3. In the presence of both zinc and iron salts in proper proportions, cinnamic aldehyde is reduced to pure cinnamyl alcohol and no more than one molecular equivalent of hydrogen is absorbed.

4. A discussion of the effect of changing other conditions is given.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

THE DISSOCIATION INTO FREE RADICALS OF SUBSTITUTED DIXANTHYLS. II. THE DISSOCIATING INFLUENCE OF THE CYCLOHEXYL GROUP

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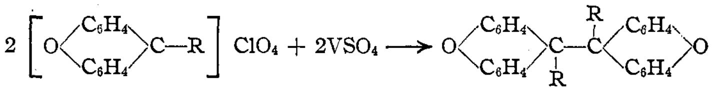
RECEIVED AUGUST 24, 1925 PUBLISHED DECEMBER 12, 1925

The discovery that many carbinols and their halochromic salts are quantitatively reduced to ethanes by vanadous salts[1] has opened the way to the preparation of derivatives of dixanthyl of Type I, where R is a *non-aromatic* residue. A study of such compounds is of particular interest



$$2\left[O\langle{}^{C_6H_4}_{C_6H_4}\rangle C{-}R\right]ClO_4 + 2VSO_4 \longrightarrow O\langle{}^{C_6H_4}_{C_6H_4}\rangle \underset{R}{C}{-}\overset{R}{C}\langle{}^{C_6H_4}_{C_6H_4}\rangle O$$

I

in connection with the problem of the existence of free radicals with other than aromatic or unsaturated groups attached to the central carbon atom. As a continuation of our study of the effect of different groups on the dissociation of such substituted dixanthyls we have now prepared by our method the following compounds: di(*p*-chlorobenzyl)-dixanthyl ($R{=}ClC_6H_4CH_2{-}$); di-*iso*-amyl-dixanthyl($R{=}(CH_3)_2CH{-}CH_2{-}CH_2{-}$); di(*n*-hexyl)-dixanthyl($R{=}C_6H_{13}{-}$) and dicyclohexyl-dixanthyl($R{=}C_6H_{11}$).

Like dibenzyl-dixanthyl,[1b] the *p*-chlorobenzyl derivative shows the characteristic properties of an ethane which dissociates into a free radical. The absorption of oxygen is very rapid. The degree of dissociation is too small to be detected by the molecular-weight determinations in freezing benzene. A solution of the dixanthyl when warmed to 80–100° loses its ability to absorb oxygen, presumably because of the usual intramolecular oxidation and reduction.

The study of the chlorobenzyl compound thus confirms our previous conclusions that an aromatic residue in the *β position* is effective in causing dissociation in the dixanthyl series, a conclusion that goes far towards disproving the postulates of the Werner-Thiele theory of valence as applied to the dissociation of ethanes.[2]

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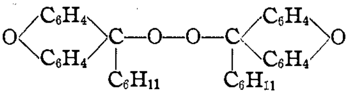
[1] Conant and Sloan, (a) THIS JOURNAL, **45**, 2466 (1923); (b) **47**, 572 (1925). (c) For the discussion of the electrochemistry of this reaction, see *ibid.*, **47**, 1959 (1925).

[2] Compare Ref. 1b, p. 576, and Schlenk and Mark, *Ber.*, **55B**, 2285–2289 (1922).

Both di-*iso*-amyl-dixanthyl and dihexyl-dixanthyl, when dissolved in bromobenzene at room temperature, slowly absorb oxygen; the rate of absorption is of the same order of magnitude as that previously observed with dibutyl-dixanthyl.[1b] The molecular weights of both substances in freezing benzene correspond to the dimolecular formula I. When their colorless solutions in methyl benzoate are warmed to the boiling point of this solvent (in the absence of oxygen), they become yellowish-brown; and when they are rapidly cooled the color completely disappears. This process may be repeated several times but when the solution is kept at the boiling point for a few minutes, the color fades to a light yellow. Similarly, a solution in molten naphthalene when heated becomes yellow, brown and finally red near the boiling point of the solvent; in a few seconds the red color fades to a light yellow. The irreversible loss of color at a high temperature is undoubtedly due to a decomposition of the molecule. The reversible color changes on heating and cooling the substance indicate that an appreciable dissociation of these dialkyl-dixanthyls takes place at temperatures higher than 100°, and probably the slow absorption of oxygen at 25° corresponds to a very small degree of dissociation even at this temperature. The parent compound, dixanthyl (R=H, Formula I), does not absorb oxygen and shows none of the properties of a dissociable ethane.

