[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

THE DISSOCIATION INTO FREE RADICALS OF SUBSTITUTED DIXANTHYLS

IV. DIXANTHYL AND DIXANTHYL-9,9'-DICARBOXYLIC ACID

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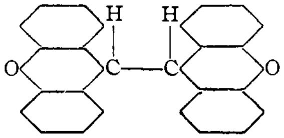
It has been shown[1] that the aryl and *sec.*-alkyl derivatives of dixanthyl are dissociated in solution at room temperature and that the primary alkyl derivatives dissociate on warming their solutions. The parent substance dixanthyl (I) differs from these derivatives in that no color develops even on boiling its solution in methyl benzoate, and at room temperature it does not combine with oxygen. There is no reason, therefore, to believe that it dissociates into a free radical even at a comparatively high temperature.[2] The carbon-carbon linkage in this compound, however, is very reactive towards certain reagents which bring about cleavage of the molecule.


I

In dilute carbon disulfide solution bromine reacts with dixanthyl forming two molecules of the perbromide of xanthyl bromide. At room temperature, dixanthyl slowly dissolves in concd. sulfuric acid, yielding a brown solution; on hydrolysis xanthanol is obtained. By analogy with the reaction of acids on dissociated ethanes one would expect xanthane as the other product in this reaction but we were unable to prove its presence in the reaction mixture. The red sodium xanthyl is rapidly formed by shaking an ether solution of dixanthyl with either sodium-potassum alloy or 40% sodium amalgam (a liquid). Tetraphenylethane is similarly cleaved by sodium-potassium alloy[3] but not by 40% amalgam. A 2% solution of dixanthyl in dibromobenzene begins to absorb oxygen at an appreciable rate at 150° and at 180–190° the oxidation is complete in five to six hours; the amount of oxygen absorbed corresponds to the for-

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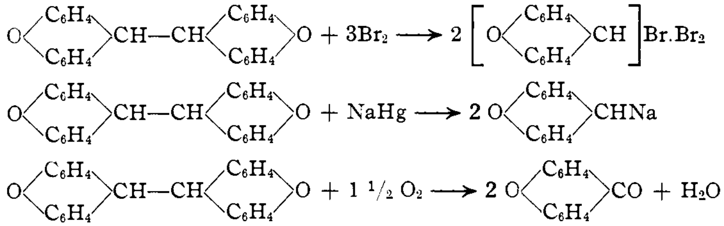
[1] Conant and Sloan, THIS JOURNAL, **47**, 572 (1925). Conant and Small, *ibid.*, **47**, 3068 (1925). Conant, Small and Sloan, *ibid.*, **48**, 1743 (1926).

[2] Conant and Sloan [THIS JOURNAL, **45**, 2468 (1923)] prepared dixanthyl by reduction of the xanthanol in strong acid solution with vanadous chloride. They believed that the colored precipitate which is first formed might contain the free xanthyl radical in the solid state. We have reinvestigated this point and have failed to obtain any evidence that the pink precipitate contains "free xanthyl." The color seems to be due to small amounts of some highly colored impurity.

[3] Ziegler and Thielmann, *Ber.*, **56B**, 1740 (1923).

mation of two molecules of xanthone. The pure compound at 225° absorbs the calculated quantity of oxygen in four to five hours, and xanthone can be isolated from the oxidation product.



$$O\left\langle\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\right\rangle CH{-}CH\left\langle\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\right\rangle O + 3Br_2 \longrightarrow 2\left[O\left\langle\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\right\rangle CH\right]Br.Br_2$$

$$O\left\langle\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\right\rangle CH{-}CH\left\langle\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\right\rangle O + NaHg \longrightarrow 2\,O\left\langle\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\right\rangle CHNa$$

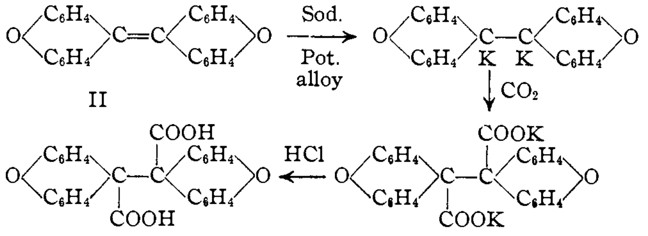
$$O\left\langle\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\right\rangle CH{-}CH\left\langle\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\right\rangle O + 1\,{}^1/_2\,O_2 \longrightarrow 2\,O\left\langle\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\right\rangle CO + H_2O$$

