because in the somewhat parallel case of the methyl ether of *m*-cresol[17] metalation takes place at the 6-position rather than between the methyl and methoxy groups.

The idea that these reagents are electrophilic was intended to offset the commonly held notion that they were nucleophilic and not to imply that the anion was inactive. Indeed, in all papers[3-5] from this Laboratory, both ions have been credited with activity that could well be simultaneous. The search for cation activity has uncovered the large field of ionic aggregates where the reactions of the reagent are dependent on the salts with which the reagent is associated. In such a highly concentrated ionic field steric factors both favorable and unfavorable are probably more in evidence than with dissolved reagents. One example is the highly specific character of the Alfin reagent which causes an outstandingly fast polymerization of butadiene, much less polymerization of isoprene and virtually no polymerization of 2,3-dimethylbutadiene.[18] Branched compounds should be very subject to steric effects on a surface. Admittedly the dissolving of the reagent in a solvent will reduce the electrophilic character, but in many cases, particularly in ether solution, a notable difference in behavior of the potassium, sodium and lithium reagents still exists even when a common anion is used. For other sodium salts which are soluble in polar solvents the electrophilic character might suffer extinction by solvation. However, Brady and Jacobovits[19] have recently found evidence for cation influence even in alcoholic and aqueous solutions.

Experiments

Amylsodium was made at −10° and 5000 r.p.m. in the "standard" proportions and in the way commonly used[20] in this Laboratory except that *n*-heptane was used as the medium instead of pentane. After the usual time allotted for a preparation each mixture was thoroughly stirred at 10,000 r.p.m. for 1.5 hours at −10° in order to provide control conditions for subsequent tests. The mixture was then carbonated on solid carbon dioxide. Three such preparations gave yields of 89, 86 and 84% of caproic acid indicative of amylsodium. The corresponding quantities of decane were 3, 4 and 7%, based on the amyl chloride used for preparing amylsodium.

Two additional preparations of the above type were then heated to 50° and held there for three hours. Carbonation showed 79 and 81% caproic acid. Decane (6%) was present in each case. From one of the experiments the water-soluble acid was determined as 4%. Earlier work[8] had shown this material to be a pentenedicarboxylic acid probably derived, as is now understood, by dimetalation of some of the pentene obtained by disproportionation of the amyl radical formed by pyrolysis. The yield of this product is computed on the basis of one carboxyl group for every amyl chloride used in preparing amylsodium. Approximately these yields agree with those expected from the previous study on pyrolysis except that the tarry acid product obtained earlier was eliminated by the use of the high-speed stirrer.

The pyrolysis was next carried out in the presence of an equivalent amount of a *t*-pentoxide which was added just before the stirring (10,000 r.p.m.) period so that the alkoxide was intimately mixed with the amylsodium. The sodium *t*-pentoxide thus added was made by addition of the theoretical amount of *t*-amyl alcohol to a standard preparation of amylsodium and the potassium alkoxide was made by addition of the alcohol to potassium. The pyrolysis in the presence of sodium *t*-pentoxide yielded, after carbonation, 33% caproic acid, 11% of decane and 34% of water-soluble acid. From the action in the presence of the potassium alkoxide the yields were 25% caproic acid, 7% decane and 21% water-soluble acid. After each experiment lumps of metallic sodium were removed.

CAMBRIDGE, MASS.

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[17] Unpublished experiments with A. E. Brachman.

[18] Unpublished experiments with R. D. Coombs.

[19] O. L. Brady and J. Jacobovits, *J. Chem. Soc.*, 767 (1950).

[20] A. A. Morton and co-workers, THIS JOURNAL, **72**, 3785 (1950).

