XXXIX.—*The Constitution of certain so-called "Mixed Azo-compounds."*

By FRANCIS R. JAPP, LL.D., F.R.S., and FELIX KLINGEMANN, Ph.D.

PART I. INTRODUCTORY AND THEORETICAL.

BETWEEN three and four years ago, Dr. Ludwig Landsberg mentioned to one of us that he had obtained by the action of sodium methoxide and methyl iodide on benzene-azo-acetone* a colourless, feebly basic compound, melting at 64°, which he had not further examined. Dr. Landsberg stated that he did not intend to continue the investigation of this compound, and very kindly allowed us to take up the subject.

Analysis showed us that, as was to be expected, the compound had been formed from benzene-azo-acetone by the substitution of a methyl-group for hydrogen. Adopting the usually accepted formula for benzene-azo-acetone,

the most probable supposition was that the methyl had displaced a hydrogen-atom of the methylene-group—a view which we put forward in a preliminary note on the subject (*Ber.*, 20, 3398). By the action of acetic anhydride on benzene-azo-acetone, we also prepared an acetyl-derivative, to which we assigned (*loc. cit.*) an analogous constitution. We shall show in the present communication, that the above formula for benzene-azo-acetone does not correctly express its constitution, and that the formulæ which we ascribed to the two derivatives just mentioned must be correspondingly modified.

As the yield of the methyl-derivative obtained by Dr. Landberg's reaction was very small,† we endeavoured to prepare the compound by splitting off carbon dioxide from benzene-azo-methacetoacetic acid, a method which would at the same time prove its constitution. We had hoped to obtain ethylic benzene-azo-methacetoacetate by the action of diazobenzene chloride on ethylic sodio-methacetoacetate, following the analogy of the reaction described by V. Meyer (*Ber.*, 10, 2075) for the preparation of ethylic benzene-azo-acetoacetate from ethylic acetoacetate and diazo-salts; but we found that the benzene-azo-group could only be introduced into the molecule of ethylic

* Benzene-azo-acetone, first described by v. Richter and Münzer (*Ber.*, 17, 1928), was discovered independently by Dr. Landsberg in the Chemical Laboratory of the Normal School of Science about the time referred to; but the investigation was abandoned after the publication of v. Richter and Münzer's memoir.

† A relatively advantageous method of carrying out the reaction is described later on.

methacetoacetate with simultaneous elimination of the acetyl-group: thus—

To the “ester” thus formed we at first assigned the formula—

(*Ber.*, **20**, 2942), regarding it as the ethyl salt of *benzene- α -azopropionic acid*—the first representative of a new class of benzene-azo-fatty acids. The acid, $\text{C}_9\text{H}_{10}\text{N}_2\text{O}_2$, was obtained by hydrolysis; and we also prepared a number of homologous “esters” and acids, under the impression that we were dealing with a new class of compounds.

The supposed benzene-azo-propionic acid, $\text{C}_9\text{H}_{10}\text{N}_2\text{O}_2$, yielded, by treatment with sodium amalgam, *benzene-hydrazopropionic acid*,

which proved to be identical with E. Fischer and Jourdan’s “phenylhydrazinepropionic acid” (*Ber.*, **16**, 2244), a fact which, however, escaped our notice at the time of our first publications on the subject (*Ber.*, **20**, 2943 and 3284). Fischer and Jourdan obtained their acid by reduction of phenylhydrazonepyruvic acid,*

On comparing our “benzene-azo-propionic acid” with phenylhydrazonepyruvic acid, we found that these two acids were also identical. It was, therefore, necessary to ascertain whether the acid had the constitution of a hydrazone, as assumed by Fischer and Jourdan, and indicated by its formation from phenylhydrazine and pyruvic acid; or that of an azo-compound, as we had all along supposed. The fact that in the reaction discovered by us, the diazo-salt expels simultaneously sodium and acetyl from the molecule of ethylic sodio-methacetoacetate might, it appeared to us, be interpreted in favour of the hydrazone formula, since in this process the bivalent group, $\text{CH}_3\cdot\text{C}\cdot\text{COOC}_2\text{H}_5$, would be formed; on the other hand, the possibility of regenerating the acid by the action of an ammoniacal solution of a cupric salt on benzene-hydrazopropionic acid as observed

* In the nomenclature of compounds formed by the action of phenylhydrazine on carbonyl-compounds we have followed the recently published suggestion of Emil Fischer (*Ber.*, **21**, 984).

by Fischer and Jourdan, indicated rather the constitution of an azo-compound. The problem, we pointed out, was of the same order as that involved in distinguishing between an isonitroso- and a nitroso-compound (*Ber.*, **20**, 3285).

Of course the question also arose, as to whether benzene-azo-acetone itself was an azo-compound or a hydrazone; and it appeared likely that in the case of this compound a study of the alkyl-derivatives obtainable by Landsberg's reaction might furnish a ready solution of the problem. If benzene-azo-acetone was an azo-compound, the alkyl-derivative would have the formula—

whereas, if it was a hydrazone (derived from pyruvic aldehyde), the alkyl would more probably attach itself to nitrogen: thus—

By the action of nascent hydrogen, an alkyl-derivative of the first formula ought to yield aniline; one of the second formula, an alkyl-aniline. In either case, the other half of the molecule would probably yield a ketene.

The method of attacking the problem was therefore analogous to that employed by Victor Meyer and Ceresole in ascertaining the constitution of the isonitroso-compounds (*Ber.*, **15**, 3071).

We preferred, however, to introduce, instead of a alkyl-group, the group $\cdot\text{CH}_2\cdot\text{COOH}$, into the molecule of benzene-azo-acetone. The resulting compound would thus yield on reduction, instead of a mixture of two bases, a base and an acid, in this way greatly facilitating the separation of the products; whilst, in order to ascertain the constitution of the compound, it was only necessary to distinguish between aniline, on the one hand, and anilidoacetic acid on the other, instead of between aniline and an alkyl-aniline.

Benzene-azo-acetone was accordingly heated with sodium ethoxide and ethylic chloracetate in alcoholic solution. The resulting "ester" was converted into the acid, which proved to have the expected formula, $\text{C}_{11}\text{H}_{12}\text{N}_2\text{O}_3$. On reduction, this acid yielded anilidoacetic acid, but no aniline. It has therefore the formula—

and "benzene-azo-acetone" is not an azo-compound at all, but a hydrazone of the formula—

—an “aldehydrazone” of pyruvic aldehyde, as distinguished from the “ketohydrazone”* derivable from the same compound.

This view was confirmed by the fact that “benzene-azo-acetone” yielded with phenylhydrazine a compound—

identical with the osazonet† of pyruvic aldehyde (methylglyoxal) prepared by v. Pechmann.

It appears, therefore, that when diazo-salts act on ethylic acetate and its analogues, or on their mono-alkylated derivatives, hydrazones are formed. R. Meyer (*Chem.-Zeit.*, 1887, 836) has shown that the compound obtained from ethylic malonate and diazo-benzene chloride is identical with the phenylhydrazone of ethylic mesoxalate, but draws the opposite conclusion to that arrived at by us, believing that the hydrazone undergoes transformation into an azo-compound.‡

* These names are formed on the analogy of “aldoxime” and “ketoxime.” “Aldehydrazone” is a contraction for “aldehydehydrazone.”

