

apparatus, a cut of which is presented, was devised to overcome the difficulty. It consists of an ordinary graduated gas burette connected with a reservoir for mercury and surrounded by a water jacket which in turn is connected with a flask containing water. The flask and jacket are so arranged that water of any desired temperature can be siphoned from the former through the latter, thus heating the gas in the burette to any temperature between 0° and 100° C. A thermometer inserted in the jacket indicates the temperature of the water. At the beginning of the experiment the water in the jacket should be at the room temperature, and the flask should hold several times the volume of the jacket. By the method of siphoning the change in temperature is so gradual that the gas is heated to the water temperature almost as rapidly as the latter passes through, and there is no danger of breaking the burette. With the apparatus each law may be deduced separately with a fair degree of accuracy. Then the two laws united and the results compared with those found mathematically from a combination of the two. The idea of absolute zero is illustrated in a very clear and convincing way. If desirable the burette may be filled with different gases, and thus it may be shown that all obey (practically) the same laws.

SOME Δ_2 -KETO-R-HEXENE DERIVATIVES.

JAMES B. GARNER.

A study of the reactions which might be brought about between benzoin and unsaturated aldehydes, ketones, and esters through the agency of cold (15° C.) alcoholic sodium ethylate, was begun several years ago¹. At that time it was found that benzoin is added to benzalacetone giving rise to a 1.5 diketone which by loss of water and ring formation, is converted into 3-4-5-triphenyl-4-oxy- Δ_2 -keto-R-hexene. This substance had previously been prepared by Professor Alexander Smith², using potassium cyanide as condensing agent³. When sodium ethylate is used as condensing agent, the yield is much greater, the reaction takes place more smoothly and the product formed is purer than when potassium cyanide is used. Knoevenagel has made an exhaustive study of the Δ_2 -keto-R-hexene de-

¹ Dissertation, Chicago, 1897, p. 17.

² Berichte, 26, 65.

³ Amer. Chem. Jour. XXII, 250.

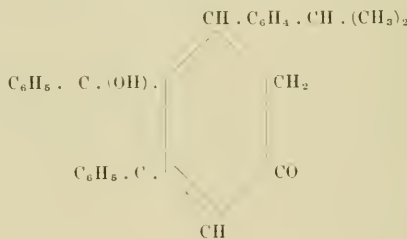
rivatives. He has found, (1) that substances of the type of acetoacetic ether and aliphatic aldehydes¹, and aromatic aldehydes², condense in the presence of diethylamine or piperidine to form 1.5 diketones, and that these diketones, with loss of water and ring formation, are converted into α_2 -keto-R-hexene derivatives; (2) that desoxybenzoin adds itself to substances of the type benzalacetylacetone forming 1.5 diketones, which, by loss of water and ring formation, yield α_2 -keto-R-hexene derivatives.

Recently the study has been extended to include the reactions which might take place between the ketols—benzoin, cuminoïn, fuoroïn, anisoïn and piperonoïn—and the unsaturated ketones—benzalacetone, cuminalacetone, p-methoxy-benzalacetone, and piperonylenacetone. In all the reactions, α_2 -keto-R-hexene derivatives are formed, except in those in which fuoroïn is used. Under no conditions has it been possible to bring about any interaction in any of the experiments in which fuoroïn is used. All of the other reactions progress smoothly and excellent yields are obtained in each case. It has been ascertained also, that in place of the unsaturated ketone, a mixture of the corresponding aldehyde and acetone may be used and the course of the reaction is in no way changed, but the yield is materially increased. To insure the completion of the reactions, however, it is necessary to boil the mixtures for fifteen minutes on the water-bath. Equal volumes of a ten per cent. solution of sodium hydroxide may be used instead of the alcoholic sodium ethylate and the same reactions will take place but the yields are very much poorer.

In the present paper the study is limited to the consideration of only those cases, which will in a general way, indicate, (1) the nature of the products formed and, (2) the extent to which the reaction is applicable.

1. ADDITION OF BENZOÏN TO CUMINALACETONE.

β -4-diphenyl-5-cumyl-4-oxo- α_2 -keto-R-hexene.



¹ Ann. 281, 25. Ann. 288, 321.

² Ann. 308, 223.