In contrast to the *n*-hexyl and di-*iso*-amyl derivatives, dicyclohexyl-dixanthyl is considerably dissociated in solution at room temperature as demonstrated by the cherry-red color of its solutions and the very rapid absorption of oxygen with the formation of the crystalline peroxide II.



$$O\begin{array}{c}C_6H_4\\C_6H_4\end{array}\underset{C_6H_{11}}{\underset{|}{C}}-O-O-\underset{C_6H_{11}}{\underset{|}{C}}\begin{array}{c}C_6H_4\\C_6H_4\end{array}O$$

II

Unfortunately the substance could be obtained only in the form of a bright yellow, amorphous precipitate which absorbed 65–80% of the calculated amount of oxygen, or as a light yellow gum. In spite of many attempts no solvent was found from which it recrystallized. Satisfactory analyses and molecular-weight determinations, therefore, are lacking. The constitution of the compound is established by its method of preparation, the analysis of its peroxide and the transformation of the latter into cyclohexylxanthydrol by treatment with sulfuric acid.

The red solutions of the yellow, crude dicyclohexyl-dixanthyl in absolute ether or bromobenzene became very faint yellow on cooling to 0°. Since on further cooling the liquid to —35°, the faint yellow color persisted, it was undoubtedly due to an impurity. When the temperature was raised to 25°, the red color was restored. This process could be repeated indefinitely. Warming a solution to 60° caused the color to deepen and on cooling to room temperature the color lightened to the original shade; at 100° the red color completely disappeared in eight minutes indicating a decomposition of the compound. When the red solution was shaken with air the color rapidly disappeared but after a few seconds reappeared. This could be repeated five or six times before the solution acquired a permanent, light yellow color. A similar phenomenon has been noted with a number of triarylmethyls and corresponds to the rapid removal of the colored, free radical from the equilibrium mixture and subsequent dissociation of the ethane.

A solution of the dicyclohexyl-dixanthyl in absolute ether was diluted in an atmosphere of pure nitrogen in a specially adapted colorimeter. The color increase on dilution corresponded to a wide deviation from Beer's law. For example, a 5% solution of material, which was at least 65% pure as determined by the oxygen absorption when diluted 6-fold, showed a depth of color 4.8 times that predicted by Beer's law.

Discussion

In spite of our failure to obtain pure crystalline dicyclohexyl-dixanthyl, the evidence is beyond doubt that this substance is considerably dissociated in solution at room temperature. This establishes clearly that the cyclohexyl group is effective in causing dissociation. Ziegler's previous study of tetraphenyl-dicyclohexylethane pointed in this direction.[3] Judging from the relative intensities of the colors of the solutions, the degree of dissociation of a 3% solution of dicyclohexyl-dixanthyl is greater than that of dibenzyl-dixanthyl. It is safe to conclude that the influence of the cylcohexyl group in causing dissociation in the dixanthyl series is greater than that of the benzyl, and may be as great as that of the phenyl group. We hope eventually to obtain a crystalline cyclohexyl compound that will enable us to make a quantitative comparison.

As previously pointed out, the existence in solution of benzylxanthyl and pentaphenylethyl[2] definitely proves that a phenyl group in the β position is capable of promoting dissociation. The existence of cyclohexylxanthyl now establishes that in free radicals of the type $Ar_2\underset{\vdots}{C}-R$ it *is not necessary that R should contain any aromatic or unsaturated residue.* The probable dissociation of the dialkyl-dixanthyls (at least above 100°) is evidence that even a saturated primary alkyl group may function as one of the groups attached to a trivalent carbon atom. The effectiveness of the cyclohexyl group as compared to the *n*-hexyl group is particularly striking. We hope that our study of other derivatives of dixanthyl will enable us

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[3] Ziegler and Schnell, *Ann.*, **437**, 227 (1924). The substance was obtained in an impure form; it combined rapidly with bromine and slowly with iodine. After a stream of air had been passed through the colorless solution of this substance for some time, the solution lost its ability to combine with iodine.

to formulate some of the factors which govern the effectiveness of nonaromatic groups in causing dissociation.[3a]

