It can be seen that the fatty acids in "refinery mud" are the same as those liberated from pure starch. Since the unsaturated portion contains only oleic and linolic acids, their amounts can be determined by solving the following equations; $x + y = 100$; $90.07x/100 + 181.42y/100 = 133.5$; x is the percentage of oleic acid and y the percentage of linolic acid; 90.07 and 181.42 are their respective theoretical iodine numbers and 133.5 is the actual experimental iodine number of the mixture of unsaturated fatty acids: whence $x = 52\%$; $y = 47\%$. Assuming that the saturated portion is entirely palmitic acid and that its iodine number under the above conditions is zero, we have: $W + Z = 100$; $133.5Z/100 = 101.5$, where W is the amount of palmitic acid in the original fatty material and Z is the combined amounts of oleic and linolic acids, the whole mixture having an iodine number of 101.5; whence $W = 23\%$; $Z = 76\%$.

From these results it may be concluded that the fatty acids liberated upon hydrolysis of corn starch (alpha amylose) consist of approximately 24% of palmitic acid, 40% of oleic acid and 36% of linolic acid.

Summary[18]

The unsaturated fatty acids liberated by the hydrolysis of corn starch free from extraneous material have been identified and their amounts determined.

New York, N. Y.

[Contribution from the Chemical Laboratory of Harvard University]

THE DISSOCIATION INTO FREE RADICALS OF SUBSTITUTED DIXANTHYLS

III. THE EFFECTIVENESS OF SECONDARY ALKYL GROUPS IN PROMOTING DISSOCIATION

By J. B. Conant, L. F. Small[1] and A. W. Sloan

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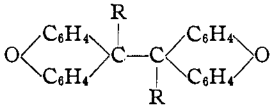
In previous papers of this series,[2] it has been shown that while dixanthyl itself (R = H, Formula I) shows none of the characteristic properties of a



I

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[18] The work embodied in this paper is taken from the first part of a thesis presented by Leo Lehrman to the Faculty of Pure Science of Columbia University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[1] Du Pont Fellow in Chemistry 1925–26.

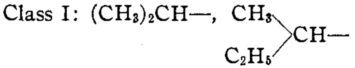
[2] Conant and Sloan, This Journal, **47**, 572 (1925). Conant and Small, *ibid.*, **47**, 3068 (1925).

dissociable ethane, many of its derivatives do. The effectiveness of certain groups in promoting this dissociation may be summarized by placing them in three classes as follows:

$(C_{10}H_7—, C_6H_5—, C_6H_{11}—,) > (C_6H_5CH_2—, ClC_6H_4CH_2—) > (n\text{-}C_4H_9—, n\text{-}C_6H_{13}—, iso\text{-amyl}) > H$
I II III

Thus solutions of diphenyl-dixanthyl ($R = C_6H_5$) or dicyclohexyl dixanthyl ($R = C_6H_{11}$) are highly colored at 25° and adsorb oxygen almost instantaneously forming peroxides, while solutions of dibenzyl-dixanthyl become colored only when warmed to 80–100°, although the oxygen absorption is very rapid even at 25°. The primary alkyl groups (Class III) are the least effective as is evidenced both by the very slow reaction with oxygen and the fact that their solutions become colored only when heated to about 140°.

We have continued our preparation and study of derivatives of dixanthyl and as a result of this further work can add the following groups to the above classification:


Class I: $(CH_3)_2CH—, \; \begin{matrix} CH_3 \\ C_2H_5 \end{matrix}\!\!>\!CH—$
Class II: $(CH_3)_2CHCH_2—, C_{10}H_7CH_2—$.
Class III: $CH_3—, C_2H_5—, C_6H_5CH_2CH_2—, C_6H_5(CH_2)_3—$.

With the exception of the α-naphthyl and phenyl derivatives which have been studied by Gomberg, it is not yet possible to compare the degree of dissociation of the various derivatives by means of molecular-weight determinations. In the case of cyclohexyl, *iso*propyl and *sec.*-butyl compounds we have been unable to obtain pure crystalline material and in the other cases the degree of dissociation is too slight to be detected by the cryoscopic methods at temperatures at which the compounds are stable. In another paper we hope to report the results of a study of the rates of oxygen absorption, the color of solutions at different temperatures and other quantitative data which should permit us to distinguish between some of the groups which are now classed together.

The present work demonstrates for the first time the great influence of secondary alkyl groups and it is evident that the effectiveness of the cyclohexyl group must be attributed largely to the fact that it is also a secondary group. Although we have been unable to obtain crystalline di-*iso*propyl-dixanthyl, or di-*sec.*-butyl-dixanthyl, their dissociation to a considerable degree at 25° in solution is clearly demonstrated by the intense red color of the solutions. This color becomes deeper on warming and fades almost completely at temperatures below 0°, but reappears on warming. Like other free radicals containing alkyl groups attached to the trivalent carbon atom, the substances are unstable, and at temperatures above 60–70°

the color disappears rapidly because of a decomposition probably involving internal oxidation and reduction. The very rapid absorption of oxygen by the highly colored solution of these free radicals yields the usual crystalline peroxides.

Di-*iso*butyl-dixanthyl and dinaphthylmethyl-dixanthyl are very similar to the benzyl and *p*-chlorobenzyl derivatives previously reported. Their colorless solutions at room temperature absorb oxygen almost as rapidly as does a solution of hexaphenylethane; in the case of the *iso*butyl compound a crystalline peroxide was obtained in good yields. It is of interest that the *iso*propyl group, so effective in the alpha position in promoting dissociation, is also effective to some extent in the beta position just as are the aryl groups.

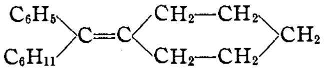
In the gamma position neither the *iso*propyl nor the phenyl group exerts a special influence which can be detected by our present methods, since di-*iso*-amyl-dixanthyl ($R = (CH_3)_2CH—CH_2—CH_2$) and di-β-phenylethyl-dixanthyl are both very like the di-*n*-butyl and di-*n*-hexyl derivatives; the same is true of the γ-phenylpropyl compound. With all these compounds the slow oxygen absorption at room temperature may be interpreted as an auto-oxidation of the ethane or as proceeding through a very small amount of free radical. The reversible development of color on heating solutions of these substances indicates that at least above about 120°, there is appreciable dissociation. It might be noted in this connection that the dimethyl and diethyl derivatives—in particular the dimethyl—absorb oxygen more slowly at 25° than the other compounds of this class and we feel quite certain that of all the alkyl groups thus far examined the methyl has the least dissociating influence.

