

COMMUNICATIONS TO THE EDITOR

A CORRECTION

Sir:

In the note on the use of ammonium acetate as a buffer [THIS JOURNAL, 54, 1911 (1932)], the implication was made that an ordinary good grade product was suitable for this purpose. Unfortunately the matter was treated by us as a passing observation and no more experimental work was done than that reported. Subsequently we have tested other samples of ammonium acetate. An unopened Kahlbaum sample gave a P_H of 6.93, which is close to neutrality, but other samples were very much more acid. Ammonium acetate recrystallized by dissolving the dry salt in five times its weight of methanol, adding a slight excess of ammonia (using as little water as possible), then adding an equal volume of acid-free ether, is reasonably stable and has always in our hands yielded a solution nearly neutral. In one case, however, the P_H value of a solution of crystals prepared approximately in this way was 6.85. Our original supply of ammonium acetate was therefore, by coincidence, somewhat unique in possessing the theoretically anticipated neutrality. We have not had time for a thorough study, but hope others may carry out such studies. We are regretful that a fuller experimental study was not made previous to the publication of our note.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF OREGON
EUGENE, OREGON
RECEIVED JULY 13, 1932
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ROGER J. WILLIAMS
CARL M. LYMAN

A PROPOSAL TO ADOPT THE STEM "XEN" OF A. W. HOFMANN'S XENYL AS
BASIS FOR NOMENCLATURE OF BIPHENYL (DIPHENYL) AND ITS
DERIVATIVES

Sir:

The study of condensed nuclei involving benzene has been materially aided through the employment of generic names for each particular grouping. In those cases, however, where two or more benzene rings are singly linked we have encountered an increasing difficulty in finding suitable terminology that is both clear and brief.

The name biphenyl (or diphenyl) has long been in use to designate the first step in the condensation of two benzene rings. It is only when we come to the consideration of well-known derivatives of biphenyl that we encounter a growing cumbersomeness in nomenclature.

For hydroxylated biphenyl compounds, the designations of ortho, meta and para phenylphenol are now meeting with favor over the correctly formed yet less euphonious corresponding terms ortho, meta and para hydroxybiphenyl; yet there is no reason why we should continue in use such

long terms as phenylphenol when we refer to a group of compounds which are of growing worth in the chemical industry and, as far as we can discern, will be of far greater worth in the future than the simple, old-time phenol.

Xenylamine, later identified as *p*-aminobiphenyl, was isolated by A. W. Hofmann from the high-boiling bases (over 330°) found in commercial aniline. This same compound was called martylamine by the same author [*Proc. Roy. Soc. (London)*, **12**, 389 (1862)] but only the former name seems to have persisted in the literature.

The confusion that arises today in the use of "biphenyl" or "biphenylyl" as a univalent group in contradistinction to "diphenyl" designating two phenyl groups is not easily dispelled. For example, *o*-aminobiphenyl—sometimes termed *o*-biphenylamine, must be readily discernible from diphenylamine and this notwithstanding that the hydrocarbon phenylbenzene remains "diphenyl" as well as "biphenyl." It would seem advisable, therefore, that we adopt some simpler means of representing a hydrocarbon base when made up of separate benzene rings singly linked.

For the present, it is hardly necessary to look beyond groupings containing more than two benzene rings singly linked, and for this reason the proposal by A. W. Hofmann [*Compt. rend.*, **55**, 901 (1862); *Jahrest. Fort. Chem.*, 344 (1862)] of the name "xenyl" for the biphenylyl radical is here considered sufficient. Its meaning should be extended to include the ortho and meta as well as the para series. The hydrocarbon of which xenyl is the univalent radical naturally must become "xenene"; the hydroxyl derivative will become "xenol" or in abbreviated form "xenol."

The preparation of ortho and para xenylamines is reported in several articles by Morgan and Walls [*J. Soc. Chem. Ind.*, **49**, 15T (1930); **50**, 94 (1931)]. "Beilstein" has adopted this term in the new editions. *Chemical Abstracts* since 1917 has used the term "xenyl" as an equivalent for *p*-biphenylyl in the name xenylamine. Hurd, in the "Pyrolysis of Carbon Compounds," page 28, makes brief mention of "xenyl" in contradistinction to phenyl and other radicals.

The diamino derivatives of "xenene" now should be looked upon as "xenylenediamine" compounds and the well-known 4,4'-biphenylenediamine or benzidine, will become 4,4'-xenylenediamine. The monocarboxylated xenene derivative would become xenencarboxylic acid or *o*-, *m*- or *p*-xenoic acid (by analogy with benzoic, naphthoic, etc., acids).

