L.—Contributions to the Knowledge of the
 β -Diketones.

By SIEGFRIED RUHEMANN and EDWIN ROY WATSON.

SOME years ago, J. Wislicenus (*Annalen*, 1899, 308, 219) published the results of the work undertaken by him in conjunction with Löwenheim, Schmidt, and Wells on the interaction of alcoholic potash with benzylideneacetophenone dibromide. They found that the compound thus formed had the formula $C_{15}H_{12}O_2$, and they regarded it as the tautomeride of dibenzoylmethane, which had been first obtained by v. Baeyer and Perkin (*Ber.*, 1883, 16, 2134) by boiling ethyl dibenzoylacetate with water, and afterwards by Claisen (*Annalen*, 1896, 291, 52) by the action of sodium ethoxide or metallic sodium on a mixture of ethyl benzoate and acetophenone. The two tautomeric forms of dibenzoylmethane could be represented by the following formulæ: $C_6H_5 \cdot C(OH) : CH \cdot CO \cdot C_6H_5$ and $C_6H_5 \cdot CO \cdot CH_2 \cdot CO \cdot C_6H_5$.

Wislicenus is inclined to regard his compound as the diketonic form, and the old dibenzoylmethane as the enol-ketonic form, because, whilst the latter dissolves in alkali with the greatest ease and yields with ferric chloride a violet-red coloration and a greyish-green precipitate with alcoholic copper acetate solution, the former is insoluble in alkali and neither gives at once a coloration with ferric chloride, nor is precipitated by copper acetate.

That Wislicenus's compound was a tautomeride of the long-known dibenzoylmethane seemed to follow from the fact that it gave the same compounds on treatment with bromine, hydroxylamine, phenylhydrazine, hydrazine, or semicarbazide. Wislicenus further showed that, although his compound remained unchanged on distillation or on boiling with acetic acid, it was transformed into the old dibenzoylmethane under the influence of mineral acids. He therefore succeeded in effecting a transformation of his compound into the other, although the reverse change could not be accomplished.

That the transformation of the one form into the other is not brought about either by boiling or under the influence of alkali seems to be incompatible with our present knowledge of tautomeric compounds. These difficulties seem to have been recognised by Wislicenus himself, for he suggested the possibility of representing his compound as benzoylphenylethylene oxide, $C_6H_5 \cdot CO \cdot CH \cdot CH \cdot C_6H_5$.

These discrepancies and the desire to prepare ketones of the acetylene series in order to examine whether they are transformed by the action of bases into heterocyclic compounds, similar to those formed

from the esters of the acetylene series (Ruhemann and Stapleton, *Trans.*, 1900, **67**, 239), have induced us to repeat Wislicenus's experiments.

Such ketones of the acetylene series have indeed been obtained by Nef (*Annalen*, 1899, **308**, 264) from the sodium compounds of the hydrocarbons of the acetylene series under the influence of acid chlorides; yet it seemed to us possible to prepare them from the olefinic ketones, just as Claisen has prepared acetylenic aldehydes from their olefinic analogues (*Ber.*, 1903, **36**, 3664).

In following Wislicenus's directions, we obtained by the action of alcoholic potash on benzylideneacetophenone dibromide a compound with precisely the same properties as those recorded by this author for his dibenzoylmethane, but our analytical results differed considerably from the numbers given by Wislicenus, and agree, not with the formula $C_{15}H_{12}O_2$ for dibenzoylmethane, but with $C_{17}H_{16}O_2$. This formula, which was, moreover, verified by a molecular weight determination, would correspond with the following constitution,

according to which the substance appears to be the ethyl ether of dibenzoylmethane, and would therefore be analogous to the corresponding esters which have lately been obtained by Lees (*Trans.*, 1903, **83**, 145). This constitution is supported by the fact that the compound $C_{17}H_{16}O_2$, on heating with hydrochloric acid, is decomposed, giving acetophenone, benzoic acid, and ethyl chloride. This reaction, therefore, takes place in accordance with the following equation :

Löwenheim, who effected the decomposition of the compound by means of concentrated caustic potash and obtained acetophenone and benzoic acid, did not observe the formation of alcohol.

