crystals of sodium nitrite were added, and then the resulting solution was cooled to 10°. A solution of about 0.6 mole of concentrated nitric acid in an equal volume of acetic acid was added during stirring while the temperature was maintained at 5–10°. After the reaction mixture had been allowed to stand 1 hour, 300 g. of mossy tin and 1 liter of hydrochloric acid were added. The resulting reaction mixture was heated on a steam-bath for four hours. At the end of this reflux period, the reaction mixture was decanted into 2 liters of concentrated hydrochloric acid. On standing, the hydrochloride of the amino alkylphenol separated. It was filtered and washed with hydrochloric acid and then with petroleum ether.

In some cases, the nitroso alkylphenol was dissolved in acetic acid and reduced as described above to give the corresponding amine hydrochloride.

Amino Alkylphenols. 1. Reduction of Nitroso Compounds. Method A.—The procedure used for the reduction of nitroso alkylphenols is described in reference 20. The nitroso compound (1.39 moles) was dissolved in 1.5 liters of water plus 300 cc. of 5 N sodium hydroxide. The solution was filtered and 1200 cc. of 5 N sodium hydroxide was added. The reaction mixture was heated to 35° and 600 g. of sodium hydrosulfite was added in small portions during stirring. The temperature of the solution rose to 60–65° and was maintained at that temperature for 0.5 hour, stirring being carried out for about 20% of the time during this period. At the end of 15 minutes, the solution became light in color and usually some of the amino alkylphenol precipitated from solution.

The addition of a kilogram of ice cooled the reaction mixture of about 20° and 500 ml. of concentrated hydrochloric acid was added. The solution was made slightly alkaline with ammonia and a small amount of sodium hydrosulfite was added to prevent oxidation during the filtering operation. The product was filtered, washed with water containing a small amount of sodium hydrosulfite and dried.

2. Coupling with Sulfanilic Acid followed by Reduction. Method B.—This procedure is described in reference 21. Sulfanilic acid (0.5 mole), an equivalent amount (25 g.) of sodium carbonate and 500 cc. of water were heated and stirred until all the sulfanilic acid had dissolved and then the solution was cooled to 15°. A solution of 37 g. (0.54 mole) of sodium nitrite in 100 ml. of water was added and the resulting solution was poured at once onto a mixture of 106 cc. (1.25 moles) of concentrated hydrochloric acid and 600 g. of ice contained in a 2-liter beaker. The resulting solution, from which some of the diazonium sulfate separates, was allowed to stand in an ice-bath for 15 to 25 minutes.

One-half mole of alkylphenol was dissolved in the warm solution obtained by dissolving 110 g. (2.75 moles) of sodium hydroxide in 600 ml. of water in a 5-liter flask. The addition of 400 g. of ice cooled the solution to 5°. In order to obtain a homogeneous solution in the case of high molecular weight phenols, it was necessary to use some 95% ethyl alcohol and then the minimum amount of water to effect solution of sodium hydroxide. To the cooled solution of alkylphenol, the diazonium salt was added and the resulting reaction mixture was allowed to stand without external cooling for 1 hour. In all cases, the solution became red but there was no separation of a precipitate.

The solution of azo dye was then heated to 45–50° and 230 g. (1.1 moles) of sodium hydrosulfite was added portionwise. The temperature of the reaction mixture rose to about 60–65° and was heated at that temperature for about 0.5 hour. The product which separated was filtered, washed with water containing a small amount of sodium hydrosulfite, and dried.

3. Reduction by Zinc and Acetic Acid. Method C.—The nitro alkylphenol was dissolved in acetic acid and then zinc dust was added during stirring until the solution became colorless. During this reduction, the temperature usually rose to about 60°. The colorless solution was cooled, filtered to remove excess zinc and the filtrate was diluted with water and cooled by the addition of ice. Ammonia was added to make the solution slightly alkaline and a small amount of sodium hydrosulfite was added to minimize oxidation of the amino compound by air. The product was filtered, washed with water containing a small amount of sodium hydrosulfite and dried.

