[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

DI-TERTIARY-BUTYLTETRAPHENYLETHANE

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A study of dialkyl dixanthyls[1] has shown the effectiveness of secondary alkyl groups in promoting the dissociation into free radicals of derivatives of dixanthyl. The close relationship between dixanthyl and tetraphenylethane would lead one to expect that the substitution of secondary and tertiary groups in this hydrocarbon would give rise to compounds with a dissociable carbon to carbon linkage. Only two such compounds have been reported in the literature. One, dicyclohexyltetraphenylethane, was prepared by Ziegler[2] in an impure condition in the course of his extensive study of dialkyl-tetraphenylethanes. Its behavior toward oxygen and halogens indicated that it contained a reactive carbon to carbon linkage. The author reported these results with some reserve because of the difficulty of obtaining an analytically pure sample and because the cleavage with sodium-potassium alloy and carbon dioxide did not result in the formation of the expected diphenylcyclohexylacetic acid. The other compound, di-*tert.*-butyltetraphenylethane was mentioned in a paper by Schlenk,[3] who stated that it did not have the "Dissoziations fähigkeit" of the hexa-aryl ethanes. This statement is surprising both in view of Ziegler's results and those obtained in this Laboratory with dixanthyl derivatives.

Schlenk prepared his compound by the action of molecular silver on a chloride, $(C_6H_5)_2CC_4H_9Cl$, which melted at 103–106°; no description of the ethane was given beyond a statement of its method of preparation.

The identity of Schlenk's hydrocarbon is very questionable. Marvel[4] has shown that the chloride which Schlenk employed is $(C_6H_5)_2C(CH_3)$-$CCl(CH_3)_2$, since it can be prepared by the addition of hydrogen chloride to diphenyl-3,3-methyl-2-butene-1 $(C_6H_5)_2C(CH_3)_2C(CH_3)=CH_2$. The structure of this hydrocarbon was definitely established. Mme. Ramart-Lucas[5] had previously shown that two isomeric chlorides may be obtained from *tert.*-butyldiphenylcarbinol. The lower melting (71–72°) is obtained directly from the carbinol at room temperature by the action of thionyl chloride; the other is obtained by dehydrating the carbinol and adding hydrogen chloride to the unsaturated hydrocarbon. The higher melting chloride may also be obtained by heating the carbinol with acetyl chloride

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[1] Conant, Small and Sloan, THIS JOURNAL, **48**, 1743 (1926).

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

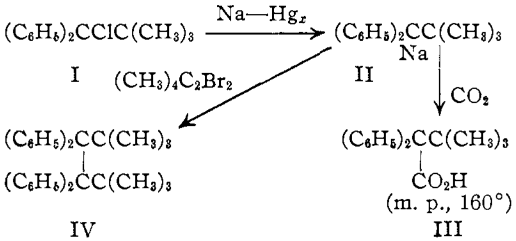
[3] Schlenk and Racky, *Ann.*, **394**, 201 (1912).

[4] Bateman with Marvel, THIS JOURNAL, **49**, 2914 (1927).

[5] Ramart-Lucas, *Compt. rend.*, **154**, 1088 (1912); *Ann. chim. phys.*, [8] **30**, 367, 390 (1913).

(Schlenk's method); its formation in this case involves a Wagner rearrangement. Marvel attempted the preparation of di-*tert.*-butyltetraphenylethane from the low melting chloride but obtained only diphenyl-3,3-methyl-2-butene-1.