The correctness of the formula, $C_{17}H_{16}O_2$, for this compound is, moreover, supported by the fact that *p*-nitrobenzylideneacetophenone dibromide, on treatment with alcoholic potash, yields the corresponding nitro-derivative, $C_{17}H_{15}(NO_2)O_2$, which, therefore, is to be regarded as the ethyl ether of *p*-nitrodibenzoylmethane,

As regards the formation of the ethyl ether of dibenzoylmethane from benzylideneacetophenone dibromide, there cannot be any doubt that the first action of the alcoholic potash is to remove 1 mol. of hydrogen bromide and to yield the bromobenzylideneacetophenone,

a compound obtained by Schmidt (*Wislicenus, loc. cit.*) by the action of potassium acetate on the dibromide. We have obtained a similar compound, namely, bromobenzylideneacetone,

by the action of alcoholic potash in the cold on the benzylideneacetone dibromide. The bromobenzylideneacetophenone is subsequently transformed into the ethyl ether of dibenzoylmethane, either by the further removal of hydrogen bromide and subsequent union of alcohol with the first formed benzoylphenylacetylene, or by the direct replacement of the bromine atom by the ethoxyl group.

This constitution shows why the compound is insoluble in aqueous caustic potash and does not give a coloration with ferric chloride or a precipitate with copper acetate. It further explains why the compound can be readily transformed into dibenzoylmethane, and why the reverse change cannot be directly effected. Moreover, all the reactions of this compound, as described by *Wislicenus*, can be readily explained on this view of its constitution.

For example, an $\alpha\gamma$ -diphenylisooxazole is formed with hydroxylamine,

The formation of $\alpha\gamma$ -diphenylisooxazole, as shown by *Wislicenus (loc. cit.)*, is preceded by that of a compound which he regarded as an oxime of dibenzoylmethane. The fact, however, that this substance, which is produced also from *v. Baeyer* and *Perkin's* dibenzoylmethane, does not yield a coloration with ferric chloride, is not in harmony with the formula $\text{C}_6\text{H}_5 \cdot \text{C}(\text{OH}) : \text{CH} \cdot \text{C}(\text{C}_6\text{H}_5) : \text{NOH}$. After having proved that *Wislicenus's* dibenzoylmethane is ethoxybenzylideneacetophenone, its reaction with hydroxylamine may be expressed as follows :

The compound would thus appear to be a hydroxylamine derivative and not an oxime. This constitution agrees with the fact that the compound does not give a coloration with ferric chloride ; it explains, also, why the substance, although unchanged by neutral solvents, is readily transformed into $\alpha\gamma$ -diphenylisooxazole under the influence of alkalis. It is thus isomerised to $\text{C}_6\text{H}_5 \cdot \text{C}(:\text{NOH}) \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{C}_6\text{H}_5$, which subsequently loses water to form the isooxazole derivative.

A ready explanation is also afforded of the action of bromine in forming the monobromo- and dibromo-benzoylmethane compounds, previously

prepared by Neufville and v. Pechmann (*Ber.*, 1890, 23, 3377) from dibenzoylmethane,

In connection with this investigation, we record the result of our experiments on the behaviour of bases towards olefinic diketones, an account of the action of benzamidine on these diketones having been lately given (*Trans.*, 1903, 83, 1371). The results obtained induced us to examine also the action of other bases on these diketones. We find that ammonia readily reacts with benzylideneacetylacetone, yielding a compound having the formula $\text{C}_{19}\text{H}_{20}\text{ON}_2$, the formation of which may be thus represented :

The constitution of the product should probably be expressed as follows :

according to which it is to be regarded as acetyldiphenylmethyltetrahydropyrimidine. This constitution is in agreement with the fact that the compound, although readily decomposed by dilute mineral acids with the formation of benzaldehyde, is yet comparatively stable towards alkalis. On heating with alkali, no ammonia is evolved, but on removing the acetyl group a compound is formed which is probably the corresponding diphenylmethyltetrahydropyrimidine.

