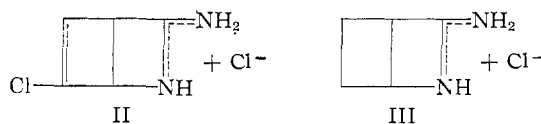


violet light above 240 $m\mu$, with only end absorption below 240 $m\mu$ (ϵ , 5600 at 220 $m\mu$). The n.m.r. spectrum of this reduction product shows a broad hydrogen peak ($\tau = 7.89$) and a pair of doublets ($\tau = 5.79, 5.66$ and $5.29, 5.15$), typical of an AB pattern. Integration showed that there are twice as many hydrogen atoms under the broad peak as in the combined doublets. Although the reduction product (as the hydrochloride), in contrast to the photoisomer, was stable upon prolonged standing in aqueous solution, addition of 0.1 *N* sodium hydroxide at room temperature resulted in the separation within two minutes and in essentially quantitative yield of a compound which, on the basis of all available evidence, appears to be *cis*-2-aminocyclobutanecarboxamide IV, (m.p. 253–255°; *Anal.* Calcd. for $C_5H_{10}N_2O$: C, 52.6; H, 8.8; N, 24.5; mol. wt., 114. Found: C, 52.95; H, 9.0; N, 24.9; mol. wt. (in glacial HOAc), 99).

On the basis of the above considerations, we feel that the photoisomer of I can only be represented by structure II, and that the reduction product must be represented by structure III. The conversion of I to II represents the first example of a valence-bond tautomerism in a six-membered aromatic system. The reaction appears to be general, for similar photoisomers were obtained from 2-aminopyridine and 2-amino-5-bromopyridine; catalytic reduction in each case yielded compound III. Furthermore, the conversion of II to IV in an over-all yield of greater than 95% promises to be representative of an extraordinarily simple route to cyclobutane derivatives. Extensions of this new photoisomerization reaction to other systems and the chemistry of the photo products are under active exploration.



Acknowledgment.—This work was supported by a research grant (CY-2551) to Princeton University from the National Cancer Institute, National Institutes of Health, U. S. Public Health Service.

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RECEIVED MAY 12, 1961

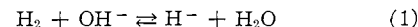
BASE CATALYZED HOMOGENEOUS HYDROGENATION

Sir:

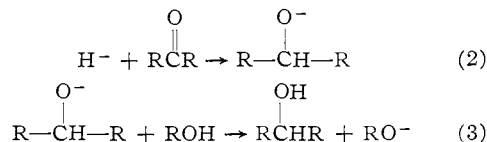
Although the reaction of molecular hydrogen with unsaturated organic molecules at moderate temperatures is generally energetically feasible, a potential barrier to the process exists which is only overcome by the use of heterogeneous catalysts or certain transition-metal complexes in homogeneous systems.¹

Two groups of observations of long standing in the literature suggested to us that simple basic catalysis of homogeneous hydrogenation also

might be achieved in suitable systems. The first of these is the base catalyzed exchange between D_2 and water,² which is pictured most easily in terms of the (admittedly very unfavorable) equilibrium



Conceivably, the small amount of hydride ion present in strongly basic systems might accomplish the reduction of an organic molecule via a sequence such as



Second, a considerable number of reactions are known in which the treatment of organic molecules with strong bases at elevated temperatures leads to oxidation with evolution of molecular hydrogen. Perhaps the oldest is the Varrentrapp reaction in which caustic fusion of oleic acid produces hydrogen, palmitic acid and acetic acid.³ Since at least one step in these processes involves dehydrogenation, they may be considered as simply the back reactions of a based catalyzed hydrogenations.

TABLE I

BASE CATALYZED HYDROGENATIONS IN *tert*-BUTYL ALCOHOL

Substrate	<i>T</i> (°C.)	H_2 (lb./in. ²)	Time, hr.	$KOC_4H_9^a$	Yield, ^b %
Benzophenone	200	1300	70	0.5	50–60
Benzophenone	180	2000	16	0	—
Benzophenone	195	1900	31	0.25	40–50
Benzophenone	230	2560	15	0	—
Benzophenone	230	2560	15	0.2	+ ^d
Benzophenone	170	2100	25	0.05	(–) ^c
Nitrobenzene	160	1900	45	0.1	+
Nitrobenzene	160	2000	49	0	—

^a Moles/mole substrate. ^b (+) indicates reduction, but yield not determined; (–) indicates no reaction. ^c Small pressure drop, but no reduction products definitely identified. ^d Teflon liner in vessel.

We now report such a base-catalyzed homogeneous hydrogenation, achieved by heating benzophenone in *tert*-butyl alcohol solution containing potassium *tert*-butoxide at 200° under 1300–2000 lb./in.² hydrogen pressure. Hydrogen is slowly absorbed and benzhydrol obtained in 40–60% yield, determined by gas chromatography, and identified by retention time, infrared spectra, and mixed melting point. No further reduction to diphenylmethane is detected.

Experiments were carried out in a small conventional stirred autoclave with nickel liner, and the effects of variables are shown in Table I. Hydrogen, *tert*-butoxide and an elevated temperature are all required for the reaction. The possibility of heterogeneous catalysis by the nickel liner is eliminated by the successful experiment using a Teflon liner.

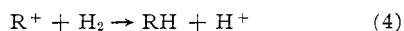
(2) K. Wirtz and K. F. Bonhoeffer, *Z. physik Chem.*, **177A**, 1 (1936); W. K. Wilmarth, J. C. Dayton and J. M. Flournoy, *J. Am. Chem. Soc.*, **75**, 4549 (1953); S. L. Miller and D. Rittenberg, *ibid.*, **80**, 64 (1958).