The results of this work seem to us to point quite clearly to the fact that secondary alkyl or alicyclic groups have an influence on the dissociation of the C—C linkage, comparable to that of aryl and unsaturated groups. Very probably tertiary alkyl groups have the same influence, but our failure to prepare *tert.*-butyl-xanthenol has prevented our testing this point in the dixanthyl series. Whether this influence of the forked aliphatic chain is to be explained on steric grounds or in terms of the absence of hydrogen atoms in critical positions, cannot yet be settled. The latter hypothesis, which was suggested to us by Dr. E. Q. Adams, is very attractive in many ways and the data we have accumulated in the dixanthyl series accord with it, but there are many difficulties in applying it generally to the dissociation of ethanes.

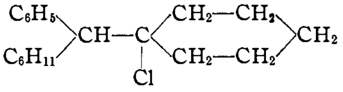
Whatever may be the reason for the action of secondary alkyl groups, it seems extremely probable that this effect is of the same order of magnitude as that of the phenyl group and like it should be cumulative. One would thus be led to predict that such compounds as hexa(*iso*propyl)ethane would dissociate in solution at temperatures not far above room temperature. The resulting free radical might undergo immediate disproportionation as in the case of ethyldiphenylmethyl,[3] but the existence of either dissociation or decomposition should be easily demonstrated. As far as we can discover, no aliphatic hydrocarbons are known which contain six secondary or tertiary alkyl groups attached to adjacent carbon atoms, nor any containing two aryl groups and four branched alkyl groups. The existence or non-existence of free radicals containing less than two unsaturated (or aryl) groups has, therefore, not yet been adequately tested.

The Structure of the Hydrocarbon Obtained from Phenyl-dicyclohexylchloromethane

Very recently the synthesis of diphenyl-tetracyclohexyl-ethane has been reported[4] and its behavior studied in relation to its possible dissociation. It was found that it was unchanged on heating to 330° in air for 30 minutes. As this stability was quite contrary to what we would have predicted from the effect of the cyclohexyl group in the dixanthyl series, we have repeated the work. We confirmed the structure of phenyl-dicyclohexyl-chloromethane by treating it with silver oxide and obtaining the original carbinol from which it was prepared; this precludes a possible rearrangement during the conversion of carbinol to chloride which we had thought possible.[5] The hydrocarbon obtained by treating the chloride with silver in boiling toluene, we found to be phenyl-cyclohexylidene-cyclohexyl-methane (II) previously prepared by Godchot, and not diphenyl-tetracyclohexyl-ethane.



II



III

This was established by molecular-weight determinations in freezing benzene and naphthalene and by the conversion of it into crystalline chlorocyclohexyl-cyclohexyl-phenylmethane (III) by treatment with hydrogen chloride in alcohol solution at 0°. The same chloride was obtained from the unsaturated hydrocarbon prepared according to Godchot's directions by dehydration of dicyclohexylphenyl carbinol. Diphenyl-tetracyclohexyl-ethane is thus to be removed from the literature. We wish to express our appreciation of the kind coöperation of Dr. Marvel who supplied us with a generous sample of his hydrocarbon, which we found to have physical and chemical properties identical with the material we prepared according to his directions.

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[3] Ziegler and Schnell, *Ann.*, **437**, 233 (1924).

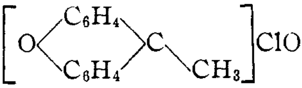
[4] Gray and Marvel, THIS JOURNAL, **47**, 2796 (1925).

[5] Schmidlin and von Escher, *Ber.*, **45**, 889 (1912).

Experimental Part

Part A[6]

Methyl-xanthydrol was prepared by the method of H. Decker,[7] by the action of methylmagnesiumiodide upon xanthone. The product was contaminated probably with xanthone, the melting point being 101–111°, instead of 96–99° as given by Decker.

Methyl-xanthyl Perchlorate,  $\left[O{<}\substack{C_6H_4\\C_6H_4}{>}C{-}CH_3\right]ClO_4$.—The perchlorate was prepared from an ether solution of the crude carbinol.

A mixture of 2.4 g. of magnesium shavings, 15 g. of methyl iodide and 10 g. of xanthone gave, on decomposition of the Grignard compound with cold ammonium chloride, a yellow ether solution which was dried with calcium chloride. The solution was filtered, and treated with 5 cc. of 60% perchloric acid, added dropwise. A heavy, red precipitate of the salt was formed. The product contained small specks of yellow material which, as shown below, was probably a purer form of the perchlorate salt. Further drying of the ether solution with calcium chloride gave more product; yield, 9.6 g., or 64.5%; m. p., 173–188°.

Anal. (Gomberg's method).[8] Calcd. for $C_{14}H_{11}ClO_5$: ClO_4, 33.96. Found: 21.55.

The low analysis was due probably to the presence of xanthone, or methylxanthydrol, or a different complex. Reduction with vanadous chloride, in hydrochloric acid solution, gave a 116% yield of crude dimethyl-dixanthyl, m. p. 135–159°, which would agree with a 100% yield of product assuming that the red salt were a mixture of 60% of the perchlorate, and 40% of the xanthydrol, indicated by the analysis given above. However, recrystallization of the crude dimethyl-dixanthyl from benzene gave a much lower yield of higher-melting product, the impurity being possibly xanthone.

In another preparation of methylxanthyl perchlorate, using the same amounts of material as given above, the Grignard reaction product being only partly soluble in ether, was filtered off, and the ether extract decomposed with cold water containing a few drops of concd. hydrochloric acid. The ether solution, after being dried with calcium chloride, was treated with a solution of 60% perchloric acid in acetic anhydride. A precipitate of 1.9 g. of brilliant red, very fine crystals formed; m. p., 185–208° (with decomposition).

Anal. Calcd. for $C_{14}H_{11}ClO_5$: ClO_4, 33.76. Found: 20.98.

From the above filtrate, the addition of 5 cc. of acetic anhydride, and 1.5 cc. more of the perchloric acid solution gave 0.28 g. of orange-yellow crystals, m. p. 209–210° (with decomposition), after darkening at 190°.

Anal. Calcd. for $C_{14}H_{11}ClO_5$: ClO_4, 33.76. Found: 32.77.

This analysis indicates that the yellow salt is the normal one.

Attempts to recrystallize the red salt from chloroform left a yellow residue of m. p. 210–212° (with decomposition), after darkening at 200°. From the chloroform solu-

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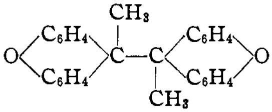
[6] Part A of the experimental portion of this paper is part of a thesis by A. W. Sloan presented to the Faculty of Arts and Sciences of Harvard University in partial fulfilment of the requirements for the degree of Doctor of Philosophy; Part B is part of a thesis of L. F. Small presented to the same Faculty for the same degree.

[7] Decker, *Ber.*, **38**, 2507 (1905).

[8] Gomberg and Cone, *Ann.*, **370**, 159 (1909).

tion, evaporation gave a brown gum which upon treatment with petroleum ether gave fine, green crystals melting at 198°, with darkening at 185°. These were not analyzed.

