elemental amorphous carbon and boron. Additional corrections were made to fit the bomb combustion to the over-all process at 25°:

$$BCH_{(liq.)} + O_{2(gas,\ 1\ atm)} \longrightarrow CO_{2(gas,\ 1\ atm)} + H_2O_{(gas,\ 1\ atm)} + B_2O_{3(amorph)}$$

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[CONTRIBUTION FROM THE SANDERS LABORATORY OF CHEMISTRY, VASSAR COLLEGE]

Compounds Related to 2,3,4-Triphenylbutyric Acid[1]

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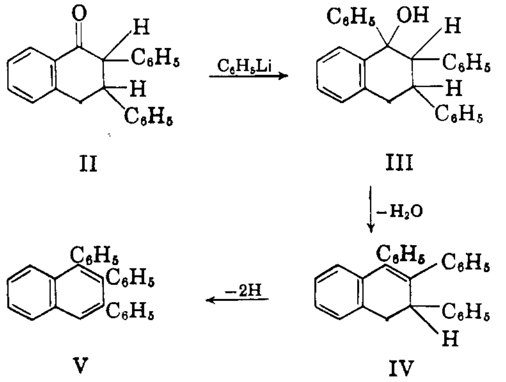
The structure of a by-product in the preparation of 2,3-diphenyltetralone from 2,3,4-triphenylbutyric acid, has been shown to be I. Various compounds related to the ester are described.

Several years ago, in the preparation of 2,3-diphenyltetralone[2,3] for use in other studies, traces of a compound I melting at 211–212° were obtained in several reactions. In one reaction in which the tetralone was prepared by treating 2,3,4-triphenylbutyryl chloride with anhydrous aluminum chloride, the yield of I was 18 g., 12% based on the weight of acid used. Analyses for carbon and hydrogen agreed with the values calculated for the tetralone but the molecular weight was much too high. Only one form of the tetralone, that melting at 147–148°, has been reported although many people have reported making it and diastereoisomers should be possible.

A series of reactions was planned which would test the hypothesis that I was an isomeric tetralone. The 147° tetralone II was treated with phenyllithium to give a new tertiary alcohol III. This alcohol was dehydrated to give the known 1,2,3-triphenyl-3,4-dihydronaphthalene[4] IV which was then dehydrogenated to give the known 1,2,3-triphenylnaphthalene[4] V. Earlier[3] the tetralone had been reduced to a secondary alcohol by aluminum isopropoxide and this alcohol had been dehydrated and dehydrogenated to give 2,3-diphenylnaphthalene.



These two series of reactions, applied to I, should have led to the same final products if I had been an isomeric tetralone. Aluminum isopropoxide was without effect on I. Phenyllithium reacted with I to give two products, neither of which could be dehydrated by heating with Lucas' reagent or with potassium hydrogen sulfate. Since I was not an isomeric tetralone, the problem was temporarily dropped.

Interest in I was aroused again when it was shown[5] that 2,3,4-triphenylbutyric acid could be cyclized by hydrogen fluoride to give a small amount of 2-phenyl-3-benzylindanone as well as the more common tetralone.

From the infrared spectrum of I, Dr. Gilbert Stork of Columbia University suggested to us that the carbonyl group might be presented as an ester. This proved to be the case. The ester resulted from the reaction of unconverted acid chloride with the enol form of the tetralone. The following chart shows the relationships of the compounds involved.

Hydrolysis of I led to the known acid VI and a neutral oil which could not be crystallized but whose infrared spectrum indicated that it was the known tetralone II. Reaction of I with phenyllithium gave the known ketone VIII[6] and a compound VII whose properties indicate that it may be isomeric with the ketone VIII. Ketone VIII was synthesized by the reaction of phenylmagnesium bromide on either the 87° or the 130° nitrile IX.[2,3] Mixed melting points showed no depression and the infrared spectra were the same. Under forcing conditions phenylmagnesium bromide also reacted with I to give VIII. The

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[1] Presented at the fall meeting of the American Chemical Society in Atlantic City in September 1959.