(3) F. Varrentrapp, *Liebigs Ann.*, **35**, 196 (1840). For more recent work, cf. R. G. Ackman, P. Linstead, B. J. Wakefield and B. C. L. Linstead, *Tetrahedron*, **8**, 221 (1960).

(1) For a review and discussion, cf. J. Halpern, *Advances in Catalysis*, **9**, 302 (1957).

While our reaction is significant in indicating a possible simple hydride ion path for hydrogenation, it is obviously limited to molecules stable under rather drastic basic conditions. We have observed a partial reduction of nitrobenzene to aniline at 160°, but acetone appears to give only aldol condensation products with little if any hydrogen uptake. We are currently exploring additional systems.

In the base catalyzed reaction we believe it is the hydrogen which is activated by conversion to hydride ion. An acid catalyzed process involving activation of the organic molecule by conversion to a carbonium ion is also conceivable.



Reaction (4) is energetically unfavorable in the gas phase by 80–100 kcal./mole but could perhaps proceed to the right in highly polar solvents by virtue of the very high solvation energy of the proton produced. Indeed, a number of examples of the modifying effect of hydrogen on $AlCl_3$ catalyzed carbonium ion reactions suggest that this may be the case.⁴

(4) Cf. for example the modifying action of hydrogen on $AlCl_3$ catalyzed hydrocarbon isomerizations, V. N. Ipatieff and L. Schmerling, *Ind. Eng. Chem.*, **40**, 2354 (1948).

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RECEIVED MAY 20, 1961

BOOK REVIEWS

Radioactive Isotopes in Biochemistry. By ENGELBERT BRODA, Professor of Chemistry, University of Vienna (Austria). D. Van Nostrand Company, Inc., 120 Alexander Street, Princeton, New Jersey. 1960. X + 376 pp. 15.5 × 23 cm. Price, \$11.50.

This book is a remarkably concise survey of principles of methodology in the use of radioactive tracers and their application to selected problems in biochemistry. The author avowedly makes no pretense to completeness in any direction. The admitted deficiencies in detail are compensated for to a large extent by more than 3200 references to the original literature, including many of the latest pertinent papers.

The first third of the text is devoted to eight chapters dealing with radioelements in biochemistry, principles of radiochemistry, radiosynthesis, isotope effects, radiation chemistry, radiation biology, protection against radiation, and measurement of radioactivity. This is followed by two chapters on the application of radioactivity to analysis of living matter and absorption and excretion of elements.

The last half of the book entails six well organized chapters on the principal problems and special topics in intermediary metabolism.

The English translation reveals a sound grasp of and feeling for both the original German and English idiom.

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Lectures on Theoretical Rheology. Third Edition. By MARKUS REINER, Dr. Techn., Professor of Applied Mechanics, Israel Institute of Technology, Member of the Israel Academy of Sciences, Sometime Research Professor, Lafayette College, Easton, Pa. Interscience Publishers, Inc., 250 Fifth Avenue, New York 1, N. Y. 1960. xvi + 158 pp. 15 × 21.5 cm. Price, \$4.85.

This revision of Professor Reiner's earlier twelve lectures (and still earlier ten lectures) is a concise and most readable introduction to a number of topics in the area of rheology. A variety of interesting historical notes are included and are of special interest in that they represent the pertinent comments, unavailable elsewhere, of one of the founders of this area of science.

The differences between this edition and the previous one are largely in the area of readability. Of the three new chapters which have been added one is confined to background calculus and algebra; the other two are very brief

discussions of normal stresses. If one excludes Professor Reiner's own numerous publications, only five or six papers out of a bibliography of perhaps a hundred were published more recently than 1945. Obviously the book was not intended to reflect the scope or results of current research. Neither is the book an encyclopedic compendium of earlier results. However, the reader who is interested in both mathematical and experimental work will find the book a readable and worthwhile introduction to the subject. Professor Reiner's exposition is very lucid and clear and the book appears to be essentially free of typographical errors except for the frequent but usually obvious omission of the dot over a symbol, used to indicate a derivative. The inclusion of pertinent background material in calculus and in fluid mechanics suggest it will be of especial interest to chemists. This reviewer would guess that any scientist becoming interested in rheology in more than an empirical way will want a personal copy of this book if he does not already own the previous edition.

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Preparativní Reakce V Organické Chemii. Díl V. Aldolisace a příbuzné reakce. By INŽ. DR. JAROMÍR PLEŠEK and INŽ. ALENA ZOBÁČOVÁ za redakce inž. dr. Miloše Hudlického. Nakladatelství Československé Akademie Věd, Vodičkova 40, Praha 2, Czechoslovakia. 1960. 976 pp. 18.5 × 24.5 cm. Price, Kčs 89,—.

"Aldolization and Related Reactions" is the fifth volume in a series entitled "Preparative Reactions in Organic Chemistry" published by the chemical section of the Czechoslovak Academy of Sciences. The authors of the present volume have attempted to present a comprehensive review of the theoretical and preparative aspects of the acid- and base-catalyzed addition of active hydrogen compounds to aldehydes and ketones, or their functional derivatives. The selection of material for inclusion in the book has been made on the basis of the similarity of reaction mechanisms. All types of synthetic organic reactions involving the addition of active hydrogen compounds to carbonyl groups are included. The book contains chapters on the addition of acetylenes to carbonyl compounds, synthesis of cyanohydrins, Strecker synthesis of α -aminoacids, reactions of nitroparaffins with carbonyl compounds, reactions of aldehydes with alkyl derivatives of heterocyclic compounds, reactions of carbonyl compounds with "ylids" and triaryl-