

shown by enzymatic and microbiological<sup>3</sup> assay to contain 50% L-lysine.

The conversion of D-lysine to L-lysine can be demonstrated manometrically by carrying out the racemization in the presence of L-lysine decarboxylase, as illustrated in Table II.

TABLE II

RACEMIZATION OF D-LYSINE BY LYOPHILIZED CELLS OF *Proteus vulgaris*

Reaction system	CO <sub>2</sub> evolved $\mu\text{M}/\text{flask}$	Residual lysine <sup>b</sup>
Complete	16.5	2.7
Minus lyophilized cells	0.7 <sup>c</sup>	20.1
Minus decarboxylase	0.0	21.0

<sup>a</sup> A Warburg flask containing 13 mg. of lyophilized cells and 20  $\mu\text{M}$  of D-lysine in 2 ml. of 0.2 M potassium phosphate buffer (pH 5.8), and 5 mg. of L-lysine decarboxylase<sup>2</sup> in 0.5 ml. of buffer was incubated at 37° for 2.5 hours; the reaction was stopped by heating contents for 2 minutes at 100°. <sup>b</sup> Quantitative paper chromatography. <sup>c</sup> The sample of D-lysine contained (enzymatic assay) about 5% L-lysine.

The simplest explanation of these results is that *Proteus vulgaris* contains a lysine racemase.

(3) With *Leuconostoc mesenteroides* P-60.

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#### THE ADDITION OF HYDROGEN ATOMS TO SOLID OLEFINS AT -195°\*

Sir:

The addition of H atoms to olefins in the gas phase at low temperatures is known to occur.<sup>1</sup> In an attempt to prepare free radicals in a condensed matrix, solid olefins were exposed at -195° to H atoms.<sup>2</sup> It was found that the H atom addition occurs and that the rate of hydrogen uptake depends strongly upon the olefin.

The experimental technique used in investigating this reaction consisted of exposing the olefin, uniformly deposited on the inner surface of a spherical, one-liter bulb immersed in liquid nitrogen, to the H atoms formed on an incandescent tungsten ribbon.<sup>3</sup> The olefin was introduced into an evacuated one-liter reaction vessel to a pressure of 2 mm. and condensed on the surface of a liquid nitrogen filled 2 cc. bulb, positioned near the center of the reaction vessel. The entire reaction vessel was immersed in liquid nitrogen and the refrigerant in the 2-cc. bulb evaporated. In this way the olefin was uniformly deposited on the reaction vessel walls. Pure hydrogen was introduced by diffusion through a heated palladium thimble. The tungsten ribbon centrally located in the vessel was heated to 1800° to produce H atoms. They reach the walls without recombining. The reaction with the olefin was followed by the pressure decrease.

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(1) K. H. Gelb and P. Harteck, *Ber.*, **66B**, 1815 (1933).

(2) F. O. Rice and M. Freamo, *THIS JOURNAL*, **75**, 548 (1953), have previously reported an attempt to hydrogenate a solid at liquid nitrogen temperature by irradiation with H atoms.

(3) I. Langmuir, *ibid.*, **34**, 1310 (1912); **36**, 417 (1915).

Rates of pressure decrease were observed for propylene, butene-1, isobutene, butadiene-1,3, pentene-1 and hexene-1. Thirty microns of hydrogen reacted completely with propylene in eight seconds. Butene-1 and isobutene reacted  $1/3$  and  $1/20$  as fast, respectively. Butadiene-1,3 and pentene-1 reacted very slowly and incompletely. Hexene-1 showed no measurable reaction. An analysis of the products of the hydrogen addition to butene-1 showed that *n*-butane, butene-2 and 3,4-dimethylhexane were formed. These results indicate that H atoms add to the terminal carbon of butene-1 to give secondary butyl radicals.<sup>4</sup> 3,4-Dimethylhexane results from dimerization while *n*-butane and butene-2 arise from a disproportionation reaction. H atom addition to butyl radicals to give *n*-butane cannot be excluded.

At least 80% of the propylene, butene-1 and isobutene could be hydrogenated at liquid nitrogen temperatures. It is apparent that considerable reaction has occurred throughout the bulk of the solid and that diffusion processes are operative. Either H atoms diffuse interstitially, or an H atom transfer from an alkyl radical to the olefin may effectively transport H atoms through the condensed phase.

This interpretation is valid provided the olefin does not reach the hot tungsten ribbon. A control experiment was performed using butene-1 and helium instead of hydrogen. The initially deposited butene-1 was the only hydrocarbon found after warm-up. It can be concluded that heat transfer from the ribbon to the surface was insufficient to evaporate the butene-1.

There is no doubt that H atom addition to some solid olefins can occur at -195°. The analytical results indicate clearly that alkyl radicals were formed. It cannot yet be stated whether these radicals are stabilized in an olefin matrix and undergo reaction on warm-up, or that they exist only in small stationary state concentrations.

(4) W. J. Moore and L. A. Wall (*J. Chem. Phys.*, **17**, 1335 (1949)) obtained similar results from a mercury sensitized hydrogenation of butene in the gas phase.

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#### THE STRUCTURE OF CITROSTADIENOL, A NATURAL 4 $\alpha$ -METHYLSTEROL

Sir:

The isolation of citrostadienol [C<sub>30</sub>H<sub>50</sub>O  $\pm$  CH<sub>2</sub>; m.p. 162-164°, [ $\alpha$ ]<sub>D</sub> +24° (all rotations in chloroform)] from Israeli grapefruit and orange peel-oil was reported recently.<sup>1</sup> The substance (a companion of  $\beta$ -sitosterol) appeared to be a doubly unsaturated 3 $\beta$ -hydroxy-steroid, except that the optical rotation data resembled those of the tetracyclic triterpenes rather than the steroids. We have now shown citrostadienol to be 4 $\alpha$ -methyl- $\Delta^{7,24(28)}$ -stigmastadien-3 $\beta$ -ol (4 $\alpha$ -methyl-24-ethylidene- $\Delta^7$ -cholesten-3 $\beta$ -ol) (I).

(1) A. Welzmann and Y. Mazur, *J. Org. Chem.*, in press.