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF NEW HAMPSHIRE AND SEVERANCE CHEMICAL LABORATORY OF OBERLIN COLLEGE]

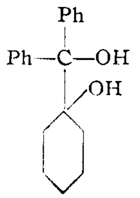
Molecular Rearrangements. I. A Study of the Pinacol Rearrangement of 1-(1-Hydroxycyclohexyl)-diphenylcarbinol[1]

BY ROBERT E. LYLE[2] AND GLORIA G. LYLE[2]

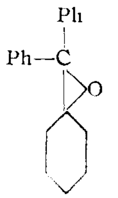
RECEIVED DECEMBER 8, 1951

1-(1-Hydroxycyclohexyl)-diphenylcarbinol (I) undergoes the pinacol rearrangement on treatment with reagents such as concentrated sulfuric acid, boron trifluoride in acetic acid, or Lucas reagent forming 2,2-diphenylcycloheptanone (IV). Zinc chloride in acetic anhydride converts the glycol I to 1-(1-phenylcyclohexyl)-phenyl ketone (III). Conclusive evidence for the structures of the rearrangement products is presented and a mechanism for the selective migration of phenyl or ring methylene groups is suggested.

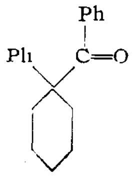
Meerwein,[3] in a previous study of the pinacol rearrangement of 1-(1-hydroxyclohexyl)-diphenylcarbinol (I), isolated a material from the treatment of I with sulfuric acid which he identified as the epoxide of cyclohexylidenediphenylmethane (II). Meerwein[3] reported further that this compound on distillation from zinc chloride produced 1-(1-phenylcyclohexyl) phenyl ketone (III). In a recent paper Cauquil and Rouzaud[4] suggested that the product of sulfuric acid treatment of I was 2,2-diphenyl-



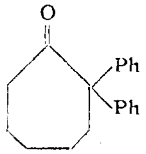
I



II



III



IV

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[1] Presented in part before the Division of Organic Chemistry at the 119th meeting of the American Chemical Society at Cleveland, Ohio, April 10, 1951.

[2] Department of Chemistry, James Hall, University of New Hampshire, Durham, New Hampshire.

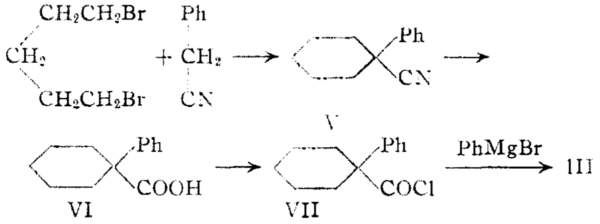
[3] H. Meerwein, *Ann.*, **396**, 200 (1913); **419**, 121 (1919).

[4] G. Cauquil and J. Rouzaud, *Compt. rend.*, **231**, 699 (1950).

cycloheptanone (IV) rather than II. They were, however, unable to present sufficient evidence to characterize the product as IV.

In connection with other research in progress in this Laboratory, it was necessary to find a direct method of preparing III from I and to characterize more completely the products of the rearrangement.

It was found that anhydrous zinc chloride with acetic anhydride as solvent smoothly converted I to III. The structure of the latter compound was shown to be 1-(1-phenylcyclohexyl) phenyl ketone (III) by an unequivocal synthesis. The alkylation of phenylacetonitrile with pentamethylene dibromide was effected by the use of potassium *t*-butoxide as the basic catalyst, producing a 59% yield of 1-phenyl-1-cyclohexanecarbonitrile (V).[5,6] This method gave a yield comparable to that reported by Weston,[6] who used sodium amide as catalyst, without requiring the long reaction time. The nitrile V was hydrolyzed to 1-phenyl-1-cyclohexanecarboxylic acid (VI)[5,6] which was converted to the acid chloride (VII) following the procedure of Weston.[6] Reaction of phenylmagnesium bromide with the acid chloride produced 1-(1-phenylcyclohexyl) phenyl ketone (III) in a 96% yield. This ketone showed no depression of melting point on mixing with the product formed by the zinc chloride–acetic anhydride rearrangement of I.