† “Osazone” is the term introduced by Fischer to denote the dihydrazone of an α -dicarbonyl-compound.

‡ This preliminary communication in the *Chemiker-Zeitung* had unfortunately escaped our notice at the time we published our first note on the identity of our “benzene-azo-propionic acid” with Fischer and Jourdan’s phenylhydrazonepyruvic acid.

Our views on the constitution of the above “mixed azo-compounds,” were first published, together with a brief account of the experimental proofs, in the Proceedings of December 15, 1887, and somewhat later in the *Berichte* (20, 3284 and 3398). Professor Victor Meyer, who arrived independently at the same conclusions, published a paper later still in the *Berichte* (21, 11), in which he discusses the theoretical question very fully, but does not contribute any fresh experimental material, although he suggests various experiments, some of which we had already described in our paper. After his paper had been sent to the *Berichte* (date of reception, 30th December, 1887), Professor Victor Meyer received the number of the Proceedings containing the account of our work, and despatched to the *Berichte* an addendum (4th January, 1888) in which he says: “Ich gestatte mir, darauf hinzuweisen, dass ich über das Thema am 13. December in der Göttinger chemischen Gesellschaft vorgetragen habe.”

We believe that, in the above sentence, Professor Victor Meyer has unintentionally conveyed the impression that he read a paper before the Göttingen Chemical Society on December 13. We understood the words in this sense, and therefore turned to the account of the meeting in question, given in the *Chemiker-Zeitung* (1887, 11, 1584), but found no mention of any such paper. Later, however, on January 8, in the number of the *Chemiker-Zeitung* following that in which an account of our work had been published, there appeared a second and “supplementary” notice of the above meeting of the Göttingen Chemical Society, in which it was stated that, in a discussion which followed on the reading of a paper by P. Jacobsen, Professor Victor Meyer had made certain remarks on the constitution of mixed azo-

The bivalent hydrazone-group, $\text{:N}\cdot\text{NHC}_6\text{H}_5$, thus corresponds with the bivalent isonitroso-group, $\text{:N}\cdot\text{OH}$. The isonitroso-compounds, as Victor Meyer has shown, are formed either by the action of hydroxylamine on a carbonyl-compound, or by the action of 'nitrous acid' on a compound containing the group CH_2 or CHR' attached to two electro-negative radicles, R' being a readily displaceable radicle (acetyl or carboxyl). Substituting, in the foregoing statement, "phenylhydrazine" for "hydroxylamine," and "diazocompound" for "nitrous acid," it describes the modes of formation of the hydrazones.

The analogy between the action of hydroxylamine and phenylhydrazine on carbonyl-compounds needs no illustration. The analogy between the action of nitrous acid and diazobenzene-compounds on ethylic acetoacetate, acetoacetic acid and their monalkyl-derivatives, is exemplified in the following equations, in which, for the sake of simplicity, free diazobenzene is employed, instead of its salts:—

1. With ethylic acetoacetate the reactions may be expressed as follows:—

2. In the case of monalkyl-derivatives of ethylic acetoacetate, the acetyl-group is expelled:—

compounds. The views embodied in these remarks were, we may say, identical with those put forward by us, and to this extent we were forestalled by Professor Victor Meyer.

Two criticisms suggest themselves on the foregoing.

In the first place, as regards the general question, although a discussion made before a learned Society may embody valuable remarks, yet if this discussion is not reported in the ordinary course along with the other work of the Society, it would be hardly fair to outsiders to regard such remarks as equivalent to publication.

Secondly, on the present and personal matter, if we had chosen to take the same course as Professor Victor Meyer, and publish our theoretical views first, leaving the experimental confirmation for later, we might have considerably anticipated the date of December 13, on which he lays so much stress.

3. When nitrous acid acts on free acetoacetic acid, or its monalkyl-derivatives, instead of on their ethyl salts, the carboxyl-group is eliminated, and isonitroso-ketones are formed. We find that in this case also diazobenzene behaves in an analogous manner. Thus, with acetoacetic acid, we have—

whilst methacetoacetic acid yields with diazobenzene the compound $\text{CH}_3\cdot\text{CO}\cdot\text{C}(\text{CH}_3)\cdot\text{N}\cdot\text{NHC}_6\text{H}_5$ (the monohydrazone of diacetyl, already prepared by v. Pechmann from diacetyl and phenylhydrazine); and ethacetoacetic acid yields the corresponding compound of the formula $\text{CH}_3\cdot\text{CO}\cdot\text{C}(\text{C}_2\text{H}_5)\cdot\text{N}\cdot\text{NHC}_6\text{H}_5$.

The so-called azo-ketones are thus monohydrazones of α -dicarbonyl-compounds. We also discovered, in the course of the present investigation, the following curious mode of formation of osazones (dihydrazones of α -dicarbonyl-compounds).

In heating phenylhydrazonepyruvic acid at 180 — 190° , until it had ceased to evolve gas, we obtained, along with oily matters, a crystalline substance of the formula $\text{C}_{16}\text{H}_{18}\text{N}_4$ (*Ber.*, **20**, 2943). We afterwards found that this compound was identical with the osazone of diacetyl, since prepared by v. Pechmann. Its formation from phenylhydrazonepyruvic acid may be expressed by the equation—

but we believe that it is in reality formed in a secondary reaction. E. Fischer and Jourdan have shown (*Ber.*, **16**, 2242) that phenylhydrazonepyruvic acid breaks up on heating, with evolution of carbon dioxide and formation of aldehydrazone (ethylidenephnylhydrazine)—

In fact, this is the chief reaction, the oily substance which we obtained consisting mainly of aldehydrazone, whilst the osazone is formed only in small quantity.

We, therefore, heated aldehydrazone at 180 — 190° , and found that the osazone of diacetyl was formed. The following equation shows the reaction:—

PART II. EXPERIMENTAL.

1. *Introduction of Monad Radicles into the Molecule of Pyruvaldehydrazone* ("Benzene-azo-acetone").

The pyruvaldehydrazone (to give the compound the name denoting the constitution to which the following experiments point) was prepared by a modification of v. Richter and Münzer's method (*Ber.*, 17, 1928). The crude product of the action of diazobenzene chloride on ethylic sodacetoacetate was first hydrolysed by warming for a few minutes with alcoholic caustic soda. Instead, however, of continuing the heating until the sodium salt thus formed was converted by the action of the caustic alkali into pyruvaldehydrazone and sodium carbonate, we added water, acidified with hydrochloric acid so as partially to precipitate the organic acid, added sodium carbonate so as to redissolve the precipitate, and then heated the liquid on a water-bath for several hours. In this way, the pyruvaldehydrazone was not exposed to the decomposing action of the caustic alkali, and was obtained in a purer condition. It separated from the hot liquid in large plates, which were filtered off, and the liquid was heated afresh until no further separation occurred. The latter portions were less pure. The compound is most conveniently purified by recrystallisation from hot benzene or methyl alcohol. As regards its physical properties, we have nothing to add to v. Richter and Münzer's description.