One of us (Ruhemann, *Trans.*, 1903, 83, 378) has shown that by the action of ammonia on ethyl benzylideneacetoacetate, a compound was formed which was regarded as benzylideneaminoacetone, $\text{C}_{10}\text{H}_{11}\text{ON}$. On account of the ease with which this substance is decomposed, the above formula could not be verified by a molecular weight determination. The behaviour of this compound is analogous to that of the substance obtained from benzylideneacetylacetone, and this makes it necessary to assign to the two compounds similar constitutions. Such considerations lead us to double the molecular weight of the compound obtained from ethyl benzylideneacetoacetate, and to regard it as ethyl diphenylmethyltetrahydropyrimidinecarboxylate. Its formation may then be expressed by the following equation :

These compounds are still under examination.

The assumption that the first step in the reaction of ammonia on benzylideneacetylacetone leads to the formation of an additive product, as indicated in the above equation, is rendered probable by the action of aniline on benzylideneacetylacetone.

These compounds interact at the ordinary temperature to form the additive product, α -anilino- $\beta\beta$ -diacetyl- α -phenylethane,

This compound, however, on heating at 100° , decomposes with the formation of benzylideneaniline and acetylacetone according to the equation:

Phenylhydrazine reacts with benzylideneacetylacetone as well as with benzylidenebenzoylacetone with development of heat, but the additive products, which may be assumed to be first formed, cannot be isolated, since, in both cases, they at once decompose forming benzaldehydephenylhydrazone.

The action of semicarbazide on benzylideneacetylacetone and benzylidenebenzoylacetone is of especial interest; in both cases, the reaction takes place between 1 mol. of the olefinic diketone and 1 mol. of the semicarbazide; water (1 mol.) is eliminated, and compounds are obtained having the formulæ $\text{C}_{13}\text{H}_{15}\text{O}_2\text{N}_3$ and $\text{C}_{18}\text{H}_{17}\text{O}_2\text{N}_3$ respectively. These compounds might be regarded as semicarbazones,

but taking into consideration the behaviour of other bases towards the olefinic diketones, there remains the alternative view that, in these cases also, additive products are first formed, which subsequently lose water to form cyclic compounds, for example:

One of us has recently shown (*loc. cit.*) that benzamidine also reacts with benzylidenebenzoylacetone forming an additive product. The fact that this compound, on heating with hydrochloric acid, decomposes and yields dibenzamide led to the view that the constitution of this compound should be represented by the formula:

This constitution, however, would not be in harmony with the results recorded in this paper, according to which the bases react additively with the olefinic diketones in such a way as to destroy the double linking. In the light of these researches, the above compound must be represented thus :

and this formula would also readily explain the formation of dibenzamide. Under the influence of hydrochloric acid, decomposition takes place, as indicated by the equation :

The benzamidine and benzoic acid in turn react in the presence of mineral acid to yield dibenzamide, thus :

The reaction of benzamidine on benzylideneacetylacetone, which, as has been shown lately (*loc. cit.*), yields diphenylmethyldihydropyrimidine, may well be explained in a similar manner by assuming that first the additive product, $\text{C}_6\text{H}_5 \cdot \text{CH}[\text{NH} \cdot \text{C}(\text{C}_6\text{H}_5) : \text{NH}] \text{CH}(\text{CO} \cdot \text{CH}_3)_2$, is formed, which then condenses to the hydropyrimidine.

The constitution of the products formed by the interaction of benzylideneacetylacetone and benzylidenebenzoylacetone with semicarbazide has not yet been definitely fixed, but without considering this problem the general hypothesis may be deduced that, in the first place, ammonia and organic bases, on reacting with the olefinic diketones, destroy the ethylene linking to form additive compounds.

This assumption may be extended to explain the behaviour of bases towards ethyl dicarboxyglutaconate and its derivatives. As shown by one of us and his pupils, ethyl benzyldicarboxyglutaconate, on treatment with ammonia, yields ethyl benzylmalonate and ethyl aminomethylenemalonate. In these cases, also, it may be supposed that the decomposition is preceded by the formation of additive products, which subsequently break up in the manner indicated by the following equation :

EXPERIMENTAL.