All these reactions are characteristic of dissociable ethanes, and when they take place with such a substance as hexaphenylethane, are usually interpreted as reactions of the free radical (for example, triphenylmethyl). With dixanthyl the reactions are slower and either require somewhat more drastic reagents (for example, 40% amalgam instead of 1% amalgam) or a higher temperature, as in the case of the absorption of oxygen. It seems to us highly improbable that these cleavage reactions of dixanthyl proceed through a free radical stage. We seem rather to be dealing with definite reactions of the *single* bond. Even in the case of the oxygen absorption of the colorless solutions of certain dialkyl dixanthyls the reaction may involve a very reactive carbon-to-carbon linkage and not a free radical. In the dixanthyl series we have at our disposal a series of compounds with considerable variations in the reactivity of the single linkage; at the top of the series are those substances like diphenyl-dixanthyl and di-*iso*propyldixanthyl which dissociate in solution at 25°; at the bottom is the hydrogen compound dixanthyl itself.

It is worth noting that the cleavage of a single bond by halogens, acids, alkali metals and oxygen is strikingly parallel to the action of the same reagents on ethylenic derivatives. The only difference is that in the case of the unsaturated compounds the molecule as a whole stays intact as only one of the two linkages is cleaved. It is very probable, therefore, that the final explanation of the variations in the reactivity of the single bond and the double bond will be found to be closely allied if not identical.

Dixanthyl-9,9′-dicarboxylic Acid and its Ester

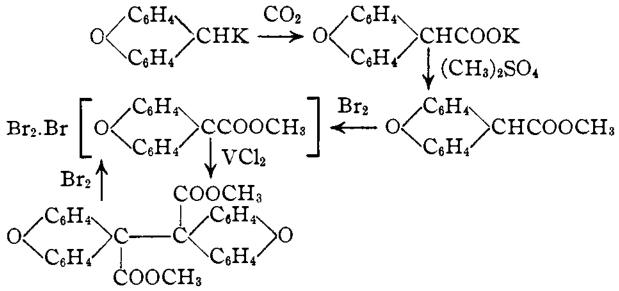
In order to compare the dissociating influence of a so-called negative group with that of aryl and alkyl groups, we have synthesized dixanthyl-9,9′-dicarboxylic acid (III) and its dimethyl ester by two methods. Dixanthylene (II) adds two atoms of alkali metal when shaken with sodium-potassium alloy. The resulting compound, on treatment with carbon dioxide, yields the salt of the dibasic acid. The reactions are outlined below; we have written the metallic compound as the potassium compound but have no evidence as to whether sodium or potassium (or perhaps both) is actually involved in the reaction.


II

III

The acid may also be obtained by the reduction of 9-bromo-xanthanoic acid with vanadous chloride. The crystalline perbromide was actually employed; it is probably a xanthylium salt and analogous to the salts of the substituted xanthanols, which we have reduced to dixanthyls in an earlier work in this Laboratory. The bromoxanthanoic acid was obtained by bromination of the xanthanoic acid formed by the action of carbon dioxide on potassium xanthyl. This in turn can be prepared by the cleavage of dixanthyl with sodium-potassium alloy or by the action of the same reagent on xanthane. The dimethyl ester of dixanthyl-9,9′-dicarboxylic acid can be prepared by a similar bromination of the methyl ester of xanthanoic acid and subsequent reduction. It may also be prepared by the methylation of the sodium salt of the dibasic acid with dimethyl sulfate.

Dimethyl dixanthyl-9,9′-dicarboxylate reacts rapidly with bromine in carbon disulfide and forms the perbromide of the bromo-xanthanoic ester. It is thus possible to go back and forth from this compound to the dixanthyl di-ester by using either aqueous vanadous chloride or bromine in carbon disulfide.



