As aconitic acid could be formed as well by the contamination of Fraction 5 by triethyl citrate, a test was made for citric acid by the pentabromoacetone method on 0.8 g. of the ester and on 0.4 g. of the free acid. Only a trace of citric acid was found. Therefore, the aconitic acid obtained must come from isocitric acid. Further proof that the acid is isocitric acid was obtained on fusing it with potassium hydroxide, the products being acetic and oxalic acids. Citric acid, on fusion with potassium hydroxide yields the same products.

The ethyl isocitrate obtained from the first lot of blackberries was levorotatory, whereas that obtained from the second and third lots was dextrorotatory. The indications are, therefore, that isocitric acid may occur in blackberries in both optically active modifications.

As its optical rotation is increased in the positive direction by uranyl salts, instead of in the negative direction as in the case of *l*-malic acid, determinations of the latter acid in its presence would be disturbed. The solubility of barium isocitrate in cold water would make its separation from barium malate difficult, and it would be better to attempt such a separation from boiling water.

Summary

Investigation of the acids of the blackberry shows that the predominating and characteristic acid is optically active isocitric acid, constituting about five-sixths of the total acids of the fruit. *l*-Malic acid was present in moderate amount, together with traces of oxalic, succinic and citric acids.

Further study is required in order to devise methods for the estimation of isocitric acid in fruits.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

THE DISSOCIATION INTO FREE RADICALS OF SUBSTITUTED DIXANTHYLS. I. DIBENZYL- AND DIBUTYLDIXANTHYL

BY JAMES B. CONANT AND ARTHUR W. SLOAN

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It was shown in a preliminary paper from this Laboratory[1] that the salts of certain organic bases and pseudo bases were reduced by vanadous chloride with the formation of substituted ethanes, the general reaction being represented by the following equations: $AX + VX_2 \longrightarrow A— + VX_3$; $2A— \longrightarrow A—A$. The discovery of this convenient method of preparing ethanes directly from the corresponding carbinols makes possible the synthesis of many interesting types of substituted ethanes hitherto

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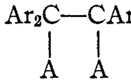
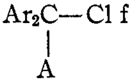
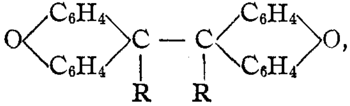
that it is identical with respect to these properties, thus confirming its identity with aconitic acid.

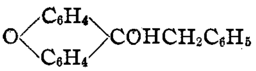
[1] THIS JOURNAL, 45, 2466 (1923).

inaccessible. Previous investigators who have attempted to prepare ethanes of the type  $\underset{\substack{|\\A}}{Ar_2C}-\underset{\substack{|\\A}}{CAr_2}$ (Ar being an aromatic group, and A a non-aromatic group) have in most instances failed because of the difficulty of preparing  $\underset{\substack{|\\A}}{Ar_2C}-Cl$ from the corresponding carbinol.[2] Very recently, Ziegler[3] has succeeded in preparing certain compounds of this general type by avoiding the classic method which requires the chloride or bromide, and employing instead a method which involves as a first step the interaction of metallic sodium and the methyl ether of the carbinol. In a certain limited field he has also been able to apply the method of preparation which depends on the action of phenylmagnesium bromide on the perchlorate.[4] The properties of the ethanes which he thus prepared are discussed below in connection with the dixanthyl derivatives which we have obtained.

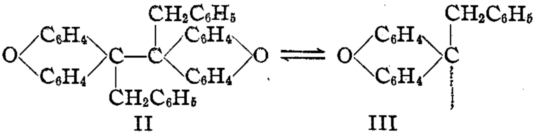
Other papers from this Laboratory will discuss the electrochemistry of the new method of preparing free radicals and its application to the preparation of ethanes from such very weak pseudo bases as triphenyl carbinol, diphenyl phenylethinyl carbinol and similar substances. In this series of communications we propose to deal with the problem of the dissociation of substituted dixanthyls of the type  where R is some group other than an aromatic hydrocarbon residue. As a first step in this inquiry, we have prepared two substances in which R is $C_6H_5CH_2$ and C_4H_9, respectively.

