semicarbazone prepared from our cyclo-octanone out of cyclohexanone and diazomethane as well as that obtained from Professor Ruzicka.

The reaction of the main portion of this fraction with piperidine did not yield homogeneous derivatives of the piperidino alcohol.

Summary

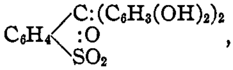
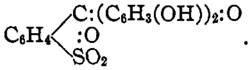
The action of diazomethane on cyclohexanone in the presence of methyl alcohol yields as the main product cycloheptanone, and in smaller quantities cyclo-octanone and an oxide isomeric with cycloheptanone.

Diazomethane with cyclopentanone leads (through cyclohexanone) to cycloheptanone as chief product, and cyclo-octanone as by-product. In this case, the oxide formed was not identified.

The reaction may be advantageously applied to the preparation of cycloheptanone and cyclo-octanone.

University, Virginia

NOTES

Note on Catechol Sulfonephthalein.—Catechol sulfonephthalein, first mentioned by Moir,[1] was prepared by substantially the method of Lubs and Clark,[2] condensing at temperatures under 100 two moles of catechol with one mole of symmetrical dichloro derivative of *o*-sulfobenzoic acid, but omitting the use of zinc chloride as condensing agent. The resulting product was analyzed for sulfur, giving 95.71 and 95.76% of the calcd. for the formula  $C_6H_4\left\langle\begin{array}{l} C:(C_6H_3(OH)_2)_2 \\ :O \\ SO_2 \end{array}\right.$, or 100.40 and 100.45% of the calcd. for the formula  $C_6H_4\left\langle\begin{array}{l} C:(C_6H_3(OH))_2:O \\ :O \\ SO_2 \end{array}\right.$. The product is amorphous, of a very deep purple color (practically black), solid but not brittle at ordinary temperatures, and moderately hygroscopic. When warmed to about 60° it is softened sufficiently to drop from a small stirring rod. Its solubilities are: miscible in all proportions with water; readily soluble in methanol, ethanol, acetone, glacial acetic acid and ethyl acetate; slightly soluble in ethyl acetoacetate, acetic aldehyde and ethyl ether; insoluble in benzene, toluene, xylene, petroleum ether, carbon disulfide, carbon tetrachloride, chloroform and acetic anhydride. Attempts at crystallization, using the first-named solvents, have been unsuccessful.

The aqueous solution of this product is found to give colors of but a fraction, about one-tenth, of the intensities of colors of other sulfonephthaleins. A noteworthy feature of several of these colors, and one not mentioned by Moir, is their tendency to change, in some cases in only a

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[1] J. Moir, *J. So. Afr. Assoc. Anal. Chem.*, **3**, 6 (1920); *C. A.*, **14**, 3607 (1920).

[2] H. A. Lubs and W. M. Clark, *J. Wash. Acad. Sci.*, **5**, 609 (1915).

few minutes. In the following table are listed the colors exhibited by 0.2 cc. of a 0.5% aqueous solution of catechol sulfonephthalein when added to 10 cc. of the solutions listed in the first column.

	Immediate color	After 5 minutes	After 20 minutes	After 1 hour	After 18 hours	After 36 hours
1.0 *N* HCl	Red	Red	Red	Red	Red	Red
0.01 *N* HCl	Yellow	Yellow	Yellow	Yellow	Yellow	Yellow
*P*H 5	Yellow	Yellow	Yellow	Yellow	Yellow	Yellow
*P*H 6	Yellow	Yellow	Yellow	Yellow	Yellow, slightly greenish	Yellowish-green
*P*H 7	Yellow, slightly greenish	Yellow, slightly greenish	Yellow, slightly greenish	Yellow, more greenish	Yellowish-green	Yellowish-green
*P*H 8	Purple, then indigo	Rich blue	Blue	Blue	Pale, inky	Yellowish-green
*P*H 9	Pinkish-purple	Pinkish-purple	Pinkish-purple	Pinkish-purple	Pinkish-purple	Yellowish-green
*P*H 10	Pinkish-purple	Pinkish-purple	Darker, surface cloudy	Less red, somewhat brownish	Light green	Yellowish-green
0.01 *N* NaOH	Indigo, becoming cloudy	Clear, fainter purple	Purple, surface green	Purple, surface green	Grass green	Pale green
1.0 *N*	Grass green	Grass green	Grass green	Grass green	Green, less intense	Pale green

