

15 min an exotherm of 8°C and production of copper bromide were observed. The gray slurry was heated at 125–130°C for 2.5 hr, cooled, and filtered to remove the unreacted copper and copper bromides. The precipitate was washed with 150 ml of acetone and 25 ml of benzene. The filtrates and washings were combined; the acetone and benzene were evaporated under reduced pressure.

Unreacted *m*-bromoanisole amounting to 154 grams was distilled from the crude product at 45–50°C (0.5 mm). Crude black residue, 30 grams (100% yield), was dissolved in 500 ml of hot, anhydrous acetone and treated twice with decolorizing carbon (10 grams). The resulting clear brown solution was concentrated to about 200 ml and 300 ml of hot methanol was added. On cooling 5b, an off-white powder was recovered, 15.3 grams (55% yield) with a melting point of 172–175°C. Reported (4) melting point is 178°C, (dec); ir (fluorolube and nujol) 3030 (w, aromatic CH), 2950 (CH₃O), 1550 (M, CNO₂), and 1350 cm⁻¹ (w, CNO₂).

3,3''-Dimethoxy-2,2',2'',4,4',4'',6,6',6''-nonanitro-*m*-terphenyl, 5c. The nitration mixture was prepared in a 2-liter, 3-necked flask by adding 151 grams (1.5 mole) of dry potassium nitrate incrementally over 30 min to 800 grams of 30% oleum (3.0 mole of SO₃). The resulting exothermic reaction raised the temperature to 70°C. Potassium sulfate precipitated as the mixture was cooled to ambient temperature. After 5b (12.75 grams, 0.30 mole) was added quickly producing a temperature rise of 8°C, the slurry was cooled and stirred for 16 hr at 27°C. The slurry was then heated at 110–113°C for 4 hr (at this temperature foaming became severe), cooled to about 40°C, and slowly quenched in 1500 grams ice.

The resulting brown aqueous solution was extracted with ethyl acetate (5 × 200 ml) and the extracts were combined, washed with water (2 × 100 ml), and dried over anhydrous magnesium sulfate. The solvent was evaporated to give 5.2 grams (25%) as an off-white powder. Recrystallization of the crude solid from 1/4 acetone/methanol gave 4.0 grams of 5c as yellow needles; mp 310°C, (dec); ir (fluorolube and nujol) 3100 (w, aromatic CH); 1540 (m, CNO₂), 1340 cm⁻¹ (m, CNO₂); nmr (dimethylsulfoxide-d₆); δ 3.94 (s, 6, CH₃O), 8.90 (s, 2, 5,5''-protons), 9.22 (s, 1, 5'-proton).

3,3''-Diamino-2,2',2'',4,4',4'',6,6',6''-nonanitro-*m*-terphenyl, 5d. 5c (1.25 grams, 1.8 mole) was dissolved in 72 ml of a tetrahydrofuran-methanol-dimethylformamide (50/20/2-v/v/v). The solution was saturated with anhydrous ammonia and stirred for 30 min. The solution turned from a yellow to a blood-red within a few minutes, and a temperature rise of 10°C was observed. The solvents were removed with reduced pressure. Methanol (50 ml) was added, and the slurry was cooled and filtered. The wet, crude product, 1.3 grams, was recrystallized by dissolving in 5 ml of hot dimethylformamide and adding 50 ml of hot methanol.

On cooling, the yellow powder, 5d, that was recovered by filtration exploded at 355°C, 0.80 grams (66% yield); ir (fluorolube and nujol) 3400 (2, NH₂), 3100 (w, aromatic CH), 1360 cm⁻¹ (m, CNO₂); nmr (dimethylsulfoxide-d₆), δ 8.74 (broad s, NH₂), 9.12 (s, 2, 5,5''-protons); 0.42 (s, 1, 5'-proton). The nmr spectrum also indicated the presence of a small amount of dimethylformamide. This solvent, which could not be removed by repeated drying with heat and vacuum, caused inaccurate elemental analysis.

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Alkyl 3-Pyridylmethyl Ketones and Derivatives

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Nine alkyl 3-pyridylmethyl ketones were prepared by the interaction of 3-picolyisodium 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 3-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 very 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 Reynolds and Levine (4) in which 3-picolyisodium was acylated 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 (3).

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Table I lists the yields of the alkyl 3-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 refractive indexes were determined with an Abbe refractometer which was checked by measuring the refractive index of distilled water and obtaining a reading of n_D^{20} 1.3330. The following examples illustrate the syntheses of the alkyl 3-pyridylmethyl ketones and the 5-alkyl-5-(3-pyridylmethyl) hydantoins.