Although steric hindrance of the carbonyl group retarded the formation of ketone derivatives, an oxime of III could be prepared by the method of Bachmann and Barton.[7] Mixtures of the two oxime derivatives likewise showed no depression of melting point.

Treatment of I with reagents such as sulfuric acid, Lucas reagent or boron trifluoride in acetic acid gave the material identified by Meerwein[3] as II and by Cauquil and Rouzaud[4] as IV. The refutation of Meerwein's work by the latter authors resulted from the difference in physical constants of II produced by peracetic acid oxidation of cyclohexylidenediphenylmethane, reported by Arbuzov and Arbuzova,[8] and the constants of the compound formed on treatment of I with sulfuric acid. Because of the possible side reactions in the peracetic acid oxidation, the synthesis of II from cyclohexylidenediphenylmethane was repeated using perbenzoic acid. The product of this reaction was identical with that reported by Arbuzov and Arbuzova.[8] Furthermore, cold concentrated sulfuric acid converted this epoxide smoothly to the material formed from I under similar conditions. This eliminated the possibility of the oxirane structure (II) as the product of the dehydration of I.

In order to show that the product of the sulfuric acid rearrangement of I was the result of ring expansion, the existence of the ketone carbonyl must be established. The steric hindrance and reduced activity of the ketone group of IV had led Meerwein[3] to make the erroneous assignment of structure II and prevented Cauquil and Rouzaud[4] from definitely establishing IV as the structure of the product of rearrangement. The procedure of Bachmann and Barton[7] could be used to give excellent yields of the oxime of IV. Additional evidence for the carbonyl group was obtained from the fact that lithium aluminum hydride reduced IV to 2,2-diphenylcycloheptanol (VIII) and that IV showed a definite maximum at 5.90 μ in the infrared spectrum. The ultraviolet spectrum (Fig. 1) showed a marked resemblance to that of 3,3-diphenylbutanone-2,[9] indicating the presence of the diphenylacetyl system in IV.

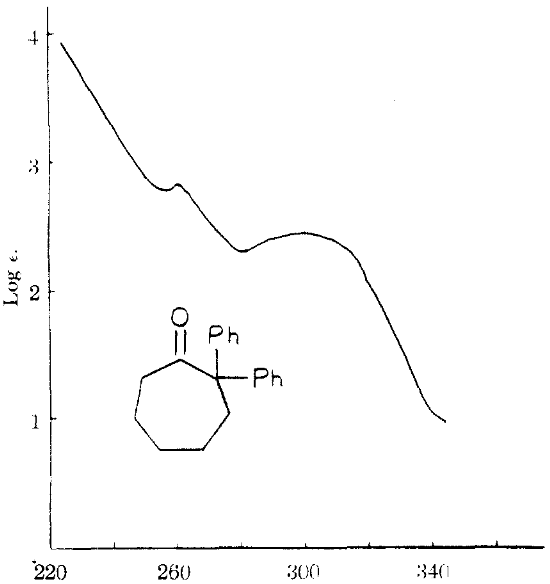


Fig. 1.

The Wallach degradation[10,11] of IV produced 2,2-diphenylcyclohexanone (XI), giving an immediately obvious proof of the structure of 2,2-diphenylcycloheptanone (IV). Illumination of a mixture of 2,2-diphenylcycloheptanone (IV) and bromine, in slight excess of two equivalents, readily produced 2,2-diphenyl-7,7-dibromocycloheptanone (IX) in good yield. Hydrolysis of IX with aqueous alcoholic potassium hydroxide gave an acidic material soluble in sodium bicarbonate. Although this acid was not identified, the structure is probably 1-hydroxy-2,2-diphenylcyclohexane carboxylic acid (X), for on oxidation with potassium permanganate it formed 2,2-diphenylcyclohexanone (XI),[12] identified by its melting point and those of its derivatives: oxime, semicarbazone and monobromide (see Table I).

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(5) F. Case, This Journal, **56**, 715 (1934).

(6) A. Weston, *ibid.*, **68**, 2345 (1946).

