[Contribution from the Department of Chemistry, Polytechnic Institute of Brooklyn]

Azo Compounds.[1] The Preparation and Oxidation of 3,7-Diphenylhexahydro-1,2-diazepine

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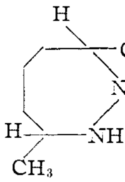
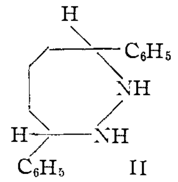
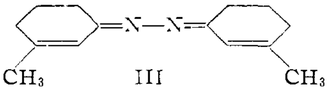
Compound II, 3,7-diphenylhexahydro-1,2-diazepine, has been prepared and characterized. Attempts to synthesize compound I, 3,7-dimethylhexahydro-1,2-diazepine, have resulted in the formation of III, the azine of 3-methyl-2-cyclohexen-1-one (III). Oxidation of II with bromine in aqueous ethanol in acid solution gave δ-bromo-δ-phenylvalerophenone (VII). The structure of VII was demonstated by dehydrohalogenation to give VIII. Alkaline permanganate oxidation of VIII gave benzoic acid and β-benzoylpropionic acid. Oxidation of VII with neutral permanganate in aqueous acetone gave the diketone IV. Reduction of VII over palladium-on-calcium carbonate gave the monoketone IX which was identical with an authentic specimen.

As part of our general program to synthesize cyclic azo compounds which would be capable of giving moderately active biradicals in solution, we have attempted the synthesis of I and II. This paper reports the successful synthesis of II and unsuccessful attempts to prepare I. In an attempted synthesis of I, heptane-2,6-dione[3] was treated with hydrazine to give in 51% yield the azine of 3-methyl-2-cyclohexene-1-one (III), instead of the expected cyclic azine. A wide variety of reaction conditions were tried without successfully changing the course of the reaction, some 45 variations being attempted. Thus III was also obtained in 19% yield from the reaction of heptane-2,6-dione with hydrazine in acid solution.


I

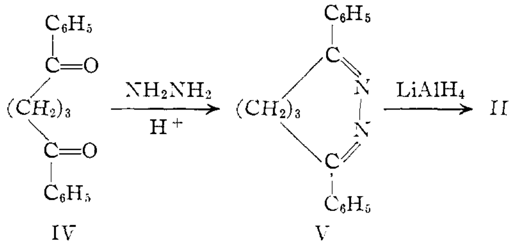

II


III

A comparison of III with the azine prepared from a known sample of 3-methyl-2-cyclohexen-1-one and hydrazine hydrate[4] demonstrated that the compounds were identical, that is, no depression of the melting point was observed by a mixed melting point determination and their infrared spectra were identical.

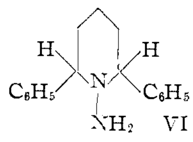
It was apparent from these results that cyclization of the diketone *via* an aldol condensation was much too facile and that it would be impossible to prepare I *via* the azine route.

Preparation of II was accomplished according to the scheme



IV was prepared in 72% yield by the method of Auger[5a] using a modification of the method of Fuson and Walker[5b] for the preparation of dibenzoylbutane. The diketone IV was treated with hydrazine hydrate and a catalytic amount of acid to give the cyclic azine V in 95% yield. The reaction was carried out in relatively dilute solution (0.16 *M*) in accord with the general knowledge of the Ruggli dilution principle.[6]

The conditions of reaction and catalyst concentration are important to obtain the high yield realized. Polymer formation is the principal side reaction. Reduction of the azine to the cyclic hydrazine II was carried out in 66% yield with lithium aluminum hydride. This reagent has recently been reported for the reduction of a hydrazine linkage to a saturated hydrazine, although to date there are relatively few examples of this interesting reduction[7a,b] with azines. The question remained as to whether the structure of II might possibly be the six-membered 1-amino compound, VI. The infrared spectrum was not definitive since the phenyl peak in the 6.25 μ area sometimes masks the NH_2 bending frequency in this region. In the 3 μ area the NH frequency would be similar to an NH_2 group and a distinction cannot be made. The pK_B of II was determined to be 5×10^{-12} in ethanol–water solution. Consequently VI was synthesized and shown to be different from II in


VI

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[1] This is the 19th in a series of papers concerned with the preparation and decomposition of azo compounds. For the previous paper in this series see C. G. Overberger, N. R. Byrd and R. B. Mesrobian, This Journal, **78**, 1961 (1956).