A solution of dixanthyl-9,9′-dicarboxylic acid in ethyl benzoate in nitrogen becomes red on heating and the color disappears on cooling; this may be repeated a number of times. The first color becomes apparent at about 105°; at 140° a two per cent. solution is light cherry-red. The color darkens on further raising the temperature but above 185° an irreversible decomposition takes place and the red color disappears. This decomposition is probably some sort of internal oxidation-reduction similar to that observed with the di-alkyl dixanthyls. Xanthanoic acid was isolated from a naphthalene solution of the dibasic acid which had been heated until the red color had appeared and then faded. A solution of the dimethyl ester showed the same reversible color changes on heating but unlike the acid the color showed no signs of fading after ten minutes at 200°; on cooling, the solution became colorless. The first color was visible at 115–120°, and above 175° the solution was cherry-red.

The red color of a solution of the ester or acid in boiling xylene was discharged by the addition of phenylhydrazine. Unfortunately, no crystalline products could be isolated from the reaction mixture. The color also disappeared when oxygen was bubbled through the hot solution. A small quantity of crystalline material was isolated from such an oxidized solution of the ester; analysis showed it to have the composition of the peroxide. The rates of oxygen absorption of the acid and ester were measured in the usual way, using bromobenzene as a solvent at room temperature, and *p*-dibromobenzene at higher temperatures. A solution of the ester at 25° absorbed no appreciable quantity of oxygen in 52 hours but the acid under the same conditions absorbed 9.3% of one mole. At higher temperatures the action is more rapid; carbon dioxide is evolved in the case of the acid and this was absorbed in sodium hydroxide before measuring the change in volume. At 120–130° a dilute solution of the acid reacted with 80% of one mole in six and a half hours. At 150–160°, a similar solution of the ester absorbed 54% in seven hours. A solution of the acid in sodium hydroxide was heated to boiling and oxygen bubbled through for three hours; xanthone was precipitated (about 20%) and on acidification considerable unchanged acid was obtained.

A comparison of the facts stated in the preceding paragraph with the behavior of other dixanthyl derivatives is of interest. The temperature at which dissociation first becomes appreciable, as judged by the appearance of color, is about the same for the ester and acid (115° for the ester, 105° for acid). It is considerably lower than the temperature required for appreciable dissociation of dimethyl-dixanthyl (about 160°) or dibutyl-dixanthyl (about 140°), but greater than that for dibenzyl-dixanthyl (about 80°). On the other hand, towards oxygen the compounds are much less reactive than the least reactive of the dialkyl dixanthyls, all of which in dilute solution absorb one mole of oxygen in less than a day, at 25°.

This marked unreactivity of the compounds towards oxygen is in accord with the only other work that has been done on the effect of negative groups on the dissociation of ethanes. Löwenbein[4] has prepared the

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[4] Löwenbein, *Ber.*, **58**, 601 (1925).

*bis*lactone of 2,2'-dioxytetraphenyl-succinic acid and has shown by colorimetric measurements that it is considerably dissociated in boiling toluene. The same author later showed that tetra-*p*-anisyl-succinonitrile begins to dissociate at 60–80° and tetraphenyl-succinonitrile at about 140°. The color of Löwenbein's free radicals was discharged by phenylhydrazine but only very slowly by oxygen; a 20% solution of the *bis*lactone in boiling xylene was decolorized by a stream of oxygen in an hour. This rate is of the same order of magnitude as the rates of oxygen absorption by the dixanthyl dibasic acid, but very different, indeed, from those observed with all other dissociable ethanes. Löwenbein has explained this unreactivity of his radicals in terms of a splitting of the free valence between the ethane carbon atom and the oxygen atom of the carbonyl group.

Experimental Part

Reactions of Dixanthyl. (a) *Bromine.*—Five cc. of a 6% solution of bromine in carbon disulfide was added to a solution of 0.2 g. of dixanthyl in 10 cc. of the same solvent. An orange precipitate was formed; after it had been filtered off and washed with petroleum ether it melted with decomposition at 151–153°. A sample of the perbromide of xanthyl bromide was prepared by the action of gaseous bromine and hydrobromic acid on a carbon disulfide solution of xanthanol;[5] it was identical with the bromide prepared from dixanthyl as shown by color, reactions and mixed melting point.