(7) W. Bachmann and M. Barton, *J. Org. Chem.*, **3**, 300 (1939).

(8) A. Arbuzov and I. Arbuzova, *Chem. Zentr.*, **104**, 2940 (1933).

(9) E. Alpen, W. Kumler and L. Strait, This Journal, **72**, 4558 (1950).

(10) O. Wallach, *Ann.*, **414**, 296 (1918); **437**, 148 (1924).

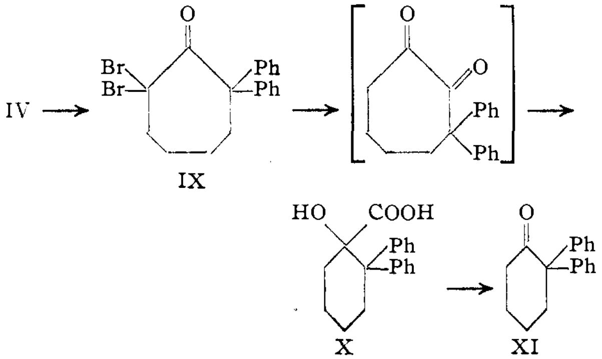
(11) E. R. Buchman and H. Sargent, *J. Org. Chem.*, **7**, 148 (1942).

(12) A. Burger and W. B. Bennet, This Journal, **72**, 5414 (1950).

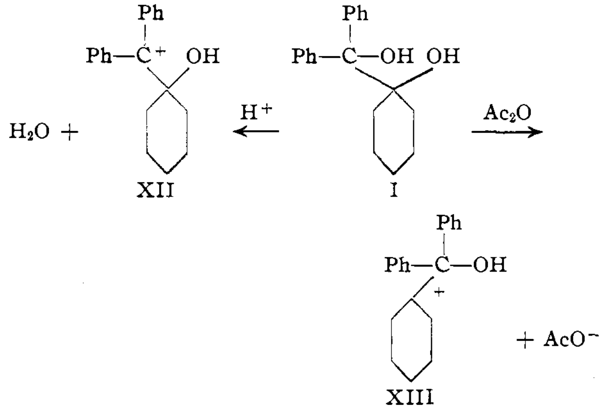
TABLE I

Compound	Obsd. m.p., °C.	Lit. m.p., °C.
2,2-Diphenylcyclohexanone (XI)	93.5-94.5	99-99.5[a]
Oxime of XI	207-208	208.5[a]
Semicarbazone of XI	237-238 (subm.)[b]	240[c]
Monobromide of XI	117.5-117.7	117-117.5[a]
Mixture of XI with authentic sample[d]	95-97[b]	
Mixture of monobromide of XI with authentic sample[d]	115.5-116.5[b]	

[a] A. Burger and W. B. Bennet, THIS JOURNAL, **72**, 5414 (1950). [b] Melting point uncorrected. [c] H. Meerwein, *Ann.*, **396**, 200 (1913). [d] The authors express appreciation to Dr. Alfred Burger for the authentic sample of 2,2-diphenylcyclohexanone.



This experimental evidence indicates that the migration of the phenyl or ring methylene groups in the unsymmetrical glycol, 1-(1-hydroxycyclohexyl)-diphenylcarbinol (I), depends largely on the solvent for the rearrangement reaction. On the basis of the currently accepted mechanism for the pinacol rearrangement, it is necessary to assume that the usual acid catalysts produce rearrangement by formation of the carbonium ion (XII) with subsequent migration of the ring methylene group; whereas, a Lewis acid with acetic anhydride as solvent causes formation of carbonium ion (XIII) followed by migration of a phenyl group.



Both experimental evidence and structural factors indicate that of the two hydroxyl groups involved the conjugate acid resulting from the protonation of the diphenylcarbinol hydroxyl group should be the more readily ionized; *i.e.*, the carbonium ion XII would be stabilized by resonance. However, in the vigorous acetylation medium of zinc chloride and acetic anhydride and in the absence of protons the monoacetoxy derivative could be an intermediate, which by elimination of the acetate ion would then yield the required intermediate carbonium ion XIII.