The hydroxyl derivatives of xenene thus become xenyl hydroxides or xenols and of these *o*-xenol and *p*-xenol are now meeting with extensive use in the chemical industry. Among the halogen derivatives we would have, for example, *o*-, *m*- or *p*-chloroxenene and other halides similarly named.

THE DOW CHEMICAL COMPANY
MIDLAND, MICHIGAN

WILLIAM J. HALE

RECEIVED AUGUST 13, 1932
PUBLISHED NOVEMBER 5, 1932

AN EQUATION RELATING VISCOSITY AND SURFACE TENSION

Sir:

An equation relating viscosity and surface tension can be obtained by combining the following equations of Batchinski [*Z. physik. Chem.*, **84**, 643 (1913)] and McLeod [*Trans. Faraday Soc.*, **19**, 38 (1923)], respectively,

$$\eta = \frac{C'}{v - w} \quad \frac{\gamma}{(D - d)^4} = C$$

where η is the viscosity, v the specific volume, w the limiting volume or approximately van der Waals b , γ the surface tension, D the density of the liquid, d the density of the vapor, and C' and C are constants for a given liquid. Below the boiling point the density of the vapor may be neglected in comparison with the density of the liquid. Neglecting d and equating v to $1/D$, we obtain

$$\gamma^{-1/4} = A \frac{1}{\eta} + B$$

where A and B are constants characteristic of the liquid.

If this equation is correct, a straight line will be obtained when $\gamma^{-1/4}$ is plotted against fluidity. When such plots were made for twenty-five liquids, water included, the deviations of the points from a straight line were within the experimental error except in the cases of ethyl ether and the alcohols, in which the surface tension at low fluidities was less than the straight-line requirements, the deviation increasing as fluidity decreases.

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DANIEL SILVERMAN
W. E. ROSEVEARE

RECEIVED SEPTEMBER 26, 1932
PUBLISHED NOVEMBER 5, 1932

THE PHOTOCHEMICAL FORMATION OF HYDROGEN PEROXIDE

Sir:

In previous communications [*J. Phys. Chem.*, **30**, 34 (1926); *THIS JOURNAL*, **49**, 2763 (1927)] the author has reported the quantum yield for the formation of hydrogen peroxide from hydrogen and oxygen by light of wave length 2536 Å. when photosensitized by mercury vapor. In making these measurements, a quartz filter containing chlorine and bromine was used. The manufacturers gave the transmission of this filter for 2536 Å. as 80%. Since these papers were published Frankenburger and Klinkhardt [*Z. physik. Chem.*, **B15**, 421 (1932)] have also reported work on this reaction in which they obtain a yield of 1.2 molecules of H_2O_2 and 1.5-2.5 molecules of H_2O per quantum absorbed. The author originally reported 6.6 molecules of H_2O_2 formed per quantum absorbed. In attempting to account for this discrepancy the filter originally used was borrowed from Princeton University and its transmission measured by Mr. Frank Benford,

in this Laboratory, using a Bausch and Lomb monochromator and receiving the transmitted energy on a thermopile. The transmissions measured are given in the accompanying table.

Wave length in Å.	Fraction of incident light transmitted	Wave length in Å.	Fraction of incident light transmitted
2475	0.24	3650	0.00
2536	.31	4047	.00
2650	.36	4350	.03
2804	.17	4916	.25
2967	.00	5461	.60
3024	.00	5770	.53

These results agree fairly well with measurements on a similar filter reported by Villars [THIS JOURNAL, 48, 1874 (1926)]. As a result of these measurements the quantum yield reported by the author will have to be reduced from 6.6 to 2.5.

In previous experiments (Ref. 1) using a closed circulatory system the author was able to show that the product of the reaction was predominantly hydrogen peroxide. Due to an unfortunate accident, this was only an estimate, but a careful check on the volume of the system made from a photograph shows that the yield was at least 75% H_2O_2 and probably much greater. It is thus possible to say that in these experiments where the gas was saturated with water vapor at 20° the yield of water vapor in the reaction is not at all in agreement with the results of Frankenburger, who found more water formed than peroxide. His objection to the mechanism postulated



on account of the endothermic nature of reaction (2) is not necessarily valid since the original product HO_2 may react with oxygen before it loses the 69 k. cal. acquired in its formation.

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SCHENECTADY, N. Y.