Dibenzyldixanthyl

When a solution of benzylxanthydrol (I) or the perchlorate in concd. hydrochloric acid is treated with vanadous chloride, a light brown precipitate is immediately formed. This precipitate may be purified by recrystallization from benzene in an inert atmosphere and one thus obtains a crystalline, colorless solid which analyzes for dibenzyldixanthyl (II). Its properties correspond to those of an ethane which dissociates into a free radical (III). Thus the substance I



I



II III

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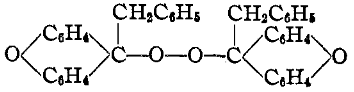
[2] *Ann.*, **394**, 201 (1912). *Ber.*, **54**, 2511 (1921). *Ber.*, **55**, 815, 819 (1922). *Ber.*, **55**, 2257 (1922).

[3] Ziegler, *Ann.*, **437**, 227 (1924).

[4] Ziegler, *Ann.*, **434**, 34 (1923).

rapidly combines with oxygen forming a crystalline peroxide (IV),

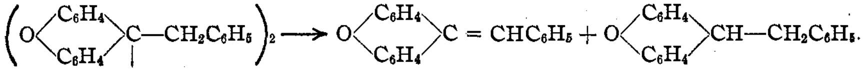


$$\mathrm{O}\Big\langle\begin{matrix}\mathrm{C_6H_4}\\ \mathrm{C_6H_4}\end{matrix}\Big\rangle\overset{\mathrm{CH_2C_6H_5}}{\overset{|}{\mathrm{C}}}-\mathrm{O}-\mathrm{O}-\overset{\mathrm{CH_2C_6H_5}}{\overset{|}{\mathrm{C}}}\Big\langle\begin{matrix}\mathrm{C_6H_4}\\ \mathrm{C_6H_4}\end{matrix}\Big\rangle\mathrm{O}$$

IV

A quantitative determination in the usual manner of the amount of oxygen absorbed[5] showed that 94–95% of the amount necessary for the formation of the peroxide was taken up in seven minutes in bromobenzene and slightly more that 100% in 25 minutes. This is equal to the ease with which well-known free radicals such as triphenylmethyl (hexaphenylethane) combine with oxygen. The crude precipitate also combines with practically the theoretical amount of oxygen, and the peroxide is readily obtained from it. A solution of the compound in benzene is very light yellow at room termperature but the color darkens to brown on warming, and fades again on cooling. Like hexaphenylethane, dibenzyldixanthyl is so little dissociated in benzene at low temperatures that the molecular weight by the freezing-point method corresponds to the bimolecular formula within our limits of error.

In the solid state the substance may be kept in an inert atmosphere many days without change. It is decomposed, however, on heating. Thus a solution of it in bromobenzene heated to 75–80° for 1.5 hour lost about half of its oxygen-absorbing power and after the same length of time at 108° failed to combine with any oxygen. The color changes of the substance in molten naphthalene also show that a decomposition takes place. Thus at the melting point of naphthalene the solution is yellow, darkens to a reddish brown when the substance is heated to 120° and lightens again as it cools; on repeating the process, however, the color deepens to a less extent and above a temperature of 130° rapidly fades to a permanent, light yellow. The reaction involved appears to be the following, which Ziegler[3] has noted with undissociated 2,2,3,3-tetraphenylbutane, $(C_6H_5)_2C(CH_3)C(CH_3)(C_6H_5)_2$, and which apparently takes place so readily with tetraphenyl-dibenzylethane that this substance has not yet been prepared.



$$\left(\mathrm{O}\Big\langle\begin{matrix}\mathrm{C_6H_4}\\ \mathrm{C_6H_4}\end{matrix}\Big\rangle\underset{|}{\mathrm{C}}-\mathrm{CH_2C_6H_5}\right)_2\longrightarrow\mathrm{O}\Big\langle\begin{matrix}\mathrm{C_6H_4}\\ \mathrm{C_6H_4}\end{matrix}\Big\rangle\mathrm{C}=\mathrm{CHC_6H_5}+\mathrm{O}\Big\langle\begin{matrix}\mathrm{C_6H_4}\\ \mathrm{C_6H_4}\end{matrix}\Big\rangle\mathrm{CH}-\mathrm{CH_2C_6H_5}.$$

Thus, from a benzene solution of dibenzyldixanthyl heated to 108° for 20 minutes, benzylidene-xanthane and a low-melting substance, probably benzylxanthane, were isolated.