Experimental Part

***p*-Chlorobenzylidene-xanthane,** $O<(C_6H_4)_2>C{=}CHC_6H_4Cl$.—To 3.0 g. of magnesium chips in dry ether was added slowly 20 g. of *p*-chlorobenzyl chloride (a considerable excess over the calculated amount is required to make all of the magnesium dissolve). When the reaction was complete, 18 g. of finely powdered xanthone suspended in dry ether was added, and the mixture stirred for 30 minutes. It was decomposed with ice and ammonium chloride, and the product after several recrystallizations from chloroform-petroleum ether was a mixture of white needles melting at 120–122°, and yellow prisms melting at 130–132°. The white needles were probably *p*-chlorobenzyl-xanthydrol, but since they lost water very easily during crystallization, they could not be obtained pure enough for analysis from any solvent. On recrystallization from 60° ligroin they were converted entirely to the yellow form; m. p., 131–131.5°; yield, about 60%, based on the xanthone employed.

Anal. Calcd. for $C_{20}H_{13}OCl$: C, 78.8; H, 4.30; Cl, 11.6. Found: C, 78.8; H, 4.41; Cl, 11.4.

Mol. wt. Subs., 0.2026: 17.4 g. of diphenylamine; $\Delta t = 0.340°$; $K = 8.6$. Calcd. for $C_{20}H_{13}OCl$: mol. wt., 304.5. Found: 300.

***p*-Chlorobenzylxanthyl Perchlorate.**—After decomposition of the product from the Grignard reaction carried out as described above, the ether layer was dried with calcium chloride, kept cool and treated very slowly with a mixture of perchloric acid and acetic anhydride (10 cc. of 60% perchloric acid in 60 cc. of acetic anhydride) until no more precipitate formed. The perchlorate crystallized in large, yellow flakes. These were filtered off, washed with dry ether and dried in a vacuum over sodium hydroxide; yield, 22 g., or 55%, based on the xanthone employed. The perchlorate may be recrystallized from boiling glacial acetic acid. It darkens at 200°, and fuses at 209° to a black melt.

The perchlorate was dried for several days over sodium hydroxide. A weighed amount was warmed gently with 10 cc. of purified benzene and 0.5 cc. of water. When it had all dissolved, it was diluted to 50 cc. and titrated with alkali, using phenolphthalein.

Anal. Calcd. for $C_{20}H_{14}O_5Cl_2$: ClO_4, 24.5. Found: 24.1.

Di(*p*-chlorobenzyl-dixanthyl)ethane, $(O<(C_6H_4)_2>\overset{|}{C}CH_2C_6H_4Cl)_2$.—Two g. of *p*-chlorobenzylxanthyl perchlorate was dissolved in 250 cc. of concd. hydrochloric acid, and the deep orange solution was filtered through asbestos to separate it from a small amount of insoluble material. This solution was cooled in an ice-bath, reduced with 20 cc. of 0.5 *M* vanadous sulfate solution and poured into 300 cc. of air-free water. After the solid had been filtered off and washed carefully, the white powder obtained was dried in carbon dioxide under diminished pressure. It was dissolved in 100 cc. of warm benzene in an atmosphere of carbon dioxide, the solution filtered and half the benzene evaporated in a vacuum. The material separated as white needles which were filtered off and dried in a stream of carbon dioxide. About 0.7 g. (m. p. in air, 147–149°,

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[3a] Recent experiments, which will be reported in detail later, show that even *secondary alkyl groups of low molecular weight* are very effective in promoting dissociation. Thus solutions of di-*iso*propyl-dixanthyl and di-(*sec.*-butyl)-dixanthyl are highly colored at 20° and have the properties characteristic of solutions of free radicals. The greater effectiveness of secondary as compared with primary alkyl groups is of particular interest. (Note added to proof, November 16, 1925.)

turning brown) was obtained; m. p. in carbon dioxide, 152° with no color change. After the substance had stood in air for 24 hours, the melting point in carbon dioxide was 137–138°; the capacity for oxygen absorption was, however, unchanged.

Anal. Calcd. for $C_{20}H_{14}OCl$: C, 78.6; H, 4.58. Found: C, 78.0; H, 4.74.

Mol. wt. (by the freezing-point method). Subs., 0.2067: 19.24 g. of *p*-chlorotoluene under nitrogen; $\Delta t = 0.100°$; $K = 5.6$. Calcd. for $C_{40}H_{28}O_2Cl_2$: mol. wt., 611. Found: 604.