Anal. For perbromide bromine: Calcd.: 38.0. Found: 38.2.

(b) *Sulfuric Acid.*—A tenth of a gram of dixanthyl was suspended in 30 cc. of concd. sulfuric acid. After 48 hours a brown solution was formed; this was filtered through asbestos, poured onto ice and neutralized. The white precipitate was taken up in ether which was then evaporated. On treating the residue with perchloric acid in dry ether, a yellow precipitate of xanthanol perchlorate (m. p. 218–219°) was obtained. It was identified by a mixed-melting-point determination.

(c) *Cleavage by Alkali Metals.*—A solution of 0.18 g. of dixanthyl in 10 cc. of absolute ether was shaken with 1 cc. of a liquid sodium-potassium alloy (10 parts of potassium and 4 parts of sodium) in dry nitrogen. The solution became red in about a minute and after two and a half hours there was a considerable red precipitate. After treating with carbon dioxide, decomposing the excess of alloy with alcohol and acidifying, 0.12 g. of xanthanoic acid, m. p. 215–217° (see below), was obtained. In a similar experiment with 40% sodium amalgam (a liquid) the solution acquired the characteristic red color of sodium xanthyl, but on working up the product after two and a half hours, only a very small amount of xanthanoic acid was obtained. One per cent. sodium amalgam gave no color even on prolonged shaking.

(d) *Oxygen Absorption.*—A tenth of a gram of dixanthyl dissolved in 9 g. of molten *p*-dibromobenzene absorbed 9.2 cc. of oxygen (N. T. P.) in 6.5 hours; at 148–155° in two other experiments, 2.7 and 2.1 cc. were absorbed in 5.75 and 6.75 hours, respectively. A blank showed that the dibromobenzene itself absorbed no oxygen under similar conditions. To oxidize 0.1 g. of dixanthyl to xanthone requires 9.3 cc. of oxygen (N. T. P.). A tenth of a gram of dixanthyl without any solvent absorbed the calculated quantity of oxygen in from 3 to 4.5 hours; xanthone was isolated and identified by mixed-melting-point determination. The apparatus used in measuring the rate of oxygen

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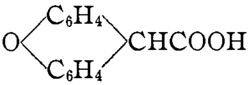
[5] Gomberg and Cone, *Ann.*, 376, 193 (1910).

absorption at elevated temperatures consisted of a bulb of about 20 cc. capacity heated in a paraffin bath and connected to a gas buret having mercury as the containing liquid.

Xanthanoic Acid.



$$O\left\langle\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\right\rangle CHCOOH$$

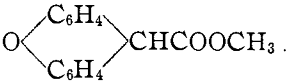
(a) **Preparation from Dixanthyl.**—In a typical run for the preparation of this acid, 2.25 g. of dixanthyl in 150 cc. of dry ether was shaken overnight with 10 cc. of sodium-potassium alloy under nitrogen in a 500 cc. glass-stoppered distilling flask with the side arm sealed off. The solution was then brick red and there was a brick-red precipitate. The flask was then cooled in a bath of ice and salt and dry carbon dioxide was passed in by breaking off the tip of the side arm. Common ether was then added and the contents of the flask were washed into a beaker. The moisture in the ether caused the alloy to coagulate so that it could easily be removed by a small glass dipper. Water was then added to dissolve the sodium salt, and the ether and water layers were separated. The alkaline water layer was acidified. This threw out a copious, very finely divided precipitate which was extracted with ether. The ether was dried over calcium chloride and evaporated. The residue was recrystallized from 50% ethyl alcohol. The product crystallized in long, white needles which softened slightly at 222° and melted at 223–224°. The yield of recrystallized product was 1.6 g.

(b) **Preparation of Xanthanoic Acid from Xanthane.**—In the preparation of the acid 0.3 g. of xanthane in 15 cc. of dry ether was shaken for ten minutes with 5 cc. of sodium-potassium alloy. The solution was brick red and there was some brick-red precipitate. This sodium xanthyl was treated with carbon dioxide, as in the previous case. A small amount of acid was obtained which was recrystallized from 50% ethyl alcohol and then from ether and petroleum ether; m. p., 218–219°. When mixed with some of the acid obtained from dixanthyl (m. p. 222–223°) the mixed melting point was 221–222°.