Dibutyldixanthyl

The reduction of butylxanthyl perchlorate with vanadous chloride in aqueous hydrochloric acid yields dibutyldixanthyl (V) which can be

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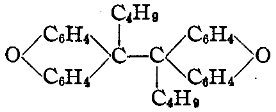
[5] Compare Gomberg, THIS JOURNAL, 39, 1652 (1917).


V


VI

obtained as a colorless, crystalline compound by recrystallization from benzene. The molecular weight in freezing benzene corresponds to the bimolecular formula within the limits of significance of our measurements. The compound combines with oxygen very slowly, about 25% of one mole being absorbed in 2.5 hours, 50% in four hours, 100% in nine hours and finally after 70 hours the absorption is practically complete, 2.75 moles of oxygen per mole of dibutyldixanthyl having been absorbed. From an ether solution which had been allowed to stand in contact with air for many hours, a small amount of solid was obtained which analyzed for dibutyldixanthyl peroxide.

Solutions of the pure compound in benzene are practically colorless and remain so when warmed. Like dibenzyldixanthyl the compound is sensitive to heat and a non-crystalline material is obtained when a benzene solution of it is heated for any length of time. Undoubtedly, the same change occurs as with the dibenzyl compound but crystalline products have not yet been identified. The oxidation of the compound by air is accompanied by the appearance of a yellow color the source of which has not been determined.

It may be regarded as an open question whether or not dibutyldixanthyl dissociates at room temperature into the free radical butylxanthyl. The slow absorption of oxygen can be interpreted as an "auto-oxidation" of the ethane molecule and not dependent on the formation of a compound containing trivalent carbon. Thus, butylxanthyl carbinol itself (or the product formed from it by the spontaneous loss of water) undergoes slow auto-oxidation, the rate, however, being considerably less than with the dibutyldixanthyl. However, we are inclined to believe that dibutyldixanthyl does dissociate to a slight extent and that it is this dissociated form which is responsible for the absorption of oxygen. The amount of dissociation may be very small or the rate of dissociation may be slow; either or both of these factors would decrease the speed of absorption of oxygen. Dixanthyl (VI), itself, does not absorb oxygen at all and in general shows no sign of dissociation.

If dibutyldixanthyl is really dissociated only to the extent of a few per cent. or less, it is obvious that special methods will have to be devised to determine such a small degree of dissociation. We hope to deal in a later paper with this problem and other aspects of the behavior of compounds which lie on the border line between dissociated and undissociated ethanes.

The Effect of Non-Aromatic Groups on the Dissociation of Ethanes

Almost all of the free radicals that have been hitherto prepared are of the type Ar_3C—, where Ar— is an aromatic nucleus. Triphenyl indyl,[6] pentaphenylethyl,[7] diphenylvinylxanthyl and diphenylvinyl-diphenylmethyl[3] $[(C_6H_5)_2C{=}CH{-}\underset{|}{C}(C_6H_5)_2]$ and its methoxy derivatives are the only known[8] examples of compounds containing trivalent carbon which have only two aromatic nuclei directly attached to the central carbon atom. Benzylxanthyl and probably butylxanthyl must now be added to this small group of interesting compounds. As far as the dissociation of *derivatives of dixanthyl* is concerned, the influence of groups can be definitely placed as $C_{10}H_5$[9] $>$ C_6H_5[9] $> C_6H_5CH_2 > C_4H_9 >$ H. It cannot be definitely predicted that this same order would hold in another series such as derivatives of tetraphenylethane since Ziegler states that the β,β-diphenylvinyl-diphenylmethyl is less associated than β,β-diphenylvinylxanthyl, whereas aromatic groups are more effective in the xanthyl series than in the hexaphenylethane series.