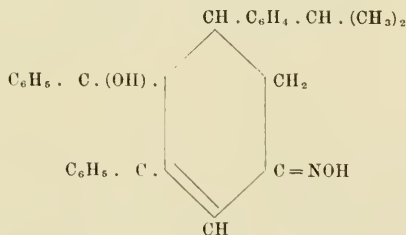
For the preparation of this Δ_2 -keto-R-hexene derivative, one molecule (6 gr.) of benzoin is dissolved in boiling absolute ethyl alcohol (100cc.), and to this solution is added one molecule (5.32 gr.) of cuminalacetone. This mixture is treated with an alcoholic solution (4cc.) of sodium-ethylate (.5 gr. sodium in 30cc. absolute ethyl alcohol). The mixture becomes deep red in color and upon standing in a cool place for two hours deposits clusters of needle-like crystals. The crystalline mass is filtered off and after washing with absolute ethyl alcohol is recrystallized twice from glacial acetic acid. Clusters of long, fine, white needles result which melt at 231° . It is insoluble in ligroin (40-60), ether, and cold alcohol, but dissolves readily in hot benzene, glacial acetic acid and chloroform.

Calculated as $C_{27}H_{26}O_2$.	Found.
C 84.80	84.67
H 6.81	6.92

If a mixture of one molecule each of cuminol (4.2 gr.) and pure acetone (1.7 gr.) is used instead of the cuminalacetone, it has been established by several comparable experiments that it is necessary that the reaction shall be carried on at the temperature of the water bath for fifteen minutes. Upon the cooling of the mixture, the Δ_2 -keto-R-hexene derivative separates in a relatively pure condition. By repeated additions of 4cc. of sodium ethylate at a time, additional quantities of the substance are obtained which make the yield almost quantitative. Experiments were made using the total quantity of sodium ethylate solution (12cc.) required for the quantitative completion of the reaction, and it was found that the reaction took an entirely different course, resulting in the formation of the sodium ethylate addition product of benzoin⁶.

The condensation takes place readily when 15 grs. of a 10% solution of sodium hydroxide are used in place of the 4cc. of sodium ethylate solution.

Orim of 3-4-diphenyl-5-cumyl-4-oxo- Δ_2 -keto-R-hexene.



⁶ Dissertation, Chicago, 1897, p. 4.

This oxim is obtained by boiling a mixture of one molecule (1 gr.) of the α_2 -keto-R-hexene derivative with three molecules (.56 gr.) of hydroxylamine hydrochloride and one and one-half molecules (.56 gr.) of sodium carbonate dissolved in ethyl alcohol (140cc.) for forty-five minutes, using a return condenser. One-half of the alcohol is distilled off and the residue on cooling deposits white crystals, which, when they have been recrystallized from a mixture of benzene and ligroin, melt at $221-3^\circ$. The substance is easily soluble in hot alcohol, cold ether, acetic acid, and hot benzene, but very sparingly soluble in hot ligroin ($40-60^\circ$).

Calculated as $C_{17}H_{27}O_2N$.

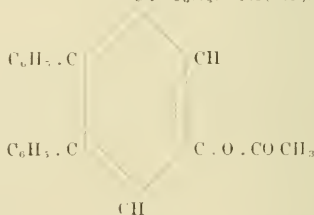
N. 3.53

Found.

3.72

3-4-diphenyl-5-cinnyl-phenol-acetate.

C. $C_{26}H_{24}$, $CH(CH_3)_2$



This body is prepared by boiling the α_2 -keto-R-hexene derivative with excess of either acetic anhydride or acetyl chloride for thirty minutes. The mixture assumes a yellowish-red tint, and yields a solid substance only when it is poured into a large excess of water. The white amorphous mass recrystallizes from hot ligroin ($40-60^\circ$) in bunches of long needles, melting at 98° . It is soluble in cold glacial acetic acid, benzene, ether and alcohol, but is sparingly soluble in ligroin.

Calculated as $C_{26}H_{26}O_2$.

C 85.72

H 6.40

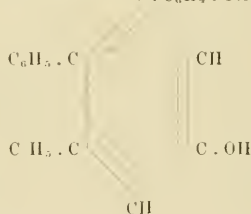
Found.

85.50

6.62

3-4-diphenyl-5-cinnyl-phenol.

C. $C_{26}H_{24}$, $CH(CH_3)_2$

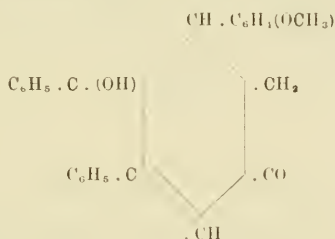


The acetate is boiled upon a water-bath with alcoholic potassium hydroxide for fifteen minutes. The mixture resulting is poured into excess of dilute hydrochloric acid, and a white mass is obtained. The amorphous phenol is recrystallized from hot alcohol. It forms white needles, which melt at 155° . It is readily soluble in cold chloroform, benzene and ether, but sparingly soluble in hot ligroin ($40-60^{\circ}$).