Anal. Calcd. for $C_{14}H_{10}O_3$: C, 74.3; H, 4.4. Found: C, 74.7; H, 4.6. Equiv. wt. by titration in 50% alcohol with standard sodium hydroxide solution (phenolphthalein indicator). Calcd. for $C_{14}H_{10}O_3$: 226. Found: 220, 226.

On heating to 290–300°, xanthanoic acid decomposes, giving carbon dioxide and xanthane. Bromination in carbon disulfide produced a dark red precipitate (m. p., 162–163°) and evolution of hydrobromic acid. The red precipitate on reduction with vanadous chloride in concd. hydrochloric acid yielded dixanthyl-9,9'-dicarboxylic acid (see below).

Methyl Xanthanoate.



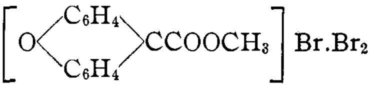
$$O\left\langle\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\right\rangle CHCOOCH_3.$$

Xanthanoic acid may be converted into its methyl ester by methylation of the sodium salt with dimethyl sulfate at 100° or by the action of thionyl chloride and absolute methyl alcohol. The ester can be recrystallized from methyl alcohol; it melts at 85–86°.

Anal. Calcd. for $C_{15}H_{12}O_3$: C, 75.0; H, 5.0. Found: C, 75.1; H, 5.0.

Mol. wt. in freezing benzene. Subs., 0.1354 g.; 0.2522 g.; solvent, 17.37 g.; Δt, 0.172, 0.320; K = 5.12. Mol. wt. Calcd. for $C_{15}H_{12}O_3$: 240. Found: 232, 233.

Perbromide of Methyl-9-Bromo-xanthanoate.

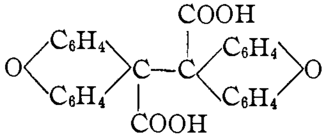


$$\left[O\left\langle\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\right\rangle CCOOCH_3\right]Br.Br_2$$

Bromination of the methyl ester in carbon disulfide yielded a red precipitate with evolution of hydrogen bromide. It was purified by washing with petroleum ether; it melted at 158–159° with decomposition.

Anal. for perbromide bromine. Calcd. for $C_{15}H_{11}O_3Br$: Br_2, 33.4. Found: 33.5.

Dixanthyl-9,9'-dicarboxylic Acid.



Preparation from Dixanthylene.—In a typical run 2.4 g. of dixanthylene, 350 cc. of dry ether and 15 cc. of sodium-potassium alloy under dry nitrogen, were shaken for 12 hours in a glass-stoppered distilling flask with the side arm sealed off. The solution was a deep reddish-purple and there was a dark precipitate. The flask was cooled in an ice-and-salt bath and carbon dioxide was introduced by breaking the tip off the side arm. Considerable white precipitate formed. The contents of the flask were washed into a beaker with common ether. The moisture caused the alloy to coagulate and it was removed with a small, glass dipper. Water was added and the mixture shaken. The two layers were then separated. The ether was sucked out of the water layer, which was turbid. The water layer was filtered four times before a clear, yellow solution was obtained. When this solution was then acidified considerable precipitate formed which quickly coagulated and was filtered off, washed well and dried. It commenced to darken at 125° and decomposed up to 155°.

Numerous attempts to purify the acid by crystallization from various solvents failed; the only way to purify the material was to dissolve in aqueous alkali, filter and reprecipitate with acid. When the acid which had been precipitated from a clear alkaline solution was redissolved after standing, there was usually a small residue of xanthone. The clear alkaline solutions slowly deposited small amounts of the same material, evidently due to oxidation by the air.

Anal. Calcd. for $C_{28}H_{18}O_6$: C, 74.7; H, 4.0. Found: C, 74.5; H, 4.3.

Equiv. wt. by titration (phenolphthalein indicator). Calcd. for $^1/_2$ $C_{28}H_{18}O_6$: 225. Found: 221, 230.