The importance of the dissociation of dibenzyldixanthyl lies in the fact that it definitely establishes *that a saturated non-aromatic group may increase the dissociation of an ethane.* The behavior of dibutyldixanthyl also points in this direction. The other free radicals mentioned above with the exception of pentaphenylethyl all have an ethylene linkage in the alpha position to the central carbon atom, and the effect of the non-aromatic group in these cases may well be attributed to its unsaturation. No such explanation is possible with dibenzyldixanthyl or dibutyldixanthyl.

The existence of the free radical benzylxanthyl is contrary to the conceptions of the Werner theory of valence. As Schlenk has pointed out in regard to the existence of pentaphenylethyl,[7] this theory would lead to the conclusion that a phenyl group in the beta position would *diminish* rather than *increase* the dissociation of the ethane. The same difficulty is met in attempting to apply any theory of alternate strong and weak affinities or alternating polarities.

Experimental Part

Benzylxanthyl Perchlorate.—This compound was prepared by the addition of 60% perchloric acid in a mixture of acetic acid and acetic anhydride to a solution of benzylxanthydrol[10] in dry ether. It was obtained as a bright yellow, crystalline precipitate; m. p., 226–227°. When it was dissolved in concd. hydrochloric acid and the solu-

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[6] Kohler, *Am. Chem. J.*, **40**, 217 (1908).

[7] Schlenk and Mark, *Ber.*, **55B**, 2285 (1922).

[8] Diphenyl-cyclohexylmethyl may also exist although it has not yet been isolated in a pure state. (Ref. 4.)

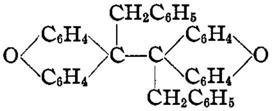
[9] Gomberg, *Chem. Reviews*, **1**, 91 (1924).

[10] Decker, *Ber.*, **38**, 2493 (1905).

tion diluted with water, a precipitate of benzylidenexanthane (m. p., 113–113.5°) was formed.

Anal. (by titration with standard alkali).[11] Calcd.: ClO_4, 26.8. Found: 26.8.

Dibenzyldixanthyl,



Preparation from the Carbinol.—A solution of 5 g. of benzylxanthydrol in 500 cc. of concd. hydrochloric acid was reduced with 40 cc. of 0.5 *N* vanadous chloride solution (prepared by the reduction of vanadium pentoxide with amalgamated zinc and acid). A tan-colored precipitate formed immediately; the mixture was diluted with 1 liter of boiled water, filtered rapidly with suction and the precipitate dried in an atmosphere of carbon dioxide. The product weighed 4.5 g.; m. p., 114–135°.

Preparation from the Perchlorate.—A solution of 2 g. of the perchlorate salt in 200 cc. of concd. hydrochloric acid was treated with 15 cc. of 0.5 *N* vanadous chloride. The mixture was diluted with boiled water and the precipitate filtered off and treated as described above; yield, 1.37 g.; m. p., 80–110°.

Preparation from Benzylidenexanthane.—Five g. of benzylidenexanthane was dissolved in 600 cc. of concd. hydrochloric acid and reduced with 40 cc. of 0.5 *N* vanadous chloride. The precipitate was filtered off and dried in the usual manner, yielding 4.9 g. of product; m. p., 124–130°.

The oxygen absorption of the crude, dry dibenzyldixanthyl was 94–97% of that calculated. The moist precipitate prepared by any one of the three methods also absorbed oxygen very rapidly, taking up nearly the calculated amount. The method and apparatus used throughout this work for obtaining the oxygen-absorbing power of the free radicals were essentially those described by Gomberg.[12] The solid was introduced into a small, thin-walled bulb which was then stoppered and placed in the absorption bottle, containing bromobenzene and connected with a gas buret. After the temperature had become constant, the bulb was broken by agitating the absorption bottle and the shaking was continued from time to time until no more gas was absorbed.

The crude dibenzyldixanthyl was purified by recrystallization from benzene and petroleum ether in an atmosphere of hydrogen in a special apparatus very similar to those employed by other investigators in the manipulation of free radicals. In this way 1.5 g. of pure product, m. p. 146.5–148.5° (in carbon dioxide), was obtained from 2.4 g. of crude material. A second recrystallization was necessary in some cases in order to obtain pure material.