[2] This paper comprises a portion of a thesis presented by J. J. Monagle in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of the Polytechnic Institute of Brooklyn.

[3] C. G. Overberger, P. Huang, T. Gibb, Jr., S. Chibnik and J. J. Monagle, This Journal, **74**, 3290 (1952).

[4] R. C. Fargher and W. H. Perkin, *J. Chem. Soc.*, **105**, 1353 (1914).

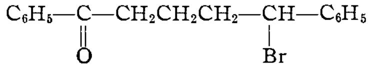
[5] (a) V. Auger, *Ann. Chem. Phys.*, [6] **22**, 358 (1891); (b) R. C. Fuson and J. T. Walker, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 169.

[6] K. Ziegler, H. Eberle and H. Ohlinger, *Ann.*, **504**, 94 (1933).

[7] (a) J. B. Class, J. G. Aston and T. S. Oakwood, This Journal, **75**, 2937 (1953); (b) R. Renaud and L. C. Leitch, *Can. J. Chem.*, **32**, 545 (1954).

its chemical and physical properties. This portion of the work will be reported separately.

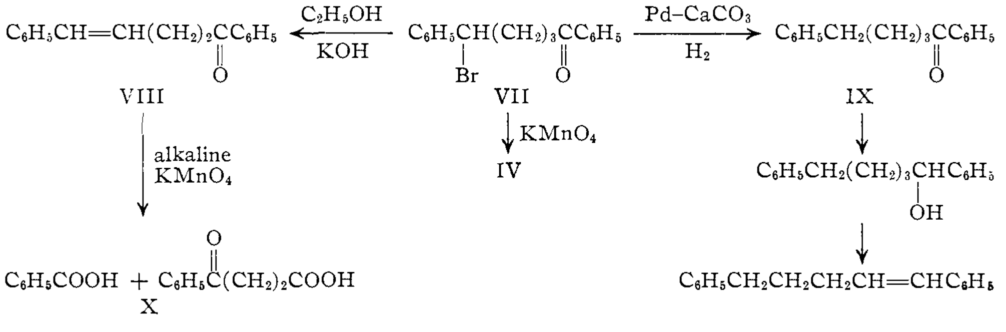
Oxidation of II was attempted with cupric chloride, air, oxygen, mercuric oxide in boiling ether, calcium hypochlorite in neutral and acid solution, hydrogen peroxide, a solution of bromine in water and ethanol and pure bromine. Oxidation only occurred with calcium hypochlorite in acid solution or with bromine in acid solution. The oxidation experiments therefore were carried out in acid solution with excess bromine as the oxidizing agent and in all cases an almost quantitative evolution of nitrogen was obtained. The only product that could be isolated and characterized was δ-bromo-δ-phenylvalerophenone (VII) in an average yield of 41%.



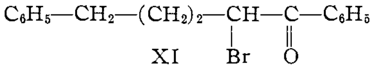
$C_6H_5-\underset{\underset{O}{\|}}{C}-CH_2CH_2CH_2-\underset{\underset{Br}{|}}{CH}-C_6H_5$

VII

The structure of VII was demonstrated in the following way. Reduction of VII over palladium-on-calcium carbonate at 3 atm. gave δ-phenylvalerophenone (IX). IX was synthesized by the method of Borsche and Wölleman[8] who hydrogenated cinnamalacetophenone to obtain the desired product. Cinnamalacetophenone was prepared in 77% yield by a method used by Kohler and Chadwell to prepare benzalacetophenone.[9] A mixed m.p. of IX obtained by the two procedures was not depressed. Infrared spectra of the two materials were identical.