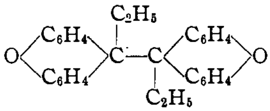
Dimethyl-dixanthyl,  $O(C_6H_4)_2C(CH_3)-C(CH_3)(C_6H_4)_2O$.—Two g. of the red perchlorate salt was dissolved in 200 cc. of concd. hydrochloric acid, and the deep green solution was diluted with 100 cc. of water and filtered. To the filtrate was added 10 cc. of 1 *N* vanadous chloride solution. A flocculent, light colored precipitate was immediately formed. It was filtered off, washed with a large amount of cold water, and dried in a vacuum desiccator under nitrogen, and over solid potassium hydroxide and phosphorus pentoxide. It weighed 1.53 g., a 116% yield; m. p., 168–172° under nitrogen.

Recrystallization of the crude material from benzene and acetone gave 0.8 g. of white crystals, m. p. 181–181.5° under nitrogen, and 0.2 g. of white crystals of slightly lower melting point.

Anal. Calcd. for $[C_{14}H_{11}O]_2$: C, 86.12; H, 5.68. Found: C, 85.97; H, 5.69.

Molecular Weight in Freezing Benzene, in an Atmosphere of Hydrogen.—The compound was so slightly soluble that only one increment could be added: 0.1212 g. in 16.86 g. of benzene; Δt = 0.093°; mol. wt. = 395.8. Calcd. mol. wt. = 390.3. K = 5120. A further addition of 0.1087 g. did not dissolve. Dimethyl-dixanthyl in 0.05 *M* solution in bromobenzene absorbed oxygen at the following rate:[9] 4 hours, 10%; 10 hours, 25%. On warming a 0.05 *M* solution of the dimethyl-dixanthyl in ethyl benzoate to 160° it acquired a faint yellow color which increased at 212° and then faded rapidly, due to decomposition.

Ethylxanthenol has been prepared by Fosse,[10] both by the action of sodium and ethyl bromide on xanthone in toluene solution, and by the Grignard reaction. The Grignard compound from 2.4 g. of magnesium, 12 g. of ethyl bromide and 10 g. of xanthone, in 150 cc. of dry ether was filtered, and the insoluble residue washed with 50 cc. of dry ether. It was then dried for ten minutes on a clay plate, during which time the white product began to turn yellow. It was decomposed with a mixture of 3 *N* ammonium chloride solution and ice. The white product was filtered off and washed with water; yield, 8.4 g. or 73.5%, based on the xanthone; m. p., 89.5–93°. Decomposition of the ether filtrate and evaporation of the ether gave 2.6 g. more of crude product; m. p., 82–148°. Recrystallization of 1.0 g. of the better material from petroleum ether gave 0.7 g. of white, crystalline ethylxanthydrol; m. p., 96–97° (Fosse, 98–100°). From a solution of the xanthydrol in ether, addition of 60% perchloric acid in an equal volume of acetic anhydride precipitated fine light yellow crystals of the perchlorate; m. p., 191–192°, with decomposition. The product was not analyzed.

Diethyl-dixanthyl,  $O(C_6H_4)_2C(C_2H_5)-C(C_2H_5)(C_6H_4)_2O$.—Two g. of ethyl-anthydrol was

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[9] The method used for determining the rate of oxygen absorption was similar to that outlined by Gomberg [THIS JOURNAL, **39**, 1662 (1917)] and employed in our previous studies. In most experiments the bottle containing the solution of the dixanthyl derivative and pure oxygen was continuously shaken. The percentage oxygenation is calculated from the weight of sample and the volume of oxygen corresponding to the formation of the peroxide.

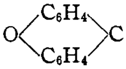
[10] Fosse and Baillon, *Bull. soc. chim.*, [4] **1**, 861 (1907).

treated with 5 cc. of water, and the resulting paste dissolved in 200 cc. of concd. hydrochloric acid. The deep yellow solution was filtered through asbestos. To the filtrate was added, during stirring, 10 cc. of 1 *N* vanadous chloride solution. Immediately a fine, light yellow flocculent precipitate was formed. After the mixture had been diluted with 600 cc. of cold water, the product was filtered off, washed well with water and dried; yield, 1.7 g., or 92%; m. p., 183–186° in nitrogen. Recrystallization of 1.65 g. from benzene and acetone gave 1.3 g. of product melting at 192.5–193° in nitrogen, and a second recrystallization raised the melting point to 194° in nitrogen.

Anal. Calcd. for $C_{30}H_{26}O_2$: C, 86.1; H, 6.2. Found: C, 85.8; H, 6.2.

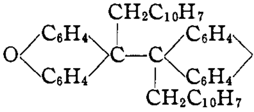
Mol. wt. (benzene, cryoscopic, hydrogen). Subs., 0.0976; benzene, 11.1; Δt, 0.011°. Calcd. for $C_{30}H_{26}O_2$, mol. wt., 418. Found: 406.

The rate of oxygen absorption measured in the usual way was as follows: 3.5 hours, 20%; 8 hours, 40%; 28 hours, 100%.

α-Naphthylmethyl-xanthenol,  $O{<}\begin{smallmatrix}C_6H_4\\C_6H_4\end{smallmatrix}{>}C(OH)CH_2C_{10}H_7(\alpha)$.—A mixture of 0.70 g. of magnesium shavings, one crystal of iodine, one small drop of ethyl iodide, and 20 cc. of dry ether in a 500cc. Wolff flask was heated to boiling under a reflux condenser, in an atmosphere of nitrogen. A solution of 4.5 g. of α-chloromethyl-naphthalene[11] in 40 cc. of dry ether was added dropwise during 40 minutes. The reaction proceeded very slowly. In three hours, the reaction was about complete. The reaction mixture was then cooled to 5° with ice water, and a suspension of 5 g. of xanthone in 60 cc. of dry ether was added from a separatory funnel during three to four minutes. Reaction was immediate. A large amount of brown product separated. The mixture was allowed to warm to room temperature, and stirring was continued for one hour. The Grignard reaction product was then poured rapidly into 150 cc. of cold water, 150 g. of ice, and 10 cc. of concd. hydrochloric acid. Floating between the yellow ether layer and the water layer was a fairly large amount of light yellow, crystalline solid which proved to be xanthone. The water layer was separated and washed with 50 cc. of ether. The combined ether layers were dried with 20 g. of anhydrous potassium carbonate.

From the ether solution, upon evaporation and separation of some xanthone, 1.26 g. of the crude xanthydrol was obtained, m. p. 112–120°, which after two crystallizations from a mixture of benzene and petroleum ether melted at 137–138°.

Anal. Calcd. for $C_{24}H_{18}O_2$: C, 85.2; H, 5.4. Found: C, 84.8; H, 5.4.