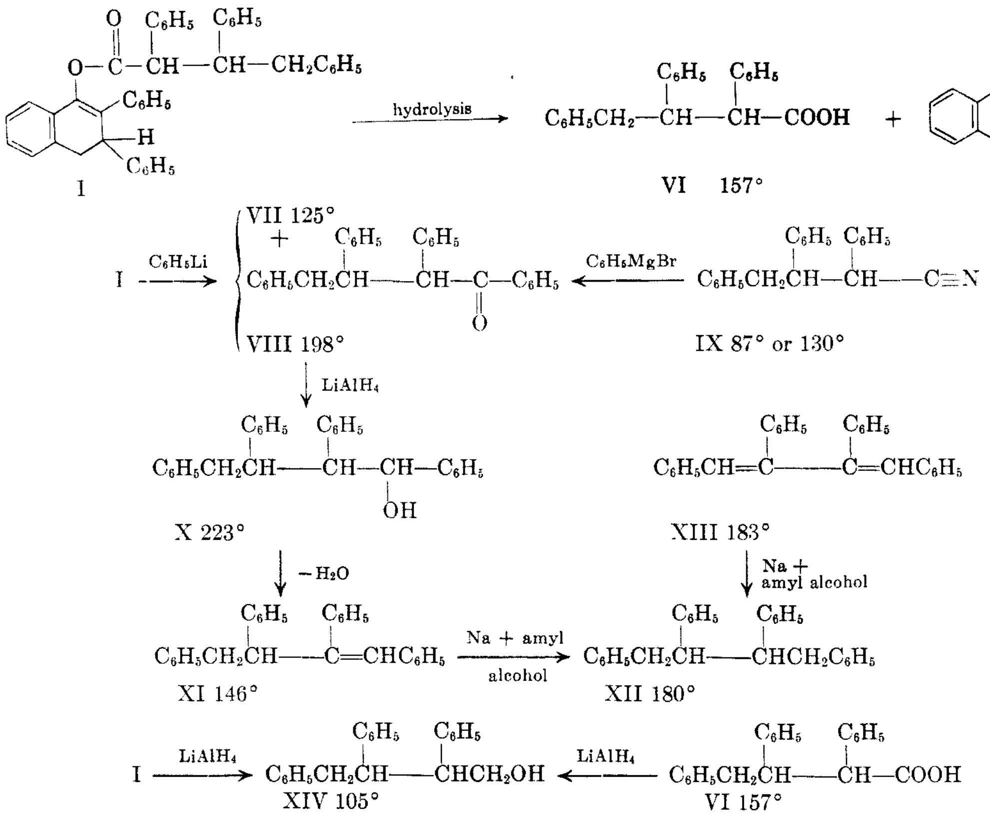
[2] H. M. Crawford, J. C. Davidson, and M. A. Plunkett, *J. Am. Chem. Soc.*, **66**, 2010 (1944).

[3] H. M. Crawford and H. B. Nelson, *J. Am. Chem. Soc.*, **68**, 134 (1946).

[4] F. Bergmann, D. Schapiro, and H. E. Eschinazi, *J. Am. Chem. Soc.*, **64**, 559 (1942).

[5] D. Lednicer and C. R. Hauser, *J. Am. Chem. Soc.*, **80**, 3409 (1959).

[6] E. Bergmann, D. Winter, and W. Schreiber, *Ann.*, **500**, 122 (1933).



ketone VIII reacted with lithium aluminum hydride to give a new secondary alcohol X, which could be dehydrated to give the known hydrocarbon XI. This, in turn, was reduced to the known hydrocarbon XII, and a mixed melting point of this hydrocarbon with an authentic sample prepared from XIII[7] showed no depression. The reaction of lithium aluminum hydride on the ester I gave a new primary alcohol XIV which was identical with the alcohol prepared by the action of lithium aluminum hydride on the 157° acid VI.

EXPERIMENTAL

Preparation of the ester I. The ester I resulted in some of the reactions for the preparation[2,3] of 2,3-diphenyltetralone II. 2,3,4-Triphenylbutyric acid was converted to the acid chloride by phosphorus pentachloride. After the removal of phosphorus oxychloride, the acid chloride was treated with anhydrous aluminum chloride to form the tetralone. This tetralone is known[8] to enolize readily, and this enol form reacted with the acid chloride to form the ester I. The ester was only slightly soluble in ether, ethanol, and ethyl acetate but could be recrystallized from chloroform or dioxane. It crystallized as cottony, white needles, melting at 211–212°. Heating with chloranil failed to dehydrogenate it and treatment with aluminum isopropoxide did not reduce it. It was reduced by refluxing with lithium aluminum hydride and it reacted readily with phenyllithium and slowly with phenylmagnesium bromide.

