes were made. These compounds, whose structures are shown in Figure 1, were prepared by condensing an α,ω-dichloro compound with a suitable α,ω-diol in the presence of an acid acceptor such as pyridine. The starting materials are given in Table I. Properties of the new cyclosiloxanes are given in Table II, and their infrared spectra are tabulated in Table III.

Experimental

The condensation reactions were carried out in toluene solution with pyridine as an acid acceptor and occasionally as a solvent for the diol as well. A typical procedure is described below.

Preparation of compound I. Into a 2-liter three-necked flask equipped with two dropping funnels, a stirrer, and drying tube, was placed a solution containing 10 ml of pyridine and 500 ml of toluene. To this were added two 300-ml toluene solutions, one containing 22.7 grams (0.05*m*) of tetra-o-tolyldisilane-1,2-diol, the other containing 6.1 ml (0.05*m*) of dichlorodimethylsilane. Both solutions were added simultaneously and at the same rate over a period of 1 hr with stirring at room temperature. The resulting mixture was stirred for a few hours and

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[1] Present address, Abcor Inc., 341 Vassar St., Cambridge, Mass. 02139. To whom correspondence should be addressed.

[2] Present address, Laboratory for Materials, Inc., P.O. Box 14, Burnt Hills, N.Y. 12027.