We have described the foregoing method because it was that by which the material employed in this investigation was obtained, but later on we give a method by which the compound can be much more readily prepared, namely, by the action of diazobenzene chloride on acetoacetic acid.

Action of Acetic Anhydride.—Pyruvaldehydrazone was boiled with excess of acetic anhydride for several hours, after which the solution was poured into water. An oil separated, which speedily became crystalline. By recrystallisation from boiling light petroleum, the compound was obtained in colourless needles melting at 93°. From a benzene solution, it is deposited in thick well-formed crystals, apparently quadratic. Analysis agreed with the formula $C_{11}H_{12}N_2O_2$.

	Substance.	CO ₂ .	H ₂ O.
I.	0.2150	0.5105	0.1151
II.	0.2265	0.5375	0.1202

III. 0.1110 gram, burnt with oxide of copper in a vacuum, gave 22.63 c.c. of a mixture of nitrogen and nitric oxide, measured dry at 19.5° and under 459 mm. pressure. After absorption of the nitric oxide there remained 22.63 c.c. of dry nitrogen at 19.5° and under 434 mm. pressure.

	Calculated for $C_{11}H_{12}N_2O_2$.	Found.		
		I.	II.	III.
C	64.70	64.75	64.72	—
H	5.88	5.94	5.89	—
N	13.73	—	—	14.05
O	15.69	—	—	—
	100.00			

The compound is therefore *acetylpyruvaldehydrazone*,

At the time when we first prepared this compound, we were under the impression that the acetyl-group had displaced hydrogen in the "methylene-group of benzene-azo-acetone" and that the compound was therefore a diketone. We consequently heated it with an excess of phenylhydrazine in alcoholic solution, but even at 200° only one oxygen-atom was displaced by the phenylhydrazone-group. The phenylhydrazone, which in reality has the formula

crystallises in pale-yellow needles, melting at 229° , readily soluble in hot, sparingly soluble in cold alcohol.

0.1013 gram, burnt with copper oxide in a vacuum, gave 22.63 c.c. of a mixture of nitrogen and nitric oxide, measured dry at 15.5° and under a pressure of 548 mm. After absorption of the nitric oxide, there remained 22.63 c.c. of dry nitrogen at 15.5° and under 543 mm. pressure.

	Calculated for $C_{17}H_{18}N_4O$.	Found.
N in 100 parts	19.04	19.06

Action of Methyl Iodide.—By heating together, in methyl alcoholic solution, equimolecular proportions of pyruvaldehydrazone, sodium methoxide, and methyl iodide, only a very small proportion of the pyruvaldehydrazone was converted into the methyl-derivative. This is due to the fact that the sodium methoxide and methyl iodide interact in great part by themselves, as if no pyruvaldehydrazone were present. We then tried whether an increase in the proportion of sodium methoxide and methyl iodide would render the conversion more complete; but the result was still unsatisfactory. The following slight modification of the process, however, by which the presence of any but a very small proportion of sodium methoxide during the progress of the reaction is avoided, gave an excellent yield.

A solution of 1 mol. proportion of pyruvaldehydrazone with 4 mol.

proportions of methyl iodide in methyl alcohol was boiled with a reflux condenser; a solution of 4 atomic proportions of sodium in methyl alcohol was allowed to drop gradually into the boiling liquid, so that the process extended over several hours; and the boiling was continued for a short time after the whole of the methoxide had been added. On pouring the contents of the flask into excess of water, an oil separated which speedily solidified; this substance was purified by recrystallisation from boiling light petroleum. It forms colourless, flat needles, melting at 64° , very soluble in alcohol, ether, and benzene, somewhat less soluble in light petroleum. It is a weak base, dissolving in concentrated hydrochloric acid, but is reprecipitated by water.

Analysis showed that it had the formula $C_{10}H_{12}N_2O$:—

	Substance.	CO_2 .	H_2O .
I.	0.2180	0.5450	0.1344
II.	0.2039	0.5098	0.1260

III. 0.1088 gram, burnt with copper oxide in a vacuum, gave 22.63 c.c. of nitrogen, measured dry at 18.2° and under 500 mm. pressure. Nitric oxide was not present.

Calculated for $C_{10}H_{12}N_2O$.		Found.		
		I.	II.	III.
C	68.18	68.18	68.18	—
H	6.82	6.85	6.86	—
N	15.91	—	—	16.12
O	9.09	—	—	—
<hr/>				
100.00				

The compound has the constitution $CH_3 \cdot CO \cdot CH \cdot N \cdot N < \begin{smallmatrix} C_6H_5 \\ CH_3 \end{smallmatrix}$.

That the methyl-group has not displaced hydrogen attached to carbon is shown by the fact that the compound is distinct from the hydrazone of diacetyl (*vide infra*).

When heated with phenylhydrazine in alcoholic solution, it yields a compound,

which crystallises in faint-yellow needles, melting at 151 — 152° , sparingly soluble in alcohol, readily soluble in ether.

0.0770 gram, burnt with copper oxide in a vacuum, gave 22.63 c.c. of a mixture of nitrogen and nitric oxide, measured dry at 15.4° and under a pressure of 471 mm. After absorption of the nitric oxide, there remained 22.63 c.c. of dry nitrogen at 15.6° and under 460 mm. pressure.

	Calculated for $C_{16}H_{18}N_4$	Found.
N in 100 parts	21.05	21.4

Action of Ethyl Iodide.—Pyruvaldehydrazone reacted in an analogous manner with sodium ethoxide and ethyl iodide, yielding the compound $CH_3 \cdot CO \cdot CH : N \cdot N (C_2H_5)C_6H_5$, which crystallised from light petroleum in thin prisms, melting at 55° . The substance had a faint reddish tinge, doubtless due to impurity.

0.1942 gram gave 0.4923 gram CO_2 and 0.1277 gram H_2O .

	Calculated for $C_{11}H_{14}N_2O$	Found.
C	69.47	69.13
H	7.37	7.30
N	14.74	—
O	8.42	—
	<hr/> 100.00	

Action of Ethylic Chloracetate.—The pyruvaldehydrazone, together with four times its molecular proportion of ethylic chloracetate, was dissolved in alcohol, and a solution of 4 atoms of sodium in alcohol was gradually added to the boiling liquid, conducting the operation as in the preparation of the methyl-derivative. Caustic soda was then added, and the solution was boiled so as to hydrolyse the “ester” which had been formed in the reaction. After expelling part of the alcohol by heating, water was added, the liquid was filtered, and the new acid was precipitated with hydrochloric acid. In order to purify the substance, it was dissolved in a cold solution of sodium carbonate, reprecipitated with hydrochloric acid and repeatedly recrystallised from boiling water. It formed yellow needles which melted with decomposition about 161 — 162° . Analysis agreed with the formula $CH_3 \cdot CO \cdot CH : N \cdot N (C_6H_5)CH_2 \cdot COOH$.

I. 0.2128 gram gave 0.4671 gram CO_2 and 0.1070 gram H_2O .

II. 0.1067 gram, burnt with copper oxide in a vacuum, gave 22.63 c.c. of a mixture of nitrogen and nitric oxide, measured dry at 16° and under 405 mm. pressure. After absorption of the nitric oxide there remained 22.63 c.c. of dry nitrogen at 16° and under 395 mm. pressure.

