The data discussed above constitute evidence that anthraquinone exists, at least partially, in a quinonoid state in ether solution; that xanthone exists entirely in a benzenoid state in ether solution and that both of these compounds exist, at least partially, in a quinonoid state in sulfuric or perchloric acid solutions. The data also indicate that benzophenone does not possess a quinonoid structure in either sulfuric or perchloric acid solutions.

Summary

Curves are presented for the quantitative absorption spectra for solutions of each of the following compounds: anthraquinone, benzophenone, and xanthone in ether and in sulfuric acid, respectively, and for ether and perchloric acid solutions of benzoquinone. The curves indicate that the colored solute which is produced when ketones are dissolved in sulfuric or perchloric acid is produced through the reactivity of the carbonyl group of the ketone. They show, furthermore, that in some instances quinoidation may also be responsible for the color.

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The Dissociation into Free Radicals of Di-tert-butyltetradiphenylethane

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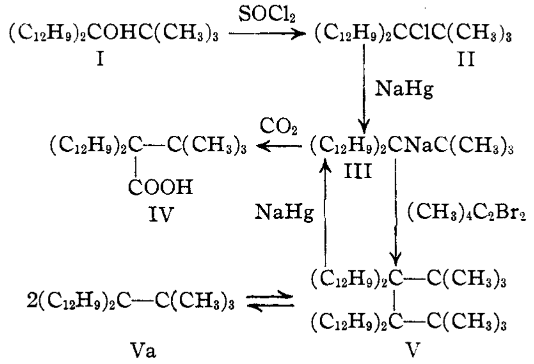
In recent years it has become evident that a branched alkyl group is effective in promoting the dissociation of a highly substituted ethane. Thus, dicyclohexyltetraphenylethane[1] and di-*tert*-butyltetraphenylethane[2] contain a very reactive carbon to carbon linkage and in the case of the latter substance clear evidence of its dissociation into a free radical can be obtained. The free radical is formed in appreciable quantities only above about 50° and at these temperatures quickly disproportionates; for this reason no molecular weight determinations could be made and it was necessary to rely on color changes and chemical reactions. In the dixanthyl series, the free radicals with a branched alkyl group on the central carbon atom are much more stable and less associated. Relatively stable solutions of cyclohexylxanthyl, *sec*-butylxanthyl and isopropylxanthyl have been prepared. The solutions of these free radicals[3] are highly colored and absorb oxygen very rapidly. Unfortunately all attempts to obtain a crystalline form of the associated free radical (the dialkyl-dixanthyl) failed. It was, therefore, impossible to carry out molecular weight determinations in this case also.

[1] Ziegler and Schnell, *Ann.*, **437**, 237 (1924).

[2] Conant and Bigelow, THIS JOURNAL, **50**, 2041 (1928).

[3] Conant, Small and Sloan, *ibid.*, **48**, 1743 (1926).

It is clearly desirable to have an example of an ethane with two aliphatic substituents which can be obtained in crystalline condition and whose dissociation into free radicals can be demonstrated by molecular weight determinations as well as by color changes and chemical reactivity. We have now been able to prepare such a compound. It is di-*tert*-butyltetradiphenylethane (V). Its method of preparation completely parallels that of the corresponding tetraphenyl compound and is summarized below.



The carbinol I was best prepared by the action of lithium diphenyl on the ethyl ester of trimethylacetic acid; the same substance was formed by the action of *tert*-butylmagnesium chloride on di-diphenyl ketone, but in this case the yield was very low. The action of thionyl chloride on the carbinol resulted in the formation of two isomeric chlorides. The lower melting of the two compounds is formed almost exclusively if the reaction temperature is kept low; on heating in benzene solution it is in part converted into the higher melting isomer. The structure of the lower melting chloride was established by its conversion into a colored sodium derivative (III) from which an acid (IV) could be obtained. The higher melting chloride was not further investigated. Undoubtedly it is a rearrangement product having a different carbon skeleton. Such a rearrangement was found to occur in the case of the corresponding phenyl compounds.

The preparation of the dissociable ethane (V and Va) followed the well-known method of Ziegler.[1] The sodium compound (III) was treated with tetramethylethylene dibromide. The preparation and subsequent recrystallization of the final product was carried out in an atmosphere of nitrogen in a special all-glass apparatus.