A. L. MARSHALL

RECEIVED SEPTEMBER 29, 1932
PUBLISHED NOVEMBER 5, 1932

DERIVATIVES OF DIOXANE

Sir:

The recent article of C. L. Butler and L. H. Cretcher [THIS JOURNAL, 54, 2987 (1932)] and the communication of R. K. Summerbell and R. Christ [*ibid.*, 54, 3777 (1932)], both connecting with our first article [Böeseken, Tellegen and Henriquez, *Rec. trav. chim.*, 50, 909 (1931) and *Proc. R. Acad.*, 34, 631 (1931)] cause us to give a brief preliminary report of the continuation of our research. While chlorinating 2,3-dichlorodioxane, we obtained

the liquid asymmetrical tetrachlorodioxane, described by Butler and Cretcher, a crystalline hexachlorodioxane and more highly chlorinated derivatives which are under investigation. More properties of the isomeric naphthodioxanes have been determined and the inquiry has been enlarged to include the derivatives with 1,3-propanediol, pyrocatechol, benzyl alcohol, ester of tartaric acid, etc. By treatment with potassium acetate we made and investigated the diacetate. We are very much astonished that our first communication, intended *inter alia* to save double work, has apparently been understood as an invitation to continue our research. After this explanation we think it will be clear that we ourselves will continue our research in all directions. The results obtained since our last article will be communicated in the near future.

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RECEIVED OCTOBER 13, 1932
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J. BÖESEKEN
F. TELLEGEN
P. COHEN HENRIQUEZ

THE REACTION OF CARBOXYLIC ACIDS WITH PHOSPHORUS PENTOXIDE

Sir:

Certain aliphatic ketones have been made by the action of phosphorus pentoxide with acids [Gal and Étard, *Compt. rend.*, **82**, 457 (1876); Kipping, *J. Chem. Soc.*, **57**, 532, 980 (1890); **63**, 452 (1893)]. An attempt to apply this reaction to trimethylacetic acid gave no ketone nor carbon dioxide but instead gave carbon monoxide and polymers of isobutylene. *n*-Butyric and isobutyric acids with excess of phosphorus pentoxide gave both carbon dioxide and carbon monoxide and formed tars. The yields and ratios of these gases were determined.

Acid	% Yield of CO and CO ₂	Ratio CO : CO ₂
<i>n</i> -Butyric	7	1:5
Isobutyric	10	5:1
Trimethylacetic	60	∞

Use of xylene as a solvent for the first two acids cut the yields of gas to 0.07 and 0.14%, respectively, but did not change the ratio of CO:CO₂. No gas was evolved when benzoic acid was treated in boiling xylene with an excess of phosphorus pentoxide.

This process is being studied as a possible means of distinguishing tertiary aliphatic acids from other types of acids.

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KENNETH C. LAUGHLIN
FRANK C. WHITMORE

THE REACTION BETWEEN NEUTRAL LEAD MERCAPTIDES AND SULFUR

Sir:

The reaction between neutral lead mercaptides and sulfur in benzene solution leads to the formation of lead disulfide and organic polysulfides [W. E. Duncan and Emil Ott, *THIS JOURNAL*, **53**, 3940 (1931)].

Preliminary work on the similar reaction with basic lead mercaptides indicated an analogous reaction with the formation of basic lead polysulfides of the type $\text{HOPbS}_x \cdot \text{PbOH}$ [Emil Ott and E. E. Reid, *Ind. Eng. Chem.*, **22**, 884 (1930); **22**, 878 (1930)].

This reaction was now studied more extensively with basic *sec.*-butyl lead mercaptide. The relatively stable yellow-orange (light reddish-brown when dry) precipitate obtained by the addition of sulfur in benzene solution was definitely established to be a mixture of basic lead polysulfides of the type mentioned above. Most mixtures may simply be described as containing the compounds with $x = 3$ and $x = 4$, but in some cases $x = 5$ is additionally present.

Thorough qualitative tests and quantitative analyses for lead, sulfur, hydrogen and carbon established composition and constitution of the products.

Since the basic *sec.*-butyl lead mercaptide cannot be prepared entirely free from neutral *sec.*-butyl lead mercaptide, a certain amount of lead disulfide is also formed, the amount of which can be predicted accurately from the analysis of the mercaptide solution. Thus no uncertainty is introduced into the final analyses. It lies in the nature of the problem that no individual compounds could be isolated; for the same reason this abbreviated communication seemed necessary.