Since *tert.*-butyldiphenylchloromethane (I) (m. p. 71–72°) easily undergoes rearrangement to the isomeric chloride, it is obviously necessary to use some reagent to remove the chlorine atom which will act very rapidly at low temperature. Forty per cent. sodium amalgam or a large excess of sodium-potassium alloy are both effective; the former is much more convenient. When a 20% solution of the low melting chloride is shaken in dry ether in nitrogen with either of these reagents at 0–10°, a vigorous reaction ensues and a brick red, metallic derivative (II) is soon formed. This metallic derivative may be isolated in the usual manner. On treatment with carbon dioxide it yields an acid (m. p. 160°) whose analysis and molecular weight (determined with the *p*-nitrobenzyl ester) correspond to *tert.*-butyldiphenylacetic acid (III). The metallic derivative may be coupled to the corresponding ethane by treating with tetramethylethylene dibromide (Ziegler's procedure). The substance obtained is very sensitive to oxygen and must be manipulated by the procedure employed in handling dissociable ethanes. It is a colorless solid (m. p. 138–141°) whose analysis and molecular weight correspond to di-*tert.*-butyltetraphenylethane (IV). On shaking an ethereal solution of this hydrocarbon with 40% sodium amalgam, a brick red metallic derivative was formed which with carbon dioxide yielded *tert.*-butyldiphenylacetic acid (m. p. 160°).



It is important to establish that the red metallic derivative formed from the low melting chloride is really a primary product of the reaction of this chloride and is not derived from the isomeric chloride which might be the result of a rearrangement. It was found that the high melting chloride when shaken with sodium-potassium alloy in ether yields a metallic derivative which is entirely different from that produced from the low melting isomer. Both the high melting chloride and the corresponding unsaturated hydrocarbon (diphenyl-3,3-methyl-2-butene-1) form the same dark red potassium compound. On treating with carbon dioxide this yields an acid of the same composition as *tert.*-butyldiphenylacetic acid but with entirely different properties (m. p. 217° as compared with 160°). No crystalline esters could be prepared for molecular weight determinations. An amorphous *p*-nitrobenzyl ester showed a molecular weight double that of the corresponding ester of *tert.*-butyldiphenylacetic acid; this indicates that the acid in question has the formula $C_{36}H_{40}O_4$. On treating with Ziegler's reagent or mercuric chloride, an oil is obtained which is not sensitive to oxygen. On treatment with sodium-potassium alloy, this oil regenerates the dark red metallic derivative as shown by the action of carbon dioxide, which yields the acid melting at 217°.

Thus, in its color and all its reactions, the metallic derivative formed from the high melting chloride or unsaturated hydrocarbon differs from the substance which is formed from the low melting chloride. This fact eliminates the possibility that the product formed by the action of sodium-potassium alloy or sodium amalgam on the true *tert.*-butyldiphenylchloromethane (low melting chloride) may be derived from its rearrangement products. We have not yet completed our study of the action of sodium-potassium alloy on the high melting chloride and will reserve for another paper a further discussion of this interesting reaction.

If an insufficient amount of sodium-potassium alloy is employed in the preparation of potassium *tert.*-butyldiphenylmethyl, the yield is much lowered and about half of the chloride is converted into a hydrocarbon isomeric with di-*tert.*-butyltetraphenylethane. The substance is not sensitive to oxygen and does not react with sodium-potassium alloy in ether after twelve hours' shaking. It seems probable that this hydrocarbon is comparable to Chichibabin's hydrocarbon (*p*-benzhydryltetraphenylmethane) which is formed by the action of metallic sodium on triphenylchloromethane.[6] The use of a 40% sodium amalgam (a liquid) avoids its formation and it is for this reason that this reagent is preferable to sodium-potassium alloy.

Properties of Di-*tert.*-butyltetraphenylethane

The new hydrocarbon is very similar in its reaction to dibenzyldixanthyl and it is clear that it contains a very labile carbon to carbon linkage. Thus, at 20° in bromobenzene it absorbs the theoretical amount of oxygen in four minutes but no peroxide could be isolated. At the same temperature it reacts with 40% sodium amalgam in benzene and ether at an appreciable rate, but not with 1% amalgam in ether; this behavior classes it with the primary alkyl dixanthyls and distinguishes it from ethanes such as hexaphenylethane[7] which are considerably dissociated in solution at room temperature. Even its dilute solutions were only very faintly colored at 25°; the difference between the slight colors of a 0.0125 molar

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[6] Schlenk and Marcus, *Ber.*, **47**, 1664 (1914).

