which was heated to reflux by an electrical heating mantle. With stirring and a nitrogen purge, a total of 152 grams of a 25% solution of peracetic acid in ethyl acetate (0.5 mole of peracetic acid) was added dropwise over a 4-hr period. The solution temperature was maintained at 100° ± 10°C by continuously removing ethyl acetate overhead.

Following the addition, the solution was stirred under reflux for 6 hr, at which time a negative peroxide test (5) was obtained. The crude reaction mixture was transferred to a 450 theoretical plate spinning-band distillation apparatus and fractionated at reduced pressure, with the progress of the reaction monitored by glc. After removing isobutyl acetate, successive fractions became progressively enriched in the major product of the reaction. A product fraction, 1.65 grams, bp, 72-73°C @ 15 mm Hg, was analyzed by glc and contained a single component. An analytical sample was obtained by preparative glc: η_D^{25} 1.4170; ν_{max}^{KBr} 3509, 2985, 2924, 1739, 1462, 1379, 1242, 1156, 1044 cm^{-1}; τ (100 MHz, $CDCl_3$) 8.78 (s, 6H), 7.93 (s, 3H), 6.06 (broad s, 3H; $-CH_2$ and $-OH$); m/e 117 ($M-CH_3$), 72 ($M-CH_3CO_2H$), 59 ($CH_3CO_2^{\oplus}$), 43 ($CH_3CO^{\oplus}$).

Based on glc area percent calculations, 2.57 grams of I was contained in other fractions; the total of 4.22 grams of I is equivalent to 6.4% of theory, based on isobutyl acetate.

2-Hydroxy-2-methylbutyl acetate (II). In the manner described above, 0.2 mole of 2-methylbutyl acetate (99.5% pure by glc) was allowed to react with 0.35 mole of peracetic acid. Following the same purification procedure, a product fraction which contained a single component (glc) was isolated; 0.80 gram, bp, 81-82.5°C @ 8 mm Hg. An analytical sample was obtained by preparative glc: η_D^{25} 1.4252; ν_{max}^{KBr} 3448, 2985, 1730, 1460, 1374, 1239, 1042 cm^{-1}; τ (100 MHz, $CDCl_3$) 9.05 (t, 3H), 8.80 (s, 3H), 8.45 (m, 2H), 7.85 (s, 3H), 7.60 (broad s, 1H), 5.98 (s, 2H); m/e 131 ($M-CH_3$), 117 ($M-CH_2CH_3$), 73 ($CH_3CO_2CH_2^{\oplus}$), 43 ($CH_3CO^{\oplus}$). Based on glc area percent calculations, 1.97 grams of II was contained in other fractions; the total of 2.77 grams of II is equivalent to 9.5% of theory, based on 2-methylbutyl acetate.

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Identity of 1,2,3,3-Tetraphenyl-1-propanol

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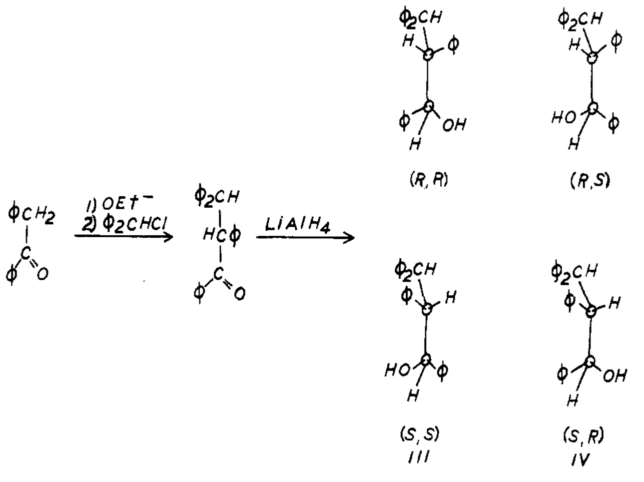
The racemates of 1,2,3,3-tetraphenyl-1-propanol were synthesized and separated. Physical constants and spectral data are presented.