The colors given by products of condensation of mixtures containing larger porportions (2.2 moles, 2.5 moles) of catechol are much the same as those shown in the table, save that the greens are much more intense.

It has been found possible to prepare a satisfactory series of color shades in the range *P*H 0 to *P*H 1.5.

Products condensed at temperatures of 130 and 160° were found to be incompletely soluble in water; these soluble portions give relatively very faint acid colors and comparatively more intense alkaline colors. Acidified aqueous solutions of the low temperature product, on vigorous boiling, showed similar color differences.

The product condensed at the lower temperature appears to be fairly pure, dilute and concentrated aqueous solutions remaining clear for many days, and no material is insoluble in sodium hydroxide[2] or in sodium bicarbonate[3] developing on long standing.

TAKOMA PARK
WASHINGTON, D. C.
CYRUS B. WOOD

RECEIVED FEBRUARY 21, 1930
PUBLISHED AUGUST 5, 1930

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[3] W. R. Orndorff and F. W. Sherwood, THIS JOURNAL, **45**, 486 (1923).

A Note on the Preparation of Monomethyldiethylmercaptoglucose.—Monomethyldiethylmercaptoglucose can be obtained by treating the monosodium derivative of diethylmercaptoglucose with methyl iodide. Emil Fischer[1] treated the monosodium diethylmercaptoglucose with methyl iodide in the presence of methyl alcohol, and thought that he regained the original diethylmercaptoglucose. However, some oily disks were formed which he did not investigate. In the present work the sodium diethylmercaptoglucose was prepared according to Fischer's method by treating the diethylmercaptoglucose with sodium ethoxide. The excess of alcohol was evaporated and the methylation was done in absence of alcohol. The solid residue was refluxed with excess methyl iodide until all dissolved. The excess of methyl iodide was evaporated and to the solid residue water was added. From this solution a substance was extracted by means of ether and chloroform which was recrystallized three times from absolute alcohol. It gave a melting point of 155°. The results of micro-analysis for carbon and hydrogen are given in the following table.

TABLE I

ANALYTICAL DATA FOR MONOMETHYLDIETHYLMERCAPTOGLUCOSE

Sample, mg.	Weighed, mg.	Calcd. for, %	Found %
5.020	H_2O, 3.600	H, 8.05	8.03
	CO_2, 8.140	C, 43.97	44.21

The results seem to indicate that the monomethyldiethylmercaptoglucose as prepared by the above method is the same as that isolated by the present author,[2] as a by-product from the preparation of pentamethyldiethylmercaptoglucose.

CONTRIBUTION FROM THE
CHEMICAL LABORATORY OF
WASHINGTON SQUARE COLLEGE
NEW YORK UNIVERSITY
NEW YORK, N. Y.
PHILIPPOS E. PAPADAKIS

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The Bromination of Hexane.—When the vapor of hexane is passed through bromine water, *p*-dibromobenzene and hexabromobenzene are said to be obtained.[1] F. O. Rice[2] has pointed out that such a transformation of hexane to an aromatic derivative seems doubtful. Since hexane spectroscopically free from benzene was available, it seemed desirable to investigate this question further.

[1] E. Fischer, *Ber.*, **27**, 673 (1894).

[2] P. E. Papadakis, THIS JOURNAL, **52**, 2147 (1930).

[1] Blair, Leabury and Wheeler, *J. Soc. Chem. Ind.*, **43**, 298T (1924).

[2] F. O. Rice, "The Mechanism of Homogeneous Organic Reactions from the Physical-Chemical Standpoint," American Chemical Society Monograph, No. 39, The Chemical Catalog Company, Inc., New York.

