TABLE I

SOME HYDROXY PEROXIDES

Peroxide	Formula	Active oxygen, % Calcd.	Found	
Hydroxy dicarbethoxymethyl[a]	$C_7H_{12}O_7$	7.7	7.55	
Di-[hydroxy dicarbethoxymethyl][b]	$C_{14}H_{22}O_{12}$	4.19	4.24	4.19
α,α'-Dihydroxydiisoamyl	$C_{10}H_{22}O_4$	7.76	7.60	
α,α'-Dihydroxydi-*n*-hexyl[c]	$C_{12}H_{26}O_4$	6.84	6.69	

[a] d^{29}_{29} 1.226; $n^{27}D$ 1.4392.
[b] d^{29}_{29} 1.216; $n^{27}D$ 1.4388.
[c] M. p. 62–63°.

yields from aqueous 30% hydrogen peroxide and *n*-hexaldehyde.

DEPARTMENT OF CHEMISTRY NICHOLAS A. MILAS
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RECEIVED DECEMBER 31, 1945

(3) From Part I of Ph.D. Thesis, M. I. T., 1939.

Diperoxalic Acid

When oxalyl chloride[1] was treated at 0° with an ice–sodium peroxide mixture, it was hoped to obtain a carbon peroxide, O=C—C=O, or one of its polymers, $\left[\begin{array}{l}O{=}C{-}C{=}O\\ \quad|\quad|\\ \quad O\quad O\end{array}\right]_x$. Neither one of these peroxides was obtained, but instead a small yield of diperoxalic acid. A higher yield of this diperacid was obtained by the following, somewhat different, procedure: To a solution of 19 g. of dry pyridine, 285 cc. of anhydrous ether containing 4 g. of hydrogen peroxide and maintained at −20°, was added, dropwise in the course of two hours and with vigorous stirring, a precooled (−10°) solution of 75 cc. of anhydrous ether containing 14.3 g. of oxalyl chloride. At the end of the reaction, the ether layer was decanted and the solid precipitate, which had separated out, extracted with two 100-cc. portions of anhydrous ether. The residue was then treated with an ice-cold mixture of 60 cc. of saturated sodium sulfate solution and 40 cc. of 85% orthophosphoric acid. The resulting mixture, after adding more solid sodium sulfate, was extracted with three 100-cc. portions of acetone which was combined with an equal volume of ether and the mixture dried and filtered. When the solvent was removed under reduced pressure, a highly viscous residue (2.2 g.) remained which failed to crystallize on standing for some time at 0°. This product was free from chlorine and nitrogenous products, and was found to be very soluble in water and chloroform. Diperoxalic acid is a powerful oxidizing agent, and, when treated with potassium iodide, it is reduced rapidly to oxalic acid.

Anal. Calcd. for $C_2H_2O_6$: (O), 26.3. Found: (O), 25.4, 25.7.

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RECEIVED DECEMBER 31, 1945

(1) Prepared according to Staudinger, *Ber.*, **41**, 3563 (1908).

(2) From Part I of Ph.D. Thesis, M. I. T., 1939. Present address: Lowell Textile Institute, Lowell, Mass.

COMMUNICATIONS TO THE EDITOR

3-*n*-PENTADECYLCATECHOL

Sir:

Recently the synthesis of 3-*n*-pentadecylcatechol (Hydrourushiol) was described by H. S. Mason.[1] This compound, the dimethyl ether of which was first synthesized in low yield about thirty years ago by Majima and Tahara,[2] and later by Backer and Haack,[3] has attracted considerable interest in view of its close relationship to poison ivy "urushiol." The scheme of synthesis which Mason found gave the best results was essentially that employed by Backer and Haack for the preparation of the dimethyl ether. However, Mason markedly improved the yields over those reported by Backer and Haack, and carried the synthesis one step further by cleaving the dimethyl ether to obtain the catechol compound.