Di-α-naphthylmethyl-dixanthyl,  $O{<}\begin{smallmatrix}C_6H_4\\C_6H_4\end{smallmatrix}{>}\overset{CH_2C_{10}H_7}{C}-\underset{CH_2C_{10}H_7}{C}{<}\begin{smallmatrix}C_6H_4\\C_6H_4\end{smallmatrix}{>}O$.—*Preparation from the Crude α-Naphthylmethyl-xanthydrol.*—The crude xanthydrol dissolved in glacial acetic acid containing a small amount of concd. hydrochloric acid, gave a white, flocculent precipitate when reduced with vanadous chloride which on drying in a desiccator under nitrogen and over phosphorus pentoxide melted at 179.5–181.5° under nitrogen.

Preparation from the Magnesium Grignard Compound.—From 1.0 g. of magnesium, 7.0 g. of xanthone and 7.1 g. of α-naphthylmethyl chloride added all at one time to 95 cc. of dry ether, under nitrogen, was obtained, after removal of 0.2 g. of unused magnesium, 13.2 g. of Grignard product, in the form of light brown crystals. It was kept in a desiccator over phosphorus pentoxide.

Two g. of the Grignard compound was treated with 5 g. of ice, giving a yellow, powdery product. After a few drops of cold dil. hydrochloric acid had been added, the

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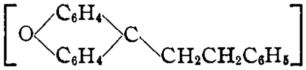
[11] Braun and Moldaenke, *Ber.*, **56,** 2165 (1923).

product was filtered off, washed with water, and dissolved in 120 cc. of glacial acetic acid and 3.5 cc. of concd. hydrochloric acid. The orange-brown solution thus obtained was cooled and treated with 10 cc. of 0.5 *N* vanadous chloride, whereupon a white flocculent precipitate was formed. It was washed first with glacial acetic acid, then with water, and dried for two hours on a porous plate, then in a vacuum desiccator over phosphorus pentoxide; yield, 0.78 g.; m. p., 174–177°, under carbon dioxide.

Attempts to crystallize the crude material were not successful. It was insoluble in most solvents. Washing with ether in an atmosphere of carbon dioxide raised the melting point to 182–183° (under carbon dioxide). From chloroform and petroleum ether, the recrystallized product had the same melting point as material washed only with chloroform (184°), but was impure as evidenced by an analysis and oxygen absorption.

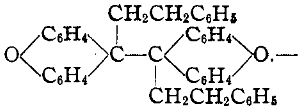
Anal. (material washed with benzene under carbon dioxide). Calcd. for $(C_{24}H_{17}O)_2$: C, 89.7; H, 5.3. Found: C, 88.9; H, 5.6.

The crude material took up oxygen rapidly in bromobenzene solution, the rate being too rapid for significant measurement. The crude material without washing thus took up 84% of the calculated amount. No peroxide could be isolated from the oxidation of an ether solution, but a 45% yield of xanthone was obtained. A solution of the material in ethyl benzoate (somewhat less than 0.05 *M*) became yellow when warmed to 100° and at 160° was brown of about the same intensity of color as a similar solution of dibenzyl-dixanthyl. At 160° the color rapidly faded to light yellow.

Phenylethyl-xanthyl Perchlorate,  $\left[O{<}\begin{matrix}C_6H_4\\C_6H_4\end{matrix}{>}C{-}CH_2CH_2C_6H_5\right]ClO_4$.—The Grignard reagent was made by dropping a solution of 19 g. of phenylethyl bromide in 30 cc. of dry ether onto a mixture of 2.4 g. of magnesium, 30 cc. of dry ether and one crystal of iodine. To this was added a suspension of 10 g. of xanthone in 50 cc. of dry ether, and the temperature was kept below 15°. After several hours, there was very little insoluble product in the brown ether solution. The whole was poured rapidly into 200 cc. of 3 *N* ammonium chloride solution at room temperature. The ether layer was separated, washed with very dil. hydrochloric acid, and dried with anhydrous sodium sulfate overnight. It was then filtered and treated with a solution of 6 cc. of 60% perchloric acid in 125 cc. of ether. After the mixture had been stirred for 20 minutes, orange-red crystals began to separate. Ten cc. of acetic anhydride was added, and the crystals were filtered off and washed with ether; yield, 2.2 g.

From the filtrate, addition of 20 cc. more of acetic anhydride gave 4.1 g. more of product; m. p., 191–193.5° (with decomposition).

Anal. Calcd. for $C_{21}H_{17}ClO_5$: ClO_4, 25.9. Found: 25.5.

Diphenylethyl-dixanthyl,  $O{<}\begin{matrix}C_6H_4\\C_6H_4\end{matrix}{>}C(CH_2CH_2C_6H_5){-}C(CH_2CH_2C_6H_5){<}\begin{matrix}C_6H_4\\C_6H_4\end{matrix}{>}O$.—Five g. of the perchlorate salt was dissolved in 500 cc. of concd. hydrochloric acid, and the solution decanted through an asbestos filter. To the clear, orange-red liquid thus obtained was added, dropwise, 40 cc. of 0.5 *N* vanadous chloride solution. A finely flocculent, light brown precipitate was formed. The mixture was poured into 1500 cc. of water, the product filtered off, and washed with 1 liter of water. It was dried in the air; yield, 3.8 g., or 102.5%; m. p., 125–160° (in air).

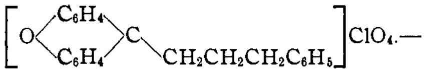
Two crystallizations from benzene and petroleum ether gave white crystals; m. p., 180–182° (under carbon dioxide).

Anal. Calcd. for $(C_{21}H_{17}O)_2$: C, 88.4; H, 6.01. Found: C, 88.3; H, 6.05.

Molecular Weight in Freezing Benzene in an Atmosphere of Hydrogen.—17.54 g. of benzene was used. The following total weights and freezing-point depressions were calculated from the second increment: 0.1697 g., $\Delta t = 0.084°$, mol. wt. = 590; 0.3486 g., $\Delta t = 0.177°$, mol. wt. = 575; av. mol. wt. = 582. Calcd. mol. wt. = 571; *K*, 5120.

The rate of oxygen absorption was as follows: 3 hours, 25%; and 10 hours, 71%. A solution of the substance in ethyl benzoate at 100° was faint yellow, at 160° was much darker, and at 212° light orange and faded rapidly.

