are disappearing. The black bass feed on them. There are many German carp in parts of the Perkiomen and Skippack Creeks; in some places they keep the dams muddy. Among Americans this fish is not regarded with much favor, although it is a favorite food fish in Bohemia. The Delaware, at Trenton, is full of large carp. Near Burlington the carp fisheries furnish Philadelphia and Trenton with nearly a ton of carp per week, consumed mostly by foreigners. The black bass are decreasing in the Schuylkill, owing to the fact that the carp eat their spawn, and also to the fact that the culm or coal dust which comes from the coal region annoys them, as they do not thrive on muddy bottoms. Often after a heavy rain in the coal regions Philadelphia water will be dirty for a week. The greatest amount comes from the Little Schuylkill, although much is dumped along the Big Schuylkill. There was some coal dust dumped along the west side of the Schuylkill between Norristown and Philadelphia which the high water and heavy rains would stir up, but this practice has been stopped.

DR. JOSEPH W. RICHARDS, President, in the chair.

SOME NEW DERIVATIVES OF DIACETYL.

BY HARRY F. KELLER AND PHILIP MAAS.

Since communicating the results obtained in studying the action of oxidizing agents upon diacetyl, we have continued our work on this diketone in several directions.

The ready and quantitative conversion of diacetyl into acetic acid by certain oxidizing agents, notably hydrogen peroxide, induced us to try whether the halogen-substituted products, dibromo-diacetyl and tetrabromo-diacetyl, would behave in an analogous manner. If they, respectively, yielded bromacetic acid and dibromacetic acid, their symmetrical structure might be regarded as definitely established. Thus:

and

While both compounds were found to be readily attacked by the oxidizing agent, only the dibromo-derivative gave something like the expected result.

A weighed quantity of this substance was treated in the cold with a moderate excess of hydrogen peroxide solution. The greasy scales gradually disappeared, and the liquid became strongly acid. Upon evaporating, it gave off hydrobromic acid, and left a residue consisting of a mixture of *bromacetic* and *glycollic* (oxyacetic) acids. This mixture was completely converted into the latter acid by prolonged boiling with water, according to the equation:

The characteristic calcium salt was prepared. It was obtained in stellar aggregations of needles, having a silky luster, insoluble in alcohol and only sparingly soluble in cold water. It contained:

	I.	II.	Calculated for (C ₂ H ₃ O ₃) ₂ Ca + 4H ² O.
Ca	15.06	15.54	15.26
H ₂ O	26.97	26.47	27.48

The salt is understood to be somewhat efflorescent, and the percentage of water therefore a little too low. The dehydrated salt gave Ca = 21.32 per cent., instead of 21.05 per cent., required by theory.

The blue copper salt was also obtained.

A mixture of several acids is produced when dibromodiacetyl is heated with nitric acid. We have not been able to effect their separation, but have reasons to believe that oxalic acid and monobromacetic acid are amongst them.

When tetrabromodiacetyl was treated with hydrogen peroxide, its yellow color disappeared slowly. A white flocculent precipitate formed while the dense powder dissolved. The colorless solution had a peculiar penetrating odor, and deposited, upon standing, another crop of the product in the

form of long, colorless needles with a silky luster. From 3 to 4 grams of this substance were thus obtained from 10 grams of the diketone.

The mother liquor, still having the characteristic odor of the crystallized product, was extracted with ether, but the latter, on evaporating, left only a small quantity of an oily liquid.

The crystals were found to be insoluble in water, and very freely soluble in alcohol, ether, benzene, glacial acetic acid and other organic solvents. From an ethereal solution very beautiful, prismatic crystals, more than a centimeter long, were obtained. They belong without doubt to the rhombic system, and consist of several prisms, the orthopinacoid and a brachydome. From the solution in acetic acid the substance is reprecipitated in the form of long, fine needles, when much water is added. It melts at 72.8° , and at higher temperatures sublimes, apparently without decomposition.

Analyses of the carefully purified substance yielded:

	I.	II.	Calculated for C_5HBr_5O .
	Per Cent.	Per Cent.	Per Cent.
C	8.13	8.04	7.94
H	.56	.26	.22
Br	87.99	88.04	88.30
O	[3.32]	[3.66]	3.53

Determinations of the molecular weight by the cryoscopic method, by means of Beckmann's apparatus and glacial acetic acid as the solvent, gave:

I.		
Used solvent	19.485	grams.
Substance	.1788	"
Depression	.084°	
II.		
Solvent	19.663	grams.
Substance	.3360	"
Depression	.146°	
I.	II.	Calculated.
461	435	452

The composition and molecular weight correspond to the formula C_5HBr_5O , which is that of *pentabromacetone*. That

this is really the compound we obtained is further proved by a comparison of the physical properties* with those observed by other chemists, as well as its behavior upon boiling with barium hydroxide; *bromoform* was produced and was identified, after distilling it in a current of steam, by its odor and boiling point, and the formation of phenylcarbylamine when the alcoholic solution was treated with aniline and caustic potash.

It is remarkable that an acetone derivative should result from the oxidation of a diketone, for methyl-ethyl ketone can be converted by oxidation into diacetyl.†

The oily product mentioned above, and which was extracted from the solution after the pentabromacetone had separated, may have been tribromacetone. It had a powerful odor, decomposed upon heating, and did not respond to the carbylamine reaction.