Action of Alcoholic Potash on Benzylideneacetophenone Dibromide.

Benzylideneacetophenone is readily prepared by Claisen's method (*Ber.*, 1887, 20, 657) by the action of sodium methoxide in methyl-alcoholic solution on a mixture of benzaldehyde and acetophenone. Its transformation into the dibromide, $C_6H_5 \cdot CHBr \cdot CHBr \cdot CO \cdot C_6H_5$, is best effected by dissolving the olefinic ketone in carbon disulphide instead of chloroform, as recommended by Wislicenus (*loc. cit.*), when almost the total quantity of the dibromide separates out; it dissolves in boiling alcohol with difficulty and, on cooling, crystallises in colourless needles which melt at 158° (according to Wislicenus at $156.5-157.5^\circ$).

0.2078 gave 0.3711 CO_2 and 0.0642 H_2O . C = 48.70; H = 3.43.

0.2017 „ 0.3618 CO_2 „ 0.0624 H_2O . C = 48.92; H = 3.43.

0.2371 „ 0.2406 AgBr. Br = 43.18.

$C_{15}H_{12}OBr_2$ requires C = 48.91; H = 3.26; Br = 43.47 per cent.

We have pointed out in the introduction that the dibromide reacts with alcoholic potash to yield the ethyl ether of dibenzoylmethane, $C_6H_5 \cdot C(O \cdot C_2H_5) : CH \cdot CO \cdot C_6H_5$, instead of dibenzoylmethane,

as stated by Wislicenus. Our mode of procedure is practically the same as employed by this author: caustic potash (2 mols.) dissolved in absolute alcohol is gradually added to the hot solution of the dibromide (1 mol.) in absolute alcohol, and the reaction is completed by digesting the mixture at 100° for about an hour. The alcohol is then distilled from the water-bath as far as possible, the residue treated with water and extracted with ether. After drying the ethereal solution with calcium chloride and evaporating off the ether, an oil is left which distils at 212° under 10 mm. pressure. The yellowish, oily distillate, when left for a short time, solidifies almost completely. The solid is only sparingly soluble in cold light petroleum (b. p. $50-80^\circ$), but readily dissolves in the hot solvent. It is readily soluble in hot alcohol and crystallises from either solvent in colourless prisms which melt at $77-78^\circ$ and have all the properties recorded by Wislicenus for his "dibenzoylmethane."

0.2037 gave 0.6020 CO_2 and 0.1190 H_2O . C = 80.60; H = 6.49.

0.1925 „ 0.5695 CO_2 „ 0.1120 H_2O . C = 80.68; H = 6.46.

0.1818 „ 0.5397 CO_2 „ 0.1052 H_2O . C = 80.96; H = 6.42.

$C_{17}H_{16}O_2$ requires C = 80.95; H = 6.35 per cent.

These numbers differ considerably from those given by J. Wislicenus, which show a close agreement with the percentage results required for dibenzoylmethane, $C_{15}H_{12}O_2$, namely, C = 80.36 ; H = 5.36 per cent.

The formula $C_{17}H_{16}O_2$ agrees also with the result of the molecular weight determination of the compound by the freezing point method.

0.405 in 22.49 benzene gave $\Delta t - 0.405^\circ$. M. W. = 256.

$C_{17}H_{16}O_2$ requires M. W. = 252.

The constitution $C_6H_5 \cdot C(O \cdot C_2H_5) : CH \cdot CO \cdot C_6H_5$ follows from the decomposition which the compound undergoes when heated with concentrated hydrochloric acid in a closed tube at $150-160^\circ$ for two hours. It thus furnishes ethyl chloride, acetophenone, and benzoic acid. The formation of ethyl chloride is sufficiently proved by the fact that on opening the cold tube hardly any pressure is noticed, but on warming, a gas escapes which burns with a green flame. The other products of decomposition have been isolated and identified as acetophenone and benzoic acid by their properties and by analysis.