Although the mechanism of the oxidation is not discussed in this paper, there are two likely positions for the bromine atom; either alpha to the ketone group, structure XI, or at the 5 or benzyl position



$C_6H_5-CH_2-(CH_2)_2-\underset{\underset{Br}{|}}{CH}-\underset{\underset{O}{\|}}{C}-C_6H_5$

as in VII. XI was synthesized by the bromination of IX in acid solution and demonstrated to be a liquid at room temperature not identical with VII. VII was dehydrohalogenated by reaction with alcoholic potassium hydroxide to give 1,5-diphenyl-4-penten-1-one (VIII), in 64% yield. An alkaline permanganate oxidation of VIII gave the known β-benzoylpropionic acid (X) and benzoic acid in 14.4 and 89% yield, respectively. Furthermore, oxidation of VII with potassium permanganate solution in aqueous acetone solution gave 1,5-diphenyl-1,5-pentanedione[5] (IV) in 70.4% yield. It was assumed in this latter case the hydrolysis of the benzyl bromide occurs to give the hydroxy compound which is then oxidized to give the diketone. It is clear that the structure of the oxidation product can only be VII.

Some derivatives of IX were also prepared and characterized as part of a general mechanisms study of oxidations of this type of hydrazine. Reduction of IX with lithium aluminum hydride gave the corresponding alcohol in high yield. Dehydration of this alcohol gave an 83% yield of 1,5-diphenylpentene-1.

Oxidation mechanisms for this type of cyclic hydrazine II and its stereochemistry will be discussed elsewhere.

Experimental[10]

Reaction of Heptane-2,6-dione with Hydrazine. (a) **Reaction in Neutral Solution.**—Heptane-2,6-dione, 4.3 g. (0.033 mole), prepared as described previously[3] and 3.84 g. (6 ml., 0.12 mole) of hydrazine were dissolved in 600 ml. of ethanol and shaken for 23 hr. The ethanol was removed by warming under reduced pressure, and the yellow viscous residue was distilled under vacuum to yield 1.82 g. (51%) of the azine of 3-methyl-2-cyclohexen-1-one, b.p. 160–190° (2.8–3 mm.). Recrystallization from an ethanol-water mixture yielded long needles, m.p. 100.5–103° (see later analyses). This material decolorized bromine in carbon tetrachloride.

(b) **Reaction in Acid Solution.**—The diketone, 2.6 g. (0.02 mole), 1 ml. (0.02 mole) of hydrazine hydrate and four drops of concentrated hydrochloric acid were dissolved in 150 ml. of ethanol and the mixture was refluxed for 2.5 hr. Water was then added to the solution, and the mixture was cooled in the ice-chest to give 0.41 g. (18.9%) of bright yellow solid, m.p. 103–105°. A mixed m.p. with the solid obtained from the reaction in neutral solution, m.p. 100.5–103°, melted at 102–105°.

Preparation of 3-Methyl-2-cyclohexen-1-one.—This ketone was prepared by the procedure of Fargher and Perkin[4] and gave 68% of a mobile water-white liquid, $n^{25.5}\text{D}$ 1.4919, b.p. 48–50° (2.3 mm.) (no yield, b.p. 197° (760 mm.) from heptane-2,6-dione).[4]

Preparation of 3-Methyl-2-cyclohexen-1-one Azine (III).—The ketone, 4.0 g. (0.036 mole), 11 ml. (0.01 mole) of hydrazine hydrate and three drops of concentrated hydrochloric acid were dissolved in 25 ml. of ethanol and the mixture refluxed for 1 hr. The solution was then poured onto ice. The product was an oil which solidified on standing to give a yellow solid. The solid was removed by filtration and dried in a vacuum desiccator over sulfuric acid to give 2.52 g. (64%) of the azine. Recrystallization from petroleum ether (b.p. 90–100°) gave a m.p. 99–103°. Continued recrystallization from petroleum ether (b.p. 28–38°) raised the m.p. to 104.8–106°. Calcd. for $C_{14}H_{20}N_2$: C, 77.73; H, 9.32; N, 12.94. Found[11]: C, 77.68; H, 9.30; N, 13.05.

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[8] W. Borsche and J. Wolleman, *Ber.*, **45**, 3713 (1912).

[9] E. P. Kohler and H. M. Chadwell, "Organic Syntheses," Coll. Vol. I, 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1941, p. 78.

[10] All melting points are corrected.

[11] Analyses by Drs. K. Ritter, Zurich, Switzerland, and F. Schwarzkopf, New York, N. Y.

A mixed m.p. of this material with that obtained from the reaction of the diketone in neutral solution, m.p. 100.5–103°, melted at 102.5–104°. The infrared spectra of the two substances were identical.

