The enhancement disappeared on standing for two to four days at room temperature, but could be restored by further irradiation. Feebly catalytic samples, prepared by annealing the standard preparation at 200° without further pumping, showed a several thousandfold increase in activity when irradiated, but the increase disappeared in a few hours, even at −78°. Irradiation during activity measurement on the assumption that short-lived states might play a role as in photosensitization gave results not greatly different from those irradiated *in vacuo* between measurements, indicating that short-lived states need not be invoked.

The reality of the radiation effect is attested by some 49 separate irradiations which produced in 38 cases appreciable increase in activity. Some instances of lack of change appear to indicate saturation of the effect, while some decreases are thought to have resulted from poisoning. No activity was induced by gamma rays in samples that had not been activated in the manner described above.

The high rate of change of activity with irradiation and the ready annealing of the change suggest that the effects observed may be attributable to electrons or positive holes trapped in special sites in the alumina lattice. Experiments intended to show more about the phenomena are in progress.

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THE STABILITY RELATIONSHIP OF 1-METHYLCYCLOPENTENE AND METHYLENECYCLOPENTANE

Sir:

Evidence bearing on the problem of stability differences that exist between isomers possessing exocyclic and endocyclic double bonds in 5- and 6-membered ring systems has been summarized by Brown, Brewster and Shechter.[1] The conclusions reached by these authors are expressed in the generalization that "reactions will proceed in such a manner as to favor the formation or retention of an exo double bond in the 5-ring and to avoid the formation or retention of the exo double bond in the 6-ring systems." Although the position adopted with respect to 6-membered ring compounds is well-supported,[2] evidence available concerning the 5-ring cases is less convincing.

In connection with a general study of heats of catalytic hydrogenation in solution, currently in progress in this Laboratory, we have had an opportunity to examine the heat changes accompanying hydrogenations of 1-methylcyclohexene, methylenecyclohexane, 1-methylcyclopentene, and methylenecyclopentane. The results obtained for these substances are listed in Table I. In each isomer pair the methylenecycloalkane shows a higher heat of hydrogenation than does the 1-methylcycloalkene, the differences being 2.1 kcal./mole for the 6-membered, and 3.8 kcal./mole for the 5-membered ring compounds. Since these values reflect differences in heat content rather than in free energy, we were prompted to investigate the equilibrium behavior of the methylene derivatives in the presence of acid. Our results for methylenecyclohexane are in complete accord with those of Wallach and his associates,[2] and it was further established that in acetic acid containing *p*-toluenesulfonic acid methylenecyclopentane is converted essentially quantitatively into 1-methylcyclopentene. The amounts of methylenecyclopentane present in the equilibrated product are too small to be detectable by infrared analysis, although trace contamination by acetate ester is indicated. The conclusion that 1-methylcyclopentene is *more* stable than methylenecyclopentane is therefore inescapable.

TABLE I

HEATS OF HYDROGENATION IN ACETIC ACID SOLUTION (25° C.)

Compound	$-\Delta H$, kcal./mole
1-Methylcyclohexene	25.70 ± 0.10
Methylenecyclohexane	27.82 ± 0.07
1-Methylcyclopentene	23.01 ± 0.04
Methylenecyclopentane	26.82 ± 0.08

A complete report of this work will be published shortly.

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RECEIVED DECEMBER 6, 1956

(1) H. C. Brown, J. H. Brewster and H. Shechter, THIS JOURNAL, **76**, 467 (1954).

(2) Of special relevance is the demonstration of O. Wallach, E. Evans, J. B. Churchill, M. Rentschler and H. Mallison, *Ann.*, **360**, 26 (1908), that various alkylidenecyclohexanes are converted into the corresponding 1-alkylcyclohexenes by the action of acid.

BOOK REVIEWS

Statistical Mechanics. Principles and Selected Applications. By TERRELL L. HILL, Naval Medical Research Institute, Bethesda, Maryland. McGraw-Hill Book Company, Inc., 330 West 42nd Street, New York 56, N. Y. 1956. xiii + 432 pp. 16 × 23.5 cm. Price, $9.00.

This book gives an excellent discussion of some of the recent advances which have been made in the applications of statistical mechanics. According to the author, "the primary aim of this volume is to provide a rather detailed account of a selected group of these developments, namely, fluctuation theory, imperfect gas and condensation theory, distribution functions, nearest neighbor (Ising) statistics, and free volume and hole theories of liquids and solids."

The book opens with introductory chapters on classical statistical mechanics, quantum statistical mechanics, and the relation of statistical mechanics to thermodynamics. The