Anal. Calcd. for $C_{40}H_{30}O_2$: C, 88.5; H, 5.6. Found: C, 88.1; H, 5.5.

Molecular Weight in Freezing Benzene in an Atmosphere of Hydrogen.—Successive increments of about 0.15 g. were added to 16.66 g. of benzene and the following total weights and freezing-point depression (Δt) were calculated from the second increment: 0.1553 g., $\Delta t = 0.091°$, mol. wt., 525, 0.3056; $\Delta t = 0.180°$, mol. wt., 522; av. mol. wt. = 523; calcd., 542; oxygen absorption of the same material on the same day, 105%.

Oxygen Absorptions.—The following results are typical: 0.38 g. of material (five days after preparation) absorbed 17.3 cc. of oxygen (19°, 756 mm.) in 40 minutes, equivalent to 102.5% of the calculated amount, of which 94.5% was absorbed in the first seven minutes; 0.48 g. (14 days after preparation) absorbed 21.2 cc. (21°, 771 mm.) or 101%; 0.288 g. of freshly recrystallized material absorbed 13.4 cc. (20°, 761), or 105%. Benzylidenexanthane failed to show any oxygen absorption in parallel experiments.

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[11] *Ann.*, **370**, 159 (1909).

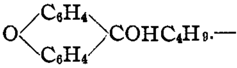
[12] Gomberg, THIS JOURNAL, **39**, 1652 (1917).

A 4.0% solution of dibenzyldixanthyl in benzene at 20° (under hydrogen) is light yellow. When the solution is warmed to 100° the color darkens to reddish brown and fades again on cooling. The process can be repeated several times. When the liquid is kept at a temperature of 108° for 20 minutes the brown color fades to a permanent light yellow; from 15 cc. of this solution were isolated 0.15 g. of benzylidenexanthane (m. p., 113–113.5°) and some material melting at 60–62° which was perhaps benzylxanthane (m. p., 71–72°).

A solution of 0.05 g. of dibenzyldixanthyl in 2 g. of molten naphthalene was light yellow and the color gradually changed to reddish brown when the liquid was heated to 130°, faded to yellow again as it cooled. The color changes could be repeated by heating and cooling but the intensity of the brown color was less each time. Above a temperature of 130° the color faded rapidly to a light yellow which was unaffected by heating the liquid to 200° or cooling it.

DIBENZYLDIXANTHYL PEROXIDE.—The moist precipitate of dibenzyldixanthyl obtained by reduction of 5 g. of benzylxanthyl perchlorate was immediately introduced into 200 cc. of ether. The dibenzyldixanthyl dissolved immediately and a fine, white precipitate of peroxide formed and was filtered off. A further amount was obtained by evaporation of the filtrate; yield, 3.1 g., or 80%; m. p., 130–139°. It could be recrystallized from benzene by keeping the temperature below 40° and adding petroleum ether. The recrystallized material melts sharply at 131°. It is decomposed when heated in benzene solution to give xanthone and other products not identified.

Anal. Calcd. for $C_{40}H_{30}O_4$: C, 83.6; H, 5.3. Found: C, 83.3; H, 5.2.

Butylxanthydrol 

$O\langle^{C_6H_4}_{C_6H_4}\rangle COHC_4H_9$

.—A solution of butylmagnesium bromide in ether was prepared in the usual way from 2.6 g. of magnesium, 60 cc. of dry ether and 14 g. of *n*-butyl bromide. This was cooled to 5° and a suspension of 10 g. of xanthone in 50 cc. of ether added during 20 minutes, the temperature being kept below 15°. After 30 minutes, the reaction mixture was poured into a mixture of 100 g. of cracked ice and 200 cc. of 3 *N* ammonium chloride solution in a vessel placed in a freezing bath. The mixture was then warmed to 20° and, after 30 minutes, the ether layer was separated and the aqueous layer extracted once with ether. The combined ethereal solutions were dried rapidly with a little calcium chloride and evaporated to a small volume under diminished pressure; a somewhat yellow, crystalline paste resulted. Petroleum ether was added and the solid filtered off and washed with petroleum ether until colorless; yield, 8.9 g., or 67%; m. p., 109–112°. Since the carbinol is slowly auto-oxidized, it was recrystallized in an atmosphere of carbon dioxide. Four g. of the crude product was dissolved in 25 cc. of benzene at 40°, the solution filtered from a small residue, and evaporated, at 20 mm. pressure and 10°, to 5 cc. Petroleum ether (10 cc.) was added, the mixture cooled in a freezing bath, the product filtered off, washed with petroleum ether and dried on a porous plate; yield 1.8 g., m. p. 106–106.5°; 0.9 g. from the filtrates, m. p., 106–107°.

