Table I. Nmr Absorption Data for Some 7-Norbornadienyl Derivatives[a]

Type of protons	II	III (*2*)	7-Acetate (*3*)	7-Chloride (*4*)
Olefinic	3.30 (3)	3.56 (m)	3.56 (3)	3.2 (3)
	3.45 (3)	3.70 (m)	3.72 (m)	3.4 (3)
Bridgehead	6.35 (6)	6.77 (m)	6.46 (6)	6.3 (6)
Bridge	5.40 (s)	6.38 (s)	5.55 (s)	5.8 (s)
tert-Butoxy		8.94		
Methyl			8.14 (s)	

[a] All values of τ in ppm relative to tetramethylsilane at 10.00. CCl_4 was the solvent except for the 7-chloride which was run in liquid SO_2 (*4*); m = unresolved multiplet; s = singlet; 3 equals triplet, etc.

consistent with the strong electron withdrawing effect of the trifluoroacetoxy group. Table II, "Comparison with Other Normal-Octane," has been deposited with the ACS Microfilm Depository Service.

It seems likely that the reaction of III with either trifluoroacetic acid (IV) or the anhydride with added IV proceeds through the norbornadienyl carbonium ion to produce II. Likewise formation of the 7-acetate from II probably proceeds through the same intermediate with the more nucleophilic acetic acid attacking preferentially to produce product. A carbonyl addition mechanism would also lead to the same product (*1*). The latter mechanism would require the formation of 7-norbornadienol and mixed anhydride. This is considered unlikely since the dienol would be a much poorer leaving group than the attacking acetic acid.

ACKNOWLEDGMENT

The authors thank Thomas Williams of Hoffmann-La Roche, Nutley, N.J., for determining the nmr spectra.

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RECEIVED for review December 14, 1970. Accepted April 28, 1971. Table II will appear following these pages in the microfilm edition of this volume of the Journal. Single copies may be obtained from the Reprint Department, ACS Books and Journals Division, 1155 16th St., N.W., Washington, D.C. 20036. Refer to author, title of article, volume, and page number. Remit by check or money order $3.00 for photocopy or $2.00 for microfiche.

Alkyl 2-Picolyl Ketones and Derivatives

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Nine alkyl 2-picolyl ketones were prepared by the interaction of 2-picolyllithium 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 2-picolyl ketones. A careful perusal of the literature revealed that most of the required ketones had been prepared, but physical properties as well as derivatives were very sparse or lacking completely. Therefore, as the ketones were prepared, some of their physical constants were determined and derivatives prepared.

The ketones were prepared by the method of Goldberg et al. (*3*) in which 2-picolyllithium was interacted with the requisite methyl ester. Typical carbonyl derivatives—i.e., oximes, semicarbazones, and 2,4-dinitrophenylhydrazones—proved to be very difficult to prepare from these ketones. Thus, hydantoin derivatives, which could be prepared with relative ease, were chosen and prepared by the method of Henze and Speer (*4*).

Table I lists the yields of the alkyl 2-picolyl 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 using a pycnometer which held 1.5291 grams of water at 4.0°C (*5*). The following examples illustrate the synthesis of the alkyl 2-picolyl ketones and the 5-alkyl-5-(2-pyridyl)hydantoins.

1-(2-Pyridyl)-3-methyl-2-pentanone. 2-Picolyllithium was prepared by the addition of 93.1 grams (1.0 mole) of 2-picoline to 84 grams (1.0 mole) of phenyllithium (from bromobenzene and lithium wire) in 1.0 liter of anhydrous ether. The addition was completed over a 30-min period and the mixture refluxed for an additional 30 min. To the rapidly stirred solution of 2-picolyllithium was added 51 grams (0.5 mole) of methyl 2-methylbutyrate dissolved in 100 ml of anhydrous ether over a 30-min period so that the ether re-

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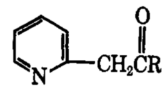
fluxed rapidly. The reaction mixture was refluxed an additional 30 min, cooled, and 190 ml of water were slowly added, after which the entire mixture was poured into 250 ml of 6*N* hydrochloric acid and 1250 grams of ice.