The possibility exists that 1-(1-phenylcyclohexyl) phenyl ketone (III) and 2,2-diphenylcycloheptanone (IV) are produced in an equilibrium mixture which allows one or the other to be isolated depending upon the solvent. It was found, however, that IV could not be converted to III by zinc chloride in acetic anhydride solution, nor could III be converted to IV by treatment with concentrated sulfuric acid, thus eliminating the possibility of an equilibrium between the products of rearrangement. Additional work is in progress in this Laboratory with the aim of elucidating the mechanism of this preferential rearrangement.

Experimental

Rearrangement of 1-(1-Hydroxycyclohexyl)-diphenylcarbinol (I) Using Zinc Chloride and Acetic Anhydride.—To a mixture of 14.4 g. (0.05 mole) of 1-(1-hydroxycyclohexyl)-diphenylcarbinol (I) and 6.3 g. of fused, pulverized zinc chloride was added 63 ml. of acetic anhydride. The mixture was heated with agitation for two minutes on a boiling water-bath and allowed to stand one hour at room temperature. The solution was poured into a mixture of 50 g. of potassium hydroxide in 400 ml. of ice and water and the precipitate filtered yielding 12.8 g. (97%) of 1-(1-phenylcyclohexyl) phenyl ketone (III), m.p. 76-76.5°; lit.,[3] m.p. 73-74°.

This ketone showed no depression in melting point when mixed with a sample of the ketone (III) prepared from the acid chloride (VII).

Preparation of the **oxime** of III was carried out according to the method of Bachmann and Barton[7] in 86% yield. After recrystallization from alcohol the oxime melted 173.5-174.5°.

Anal. Calcd. for $C_{19}H_{21}NO$: C, 81.67; H, 7.58. Found: C, 81.24; H, 7.53.

1-Phenyl-1-cyclohexanecarbonitrile (V).—A solution of 0.16 mole of potassium *t*-butoxide was prepared from 6.2 g. potassium and 125 ml. *t*-butyl alcohol in a 500-ml. 3-necked flask equipped with mercury-sealed stirrer, dropping funnel and reflux condenser. Maintaining the solution at reflux temperature a mixture of 18.4 g. (0.08 mole) of pentamethylene dibromide and 9.4 g. (0.08 mole) of phenylacetonitrile in 50 ml. of *t*-butyl alcohol was added dropwise over a period of one hour. The mixture was refluxed and stirred an additional four hours after which the *t*-butyl alcohol was removed by distillation and the reaction mixture poured into water. The water solution was extracted with three 50-ml. portions of ether and the extracts dried over calcium chloride. Fractional distillation of the ethereal solution gave 8.7 g. (59%) of 1-phenyl-1-cyclohexanecarbonitrile (V), b.p. 110-115° at 0.7 mm., n^{25}_{D} 1.5327; lit.[6] b.p. 125-127° at 3 mm., n^{26}_{D} 1.5330.

1-Phenyl-1-cyclohexanecarboxylic Acid (VI).—The hydrolysis of the nitrile (V) was accomplished by refluxing 8.7 g. (0.047 mole) of 1-phenyl-1-cyclohexanecarbonitrile (V) with 7.8 g. (0.14 mole) of potassium hydroxide in 125 ml. of β,β'-dihydroxyethyl ether for three hours. The solution was poured into 75 ml. of water and extracted with two 30-ml. portions of ether to remove any unreacted nitrile or amide. The aqueous solution was acidified with hydrochloric acid and extracted with three 30-ml. portions of ether. The combined acidic extracts were dried over sodium sulfate and the ether removed leaving 9.0 g. (94%) of the acid, which, on recrystallization from benzene, melted 123-124°; lit.[6] m.p. 123-124°.