Di-*tert*-butyltetradiphenylethane was obtained in the form of light orange crystals which melted at 136–137° (out of contact with air). We believe that the absolutely pure ethane would be colorless but were not able to obtain a colorless sample. Solutions of the compound have a strong orange-red color at room temperature. The intensity of the color of a 0.007 molar solution in toluene was markedly decreased by cooling to $-80°$

and noticeably diminished even by cooling to 0°. On freezing the solvent by immersion in liquid air, a pale yellow solid was obtained. Warming to room temperature restored the color. At 80° the color of the solution became more intense but then rapidly faded due to disproportionation. The same reaction proceeds more slowly at room temperature; the color of one solution, for example, was diminished to about a fourth after standing for fifteen hours in the dark at room temperature. *Tert*-butyl-di-(diphenyl)-methane was isolated in considerable amounts from a solution whose color had been destroyed by warming to 45° for 2.2 hours. The other product of the disproportionation was not isolated but is probably an unsaturated hydrocarbon since the residual oil from which the methane crystallized decolorized a chloroform solution of bromine.

The molecular weight was determined by the freezing point method in benzene, special precautions being taken to exclude air. Values of 473 and 490 were found in a 0.006 molar solution. This corresponds to a degree of dissociation of 0.74 and 0.69, respectively. The evidence is thus conclusive that the compound is largely dissociated even at 5°.

Solutions of the ethane absorb oxygen with great rapidity and are thereby decolorized. The amount of oxygen corresponding to peroxide formation is taken up at once and then an additional quantity (half a mole) is absorbed slowly. No peroxide could be isolated but a 70% yield of di-diphenyl ketone was obtained. This is similar to the formation of xanthone by the autoxidation of the dialkyl-dixanthyls.[4] A solution of the ethane forms the sodium compound rapidly when treated with 1% sodium amalgam.

It would be interesting to obtain a quantitative comparison of the relative effectiveness of a secondary and a tertiary group in promoting dissociation. This has never been done, though it is clear from the qualitative evidence that the two groups are very similar to each other but very different from a primary group. With the hope of making such a comparison we endeavored to prepare dicyclohexyltetradiphenylethane. In this case we prepared the methyl ether of the carbinol and prepared the free radical from it by the method of Ziegler and Schnell.[1] An orange-colored solution of a dissociable ethane appeared to be formed when the violet sodium derivative was treated with tetramethylethylene dibromide. The color soon faded, however, and no product could be isolated which would absorb oxygen. Evidently the disproportionation in this case is so rapid that it is complete at room temperature in a short time. A similar rapid decomposition has been found to occur with dicyclohexyltetraphenylethane.[1] The transitory orange color indicates, however, that the ethane was present for a short time and was considerably dissociated. Evidently there is little hope of doing quantitative work with this compound, however.

(4) THIS JOURNAL, **47**, 572 (1925); **47**, 3068 (1925).

Experimental

Tert-butyl-di-diphenylcarbinol.—Lithium diphenyl was prepared from *p*-bromodiphenyl and lithium by the action of the bromide on metallic lithium under dry ether in an atmosphere of nitrogen. The procedure was the same as that employed by Ziegler and Colonius[5] in the preparation of lithium phenyl. The dark brown solution of lithium diphenyl from 0.6 g. of lithium and 10 g. of bromodiphenyl was treated with 2.8 g. of ethyl trimethylacetate in ether solution. After two hours' heating under a return condenser the mixture was decomposed with cold water. The product was recrystallized from ether and petroleum ether. The yield was 5.5 g.; the melting point was 129–130°.

Anal. Calcd. for $C_{24}H_{28}O$: C, 88.7; H, 7.2. Found: C, 88.8; H, 7.5.

In the preparation of the carbinol from the ketone and tertiary-butylmagnesium chloride a number of interesting phenomena were observed which are worthy of further study. When the finely ground solid ketone (di-diphenyl ketone) was added to the Grignard reagent, it dissolved at once forming a bright green solution with evolution of heat. The color of this solution fades rather rapidly to a yellowish orange; even an excess of ketone fails to make the green color permanent. The yellow solution when treated with water gives a very small quantity of carbinol (5% yield) and the rest of the material as unchanged ketone. Boiling the solution for many hours with and without the addition of benzene, toluene or xylene or even heating to 150° in ether in a sealed tube for eight hours failed to increase the carbinol yield to more than 10%; the amount of recovered ketone, however, diminished, non-crystalline products taking its place.

