Anal. Calcd. for $C_{17}H_{21}O_2NS$: S, 10.57. Found: 10.60, 10.60, 10.73.

N-Methyl-N-β-phenethyl-p-toluenesulfonamide, p-$CH_3C_6H_4SO_2NCH_3CH_2CH_2C_6H_5$, white crystals from ether-petroleum ether, m. p. 44–45°.

Anal. Calcd. for $C_{16}H_{19}O_2NS$: S, 11.08. Found: 11.04.

N-Di-p-toluenesulfonylbenzylamine, (p-$CH_3C_6H_4SO_2)_2NCH_2C_6H_5$, m. p. 161°.

Anal. Calcd. for $C_{21}H_{21}O_4NS_2$: S, 15.44. Found: 15.38.

N-Di-p-toluenesulfonyl-β-phenethylamine, $(CH_3C_6H_4SO_2)_2NCH_2CH_2C_6H_5$, m. p. 101°.

Anal. Calcd. for $C_{22}H_{23}O_4NS_2$: S, 14.94. Found: 14.93.

Summary

Data are presented on the preparation and on the base strengths of some amines.

CAMBRIDGE 38, MASSACHUSETTS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

THE STRUCTURE OF THE HYDROCARBON $C_{17}H_{18}$ OBTAINED BY THE DEHYDRATION OF *TERT.*-BUTYLDIPHENYLCARBINOL

BY DOROTHY E. BATEMAN[1] WITH C. S. MARVEL

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Some time ago Schlenk and Racky[2] reported the preparation of tetraphenyldi-*tert.*-butylethane and asserted that this product was a stable hydrocarbon which did not show any of the characteristics of the hexaarylethanes. The recent work of Conant and his students[3] on derivatives of dixanthyl has shown that certain aliphatic groups substituted for the hydrogens of what might be considered the ethane carbons in dixanthyl have almost as great a tendency to cause dissociation into free radicals as do phenyl groups in these positions. It has been shown that di-*sec.*-butyldixanthyl is dissociated to about the same degree as diphenyldixanthyl. One might expect from analogy then that a *tert.*-butyl group would have a strong tendency to produce dissociation. It would appear that the compound described by Schlenk needs to be reinvestigated, especially since his conclusions rest on rather incomplete experimental results.

In reviewing the subject in the literature it was found that Schlenk prepared diphenyl-*tert.*-butylmethyl chloride from diphenyl-*tert.*-butyl carbinol and acetyl chloride and obtained a product which melted at

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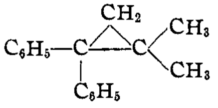
[1] This communication is an abstract of a thesis submitted by Dorothy E. Bateman in partial fulfilment of the requirements for the degree of Doctor of Philosophy, in Chemistry, at the University of Illinois.

[2] Schlenk and Racky, *Ann.*, **394**, 202, 211, 212 (1912).

[3] (a) Conant and Sloan, THIS JOURNAL, **47**, 572 (1925); (b) *ibid.*, **47**, 3068 (1925); (c) Conant, Small and Sloan, *ibid.*, **48**, 1743 (1926).

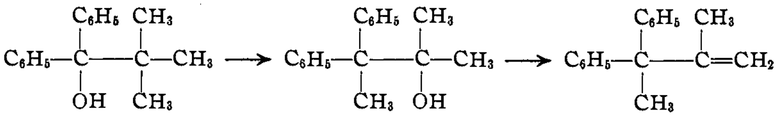
103–106°. About the same time Mme. Ramart-Lucas[4] prepared this carbinol and obtained from it two isomeric chlorides, one melting at 71–72° and the other at 108–109°. The lower-melting chloride on hydrolysis gave the original carbinol and must have had the corresponding structure. It was further observed that the carbinol was easily dehydrated to give a hydrocarbon $C_{17}H_{18}$ which would add hydrogen chloride to give the higher-melting chloride mentioned above.