[7] Conant and Garvey, THIS JOURNAL, **49**, 2599 (1927).

solution at 30° and 0° however, was definite. A 0.05 molar solution on warming to 50° became lemon yellow; on cooling the color faded. This could be repeated a number of times. At 100° the color was brighter and seemed to represent the maximum, since a similar experiment at 130° gave no deeper shade. If the solutions are kept at 100° or higher for more than a few minutes they acquire an orange-yellow color which does not fade on cooling. This permanent color is apparently connected with the rapid decomposition of the ethane at elevated temperatures. This decomposition was studied by molecular weight determinations by the freezing point method in *p*-chlorotoluene (in the complete absence of oxygen). Six minutes' heating at 100° of a 5% solution was sufficient to lower the apparent molecular weight from 390 to 266 and twelve minutes at the same temperature lowered it to 227 (theoretical value for complete cleavage 223); further heating was without effect. We have not been able to isolate and identify the products of this thermal decomposition but it is presumably a disproportionation reaction; this reaction seems to be characteristic of free radicals which contain alkyl groups attached to the methyl carbon atom.

A comparison of the facts summarized above with the well-known behavior of hexaphenylethane shows that the tertiary butyl group is somewhat less effective than the phenyl group in promoting dissociation. At room temperature the dilute solutions of di-*tert.*-butyltetraphenylethane must contain less than a few per cent. of the free radical; at 50°, however, the amount of the dissociated form is certainly appreciable. As a rough basis of comparison, we estimate that in a 0.05 molar solution the following substances are just appreciably dissociated (a few per cent.) at the following temperatures: hexaphenylethane, 0°; di-*iso*propyldixanthyl, 0°; di-*tert.*-butyltetraphenylethane, 50°; dibenzyldixanthyl (and di-*iso*butyl dixanthyl), 75°; dibutyldixanthyl, 130°. If the temperature coefficient of the logarithm of the equilibrium constant is nearly alike for all these substances, these temperatures are a measure of the relative free energy of dissociation in solution.

It has long been known that the xanthyl group is considerably more effective than two phenyl groups in causing dissociation. The fact that di-*iso*propyldixanthyl is appreciably dissociated at 0° and di-*tert.*-butyltetraphenylethane only at 50° is thus consistent with the idea that secondary and tertiary alkyl groups are approximately equivalent in their dissociating influence. Unfortunately no facts are as yet available which enable us to make a direct comparison of these two classes of alkyl groups. It may be pointed out in conclusion that the somewhat greater influence of the phenyl group as compared to the tertiary butyl group may not reside in the unsaturated nature of the phenyl group. If the presence or absence of hydrogen atoms in the α- and β-positions are a determining factor, one should really compare the phenyl group with such a tertiary group as $C(CH(CH_3)_2)_3$. The accumulation of evidence in recent years certainly points to the conclusion that the lability of a carbon–carbon linkage is to a large extent a function of the branching of the carbon chain with the corresponding elimination of hydrogen atoms in critical positions.

Experimental Part

***Tert.*-butyldiphenylcarbinol and *Tert.*-butyldiphenylchloromethane.**—The carbinol was prepared by three different methods: by the reaction of *tert.*-butylmagnesium chloride on benzophenone, by the reaction of phenylmagnesium bromide on trimethylacetophenone and by the reaction of phenylmagnesium bromide on ethyl trimethylacetate.[3,4] The latter method proved the most satisfactory. The preparation of the chloride followed the directions of Mme. Ramart-Lucas.[5] From 10 g. of carbinol and 6.0 g. of thionyl chloride, 8.5 g. of chloride melting at 71° was obtained; at no time in the preparation was the material heated above room temperature.

Preparation of *Tert.*-butyldiphenylmethyl Sodium.—Five grams of the low melting chloride was dissolved in 25 cc. of dry ether in a side-arm test-tube and to this solution was added 10 cc. of 40% sodium amalgam. The air in the test-tube was replaced with pure nitrogen and the tube shaken by hand, with frequent cooling in an ice-bath. The reaction was very brisk, heat was given off and a gray suspension of sodium chloride was rapidly formed. In about five minutes the characteristic brick red color of the sodium derivative appeared. This grew rapidly deeper and the solution became quite thick. The tube was then shaken for about twelve hours on a machine. The sodium derivative is somewhat soluble in ether but is almost insoluble in petroleum ether; it may be partially purified by washing with this solvent.