In view of the current interest in 3-*n*-pentadecylcatechol, because of its possible use as a standard agent for the diagnosis and therapy of poison ivy dermatitis, we are prompted to point out that it was synthesized in our laboratory in minimum over-all yield of 57% from *o*-veratraldehyde over two years ago. The synthesis was not published at that time inasmuch as it was a duplication of the work of Backer and Haack except for the improved yields and the additional ether cleavage step. However, the fact that we had synthesized 3-*n*-pentadecylcatechol was made clear in a later article.[4] Furthermore, the data in this article showing the 100% correlation of hypersensitiveness to poison ivy and to standard acetone solutions of 3-*n*-pentadecylcatechol involving patch tests on 21 patients made obvious the possible use of this synthetic compound as a standard agent for the diagnosis and therapy of poison ivy dermatitis. It would appear that Mason overlooked this article since no reference to it was made in his description of the synthesis nor in his statements in regard to the use of 3-*n*-pentadecylcatechol as a standard allergen.

(1) Mason, THIS JOURNAL, **67**, 1538 (1945).
(2) Majima and Tahara, *Ber.*, **48**, 1606 (1915).
(3) Backer and Haack, *Rec. trav. chim.*, **57**, 225 (1938).
(4) Keil, Wasserman and Dawson, *J. Exptl. Med.*, **80**, 275 (1944.)

Since our method of cleaving the dimethyl ether gives comparable, if not better, yields of pure 3-*n*-pentadecylcatechol, and takes less time and effort than the procedure described by Mason, it seems worth while to outline it here in some detail.

The cleavage of the 3-*n*-pentadecylveratrole to yield pure 3-*n*-pentadecylcatechol was best accomplished in the following way. Three grams of the veratrole compound, 3 g. of anhydrous aluminum chloride and 30 cc. of dry chlorobenzene were refluxed for three hours, cooled, poured on ice, washed with 50% methanol solution, and the chlorobenzene layer evaporated under vacuum. The residue on molecular distillation yielded 2.5 g. (91%) of crude catechol compound melting at 52–59°. After three recrystallizations from petroleum ether, 2.1 g. (76%) of pure 3-*n*-pentadecylcatechol melting at 59–60° was obtained in the form of short white needles.

Anal. Calcd. for $C_{21}H_{36}O_2$: C, 78.69; H, 11.32. Found: C, 78.97; H, 11.30.

In the conversion of *o*-veratraldehyde to pure 3-*n*-pentadecylcatechol, an over-all yield of 57% was obtained.

During the past two years we have been using 3-*n*-pentadecylcatechol as a standard agent for the diagnosis of poison ivy hypersensitiveness and for demonstrating cross reactivity between poison ivy and other members of the anacardiaceae.[4,5,6,7] The optimal concentrations for these tests were found to lie between 0.1 and 1.0% in a suitable non-irritating carrier such as acetone or isoamyl acetate.

(5) Keil, Wasserman and Dawson, *Science*, **102**, 279 (1945).
(6) Keil, Wasserman and Dawson, *Indust. Med.*, **14**, 285 (1945).
(7) Keil, Wasserman and Dawson, *J. Allergy*, **16**, 275 (1945).

DEPARTMENT OF CHEMISTRY CHARLES R. DAWSON
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RECEIVED SEPTEMBER 24, 1945

CONCERNING A PROPOSED MODIFICATION OF THE BRUNAUER-EMMETT-TELLER THEORY OF MULTIMOLECULAR ADSORPTION

Sir:

In a recent paper, Pickett[1] proposed a modification of the BET[2] theory of multimolecular adsorption. This modification does not affect the familiar equation

$$\frac{v}{v_m} = \frac{cx}{(1 - x)(1 - x + cx)} \qquad (1)$$

which holds for adsorption on a free surface. It applies, rather, to adsorption in those cases where the maximum number of adsorbed layers (n) is restricted.

(1) Gerald Pickett, THIS JOURNAL, **67**, 1958 (1945).
(2) S. Brunauer, P. H. Emmett and E. Teller, *ibid.*, **60**, 309 (1938).

When n is finite, the BET theory does not predict complete filling of capillaries at saturation pressure. This is generally considered to be an unsatisfactory feature of the theory. Pickett's modification eliminates this feature and seems to improve the range of agreement with experimental data in a number of cases.

The equations obtained by Pickett follow from his assumption that there is a "decrease in probability of escape from an elemental area covered with n layers (the maximum number possible in the limited space) as adjacent elemental areas also become covered with n layers." Specifically, he assumes that the probability of escape from the n-th layer is reduced by a factor of $1 - x$. It is pointed out that there is an alternative but logically equivalent way of expressing this assumption. Since the two alternatives are equivalent we shall confine our attention to the first statement, given above, as it is more amenable to analysis (the second statement has a certain intuitive appeal but is more difficult to interpret).