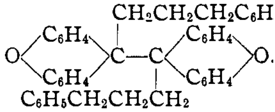
Phenylpropyl-xanthyl Perchlorate,



$\left[O{<}\begin{matrix}C_6H_4\\C_6H_4\end{matrix}{>}C{-}CH_2CH_2CH_2C_6H_5\right]ClO_4$.—The Grignard reagent was made by adding, dropwise, a solution of 6.7 g. of phenylpropyl chloride in 40 cc. of dry ether, to a mixture of 1.2 g. of magnesium, one crystal of iodine, and 4 drops of methyl iodide, in 40 cc. of dry ether. At the end of one and a half hours, the solution was almost clear. The solution was cooled with ice, and to it was added, a few cubic centimeters at a time, during stirring, a suspension of 5 g. of xanthone in 30 cc. of dry ether. The reaction was immediate. After several hours the mixture was poured into 100 cc. of 3 *N* ammonium chloride solution, and 150 g. of ice. The water layer was extracted with 75 cc. of ether, and the combined ether layers were treated with very dilute hydrochloric acid. After further washing with water, the ether solution was dried with calcium chloride. It was then filtered, diluted with 200 cc. of dry ether, and cooled with ice. Dropwise addition of 7 cc. of a 1:1 solution of 60% perchloric acid in acetic anhydride threw out at first a rather gummy product, which within a few minutes changed to fine yellow crystals; yield, 5.7 g., or 56%; m. p., 181–183.5° (with decomposition). As indicated by the analysis the salt was probably contaminated with some carbinol.

Anal. Calcd. for $C_{22}H_{19}ClO_5$: ClO_4, 24.9. Found: 19.1.

Diphenylpropyl-dixanthyl,



$O{<}\begin{matrix}C_6H_4\\C_6H_4\end{matrix}{>}\overset{CH_2CH_2CH_2C_6H_5}{C}{-}\underset{C_6H_5CH_2CH_2CH_2}{C}{<}\begin{matrix}C_6H_4\\C_6H_4\end{matrix}{>}O$.—Two g. of the perchlorate salt was dissolved in 400 cc. of concd. hydrochloric acid. The orange-colored solution was filtered through asbestos, and treated with 6.0 cc. of 1 *N* vanadous chloride solution, added dropwise. A flocculent, light colored product was formed immediately. The mixture was thrown into 600 cc. of cold water, and allowed to stand for a few minutes. The product rose to the top of the water. After as much of the liquid had been siphoned off as possible, the residue was diluted again with 500 cc. of water. The coagulated white product was then filtered off, washed with water, and dried on a porous plate; yield, 1.46 g. or 97.5%; m. p., 169–180° (under nitrogen).

Recrystallization from benzene and petroleum ether, in an atmosphere of nitrogen, gave 1.0 g. of white crystals; m. p., 190° (under nitrogen).

Anal. Calcd. for $C_{44}H_{38}O_2$: C, 88.3; H, 6.4. Found: C, 88.4; H, 6.5.

Mol. wt. (benzene, cryoscopic, hydrogen). Subs., 0.0877; benzene 11.5; Δt 0.063°. Calcd. for $C_{44}H_{38}O_2$: *mol. wt.* 598. Found: 629.

The rate of oxygen absorption was as follows: 1 hour, 4%; 5 hours, 25%; 12.5 hours, 50%. When heated, a 0.05 *M* solution became faint yellow at 100° and showed the same depth of color, on being heated to 212°, as the phenylethyl compound.

Part B

*iso***Propyl-xanthenol,** $O<(C_6H_4)_2>COHC_3H_7$.—Twenty g. of *iso*propyl bromide was dropped slowly onto 3.9 g. of magnesium in 50 cc. of dry ether, and the mixture was stirred until the magnesium had dissolved, cooled to 0°, and 20 g. of finely powdered solid xanthone (60% of the calculated amount) was added in small lots. A vigorous reaction took place, and the ether solution turned green at first, then red, and after an hour's stirring changed to a brown pasty mass. It was decomposed with ice and ammonium chloride and extracted twice with ether. One half of the ethereal solution was evaporated, and on scratching, and diluting with petroleum ether (b. p., 40–50°), yielded 7.4 g. of white crystals. It was recrystallized from 40–50° petroleum ether; m. p., 75°. *isoPropyl-xanthenol* is exceedingly soluble in alcohols, ether, benzene, ethyl acetate, chloroform and high-boiling ligroin, and sparingly soluble in cold, low-boiling petroleum ether. Its solution in concd. sulfuric acid is deep red by transmitted light and green by reflected light. It may be recovered unchanged from this solution by dilution with water.

Anal. Calcd. for $C_{16}H_{16}O_2$: C, 80.0; H, 6.67. Found: C, 79.9; H, 6.67.

*iso***Propyl-xanthyl Perchlorate,** $[O<(C_6H_4)_2>CC_3H_7]ClO_4$.—The remaining ethereal solution from the Grignard reaction was treated with a mixture of 6 volumes of acetic anhydride and 1 volume of 70% perchloric acid. Due to a secondary reaction between *iso*propylmagnesium bromide and xanthone, there is a dimolecular product present, of the formula $C_{26}H_{18}O_4$ (m. p., 164°) which also forms a perchlorate, dark red in color. The formation of this perchlorate may be avoided by taking a definite fraction of the ether solution, and adding the perchloric acid mixture from a buret. The amount of perchloric acid necessary for the precipitation of the yellow *iso*propyl-xanthyl perchlorate, but insufficient for the formation of the red perchlorate may thus be determined. In this way the yellow perchlorate may be obtained practically free from the red; yield, 12 g.; total yield of *iso*propyl derivative, based on xanthone, 67%. The perchlorate is insoluble in carbon tetrachloride and benzene, slightly soluble in boiling acetic acid, from which it crystallizes in large feathery crystals. It turns black at 200°, and decomposes at 210–211° (uncorr.) with gas evolution. The perchlorate dissolves in concd. sulfuric acid with development of an orange color, and on dilution of this solution with water, *iso*propyl-xanthenol is obtained.

Anal. Subs., 0.2063, 0.2029, 0.2214: 0.0450 *N* KOH, 14.91 cc., 14.80 cc., 15.50 cc. Calcd. for $C_{16}H_{15}O_5Cl$: ClO_4, 30.85. Found: 32.35, 32.67, 31.32.

Crude Di-isopropyl-dixanthyl.—A solution of 1 g. of *iso*propyl-xanthyl perchlorate in a cold mixture of 60 cc. of glacial acetic acid and 20 cc. of concd. sulfuric acid was cooled in ice and, in an atmosphere of carbon dioxide, treated with 8 cc. of molar vanadous chloride. The orange solution turned very dark. It was poured into 400 cc. of boiled water, the solid filtered off and washed rapidly, and dried in carbon dioxide under diminished pressure. A fine, yellow powder was obtained which was exceedingly sensitive to air, sintering and turning black on the slightest exposure. It is very soluble in ether, petroleum ether, benzene, acetone, chloroform, ethyl acetate, carbon disulfide and butyl alcohol; it is sparingly soluble in methyl or ethyl alcohol, but does not give crystals from these. The solutions are colored deep red, and become nearly colorless at —20°. At 100° the color is very deep, but fades to pale yellow after one and a half minutes at this temperature.