	Calculated for $C_{11}H_{12}N_2O_3$	Found.	
		I.	II.
C	60.00	59.86	—
H	5.45	5.58	—
N	12.73	—	13.25
O	21.82	—	—
	<hr/> 100.00		

Action of Nascent Hydrogen on the Acid $C_{11}H_{12}N_2O_3$.—The acid was dissolved in alcohol and treated with excess of tin and hydrochloric acid. The tin was then precipitated with sulphuretted hydrogen, the solution evaporated to dryness, the residue extracted with ether,* and the substance remaining on evaporation of the ether recrystallised from hot water. The aqueous solution on cooling deposited small crystals, with a slight brownish tinge, melting at $126-127^\circ$. (M. p. of anilidoacetic acid $126-127^\circ$; P. Meyer). In all its properties, excepting the slight brown colour, it was indistinguishable from a specimen of anilidoacetic acid prepared from bromacetic acid and aniline. As the quantity was too small for further purification we analysed it direct.

0.0926 gram, burnt with copper oxide in a vacuum, gave 22.63 c.c. of a mixture of nitrogen and nitric oxide, measured dry at 15° and under 253 mm. pressure. After absorption of the nitric oxide, there remained 22.63 c.c. of dry nitrogen at 15° and under 246 mm. pressure.

	Calculated for $NH(C_6H_5) \cdot CH_2 \cdot COOH$.	Found.
N in 100 parts	9.27	9.54

Anilidoacetic acid was also obtained by reducing the acid $C_{11}H_{12}N_2O_3$ with sodium amalgam in aqueous solution. No aniline was formed; but a strong smell of a ketine was perceived. We reduced simultaneously isonitrosoacetone with sodium amalgam and perceived the same smell.

The acid, $CH_3 \cdot CO \cdot CH : N \cdot N(C_6H_5) \cdot CH_2 \cdot COOH$, is therefore broken up by the nascent hydrogen with separation of the nitrogen-atoms, one-half of the molecule yielding anilidoacetic acid, the other a ketine. The formation of anilidoacetic acid from this acid proves that the latter has the constitution here assigned to it, and thus, indirectly, that the so-called "benzene-azo-acetone" is *pyruvaldehydrazone*.

2. Action of Phenylhydrazine on some Ketonic Compounds containing the Phenylhydrazone-group.

Action on Ethylic Phenylhydrazone-acetoglyoxylate ("Benzene-azo-acetoacetate").—10 grams of ethylic phenylhydrazone-acetoglyoxylate and 5.5 grams of phenylhydrazine were heated with glacial acetic acid in a sealed tube for an hour, at $120-130^\circ$. On cooling, the tube

* As the substance here extracted was anilidoacetic acid, we would point out that Schwebel's statement (*Ber.*, 10, 2046) that this acid is insoluble in ether is incorrect. Michaelson and Lippmann, the discoverers of anilidoacetic acid, say (*Annalen*, 139, 236): "It is fairly soluble in water, less soluble in ether." This is correct. The statement as to its insolubility in ether has passed into Beilstein's *Handbuch*.

was found to be filled with red needles, with a characteristic blue reflex; these, after crystallisation from glacial acetic acid, melted at 155°. These properties pointed to the identity of the compound with Knorr's (1)-phenyl-(3)-methylpyrazolone-(4)-azobenzene (*Annalen*, **238**, 183), which this author obtained by the action of diazobenzene salts on phenylmethylpyrazolone, and to which he assigns the constitution—

In the present case it is formed according to the equation—

A nitrogen determination gave the following result:—

0.0967 gram, burnt with copper oxide in a vacuum, gave 22.63 c.c. of a mixture of nitrogen and nitric oxide, measured dry at 18°, and under 556 mm. pressure. After absorption of the nitric oxide, there remained 22.63 c.c. of dry nitrogen at 18°, and under 550 mm. pressure.

	Calculated for $\text{C}_{16}\text{H}_{14}\text{N}_4\text{O}$.	Found.
N in 100 parts	20.14	20.06

Although ethylic phenylhydrazone-acetoglyoxylylate must be regarded as a hydrazone, we should not like positively to affirm the same of the pyrazolone-derivative obtained from it in the foregoing reaction. It is quite conceivable that in the formation of this compound the hydrazone-group is transformed into an azo-group; and, indeed, the extremely pronounced colour of Knorr's compound would rather indicate the occurrence of such a change.*

Action on Phenylhydrazone-acetoglyoxylic Acid.—When phenylhydrazone-acetoglyoxylic acid is warmed with phenylhydrazine in alcoholic solution, *osazone-acetoglyoxylic acid*—

separates almost immediately in slender, yellow needles, melting at 209°. This acid was obtained by Knorr (*Annalen*, **238**, 195) by the action of phenylhydrazine on rubazonic acid. Knorr gives the melting point at 212°.

* Compare also Bernthsen, *Ber.*, **21**, 743.

0.1048 gram, burnt with copper oxide in a vacuum, gave 22.63 c.c. of a mixture of nitrogen and nitric oxide, measured dry at 15.8° and under 572 mm. pressure. After absorption of the nitric oxide, there remained 22.63 c.c. of dry nitrogen at 16° and under 555 mm. pressure.

	Calculated for $C_{16}H_{16}N_4O_2$.	Found.
N in 100 parts	18.92	19.00

When heated with acetic acid, this compound parts with the elements of 1 mol. H_2O , and yields the foregoing phenylmethylpyrazolone-azobenzene, melting at 155°.*

Action on Pyruvaldehydrazone.—Pyruvaldehydrazone and phenylhydrazine, when heated together in alcoholic solution, react, yielding the compound—

It is deposited from hot alcohol, in which it is only sparingly soluble, as a yellowish crystalline powder, melting at 145°. It dissolves in concentrated sulphuric acid in the cold with an olive-green colour, which speedily changes to slate-blue, and finally, after standing for some hours, to violet. A drop of the blue or violet solution, poured into a porcelain basin and breathed upon, becomes first green, and afterwards yellow.

0.0889 gram, burnt with copper oxide in a vacuum, gave 22.63 c.c. of a mixture of nitrogen and nitric oxide, measured dry at 16.2°, and under 561.5 mm. pressure. After absorption of the nitric oxide, there remained 22.63 c.c. of dry nitrogen at 16.5° and under 551 mm. pressure.

	Calculated for $C_{15}H_{16}N_4$.	Found.
N in 100 parts	22.22	22.08

Assuming that the above formula is correct, the compound should be identical with the osazone of pyruvaldehyde (methylglyoxal) obtained by v. Pechmann by the action of phenylhydrazine on pyruvaldehyde and also by heating isonitrosoacetone with phenylhydrazine in acetic acid solution (*Ber.*, 20, 2543). We therefore prepared the

* After the above was already in type, we received No. 6 of the *Berichte*, 1888, in which Knorr describes the formation of phenylmethylpyrazolone-azobenzene from osazone-acetoglyoxylic acid, and points out its identity with phenylhydrazone-phenylmethylketopyrazolone (*Ber.*, 21, 1203). Knorr is of opinion that the compound is a hydrazone.