Oxidation with Oxygen.—Half a gram of the acid was dissolved in 15 cc. of 5% sodium hydroxide, the solution diluted to 30 cc. and heated to boiling for three hours under a return condenser while a current of oxygen was bubbled through. After cooling and standing overnight, 0.075 g. of xanthone was filtered off. On acidification considerable dixanthyl-9,9'-dicarboxylic acid was obtained, somewhat pink in color. It melted, with decomposition, at 110–150° and was further identified by analysis. (Found: C, 74.0; H, 4.3.)

When the acid was dissolved in *p*-dibromobenzene and heated in oxygen at 150–160° there was no change in volume after seven hours. However, when the apparatus was disconnected and the bulb submerged in concd. potassium hydroxide, 6 cc. was drawn into the bulb, showing that carbon dioxide was formed. For further experimentation a tube filled with slightly moist potassium hydroxide was inserted between the reaction bulb and the gasometer. With this apparatus a solution of 0.15 g. of the acid in 7 g. of dibromobenzene absorbed oxygen as follows: at 120–130°, 80% of one mole in 6.5 hours and 100% in 13 hours.

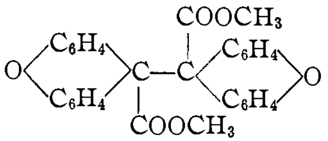
The rate of oxidation by oxygen in bromobenzene at 25° was determined in the usual manner. Only 9.3% of one mole was absorbed in three days.

Color on Heating.—A solution of 0.225 g. of the acid in 10 cc. of ethyl benzoate was heated in an atmosphere of nitrogen. The temperature was fixed by plunging the tube in a hot paraffin bath. At 90° there was no color; at 105° the first color became apparent, which faded on cooling. This was repeated. At 150° the color became a light cherry-red; this faded on cooling, but the solution remained somewhat more colored than it was originally. At 180–200° the red color faded to yellow in about five minutes.

A sample of 0.2 g. of the acid was mixed with 10 g. of naphthalene and heated in a paraffin bath under nitrogen until the color faded. When cold, the tube was broken. The contents were dissolved in ether and this solution was extracted with sodium carbonate. Both the ether and the alkaline layers were yellow. The precipitate formed by the acidification of the alkali layer did not coagulate and was, therefore, extracted with ether, which was dried and evaporated. A yellow oil and a few crystals were obtained. This product was taken up in hot 50% ethyl alcohol and the solution filtered from a few crystals which melted above 240° and were not identified. When cold, the solution was filtered but no product was obtained. It was then extracted with ether which was dried and evaporated. Gummy crystals were obtained. They were washed in 50% ethyl alcohol. In this way a small quantity of crystals of xanthanoic acid was obtained (m. p. 218–220°) and identified by a mixed-melting-point determination.

When a solution of the acid in xylene was heated almost to boiling, the reddish color of the radical was quite apparent. When a solution of phenylhydrazine in xylene was added to this hot solution the radical color faded at once. No precipitate was formed. Several attempts to isolate xanthanoic acid from this reaction mixture failed, the only product being a yellow oil.

Dimethyl Dixanthyl-9,9′-dicarboxylate,



$$O\left\langle\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\right\rangle \underset{\substack{|\\COOCH_3}}{C}—\overset{\substack{COOCH_3\\|}}{C}\left\langle\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\right\rangle O$$

The dibasic acid was converted to its dimethyl ester by boiling a solution of it in 5% sodium hydroxide with dimethyl sulfate, the gummy precipitate being filtered from the still strongly alkaline solution. It was also prepared by the reduction of the perbromide of bromo-xanthanoic ester as follows. A solution of 0.5 g. of the perbromide in 125 cc. of concd. hydrochloric acid was treated with 3 cc. of 0.5 *N* vanadous chloride. A pinkish precipitate was formed. It was dissolved in ether, the solution extracted with aqueous sodium hydroxide, the ether solution then dried and the ether evaporated. A flaky, amorphous solid was left, melting over the range 90–110°. The ester could not be crystallized from any solvent that was found. On evaporating a dry ether solution it was obtained as an amorphous, flaky solid; an alcoholic solution evaporated in a vacuum left a yellow gum which hardened to a pliable solid. A similar solid could be obtained by precipitation with water from methyl alcohol. All samples melted indefinitely between 85 and 110°, but could be dried in a vacuum for analysis and molecular-weight determination.