It appears to the present writer that Pickett's assumption can be criticized on the following grounds:

(1) If there is a decrease in probability of escape from an elemental area covered with n layers as adjacent elemental areas become covered with n layers, there is also a decrease in probability of escape from elemental areas covered with 1, 2, 3 . . ., layers as adjacent elemental areas become covered with n layers.

(2) If there is a decrease in probability of escape (rate of evaporation) as adjacent elemental areas become covered with n layers, there is also an identical decrease in the rate of condensation, according to the principle of microscopic reversibility. Hence, multiplying only the right-hand member of the equation

$$as_{n-1}p = bs_n e^{-E_L/RT} \qquad (2)$$

by the factor $1 - x$ is not justified. The same is true if, in Equation (2), n is replaced by 1, 2, 3, . . . (when n is replaced by 1, E_L is replaced by E_1).

(3) Even if the multiplication of the right-hand member of Equation (2) by a factor were justified, the function $1 - x$ seems to be advantageous only because it has (a) simplicity, (b) "correct" boundary values, and (c) it allows the fundamental assumption to be restated in the alternative form mentioned above.

(4) A treatment of the problem, using statistical mechanics,[3] leads to the BET result rather than to the result obtained by Pickett. In the statistical treatment, no assumptions regarding mechanism need be made. It suffices to consider only possible states of the system.

The conclusion of the present writer is that, although Pickett's equations may improve the agreement with experimental data in some cases,

(3) T. L. Hill, *J. Chem. Phys.*, in press.

his modification should not be considered a really fundamental improvement over the BET theory.

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RECEIVED DECEMBER 10, 1945

STREPTOMYCES ANTIBIOTICS. V. N-METHYL-*l*-GLUCOSAMINE FROM STREPTOMYCIN

Sir:

Streptomycin has been degraded to a new product which has been established as N-methyl-*l*-glucosamine.

Acid hydrolysis of methyl streptobiosaminide dimethyl acetal[1] followed by acetylation yielded a pentaacetyl derivative of a hexosamine; m. p. 160.5–161.5° (micro-block), $[\alpha]^{25}D$ −100° (*c*, 0.7 in chloroform). *Anal.* Calcd. for $C_{17}H_{25}NO_{10}$: C, 50.62; H, 6.25; N, 3.47; CH_3CO, 53.3; mol. wt., 403. Found: C, 50.51; H, 6.24; N, 3.76; CH_3CO, 49.2; mol. wt., 414 (cryoscopic in benzene). The hydrochloride of the hexosamine was obtained from the pentaacetyl derivative by hydrolysis with hydrochloric acid; m. p. 160–163° (micro-block), $[\alpha]^{25}D$ −103° (initial), −88° (final) (*c*, 0.6 in water). *Anal.* Calcd. for $C_7H_{15}NO_5 \cdot HCl$: C, 36.60; H, 7.02; CH_3N, 6.5. Found: C, 36.65; H, 6.86; CH_3N, 6.8. Treatment of the hydrochloride with silver oxide gave the free base as a colorless gum; $[\alpha]^{25}D$ −65° (*c*, 1.0 in methanol). Acetylation of the free base in the presence of methanol gave the N-acetyl derivative; m. p. 165–166° (micro-block), $[\alpha]^{25}D$ −51° (*c*, 0.4 in water).

The phenylosazone prepared from the hexosamine melted at 205° (capill.).[2] A phenylosotriazole, prepared[3] from this osazone, melted at the same temperature (196–197°) as the corresponding derivative of *d*-glucose, and the specific rotation was of equal magnitude but opposite in sign.

Oxidation of the free hexosamine with mercuric oxide gave an acid which had the same melting point (m. p. 230–232°) reported for N-methyl-*d*-glucosamic acid.[4] Again, the rotation was of the same magnitude but opposite sign.

Hydrolysis of the product of the reaction between *l*-arabinose, methylamine and hydrogen cyanide gave an acid which was identical with the "natural" acid described above. When the synthetic acid was converted to the lactone, reduced and acetylated, the product was found to be identical with the pentaacetyl derivative of the "natural" hexosamine. Thus, the configurations about C_3, C_4, and C_5 of the hexosamine are those at carbons 2, 3, and 4 of *l*-arabinose (or carbons 3, 4 and 5 of *l*-glucose).