Pure (99.5%) nitrogen gas was first passed through concentrated sulfuric acid and bubbled through 20 g. of the pure hexane in a distilling flask. The arm of this flask was connected with a bubbler containing water with an excess of bromine. Five hours were required to vaporize the hexane, and examination of the bromine solution revealed no benzene bromides. Repeating with the bromine solution kept below zero and the hexane vaporized in the course of forty hours, no benzene bromides were found. A large amount of the hexane was recovered.

Repeating under the same conditions, but with the bromine solution exposed to a 100-watt Mazda lamp, again no benzene bromides were obtained.

When one gram of benzene was added to the hexane, and the vaporization carried out in the cold and in the dark, some benzene bromides were readily obtained.

The production of the derivatives mentioned in the literature can therefore be traced to hexane slightly contaminated with benzene.

This work was done at the suggestion of Dr. M. S. Kharasch, of the University of Chicago.

CONTRIBUTION FROM THE
DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CHICAGO
CHICAGO, ILLINOIS.

FRANCIS M. PARKER

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Determination of Halogens in Organic Compounds.—We wish to thank Professor Robertson[1] for calling our attention to his papers, which we overlooked, probably because we were searching for a general method for the determination of chlorine, bromine and iodine and Robertson's method is, as he states, not suitable for iodine compounds.

We have tested his method using samples of about 0.15 g. of bromobenzene and obtained low results, a tendency to which Robertson also calls attention. Duplicates checked less closely than by our method.

The use of sodium peroxide instead of arsenite is obviously optional in either method, but the latter was decided upon after a trial of both reagents.

The time required depends upon whether the gravimetric or volumetric method is used. We needed eighty-five minutes by the gravimetric method with Robertson's apparatus.

The principal advantages of our method[2] are: (1) it is a general method applicable to compounds of chlorine, bromine and iodine.

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[1] Robertson, THIS JOURNAL, **52,** 3023 (1930).

[2] Thompson and Oakdale, *ibid.,* **52,** 1195 (1930).

(2) It can be used with low-boiling compounds such as ethyl bromide. (3) Metals in the residue may be very easily determined. (4) The accuracy is greater than in Robertson's method, as shown by a comparison of analyses. (5) The use of oxygen and platinized asbestos is never necessary. (6) There is no danger of the reaction becoming too violent or of the projection of particles onto the walls of the flask. (7) The time required is less, particularly because it has been found since publication of the last paper by Willard and Thompson,[3] that the apparatus described by them for the micro determination of halogens can also be used for samples as large as 0.1–0.2 g. This results in a saving of time as well as of space required for the apparatus. For samples of 0.01–0.02 g. an apparatus about half the size of this, or only 28 cm. high, works perfectly.

Contribution from the
Chemical Laboratory
University of Michigan
Ann Arbor, Michigan

J. J. Thompson
U. O. Oakdale

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COMMUNICATIONS TO THE EDITOR

THE HEAT OF FORMATION OF MOLECULAR OXYGEN

Sir:

In a recent communication Copeland[1] has reported a value for the heat of formation of molecular oxygen of 165,000 cal. We have been engaged in a similar determination by an experimental method which differs only in minor details from the method used by Copeland. The results of our first determinations were in substantial agreement with those reported by Copeland, the average of a number of runs being about 160,000 cal. When we checked the method for possible errors we discovered that we were getting spurious heat effects in the calorimeter. When we took precautions to eliminate these heat effects we obtained as the average of a number of fairly consistent runs 131,000 cal. We do not find any evidence that metastable atoms reach the calorimeter.

Chemical Laboratory
University of Illinois
Urbana, Illinois

W. H. Rodebush
S. M. Troxel

Received June 27, 1930
Published August 5, 1930

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[3] Willard and Thompson, This Journal, **52**, 1893 (1930).

[1] Copeland, *ibid.*, **52**, 2581 (1930).