The ether phase was separated and extracted several times with 6*N* hydrochloric acid, the aqueous extracts were combined and treated with 20% sodium hydroxide solution until a pH of 6.2 was reached. Solid sodium bicarbonate was added until a pH of 7.5 was reached. The basic mixture was extracted with ether until the extracts no longer gave a blue-green color with alcoholic iron III chloride. The ether extracts were combined and dried over anhydrous sodium sulfate. The ether was removed by flash distillation, and the ketone was distilled through a Nester-Faust annular Teflon spinning-band column under reduced pressure. Obtained were 52 grams (58%) of 1-(2-pyridyl)-3-methyl-2-pentanone, bp 88°C (0.7 mm), n^{20}_D 1.5216, d_4^{20} 1.009. A picrate was prepared by the method of Shriner et al. (*5*), mp 84.5–6.5°C.

5-*sec*-Butyl-5-(2-pyridinyl)hydantoin. A mixture of 4.5 grams of ammonium carbonate, 1.3 grams of potassium cyanide, and 1.0 gram of 1-(2-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, and cooled. The hydantoin precipitate was removed by filtration and recrystallized from water, mp 205–6°C.

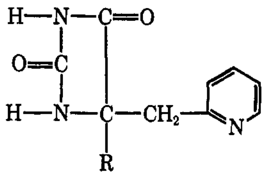
Table I. Alkyl 2-Picolyl Ketones

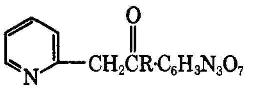


R	% Yield	Bp, °C/mm	n^{20}_D	d_4^{20}
CH_3	20	79/1.9[a]	1.5282	1.072
C_2H_5	33	80/0.6[b]	1.5210	1.051
n-C_3H_7	49	94/1.7[c]	1.5195	1.027
iso-C_3H_7	48	84/0.7[d]	1.5203	1.026
n-C_4H_9	47	108/1.3[e]	1.5148	1.009
iso-C_4H_9	56	96/1.1[f]	1.5173	1.005
sec-C_4H_9[g]	58	88/0.7	1.5216	1.009
tert-C_4H_9[g]	49	98/1.8	1.5235	1.010
n-C_5H_{11}	52	112/1.0[h]	1.5146	0.998

[a] Reported bp 74–5°/1.5 mm (*3*). [b] Reported bp 99–103°/5 mm (*3*). [c] Reported bp 123°/10 mm (*2*). [d] Reported bp 79–85°/2 mm (*3*). [e] Reported bp 136°/10 mm (*2*). [f] Reported bp 114–17°/6 mm (*3*). [g] Elemental analyses (C, H, and N) in agreement with theoretical values have been obtained and submitted for review. [h] Reported bp 151°/10 mm (*2*).

Table II. Hydantoin[a] and Picrate[a] Derivatives of Alkyl 2-Picolyl Ketones





R	Mp, °C	Mp, °C
CH_3	202-3	140-1[b]
C_2H_5	163.5-4.5	146-7[c]
n-C_3H_7	184.5-5.5	130-1
iso-C_3H_7	212-13	146-7[d]
n-C_4H_9	171.5-2.5	116-17
iso-C_4H_9	165.5-7.5	103-4[e]
sec-C_4H_9[f]	205-6	84.5-6.5[f]
tert-C_4H_9	246-7	129-30
n-C_5H_{11}	122-3	85.5-6.5

[a] Elemental analyses (N) in agreement with theoretical values have been obtained and submitted for review. [b] Reported mp 140–0.5° (*1*). [c] Reported mp 144.2–5.5° (*3*). [d] Reported mp 144.5–5.2 (*3*). [e] Reported mp 103–3.8 (*3*). [f] Elemental analyses (C, H, and N) in agreement with theoretical values have been obtained and submitted for review.

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Preparation of Sulfate Esters with Various Carbodiimides and Solvents

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Dicyclohexylcarbodiimide (DCC), sulfuric acid, and various nucleophiles reacted in the solvent dimethylformamide (DMF) to produce sulfated products (*3, 5–7*). Under these reaction conditions monoalkyl sulfates and/or dialkyl pyrosulfates were prepared from alcohols, phenols, mercaptans, and hydroxamates. When the reaction was conducted under dilute conditions (*3*), only unhindered alcohols were sulfated. The DCC-mediated reaction in DMF was selective, gave good yields, permitted short reaction times, and facilitated the use of an ^{35}S-label. Although the DCC-mediated sulfation gives excellent yields of monoalkyl sulfates, the formation of the relatively insoluble voluminous dicyclohexylurea impeded the direct isolation of the monoalkyl sulfate. Rather large volumes of methanol were required to elute the dicyclohexylurea in the DEAE-cellulose column isolation technique (*5, 7*).

Since only DCC and DMF were used in the previous studies,

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