Methylation of *d*-glucosamine, followed by acetylation, yielded pentaacetyl-N-methyl-*d*-glucosamine; m. p. 160.5–161.5° (micro-block), $[\alpha]^{25}D$ +101°. The properties of this compound are identical with those of the pentaacetyl derivative described above except for the sign of rotation.

With these data and the reported configuration of carbon atom 2 of *d*-glucosamine,[5] it is concluded that the configuration at carbon atom 2 of the hexosamine is also that of *l*-glucose and the degradation product is N-methyl-*l*-glucosamine.

(1) Brink, Kuehl and Folkers, *Science*, **102**, 506 (1945).

(2) *l*-Glucose phenylosazone, m. p. 205°; Fischer, *Ber.*, **23**, 374 (1890).

(3) Haskins, Hann and Hudson, THIS JOURNAL, **67**, 939 (1945).

(4) Votoček and Lukeš, *Chem. Listy*, **29**, 308 (1935).

(5) Haworth, Lake and Peat, *J. Chem. Soc.*, 271 (1939).

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RECEIVED FEBRUARY 26, 1946

NEIGHBORING GROUPS AND REACTIVITY

Sir:

Heretofore, we have stressed the stereochemical consequences of participation by neighboring groups[1] such as OAc, Br, OCH_3, etc., in replacement reactions. We have recently completed rate measurements which bring out the striking connection between reactivity and this participation.

First order rate-constants of solvolysis at 75° in glacial acetic acid of a series of 2-substituted cyclohexyl *p*-bromobenzenesulfonates give the following relative reactivities: unsubstituted, 1.00; *trans*-2-OAc, 0.240; *trans*-2-Br, 0.101; *trans*-2-OCH_3, 0.057; *trans*-2-Cl, 4.9×10^{-4}; *cis*-2-OAc, 3.8×10^{-4}; *cis*-2-$OSO_2C_6H_4Br$, 7.7×10^{-5}; *trans*-2-$OSO_2C_6H_4Br$, 6.9×10^{-5}. Similarly, acetolysis rates at 23.6° of cyclohexyl *p*-toluenesulfonates give the relative reactivities: *trans*-2-I, 1800; unsubstituted 1.00.

The effects of a halogen substituent similar to those above are seen also in the rough values of relative reactivities of alcohols to fuming hydrobromic acid or concentrated hydrochloric acid at room temperature. One reactivity sequence obtained in this way is: *trans*-2-iodocyclohexanol 1000; cyclohexanol 1; *trans*-2-bromocyclohexanol 0.08; *trans*-2-chlorocyclohexanol 1.6×10^{-4}.

In the relatively reactive substituted cyclohexyl compounds (which are typical of most of the cases where stereochemical evidence for participation exists) the neighboring group supplies a large driving force for the rate-determining ionization of the departing group. This partially neutralizes or completely overbalances (as for I) the rate-retarding inductive effect. The sequence I > Br > Cl is to be expected. As in the case of the acetoxy group, the driving force is supplied from the *trans*-position and poorly if at all from the *cis*-position. In the case of the

(1) Winstein and Seymour, THIS JOURNAL, **68**, 119 (1946), and previous articles in the series.

di-*p*-bromobenzenesulfonates little if any driving force is supplied by the poorly nucleophilic neighboring group even in the *trans*-position.

When the carbon atom being substituted is of a structural type more favorable for something approximating a carbonium ion mechanism, the effect of a neighboring bromine atom is more nearly given by consideration of the inductive effect alone. From our solvolysis rates of dibromides, relative reactivities are: $C_6H_5CHBrCH_3$[2a] 1000, $C_6H_5CHBrCH_2Br$ 1.00 in ethanol at 55°; $(CH_3)_2CBrCH_3$[2b] 6000, $(CH_3)_2CBrCH_2Br$ 1.00 in 80% ethanol at 25°. In fact, in the case of isobutylene dibromide the neighboring bromine atom is similar in effect to that of the chlorine atom in isobutylene dichloride, for which Kharasch and co-workers[3] have estimated a retarding factor of 4000 at 79°.