***Tert.*-butyldiphenylacetic Acid.**—The sodium compound formed from 5 g. of low melting chloride was decomposed with carbon dioxide and the acid isolated in the usual manner. The freshly precipitated, amorphous acid tended to sinter together into a gummy mass; hence the precipitation, washing and filtration were done in chilled solutions and as rapidly as possible. The yield of crude acid was 3 g., about 60%. The acid may be recrystallized from a mixture of methyl alcohol and water. It melts at 160°.

Anal. Calcd. for $C_{18}H_{20}O_2$: C, 80.5; H, 7.4. Found: C, 80.6, 80.3; H, 7.5, 7.4.

Combining weight with NaOH. Calcd. for $C_{28}H_{20}O_2$, 268. Found: 271, 264, 268.

***p*-Nitrobenzyl Ester.**—The *tert.*-butyldiphenylacetic acid was converted into the *p*-nitrobenzyl ester by warming for one hour on the steam-bath an alcoholic solution of the sodium salt with *p*-nitrobenzyl bromide. The ester was recrystallized from alcohol; it melted at 77°; 1.6 g. of acid yielded 1.5 g. of ester.

Anal. Calcd. for $C_{25}H_{25}O_4N$: C, 74.4; H, 6.25. Found: C, 74.2; H, 6.5.

Mol. Wt. (by the cryoscopic method in benzene). Benzene, 9.39 g.; calculations from the second increment. Subs., 0.1949: Δt = 0.274°, m. w. = 388; subs., 0.1595, Δt = 0.222°, m. w. = 392. Calcd. for $C_{25}H_{25}O_4N$: 403.

Di-*tert.*-butyltetraphenylethane, $C_4H_9(C_6H_5)_2CC(C_6H_5)_2C_4H_9$.—The preparation of the sodium derivative was carried out in a 500-cc. round-bottomed flask to which a side tube and stopcock were attached at right angles to the mouth. The side tube is bent below the stopcock at 45°. In this flask 5 g. of the low melting chloride was dissolved in 50 cc. of dry ether and 15 cc. of 40% sodium amalgam was added. In the mouth of the flask was placed a cloth filter backed by copper gauze, the filter being held in place by a cork ring which fitted tightly into the neck of the flask. The mouth of the tube was closed by a one-holed rubber stopper fitted with a glass stopcock.

The air in the flask was removed by evacuation and replacement with pure, dry nitrogen; the flask was shaken vigorously by hand, with cooling in ice as necessary. In about five minutes the red color of the sodium derivative appeared, the suspension in the flask becoming quite thick. At this point the shaking was carried on in a shaking machine; this was continued for about sixteen hours.

At the end of this time the reaction was considered complete; the excess amalgam was removed by suction through the side arm. Twenty-five cc. of low boiling petroleum ether was added to decrease the solubility of the sodium derivative, the mother liquors were removed by filtration with suction through the cloth filter and the filter cake was washed with petroleum ether. The flask was immersed in an ice-bath with the rubber stopper uppermost and 25 cc. of dry ether sucked in through the filter. Tetramethyl ethylene bromide (1.5–2.5 g.) dissolved in 10 cc. of dry ether was then added in small portions with constant shaking. The course of the reaction was followed by the change of color from red to colorless.

The colorless solution of the ethane was filtered from the sodium bromide in an atmosphere of nitrogen. The solution was concentrated by evaporation under diminished pressure until crystals of the ethane began to form. An equal volume of petroleum ether was added and the crystallization of the ethane made as complete as possible by cooling to -10 °. The crystals were filtered off in an atmosphere of nitrogen, washed with small quantities of petroleum ether and dried at room temperature in a stream of nitrogen. The apparatus was then opened to the air and the solid transferred to a Fischer pistol in which it was kept in an atmosphere of nitrogen. All the manipulations except the final transfer were carried out in an atmosphere of nitrogen carefully freed from oxygen and moisture. A slight modification of the usual type of apparatus employed in such work made possible the filtration from the sodium bromide and the crystallization of the ethane.