Di-*p*-chlorobenzyl-dixanthylethane could also be prepared as follows. Five g. of *p*-chlorobenzylxanthyl perchlorate was suspended in 300 cc. of glacial acetic acid, and the solution treated slowly with 50 cc. of concd. sulfuric acid. A clear brown-yellow solution was obtained. This was reduced with 35 cc. of *M* vanadous chloride, and precipitated by pouring into 1 liter of air-free water. It was washed free from acid and dried in nitrogen. After recrystallization twice from a mixture of 9 parts acetone and 1 part of carbon disulfide, 1.6 g. was obtained; m. p., 149–150°, in carbon dioxide.

OXYGEN ABSORPTION.—A solution of 0.28 g. of di-*p*-chlorobenzyl-dixanthyl-ethane in 20 cc. of bromobenzene took up 10.2 cc. of oxygen at 20.8° in four minutes, 100% of the amount calculated for the formation of a peroxide. Another sample which had stood in air for 48 hours took up 110% in five minutes and no further amount after this time.

EFFECT OF HEAT.—A number of bulbs containing each 0.1 g. of di-*p*-chlorobenzyl-dixanthylethane were filled with bromobenzene in an atmosphere of hydrogen and subjected to heat, to determine the effect upon the oxygen-absorbing capacity of the ethane. (I) Blank absorption: (bulb not heated) absorbed 4.5 cc. in nine minutes, = 112% of the calculated amount; (II) heated at 60° for one hour: absorbed 3.9 cc. in ten minutes, = 105%; (III) heated at 80° for one hour: absorbed 2.8 cc. in eight minutes, = 77%; (IV) heated at 100° for one hour: absorbed no oxygen.

***iso*-Amylxanthydrol,** $O<(C_6H_4)_2>COHC_5H_{11}$.—A solution of 5.1 g. of magnesium in 100 cc. of dry ether was treated slowly with 32 g. of *iso*-amyl bromide. A vigorous reaction took place, and the magnesium was completely dissolved after two hours' stirring; 20 g. of finely powdered solid xanthone was then added in small quantities. The mixture turned deep green, and finally precipitated a yellow solid. It was decomposed with ice and ammonium chloride, and the product after two recrystallizations from 90° ligroin was a white crystalline powder; m. p., 95–97°; yield, 6 g. The residues from recrystallization, on treatment with the perchloric acid-acetic anhydride mixture, yielded 21.5 g. of perchlorate; total yield, about 80%.

Anal. Calcd. for $C_{18}H_{20}O_2$: C, 80.6; H, 7.51. Found: C, 81.0; H, 7.48.

The *iso*-amylxanthyl carbinol slowly decomposed in contact with air. After two months in a desiccator it yielded nearly the calculated amount of xanthone, and the odor characteristic of *iso*-amyl alcohol or aldehyde was noticeable.

***iso*-Amylxanthyl Perchlorate.**—To the dry ether solution resulting from the reaction of *iso*-amylmagnesium bromide and xanthone was added very slowly a mixture of 6 parts of acetic anhydride and 1 part of 60% perchloric acid, until no more precipitate was formed. The perchlorate separated as long, yellow needles. When the perchloric acid mixture was added too rapidly, the precipitate came down very fine and was red, but was apparently identical with the yellow needles; m. p., 165°.

Anal. Calcd. for $C_{12}H_{13}O_5Cl$: ClO_4, 28.39. Found: 28.22.

Di-*iso*-amyl-dixanthylethane, $(O<(C_6H_4)_2>\overset{|}{C}C_5H_{11})_2$.—Five g. of *iso*-amylxanthyl perchlorate was dissolved in 150 cc. of concd. hydrochloric acid, and the orange solution treated with 50 cc. of 0.5 *M* vanadous sulfate slowly, during cooling. A heavy, white precipitate separated. The mixture was poured into ice water, filtered and washed well, and after drying in carbon dioxide the resulting white powder was recrystallized in a carbon dioxide atmosphere from 200 cc. of acetone. It separated in large, white crystals, weighing 3.4 g. (95% yield); m. p. in air, 137–145°; m. p. in carbon dioxide, 158–160°.

Anal. Calcd. for $C_{18}H_{19}O$: C, 86.0; H, 7.58. Found: C, 86.0; H, 7.64.