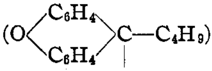
Anal. Calcd., C, 80.3; H, 7.1. Found: C, 79.5, 79.3; H, 6.9, 6.9.

As evident from the above analyses, the carbinol was not quite pure; because of its sensitiveness it could not be obtained in any purer condition. It cannot be dried over sulfuric acid for it loses water, probably forming butylidene xanthane. It takes up oxygen from the air slowly, giving non-crystalline products, and the solid after several days' exposure to air turns into a sticky mass. Three-tenths g. was placed in the usual apparatus for determining oxygen capacity and dissolved in bromobenzene by breaking the small bulb; in the first four hours there was an increase of gas volume of 4 cc., due perhaps to the loss of water from the compound and consequent increase in the pressure of the previously dry system. After 72 hours, there was a contraction of 9.1 cc. (21°, 760 mm.) and after 102 hours the absorption was complete, a total of 16.2 cc. (21°, 763 mm.) having been absorbed. This corresponds to 1.1 atoms of oxygen per molecule of carbinol, which is only about half that required for the oxidation of the carbinol (or butylidenexanthane) to xanthone and aldehyde. The nature of the products of the auto-oxidation have not been determined.

Butylxanthyl Perchlorate.—The ether solution containing the crude carbinol prepared from 10 g. of xanthone, as described above, was treated with 12 cc. of 60% perchloric acid. A fine, orange, crystalline precipitate formed which was filtered off, washed several times with ether and dried on a porous plate; yield, 11.4 g., or 66%; m. p., 187–189°. This compound is much more stable than the carbinol but after standing for a week exposed to air it develops an unpleasant odor indicating some decomposition.

Anal., by hydrolysis and titration with standard alkali. Calcd.: ClO_4, 29.5. Found: 29.6.

Dibutyldixanthyl,



$\left(O{<}^{C_6H_4}_{C_6H_4}{>}C-C_4H_9\right)_2$

Two g. of the perchlorate was dissolved in 150 cc. of concd. hydrochloric acid, a clear, orange solution resulting. This was diluted with 100 cc. of water, filtered from a very small residue and reduced with 30 cc. of 0.5 *N* vanadous chloride. A tan-colored precipitate immediately formed and was filtered off, washed with water and dried in an atmosphere of hydrogen over sulfuric acid; yield of crude dry material, 1.4 g., or 97%; m. p., 119–147°.

The material was recrystallized from benzene, the temperature never being higher than 30°. The crude material (1.36 g.) was dissolved in 40 cc. of benzene at room temperature (no precautions being taken to exclude air). A small amount of residue was filtered off and the filtrate evaporated to 5 cc. at 15–20° and 100 mm. A white, crystalline powder separated, which was filtered off, washed with a little benzene and dried on a porous plate; yield, 0.88 g.; m. p., 145–157°. The filtrate yielded 0.15 g. of purer material (m. p., 155–158.5°). A second crystallization of the combined products yielded 0.74 g. of pure product; m. p., 158–158.5°.

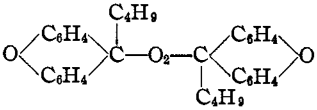
Anal. Calcd.: C, 86.1; H, 7.2. Found: C, 86.2; H, 7.4.

Molecular Weight in Freezing Benzene under Hydrogen.—A. Successive increments were added to 12.06 g. of benzene, the depression caused by the first increment being discarded: 0.1476 g., $\Delta t = 0.139°$, mol. wt., 451; 0.3071 g., $\Delta t = 0.284°$, mol. wt., 459; av. mol. wt. = 455; calcd., 474.