The structure of the hydrocarbon was studied by Mme. Ramart-Lucas.[5] Several structures were suggested and disproved. Oxidation of the compound produced benzophenone, acetophenone and an acid which melted at 172–173° and to which from analyses the empirical formula $C_{17}H_{18}O_2$ was given. The structure which was favored seemed to be that of diphenyl-1,1-dimethyl-2,2-cyclopropane (I) which contained the cyclopropane ring. However, the above formula does not explain the formation of acetophenone as an oxidation product and it is difficult to conceive of its oxidation to an acid, $C_{17}H_{18}O_2$.



I

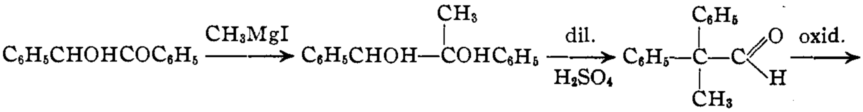
In order to draw any conclusions concerning the work of Schlenk, it seemed necessary first to establish the structure of this unsaturated hydrocarbon and of the higher-melting chloride which was used in his experiments. The structure for the hydrocarbon which seemed most probable in advance was that of diphenyl-2,3-methyl-2-butene-1 (II), which would be the dehydration product of the carbinol (III) that would be formed if the original carbinol, *tert.*-butyldiphenylcarbinol (IV), were to undergo a Wagner rearrangement.



$$C_6H_5\text{—}\underset{OH}{\overset{C_6H_5}{C}}\text{——}\underset{CH_3}{\overset{CH_3}{C}}\text{—}CH_3 \longrightarrow C_6H_5\text{—}\underset{CH_3}{\overset{C_6H_5}{C}}\text{——}\underset{OH}{\overset{CH_3}{C}}\text{—}CH_3 \longrightarrow C_6H_5\text{—}\underset{CH_3}{\overset{C_6H_5}{C}}\text{——}\overset{CH_3}{C}{=}CH_2$$

IV III II

In order to test this prediction, a sample of diphenyl-3,3-methyl-2-butene-1 was prepared by the following series of reactions



$$C_6H_5CHOHCOC_6H_5 \xrightarrow{CH_3MgI} C_6H_5CHOH\text{—}\overset{CH_3}{C}OHC_6H_5 \xrightarrow[H_2SO_4]{dil.} C_6H_5\text{—}\underset{CH_3}{\overset{C_6H_5}{C}}\text{—}C\left\langle{}^{O}_{H}\right. \xrightarrow{oxid.}$$

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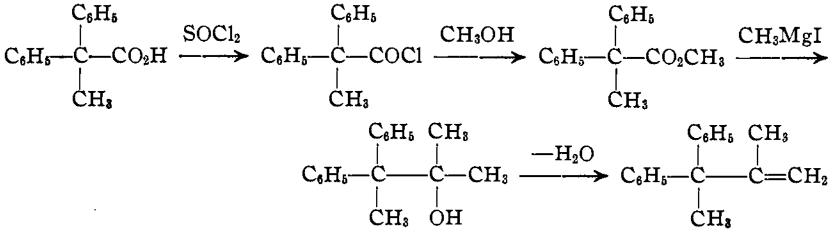
[4] Ramart-Lucas, (a) *Compt. rend.*, **154**, 1088 (1912); (b) *Ann. chim. phys.*, [8] **30**, 367, 390 (1913).

[5] Ref. 4 b, p. 406.

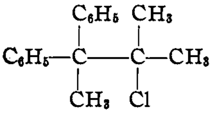


$$C_6H_5-\underset{CH_3}{\overset{C_6H_5}{C}}-CO_2H \xrightarrow{SOCl_2} C_6H_5-\underset{CH_3}{\overset{C_6H_5}{C}}-COCl \xrightarrow{CH_3OH} C_6H_5-\underset{CH_3}{\overset{C_6H_5}{C}}-CO_2CH_3 \xrightarrow{CH_3MgI}$$

$$C_6H_5-\underset{CH_3}{\overset{C_6H_5}{C}}-\underset{OH}{\overset{CH_3}{C}}-CH_3 \xrightarrow{-H_2O} C_6H_5-\underset{CH_3}{\overset{C_6H_5}{C}}-\overset{CH_3}{C}=CH_2$$

The diphenylmethylacetaldehyde was prepared from benzoin as described by Tiffeneau and Dorlencourt[6] and was oxidized with alkaline permanganate solution to diphenylmethylacetic acid. The esterification of this acid and the reaction of the ester with the Grignard reagent were carried out in the usual manner. The carbinol was not isolated but was dehydrated directly.