The ethane was recrystallized from a mixture of ether and petroleum ether in an atmosphere of nitrogen. It melted at 138–141° in nitrogen to a red melt; in air it melts at 40–50°. It is stable indefinitely in the dark under pure dry nitrogen and is not affected by subdued daylight. In the air the dry crystals become slightly sticky in about a half hour, and in twelve to eighteen hours it turns into a sticky brown mass. The weight of the sample decreases during this process; in sixteen hours the sample loses about 2% of its original weight. In two instances the crystals, on being removed from the recrystallizing machine, decomposed almost instantaneously to a yellow oil; white fumes smelling something like benzophenone were given off, and the oil became too hot to touch. The whole yield did not undergo this decomposition; the unchanged powder, guarded from contact with the oil, usually, although not always, did not decompose, but if any part of a sample came in contact with the oil, it decomposed in turn. This decomposition may be due to impurities or to moisture. In one of the cases in which the formation of the oil occurred, the sample had been dried for only a half hour; however, a small sample of the pure ethane slightly moistened with petroleum ether did not decompose on short exposure to air.

Anal. Calcd. for $C_{34}H_{38}$: C, 91.4; H, 8.6. Found: C, 90.6, 91.6; H, 8.5, 9.0.

Molecular weight (cryoscopic in an atmosphere of nitrogen). (a) Benzene (8.08 g. of solvent). Subs., 0.0766 g.: Δt = 0.125°, mol. wt. = 372; subs., 0.1491, Δt = 0.205°, mol. wt. = 440.

(b) In *p*-chlorotoluene (10.7 g.) (first increment disregarded). Subs., 0.2106 g.: Δt = 0.272°, mol. wt. = 404; subs., 0.1769 g.; Δt = 0.222°, mol. wt. = 418. Calcd. for $C_{34}H_{38}$ = 446.

Oxygen Absorptions.—The method used was the same as that employed in the previous work on free radicals in this Laboratory. The bottle containing the bromobenzene solution of the ethane and oxygen was shaken vigorously. The percentage oxygenation was calculated from the weight of the sample and the volume of oxygen corresponding to the formation of a peroxide. A 0.05 molar solution in bromobenzene absorbed oxygen at 14° at the following rate: two minutes, 70%; five minutes, 106%; eight minutes, 122%; twenty-five minutes, 126%; twenty hours, 165%. These results were reproducible within a few per cent. No peroxide could be isolated from the oxygenation in ether or other solvents.

Cleavage with Alkali Metals.—A determination of the activity of the ethane toward the alkali metals was carried out according to the method previously described.[7] The ethane was rapidly cleaved by sodium-potassium alloy in ether and also in benzene; it was not, however, acted on by 1% amalgam in ether. It was cleaved by 40% sodium amalgam in ether and also in benzene. In all these runs, 0.10 g. (0.00025 moles) of the ethane was placed in a small test-tube with a constricted neck. After the air in the tube had been displaced by pure dry nitrogen, 5 cc. of the solvent and 1 cc. of liquid alloy or amalgam were introduced through a separatory funnel. The tube was then sealed off at the constriction and shaken vigorously by hand for five minutes. In all cases in which color was reported, it developed practically at once; the tube containing the 1% alloy was shaken on a machine for twenty-four hours without the development of color. The metal derivative formed in all these cases, when decomposed with carbon dioxide, yielded the *tert.*-butyldiphenylacetic acid (m. p. 160°).

