

products occurring in initial stages of oxidation of paraffins and olefins. The results seem significant in that they indicate the "initial point of oxygen attack" in the gas-phase oxidation of hydrocarbons.

Experiments were carried out by mixing atom-rich hydrogen from a Wood's discharge tube with a hydrocarbon mixture. The gases reacted at 20° and products were condensed at liquid nitrogen temperature. Results (from experiments with hydrogen, hydrocarbon and oxygen in the ratio of 3:1:1; hydrogen about 60% dissociated; total pressure, 0.4 mm.; total gas velocity, 300-400 cm./sec.) in Table I show the main carbonyl products present from oxidation of C<sub>4</sub> hydrocarbons. Ratios of aldehyde or ketone to hydrocarbon as high as 0.20 resulted.

Hydrocarbon oxidized	TABLE I Main carbonyl products
<i>n</i> -Butane	Acetaldehyde
Isobutane	Acetone, formaldehyde
1-Butene	Propionaldehyde, formaldehyde
1,3-Butadiene	Acrolein, formaldehyde, glyoxal

(Each product was definitely identified by precipitating with 2,4-dinitrophenylhydrazine, separation by fractional recrystallization and determination of melting points and mixed melting points with pure compounds.) The aldehyde or ketone first listed for each particular hydrocarbon was present in largest amount; some formaldehyde was also present in the *n*-butane products. Peroxides and other products were also present.

Insufficient evidence is available to determine the exact mechanism but the results clearly show that oxidation initially occurs at tertiary in preference to secondary and secondary in preference to primary C-H bonds. Oxidation occurs at a double bond if present.

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## RESOLUTION OF AN ALIPHATIC TERTIARY ALCOHOL

Sir:

We wish to report the partial resolution of 2,4-dimethyl-4-hexanol (I, methylethylisobutylcarbinol), apparently the first successful resolution of an aliphatic tertiary alcohol in which the hydroxyl group is attached to the asymmetric carbon atom.<sup>1</sup>

The racemic alcohol I, b. p. 152-153° (760 mm.);  $n_D^{18}$  1.4277;  $n_D^{28}$  1.4234, was synthesized according to Clarke<sup>2</sup> and converted to its hydrogen

(1) Paolini and Divizia, *Atti accad. Lincei*, (5) **23**, 171 (1914), have claimed the partial resolution of *dl*-linalool ( $\alpha = 1.7^\circ$  instead of  $\alpha = 20^\circ$  for the natural product) without furnishing evidence that the optical activity is due to resolved linalool rather than to a resolved impurity.

(2) Clarke, *THIS JOURNAL*, **30**, 1144 (1908), reported b. p. 151° (768 mm.);  $n_D^{18}$  1.4286.

phthalate (II) by adding a benzene solution of the potassium salt of I to a benzene solution of phthalic anhydride according to the general procedure of Fuller and Kenyon.<sup>3</sup> The liquid II was purified by crystallizing its barium salt, m. p. 84-86°, from ether-pentane.

*Anal.* Calcd. for C<sub>32</sub>H<sub>42</sub>O<sub>8</sub>Ba·H<sub>2</sub>O: C, 54.13; H, 6.25; Ba, 19.35. Found: C, 54.38; H, 6.54; Ba, 18.94.

The brucine salt from 139 g. of II, m. p. 139.5-140.5° (A),  $[\alpha]_D^{28} - 7.8^\circ$  [ $c = 6.3\%$ ],<sup>4</sup> crystallized in heavy prisms from acetone. After a fourteen-step systematic fractional crystallization, the brucine salt, m. p. 141-142° (B), comprising the head fraction crystallized as tight, hemispherical pellets,  $[\alpha]_D^{26} - 4.8^\circ$  [ $c = 9.8\%$ ].<sup>4</sup>

*Anal.* Calcd. for C<sub>39</sub>H<sub>48</sub>O<sub>8</sub>N<sub>2</sub>: C, 69.62; H, 7.19; N, 4.16. Found: C, 69.91, 70.32; H, 7.04, 7.15; N, 4.59, 4.11.

On regeneration the brucine salt (B) gave II,  $[\alpha]_D^{26} + 7.3^\circ$  [ $c = 8.0\%$ ,  $\alpha = 0.59^\circ$ ]. The curve obtained by melting mixtures of A and B showed a minimum at 136° indicating that A is a 1:1 compound of brucine -(+)-II and brucine -(-)-II.

The recovery of I was effected by adding an ethereal solution of 9.0 g. of II,  $[\alpha]_D^{27} + 5.5^\circ$  [ $c = 8.5\%$ ],<sup>4</sup> to six equivalents of ethylmagnesium bromide. The optically active I (2.0 g.) had the following properties: b. p. 78-80° (52 mm.); 152° (760 mm.);  $n_D^{18}$  1.4259;  $[\alpha]_D^{27} - 2.6^\circ$  [ $c = 5.1\%$ ,  $\alpha = -0.13^\circ$ ].

*Anal.* Calcd. for C<sub>8</sub>H<sub>18</sub>O: C, 73.78; H, 13.93. Found: C, 73.55; H, 14.02.

During the preliminary distillation of the (-)-I there was formed some olefin, b. p. 112-115°, which showed no optical activity. A sample of II, 13.7 g.,  $[\alpha]_D^{28} - 2.7^\circ$  [ $c = 5.1\%$ ],<sup>4</sup> from the tail fraction gave (+)-I (2.7 g.),  $[\alpha]_D^{28} + 1.5^\circ$  [ $c = 5.9\%$ ,  $\alpha = 0.09^\circ$ ]; b. p. 152° (760 mm.);  $n_D^{28}$  1.4234.

The infrared spectra of racemic I, partially resolved (+)-I and partially resolved (-)-I were identical in all details between 700 and 4000 wave numbers. We are indebted to Professor Ralph S. Halford and to Mr. Abraham Savitzky for these measurements.

(3) Fuller and Kenyon, *J. Chem. Soc.*, **125**, 2304 (1924).

(4) All optical rotations were measured in 95% ethanol.

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## PENICILLIN AMIDE

Sir:

In considering methods for obtaining the amide of penicillin, both the symmetrical anhydride<sup>1</sup> and a mixed penicillin anhydride were considered as

(1) Carpenter, *THIS JOURNAL*, **70**, 2964 (1948).