Action of Alcoholic Potash on p-Nitrobenzylideneacetophenone Dibromide.

The action of alcoholic potash on benzylideneacetophenone dibromide is analogous to the behaviour of the same reagent towards the *p*-nitrobenzylideneacetophenone dibromide, the latter reaction giving rise to the ethyl ether of *p*-nitrodibenzoylmethane :

p-Nitrobenzylideneacetophenone is formed by adding dilute caustic soda to an alcoholic solution of *p*-nitrobenzaldehyde and acetophenone. It was thus prepared by Sorge (*Ber.*, 1902, 35, 1068), who also transformed it into the dibromide. We find that the union of bromine with the olefinic ketone takes place more readily than stated by this investigator, and that it is completed when the solution of both reagents in chloroform has been left overnight. The dibromide, which separates out on concentrating the solution, has been once recrystallised from chloroform, when it is obtained in yellow needles. On gradually adding the exact quantity of alcoholic potash (2 mols.) dissolved in absolute alcohol to the hot alcoholic solution of *p*-nitrobenzylideneacetophenone dibromide (1 mol.), potassium bromide separates out and the solution turns deep red. After digesting the mixture for an hour at 100° , the alcohol is distilled from the water-bath and the residue extracted with ether. On evaporating off the ether, a dark oil is left behind which partially solidifies in the course of 2—3 days ; the solid is collected at the pump and dissolved in hot dilute alcohol, from which solvent it separates in yellow needles which,

after two crystallisations from the same solvent, melt constantly at $89-90^{\circ}$.

0.1993 gave 0.5018 CO_2 and 0.0923 H_2O . $\text{C} = 68.62$; $\text{H} = 5.14$.

0.1965 „ 8.4 c.c. moist nitrogen at 17° and 744.5 mm. $\text{N} = 4.85$.

0.1959 „ 8.4 c.c. „ at 19° and 755.5 mm. $\text{N} = 4.89$.

$\text{C}_{17}\text{H}_{15}\text{O}_4\text{N}$ requires $\text{C} = 68.68$; $\text{H} = 5.05$; $\text{N} = 4.71$ per cent.

p-Nitrodibenzoylmethane is readily soluble in alcohol, chloroform, or ether and insoluble in cold potash, but on warming with the alkali, however, decomposition takes place, and the odour of acetophenone is perceptible.

Action of Alcoholic Potash on the Benzylideneacetone Dibromide.

In preparing benzylideneacetone, we have followed the directions given by Claisen and Ponder (*Annalen*, 1884, 223, 139). This compound readily takes up bromine and yields the dibromide, $\text{C}_6\text{H}_5\cdot\text{CHBr}\cdot\text{CHBr}\cdot\text{CO}\cdot\text{CH}_3$, but for this purpose we find it advisable to employ carbon disulphide rather than chloroform as a solvent (compare Claisen and Claparède, *Ber.*, 1881, 14, 2461), since the yield is better and the product is at once obtained in a pure state. On adding caustic potash (2 mols.), dissolved in absolute alcohol, to the warm alcoholic solution of the dibromide (1 mol.), potassium bromide separates, and the solution turns red without further heating. The alcohol was not distilled off, as in the previous cases, but the solution was diluted with water and extracted with ether. After removing the ether, a yellow oil was obtained boiling at $150-151^{\circ}$ and $169-170^{\circ}$ under 10 and 20 mm. pressure respectively.

This compound was bromobenzylideneacetone, $\text{C}_6\text{H}_5\cdot\text{CBr}\cdot\text{CH}\cdot\text{CO}\cdot\text{CH}_3$, which, however, as indicated by the analysis, was not quite pure, but probably contained a little of the ethyl ether of benzoylacetyl-methane.

0.2063 gave 0.4023 CO_2 and 0.0839 H_2O . $\text{C} = 53.18$; $\text{H} = 4.51$.

0.2264 „ 0.1775 AgBr . $\text{Br} = 33.39$.