1-(1-Phenylcyclohexyl) Phenyl Ketone (III).—A solution of 4.85 g. (0.022 mole) of the acid chloride of 1-phenyl-1-cyclohexanecarboxylic acid (VII), prepared from VI by the method of Weston,[6] in 50 ml. of absolute ether was placed in a 500-ml. 3-necked flask fitted with condenser, mercury-sealed stirrer and dropping funnel. The system was filled with nitrogen and 0.029 mole of phenylmagnesium bromide in 40 ml. of ether was added slowly. The resulting mixture was refluxed and stirred for one hour, cooled and treated with ice and hydrochloric acid. The ether layer was separated and the water layer extracted three times with 50-ml. portions of ether. After drying the combined ether extracts over sodium sulfate, the ether was removed leaving 5.6 g. (96%) of the ketone (III) which was recrystallized from alcohol and melted at 75–77°.

The Epoxide of Cyclohexylidenediphenylmethane (II).—A solution of 5.0 g. (0.02 mole) of cyclohexylidenediphenylmethane in 20 ml. of chloroform was cooled to 16°. A slight molar excess of perbenzoic acid in 40 ml. of chloroform was added dropwise to the stirred solution while maintaining the temperature at 16°. The mixture was stirred for four hours at room temperature, and 40 ml. of water was added. The chloroform layer was removed and the water layer extracted twice with 20 ml. of chloroform. The combined extracts were washed with two 20-ml. portions of 5% potassium hydroxide solution and dried over sodium sulfate. The chloroform was removed by distillation leaving 4.62 g. (87%) of the epoxide of cyclohexylidenediphenylmethane (II). On recrystallization from alcohol the material melted 120.5–121°; lit.[8] 121–121.5°.

Rearrangement of the Epoxide of Cyclohexylidenediphenylmethane (II).—In a 50-ml. erlenmeyer flask containing 15 ml. concentrated sulfuric acid cooled to 0° in an ice-salt-bath was placed 2.0 g. (0.008 mole) of the epoxide of cyclohexylidenediphenylmethane (II). The mixture was allowed to stand one hour at 0° and then poured into 50 ml. of water. The precipitate was filtered and recrystallized from alcohol yielding 1.7 g. (85%) of **2,2-diphenylcycloheptanone (IV)**, m.p. 92–94°. A sample of this material when mixed with the product IV from the sulfuric acid rearrangement of I showed no depression of melting point.

The preparation of the **oxime** of 2,2-diphenylcycloheptanone was carried out according to the procedure described by Bachmann and Barton[7] producing a material which melted 190.5–192° after recrystallization from alcohol. A mixture of the oxime prepared from the product of the rearrangement of I with the oxime prepared from the rearrangement of II showed no depression of melting point.

Anal. Calcd. for $C_{19}H_{21}NO$: C, 81.67; H, 7.58. Found: C, 81.70; H, 7.69.

2,2-Diphenylcycloheptanol (VIII).—A suspension of 1.9 g. (0.05 mole) of lithium aluminum hydride in 60 ml. of dry ether was prepared in a 3-necked flask equipped with dropping funnel, mercury-sealed stirrer and condenser. To this solution 5.28 g. (0.02 mole) of 2,2-diphenylcycloheptanone (IV) in 20 ml. of ether was added while maintaining the mixture at reflux temperature. After stirring the solution for 1/2 hour, water was added dropwise until all reaction had ceased. The mixture was poured into ice and 100 ml. of 10% sulfuric acid solution was added. The ether layer was separated and the water layer extracted once with 25 ml. of ether. After removal of the ether, the product distilled at 185–192° at 0.9 mm. Recrystallization from ligroin gave 4.39 g. (82.5%) of 2,2-diphenylcycloheptanol (VIII), m.p. 52–53.5°.

Anal. Calcd. for $C_{19}H_{22}O$: C, 85.67; H, 8.33. Found: C, 85.75; H, 8.31.

The benzoate ester derivative of 2,2-diphenylcycloheptanol, after recrystallization from ligroin, melted 98–100.5°.