Knorr converts the osazone into the pyrazolone-compound by dissolving it in caustic alkali and precipitating with acetic acid.

compound by the latter method, and found that it agreed in all its properties with that above described.

3. *Action of Diazo-salts on Monalkyl-derivatives of Ethylic Acetoacetate : Formation of Hydrazones of α -Ketonic Acids.*

Ethyl Methacetoacetate and Diazobenzene Chloride.—An aqueous solution of diazobenzene chloride was gradually added in equimolecular proportion to an alcoholic solution of ethylic sodiomethacetoacetate, cooling during the process. The liquid became deep red, and towards the end of the operation a dark-red oil separated. Water was then added to complete the precipitation, after which the oil generally solidified. When this did not occur, the oil was washed with water in a separating funnel and then mixed with alcohol, which caused it to become solid and crystalline. The solid substance was recrystallised several times, first from alcohol, afterwards from light petroleum, by which means it was obtained in yellow needles, melting at 117° .

Analysis led to the formula $C_{11}H_{14}N_2O_2$:—

I. 0.2050 gram gave 0.4820 gram CO_2 and 0.1255 gram H_2O .

II. 0.1123 gram, burnt with copper oxide in a vacuum, gave 22.63 c.c. of nitrogen, measured dry at 17.6° , and under 438 mm. pressure. Nitric oxide was not present.

	Calculated for $C_{11}H_{14}N_2O_2$.	Found.	
		I.	II.
C	64.08	64.12	—
H	6.80	6.80	—
N	13.59	—	13.70
O	15.53	—	—
	<hr/> 100.00		

The acid was readily obtained by warming the "ester" with an alcoholic solution of caustic soda and precipitating with hydrochloric acid. It crystallises from hot benzene in yellowish needles, melting with evolution of gas at 185° . It dissolves in cold concentrated sulphuric acid with a yellow colour, which soon changes to a deep-red. On allowing a drop of the concentrated red solution to flow about in a porcelain basin, and breathing on it, the colour changes to blue.

Analysis gave figures agreeing with the formula $C_9H_{10}N_2O_2$:—

I. 0.2202 gram gave 0.4893 gram CO_2 and 0.1126 gram H_2O .

II. 0.1101 gram, burnt with oxide of copper in a vacuum, gave 22.63 c.c. of nitrogen, measured dry at 23.4° , and under 501 mm. pressure. Nitric oxide was not present.

	Calculated for $C_9H_{10}N_2O_2$.	Found.	
		I.	II.
C	60.67	60.60	—
H	5.62	5.68	—
N	15.73	—	15.68
O	17.98	—	—
	<hr/> 100.00		

This acid proved, as already mentioned, to be identical with E. Fischer and Jourdan's *phenylhydrazonepyruvic acid*,

(*Ber.*, 16, 2241). Fischer and Jourdan give the melting point of their acid at 169° ; but, later, Fischer (*Ber.*, 17, 578) stated that this was a misprint for 192° , which he gives as the true melting point of the acid.* We therefore carefully purified specimens of acid prepared both by our method and by that of Fischer and Jourdan, but in

* In an earlier communication on this subject (*Ber.*, 20, 3285), we unfortunately overlooked Fischer's correction, and stated that Fischer and Jourdan had given the melting point "much too low." Our attention was called to the oversight by V. Meyer (*Ber.*, 21, 18). Fischer's correction appears to have escaped notice in another quarter: thus Sandmeyer, in a paper emanating from the laboratory of the Zürich Polytechnic (*Ber.*, 20, 641), identifies pyruvic acid by means of its phenylhydrazone, which, according to him, "after dissolving once in dilute ammonia and precipitating with hydrochloric acid, showed the correct melting point of 169° ."

Since the foregoing was written, Professor Fischer has alluded to the subject of the melting point of phenylhydrazonepyruvic acid (*Ber.*, 21, 987). After pointing out that the acid, as a substance which decomposes in melting, will show too low a melting point unless rapidly heated, he adds:—"It was evidently from this cause that Messrs. Japp and Klingemann, who have overlooked both my corrected statement as to the melting point" [*i.e.*, that 169° was a misprint for 192°], "and my remarks on the mode of heating, found the melting point of the compound first at 182° and afterwards at 185° ."

There is a point here which calls for correction. We stated (*Ber.*, 20, 3285) that, in our first communication, the melting point of the compound "was erroneously given at 182° , instead of at 185° ." Professor Fischer somewhat hastily concludes that "erroneously given" is synonymous with "erroneously found." As a matter of fact, the error in question was an error in transcribing, although we did not specify this at the time, imagining that the cause of such an error—whether a misprint, as in Professor Fischer's case, or otherwise—could be of interest to no one save the authors.

We have already expressed our regret that we overlooked Professor Fischer's correction. As regards the other oversight—of Professor Fischer's "remarks on the mode of heating"—we would point out that we expressly stated that the compound decomposed in melting, and we are under the impression that the precaution to be taken in determining the melting point of substances of this character was

neither case could we succeed in raising the melting point above 185° , which we must therefore regard as the correct melting point.

Both acids, on heating, yielded a crystalline compound of the formula $C_{16}H_{18}N_4$ —diacetylosazone (*vide supra*)—together with oily matters.

We also found that Fischer and Jourdan's acid gave the above characteristic colour reaction with concentrated sulphuric acid.

Fischer and Jourdan give the melting point of the ethyl salt of their acid at 114 — 115° . We found, for the ethyl salt prepared as above described, the melting point 117° .

The metallic salts appear to be very unstable, and could not be obtained in a state fit for analysis.

We reduced the acid obtained by the above method with sodium amalgam. By moderate reduction of the sodium salt in aqueous solution with sodium amalgam, a hydrazo-acid was obtained, which was precipitated on acidifying with hydrochloric acid, avoiding an excess, which was found to redissolve the hydrazo-acid. It crystallised from methyl alcohol in slender, colourless needles, which on exposure to air become yellow, especially when moist. We found the melting point at 170° , but had not sufficient substance for further recrystallisation; the true melting point is 172° * (see later on). The substance evolves gas in melting. Analysis gave figures agreeing with the formula $C_9H_{12}N_2O_2$:—

I. 0.1910 gram gave 0.4207 gram CO_2 and 0.1174 gram H_2O .

II. 0.0978 gram, burnt with copper oxide in a vacuum, gave 22.63 c.c. of a mixture of nitrogen and nitric oxide, measured dry at 16.8° and under 435 mm. pressure. After absorption of the nitric oxide, there remained 22.63 c.c. of dry nitrogen at 16.9° and under 430 mm. pressure.

	Calculated for $C_9H_{12}N_2O_2$.	Found.	
		I.	II.
C	60.00	60.07	—
H	6.67	6.83	—
N	15.55	—	15.58
O	17.78	—	—
	<hr/> 100.00		

known before Professor Fischer illustrated it in the case of the hydrazones. We made a point of heating as rapidly as is practicable.

Professor Fischer's explanation will hardly account for the fact that in the case of the corresponding hydrazo-acid—also a compound which decomposes in melting—we found the melting point 20° higher than he did.