B. Another sample was added to 17.02 g. of benzene: 0.1192 g., $\Delta t = 0.081°$, mol. wt., 443°; 0.2606 g., $\Delta t = 0.175$, mol. wt., 448; av. mol. wt. = 445; calcd., 474.

Oxygen absorption.—The pure substance (0.318 g.) was introduced into the usual apparatus containing bromobenzene. After 100 minutes, 2.4 cc. was absorbed; 285 mins., 8.0 cc.; 400 mins., 11.2 cc.; 1261 mins. 25.25 cc.; 1522 mins., 28.0 cc.; 4163 mins., 38.45 cc.; 5600 mins., 37.75 cc.; 7055 mins., 37.35 cc., all at 20°, 768 mm. Calcd. on the basis of one mole (2 atoms of oxygen) per mole of dibutyldixanthyl, these absorptions correspond to the following percentage absorptions by interpolation: 25%, 2.3 hours; 50%, 4.2 hours; 100%, 8.8 hours; 150%, 15.5 hours; 200%, 25.3 hours; 275% (complete) 70 hours. Dixanthyl (m. p., 204–205°) in a parallel experiment showed no absorption after 2 days.

DIBUTYLDIXANTHYL PEROXIDE,



$O{<}^{C_6H_4}_{C_6H_4}{>}\overset{C_4H_9}{C}-O_2-\underset{C_4H_9}{C}{<}^{C_6H_4}_{C_6H_4}{>}O$

.—A colorless solution of 0.34 g. of recrystallized dibutyldixanthyl in 25 cc. of ether was filtered into a small flask which was then closed with a calcium chloride tube and allowed to remain overnight. By morning, a few colorless crystals of peroxide had formed. Shaking separated more crystals, smaller in size. After another day, the light yellow ether solution was decanted from the crystals which were then washed with a small amount of ether and dried; yield 0.19 g., or 52%; m. p., 182–183.5°, with evolution of gas at 183.5°.

Evaporation of the ether solution gave 0.02 g. of inferior product melting at 158–160°.

The peroxide was found to be quite stable in air, its melting point not changing after a week's exposure.

Anal. Calcd.: C, 80.6; H, 6.8. Found: C, 80.3; H, 6.9.

Summary

1. Dibenzyldixanthyl has been prepared by reducing benzylxanthydrol with vanadous chloride. It behaves as though it dissociated into a free radical in solution, rapidly absorbing oxygen to form a peroxide and giving the usual color changes when heated and cooled. Its molecular weight in freezing benzene corresponds to a dissociation of less than 4%.

2. Dibutyldixanthyl has been prepared by reducing butylxanthyl perchlorate with vanadous chloride. It is bimolecular in freezing benzene within the limits of error of the cryoscopic method. It absorbs oxygen slowly, forming a peroxide. It is probably slightly dissociated in solution.

3. Solutions of dibenzyldixanthyl and dibutyldixanthyl are decomposed by heat. The change apparently involves the formation of monomolecular saturated and unsaturated hydrocarbons.

4. The effectiveness of the benzyl group as compared with hydrogen or an alkyl group in causing the dissociation of an ethane does not accord with certain theories of valence.

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EVIDENCE OF A NEW AMINO ACID IN PROTEINS[1]

BY ROSS AIKEN GORTNER AND WALTER F. HOFFMAN

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While determining the nitrogen distribution of a series of proteins (Hoffman and Gortner,[2] 1924) according to the Van Slyke method,[3] the phosphotungstates of the basic amino acids, arginine, histidine, lysine

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[1] Published with the approval of the Director, as paper No. 508, Journal Series, Minnesota Agricultural Experiment Station.

[2] Hoffman and Gortner, "Physico-chemical Studies on Proteins. I. The Prolamines—Their Chemical Composition in Relation to Acid and Alkali Binding." Second Colloid Symposium Monograph, Chemical Catalog Company, New York (in press).

[3] Van Slyke, *J. Biol. Chem.*, **10**, 15 (1911).