imposable. Ir (cm^{-1}): 1665 (amide I); 1530 (amide II); 3300 (NH stretch); 812,803 (*p*-substituted aromatic).

Acknowledgment

The author is grateful to Lois Kamarowski for the ir spectra.

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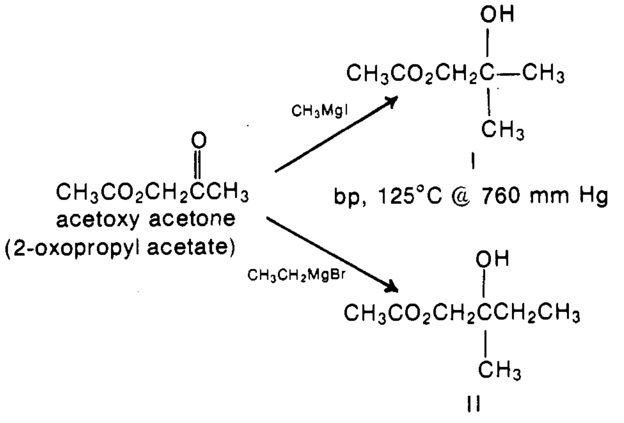
Preparation of 2-Hydroxy-2-methylpropyl Acetate and 2-Hydroxy-2-methylbutyl Acetate

Michael A. Harpold
Research and Development Department, Chemicals and Plastics, Union Carbide Corp., South Charleston, W. Va. 25303

2-Hydroxy-2-methylpropyl acetate (I) and 2-hydroxy-2-methylbutyl acetate (II) were prepared by the (peracetic acid-induced) free-radical hydroxylation of isobutyl acetate and 2-methylbutyl acetate, respectively. Both I and II were identified on the basis of nuclear magnetic resonance (nmr), infrared, mass spectroscopic, and elemental analysis data.

In 1903 Kling (2) reported the preparation of 2-hydroxy-2-methylpropyl acetate (I) and 2-hydroxy-2-methylbutyl acetate (II) by the following reactions:



acetoxy acetone
(2-oxopropyl acetate)

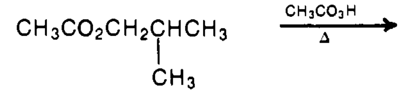
I
bp, 125°C @ 760 mm Hg

II
bp, 152–158°C @ 10 mm Hg

In 1914 Menge (3) prepared II by the reaction of "freshly fused potassium acetate and methylethylglycol chlorhydrin," but reported a boiling point of 94–94.5°C at 16 mm Hg. Menge's synthesis of II was supported by elemental analysis and cryoscopic molecular weight data.

Recently, Van Sickle (4) prepared I by the reaction of sodium acetate and 1,2-epoxy-2-methylpropane but reported only nmr data to identify I.

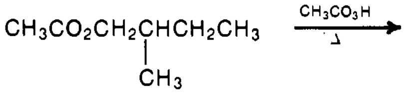
We prepared both I and II by means of the (peracetic acid-induced) free-radical hydroxylation (1) of isobutyl acetate and 2-methylbutyl acetate, respectively. These esters were allowed to react with peracetic acid at approximately 100°C, thereby effecting hydroxylation at the tertiary carbon atoms.



$$CH_3CO_2CH_2\underset{CH_3}{CH}CH_3 \xrightarrow[\Delta]{CH_3CO_3H}$$

isobutyl acetate
(2-methylpropyl acetate)

I, bp, 72–73°C @ 15 mm Hg



$$CH_3CO_2CH_2\underset{CH_3}{CH}CH_2CH_3 \xrightarrow[\Delta]{CH_3CO_3H}$$

2-methylbutyl acetate

II, bp, 81–82.5°C @ 8 mm Hg

Both I and II are clear, colorless liquids with distinctly ethereal odors; infrared, nmr, mass spectroscopic, and elemental analysis data were consistent with the structural assignments.

On the basis of our results, neither I nor II appears to have been prepared by Kling; the data reported by Menge are consistent with our identification of II, and the nmr spectrum reported by Van Sickle is equivalent to our spectrum for I.

Experimental

Gas-liquid chromatography (glc) was conducted with a F/M Model 720 chromatograph by use of 60 ml/min of helium as the carrier gas. For analytical purposes a 12-ft × 1/4-in. column containing 10% Si-550 on Chromosorb W (not acid washed) was operated at 150°C; preparative glc was carried out at 130°C with a 10-ft × 1/4-in. column containing 20% SE-30 on Chromosorb S, 60–80 mesh. Elemental analyses (C, H) in agreement with theoretical values were obtained and submitted for review.

2-Hydroxy-2-methylpropyl acetate (I). A 250-ml round-bottomed flask was equipped with a thermometer, magnetic stirring bar, nitrogen purge tube, dropping funnel, and a distillation head. The flask was loaded with 58.1 grams (0.5 mole) of isobutyl acetate (99.8% pure by glc) 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

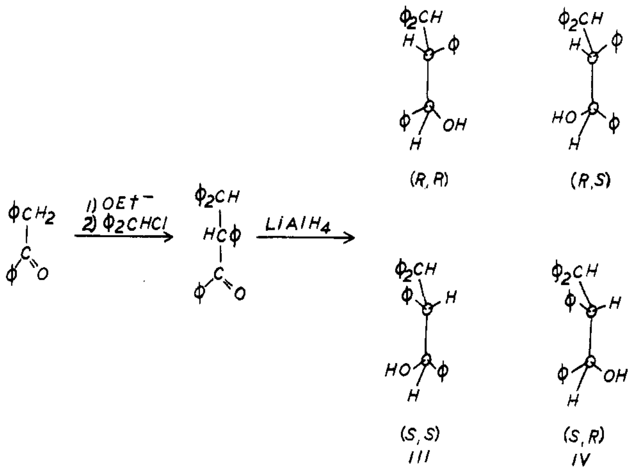
Sofia Pappatheodorou and Clarence G. Stuckwisch[1]

Department of Chemistry, University of Miami, Coral Gables, Fla. 33124

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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[1] To whom correspondence should be addressed.