$\text{C}_{10}\text{H}_9\text{OBr}$ requires $\text{C} = 53.33$; $\text{H} = 4.0$; $\text{Br} = 35.55$ per cent.

On adding phenylhydrazine to the alcoholic solution of bromobenzylideneacetone and slightly warming, a crystalline precipitate slowly separates, consisting of the phenylhydrazone,

This substance crystallises from alcohol in yellow, glistening plates which melt and decompose at 97° .

0.1831 gave 14.2 c.c. moist nitrogen at 20° and 763 mm. $\text{N} = 8.90$.

$\text{C}_{16}\text{H}_{15}\text{N}_2\text{Br}$ requires $\text{N} = 8.89$ per cent.

Bromobenzylideneacetone is analogous to the bromobenzylideneacetophenone, $C_6H_5 \cdot CBr : CH \cdot CO \cdot C_6H_5$, which Schmidt (*loc. cit.*) obtained by the action of potassium acetate on benzylideneacetophenone dibromide. We have as yet not heated the bromobenzylideneacetone with alcoholic potash, but we propose to carry out this experiment with the view of examining whether in this case the corresponding ethyl ether, $C_6H_5 \cdot C(O \cdot C_2H_5) : CH \cdot CO \cdot CH_3$, of acetylbenzoylmethane is produced.

Action of Ammonia and Organic Bases on Olefinic Diketones.

One of us has shown lately (Trans., 1903, 83, 1371) that, in the first place additive products are formed by the action of benzamidine on these diketones, and such a product has been isolated on treating benzamidine with benzylidenebenzoylacetone. We have already stated (p. 459) that other bases form with these diketones similar additive products, which, however, are unstable and readily give rise to other compounds.

Action of Ammonia on Benzylideneacetylacetone and Benzylidenebenzoylacetone.

The solution of benzylideneacetylacetone in excess of alcoholic ammonia, when left overnight, deposits colourless plates. These are insoluble in ether, but readily dissolve in hot alcohol and melt somewhat indefinitely at 147° .

0.2010 gave 0.5739 CO_2 and 0.1248 H_2O . $C = 77.87$; $H = 6.89$.

0.1844 „ 15.4 c.c. moist nitrogen at 12° and 749 mm. $N = 9.71$.

0.1865 „ 15.4 c.c. „ „ „ 15° and 755 mm. $N = 9.66$.

$C_{19}H_{20}ON_2$ requires $C = 78.08$; $H = 6.85$; $N = 9.59$ per cent.

With regard to the constitution of this compound, we have already (p. 459) expressed the view that it is acetyldiphenylmethyltetrahydropyrimidine. It dissolves in cold dilute mineral acids, but on warming the solution, decomposition takes place, which is indicated by the formation of benzaldehyde. The compound is more stable towards alkalis for, on boiling with alcoholic potash, no odour of benzaldehyde is perceptible, but it loses the acetyl group and yields a substance which is most probably diphenylmethyltetrahydropyrimidine. This product is isolated by distilling off the alcohol from the water-bath and adding water to the residue; a yellow oil is thus precipitated, whilst the aqueous solution contains acetic acid, which has been identified by its general reactions. The oil, which rapidly solidifies and crystallises from dilute alcohol in yellow leaflets, is still under examination.

The action of alcoholic ammonia on benzylidenebenzoylacetone differs from the preceding condensation. In this case, the solution turned yellow, but did not deposit a solid, even after a long time. On adding water to the solution, a viscous product was precipitated which could not be induced to crystallise.

Action of Aniline on Benzylideneacetylacetone.

A mixture of equal quantities of benzylideneacetylacetone and aniline, when left for a short time, develops heat and becomes solid. After washing with a little alcohol, the product is dissolved in hot dilute alcohol; the solution, on cooling, deposits colourless needles which melt at 113° .

0.2010 gave 0.5646 CO_2 and 0.1248 H_2O . $\text{C} = 76.60$. $\text{H} = 6.89$.

0.2367 „ 11 c.c. moist nitrogen at 22° and 732 mm. $\text{N} = 5.04$.

0.2384 „ 11 c.c. „ „ „ 21° and 733 mm. $\text{N} = 5.03$.