Preparation of Dibenzoylpropane (1,5-Diphenylpentane-1,5-dione).—The procedure was similar to that described by reference 5. From 142.2 g. (1.07 moles) of glutaric acid (dried over sulfuric acid in a vacuum desiccator), 217 ml. (3 moles) of thionyl chloride and 300 g. (2.25 moles) of anhydrous aluminum chloride in 1.5 l. of dry benzene, there was obtained a solid which was recrystallized from 700 ml. of ethanol, 205 g. (76%) of cream colored crystals, m.p. 65–67° (reported,[5a] m.p. 62–63°, no yield, same general procedure, also[12] 65% yield by condensation of phenylacetoacetic ester with formaldehyde, m.p. 67.5° and[13] no yield, by condensation of phenylacetoacetic ester with methylene iodide, m.p. 67.5°).

Preparation of 3,7-Diphenyl-4,5-dihydro-1,2-diazepine (Dibenzoylpropane Azine).—Dibenzoylpropane, 50.4 g. (0.2 mole), was dissolved in 1200 ml. of commercial absolute ethanol. To this was added 10 ml. of hydrazine hydrate (0.2 mole) and 2 ml. of concentrated hydrochloric acid, and the solution refluxed for 4 hr. While still hot the solution was poured into a mixture of ice and water. The white solid was collected by suction filtration and dried overnight in air and then over sulfuric acid in a vacuum desiccator to give 47.4 g. (95%) of pure white solid, m.p. 159.8–161.4°. The product was recrystallized from acetone to give a m.p. 162.8–164.2°. Ultraviolet spectra showed one peak at 261 mμ, while infrared spectra showed peaks at 6.3, 6.4, 6.65 and 6.85 μ, consistent with the proposed structure. Calcd. for $C_{17}H_{16}N_2$: C, 82.22; H, 6.49; N, 11.28; mol. wt., 252. Found: C, 82.13; H, 6.57; N, 11.14; mol. wt., 248.

Preparation of 3,7-Diphenylhexahydro-1,2-diazepine.—To a suspension of 7.6 g. (0.20 mole) of lithium aluminum hydride in 400 ml. of anhydrous ether was added, over a period of 3.5 hr., a solution of 15.2 g. (0.06 mole) of the crude dibenzoylpropane azine in 250 ml. of redistilled tetrahydrofuran. The mixture was stirred vigorously during the addition. Gentle refluxing occurred during the addition and a yellow-green color developed. After the addition was completed the solution was stirred for about 2 hr. The excess lithium aluminum hydride was decomposed by the dropwise addition of ethanol until the yellow color disappeared, followed by the dropwise addition of water until decomposition was complete. The mixture was filtered with suction and the solid hydroxides were washed repeatedly with ether. The filtrate and washings were dried over magnesium sulfate and removal of the solvent gave a yellow-green oil which was distilled to give two fractions. The low boiling fraction amounted to 10.1 g. (66%) of a viscous yellow-green oil, b.p. 200–202° (2.0 mm.), $n^{21.5}_{D}$ 1.6189, $d^{27.5}_{4}$ 1.086. The infrared spectra indicated at N–H stretching frequency at 3.0 μ. Calculated for $C_{17}H_{20}N_2$: C, 80.92; H, 7.99; N, 11.10. Found: C, 81.01; H, 7.84; N, 11.17.

A picrate was formed by dissolving a small amount of the hydrazine in absolute ether and adding, in excess, a solution of picric acid in absolute ether, m.p. 137.5–138.8°. Calcd. for $C_{23}H_{23}N_5O_7$: C, 57.37; H, 4.81; N, 14.54. Found: C, 57.36; H, 4.65; N, 14.40.

The base strength of the cyclic hydrazine was determined in ethanol–water solution (50%), considering the compound as a mono-base. The calculated amount of standard hydrochloric acid solution was added to bring the compound to the half neutralization point. Measurement of the *p*H at this point yielded the *pK* of the base, 5×10^{-12}.

A correction factor was necessary to compensate for the presence of ethanol in the system.[14] This was determined empirically by adding a calculated amount of acid to the same volume of solution used in the base measurements and measuring the *p*H. The difference between the observed and calculated *p*H values was the correction factor used. The *p*H measurements were carried out with a Beckman model G *p*H meter and the corrected value of the *p*H obtained was 2.71.