Color Changes on Heating.—A 0.05 molar solution of the ethane in ethyl benzoate in an atmosphere of nitrogen at room temperature showed a faint but definite coloration. When heated for thirty seconds in a water-bath at 50°, a light lemon-yellow color appeared. This color disappeared when the tube was plunged into an ice-bath. This could be repeated several times. A similar solution heated for thirty seconds at 100° was a bright lemon-yellow color; when the tube was immersed in ice and water the color vanished immediately. Heated again at 100° for two and one-half minutes, the color reappeared; on subsequent cooling the color faded but did not entirely disappear, indicating that the latter was due to a different cause. The color at 130° after forty-five seconds was the same shade as at 100°. If these solutions are heated to 100° for three hours, the yellow color first formed passes through a brownish-yellow into a bright orange color.

Decomposition of the Ethane in Solution on Heating.—The rate of disproportionation at 100° was measured by the decrease of apparent molecular weight in *p*-chlorotoluene by the cryoscopic method. The apparatus was of special construction and was kept filled with oxygen-free nitrogen. The results are tabulated below; the somewhat low initial molecular weight was probably due to the fact that the sample employed was only crystallized once.

TABLE I

DECOMPOSITION OF THE ETHANE ON HEATING

Sample, g.	Solvent, g.	Heating period Time, min.	Heating period Temp., °C.	Freezing point depression, °C.	Apparent mol. wt.
0.4078	10.70	0	20	0.547	390
.5241	10.70	3	100	.880	312
.5241	10.70	6	100	1.032	266
.5241	10.70	9	100	1.146	139
.5241	10.70	12	100	1.208	227
.5241	10.70	17	100	1.221	224
.5241	10.70	22	100	1.212	226

A sample removed at the end of the experiment had no oxygen absorption capacity. When heated to 100° for the first time, a bright yellow color was observed; on cooling this faded slightly but a marked color remained. After the first heating, no variation in color was observed between the hot and cold solutions. No orange color developed.

Isomeric Ethane.—Four and one-half g. of low melting chloride, dissolved in 40 cc. of dry ether, was shaken with 2 g. of sodium-potassium alloy for twenty-four hours. At the end of this time the solution had acquired a light red color. Carbon dioxide was introduced and the *tert.*-butyldiphenylacetic acid obtained in the usual manner. The ethereal layer containing the non-acid material yielded crystals on evaporation. These were washed with a little ether, filtered and recrystallized from alcohol and ether; yield, 1.7 g.; m. p. 145°.

Anal. Calcd. for $C_{34}H_{38}$: C, 91.4; H, 8.6. Found: C, 91.0; H, 8.52.

Mol. wt. by the freezing point method in 9.81 g. of benzene. Subs., 0.2748 g.: $\Delta t = 0.352°$, m. w. = 411; subs., 0.4122 g.: $\Delta t = 0.517°$, m. w. = 419. Calcd. for $C_{34}H_{38}$: m. w. = 446.

The substance did not react with oxygen or with sodium-potassium alloy after twelve hours' shaking in ether.

Potassium Derivative from Isomeric Chloride and from Diphenyl-3,3-methyl-2-butene-1.—The unsaturated hydrocarbon (diphenyl-3,3-methyl-2-butene-1) and the corresponding chloride were prepared according to Marvel's directions.[4] When a 20% solution of either of these substances in anhydrous ether was shaken with sodium-potassium alloy (2 g. per 25 cc. of solution), a dark red potassium derivative was formed. This substance was not identical with the red metallic derivative formed from *tert.*-butyldiphenylchloromethane, as the following experiments prove.

(a) **Decomposition with Carbon Dioxide.**—The suspension of the metallic derivative was treated with carbon dioxide and the acid obtained in the usual manner. It was precipitated from an aqueous solution of its sodium salt by the addition of mineral acid as a white, amorphous solid. The yield was about 32%. It could be recrystallized by solution in methyl alcohol at room temperature, addition of water to incipient turbidity and setting aside; m. p. 218–224° with decomposition.

Anal. Calcd. for $C_{18}H_{20}O_2$: C, 80.5; H, 7.4. Found: C, 80.8, 80.2; H, 7.61, 7.23.
Combining weight with NaOH, calcd. for $C_{18}H_{20}O_2$: 268. Found: 267, 258.