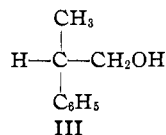
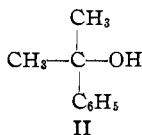
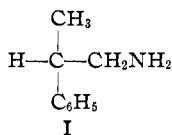
DEPARTMENT OF CHEMISTRY
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BALTIMORE, MARYLAND
RECEIVED OCTOBER 21, 1932
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WALLACE E. DUNCAN
EMIL OTT

REARRANGEMENTS BY THE ACTION OF NITROUS ACID ON AMINES OF THE TYPE $\text{CH}_3\text{CH}(\text{C}_6\text{H}_5)\text{CH}_2\text{NH}_2$

Sir:

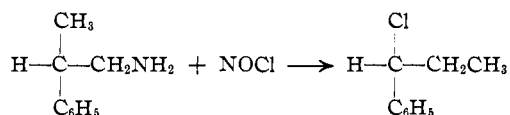
The amine I on treatment with nitrous acid should form, on the basis of observations made on aliphatic amines of this type, two isomeric carbinols,



II in predominating proportion and III in much smaller proportion. In the case of the optically active amine, the first carbinol should be optically

inactive. Similar effects should be expected from the action on the amine of NOCl or NOBr. The active halides should be expected to be the primary. This assumption was made by Levene, Mikeska and Passoth [*J. Biol. Chem.*, **88**, 27 (1930)] and was made the basis of the correlation of the substituted phenylacetic to phenylpropionic acids by Levene and Marker [*ibid.*, **93**, 749 (1931)].

We now find that the active halide obtained by the action of nitrosyl halides on the amine is not a primary but a secondary halide. Thus, in course of the reaction an unexpected rearrangement takes place



inasmuch as this halide leads to $\begin{array}{c} \text{COOH} \\ | \\ \text{H}-\text{C}-\text{C}_2\text{H}_5 \\ | \\ \text{C}_6\text{H}_5 \end{array}$.

A similar rearrangement takes place in the case of 1,1-ethylphenylethylamine (Ref. 2).

It may be mentioned here that the dextrorotatory substituted phenylacetic acids are now correlated to levorotatory substituted 3-phenylpropionic acids on the basis of new evidence. The details will be published in the *Journal of Biological Chemistry*.

THE ROCKEFELLER INSTITUTE
FOR MEDICAL RESEARCH
NEW YORK, N. Y.

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P. A. LEVENE
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ALEXANDRE ROTHEN

THE COLORIMETRIC DETERMINATION OF FLUORINE IN WATER WITH FERRIC THIOCYANATE

Sir:

In the determination of fluorine in water it has been found most satisfactory to use a colorimetric method based on the fact that the complex ion formed in the reaction between a fluoride and ferric chloride does not give the characteristic iron color with ammonium thiocyanate. Thus, with more iron than is necessary to react with the fluoride, the color is less than that produced by the same amount of iron without fluoride. By determining colorimetrically the quantity of iron reacting with the ammonium thiocyanate, the quantity withdrawn by the fluoride may be found by difference and its equivalent in fluoride read from a curve which has been made by plotting the effect of definite amounts of fluoride upon the amount of iron used in the determination.

The alkalinity of the sample of water must be neutralized and if the volume of the sample is much over 50 cc., it must be evaporated to about

this volume. By using 5 cc. of ferric chloride solution (0.1 g. of iron and 30 cc. of *N* hydrochloric acid in 1 liter) with 10 cc. of ammonium thiocyanate solution (24 g. in 1 liter) in a volume of 75 cc., as little as 0.025 mg. of fluorine in 100 cc. of the sample of water may be determined. If the sample contains more than 0.4 mg. of fluoride, a smaller sample should be taken or more iron used, which necessitates making a new curve for the larger amount of iron. It is important that the acidity, temperature, and volume be more carefully controlled than in the usual thiocyanate determination.

Sulfate produces a similar but very much smaller effect upon the red color but this is also quantitative and a curve showing the effect of definite amounts of sulfate in terms of iron or of fluorine may be made. Then, for each sample, the effect of the sulfate present may be subtracted to obtain the true fluoride content. For example, 200 parts per million of sulfate produced a fading effect equivalent to 0.5 part of fluorine when a 100-cc. sample was used. If the fading of the sample containing this amount of sulfate indicated a fluoride content of 3.7 parts per million, 0.5 part must be subtracted to obtain the true fluoride content of the sample.

Chloride produces a slight fading but for quantities below 500 parts per million this is so small that it may be ignored in a 100-cc. sample. For quantities above 500 parts per million, about 0.1 part per million of fluorine must be subtracted for each 500 parts of chloride present. The chloride added as hydrochloric acid to neutralize the alkalinity must, of course, be taken into consideration. The effect of sulfate and chloride is the same whether they are present as calcium, magnesium, or sodium salts. The amount of nitrate usually found in natural waters has no effect.

This method is particularly adapted to the determination of the small amounts of fluoride to be expected in most natural waters.

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MARGARET D. FOSTER

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