Oxidation of 3,7-Diphenylhexahydro-1,2-diazepine.—The freshly distilled hydrazine, 10.30 g. (0.0408 mole), was dissolved in 100 ml. of ethanol, 60 ml. of water was then added and the mixture cooled to 6°. A solution of 50 ml. of concentrated hydrochloric acid in 90 ml. of water was added and the solution was stirred and cooled to 2°. The solution, which had become opaque after the addition of water, became only slightly turbid when the acid was added. To this cold, vigorously stirred solution was added 13.1 g. (0.0816 mole) of bromine over a period of 9 hr. Nitrogen evolution was noted within 15 seconds after the addition of the first drop of bromine. The total nitrogen evolved was 792 ml. (corrected to standard conditions) or 86.5% of the theoretical. In other experiments designed to measure only nitrogen, 95% of the total nitrogen was evolved. A yellow-white solid was deposited as the oxidation progressed. After the addition was completed, the stirring was stopped and the solution filtered with suction to remove the yellow tinged solid. Thorough washing with water removed the yellow color. The wet solid was pressed out on a Buchner funnel and then immediately dissolved in 300 ml. of methylene chloride. The water which separated was removed, and the remaining solution was dried over magnesium sulfate. The yellow aqueous solution was extracted with five 50-ml. portions of methylene chloride, and the extracts were combined and dried over magnesium sulfate. The methylene chloride solutions were filtered and evaporated separately in an air stream. The solution containing the yellow solid deposited 11.7 g. (90%, based on bromoketone) of white solid tinged with yellow, m.p. 85–99°. Recrystallization of this solid from a chloroform-petroleum ether (b.p. 28–38°) solution raised the melting point to 116.8–117.2°. Yields of purified material averaged 41%. This material gave a positive test with the 2,4-dinitrophenylhydrazine reagent.[15] Calcd. for $C_{17}H_{17}BrO$: C, 64.36; H, 5.40; Br, 25.19. Found: C, 64.27; H, 5.58; Br, 24.95.

Hydrogenolysis of 5-Bromo-1,5-diphenyl-1-pentanone.—The bromoketone VII, 2.0 g. (0.0063 mole), was suspended in 80 ml. of ethanol and hydrogenated at 40 lb. pressure with 0.4 g. of palladium-on-calcium carbonate. When the rate of hydrogen uptake had decreased, the mixture was filtered to remove catalyst. The solid on the filter paper was washed with several portions of ethanol, and the washings combined with the filtrate. The volume of the solvent was reduced to about 20 ml. by warming under reduced pressure. The remaining light green solution was cooled at Dry Ice temperatures and gave 0.72 g. (48.3%) of 1,5-diphenyl-1-pentanone, m.p. 42.8-44.8°; m.p. oxime[16] 77.4–78.6° (m.p. 47°, ketone; oxime, 81–82).[8]

A mixed melting point of this material with an authentic sample, 1,5-diphenyl-1-pentanone (IX), m.p. 42.8-44.8, melted at 42.4–43.8°. Comparison of the infrared spectra demonstrated that the compounds were identical.

Preparation of Cinnamalacetophenone.—From 56 g. (1.3 moles) of sodium hydroxide in 500 ml. of water and 425 ml. of ethanol, 132.1 g. (1.1 moles) of acetophenone and 145 g. (1.1 moles) of cinnamaldehyde, there was obtained 244 g. of product, m.p. 91–98°. Recrystallization from a mixture of 500 ml. of ethanol and 350 ml. of methyl acetate gave 188.4 g. (73%) of yellow crystalline solid, m.p. 100.4–102.0° (reported,[17] no yield, m.p. 102°).

Preparation of 1,5-Diphenyl-1-pentanone (IX).—The ketone was prepared from cinnamalacetophenone by the method of Borsche.[8] The procedure yielded a liquid, b.p. 138–145° (0.25-0.3 mm.), n^{25}_{D} 1.5659 (reported,[8] no yield, b.p. 225-226° (16 mm.), m.p. 47°). Recrystallization from petroleum ether (b.p. 28–38°) gave a 78.5% yield of the ketone, m.p. 42.8–44.8°.