With these latter structural types and also with substances such as the very unreactive cyclohexyl compounds we still have little stereochemical evidence regarding participation.

We shall publish a detailed discussion and account of this work as soon as circumstances permit.

(2) (a) Hughes, Ingold, *et al.*, *J. Chem. Soc.*, 899 (1940); (b) Cooper and Hughes, *ibid.*, 1183 (1937).

(3) Brown, Kharasch and Chao, THIS JOURNAL, **62**, 3435 (1940).

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RECEIVED NOVEMBER 17, 1945

NEW BOOKS

The Bacterial Cell in its Relation to Problems of Virulence, Immunity and Chemotherapy. By RENÉ J. DUBOS. George Fabyan Professor of Comparative Pathology and Professor of Tropical Medicine, Schools of Medicine and Public Health, Harvard University. Member of the Rockefeller Institute. With an addendum by C. F. ROBINOW, Strangeways Laboratory, Cambridge, England. Harvard University Press, Cambridge, Massachusetts, 1945. xix + 460 pp. Illustrated. 21.5 × 15 cm. Price $5.00.

During the course of years a large number of observations have been accumulated concerning the physical, chemical and biological properties of bacteria. Dr. Dubos' purpose in this book is to correlate these largely unrelated observations made during the study of practical problems, in order to obtain an insight into the nature and properties of "cellular structures which cannot be recognized by microscopical observation" and "to interpret the phenomena of infectious processes in terms of the biochemical architecture of the bacterial cell." A quotation from Claude Bernard placed at the beginning indicates that it is the author's intention to prepare an architect's plan into which the bricks of individual observations will fit.

The impression of the reviewer is that Dubos has eminently succeeded in his purpose. There is no other book in which the actual results of individual studies are better presented for the understanding of general problems. The successive chapters of the book lead us through the cytology of bacteria and their physiochemical and staining properties, the analysis of cellular structures by biochemical and biological methods, such as the action of enzymes, antibodies and bacteriophage, the variability of bacteria, the nature of bacterial virulence, immunity, and the bacteriostatic and bactericidal agents. The discussion of these subjects is sufficiently complete for those who are not specialists in any particular field and gives an excellent summary of the present status of research. The discussion of the general aspects of these subjects should appeal to the specialists. References covering 70 pages furnish bibliography for further reading.

The reviewer was most impressed by the keen perception of the biological nature of bacteriological problems. It is pointed out in the introduction that many bacteria which were thought to be the simplest living organisms build up from inorganic material the complex organic substances and most of the enzymes and accessory substances which are present in higher plants and animals. The recognition of the probably insoluble complexity of biological phenomena puts our problems and the knowledge we possess into proper perspective. The chapters on the virulence of bacteria, immunity and chemotherapy are especially illuminating in the manner in which they present the little that is known against the background of the complexity of the problems. The most important practical discoveries, in chemotherapy for example, were made without any understanding of the basic principles on which they depend. It is evident that the increase of our knowledge concerning these principles would further more than anything else the study of practical problems.

The book is delightful reading for those who are interested to know how the general problems of his science appear to an eminent investigator. It is hoped that by stimulating interest in these problems it will be a very useful book.

LOUIS DIENES

Wood Products for Fertilizer. Report of Conference at Orono, Maine, June 29, 1945. Northeastern Wood Utilization Council, P. O. Box 1577, New Haven 6, Conn. 72 pp. 15 × 23 cm. Price, $1.00.

The Northeastern Wood Utilization Council was organized in 1942 for a concerted attack on the problem of low grade wood and wood waste. It is concerned with applied research. The foreword to this Report also states,"—In view of the fertilizer requirements of the Northeast and the possible use for this purpose of lignin and other forms of wood waste, a special meeting—was held—in coöperation with the University of Maine—". The report gives the full text of the following papers and a summary of the discussion: "Fertilizer Requirements of the Northeast," "The Value of Wood Ashes as Fertilizer," "The Use of Lignin in Potato Fertilizer," "The Use of Sawdust, Shavings and Superphosphate with Dairy Manure," "Comparisons of Sawdust and Wheat Straw for Bedding," "Action of Soil Bacteria on Wood Products," "Fundamentals of Lignin Chemistry as Applied to Fertilizer," "Research on