* The melting point (162°) given in our first publication on this subject (*Ber.*, 20, 2943) is too low. The substance had not been sufficiently purified.

This acid would be *benzene- α -hydrazopropionic acid*,

Fischer and Jourdan (*Ber.*, **16**, 2244) obtained this acid by the reduction of phenylhydrazonepyruvic acid, but assign to it the melting point 152—154°. We therefore prepared phenylhydrazonepyruvic acid from phenylhydrazine and pyruvic acid, and reduced it with sodium amalgam. The hydrazo-acid thus obtained was identical with the foregoing, and after repeated recrystallisation from methyl alcohol had a constant melting point of 172°.

Aniline is always formed in this reduction, as observed by Fischer and Jourdan. We therefore endeavoured to isolate the other product which would be formed by the breaking up of the molecule of the hydrazo-acid by reduction—alanine. A quantity of phenylhydrazonepyruvic acid was dissolved in dilute caustic soda and treated with excess of sodium amalgam on the water-bath. The aniline which was formed was then extracted with ether; the alkaline aqueous solution was slightly acidified with hydrochloric acid, thus precipitating a small quantity of the hydrazo-acid, which was removed by filtration; the filtrate was evaporated to dryness, and the residue treated with boiling absolute alcohol to extract the alanine hydrochloride, which remained as a crystalline residue on evaporating the alcohol; this residue was boiled with water and litharge; the filtered solution, containing the lead salt of alanine, was precipitated with sulphuretted hydrogen; and the filtrate from the lead sulphide was evaporated to a small bulk and then mixed with an excess of alcohol. Alanine separated in slender white needles. The alanine thus obtained had a sweet taste; sublimed above 200°, and gave on analysis :—

	C.	H.	N.
Calculated for $\text{C}_3\text{H}_7\text{NO}_2$..	40.45	7.86	15.73 per cent.
Found	40.38	8.03	15.61 „

Ethyllic Methacetoacetate and o-Diazotoluene Chloride.—The reaction was conducted as in the former case. The “ester” was obtained as a red oil which did not solidify, even in a freezing mixture: it was therefore hydrolysed by heating with caustic soda and alcohol. The acid was precipitated with hydrochloric acid and purified by recrystallisation from benzene. It formed small yellowish laminæ, melting, with evolution of gas, at 156°. It is identical with Raschen's *o-tolyldiazopropionic acid* (*Annalen*, **239**, 228), which we prepared from pyruvic acid and *o*-tolylhydrazine hydrochloride for the purpose of comparing it with our compound. Raschen gives

the melting-point at 158—159°. The acid prepared by our method gave the following figures on analysis:—

I. 0.2214 gram gave 0.5051 gram CO₂ and 0.1221 gram H₂O.

II. 0.0988 gram, burnt with copper oxide in a vacuum, gave 22.63 c.c. of a mixture of nitrogen and nitric oxide, measured dry at 15.7° and under 412 mm. pressure. After absorption of the nitric oxide, there remained 22.63 c.c. dry nitrogen at 16° and under 408 mm. pressure.

	Calculated for C ₁₀ H ₁₂ N ₂ O ₂ .	Found.	
		I.	II.
C	62.50	62.22	—
H	6.25	6.13	—
N	14.58	—	14.67
O	16.67	—	—
	<hr/> 100.00		

The hydrazo-acid, which had not hitherto been prepared, was obtained by reducing the acid from *o*-diazotoluene and ethylic meth-acetoacetate with sodium amalgam. The acid was precipitated by careful addition of hydrochloric acid and recrystallised from methyl alcohol. It formed tufts of small, colourless needles, melting at 143°. This melting point is possibly too low, as the quantity of substance was insufficient for further recrystallisation.

	Substance.	CO ₂ .	H ₂ O.
I.....	0.1911	0.4306	0.1262
II.....	0.2048	0.4617	0.1331

III. 0.0998 gram, burnt with copper oxide in a vacuum, gave 22.63 c.c. of nitrogen, measured dry at 20° and under 412 mm. pressure. Nitric oxide was not present.

	Calculated for C ₁₀ H ₁₄ N ₂ O ₂ .	Found.		
		I.	II.	III.
C	61.86	61.45	61.48	—
H.	7.22	7.33	7.22	—
N	14.43	—	—	14.39
O	16.49	—	—	—
	<hr/> 100.000			

The acid is consequently the expected *o*-toluenehydrazopropionic acid,

o-Toluidine was regenerated during the reduction.

Ethyl Methacetoacetate and p-Diazotoluene Chloride.—In this case, the “ester,” when precipitated with water, solidified. It was deposited in yellowish laminæ from light petroleum, and in needles from alcohol, melting at 106°.

	C.	H.	N.
Calculated for $C_{12}H_{16}N_2O_2$..	65.45	7.27	12.73 per cent.
Found	65.64	7.33	13.05 „

The “ester” was hydrolysed with alcoholic caustic soda. The precipitated acid was recrystallised from benzene, from which it was deposited in yellow laminæ melting at 162° with evolution of gas

	C.	H.	N.
Calculated for $C_{10}H_{12}N_2O_2$..	62.50	6.25	14.58 per cent.
Found	62.48	6.28	14.54 „

This acid is identical with Raschen's *p-tolylhydrazonopyruvic acid* (*Annalen*, **239**, 224), which we prepared for comparison. Raschen gives the melting point of the acid at 158—160°; that of the ethyl salt at 106—107°.

The hydrazo-acid was not prepared.

Ethyl Ethacetoacetate and Diazobenzene Chloride.—In this case, diazobenzene chloride was added to the molecular proportion of ethyl sodethacetoacetate dissolved in alcohol. The new “ester,” when precipitated with water, did not solidify, and was therefore hydrolysed with alkali. The acid, precipitated with hydrochloric acid, was purified by recrystallisation from benzene, which deposited it in yellow needles, with a silky lustre, melting with decomposition at 152°.

I. 0.1984 gram gave 0.4543 gram CO_2 and 0.1139 gram H_2O .

II. 0.0927 gram, burnt with copper oxide in a vacuum, gave 22.63 c.c. of nitrogen, measured dry at 16° and under 384 mm. pressure. Nitric oxide was not present.

	Calculated for $C_{10}H_{12}N_2O_2$.	Found.	
		I.	II.
C	62.50	62.44	—
H	6.25	6.37	—
N	14.58	—	14.63
O	16.67	—	—
	<hr/> 100.00		

The acid is *phenylhydrazonopropionylformic acid*,

In the preliminary account of these reactions which we published (*Ber.*, **20**, 2943), we described this acid, regarding it, however, as "benzene- α -azobutyric acid." Later, W. Wislicenus and E. Arnold (*Ber.*, **20**, 3395) described an acid obtained from propionylformic acid and phenylhydrazine, which ought to be identical with the foregoing. They state that it crystallises from dilute alcohol in laminae melting at 144—145°.