The ester (1.5 g.) was heated with potassium hydroxide (1.3 g.) in diethylene glycol. The alkaline solution was extracted with ether. Evaporation of this ether solution did not yield any solid but the infrared spectrum of the oil was the same as that for the known tetralone. Small amounts of the tetralone are always difficult to crystallize, probably due to the tendency to enolize. The acid from the hydrolysis was isolated from the alkaline solution by acidifying and extracting with ether. The ether was evaporated and the acid crystallized from benzene–petroleum ether (b.p. 60–70°). It melted at 155–157° and a mixture of the hydrolysis product with a known sample of the acid VI melted at 155–157°. The yield was 84%. The infrared spectrum of I showed absorption at 5.75 μ and 8.95 μ.

Anal. Calcd. for $C_{44}H_{36}O_2$: C, 88.56; H, 6.08; Mol. Wt., 597. Found: C, 88.46; H, 6.48; Mol. Wt., 560.

Preparation of 1,2,3-triphenyl-1-hydroxy-1,2,3,4-tetrahydronaphthalene, III. About 0.03 mole of phenyllithium in ether was added to an ether solution of 3 g. (0.01 mole) of the tetralone II. The ether boiled vigorously. After standing for 2 hr. the grey solution was decomposed with ice water. The ether layer was allowed to evaporate and the heavy oil was stirred with diisopropyl ether. The resulting solid was crystallized from ethanol–ethyl acetate to give colorless needles melting at 168.5–169.5°. The yield was 70%.

Anal. Calcd. for $C_{28}H_{24}O$: C, 89.32; H, 6.42. Found: C, 89.31; H, 6.30.

Preparation of 1,2,3-triphenyl-3,4-dihydronaphthalene, IV. One gram of the tertiary alcohol III was heated on the steam bath for 1 hr. with 10 ml. of benzene and 20 ml. of Lucas' reagent. The benzene layer, after washing with sodium carbonate solution, was heated and diluted with petroleum ether (b.p. 60–70°). The resulting solid (0.88 g., 92%) melted at 176–177°, the melting point recorded[4] for this compound.

Preparation of 1,2,3-triphenylnaphthalene V. Dehydrogenation of 0.5 g. of IV by heating at 280–300° for 22 hr. with 0.5 g. of selenium gave the known[4] 1,2,3-triphenylnaphthalene, melting at 153–154°.

Reaction of I *with phenyllithium and with phenylmagnesium*

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(7) L. I. Smith and H. Hoehn, *J. Am. Chem. Soc.*, **63**, 1184 (1941). A sample of this compound was kindly supplied by Dr. Lee Irvin Smith.

(8) F. Bergmann and J. Szmuszkovic, *J. Am. Chem. Soc.*, **68**, 1662 (1946).

bromide. About 0.03 mole of phenyllithium was added to an ether suspension of 3 g. of I. The ether boiled vigorously and I dissolved. After standing for 2 hr. the mixture was decomposed with ice water. The ether layer was allowed to evaporate slowly. Two products could be isolated from the deep magenta colored solution by careful crystallization. The less soluble material, the ketone VIII, separated first and could be recrystallized from chloroform-methanol or from ethyl acetate to give white crystals melting at 198–199°. The more soluble compound VII could be crystallized from benzene–petroleum ether (b.p. 60–70°) and melted at 125–126°.

The ester I (2 g., 0.0033 mole) was treated with excess phenylmagnesium bromide in toluene and heated on the steam bath for 18 hr. after the ether had boiled off. The magnesium compounds were dissolved in ammonium chloride solution and the toluene layer was added to water and steam distilled to remove the toluene. An ether extract of the water layer gave 30% of VIII. None of the lower melting compound VII was isolated from this reaction. A mixed melting point of the ketone from the ester and the ketone made from IX showed no depression. Both VII and VIII gave identical infrared spectra with absorption at 6 μ characteristic of a conjugated ketone.

Anal. Calcd. for $C_{28}H_{24}O$: C, 89.32; H, 6.42; Mol. Wt., 376.5. Found: for VII: C, 89.26, 89.84; H, 7.03, 6.41; Mol. Wt., 381. Found: for VIII: C, 88.71, 89.82; H, 6.31, 6.55; Mol. Wt., 364.