The hydrocarbon obtained in this way agreed in all of its properties with the one obtained by the dehydration of *tert.*-butyldiphenylcarbinol. In order to complete the identification, dry hydrogen chloride was added to both samples and a chloride melting at 102–106° was obtained in each case. There can be no further question concerning the constitution of the hydrocarbon. The higher-melting chloride obviously has the formula



$$C_6H_5-\underset{CH_3}{\overset{C_6H_5}{C}}-\underset{Cl}{\overset{CH_3}{C}}-CH_3$$

The structure thus established for the hydrocarbon explains how both acetophenone and benzophenone can be obtained on oxidation. However, this compound could not give a seventeen carbon atom acid on oxidation. It might be expected to give some diphenylmethylacetic acid. The acid obtained by Mme. Ramart-Lucas melted at 172–173°, which is the melting point of diphenylmethylacetic acid. Some difficulty was encountered in attempting to duplicate the chromic acid oxidation of the hydrocarbon. However, ozone easily oxidized it to the ketone, diphenylmethylacetone, which on oxidation with sodium hypobromite solution gave diphenylmethylacetic acid melting at 174°. This acid is identical with the sample prepared by the oxidation of diphenylmethylacetaldehyde. There seems to be very little question that the acid previously thought to have the formula $C_{17}H_{18}O_2$ in reality has the composition $C_{15}H_{14}O_2$.

Since in his work Schlenk[2] used the chloride melting at 106° in his Würtz reaction to prepare a hexa-substituted ethane, it is quite obvious that he did not obtain tetraphenyl-di-*tert.*-butylethane but probably a hydrocarbon of the structure.

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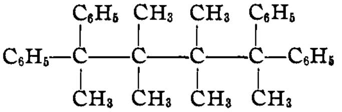
[6] Tiffeneau and Dorlencourt, *Ann. chim. phys.*, [8] **16**, 254 (1909).



$$\begin{array}{ccccccccccc} & & C_6H_5 & & CH_3 & & CH_3 & & C_6H_5 & & \\ & & | & & | & & | & & | & & \\ C_6H_5 & - & C & - & C & - & C & - & C & - & C_6H_5 \\ & & | & & | & & | & & | & & \\ & & CH_3 & & CH_3 & & CH_3 & & CH_3 & & \end{array}$$

A few attempts to couple the lower-melting chloride to give an ethane produced only the unsaturated hydrocarbon described before.

Experimental Part

Tert.-**Butyldiphenylcarbinol.**—The method of Schlenk[7] was used for this preparation. From 325 g. of phenylmagnesium bromide in 1 liter of dry ether and 114 g. of ethyl trimethylacetate there was obtained 135 g. of carbinol; b. p. 148–150° at 2.5 mm.; n_D^{20} 1.5748. The constants given by Mme. Ramart-Lucas[8] are n_D^{25} 1.57306; b. p. 178–180° at 11 mm.

Dehydration of *Tert.*-**Butyldiphenylcarbinol.**—In attempting to prepare the bromide from the carbinol, 24 g. of the latter was dissolved in 160 cc. of dry benzene and treated with 24 cc. of acetyl bromide. The mixture was allowed to stand for about 24 hours. The benzene was removed under reduced pressure and the residue distilled at about 3–3.5 mm. At this pressure the product boiled at 125–128°; d_4^{20} 1.0007; n_D^{20} 1.5730; M_D 73.03. The physical constants reported previously[9] are d_4^{25} 1.0031; N_D^{25} 1.57589; observed M_D 73.23.