Mol. wt. (in freezing benzene under nitrogen). Subs., 0.1064, 0.3588, 0.1490, 0.3622, 0.5912: g. of solvent, 16.0, 16.0, 18.86, 18.86, 18.86; Δt, 0.070°, 0.240°, 0.075°, 0.190°, 0.320°; K, 5.12. Calcd. for $C_{36}H_{38}O_2$: mol. wt., 502. Found: 487, 480, 540, 518, 501; av., 505.

Oxygen Absorption.—A solution of 0.4 g. of di-*iso*-amyl-dixanthylethane in 20 cc. of bromobenzene absorbed 17.4 cc. of oxygen in six hours, and in 30 hours absorbed 34.6 cc. at 21°, 180% of the amount required for peroxide formation. The end product of this oxidation was identified as xanthone.

Color Changes on Heating.—Di-*iso*-amyl-dixanthylethane in naphthalene gave a colorless solution at 80° under carbon dioxide. As the solution was heated, it turned brown and finally deep red at the boiling point of naphthalene. After the liquid had been boiled for 15 or 20 seconds, the color rapidly faded to a permanent pale straw. In methyl benzoate, the ethane gave a colorless solution, which became yellow when heated, and at the boiling point was yellow-brown. The color disappeared completely as the liquid cooled. This reversal could be repeated many times. When kept at the boiling point of methyl benzoate for a few minutes, the solution slowly became permanently colorless.

***n*-Hexylxanthyl Perchlorate,** $ClO_4[(O<(C_6H_4)_2)>CC_6H_{13}]$.—When 3.3 g. of magnesium in 50 cc. of absolute ether was treated with 22.4 g. of *n*-hexyl bromide and a crystal of iodine, the reaction was vigorous. After the magnesium had dissolved, xanthone was added slowly until it ceased to dissolve; 17 g. or 60% of the calculated amount was used. After standing overnight, the mixture was decomposed with ice and ammonium chloride. Attempts to isolate a carbinol were without success. A thin, yellow, fluorescent oil, smelling strongly like rancid fat, was the purified product. When treated in dry ether in the usual way, this yellow oil yielded 29 g. of yellow, crystalline perchlorate, a 92% yield based on the xanthone employed; m. p., 126–127°. It is sparingly soluble in glacial acetic acid, about 1 g. in 200 g. at 25°. The perchlorate slowly decomposes, and after several months changes color and has a very strong odor.

Anal. Calcd. for $C_{19}H_{21}O_5Cl$: ClO_4, 27.35. Found: 27.25.

Di-*n*-hexyl-dixanthylethane, $(O<(C_6H_4)_2>\overset{|}{C}—C_6H_{13})_2$.—A solution of 5 g. of *n*-hexylxanthyl perchlorate in 300 cc. of glacial acetic acid was treated with 70 cc. of concd. sulfuric acid. It was reduced with 30 cc. of *M* vanadous chloride. A heavy, white precipitate formed. The mixture was poured into two liters of ice water, and the solid filtered, washed and dried for 24 hours in a vacuum. The white powder obtained was dissolved in 40 cc. of boiling acetone, in the absence of air, the solution filtered and the substance crystallized; yield, 2.2 g., or 60%; m. p., 138° in carbon dioxide (m. p. in air, 119–133°, turning yellow). It was soluble in boiling acetone (1 part in 18), in acetone at 0° (1 part in 80), slightly soluble in boiling benzene and in boiling ligroin (70°), and practically insoluble in cold benzene, ligroin and ethyl alcohol.

Anal. Calcd. for $C_{38}H_{42}O_2$: C, 86.0; H, 7.97. Found: C, 85.9; H, 8.05.

Mol. wt. Subs., 0.1997, 0.4014: *p*-chlorotoluene (under nitrogen), 20.0 g., 20.0 g.; Δt, 0.108°, 0.220°; K, 5.6.

Subs., 0.1525, 0.2098: benzene, 15.71 g., 16.87 g.; Δt, 0.095°, 0.115°; K, 5.12.

Calcd. for $C_{38}H_{42}O_2$: mol. wt., 530. Found: in *p*-chlorotoluene, 519, 512; in benzene, 524, 554.

OXYGEN ABSORPTION.—Di-*n*-hexyl-dixanthylethane in solution reacts only slowly with oxygen, but it cannot be obtained pure by crystallization in contact with air. Warm solutions in contact with air became quickly colored with a yellow-green fluorescence, cold solutions more slowly. The product is a mixture of the ethane with xanthone and some oily material; 0.70 g. of the pure ethane in 20 cc. of bromobenzene absorbed at 25° the amounts of oxygen given below.