Bromination of 1,5-Diphenyl-1-pentanone.—To a solution of 8.5 g. (0.035 mole) of the ketone in 150 ml. of chloroform was added 5.7 g. (0.035 mole) of bromine over a period of 1.5 hr. The temperature climbed from 20.5 to 23° during the course of the reaction. The orange bromine color disappeared very slowly at the beginning of the reaction, then more rapidly until at approximately the point of half addition the color disappeared immediately after addition. A strong evolution of hydrogen bromide was noted as the reaction progressed. As the reaction approached completion, the bromine color was not discharged.

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(12) F. R. Japp and A. C. Michie, *J. Chem. Soc.*, **79**, 1000 (1901).

(13) J. Wislicenus and C. K. Kuhn, *Ann.*, **302**, 216 (1899).

(14) N. F. Hall and M. R. Sprinkle, THIS JOURNAL, **54**, 3469 (1932).

(15) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 3rd Ed., John Wiley and Sons, Inc., New York, N. Y., 1948, p. 171.

(16) Reference 15, p. 202.

(17) Z. Zafiriadis, *Compt. rend.*, **228**, 852 (1949).

After the addition of bromine was completed, the bright orange solution was evaporated under reduced pressure to yield a light tan viscous residue. This material was cooled at Dry Ice temperatures for 2 months, but failed to crystallize. Distillation yielded 8.96 g. (80.7%) of clear oil, $n^{25.5}_{\mathrm{D}}$ 1.5885, the α-bromo-δ-phenylvalerophenone. Calcd. for $C_{17}H_{17}BrO$: C, 64.36; H, 5.40; Br, 25.19. Found: C, 64.46; H, 5.49; Br, 25.13.

Permanganate Oxidation of δ-Bromo-δ-phenylvalerophenone.—To a solution of 1.0 g. (0.0031 mole) of the bromoketone in 50 ml. of water and 30 ml. of acetone was added 1.4 g. (0.009 mole) of potassium permanganate. The solution was stirred vigorously for 26 hours. The purple solution was then filtered to remove manganese dioxide. The solid was washed with several portions of acetone and the washings added to the filtrate.

The remaining permanganate ion was reduced by adding 10 ml. of saturated sodium bisulfite solution. The solution was filtered and washed again. The combined filtrates and washings were then evaporated under reduced pressure to a volume of 60 ml. A white solid precipitate appeared during the evaporation, 0.72 g. (92.1%), which proved to be crude 1,5-diphenylpentane-1,5-dione, m.p. 55–57°. Recrystallization from an ether–petroleum ether (b.p. 28–38°) solution gave 0.45 g. (57%), m.p. 63.0–64.0°. A mixed melting point with an authentic sample, m.p. 65–67°, melted at 63.8–65.2. Infrared spectra of the two materials were identical.

Preparation of 1,5-Diphenyl-4-penten-1-one.—A suspension of 2.69 g. (0.0084 mole) of the bromoketone and 1.12 g. (0.02 mole) of potassium hydroxide in 75 ml. of absolute ethanol was refluxed for 1.25 hr. The cooled, yellow solution when filtered yielded 0.82 g. of potassium bromide (82%). The excess potassium hydroxide was neutralized by the addition of concentrated hydrochloric acid. The solids were filtered and washed with several portions of ethanol. The combined filtrate and washings were evaporated and the light tan residue distilled to give 1.28 g. (64%) of clear yellow oil, b.p. 182–183° (3.5 mm.), $n^{25.5}_{\mathrm{D}}$ 1.5922. Calcd. for $C_{17}H_{16}O$: C, 86.40; H, 6.83. Found: C, 86.47; H, 6.53.

Oxidation of 1,5-Diphenyl-4-penten-1-one.—Potassium permanganate, 1.9 g. (0.012 mole), and a solution 1.02 g. (0.0043 mole) of VIII in a mixture of 25 ml. of water and 30 ml. of acetone were stirred at room temperature for 18 hr. The excess permanganate was removed by treatment with a saturated sodium bisulfite solution. Removal of the precipitated manganese dioxide left a cloudy filtrate and an insoluble oil. Repeated refluxing with basic permanganate solution did not completely remove the oil.