Calculated as $C_{27}H_{24}O$.	Found.
C 89.00	88.96
H 6.60	6.87

II. ADDITION OF BENZOIN TO ANISYLIDEN ACETONE.

3-4-Diphenyl-5-anisyl-4-oxy- Δ_2 -keto-R-hexene.



The 3-4-diphenyl-5-anisyl-4-oxy- Δ_2 -keto-R-hexene is prepared by the condensation of one molecule (6 gr.) of benzoin, either with one molecule (5 gr.) anisylidenacetone, or with one molecule each of anisaldehyde (3.9 gr.) and of pure acetone (1.7 gr.) under exactly the same conditions which were used in the preparation of 3-4-diphenyl-5-cumyl-4-oxy- Δ_2 -keto-R-hexene. The substance crystallizes in bunches of needles, either from hot glacial acetic acid, or absolute alcohol, and melts at 233.5° . However the amount of alcohol required is large—for each gram, 70cc. of hot absolute alcohol are required. It is soluble in hot benzene and chloroform, but insoluble in ether and ligroin ($40-60^{\circ}$). With cold concentrated sulphuric acid, a deep red coloration is produced.

Calculated as $C_{25}H_{22}O_3$.	Found.
C 81.08	80.91
H 5.95	6.03

Oxim of the 3-4-diphenyl-5-anisyl-4-oxy- Δ_2 -keto-R-hexene.

For the preparation of the oxim, a method, analogous to that described in the preparation of the oxim of 3-4-diphenyl-5-cumyl-4-oxy- Δ_2 -keto-R-hexene, is used. After recrystallization from hot alcohol, it melts at 196° .

It is soluble in hot glacial acetic acid, chloroform, and benzene, but insoluble in ether and ligroin (40-60°).

Calculated as $C_{25}H_{23}O_3N$.	Found.
N. 3.63	3.85

Acetate of 3-4-diphenyl-5-anisyl-phenol.

This product is obtained by boiling the α_2 -keto-R-hexene derivative with acetyl chloride on the water-bath for ten minutes. The mixture assumes a deep red coloration. Nothing separates on cooling. When excess of water is added, however, an amorphous mass separates which, upon crystallization from hot ligroin (40-60°) or from aqueous alcohol, melts at 141⁵-2°. It is soluble readily in cold benzene, ether, glacial acetic acid and chloroform; sparingly soluble in hot benzene and aqueous alcohol.

Calculated as $C_{27}H_{22}O_3$.	Found.
C 82.22	82.10
H 5.59	5.84

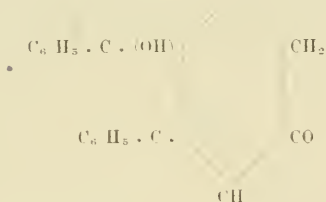
3-4-diphenyl-5-anisyl-phenol.

The acetate upon saponification with alcoholic potassium hydroxide yields the phenol. The reaction requires only fifteen minutes heating upon the water-bath to complete it. The product, which is obtained when the resulting solution is poured into dilute hydrochloric acid, is recrystallized from a mixture of alcohol and ligroin (40-60°) and melts at 159-60°. It is readily soluble in cold ether, benzene, chloroform and acetic acid, and almost insoluble in hot ligroin.

Calculated as $C_{25}H_{20}O_2$.	Found.
C 85.24	85.17
H 5.68	5.93

This phenol reacts vigorously at the ordinary temperature with cold concentrated nitric acid and yields nitro derivatives. These nitro bodies will be investigated later.

III. ADDITION OF BENZOIN TO PIPERONYLACETONE.

3-4-diphenyl-5-piperyl-4-oxy-₂-keto-R-hexene.

One molecule (6 gr.) of benzoïn and one molecule (5.9 gr.) of piperonylenacetone are dissolved in hot absolute ethyl alcohol (100cc.) and a solution (4cc) of sodium ethylate (.5 gr. sodium in 30cc. absolute alcohol) is added. As in all these condensation reactions with sodium ethylate, this mixture assumes a deep red coloration. Upon standing for two hours rosettes of yellow needle-like crystals separate. These crystals, upon recrystallization from glacial acetic acid, are obtained in fine white glittering needles, melting at 240°. The substance is soluble in hot chloroform; sparingly soluble in hot benzene and alcohol; and insoluble in ether and ligroïn (40-60°).