Time, hrs.	1.5	2.5	18.0	22.0	29.0	55.0
Oxygen, cc.	6.9	9.3	36.6	44.0	61.0	68.1
Absorption, %	21.2	28.8	113	137	189	209

No further absorption took place.

The color changes of di-*n*-hexyl-dixanthylethane were similar to those of di-*iso*-amylethane. A colorless solution in methyl benzoate, in a carbon dioxide atmosphere, when heated to the boiling point, became yellowish-brown and colorless again when rapidly cooled. Heating again restored the color, which slowly faded out during the boiling to a permanent, very pale yellow. The solution in naphthalene was colorless at 80°. When heated, it turned yellow, then brown, and at the boiling point, red. After 10 to 15 seconds' boiling, the color slowly faded to pale straw which was permanent.

Cyclohexylxanthydrol, $O<(C_6H_4)_2>COHC_6H_{11}$.—Two g. of magnesium in absolute ether was treated slowly with 10 g. of chlorocyclohexane, in an atmosphere of hydrogen (to avoid possible reaction with oxygen).[4] The reaction required about two hours for completion. Ten g. of finely divided xanthone was added in small portions, and reacted vigorously. After 12 hours, the mixture was decomposed with ice and ammonium chloride and yielded 9.8 g. of white crystals; m. p., 152°; yield, 66%. Repeated recrystallization from a mixture of benzene and ligroin gave a product, m. p. 158–159°, which was very soluble in alcohol, ether and benzene, but only slightly soluble in ligroin.

Anal. Calcd. for $C_{19}H_{20}O_2$: C, 81.0; H, 7.15. Found: C, 80.9; H, 6.88.

Cyclohexylxanthyl Perchlorate.—Treatment of a dry ethereal solution of cyclohexylxanthydrol with the usual mixture of perchloric acid and acetic anhydride gave a 70% yield of perchlorate, but it was found more advantageous to form the perchlorate directly from the crude product of the Grignard reaction as follows.

A solution of 6.2 g. of magnesium in dry ether was treated with 30 g. of chlorocyclohexane; 37. g. of dry powdered xanthone was added in small portions. The ether solution resulting from decomposition of the product with ice and ammonium chloride was dried with calcium chloride, cooled in ice and treated with perchloric acid-acetic anhydride mixture until no more perchlorate precipitated. The perchloric acid must be added very slowly as otherwise the product separates as a red oil, which subsequently forms yellow crystals. When the addition is slow enough, the material is obtained as fine, yellow needles. The product was filtered off and washed with 100 cc. of dry ether; yield, 53.5 g., or 78%. The compound turns brown at 160° and fuses at 163° to a black melt. It may be recrystallized from hot glacial acetic acid in which it is sparingly soluble.

Anal. Calcd. for $C_{19}H_{19}O_5Cl$: ClO_4, 27.44. Found: 27.42.

The perchlorate could be reconverted to the carbinol as follows. One g. of cyclohexylxanthyl perchlorate was dissolved in 60 cc. of glacial acetic acid and 20 cc. of concd. sulfuric acid. The deep red, fluorescent solution was poured onto ice, and the white precipitate obtained was washed, dried and crystallized from ether; yield, 0.66 g., or 86%; m. p., 159–160°. The substance was identified by a mixed melting point.

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[4] *Bull. soc. chim.*, [3] **29**, 1051 (1903).

Formation of Dicyclohexyl-dixanthyl by Reduction of Cyclohexylxanthyl Perchlorate.—Two g. of cyclohexylxanthyl perchlorate was dissolved in 120 cc. of glacial acetic acid and 40 cc. of concd. sulfuric acid and reduced with 20 cc. of *M* vanadous chloride solution, in a carbon dioxide atmosphere. During reduction the intensely red fluorescent solution lost its color and a light brown precipitate was formed. The mixture was poured into 500 cc. of air-free water, filtered, and the resulting light yellow powder washed thoroughly. This was dried in a vacuum desiccator in an atmosphere of nitrogen or carbon dioxide. *This material was used in the experiments reported below.* When the dry yellow powder so obtained was exposed to the air for even an instant, vigorous oxidation took place, the material charring and giving off an odor as of burnt sugar. Therefore, the solution of this material and its transfer from one container to another was performed in an atmosphere of carbon dioxide or nitrogen. A similar phenomenon has been observed with finely divided precipitates of hexaphenylethane. The reduction may also be carried out in hydrochloric acid by dissolving 2 g. of perchlorate in 120 cc. of concd. hydrochloric acid, and adding 20 cc. of vanadous chloride. The yield of the ethane as indicated by oxygen absorptions was not quite as high as when the acetic acid-sulfuric acid mixtures were used as solvent.