In connection with a study of the addition of organometallic compounds to conjugate systems, it became necessary to establish the identity of 1,2,3,3-tetraphenyl-1-propanol. The literature references to the compound in question leave its identity in doubt. Zinin (*4*) reduced 1,2,3,3-tetraphenylpropenone [I] and 1,2,3,3-tetraphenylpropanone [II] with sodium amalgam in boiling ethanol and obtained 1,2,3,3-tetraphenyl-1-propanol melting at 132°C. Japp and Klingemann (*1*) obtained similar results when they reduced I with sodium in boiling amyl alcohol. However, Kohler and Mydans (2), with sodium amalgam in ethanol-benzene with II, obtained an oil which resisted crystallization. Acetone converted their product to its acetonate which melted at 160-161°C.

Since 1,2,3,3-tetraphenyl-1-propanol has two different asymmetric centers, syntheses starting with the racemic ketone should give two racemates, III (R,R) (S,S) and IV (R,S) (S,R).



We synthesized the racemic ketone, II, by an alternate procedure, reduced it to the alcohol, and separated the latter into its enantiomeric pairs, III (R,R) (S,S) and IV (R,S) (S,R). Identity was established by analyses and from spectral characteristics.

Experimental

Melting points were determined on a Thomas-Hoover melting apparatus calibrated with melting-point standards

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supplied by Arthur H. Thomas Co. The ir data of Table I and nmr data of Table II were obtained on a Perkin-Elmer 621 and a Varian HA-100, respectively. The remainder of the ir and nmr spectra were obtained on a Beckman IR-10 and a Hitachi Perkin-Elmer R-20. A Perkin-Elmer Model 270 was used for mass spectral determinations. The gas chromatography was done on a Tracor MT-220 chromatograph with hydrogen flame ionization detector. The column chromatography was performed with the aid of a Buchler 3-4004 automatic fraction collector converted for preparative scale work by the adapter assembly 3-4044.

(R,S)-1,2,3,3-tetraphenylpropanone. Thirty-eight ml of ethanol was added dropwise to 3.0 grams (0.13 mole) of powdered sodium in a flask equipped with a magnetic stirrer, condenser, and nitrogen inlet. After evolution of hydrogen ceased, 25 grams (0.13 mole) of benzyl phenyl ketone was added. The mixture was heated until the ketone dissolved, forming a viscous, red solution. To the cooled solution was added 23.5 ml (0.13 mole) of benzhydryl chloride. The mixture was heated at 70°C for 15 min, during which time a white precipitate formed. The precipitate was collected on a filter and was then dissolved in chloroform (~500 ml).

The chloroform solution was filtered to remove insoluble material; the filtrate was concentrated to 100 ml and treated with 200 ml of hot absolute ethanol. On cooling, white crystals were deposited; yield, 24%; mp, 177–180°C. Recrystallized from chloroform–ethanol, the product melted at 180–181°C; literature mp, 180–181°C (3). Ir (KBr): C═O stretch, 1685 cm^{-1}; C—H aromatic stretch, 3000–3100 cm^{-1}; C—H out-of-plane bend, 690–768 cm^{-1}. Nmr ($CDCl_3$): δ 5.18 (1H) (d); δ 5.85 (1H) (d); δ 7.4–7.9 (18 H) (m); δ 8.3–8.5 (2H) (m).

Table I. Ir Spectra of Racemates of 1,2,3,3-Tetraphenyl-1-propanol

Absorption, cm^{-1}		
Mp, 164–164.5°C	Mp, 121–122°C	Assignment
3600	3572	[O—H] stretch
3086–3002	3084–3002	[C—H] stretch aromatic
2930, 2912	2920; 2895	[C—H] stretch aliphatic
1966–1742	1950–1733	[C—H] overtone bend, monosubstituted aromatic
1599–1450	1594–1450	[C—C] stretch aromatic ring
755–683	774–681	[C—H] out-of-plane bend aromatic

Table II. Nmr Spectra (in $CDCl_3$) of Racemates of 1,2,3,3-Tetraphenyl-1-propanol