OXYGEN ABSORPTION.—The red solutions of di-*iso*propyl-dixanthyl became colorless quickly when shaken with air. The color slowly returned and was removed again by air, just as with solutions of hexaphenylethane; 0.5 g. of perchlorate was reduced as described above, and an oxygen absorption made on the wet precipitate. It took up 16.1 cc. in two minutes, or 94% of the amount calculated on perchlorate used.

*iso***Propyl-xanthyl Peroxide,** $O<(C_6H_4)_2>CC_3H_7—O_2—C_3H_7C<(C_6H_4)_2>O$.—Six g. of *iso*propyl-xanthyl perchlorate was reduced as described above, and the precipitate extracted with ether. The ether solution, dried and shaken with air, gave on evaporation

1.5 g. of white crystals; m. p., 124–127°; yield, 33%. After three recrystallizations from a mixture of equal parts of benzene and 95% alcohol, it gave 0.99 g.; m. p., 130°, with gas evolution. It is soluble in benzene and ether, and sparingly so in ethyl alcohol.

Anal. Calcd. for $C_{32}H_{30}O_4$: C, 80.4; H, 6.28. Found: C, 80.4; H, 6.31.

Mol. wt. Subs., 0.2252, 0.4000: benzene 15.35, 15.35; Δt 0.165, 0.277. Calcd. for $C_{32}H_{30}O_4$: mol. wt., 478. Found: 455, 482.

Decomposition of the Peroxide.—The pale yellow solution of 0.20 g. of peroxide in 5 cc. of cold concd. sulfuric acid soon turned brown, with green fluorescence. After five minutes it was poured onto 50 g. of ice. The brown precipitate thus formed was extracted with ether, washed with sodium carbonate, dried and filtered from a little charred material; 0.08 g. of *iso*propyl-xanthenol was obtained, identified by a mixed melting-point determination, and by the formation of the yellow *iso*propyl-xanthyl perchlorate.

sec.-**Butyl-xanthenol,** $O<(C_6H_4)_2>COHC_4H_9$.—Five g. of magnesium in 100 cc. of dry ether was treated slowly with 30 g. of *sec.*-butyl bromide. After the reaction started, the mixture was kept cold in an ice-bath. When all the magnesium had dissolved, 30 g. of solid powdered xanthone was added in small increments during two hours, the temperature being kept at 0°. The gray solution turned dark red. It was stirred for an hour at room temperature after the addition of the xanthone, and then decomposed with ammonium chloride solution. The ether layer was evaporated, and deposited 5 g. of white crystals of melting point 164°.[12] The filtrate crystallized only after seeding with some crystals obtained by hydrolysis of *sec.*-butyl-xanthyl perchlorate. The seeded liquid was diluted with a little petroleum ether (b. p., 25°) and kept for many hours at —10°. It yielded 2.6 g. of crystals, which were recrystallized from petroleum ether (b. p., 30–40°); m. p., 70°. It is very soluble in all ordinary solvents except low-boiling petroleum ether.

Anal. Calcd. for $C_{17}H_{18}O_2$: C, 80.3; H, 7.09. Found: C, 80.1; H, 7.04.

sec.-**Butyl-xanthyl Perchlorate,** $[O<(C_6H_4)_2>CC_4H_9]ClO_4$.—The filtrate from which *sec.*-butyl-xanthenol was separated, was diluted with 200 cc. of dry ether and treated carefully with the perchloric acid-acetic anhydride mixture as described under *iso*propyl-xanthyl perchlorate, to avoid the formation of any of the undesirable red perchlorate. *sec.*-Butyl-xanthyl perchlorate separated as fine, orange-yellow crystals, which could be recrystallized from boiling glacial acetic acid. It turns dark at 158° and melts with gas evolution at 161°; yield, 18 g.; total yield of *sec.*-butyl derivatives, based on xanthone, 41%.

Anal. Subs., 0.2046, 0.2070: 0.0450 *N* KOH, 13.80, 13.73 cc. Calcd. for $C_{17}H_{17}O_5Cl$: ClO_4, 29.57. Found: 30.19, 29.69.

The material resulting from this hydrolysis was *sec.*-butyl-xanthenol; m. p., 70°.

Crude Di-*sec.*-butyl-dixanthyl.—*sec.*-Butyl-xanthyl perchlorate dissolves readily in concd. hydrochloric acid or in acetic acid containing 25% of concd. sulfuric acid. By reduction of these solutions, di-*sec.*-butyl-dixanthyl is obtained. Four g. of *sec.*-butyl-xanthyl perchlorate was dissolved in 150 cc. of concd. hydrochloric acid, and the orange solution treated with 30 cc. of molar vanadous chloride solution. The resulting mixture was poured into water, and the solid was filtered off and washed. After drying in nitrogen it gave a fine, yellow powder which was very sensitive to air. It was exceedingly soluble in chloroform, acetone, benzene and petroleum ether (b. p., 30°). From the last-mentioned solvent it separated as a yellow gum on cooling to —20°,

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[12] This compound was obtained in varying amounts in nearly all of the syntheses using xanthone and alkylmagnesium halides. See under *iso*propyl-xanthyl perchlorate. It will be further described in a later paper.

but was not obtained crystalline. It gave crimson solutions in these solvents at room temperature. This color changed reversibly with temperature and was discharged quickly on exposure to air, with formation of the peroxide. In acetone solution under nitrogen the material was faintly yellow at —32°. This color began to deepen at —16°, and at 0° was orange-red. If the color at 0° is assigned the value 10, colors at —16°, +13°, 25°, 60°, 80°, 100°, were approximately 2, 30, 40, 55, 65, 80. After 21 minutes at 100°, the color rapidly faded to a shade identical with that shown at —32°.

OXYGEN ABSORPTION.—One g. of *sec.*-butyl-xanthyl perchlorate was reduced in acetic-sulfuric acid mixture, and an absorption made on the crude wet precipitate. It took up 27.8 cc. of oxygen in one minute, or 78% of that calculated for peroxide formation.

***sec.*-Butyl-xanthyl Peroxide,** $O<(C_6H_4)_2>CC_4H_9—O_2—CC_4H_9<(C_6H_4)_2>O$.—Four g. of *sec.*-butyl-xanthyl perchlorate was dissolved in 100 cc. of cold acetic acid and 25 cc. of concd. sulfuric acid. This solution was reduced with 20 cc. of vanadous chloride solution, precipitated in water, the precipitate filtered off and washed, and while wet dissolved in ether. The color of the ether solution was destroyed by shaking with air. Evaporation yielded 0.8 g. of white crystals and some oily material. This was recrystallized by dissolving in a small amount of warm benzene and slowly adding absolute ethyl alcohol. After seven recrystallizations, 0.5 g. was obtained melting at 133–134° with gas evolution. The presence of a small amount of dixanthylene, resulting from reduction of the red perchlorate mentioned before, makes this peroxide difficult to purify. It is soluble in benzene and ether, insoluble in ethyl alcohol.