The wet product from the reduction of 0.5 g. of cyclohexylxanthyl perchlorate took up 14 cc. of oxygen in bromobenzene in one minute, which is 84% of the absorption calculated from the perchlorate used; 0.44 g. of the ethane dried in nitrogen for 12 hours absorbed 12.7 cc. of oxygen at 22°, equivalent to 65% of the calculated. This low value may have been due either to some decomposition or to leakage of oxygen, since with freshly prepared material over 80% absorption was consistently obtained.

The ethane is very soluble in all the common solvents excepting methyl alcohol. Attempts were made to recrystallize from ether, acetone, benzene, ethyl alcohol, methyl alcohol, high- and low-boiling ligroin and chloroform. From none of these solvents did crystalline material separate on cooling, and upon evaporation in vacuum, a viscous yellow gum was obtained, which would take up oxygen, and redissolve to a red solution. When methyl alcohol was slowly added to a solution of the ethane in ether in an atmosphere of carbon dioxide, a fine yellow precipitate separated. This was filtered off, washed with cold methyl alcohol, and dried in a stream of carbon dioxide. This material was at least in part active, since it took up 45% of the calculated amount of oxygen; m. p. in air, 109–110°, turning brown at 105°; m. p. in carbon dioxide, 110–113°, forming a red melt. It may have consisted in part of an addition compound with methyl alcohol as the following analyses indicate.

Anal. Calcd. for $C_{38}H_{38}O_2$: C, 86.7; H, 7.28. Calcd. for $C_{38}H_{38}O_2.CH_3OH$: C, 82.5; H, 7.45. Found: C, 83.9; H, 7.44.

Properties of the Crude Dicyclohexyl-dixanthyl.—The light yellow dicyclohexyl-dixanthylethane obtained directly from the reduction as described above dissolved in all of the common organic solvents to give a deep cherry-red solution. When such solutions in absolute ether or bromobenzene were cooled to 0°, their color faded to a very faint yellow. On further cooling the liquid to —35°, this faint yellow color persisted and is, therefore, probably due to impurities. When warmed to room temperature the solution regained its color, the reappearance of the color being most marked between 0° and 15°. This process could be repeated indefinitely. When the liquid was heated to 60°, the color became even deeper, and diminished again as the solution cooled. When the red solution of the ethane in any solvent was shaken with air, the color disappeared, reappearing after a few seconds' standing. This was repeated five or six times before the solution became a permanent light yellow. In the case of ether solutions, the white crystalline peroxide precipitated; from other solvents it separated only after evaporation. Sealed bulbs of the red solution in ether and in bromobenzene were exposed to diffuse daylight for a month. The red color disappeared in this time, and a yellow, strongly fluorescent solution remained.

Change of Color on Dilution.—A Bausch and Lomb type of Dubosq colorimeter was arranged for use with an atmosphere of nitrogen by fitting small rubber balloons over the cups and prisms, with suitable tubes for admitting nitrogen and the solution and the diluting solvent. Dilution experiments carried out with normal colored substances in ether and alcohol solutions gave results agreeing with Beer's dilution law, with an average error of less than 5%.

Three cc. of a solution of dicyclohexyl-dixanthyl-ethane in ether was introduced into each cup of the colorimeter, giving perfectly matched colors. The material in one cylinder was then diluted with measured volumes of air-free ether from an attached buret, the color obtained being matched each time with that in the undiluted cylinder, and the color intensity calculated from the depth of solution under the prism. Adequate stirring was obtained by a slow stream of pure nitrogen bubbling through the liquid, which was stopped at the moment of reading.

DATA.—V_1 and V_2 are the volumes of solution in the left and right cylinders, d_1 and d_2, the depths of solution under the prisms, and C_1 and C_2, the colors of solution. The initial color is considered 10 and $C_2 = C_1d_1/d_2$.

With approximately a 5% solution in ether of the crude, dry material at 20° the following results were obtained.