$\text{C}_{18}\text{H}_{19}\text{O}_2\text{N}$ requires $\text{C} = 76.86$; $\text{H} = 6.76$; $\text{N} = 4.98$ per cent.

This additive compound, $\text{C}_6\text{H}_5\cdot\text{CH}(\text{NH}\cdot\text{C}_6\text{H}_5)\cdot\text{CH}(\text{CO}\cdot\text{CH}_3)_2$, is somewhat unstable, and when heated on the water-bath it readily decomposes into acetylacetone and benzylideneaniline. This mixture, on cooling, partially solidifies; the adhering oil is pressed out from the solid, and the latter dissolved in hot dilute alcohol. On cooling, a white emulsion is produced in the solution, which gradually deposits a compound crystallising in colourless plates melting at 50 — 51° . This compound was identified as benzylideneaniline by the foregoing properties and by analysis.

The additive compound is also formed on heating the mixture of aniline and benzylideneacetylacetone at 100° .

Action of Phenylhydrazine on Benzylideneacetylacetone and Benzylidenebenzoylacetone.

On mixing benzylideneacetylacetone (3 grams) and phenylhydrazine (2 grams), heat was developed and a semi-solid product results, which crystallised from dilute alcohol in almost colourless needles melting at 155 — 156° , and was identified by these properties and by analysis as benzaldehydephenylhydrazone.

Benzylidenebenzoylacetone reacts with phenylhydrazine in a similar manner; an alcoholic solution of these reagents, when boiled and subsequently cooled, deposits needles melting at 155 — 156° .

0.2069 gave 0.6010 CO_2 and 0.1165 H_2O . $\text{C} = 79.26$; $\text{H} = 6.25$.

0.2032 „ 25.5 c.c. moist nitrogen at 16° and 743 mm. $\text{N} = 14.29$.

$\text{C}_{13}\text{H}_{12}\text{N}_2$ requires $\text{C} = 79.59$; $\text{H} = 6.12$; $\text{N} = 14.28$ per cent.

Action of Semicarbazide on Benzylideneacetylacetone and on Benzylidenebenzoylacetone.

Semicarbazide hydrochloride (1 mol.), dissolved in water, is mixed with a solution of sodium (1 atom) in alcohol, and then treated with benzylideneacetylacetone (1 mol.); heat is developed, and after a short time a precipitate is formed which dissolves in alcohol with difficulty and, on cooling, crystallises in yellow plates, which melt at 210° with evolution of gas.

0.2030 gave 0.4728 CO_2 and 0.1147 H_2O . $\text{C} = 63.52$; $\text{H} = 6.27$.

0.1604 „ 24.5 c.c. moist nitrogen at 18° and 746.5 mm. $\text{N} = 17.31$.

$\text{C}_{13}\text{H}_{15}\text{O}_2\text{N}_3$ requires $\text{C} = 63.67$; $\text{H} = 6.12$; $\text{N} = 17.14$ per cent.

Benzylidenebenzoylacetone reacts with semicarbazide under the same conditions. The white, crystalline precipitate which separates is insoluble in water, sparingly soluble in boiling alcohol, and melts at 230° with evolution of gas. For analysis, the compound was washed successively with water and alcohol.

0.2013 gave 0.5174 CO_2 and 0.1034 H_2O . $\text{C} = 70.10$; $\text{H} = 5.70$.

0.1679 „ 19.5 c.c. moist nitrogen at 9° and 744.5 mm. $\text{N} = 13.68$.

$\text{C}_{18}\text{H}_{17}\text{O}_2\text{N}_3$ requires $\text{C} = 70.35$; $\text{H} = 5.53$; $\text{N} = 13.68$ per cent.

Further experiments are required in order to decide whether these substances are cyclic compounds, as indicated in the introduction, or whether they are mono-semicarbazones of benzylideneacetylacetone and benzylidenebenzoylacetone, but at present we are inclined to hold the latter view.

GONVILLE AND CAIUS COLLEGE,
CAMBRIDGE.