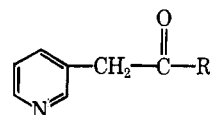
1-(3-Pyridyl)-3-methyl-2-pentanone. A sodium dispersion was prepared from 53 grams (2.3 moles) of sodium in 68 ml of decane with approximately 0.5-ml oleic acid as the dispersion agent (2). To this sodium dispersion was added 750 ml of anhydrous benzene, and the temperature was adjusted to $55 \pm 5^\circ\text{C}$. 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 would rise, 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 $55^\circ \pm 5^\circ\text{C}$. The mixture was cooled to $0^\circ \pm 5^\circ$, and 90 grams (0.9 mole) of diisopropyl amine in 126 ml of benzene was added, after which the mixture was stirred for an additional hour at $0^\circ \pm 5^\circ$. To the solution of sodium diisopropyl amide was added 85 grams (0.9 mole) of 3-picoline in 89 ml of benzene, to give the 3-pyridylmethylsodium. The mixture was stirred for an additional 30 min at $0^\circ \pm 5^\circ$, and 51 grams (0.45 mole) of methyl 2-methylbutyrate in 58 ml of benzene was added. After 1 additional hr of stirring at $0^\circ \pm 5^\circ$, 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 33.4 grams (42%) of 1-(3-pyridyl)-3-methyl-2-pentanone, bp $89/(0.2\text{ mm})$, n_D^{20} 1.5031, d_4^{20} 1.008. A picrate was prepared by the method of Shriner et al. (5), mp $132.5\text{--}3^\circ\text{C}$.

5-sec-Butyl-5-(3-pyridylmethyl) hydantoin. A mixture of 4.5 grams of ammonium carbonate, 1.3 grams of potassium cyanide, and 1.0 gram of 1-(3-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

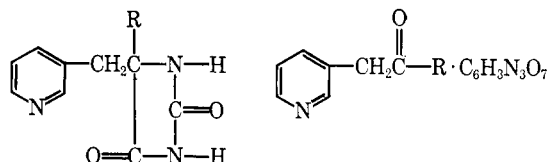
Table I. Alkyl 3-Pyridylmethyl Ketones



R	Yield, %	Bp, °C/mm	n_D^{20}	d_4^{20}
CH ₃	12	79/0.5 ^a	1.5176	1.064
C ₂ H ₅	30	86/0.3 ^b	1.5144	1.054
<i>n</i> -C ₃ H ₇ ^c	30	93/0.5	1.5084	1.048
iso-C ₃ H ₇	25	88/0.3 ^d	1.5058	1.024
<i>n</i> -C ₄ H ₉ ^c	19	103/0.9	1.5044	1.017
iso-C ₄ H ₉	30	114/1.3	1.5001	1.005
sec-C ₄ H ₉ ^c	42	89/0.2	1.5031	1.008
tert-C ₄ H ₉	24	103/0.9 ^e	1.5030	1.016
<i>n</i> -C ₅ H ₁₁ ^c	17	120/0.6	1.4998	0.997

^a Reported bp $119\text{--}23^\circ/1.0\text{ mm}$ (1). ^b Reported bp $103\text{--}104^\circ/2.53\text{ mm}$ (4). ^c Elemental analyses (C, H, and N) in agreement with theoretical values have been obtained and submitted for review. ^d Reported bp $105\text{--}106^\circ/2.0\text{ mm}$ (4). ^e Reported bp $110\text{--}111^\circ/2.48\text{ mm}$ (4).

Table II. Hydantoin^a and Picrate^a Derivatives of Alkyl 3-Pyridylmethyl Ketones



R	Mp, °C	Mp, °C
CH ₃	226.5–8.5	157–8 ^b
C ₂ H ₅	203.5–4.5	112–3 ^c
<i>n</i> -C ₃ H ₇	211.5–2.5	109.5–10.5
iso-C ₃ H ₇	207.5–8.5	134–5 ^d
<i>n</i> -C ₄ H ₉	152–3	126–6.5
iso-C ₄ H ₉	207.5–8.5	135–7
sec-C ₄ H ₉	242.5–4.5	132.5–3
tert-C ₄ H ₉	269–70	152.5–4.5 ^e
<i>n</i> -C ₅ H ₁₁	150–1	126–7.5

^a Elemental analyses (N) in agreement with theoretical values have been obtained and submitted for review. ^b Reported mp $154.0\text{--}5.1^\circ$ (4). ^c Reported mp $111.2\text{--}2.2^\circ$ (4). ^d Reported mp $132.8\text{--}3.6^\circ$ (4). ^e Reported mp $152.1\text{--}2.8^\circ$ (4).

hydrochloric acid to pH 6–7, and cooled. The hydantoin precipitate was removed by filtration and recrystallized from water, mp $242.5\text{--}4.5^\circ\text{C}$.

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