Calculated as $\text{C}_{25}\text{H}_{20}\text{O}_4$.	Found.
C 78.12	78.00
H 5.21	5.38

The method above described for the preparation of 3-4-diphenyl-5-piperyl-4-oxy-₂-keto-R-hexene does not progress as smoothly and as completely as when one molecule each of piperonal (4.25 gr.) and of pure acetone (1.7 gr.) is used in place of the piperonylenacetone, and the reaction is carried out at the temperature of the water-bath. The crystals obtained by this method are very pure and clean, and the yield is almost quantitative, especially if the mother liquor is treated again with more sodium ethylate and the mixture again boiled.

Ten per cent. sodium hydroxide solution also effects the condensation. However the yield is poor.

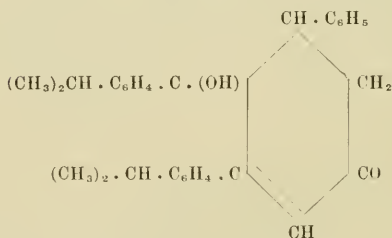
Oxim of 3-4-diphenyl-5-piperyl-4-oxy- Δ_2 -keto-R-hexene.

This oxim is prepared in an analogous method to that described previously for the preparation of oxims. When recrystallized from a mixture of alcohol and ligroin, crystals are formed melting at 190–1°. It is soluble in hot alcohol, cold ether, chloroform, and hot benzene, and is insoluble in ligroin (40–60°.)

Calculated as $C_{25}H_{21}O_4N$.	Found.
N 3.51	3.78

IV. ADDITION OF CUMINOIN TO BENZALACETONE⁷.

3-4-dicumyl-5-phenyl-4-oxy- Δ_2 -keto-R-hexene.



Cuminoin, in general, reacts less rapidly than benzoin and the yields of Δ_2 -keto-R-hexene derivatives are poorer.

One molecule (6 gr.) of pure cuminoin⁸ and one molecule (3 gr.) of pure benzalacetone dissolved in hot absolute ethyl alcohol (60cc.) are treated with a solution (6cc.) of sodium ethylate (.5 gr. sodium in 30cc. absolute alcohol). Upon the addition of the sodium ethylate, the mixture turns deep red, and after standing for six hours clusters of needles separate. By recrystallizing twice from glacial acetic acid, pure 3-4-dicumyl-5-phenyl-4-oxy- Δ_2 -keto-R-hexene is obtained. It melts at 214°. It is soluble in cold acetic ether, chloroform, hot benzene and ligroin (110–120°); insoluble in cold alcohol, ligroin (40–60°), and ether. The yield is about 27% of the theoretical.

Calculated as $C_{30}H_{32}O$.	Found.
C 84.90	84.77
H 7.54	7.83

⁷ Dissertation, Chicago, 1897, p. 19.

⁸ Berichte, XXVI, 64.

Origin of the 3-4-dicumyl-5-phenyl-4-oxo- Δ_2 -keto-R-hexene.

A molecule of the substance dissolved in alcohol was boiled with three molecules of hydroxylamine hydrochloride for an hour. On cooling, nothing appeared, but after the larger portion of the alcohol had been distilled off in the water-bath a solid separated, which on being well washed with water and recrystallized from a mixture of benzene and ligroin (40–60°) gave fine white needles melting at 208°. It may be recrystallized also from aqueous alcohol. The analysis shows it to be the monoxim.

Calculated as $C_{30}H_{33}O_2N$.	Found.
3.11	N 3.30

The substance is easily soluble in cold acetic acid, benzene, and acetic ether; insoluble in ligroin (40–60°).

3-4-dicumyl-5-phenyl-phenol acetate.

This body can easily be prepared by boiling the Δ_2 -keto-R-hexene derivative with a mixture of acetic anhydride and anhydrous sodium acetate for forty-five minutes, or until the mixture becomes decidedly pink in color. The solution is then poured into a large amount of cold water and allowed to settle. After recrystallization from glacial acetic acid, it is obtained in large bunches of long radiating fibers, and melts, when pure, at 122°. It is soluble in cold benzene, chloroform, ether, and ligroin (40–60°), in hot alcohol and acetic acid.