4. Preparation from Hydrochlorides. Method D.—The hydrochloride of the amino alkylphenol was dissolved in methanol, and an ammonia solution containing a small amount of sodium sulfite was added to make the solution slightly alkaline. Addition of water containing a small amount of sodium hydrosulfite caused precipitation of the product which was filtered and dried.

5. Purification of Amino Alkylphenols.—Aromatic–aliphatic solvent combinations, such as toluene–petroleum ether, were found to be very satisfactory for recrystallization of most of the amino alkylphenols reported in this work. Some oxidation in these solutions did occur in certain cases, but it could be minimized by avoiding moisture.

The use of methanol or ethanol in combination with water was satisfactory in most cases, but oxidation in solution was greater than in the hydrocarbon solvent combinations. It was found that the use of water containing a small amount of sodium sulfite or sodium hydrosulfite in these recrystallizations minimized the oxidation and gave very satisfactory results.

Acknowledgment.—The author wishes to express his appreciation to Dr. G. E. P. Smith, Jr., for his advice and encouragement in this work. The interest of Dr. F. W. Stavely and Dr. R. F. Dunbrook in this investigation is greatly appreciated and the author wishes to thank the Firestone Tire & Rubber Company for permission to publish this material. Acknowledgment is made of the assistance of Mr. Adolph Para in most of the experimental work of this paper.

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(20) C. S. Marvel, "Organic Syntheses," Vol. XI, John Wiley and Sons, Inc., New York, N. Y., page 8.

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sym-Tetraphenylacetone. II. Its Reactions and Derivatives

BY DOUGLAS O. DEAN,[1a] WILLIAM B. DICKINSON,[1b] GEORGE B. HOEY[1c] AND CHAS. T. LESTER[2]

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As a continuation of our studies on tetraphenylacetone,[3] I, we have prepared several of its substituted derivatives and examined its behavior toward a variety of carbonyl reagents. Only lithium aluminum hydride reacted with the carbonyl group. Six other carbonyl reagents failed to react.[4] A Huang-Minlon modification of the Wolff–Kishner reduction[5] cleaved I to diphenylmethane.[6]

When treated with oxygen in the presence of base, I was cleaved almost quantitatively to benzophenone and diphenylacetic acid.[7] The reaction of I with oxygen in the presence of acid will be reported at a later date.

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(1) Taken in part from (a) Ph.D. Dissertation, D. O. Dean, Emory University, 1950; (b) M.S. Thesis, W.B. Dickinson, Emory University, 1947; and (c) Ph.D. Dissertation, G. B. Hoey, Emory University, 1954.

(2) Responsible co-author.

(3) D. O. Dean, W. B. Dickinson, O. R. Quayle and C. T. Lester, THIS JOURNAL, **72**, 1740 (1950).

(4) D. Vorlander and E. Rack, *Ber.*, **56B**, 1125 (1923), have reported the inertness of I toward several carbonyl reagents.

(5) Huang-Minlon, THIS JOURNAL, **68**, 2387 (1946).

(6) The other product of the cleavage should be diphenylacetic acid, which could, under the experimental conditions, decarboxylate to form additional diphenylmethane. The quantity of hydrocarbon isolated exceeded the theory for a simple cleavage and was 73% of theory for cleavage followed by decarboxylation. No diphenylacetic acid was isolated.

(7) W. von E. Doering and R. M. Haines, THIS JOURNAL, **76**, 482 (1954). An interesting by-product of this reaction was a 3% yield of α-hydroxy-*sym*-tetraphenylacetone.