After the excess permanganate had been removed as above, the filtrate was acidified with concentrated sulfuric acid. A light tan solid, 0.14 g., separated and was removed by filtration.

The oil was taken up in ether, the ether solution dried and removed to give a brown oil, 0.46 g., which crystallized on standing. This oil was dissolved in 10 ml. of 10% sodium carbonate solution and then acidified with concentrated hydrochloric acid to give 0.31 g. of benzoic acid, m.p. 116.8–119°. The filtrate from this acidification and from the original solution were combined and extracted with ether. The extracts were dried over magnesium sulfate and the solvent removed, leaving 0.75 g. of a clear brown pungent oil. Crystallization of this material from ether–petroleum ether (b.p. 28–38°) gave β-benzoylpropionic acid, 0.11 g. (14.4%), m.p. 113.0–115.4°. A mixed melting point with an authentic sample, m.p. 116.3–118.0°, melted at 115.6–117.4°. Comparison of their infrared spectra demonstrated that the materials were identical.

The residue from the recrystallization of the β-benzoylpropionic acid and the 0.14 g. of brown solid obtained from the initial acidification of the oxidation mixture were combined and sublimed, giving 0.24 g. of tan solid, m.p. 97–110°. Two resublimations gave 0.09 g. of benzoic acid, m.p. 115–118°. Recrystallization from ether raised the melting point to 122–123°. A mixed melting point with an authentic sample, m.p. 121.5–123°, melted at 121.4–122.8°. Continued sublimation of the residue yielded an additional 0.07 g. of benzoic acid (total yield 0.47 g. (89%)).

Preparation of 1,5-Diphenyl-1-pentanol.—To a suspension of 3.8 g. (0.1 mole) of lithium aluminum hydride in 400 ml. of absolute ether in a 2-liter flask was added with stirring a solution of 18.2 g. (0.0764 mole) of 1,5-diphenyl-1-pentanone in 200 ml. of absolute ether. The solution was added over a period of 20 minutes, and the mixture was allowed to stir for an additional hour and 10 minutes. The complex and excess hydride were then destroyed, first by the dropwise addition of ethanol until refluxing became less violent, then by the addition of water until the decomposition was complete. The precipitate which formed during the period that the ethanol was being added made stirring difficult and caused considerable foaming. At the end of the decomposition, the ether solution was water white. The mixture was filtered to remove the precipitated hydroxides and dried over magnesium sulfate. The solvent was removed and the clear, slightly yellow residue distilled to give 16.95 g. (92.0%), b.p. 163–167° (1.2–1.3 mm.), $n^{25.5}_{\mathrm{D}}$ 1.5580, $d^{25.5}_{4}$ 1.029 (reported,[15] no yield, by high pressure hydrogenation of 1,5-diphenyl-1-pentanone, b.p. 332–333° (760 mm.), n^{20}_{D} 1.5562, d^{20}_{4} 0.961, and[8] no yield, by reduction of 1,5-diphenyl-1-pentanone with sodium in alcohol, b.p. 217° (12 mm.). Calcd. for $C_{17}H_{20}O$: C, 84.95; H, 8.39. Found: C, 85.10; H, 8.55.

Preparation of 1,5-Diphenyl-1-pentene.—To a solution of 25.3 g. (0.105 mole) of 1,5-diphenyl-1-pentanol in 150 ml. of dry benzene was added 8.95 g. (0.063 mole) of phosphorus pentoxide. The mixture was refluxed for 2 hr. and then decanted while hot from the brown sludge. When cool, the solution was washed with two 50-ml. portions of 10% sodium hydroxide and once with 50 ml. of water. The solution was dried overnight over magnesium sulfate and filtered. The solvent was removed by distillation under reduced pressure, and the cloudy residue was distilled to give 19.2 g. (82.4%), b.p. 128–130° (0.7 mm.), $n^{25.5}_{\mathrm{D}}$ 1.5832 (reported,[8] 36% yield by dehydration of 1,5-diphenyl-1-pentanol with zinc chloride, b.p. 186° (11 mm.)). Calcd. for $C_{17}H_{18}$: C, 91.84; H, 8.16. Found: C, 91.85; H, 8.23.

Infrared Spectra.—A Perkin–Elmer model 21 double beam recording spectrophotometer was employed with a NaCl prism to study the 2–15 μ range.

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