Tert-butyl-di-(diphenyl)-chloromethane.—Thionyl chloride (2 g.) and 5.5 g. of carbinol were allowed to interact at −15° for several hours. After warming to room temperature and standing one day the slight excess of thionyl chloride was removed by evacuation of the container; dry ether was added and removed by evacuation several times. The residue crystallized from a concentrated ether solution and was recrystallized from a mixture of ether and petroleum ether. The yield was 5.3 g.; the crystalline solid melted at 105–106°. Recrystallization from boiling benzene resulted in the formation of considerable quantities of the higher melting chloride; this is also formed in considerable quantities if the action of thionyl chloride takes place at 25°.

Anal. Calcd. for $C_{29}H_{27}Cl$: C, 84.7; H, 6.6. Found: C, 84.8; H, 6.1.

Higher Melting Isomeric Chloride.—In addition to the methods of preparing this substance mentioned in the preceding paragraph, another source may be noted. The treatment with thionyl chloride of the viscous residues from the interaction of *tert*-butyl magnesium chloride with di-diphenyl ketone yielded a small amount of material. It melted at 181° and differs from the lower melting isomer by being practically insoluble in ether.

Anal. Calcd. for $C_{29}H_{27}Cl$: C, 84.7; H, 6.6. Found: C, 84.9; H, 6.9.

Tert-butyl-di-(diphenyl)-acetic Acid.—A solution of 2 g. of the chloride (m. p. 105–106°) in dry ether was shaken with 40% amalgam in dry nitrogen for twenty-four hours. During the first stages of the reaction it was necessary to cool the flask as considerable heat was evolved. The deep red solution of the sodium compound was treated with dry carbon dioxide and the acid isolated in the usual manner. It was first obtained in an amorphous condition by precipitating from an ethereal solution with petroleum ether. This material yielded a crystalline substance when crystallized from glacial acetic acid. The yield of crystalline acid was 0.8 g. which melted at 178–181° after recrystallization from acetic acid.

Anal. Calcd. for $C_{30}H_{28}O_2$: C, 85.7; H, 6.7. Found: C, 85.7; H, 6.9. *Neutral equivalent* (with sodium hydroxide). Calcd.: 420. Found: 383, 382. Molecular

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[5] Ziegler and Colonius, *Ann.*, **479**, 147 (1930).

weight (micro method in camphor), 390. Attempts to obtain a crystalline methyl ester were unsuccessful.

Tert-butyl-di-(diphenyl)-methane.—The red sodium derivative from 2 g. of chloride was decomposed with moist ether. In this way 1 g. of crystalline product was obtained which melted at 178–179°.

Anal. Calcd. for $C_{29}H_{28}$: C, 92.7; H, 7.3. Found: C, 92.8; H, 7.5.

Di-tert-butyltetradiphenylethane.—For the preparation of this compound a special apparatus was constructed which consisted of a Pyrex tube 30 cm. long and 3 cm. wide to which was attached a 4-mm. slanting bore stopcock, an 8-mm. Pyrex tube side-arm, and a bulb of 3 cm. diameter, by means of a piece of 2 mm. capillary tubing; at the other end was attached an 8-mm. slanting bore stopcock; 2.5 g. of the low melting chloride was put in the apparatus against a stream of pure dry nitrogen; this was followed by 50 cc. of dry ether, and 5 cc. of 40% sodium amalgam. The nitrogen entered at the small upper stopcock while the lower large one was closed. After sealing off the side-arm the apparatus was evacuated and filled with pure nitrogen. The mixture was then shaken by hand with frequent cooling until no more heat was evolved; then it was shaken on the machine for another twenty-four hours. The amalgam was then decanted into the attached bulb and removed by sealing it off. Then an ether solution of 1–1.5 g. of tetramethylethylene dibromide was slowly added until the deep red color of the sodium derivative changed to the orange color of the free radical. The lower stopcock of the apparatus was then attached through a one-holed rubber stopper to a sintered glass Gooch crucible with attached stopcock, which was in turn connected to a special crystallization apparatus by means of another one-holed rubber stopper. The crystallization apparatus consisted of two 200-cc. round-bottomed flasks joined together by a short piece of 20-mm. Pyrex tubing which contained an alundum filter plate. One of the flasks, which was attached to the Gooch crucible, had a stopcock sealed on to permit of evacuation and refilling with nitrogen; the other was closed with a solid rubber stopper. Preliminary experiments showed that the hydrocarbon was very sensitive to oxygen and acids, the latter stimulating disproportionation reactions. To avoid this as far as possible, all of the apparatus was washed with a solution of ammonium hydroxide and dried in a vacuum, and where possible heated to drive out all moisture or adsorbed gases. The rubber stoppers employed were of new stock and were boiled in dilute sodium hydroxide, washed with distilled water, and dried over calcium chloride in a desiccator that had been evacuated, filled with pure nitrogen and then re-evacuated. The crystallizing apparatus and Gooch crucible were carefully evacuated and filled with pure nitrogen several times and then finally evacuated to a pressure of about one millimeter of mercury. Then the large stopcock was opened and the solution filtered into the crystallization apparatus free from the suspended sodium chloride and bromide. The apparatus was then tilted and the solution filtered into the second flask through the alundum disk. The Gooch crucible was removed and its place taken by a solid rubber stopper; during this operation a rapid stream of nitrogen was run into the apparatus and out the neck of the first flask to prevent back diffusion of air. The solution was concentrated by evacuation to induce crystallization. After standing for two hours to ensure complete crystallization the liquid was filtered from the crystals into the first flask through the alundum disk, where it was evaporated to dryness. The solid was transferred to a storage flask in a box filled with carbon dioxide.