Anal. Calcd. for $C_{34}H_{34}O_4$: C, 80.6; H, 6.72. Found: C, 80.9; H, 6.65.

***iso*Butyl-xanthenol,** $O<(C_6H_4)_2>COHC_4H_9$.—Seven g. of magnesium in 100 cc. of dry ether was treated at 0° with 40 g. of *iso*butyl bromide. To the product of this reaction was added 52 g. of solid xanthone in small increments, and the temperature kept at 0°. After 12 hours, the yellow crystalline mass was decomposed with ammonium chloride. The ether layer immediately began to deposit fine white crystals of the compound melting at 164° described under *iso*propyl-xanthyl perchlorate. Ten g. of this material was obtained. The filtrate on slow evaporation and prolonged cooling gave 17 g. of white crystals; m. p., 107–117°. It is very soluble in benzene and ether, slightly soluble in ligroin. Successive recrystallizations lowered this melting point, probably due to loss of water with formation of *iso*butylidene-xanthene. Slow evaporation of solvent in the cold gave a mixture of large, colorless crystals of the xanthenol and clusters of yellow needles—the unsaturated compound. These were separated mechanically. The colorless crystals were crushed, washed with cold ligroin and dried in a vacuum. They were analyzed without further purification. *iso*Butyl-xanthenol melted at 115–117°, with gas evolution.

Anal. Calcd. for $C_{17}H_{18}O_2$: C, 80.3; H, 7.09. Found: C, 80.4; H, 6.92.

***iso*Butyl-xanthyl Perchlorate,** $(O<(C_6H_4)_2>CC_4H_9)ClO_4$.—The filtrate from which *iso*butyl-xanthenol was obtained was diluted to 200 cc. with dry ether and treated slowly with perchloric acid-acetic anhydride mixture as described under *iso*propyl-xanthyl perchlorate. *iso*Butyl-xanthyl perchlorate separated as fine, light yellow crystals; yield, 16 g.; total yield of *iso*butyl derivative calculated on xanthone used, 43%. The perchlorate is fairly soluble in boiling acetic acid, but decomposes very rapidly at this temperature to give a deep green solution. It may be recrystallized from acetic acid at 60° with but slight decomposition, and then forms yellow crystals, turning green at about 167°, and melting to a black liquid at 200–204° with gas evolution. It is soluble in concd. hydrochloric acid to give a deep orange solution.

Anal. Subs., 0.1721 g., 0.2022 g.: 0.0450 *N* KOH, 11.87 cc., 13.91 cc. Calcd. for $C_{17}H_{17}O_5Cl$: ClO_4, 29.57. Found: 30.85, 30.75.

Di-*iso*butyl-dixanthyl, $O<(C_6H_4)_2>CC_4H_9{-}C_4H_9C<(C_6H_4)_2>O$.—*iso*Butyl-xanthenol dissolved readily in concd. hydrochloric acid forming an orange colored solution, and reduction of this solution yielded di-*iso*butyl-dixanthyl. Better yields of this substance were obtained by reduction of the hydrochloric acid solution of *iso*butyl-xanthyl perchlorate. Seven g. was dissolved in 300 cc. of concd. hydrochloric acid, the solution cooled to 0° and reduced with 35 cc. of molar vanadous chloride. This mixture was immediately poured into 500 cc. of air-free water, the substance filtered off and washed thoroughly. The precipitate was dried as completely as possible by pressing between filter papers, and dried for 12 hours in nitrogen under diminished pressure. The semi-crystalline material was placed in the recrystallization apparatus with a little anhydrous sodium sulfate and in an atmosphere of nitrogen was dissolved in about 200 cc. of warm acetone. The acetone for this purpose must be completely freed from oxygen. The solution was filtered and evaporated to about one-third its volume, when crystals appeared. After cooling, the liquid was decanted, and the compound recrystallized from 100 cc. of fresh acetone. The crystals were filtered out and dried under diminished pressure in a slow stream of nitrogen. When dry they were unaffected by short exposures to air; yield, 1.9 g.; m. p., in air 125–135°; in nitrogen they turned yellow at 138°, melted at 139° to give a deep red liquid. In 30 seconds this color faded completely.

Anal. Calcd. for $C_{34}H_{31}O_2$: C, 86.1; H, 7.17. Found: C, 86.0; H, 6.65.

Mol. wt. (benzene, cryoscopic, under nitrogen). Subs., 0.1542, 0.2622: benzene, 15.05, 15.05; Δt 0.114°, 0.199°. Calcd. for $C_{34}H_{34}O_2$: mol. wt., 474. Found: 460, 448.

OXYGEN ABSORPTION.—Di-*iso*butyl-dixanthyl showed very remarkable color phenomena in contact with oxygen. When dissolved in air-free solvents it gave a colorless solution at room temperature. When oxygen was admitted, the upper layer of solvent began to show a yellow color. On shaking, the solution took on an intense yellow-brown color, deeper than the color of triphenylmethyl solutions. On standing for about 40 seconds, this color slowly faded but was renewed by shaking again with oxygen. With a sample of 0.7 g. in 30 g. of bromobenzene, this was repeated 14 times before the color failed to appear. At this point oxygen absorption also stopped. The final color of the solution was pale yellow. It seems as though this color must be due to the formation of an unstable colored addition compound between *iso*butyl-xanthyl and oxygen, which slowly rearranges to the colorless peroxide, which can be isolated from these solutions. Such a phenomenon has not been observed in the case of any of the triarylmethyls, although oxidation of di-biphenylene-diphenylethane gives an intensely red solution. The color in this case is permanent, however, and does not seem to be connected with the simultaneous peroxide formation.

A solution of 0.67 g. of di-*iso*butyl-dixanthyl in 30 g. of bromobenzene took up 34.0 cc. of oxygen in three minutes at 20°, 30 cc. being absorbed in the first minute. This corresponds to 100% of the calculated amount for peroxide formation.

Color.—Di-*iso*butyl-dixanthyl dissolves without color in air-free solvents. When such solutions are warmed in an atmosphere of nitrogen, a yellow color begins to appear at 50° to 60°. A 0.05 *M* solution in ethyl benzoate at 100° showed a color of about the intensity of that of triphenylmethyl at room temperature, but with more of a red shade. This color faded completely when the liquid was cooled again. At the boiling point of ethyl benzoate the color was a strong crimson. After 10 to 15 seconds at this temperature the color rapidly faded to a permanent, pale straw.

***iso*Butyl-xanthyl Peroxide,** $O<(C_6H_4)_2>CC_4H_9{-}O_2{-}CC_4H_9<(C_6H_4)_2>O$.—Three g. of *iso*butyl-xanthenol was dissolved in 150 cc. of concd. hydrochloric acid and reduced as described above. The wet precipitate was extracted with ether, and this on slow evaporation gave 1:0 g. of *iso*butyl-xanthyl peroxide; m. p., 177° with gase volution. It was soluble in benzene, sparingly so in ethyl alcohol or petroleum ether. It was best purified from alcohol containing 10% of benzene.