Racemate melting at 164–164.5°C			Racemate melting at 121–122°C		
Shift, δ	Relative area	Assignment	Shift, δ	Relative area	Assignment
1.82 (d)	1	Hydroxyl proton	2.10 broad (s)	1	Hydroxyl proton
3.71 pair of (d)'s	1	Methine proton on C_2	4.21 (m)	2	Methine protons on C_2 and C_3
4.85 (m)	2	Methine protons on C_1 and C_3	4.94 (d)	1	Methine proton on C_1
7.14 (m)	20	Phenyl protons	7.11 (m)	20	Phenyl protons

Reduction of 1,2,3,3-tetraphenylpropanone. In a 250-ml flask equipped with an addition funnel, reflux condenser, nitrogen inlet, and a magnetic stirrer was placed a solution of 1.5 grams (40 mmol) of lithium aluminum hydride in 10 ml of tetrahydrofuran. The solution was cooled in an ice-water bath, and 3.62 grams (10 mmol) ketone in 30 ml of tetrahydrofuran was added dropwise. The mixture was refluxed for 1.0 hr, cooled in an ice bath, and the excess lithium aluminum hydride was destroyed by successive, dropwise addition of 1.5 ml of H_2O, 1.1 ml of 10% sodium hydroxide, and 5.3 ml of water.

The mixture was filtered, and the filtrate evaporated in a rotary still. The residual oil was taken up in ~300 ml of alcohol, and the resulting cloudy solution was cleared by filtration. Concentration of the filtrate to 150 ml yielded 1.5 grams of a white solid melting at 118–145°C. Gas chromatography, with 5% OV-210 on 100–120 mesh Gas Chrom Q at 200°C, N_2 flow rate 115 ml/min, showed two principal components in the mixture at relative retentions of 1.12.

The mixture was separated by column chromatography on a 1.5 × 30-cm column filled with 30 grams of 10% deactivated silica gel. A 1.5-gram sample was mixed with about 1 gram of 10% deactivated silica gel and slurried in ethyl ether. This slurry was evaporated almost to dryness and then placed on the chromatographic column. The fraction collector was set for time-flow collection (250 ml per fraction). The mixture was developed on the column with 10 liters of hexane, eluted successively with 10 liters of 10% carbon tetrachloride-90% hexane (vol-vol) and 2.0 liters of 2% ethyl acetate-98% hexane (vol-vol). The elution was monitored by gas chromatography.

Fractions 41–80 contained a compound which, after three crystallizations from hexane and two from ethanol, melted at 164–164.5°C. *Anal.* Calcd for $C_{27}H_{24}O$: C, 88.97; H, 6.64. Found: C, 88.59; H, 6.56. Fractions 81–88 contained a second component which, after decolorization in ethanol and two crystallizations from isooctane, melted at 121–122°C. *Anal.* Calcd for $C_{27}H_{24}O$: C, 88.97; H, 6.64. Found: C, 88.83; H, 6.55.

Of the two racemates, only the higher melting formed an acetonate on crystallization from acetone. The melting point of the acetonate, 162–163°C, corresponds to that of Kohler and Mydans' compound (2). Ir (KBr): C═O stretch, 1710 cm^{-1}.

Spectral Data and Conclusions

The ir spectra of the two racemates are similar and compatible with the assigned structure, 1,2,3,3-tetraphenyl-1-propanol (Table I).

The mass spectra are also consistent with the structures of the alcohols. The highest *m/e* peak was 257 and corresponds to the commonly observed cleavage of the C—C bond next to oxygen in alcohols with elimination of the heavier fragment. The base peak at 167 corresponds to the benzhydryl fragment, and a peak at 107 was assigned to the benzylic alcohol fragment. The nmr spectra show that the proton environments in the two racemates are different. Comparisons and assignments are given in Table II.

In assigning absorptions for the lower melting racemate, there was difficulty in determining which of the two hydrogens, on C_1 or C_3, absorbs more downfield. Both of these should be doublets, and both overlap in the spectrum 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

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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*).

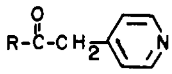
Table I lists the yields of the alkyl 4-pyridylmethyl ketones as well as some of their physical constants. Table II lists the data on the hydantoin and picrate derivatives.

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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