A more convenient method of dehydration was found. Sixty g. of the carbinol and a few grams of *p*-toluenesulfonic acid were placed in a small flask and heated on a boiling water-bath for about two hours. The mixture was treated with ether and the *p*-toluenesulfonic acid was removed by washing with dilute sodium carbonate solution and water. The ether solution was dried over sodium sulfate, filtered and evaporated. The residue was distilled under reduced pressure. The yield was 45 g. (81% of the theoretical amount) of hydrocarbon boiling at 125–128° at 3–3.5 mm.

Diphenylmethylacetic Acid.—Diphenylmethylacetaldehyde was prepared according to the directions of Tiffeneau and Dorlencourt.[6] Benzoin and methylmagnesium iodide gave methyldihydrobenzoin in about 75% yields. This compound on rearrangement by boiling with 20% sulfuric acid solution gave diphenylmethylacetaldehyde in 60–70% yields.

In a flask fitted with a reflux condenser and mechanical stirrer were placed 136 g. of the aldehyde and a solution of 220 g. of potassium permanganate and 90 g. of sodium carbonate in 800 cc. of water. The mixture was refluxed with stirring until the color of the permanganate solution had disappeared. The solution was filtered to remove the manganese dioxide, extracted with ether to remove indifferent substances and then acidified with sulfuric acid. On filtering and drying, 80 g. of the acid was obtained. This was purified by recrystallization from 95% alcohol. The acid thus obtained weighed 61.5 g., melted at 172–174° and gave a neutral equivalent of 227.4 as compared with the calculated value, 226.

Methyl Diphenylmethylacetate.—A mixture of 59 g. of diphenylmethylacetic acid and 41 g. of thionyl chloride was refluxed on a steam-bath until solution was complete and no more sulfur dioxide and hydrogen chloride were being evolved. The excess thionyl chloride was removed by heating the reaction mixture under reduced pressure on a water-bath. About 20 g. of absolute methyl alcohol was added to the residue and the solution was refluxed for about four hours. It was then dissolved in ether and the

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[7] Ref. 2, p. 211.

[8] Ref. 4b, p. 367.

[9] Ref. 4b, p. 391.

solution was washed with sodium carbonate solution and water. The ether solution was dried over sodium sulfate, filtered and evaporated. The residue was distilled under reduced pressure and the portion boiling at 149–152° at 3 mm. was collected. The yield of ester was 46.5 g. (70% of the theoretical amount). It was a viscous liquid; n_D^{20} 1.5691; d_4^{20} 1.1206; M_D, calcd., 70.43; obs., 70.13.

Anal. Subs., 0.2030: CO_2, 0.6018; H_2O, 0.1220. Calcd. for $C_{16}H_{16}O_2$: C, 80.0; H, 6.67. Found: C, 80.89; H, 6.72.

Diphenyl-3,3-methyl-2-butene-1.—To 15 g. of magnesium turnings and 400 cc. of dry ether was added 90 g. of methyl iodide. When the Grignard reagent was formed, 45 g. of methyldiphenylmethylacetate was added, the mixture was allowed to stand for several hours and then refluxed on a water-bath for about one hour. The solution was treated with ammonium chloride solution to decompose the excess Grignard reagent and to dissolve the basic magnesium salts. The ether layer was separated and the aqueous layer was extracted with two small portions of ether. The ether solutions were combined, the ether was evaporated and the residual oil treated with about 5 g. of *p*-toluenesulfonic acid and heated to 125° for about 10 to 15 minutes. It was then dissolved in ether and the acidic material removed by washing the solution with dilute sodium carbonate solution. The ether was evaporated and the residue was refluxed with alcoholic potassium hydroxide solution to hydrolyze any unreacted ester. This solution was evaporated until the alcohol was removed and then water was added. The insoluble oil was collected in ether, the ether solution dried over sodium sulfate, filtered and evaporated. The residue was fractionated under reduced pressure and the main fraction collected at 132–133° at 4.5 mm.

Anal. Subs., 0.2067: CO_2, 0.6903; H_2O, 0.1488. Calcd. for $C_{17}H_{18}$: C, 91.89; H, 8.11. Found: C, 91.09; H, 8.05.

The physical constants of this hydrocarbon and of the one obtained by the dehydration of *tert.*-butyldiphenylcarbinol are as follows.