Anal. Calcd. for $C_{34}H_{34}O_4$: C, 80.6; H, 6.72. Found: C, 81.0, 81.0; H, 6.68, 6.48.

Mol. wt. (benzene, cryoscopic). Subs., 0.2003, 0.1595: benzene 15.52, 17.88; Δt, 0.155°, 0.092°. Calcd. for $C_{34}H_{34}O_4$, mol. wt., 506. Found: 427, 497.

Constitution of Dicyclohexyl-phenyl-chloromethane.[13]—Dicyclohexyl-phenyl-carbinol was prepared according to the method used by Gray and Marvel from 24 g. of magnesium, 110 g. of chlorocyclohexane and 42 g. of ethyl benzoate; 45 g. of product was obtained, which melted at 82–83°, as found by Rheinboldt and Roleff.[14] By treatment of this material with acetyl chloride, the chloride,[13] m. p. 122°, was obtained; 6 g. of this chloride was dissolved in 100 cc. of acetone freshly distilled from permanganate, and the moist silver oxide obtained from 17 g. of silver nitrate was added. The mixture was refluxed for two and a quarter hours. It was filtered from silver chloride and silver oxide, and the solvent evaporated. The resulting viscous liquid was distilled in a vacuum, and three fractions were taken. The middle fraction, b. p. 155–157° (1 mm.), crystallized on dilution with petroleum ether and scratching, yielding dicyclohexyl-phenyl-carbinol, m. p. 83°, identified by a mixed melting point.

Reduction of Dicyclohexyl-phenyl-chloromethane.—Following the procedure of Gray and Marvel, 5.5 g. of dicyclohexyl-phenyl-chloromethane was refluxed in 175 cc. of dry toluene with 14 g. of molecular silver for 35 hours. The toluene was distilled under diminished pressure, and the viscous residue distilled in a vacuum. It distilled almost completely at 134–135° (0.3 mm.). A colorless, viscous liquid was obtained; n_D^{23}, 1.545: d_4^{20}, 0.982.

Anal. Subs., 0.1848: CO_2, 0.6073; H_2O, 0.1691. Calcd. for $C_{38}H_{54}$: C, 89.41; H, 10.59. Calcd. for $C_{38}H_{52}$, or $C_{19}H_{26}$: C, 89.76; H, 10.24. Found: C, 89.63; H, 10.24.

Mol. wt. (benzene, cryoscopic). Subs., 0.1428, 0.2370, 0.2272, 0.4299: benzene, 17.37, 17.37, 20.75, 20.75; Δt, 0.197, 0.317, 0.262, 0.512. Calcd. for $C_{19}H_{26}$: mol. wt., 254. Found: 214, 220, 214, 207. Naphthalene, cryoscopic, Subs., 0.2057: naphthalene, 15.36; Δt, 0.395, mol. wt., 234.

A small amount of this liquid was heated in nitrogen in a sealed tube for 30 minutes at 330°. Molecular weight after this treatment.

Subs., 0.3258, 0.5468: benzene, 18.83, 18.83; Δt 0.343, 0.577. Found: mol. wt., 257, 258.

Reaction with Hydrochloric Acid.—Into a solution of 0.40 g. of the supposed tetracyclohexyl-diphenylethane in the minimum amount of absolute alcohol at 0° dry hydrochloric acid was bubbled at this temperature until the liquid was saturated. The solution turned pink, and a white, oily material separated, together with a few crystals. The mixture was warmed to 50° and enough absolute alcohol added to dissolve the oil at this temperature. It was cooled to 0°, and again saturated with hydrochloric acid. On cooling to —23° and scratching, a heavy mass of crystals

[13] Gray and Marvel, THIS JOURNAL, **47**, 2800 (1925).

[14] Rheinboldt and Roleff, *J. prakt. Chem.*, **109**, 188 (1925).

appeared. These were filtered off, and the solution again was saturated with hydrochloric acid at 0°, when more crystals separated; yield, 0.347 g., or 76% of that calculated for addition of hydrochloric acid to $C_{19}H_{26}$; m. p., 52–53°. They were recrystallized by dissolving in absolute alcohol at 48° and cooling; m. p., 54–55°.

Anal. Calcd. for $C_{19}H_{27}Cl$: Cl, 12.21. Found: 12.25.

Mol. wt. (benzene, cryoscopic). Subs., 0.2090: benzene, 15.87; Δt, 0.262. Calcd. for $C_{19}H_{27}Cl$: mol. wt., 290.5. Found: 257.

The identity of the chloride was established by a mixed melting point with chlorocyclohexyl-cyclohexyl-phenylmethane prepared as follows: 2.5 g. of dicyclohexyl-phenyl-carbinol was distilled from an equal amount of potassium acid sulfate;[15] a clear, viscous liquid, cyclohexylidene-cyclohexyl-phenylmethane, distilled from the mixture at about 180° (10–15 mm.); $n_D^{23} = 1.546$; $d_4^{20} = 0.987$. When this liquid was dissolved in absolute alcohol and the solution treated with hydrochloric acid as described above, a white chloride was obtained, m. p. 55°, which did not depress the melting point of the previously described chloride.

Summary

1. The following derivatives of dixanthyl have been prepared by the reduction of the corresponding carbinols or perchlorates with vanadous salts: dimethyl-dixanthyl, diethyl-dixanthyl, di(β-phenylethyl)-dixanthyl, di(γ-phenylpropyl)-dixanthyl. Solutions of these substances absorb oxygen slowly at 25°; at about 140°, the solutions undergo reversible color changes which point to appreciable dissociation at this temperature.

2. Di-*iso*butyl-dixanthyl and di-(α-naphthylmethyl)-dixanthyl have been prepared. They form colorless solutions which absorb oxygen with great rapidity at 25°; at 60° and above, the solutions become colored and on cooling the color disappears.

3. Di-*iso*propyl-dixanthyl and di-*sec.*-butyldixanthyl have been prepared in an impure condition. Their solutions are highly colored at 25° and absorb oxygen very rapidly, forming peroxides. The color changes on warming and cooling are similar to those observed with all dissociable ethanes. As evidenced by the color and behavior of the solutions, these dixanthyls must be considerably dissociated in solution at 25°. The effectiveness of secondary alkyl groups in promoting dissociation is thus established.

4. An investigation of the action of silver on phenyl-dicyclohexyl-chloromethane has shown that the reported formation of diphenyl-tetracyclohexyl-ethane is erroneous; the product of the reaction is phenyl-cyclohexylidene-cyclohexyl-methane.

CAMBRIDGE 38, MASSACHUSETTS

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[15] Godschot, *Bull. soc. chim.*, [4] **7**, 961 (1910).