The product was a mass of orange crystals weighing about one gram. The compound melted at 136–137° to a deep ruby red melt, under nitrogen; as the temperature was further raised the color faded between 145 and 150° and the mass solidified. At 160° it again began to melt and was completely melted at 175°. The methane, which is one of the products of a disproportionation reaction, melts at 178–179°. Obviously a very rapid disproportionation reaction proceeded at 150°.

The compound and its solutions are very sensitive to atmospheric oxygen; momentary exposure invariably results in immediate decolorization and consequent loss of activity. Therefore great care had to be taken in the manipulation of the product.

Anal. Calcd. for $C_{58}H_{54}$: C, 92.7; H, 7.3. Found: C, 91.5, 91.2; H, 7.7, 7.0. Molecular weights: Cryoscopic in benzene. Calcd. for $C_{58}H_{54}$, 750; for $C_{29}H_{27}$, 375. 43.5 g. of solvent (50 cc.), subs. 0.2086 g., $\Delta t = 0.052°$, m. w. = 473; 21.75 g. of solvent (25 cc.), subs. 0.1154 g., $\Delta t = 0.055°$, m. w. = 490. These values correspond to a degree of dissociation of 0.74 and 0.69, respectively.

Reactions of Di-tert-butyl-tetra-(diphenyl)-ethane. (a) Oxygen Absorption.—0.292 g. of crystalline ethane dissolved in bromobenzene absorbed 9 cc. of oxygen practically instantaneously (calcd. for 1 mole O_2, 9.5 cc.); after five minutes 10.1 cc., after two hours 13.8 cc. and after four hours 170% of one mole; there was no further absorption. In another similar experiment 0.226 g. absorbed 1.5 moles of oxygen in three hours and 0.14 g. of di-(diphenyl) ketone was recovered from the solution.

(b) Cleavage with Alkali Metals.—0.1 g. of the ethane was treated with an excess of 40% sodium amalgam in ether under nitrogen. After a few minutes' shaking the characteristic red color of the sodium derivative appeared. Carbonation yielded the same acid as formed from the chloride; it was identified by melting point, and by mixed melting with known acid. Another experiment was made using 1% amalgam in place of the 40% amalgam, and yielded identical results.

(c) Color Changes on Heating and Cooling.—About 0.1 g. of the ethane was sealed up in an inert atmosphere with 20 cc. of pure toluene. The solution had a bright red-orange color. Heating to 50° intensified the color and cooling to room temperature again diminished it. Cooling to −78° did not completely remove the color but did change it to a pale yellow orange. Cooling to the temperature of liquid air did, however, remove completely the red component and left the frozen solution a pale yellow. Warming the mixture to room temperature always restored the color. Heating the solution to 80° produced a momentary intensification which was immediately followed by a fading to a pale yellow which persisted and was not influenced by changes in temperature.