The *p*-nitrobenzyl ester was prepared by the action of *p*-nitrobenzyl bromide on an aqueous solution of the sodium salt of the acid. The ester was an amorphous yellow powder. All attempts to recrystallize it were unavailing.

Mol. wt. by the micro method in camphor. Subs., 0.0105 g.; camphor, 0.1141 g.: $\Delta t = 5.2°$, m. w. = 705; subs., 0.0273 g.; camphor, 0.1078 g.: $\Delta t = 14.6°$, m. w. = 695. Calcd. for $C_{50}H_{48}O_8N_2$: 804.

Attempts to prepare a crystalline methyl ester and an amide yielded only amorphous, gummy materials.

(b) **Decomposition with Tetramethylethylene Dibromide.**—When the metallic derivative was treated with tetramethylethylene dibromide in the manner described above, the color disappeared. The resulting ether solution on evaporation in nitrogen yielded an oil which failed to crystallize. This oil did not absorb oxygen at any measurable rate in bromobenzene solution. On shaking an ethereal solution of it with sodium-potassium alloy, the dark red metallic derivative was formed. On treating with carbon dioxide, the acid melting at 218–224° was obtained.

Summary

1. Di-*tert.*-butyltetraphenylethane has been prepared from sodium *tert.*-butyldiphenylmethyl. This was formed when the corresponding chloride was treated with a large excess of sodium-potassium alloy or 40%

sodium amalgam. No rearrangement was involved in this reaction since the isomeric chloride was shown to yield an entirely different metallic compound when treated with the alloy.

2. Di-*tert.*-butyltetraphenylethane absorbs oxygen rapidly in solution at 25°. On heating a dilute solution to 55° a reversible color change indicative of dissociation appears. On heating for a few minutes in solution at 100°, in the absence of air, it disproportionates completely. These results show that the effect of the tertiary alkyl group in promoting the dissociation of the carbon linkage is similar to the effect of the secondary groups studied in the dixanthyl series.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE POLARIMETRY SECTION, BUREAU OF STANDARDS, UNITED STATES DEPARTMENT OF COMMERCE]

RELATIONS BETWEEN ROTATORY POWER AND STRUCTURE IN THE SUGAR GROUP.

XVIII. ALPHA-METHYL *d*-LYXOSIDE TRIACETATE[1,2]

BY F. P. PHELPS AND C. S. HUDSON

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In Article VII[3] it was assumed that the alpha forms of methyl *d*-xyloside and *d*-lyxoside possess the same ring structure and the rotation of the latter was calculated from that of the former by use of the known difference of rotation between the alpha forms of methyl *d*-glucoside and *d*-mannoside, which at that time were supposed to have like ring structures. Subsequent results[4] indicated, however, that the glucoside possesses a 1,4-ring and the mannoside a 1,5-ring and consequently in Article XII[5] it was suggested that α-methyl *d*-lyxoside does not possess the 1,5-ring of methyl *d*-xyloside but rather a 1,4-ring. The 1,3-ring appeared to be excluded because 1,3-ring glycosides in the mannose and rhamnose series are hydrolyzed very rapidly by dilute acids, whereas α-methyl lyxoside is hydrolyzed far more slowly even by stronger acid solutions. It has now been sought to obtain further evidence on this question of the possibility of a 1,3-ring structure in α-methyl *d*-lyxoside by examining the behavior of its fully acetylated derivative, a triacetate, toward alkaline saponification. It has been found that the acetates of methyl mannoside[6] and methyl rhamnoside,[7] of the 1,3-ring type, retain one acetyl group (presumably that

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[1] Publication approved by the Director of the Bureau of Standards.

[2] Article XVII was published in THIS JOURNAL, **48**, 2435 (1926).

[3] Hudson, *ibid.*, **47**, 272 (1925).

[4] Hudson, *ibid.*, **48**, 1424, 1434 (1926).

[5] Phelps and Hudson, *ibid.*, **48**, 503 (1926).

[6] Dale, *ibid.*, **46**, 1046 (1924).

[7] Fischer, Bergmann and Rabe, *Ber.*, **53**, 2362 (1920).