

0.2% or 0.005° for deuterium; 0.3% or 0.007° for tritium. Other sources of error, namely, the radioactive heat (amounting to  $8.63 \times 10^{-6}$  watt/std. cc. of gas<sup>19</sup>) and possible rapid equilibration between ortho and para forms of tritium seem to be inapplicable in the present measurements.

(19) G. H. Jenks, J. A. Ghormley and F. H. Sweeton, *Phys. Rev.*, **75**, 701 (1949).

### Summary

1. The vapor pressures of hydrogen, deuterium and tritium have been measured up to three atmospheres.

2. Triple points and heats of vaporization and of sublimation have been derived from the vapor pressures.

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## NOTES

### Simple Preparation of Optically Active Secondary Alcohols<sup>1</sup>

By AKSEL A. BOTHNER-BY

It has been well established that reduction of some classes of organic compounds by lithium aluminum hydride is accomplished by transfer of a hydride ion to an electrophilic center of the molecule being reduced.<sup>2</sup> The nature of the ions or neutral molecules donating the hydride ion has not been determined, but a reasonable hypothesis is that in the reduction of a ketone, the forms  $Al(OR)_mH_n$  are present, where  $-OR$  represents the alkoxy group derived from the ketone, and  $m$  and  $n$  are small integers. If this is the case, partial reaction of lithium aluminum hydride with *d*-camphor would give a species capable of asymmetric reduction of ketones. Similar asymmetric reductions have been reported by Vavon and co-workers,<sup>3</sup> Mosher and LaCombe,<sup>4</sup> and Doering.<sup>5</sup> Reductions of methyl ethyl ketone and pinacolone with lithium aluminum hydride-*d*-camphor have been performed. Table I shows for three runs the ketone reduced, the number of moles of lithium aluminum hydride, *d*-camphor and ketone used, and the boiling point and optical activity of the alcohol obtained.

TABLE I

Ketone reduced	Moles			B.p., °C.	[α] <sub>D</sub> <sup>20</sup>
	LiAlH <sub>4</sub>	<i>d</i> -Camphor	Ketone		
Methyl ethyl	0.100	0.200	0.200	99.5-100	+2.50
Pinacolone	.118	.118	.354	118-120	+0.04
Pinacolone	.111	.222	.222	118-120	+0.82

#### Experimental

The reductions were in each case similar to the following: **Optically Active *s*-Butyl Alcohol.**—To a stirred solution of 3.80 g. of lithium aluminum hydride in 300 ml. of ether under nitrogen, was added dropwise a solution of 30.0 g. of *d*-camphor in 50 ml. of ether. Addition required one-half hour. A mixture of 15.0 ml. of methyl ethyl ketone and 50 ml. of ether was then dropped in over one-half hour, followed immediately by 100 ml. of 17% HCl. Stirring was continued until two clear layers were present. The layers were separated, and the ether layer, after drying with calcium

(1) Work done under the auspices of the Atomic Energy Commission.

(2) L. W. Trevoy and W. G. Brown, *THIS JOURNAL*, **71**, 1675 (1949).

(3) (a) Vavon and Angelo, *Compt. rend.*, **224**, 1435 (1947); (b) Vavon, Riviere and Angelo, *ibid.*, **221**, 959 (1946).

(4) Mosher and LaCombe, *THIS JOURNAL*, **72**, 3994 (1950).

(5) W. von E. Doering, *ibid.*, **72**, 631 (1950).

chloride pellets, was fractionated through a small Vigreux column. The *d*-isoborneol solidified in the pot. The distillate was refractionated twice to obtain 10.0 g. of *s*-butyl alcohol;  $n_D^{20}$  1.3975, b.p. 97-100°,  $d_4^{20}$  0.8084.

A subsequent fractionation through a 40-plate column packed with glass helices gave alcohol having  $n_D^{20}$  1.3974, b.p. 99.5-100.0°,  $d_4^{20}$  0.8081,  $[\alpha]_D^{25} +2.50$ °.

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### Δ<sup>5,7</sup>-Steroids. IV.<sup>1</sup> 7-Dehydrocholesteryl Methyl Ether

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In this note we wish to record the preparation in a pure state of 7-dehydrocholesteryl methyl ether from cholesteryl methyl ether *via* the NBS<sup>2</sup> method.<sup>1,3</sup> This compound has been described previously only in the patent literature,<sup>4</sup> and was prepared by a modified Windaus method.<sup>5</sup>

Cholesteryl methyl ether in petroleum ether was brominated with NBS, and the intermediate bromo compound (not isolated) was dehydrobrominated with *s*-collidine in xylene in the usual manner<sup>1</sup> of this Laboratory. This gave a mixture of the desired Δ<sup>5,7</sup>-ether and the expected by-product, Δ<sup>4,6</sup>-cholestadienyl methyl ether. Recrystallization from acetone gave the pure Δ<sup>5,7</sup>-ether, m. p. 123-125°. This m. p. is in contrast to that given by Rosenberg and Turnbull, Jr.,<sup>4</sup> m. p. 109-111°. Our product was further characterized by optical rotatory power, ultraviolet and infrared absorption spectra (Fig. 1, cholesteryl methyl ether included for comparison purposes).

The material in the mother liquors<sup>4</sup> was tri-angulantly recrystallized from acetone and acetone-methanol. This gave an additional quantity of Δ<sup>5,7</sup>-ether, and a constant melting mixture of

(1) Paper I, Bernstein, Sax and SubbaRow, *J. Org. Chem.*, **13**, 837 (1948); Paper II, Bernstein, Binovi, Dorfman, Sax and SubbaRow, *ibid.*, **14**, 433 (1949); Paper III, Bernstein, Oleson, Ritter and Sax, *THIS JOURNAL*, **71**, 2576 (1949).

(2) NBS = N-bromosuccinimide.

(3) Bide and Wilkinson, British Patent 614,194 (Dec. 10, 1948); *C. A.*, **43**, 5810 (1949), have claimed to have prepared several 7-dehydrocholesteryl ethers, *e.g.*, ethyl ether, by the NBS method, but this work is not definitive.

(4) Rosenberg and Turnbull, Jr., U. S. Patent 2,386,636 (Oct. 9, 1945).

(5) Windaus, Lettré and Schenck, *Ann.*, **520**, 98 (1935); Haslewood, *J. Chem. Soc.*, 224 (1938).