By reduction of the sodium salt of the above acid in aqueous solution with sodium amalgam, *benzene- α -hydrazobutyric acid*,

was obtained. The hydrazo-acid, precipitated by hydrochloric acid, avoiding an excess, and recrystallised from methyl alcohol, formed small colourless needles. The compound exhibits a peculiar behaviour on heating. At 165°, it softens, without distinctly melting, and a substance which colours the sulphuric acid in the melting-point bulb violet distils out of the capillary tube; then the contents of the tube again become solid; and before the temperature of 245° is reached, at which a slight residue still left in the capillary tube melts, nearly everything has sublimed out of the tube. The substance was dried over sulphuric acid for analysis.

	Substance.	CO ₂ .	H ₂ O.
I	0.2098	0.4763	0.1395
II	0.2047	0.4645	0.1337

III. 0.0970 gram, burnt with copper oxide in a vacuum, gave 22.63 c.c. of a mixture of nitrogen and nitrous oxide, measured dry at 20° and under 406 mm. pressure. After absorption of the nitric oxide, there remained 22.63 c.c. of dry nitrogen at 20°, and under 402 mm. pressure:—

		Found.		
		I.	II.	III.
C	Calculated for C ₁₀ H ₁₄ N ₂ O ₂ . 61.86	61.91	61.88	—
H	7.22	7.39	7.25	—
N	14.43	—	—	14.51
O	16.49	—	—	—
<hr/>				
100.00				

4. Action of Diazo-salts on Ketonc Acids : Formation of Monohydrazones of α -Dicarbonyl-compounds.

Acetoacetic Acid and Diazobenzene Chloride.—65 grams of ethylic acetoacetate were dissolved in a solution of 30 grams of caustic

potash in 1120 grams of water, and allowed to stand for 24 hours, after which the solution was acidified with hydrochloric acid in order to liberate the acetoacetic acid. A solution of the molecular proportion of diazobenzene chloride (from 47 grams of aniline and 35 grams of sodium nitrite), *containing a slight excess of hydrochloric acid*, was then added. The acid solutions remain clear when first mixed; then a separation of pyruvaldehydrazone ("benzene-azo-acetone"), $\text{CH}_3\cdot\text{CO}\cdot\text{CH}:\text{N}\cdot\text{NH}\cdot\text{C}_6\text{H}_5$, commences, accompanied by an evolution of carbon dioxide; but the reaction takes place very slowly, and is not quite complete even at the end of eight hours. It is therefore better to add to the acid solution, after mixing, an excess of a solution of sodium acetate; the reaction then takes place rapidly, and an almost quantitative yield of a practically pure product is obtained. In both cases, the pyruvaldehydrazone separates in a crystalline form. It is probably advisable to use rather less diazo-salt than the theory requires.

After recrystallising twice from benzene, the pyruvaldehydrazone showed the proper melting point, $149-150^\circ$. It yielded a phenylhydrazine-derivative melting at 145° , which gave with concentrated sulphuric acid the characteristic colour reaction (p. 531).

The above is, both as regards yield and purity of the product, by far the best method as yet known of preparing pyruvaldehydrazone.

Methacetoacetic Acid and Diazobenzene Chloride.—The operation was conducted as in the foregoing experiment, substituting 72 grams of ethylic methacetoacetate for the ethylic acetoacetate. On adding sodium acetate to the hydrochloric acid solution of methacetoacetic acid and diazobenzene chloride, *diacetylhydrazone*,

separated in minute needles with evolution of carbon dioxide. The crude product was treated with sodium carbonate to remove any phenylhydrazonopyruvic acid that might have been formed from unhydrolysed ethylic methacetoacetate, and then recrystallised from hot benzene, which deposited it in yellow, tabular crystals, mostly grouped staircase-fashion, melting at 133° .

0.2350 gram gave 0.5847 gram CO_2 and 0.1414 gram H_2O .

	Calculated for $\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}$.	Found.
C	68.18	67.85 per cent.
H	6.82	6.68 ,,

The monophenylhydrazone of diacetyl has been prepared from diacetyl and phenylhydrazine by v. Pechmann (*Ber.*, 20, 3164), who

gives the melting point at 133° , with which our determination exactly agrees.

On pouring a concentrated aqueous solution of phenylhydrazine hydrochloride into a hot alcoholic solution of the above monohydrazone, the *osazone*, $\text{CH}_3\cdot\text{C}\cdot\text{N}\cdot\text{NH}\cdot\text{C}_6\text{H}_5$, separates as a yellow crystalline powder melting at 243° . v. Pechmann (*loc. cit.*) gives 242° as the melting point of diacetylosazone, which we also prepared from diacetyl and phenylhydrazine, and found identical in all its properties with the compound obtained by us. A nitrogen determination was made with our compound:—

0.1074 gram, burnt with copper oxide in a vacuum, gave 22.63 c.c. of a mixture of nitrogen and nitric oxide, measured dry at 11° and under 627 mm. pressure. After absorption of the nitric oxide, there remained 22.63 c.c. of dry nitrogen at 11° and under 621 mm. pressure.

	Calculated for $\text{C}_{16}\text{H}_{18}\text{N}_4$.	Found.
N in 100 parts	21.05	20.88

Diacetylosazone gives a colour-reaction with concentrated sulphuric acid. It dissolves in the cold with a brown colour; but this speedily changes to a claret-red, which in thin layers appears green.

Ethacetoacetic Acid and Diazobenzene Chloride.—The experiment was performed as in the preceding cases, except that the ethylic ethacetoacetate required longer shaking with the caustic potash solution to make it dissolve, and owing to the greater difficulty with which it is hydrolysed, it was allowed to stand in alkaline solution for 48 hours instead of for 24. In this case, the propionylacetylhydrazone $\text{C}_2\text{H}_5\cdot\text{C}\cdot\text{N}\cdot\text{NHC}_6\text{H}_5$, separated as a red oil on the addition of sodium $\text{CH}_3\cdot\text{CO}$

acetate to the hydrochloric acid solution of ethacetoacetic acid and diazobenzene chloride. On dissolving this oil in a small quantity of alcohol, the new compound was deposited in a solid form. The product was treated with sodium carbonate to remove any acid. From concentrated solutions in hot benzene, it crystallised in yellow needles or prisms radiating from a point; from dilute solutions, in large, transparent plates. It melted at $116\text{--}117^{\circ}$.

In spite of the apparent purity of the substance, the carbon was found to be 1 per cent. too low on analysis, and the hydrogen was also too low. Only after repeated recrystallisation from benzene were numbers obtained agreeing fairly well with the theory:—

	Substance.	CO_2 .	H_2O .
I	0.2669	0.6762	0.1748
II	0.2333	0.5908	0.1506

	Calculated for $C_{11}H_{14}N_2O$.	Found.	
		I.	II.
C	69·47	69·09	69·06
H	7·36	7·28	7·17

Even in these analyses, the hydrogen is too low. We suspect, therefore, that the substance was contaminated with a small quantity of pyruvaldehydrazone, which would be formed if the ethylic eth-acetoacetate contained, as it very easily might, unchanged ethylic acetoacetate. We find that propionylacetylhydrazone and pyruvaldehydrazone crystallise together.

Possibly a small quantity of the same impurity, formed in the same way, was present in the specimen of diacetylhydrazone which we analysed (*ante*), in which the hydrogen was also found too low.