Calculated for $C_{32}H_{32}O_2$.	Found.
85.71	C 85.60
7.14	H 7.55

The acetyl derivative, when hydrolyzed by means of alcoholic potash yields 3-4-dicumyl-5-phenylphenol.

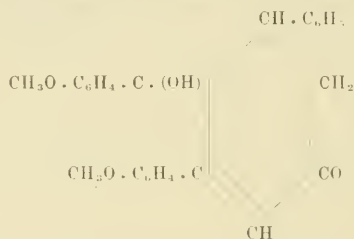
By warming the acetate in a water-bath for ten minutes with four molecules of alcoholic potash and pouring into dilute hydrochloric acid, an amorphous mass is obtained which crystallizes from warm alcohol in large thin plates, melting at 137°. This substance is soluble in cold acetic ether, benzene, chloroform, ether and hot ligroin (40–60°); insoluble in caustic soda.

Calculated as $C_{30}H_{30}O$.	Found.
C 88.66	88.26
H 7.39	7.99

The addition reactions of cumminoin with cuminalacetone, piperonylenacetone and anisylidenacetone are being studied at present, and I hope to be able soon to publish the results obtained.

V. ADDITION OF ANISOIN TO BENZALACETONE.

β-4-dianisyl-5-phenyl-4-oxo-Δ₂-keto-R-hexene.



Anisoin adds itself to the ethylene grouping much more readily than either cumminoin or benzoin to yield the expected 1.5 diketone, but the readiness with which this 1.5 diketone loses water to form the corresponding Δ_2 -keto-R-hexene derivative is markedly less. In fact the 1.5 diketone constitutes the major portion of the reaction product. Attempts to prepare the 1.5 diketone pure, *i. e.*, free from the Δ_2 -keto-R-hexene derivatives, have failed partially. However, its approximate melting point has been obtained, namely, 168-174°. When boiled with the ordinary solvents in which it is soluble, the 1.5 diketone loses water and forms the Δ_2 -keto-R-hexene derivative, which melts at 207°.

The mixture of the 1.5 diketone and the Δ_2 -keto-R-hexene derivative is prepared as follows:

One molecule (4.4 gr.) of anisoin and one molecule (2.38 gr.) of benzalacetone are dissolved in absolute ethyl alcohol (62cc.) and to the mixture sodium ethylate solution (4cc.) is added. The solution becomes deep red and upon standing for two hours deposits a large mass of crystals (2.4 gr.). The solid is filtered off and washed well with absolute alcohol. A trial determination of the melting point shows that the product is a mixture. It melts at 168-74° and 204°. The mother liquor from the crystals upon treatment with more sodium ethylate solution yields more of the same products (.4 gr.) Upon recrystallization from either of three solvents—benzene, alcohol or acetic acid—fine white needle-like crystals are

obtained, having a constant melting point of 207° . It is soluble in chloroform, slightly soluble in ligroin, and insoluble in ether.

Calculated as $C_{26}H_{24}O_4$.	Found.
C 78.00	77.62
H 6.00	6.13

The acetate and oxim have been prepared, but as yet no analyses have been made, but the physical properties determined correspond very closely with those of the other α -keto-R-hexene derivatives which I have prepared.

An investigation of the reaction of anisoin with cuminalacetone, piperonylenacetone and anisylidenacetone is being carried on.

GEOLOGY OF THE JEMEZ-ALBUQUERQUE REGION, N. M.

ALBERT B. REAGAN.

(Abstract.)

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GENERAL DESCRIPTION.

The Jemez-Albuquerque Region described in this paper, is in north-western New Mexico between longitude $106^{\circ} 20'$ and 107° W. and latitude 35° and 36° N. Roughly speaking, it is a triangle with its apex toward the south. It is bounded on the southeast by the San Dia Mountains, on the southwest by the Rio Puerco, and on the north by the upper plateau of the Jemez Mountains. Its principal river is the Rio Grande, and its commercial center is Albuquerque. The Santa Fe Railroad enters the region at the northeast, near Thornton, and passes through it, just to the east of the Rio Grande to Albuquerque. At this point the road branches, one branch of the system going to El Paso, Texas, the other, the Atlantic and Pacific, to California and the Pacific coast.

GENERAL SURVEY.

This section, as a whole, is one vast desert area, sparsely covered with grass, piñones, red cedar, sage brush and cactus, except in the valleys where there is sufficient water for irrigation. In these valleys corn, wheat, fruit and beans are raised by the natives and Mexicans. To consider the