V_1 Cc.	d_1 Mm.	C_1	V_2 Cc.	d_2 Mm.	C_2 found	C_2 calcd. (Beer's law)	Increase in color
3	10.7	10	3.1	10.0	10		
			8.1	10.0	10	3.8	2.6 times
			13.1	7.1	14.1	2.4	5.9 times

When air was bubbled through the solution, the color faded to pale yellow and dilution of this solution then followed Beer's law.

In another experiment 0.87 g. of crude dicyclohexyl-dixanthyl-ethane, which was at least 65% active material as shown by oxygen absorption, was dissolved in 20 g. of dry air-free ether, giving a light red, clear solution containing about 3% of ethane. The results may be summarized as follows: 2.5 volumes' dilution increased the color 3.1 times; dilution to 4.5 volumes, 4 times; dilution to 6 volumes, 4.8 times. Further dilution gave only a very slight increase in color.

Cyclohexylxanthyl Peroxide, $O<(C_6H_4)_2>C(C_6H_{11})—O_2—C(C_6H_{11})<(C_6H_4)_2>O$.—Two g. of cyclohexylxanthyl perchlorate in 120 cc. of glacial acetic acid and 40 cc. of concd. sulfuric acid was reduced with 12 cc. of M vanadous chloride solution, precipitated in water, and the washed precipitate was dissolved in ether. Shaking with air quickly decolorized the deep red solution, which was then dried with calcium chloride and on slow evaporation deposited large, colorless crystals. These were filtered out and washed with cold ethyl alcohol; yield, 0.5 g.; m. p., 143–145°. The peroxide was recrystallized by dissolving it in a small amount of benzene and adding absolute ethyl alcohol very slowly. The pure product melted at 147–148°, with the evolution of gas and formation of a yellow melt. The peroxide is very soluble in chloroform and benzene, slightly soluble in ether, and nearly insoluble in boiling ethyl alcohol, methyl alcohol or 90° ligroin.

Anal. Calcd. for $C_{38}H_{38}O_4$: C, 81.7; H, 6.86. Found: C, 81.6; H, 6.81.

Mol. wt. Subs., 0.2034, 0.4307: benzene, 17.02; Δt, 0.115°, 0.230°. Calcd. for $C_{38}H_{38}O_4$: mol. wt., 558. Found: 533, 564.

Cyclohexylxanthyl peroxide dissolves in concd. sulfuric acid to give an orange-yellow solution, very much like that obtained from triphenylmethyl peroxide in sulfuric acid. As with the latter, the carbinol can be obtained from this colored solution;

0.38 g. of cyclohexylxanthyl peroxide was dissolved in 2.5 cc. of cold, concd. sulfuric acid. At first a yellow solution was obtained. There was little charring and a fluorescent green solution resulted with a few black particles in it. After five minutes, it was poured onto cracked ice and a cloudy brown suspension resulted. The precipitate was filtered off, washed and dissolved in ether, the solution filtered and the ether evaporated. White crystals separated; m. p., 151–155°. After one recrystallization from benzene-ligroin mixture, these yielded 0.12 g. of carbinol, m. p. 157–159°, identified as cyclohexylxanthydrol by mixed-melting-point determinations. The peroxide when heated to 145–150° in hydrogen decomposes violently. A quantitative experiment with 0.3 g. of material yielded 86% of the calculated amount of xanthone and a yellow liquid.

Summary

1. The following derivatives of dixanthyl have been prepared by reduction of the perchlorates of the corresponding derivatives of xanthydrol: di-(*p*-chlorobenzyl)dixanthyl; di-*iso*-amyl-dixanthyl; di-*n*-hexyl-dixanthyl; and in an impure condition, dicyclohexyl-dixanthyl.

2. The behavior of the *p*-chlorobenzyl compound is analogous to that of the dibenzyl-dixanthyl previously prepared in this Laboratory and confirms our conclusions that an aromatic group in the β position is effective in causing dissociation in the dixanthyl series.

3. Di-*iso*-amyl-dixanthyl and di-*n*-hexyl-dixanthyl absorb oxygen slowly at room temperature. Their solutions when heated undergo reversible color changes which point to an appreciable dissociation at higher temperatures.

4. The properties of the solutions of the crude dicyclohexyl-dixanthyl show that this substance is considerably dissociated in solution at room temperature. The red solutions on dilution show wide deviations from Beer's law and rapidly absorb oxygen, becoming light yellow and yielding a crystalline peroxide. The effectiveness of an alicylic group in promoting dissociation has thus been established.

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