The *osazone* of propionylacetyl, $C_2H_5 \cdot C:N \cdot NHC_6H_5$, $CH_3 \cdot C:N \cdot NHC_6H_5$, was obtained by heating an alcoholic solution of the foregoing compound with phenylhydrazine hydrochloride and sodium acetate. It crystallises from benzene in yellow needles melting at 162° , which give with concentrated sulphuric acid exactly the same colour-reaction as the *osazone* of diacetyl (p. 540).*

0·1012 gram, burnt with copper oxide in a vacuum, gave 22·63 c.c. of a mixture of nitrogen and nitric oxide measured dry at 14° and under 557 mm. pressure. After absorption of the nitric oxide, there remained 22·63 c.c. of dry nitrogen at 14° and under 553 mm. pressure.

	Calculated for $C_{17}H_{20}N_4$.	Found.
N in 100 parts	20·00	19·51

5. Action of Heat on Hydrazones of Ketonic Acids and on Aldehydrazones: Formation of Osazones.

Action of Heat on Phenylhydrazonepyruvic Acid.—A quantity of phenylhydrazonepyruvic acid was heated in an oil-bath at 180 — 190° until gas ceased to be evolved. From the dark-coloured oil thus obtained, a crystalline substance separated on adding alcohol. It was

* No. 6 of the *Berichte*, received after the above was in type, contains an account of the hydrazones of propionylacetyl by v. Pechmann. The author prepared these compounds by the direct action of phenylhydrazine on propionylacetyl. He finds that the monohydrazone obtained in this way is distinct from our compound, and he therefore assigns to it the formula—

For the *osazone* he finds the melting point at 161 — $162\frac{1}{2}^\circ$, agreeing with our determination.

washed with hot alcohol, in which it is only sparingly soluble, and dried for analysis. It formed a yellow crystalline powder, melting at 238° . Analysis led to the formula $C_{16}H_{18}N_4$.

I. 0.1717 gram gave 0.4536 gram CO_2 and 0.1041 gram H_2O .

II. 0.1047 gram, burnt with copper oxide in a vacuum, gave 22.63 c.c. of a mixture of nitrogen and nitric oxide, measured dry at 14.7° and under 617 mm. pressure. After absorption of the nitric oxide, there remained 22.63 c.c. of dry nitrogen at 15° and under 610 mm. pressure.

	Calculated for $C_{16}H_{18}N_4$.	Found.	
		I.	II.
C	72.18	72.04	—
H	6.77	6.73	—
N	21.05	—	20.78
	<hr/> 100.00		

The compound was soluble in cold concentrated sulphuric acid with a brown colour, changing afterwards to a claret-red, which in thin layers appeared green.

The formula and the colour-reaction with sulphuric acid are therefore those of *diacetyllosazone* (p. 540), with which the compound is indeed identical. The difference in the melting point— 238° instead of 242° —is due to the fact that the substance, owing to the smallness of the quantity available, was not recrystallised. The yield is very small.

The formation of the osazone of diacetyl in the above reaction may be expressed thus:—

Action of Heat on Aldehydrazone.—As already mentioned, Fischer and Jourdan have shown (*loc. cit.*) that the oil which is obtained on heating phenylhydrazonopyruvic acid mainly consists of aldehydrazone (ethylidenephénylhydrazine)—

It therefore seemed possible that the osazone of diacetyl had been formed from the aldehydrazone in a secondary reaction according to the equation—

We therefore heated aldehydrazone with a reflux condensing-tube for three hours. On adding alcohol to the liquid product, the expected osazone separated as a crystalline powder. It was identified by its melting point (237—238°) and by the reaction with sulphuric acid. The yield is very small, but may be somewhat increased by passing air through the aldehydrazone during the heating process.

The osazone obtained by the above methods was carefully compared with a specimen prepared from diacetyl and phenylhydrazine.

Action of Heat on the Tolyldhydrazonopyruvic Acids.—*o*-Tolyldhydrazonopyruvic acid, when heated for some time at its melting point, yielded in like manner *diacetyl-o-tolylosazone*,

which separated from the oily product of the reaction on adding alcohol. It formed a yellow crystalline powder melting at 198°, sparingly soluble in alcohol. The sulphuric acid reaction is not characteristic; the compound dissolves in the concentrated acid with a brown colour which afterwards changes to a reddish-brown.

The same compound was obtained by heating an aqueous solution of diacetyl with *o*-tolyldhydrazine hydrochloride and sodium acetate.

I. 0.0827 gram, burnt with copper oxide in a vacuum, gave 22.63 c.c. of a mixture of nitrogen and nitric oxide, measured dry at 15.5° and under 448 mm. pressure. After absorption of the nitric oxide, there remained 22.63 c.c. of dry nitrogen at 15.5° and under 444 mm. pressure.

II. 0.0754 gram, burnt with copper oxide in a vacuum, gave 22.63 c.c. of a mixture of nitrogen and nitric oxide, measured dry at 14° and under 402 mm. pressure. After absorption of nitric oxide, there remained 22.63 c.c. of dry nitrogen at 14° and under 400 mm. pressure.

	Calculated for $\text{C}_{18}\text{H}_{22}\text{N}_4$.	Found.	
		I.	II.
N in 100 parts	19.05	19.08	18.92

Analysis I was made with a preparation obtained from *o*-tolyldhydrazonopyruvic acid; analysis II with a preparation from diacetyl and *o*-tolyldhydrazine.

p-Tolyldhydrazonopyruvic acid yields, when heated, *diacetyl-p-tolylosazone*, $\begin{array}{c} \text{CH}_3\cdot\text{C}\cdot\text{N}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_3 \\ \text{CH}_3\cdot\text{C}\cdot\text{N}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_3 \end{array}$ (1, 4). It was separated like the foregoing compounds of this class, and formed a yellow, crystalline powder

544 SHENSTONE AND CUNDALL: INFLUENCE OF TEMPERATURE

melting at 229—230°. It dissolves in cold concentrated sulphuric acid with a brown colour, which changes, through yellow and greenish-yellow, to green.

0.1101 gram, burnt with copper oxide in a vacuum, gave 22.63 c.c. of a mixture of nitrogen and nitric oxide, measured dry at 11° and under 585 mm. pressure. After absorption of the nitric oxide, there remained 22.63 c.c. of dry nitrogen at 11° and under 580 mm. pressure.

	Calculated for $C_{18}H_{22}N_4$.	Found.
N in 100 parts	19.05	19.02

The same compound was obtained by the action of *free p*-tolylhydrazine on diacetyl in ethereal solution. Curiously enough, when we attempted to prepare the compound, like its ortho-isomeride, by heating an aqueous solution of diacetyl with *p*-tolylhydrazine hydrochloride and sodium acetate, only the *mono-p*-tolylhydrazone, $CH_3 \cdot C : N_2H \cdot C_6H_4 \cdot CH_3$ (1, 4), was formed. It crystallises from benzene $CH_3 \cdot CO$ in slender yellow needles melting at 161°. A nitrogen determination gave 14.91 per cent. Calculated: N 14.73 per cent.

*Normal School of Science,
South Kensington.*