Reaction of 2,3,4-triphenylbutyronitrile with phenylmagnesium bromide. Approximately 0.03 mole of phenylmagnesium bromide was added to 0.02 mole of either form[2] of 2,3,4-triphenylbutyronitrile and the mixture was refluxed for 2 hr. Dilute hydrochloric acid was then added, the ether evaporated, and the mixture heated on the steam bath for 1 hr. The solid was filtered from the cooled mixture and crystallized from ethyl acetate. It melted at 197–198° and a mixed melting point with the ketone made from the ester I was 197–198°. The yield was 56%. The infrared spectrum was the same as that for the ketone made from the ester. This compound was described earlier.[6] It was made by adding benzylmagnesium chloride to 1,2,3-triphenylpropen-2-one-1. The resulting ketone, melting at 178°, was isomerized to the form melting at 198°.

Reduction of 1,2,3,4-tetraphenylbutanone-1, VIII. A mixture of 1 g. of the ketone VIII and 0.75 g. of lithium aluminum hydride in 40 ml. of ether was refluxed for 1 hr. and allowed to stand overnight. The excess lithium aluminum hydride was decomposed with ethyl acetate, then water was added and the layers separated. Needles of the alcohol X began to separate from the ether solution at once. Recrystallization from ethanol-chloroform gave a quantitative yield of colorless needles melting at 223–225°. The infrared spectrum showed no carbonyl absorption at 6 μ but a broad band at 9 μ characteristic of a secondary alcohol group.

Anal. Calcd. for $C_{28}H_{26}O$: C, 88.84; H, 6.92. Found: C, 88.4; H, 6.86.

Dehydration of 1,2,3,4-tetraphenylbutanol-1, IX. This alcohol was not dehydrated by heating with Lucas' reagent but heating 2.5 g. of the alcohol in 50 ml. of benzene with 0.5 g. of *p*-toluenesulfonic acid for 4 hr. did bring about the loss of water. The benzene solution was washed with water and allowed to evaporate slowly. The resulting solid (0.9 g., 43%) was recrystallized from benzene-methanol and melted at 149–150°. This hydrocarbon has been described as melting at 147–148°.[9]

Reduction of 1,2,3,4-tetraphenylbutene-1, XI. Five hundred milligrams of the hydrocarbon XI, 1.5 g. of sodium, and 15 ml. of isoamyl alcohol were refluxed for 1.5 hr. and allowed to stand overnight. The solid which separated (0.36 g., 70%) was filtered and crystallized from benzene-methanol. It melted at 180–180.5° and the mixed melting point with a known sample of 1,2,3,4-tetraphenylbutane was not depressed. The known sample of XII was made by reducing 350 mg. of 1,2,3,4-tetraphenylbutadiene-1,3, XIII[7] with sodium and amyl alcohol.

Reduction of I *with lithium aluminum hydride.* One gram of lithium aluminum hydride and 1.5 g. of I were refluxed in ether for 3 hr. The excess lithium aluminum hydride was decomposed with ethyl acetate and water was then added. The ether solution gave 0.67 g. (88%) of colorless needles of XIV. The alcohol was very soluble in most solvents but could be crystallized from methanol and either water or petroleum ether (b.p. 60–70°). It melted at 105–106° and was identical with the 2,3,4-triphenylbutanol-1 prepared in 35% yield by reducing the 157° 2,3,4-triphenylbutyric acid VI. The mixed melting point was not depressed and both samples showed absorption in their infrared spectra at 9.7 μ, characteristic of a primary alcohol.

Anal. Calcd. for $C_{22}H_{22}O$: C, 87.37; H, 7.33. Found: C, 86.82; H, 7.27.

Compound VII, whose analyses and infrared spectrum indicate that it is an isomer of VIII, was reduced by lithium aluminum hydride to a compound melting at 117–119°. Unfortunately most of this compound was lost. A less pure sample, after being heated with *p*-toluenesulfonic acid showed by infrared spectrum that it was a hydrocarbon. It contained 92.7% carbon and 6.7% hydrogen. This could be an isomer of XI.

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POUGHKEEPSIE, N. Y.

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(9) F. Bergmann, *J. Org. Chem.*, **6**, 543 (1941).