Anal. Calcd. for $C_{26}H_{26}O_2$: C, 84.29; H, 7.07. Found: C, 84.09; H, 6.89.

Wallach Degradation[10,11] of 2,2-Diphenylcycloheptanone (IV).—A 500-ml. round-bottom flask was arranged for reflux while being illuminated and heated by a 150-watt Mazda bulb. A solution of 18 g. (0.068 mole) of 2,2-diphenylcycloheptanone (IV) in 150 ml. of carbon tetrachloride and 1 ml. of 48% hydrobromic acid was placed in the flask and illuminated while 27 g. of bromine dissolved in 35 ml. of carbon tetrachloride was added slowly. After a short induction period the reaction began with vigorous evolution of hydrogen bromide. After all the bromine was added, the reaction mixture was illuminated for eight additional hours. The solvent was removed by distillation at reduced pressure and the residue crystallized by the addition of petroleum ether. Separation of the solid by filtration gave 20–23 g. (70–80%) of crude **2,2-diphenyl-7,7-dibromocycloheptanone (IX)**. On recrystallization from benzene, the solid melted from 166–167°.

Anal. Calcd. for $C_{19}H_{18}OBr_2$: Br, 37.9. Found: Br, 37.7.

A solution of 4.45 g. of IX and 4.45 g. of potassium hydroxide in 45 ml. of ethanol and 15 ml. of water was refluxed for 10.5 hours and then allowed to stand overnight. The solution was poured into 150 ml. of water and extracted with two 35-ml. portions of ether. The ether extracts were extracted once with 10% sodium hydroxide. The combined alkaline layers were treated with an additional 10 g. of potassium hydroxide and heated overnight on a steam-bath. The basic solution was acidified and allowed to stand until the precipitate had coagulated. After the solid was removed by filtration and dried, the yield was 1.95 g. of acid, supposedly 2,2-diphenylcyclohexanecarboxylic acid (X).

A portion of this acid (1.5 g.) was dissolved in 75 ml. of glacial acetic acid and to this solution was added slowly 2.4 g. of potassium permanganate dissolved in 110 ml. of 3 *N* sulfuric acid. The mixture was allowed to stand for 15 minutes after all the permanganate solution was added. The excess permanganate was decolorized with sodium bisulfite and the mixture poured into 300 ml. of water. The water solution was extracted with four 50-ml. portions of ether. The ether was extracted with water until most of the acetic acid had been removed and finally extracted twice with 20-ml. portions of 5% sodium hydroxide to remove last traces of acetic acid and unoxidized starting material. The ether was dried over calcium chloride and removed by evaporation. The remaining oil slowly crystallized yielding 0.88 g. (46% yield from dibromide) of 2,2-diphenylcyclohexanone (IX) which, after recrystallization from ethanol, melted at 93.5–94.5°; lit.[12] 99–99.5°.

Following the procedure of Burger and Bennet[12] the oxime and monobromo derivatives were prepared. Synthesis of the semicarbazone was accomplished by using an adaptation of the preparation of the oxime.

Attempted Rearrangement of 1-(1-Phenylcyclohexyl) Phenyl Ketone (III).—To 10 ml. of concentrated sulfuric acid cooled to zero degrees was added 1 g. of 1-(1-phenylcyclohexyl) phenyl ketone (III). The mixture was treated in a manner identical to that used for the conversion of 1-(1-hydroxycyclohexyl)-diphenylcarbinol (I) to 2,2-diphenylcycloheptanone (IV).[3] Recrystallization from methanol of the solid gave 0.90 g. of recovered III which melted from 73–74°; lit.[3] m.p. 73–74°.

Attempted Rearrangement of 2,2-Diphenylcycloheptanone (IV).—The treatment of 1 g. of IV under conditions given above for the rearrangement of I to III yielded, after recrystallization from methanol, 0.94 g. of recovered IV, m.p. 90–91°; lit.[3] m.p. 92–94°.

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