Table I

Physical Constants

Compound	B. p., °C.	d_4^{20}	n_D^{20}	M_D	
				Calcd.	Obs.
Diphenyl-3,3-methyl-2-butene-1	132–133 at 4.5 mm.	1.0060	1.5757	73.05	73.03
$C_{17}H_{18}$ from *tert.*-butyldiphenylcarbinol	125–128 at 3.5 mm.	1.0007	1.5730	...	73.08

A second fraction which boiled a little higher was collected. Its index of refraction was near that of the main fraction but analysis showed that it contained some oxygen.

The identification of the two hydrocarbons as samples of the same compound was completed by taking small samples of each in an absolute alcohol-ether solution and treating with dry hydrogen chloride. On standing the solid chloride separated and on recrystallization from alcohol and ether mixture it melted at 102–106° in each case. A mixed melting point showed no depression.

Ozonization of Diphenyl-3,3-methyl-2-butene-1.—A mixture of air and ozone was bubbled through a solution of 45 g. of the unsaturated hydrocarbon (obtained by the dehydration of diphenyl-*tert.*-butylcarbinol) in 200 cc. of glacial acetic acid for four hours.[10] More acetic acid was added from time to time to replace that lost by evaporation. The solution was then treated with water and the acetic acid neutralized with 20% sodium hydroxide solution. The ketone was collected in ether, the ether solution dried over sodium sulfate, filtered and evaporated. The ketone was distilled under reduced pressure. The yield was 32 g. of a yellow oil; b. p. 132–135° at 2 mm.; d_4^{20} 1.069; n_D^{20} 1.5748; M_D, calcd., 68.91; found, 69.21. This compound is described[11] as a solid melting at 41–41.5° and boiling at 310–311°. Our product did not solidify on standing for several days. It was analyzed as a check on its purity.

Anal. Subs., 0.2139: CO_2, 0.6703; H_2O, 0.1382. Calcd. for $C_{16}H_{16}O$: C, 85.71; H, 7.14. Found: C, 85.51; H, 7.23.

Oxidation of Diphenyl-3,3-butanone-2 to Diphenylmethylacetic Acid.—In a 500 cc. round-bottomed flask, fitted with a mechanical stirrer, was placed a solution of 16.5 g. of sodium hydroxide in 140 cc. of water. The solution was cooled to 0° in an ice-salt bath and to the well-stirred solution was added 24 g. of bromine. The temperature was held at 0° during this addition. To the cold solution 11.4 g. of diphenyl-3,3-butanone-2 was added and the mixture was cooled and stirred for about three hours and then allowed to come to room temperature and stirred for another three hours. The flask was fitted with a condenser for distillation and the solution was distilled as long as bromoform came over with the water. It was necessary to add water to the reaction mixture from time to time. When the hydrolysis was complete, the alkaline reaction mixture was extracted with ether to remove unoxidized ketone and then acidified with dilute sulfuric acid. The acid which precipitated was filtered and recrystallized from 95% alcohol. It then melted at 173–174° and when mixed with a sample of diphenylmethylacetic acid prepared from diphenylmethylacetaldehyde showed no depression in the melting point.

Attempts to Prepare Di-*tert*.-butyltetraphenylethane.—*Tert*.-butyldiphenylmethyl chloride was shaken with molecular silver in anhydrous toluene for long periods but the only product that could be isolated was the unsaturated hydrocarbon described above. It was also treated with magnesium in ether and then with cupric chloride. A brisk reaction occurred with magnesium but the unsaturated hydrocarbon was the only product that was isolated. The carbinol gave a deep red color with sulfuric acid but attempts to reduce the compound with vanadous chloride were unsuccessful.

Summary

1. The hydrocarbon $C_{17}H_{18}$ obtained by the dehydration of *tert*.-butyldiphenylcarbinol has been identified as diphenyl-3,3-methyl-2-butene-1.

URBANA, ILLINOIS

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[10] The procedure described by Noller with Adams, THIS JOURNAL, **48**, 1076 (1926) was followed.

[11] Thörner and Zincke, *Ber.*, **11**, 1989 (1878).