Anal. Calcd. for $C_{30}H_{22}O_6$: C, 75.3; H, 4.6. Found: C, 75.2; H, 4.9.

Mol. wt. in freezing benzene. Subs., 0.2708 g., 0.5876 g. Solvent, 17.37 g.; Δt, = 0.208°, 0.419°. Mol. wt. Calcd.: 478. Found: 393, 414.

A solution of the ester in ethyl benzoate (0.24 g. in 10 cc.) heated in nitrogen showed a faint color at 115°; at 125° the color was deeper and faded on cooling. This could be repeated many times. Above 125° the color deepened, being cherry-red at 170°. It did not fade on keeping at 200° for ten minutes, but faded on cooling; on again heating to 200° the cherry-red color deepened as before. These experiments were performed both with the material prepared by esterification of the dibasic acid and by reduction of the perbromide; the reversible appearance of color was the same with both samples.

A solution of the ester in carbon disulfide (0.14 g. in 8 cc.) when treated with bromine gave a red precipitate *without* evolution of hydrogen bromide. This precipitate was shown to be the perbromide of methyl bromo-xanthanoate by mixed melting point (158–159°) and by analysis.

Oxygen Absorption.—When 0.14 g. of the dimethyl ester was dissolved in 10 cc. of bromobenzene in the usual oxygen-absorption apparatus, there was no absorption in 52 hours.

The oxygen absorption at high temperatures was determined in the same apparatus which was used for the acid, using 0.14 g. of the ester and 7 g. of *p*-dibromobenzene. The absorption at 120–130° was 36.4% of one mole in seven hours. At 150–160° it was 53.4% of one mole in seven hours and 87.7% of one mole in 11 hours.

Two samples of 0.1 g. of the dimethyl ester were dissolved in 5 cc. of xylene in test-tubes under nitrogen and the solutions heated to boiling. The color deepened to a decided red tint. A stream of nitrogen was passed into the first, just above the surface of the liquid. The color remained in this solution for 35 minutes and then faded on cooling. Fifteen minutes later the color again deepened when the solution was heated, and faded on cooling. Ten minutes later this was again repeated. A stream of oxygen was bubbled through the second tube while the xylene was boiling. The red color faded in about five minutes and there was no further change on subsequent heating and cooling. The xylene was steam distilled from the second solution, leaving a yellow oil. Attempts to crystallize this oil from methyl alcohol yielded a small quantity of white crystals, m. p. 176°, with gas evolution. Further small quantities of this product were obtained in subsequent, similar runs.

Anal. Subs., 0.01137: CO_2, 0.02922; H_2O, 0.00426. Calcd. for $C_{30}H_{22}O_8$: C, 70.6; H, 4.3. Found: C, 70.1; H, 4.2.

A red solution of the ester in boiling xylene was treated with phenylhydrazine in nitrogen. After seven minutes at the boiling point, the color had faded and no more color was developed on subsequent heating and cooling. No crystalline products could be isolated from the reaction mixture.

Summary

1. The following cleavage reactions of dixanthyl have been demonstrated: (a) with bromine in dilute carbon disulfide; (b) with sodium-potassium alloy and 40% sodium amalgam; (c) with concd. sulfuric acid; (d) oxidation by oxygen above 150°. There is a striking parallel between these reactions of the single carbon bond and addition reactions of ethylenic compounds.

2. Dixanthyl-9,9′-dicarboxylic acid and its dimethyl ester have been synthesized by two methods. Solutions of these compounds, when heated above 100°, show reversible color changes characteristic of dissociable ethanes. Judged by the temperature required for appearance of radical color, the carboxy and carbomethoxyl groups have a slightly greater dissociating influence than primary alkyl groups. In spite of this, the compounds are only very slowly oxidized by oxygen even above 100°.

Cambridge, Massachusetts