(d) Decomposition of the Ethane in Solution.—About 0.1 g. of the ethane was dissolved in 20 cc. of oxygen-free benzene and sealed up in an atmosphere of nitrogen. It was then placed in the dark at room temperature and allowed to remain in that condition in order to observe whether any spontaneous change or disproportionation took place in solution at room temperatures. After twenty-four hours the color had faded to about one-fourth of its original intensity. After two days the red component of the color was gone and the solution was of a pale yellow color. In another experiment the solution of 0.123 g. of the ethane in 50 cc. of benzene was heated to 45°; the color had faded to one-fourth of its original intensity by the end of an hour and a half, and was completely gone after two and two tenths hours. The solution was evaporated to dryness, redissolved in ether and concentrated to induce crystal formation. The product was 0.065 g. of a crystalline material which after recrystallization melted at 173–175°. It was identified as *tert*-butyl-di-(diphenyl)-methane by mixed melting point. The remaining mother liquor was evaporated to dryness and redissolved in ether in an attempt to get a crystalline product. Only an oil remained that decolorized small amounts of a chloroform solution of bromine. In another experiment 0.1154 g. of the ethane was dissolved in 25 cc. of benzene in the molecular weight apparatus, the molecular weight was, by the freezing point lowering, 490. This solution was allowed to stand for fifteen hours, after which its color had lost about three-fourths of its original intensity, and then heated to 45° and kept there until the color was completely gone. The molecular weight of the dissolved material was again taken and indicated a value of 236. The theoretical value for disproportionation into two molecules is 375, and into three molecules, 250. Thus, more than two fragments appear to be formed in the process.

Cyclohexyl-di-(diphenyl)-carbinol.—A solution of 10 g. of *p*-bromodiphenyl was added to 0.6 g. of metallic lithium, in the same manner as described for the preparation of the *tert*-butyl analog. After this reaction was over, the mixture was treated with a solution of 3.1 g. of methyl hexahydrobenzoate dissolved in dry ether. The reaction mixture, after refluxing for two hours, was decomposed with cold water and worked up in the usual way. The yield was 7 g. of a crystalline product which, after recrystallization from ether and petroleum ether, melted at 126–127°.

Anal. Calcd. for $C_{31}H_{30}O$: C, 88.9; H, 7.2. Found: C, 88.6, 89.2; H, 6.8, 7.4.

Methyl Ether of Cyclohexyl-di-(diphenyl)-carbinol.—The carbinol (0.5 g.) was dissolved in the minimum amount of cold methyl alcohol, and enough sulfuric acid dissolved in a little methyl alcohol was added to make the total acid concentration about 2.5% by weight. After a few hours, crystals started to form, and at the end of twenty-four hours crystallization was complete. The yield was 0.5 g. of white needles melting at 140–141°; recrystallization from boiling methyl alcohol raised the melting point to 141.5–142.5.

Anal. Calcd. for $C_{32}H_{32}O$: C, 88.8; H, 7.5. Found: C, 88.8; H, 7.7. Methoxyl calcd., 7.35. Found, 7.2.

Di-cyclohexyltetradiphenylethane.—The procedure was identically that used in the preparation of the tertiary butyl analog. Two grams of the ether was used with 5 cc. of the 40% sodium amalgam. The mixture was shaken on a machine for twenty-four hours. The deep violet color of the sodium compound was discharged with a solution of tetramethylethylene dibromide in ether. The solution changed in color to a deep orange which faded after half an hour to a very pale yellow-orange. The latter color change was accompanied by the deposition of a mass of stringy crystals which would not redissolve in ether and which were completely inactive to oxygen. Approximately 0.5 g. was formed. The residual ether solution, on concentration out of contact with air, deposited another half gram of an ether-soluble crystalline material which was likewise inactive to oxygen. Therefore neither of these substances could be the desired ethane. The nature of the apparent disproportionation products was not determined.

Summary

1. Di-*tert*-butyl-tetradiphenylethane has been prepared from sodium *tert*-butyldidiphenylmethyl. This was formed by the treatment of the corresponding chloride with an excess of 40% sodium amalgam.

2. Di-*tert*-butyltetradiphenylethane absorbs oxygen rapidly in solution at room temperature; the oxidation product formed is di-diphenyl ketone. The solutions of the ethane are highly colored even at 0° and readily undergo a reversible color change. Heating for a few hours at 45° or allowing to stand at room temperature for two days causes a disproportionation with concomitant loss of color and activity. The molecular weight of the ethane in dilute solution indicates a degree of dissociation of from 0.69 to 0.74.

3. A solution of di-cyclohexyl-tetradiphenylethane has been prepared and found to undergo disproportionation so rapidly that the isolation of a solid compound was impossible. The color of the solution indicated considerable dissociation in dilute solution at room temperature.

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