Attempts to oxidize tetrabromodiacetyl with nitric acid have not as yet given any definite results. Although the substance dissolves rapidly on warming in the concentrated, especially the red fuming, acid, the greater part of it separates again, on cooling or diluting with water, in large yellow crystals.

Cyanohydrins.—Another class of diacetyl derivatives to which we have lately given some attention, are the cyanohydrins.

Fittig and one of us have shown that diacetyl and hydrocyanic acid unite quantitatively to form a dicyanohydrin, and that this may be readily converted into dimethylracemic acid.

* The melting point is given by Beilstein (3d ed., p. 989) as 76°. Although we repeated the determination several times, using material purified with scrupulous care, and the best thermometers, it invariably gave the same result 72·8°.

† Fileti and Ponzio, *Gazz. chim. ital.*, **25**, 233.

Our recent experiments were undertaken—

(1) To attempt the preparation of a monocyanohydrin of diacetyl.

(2) To produce halogen-substituted cyanohydrins.

If we succeeded in converting the latter into the corresponding acids, we would have the first derivatives of tartaric acid in which hydrogen is replaced by halogen.

Diacetyl and hydrocyanic acid (30 per cent. solution) were brought together in molecular proportions. A rise of temperature and the vanishing of the yellow color indicated that combination was taking place. The liquid was gently heated, and then allowed to stand for some time in a warm place. After extracting with ether, and evaporating this solvent, there remained a colorless, viscous liquid. This was placed over dehydrating materials, and repeatedly cooled to very low temperatures, without showing any signs of crystallizing or congealing. It was doubtless the expected compound, though probably very impure. We now attempted to produce the corresponding acid

by treatment with strong hydrochloric acid. This was tried in a number of ways; but although even the most concentrated acid (saturated at 0°) had no appreciable effect at ordinary

temperatures, the slightest warming destroyed the compound, with formation of dark resinous products, from which an acid of definite composition could not be isolated.

More encouraging were the results of our experiments upon dibromodiacetyl. It was found to combine with hydrocyanic acid quite readily, and yielded a well-crystallized dicyanohydrin. From the ethereal extract it was obtained in fine colorless crystals, having a strong luster, and melting with decomposition at 177° .

Its composition is established by these determinations:

	Found.		Calculated.
	I. Per Cent.	II. Per Cent.	Per Cent.
N	9'38		9'39
Br	54'35	54'74	53'69

The excess of bromine is probably due to the formation of calcium cyanide when the substance is ignited with lime.

Experiments are in progress to transform the nitrile into the acid; the amide of the acid has been obtained in small quantities.

We have also found that tetrabromodiacetyl can be made to combine without difficulty with two molecules of hydrocyanic acid. The resulting body seems to be analogous to the tetrachlorodiacetyl dicyanohydrin described by Levy and Witte.* As yet, however, we have not prepared a sufficient quantity to warrant the publication of definite data.

Dichlorodiacetyl.—As Levy and his pupils† obtained their tetrachlorodiacetyl by a complicated process, the action of potassium chlorate and hydrochloric acid on chloranilic acid, we have tried to prepare it by direct chlorination of diacetyl. It was found that at first the action of chlorine upon the diketone, dissolved in carbon disulphide or chloroform, is quite energetic, but the only product we have so far obtained proves to be dichlorodiacetyl. It closely resembles the dibromo-derivative; soluble in carbon disulphide, chloroform, boiling petroleum ether and warm benzene, it crystallizes in

* *Ann.*, **254**, 98.

† *Ann.*, **249**, 93.

yellowish, unctuous scales, melting at 124.5° . A chlorine determination gave:

	Found. Per Cent.	Required for $C_7H_4Cl_2O$. Per Cent
Cl	45.63	45.80

LABORATORY OF THE CENTRAL HIGH SCHOOL, PHILADELPHIA.

CORRESPONDENCE.

INTERNATIONAL GEOLOGICAL CONGRESS, SEVENTH SESSION, ST. PETERSBURG, 1897.

REPORT OF DR. JOSEPH W. RICHARDS, Delegate of the Institute.

To the President and Members of the Franklin Institute:

Your delegate to the Seventh International Geological Congress, assembled in St. Petersburg at the invitation of the Tsar, respectfully submits the following report:

The Congress was in session from August 29th to September 4th.

Previously to its opening, a number of the delegates participated in an excursion of fourteen days in Esthonia, under the direction of Fr. Schmidt; others in a trip of seven days into Finland, under the direction of I. Sederholm and W. Ramsay; while others, to the number of 120, embraced the opportunity offered to visit the Ural Mountains, and enjoyed an expedition of twenty-nine days in eastern Russia, from Moscow to Ekaterinsbourg and Perm. The members who participated in these expeditions were delighted with the lavish hospitality everywhere showered upon them, and will carry to their homes, in all quarters of the world, lasting remembrances of Russia's friendliness to the representatives of geological science.

It may here be remarked that, after the closing of the Congress, there is organized a trip of thirty days through Southern Russia and the Caucasus (*via* Moscow, Nijni, the Volga, Astrakhan, the Caspian Sea, Petrovsk, Vladi-Kavkaz, Tiflis, Baku, Batoum, Kertch, Sevastopol to Odessa), which will be partici-