I is readily monobrominated, but has resisted all efforts to produce a dibromo derivative. α-Bromo-*sym*-tetraphenylacetone (II) reacts readily with methanol, ethanol and aqueous sodium carbonate to yield the corresponding methoxy (III), ethoxy[8] (IV) and hydroxy (V) derivative

$$\underset{\text{II}}{Ph_2CBrCOCHPh_2} + ROH \longrightarrow \underset{\substack{\text{III, R = Me}\\ \text{IV, R = Et}\\ \text{V, R = H}}}{Ph_2C(OR)COCHPh_2}$$

The infrared spectrogram of III and of V reveals a strong absorption at 5.85 μ (carbonyl). The infrared spectrogram of V also shows a strong absorption at 2.92 μ (hydroxyl). An active hydrogen determination of V shows the presence of 2 active hydrogens.[9]

The active hydrogen determination of II gave results indicating 100% enolization and 100% addition. However, only I was formed in this reaction and it was isolated quantitatively. While the gas evolved was not analyzed, these results suggest[10]

$$Ph_2CBrCOCHPh_2 + 2MeMgI \longrightarrow (Ph_2CCOCHPh_2)MgI + C_2H_6 + MgBrI$$

Experimental[11]

Attempted Preparation of Carbonyl Derivatives of I.—Using vigorous and prolonged conditions I was recovered unchanged on treatment with hydrazine, phenylhydrazine, 2,4-dinitrophenylhydrazine, semicarbazide, hydroxylamine (a sealed tube reaction was not tried), and thioglycolic acid.[12] An active hydrogen determination showed 91% enolization and no addition.

Reduction of I by Lithium Aluminum Hydride.—The reaction was run in the regular manner.[13] From 9 g. of I, 8.3 g., 92%, of tetraphenylisopropyl alcohol, m.p. 107–108°, was produced. *Anal.* Calcd. for $C_{27}H_{24}O$: C, 88.97; H, 6.64. Found: C, 88.75; H, 6.76.

Attempted Huang-Minlon Reduction of I.—Following the procedure in the literature,[5] 6.93 g., 73%, of diphenylmethane, m.p. and mixture m.p. 26–27°, was isolated from the reaction of 10 g. of I. In a qualitative test 0.5 g. of I was refluxed for 15 hours with ethanolic potassium hydroxide. A small amount of diphenylacetic acid was isolated. While diphenylmethane was not isolated, its unmistakably characteristic odor pervaded the apparatus. This test shows that hydrazine is not necessary for the cleavage of I.

Autooxidation of I.[7]—A solution of 0.04 mole (14.5 g.) of I and 0.08 mole of potassium *t*-butoxide in 400 ml. of anhydrous *t*-butyl alcohol was heated at 60–65° for five hours while passing in a stream of oxygen. After removal of 200 ml. of solvent by distillation, 100 ml. of water was added and an additional 100 ml. of solvent distilled. The residue was steam distilled, yielding 2.6 g. (0.014 mole) of benzophenone, m.p. 50°, which separated from the distillate. Extraction of the distillate with ether and reaction with excess semicarbazide hydrochloride gave 4.9 g. (0.021 mole) of benzophenone semicarbazone, m.p. 164–165°. This represents a total of 0.035 mole or 87.5% of benzophenone. The alkaline residue from the steam distillation was filtered and the white crystalline material (1.22 g.) was recrystallized from ethanol, yielding 0.55 g., 3.8%, of V, m.p. and mixture m.p. 117–118°. The alkaline solution remaining was boiled with Norite, filtered and acidified, giving 7.0 g. (0.033 mole), 82.5%, of diphenylacetic acid, m.p. 144–145°. When the experiment was repeated, using nitrogen instead of oxygen, I was recovered quantitatively.

Preparation of II.—A solution of 54 g. of I and 50 ml. of bromine in 900 ml. of carbon tetrachloride was heated at 50–60° under reflux for 72 hr. The reaction mixture was irradiated with three ordinary 200 watt light bulbs. After cooling the solution was poured into 800 ml. of cold 10% sodium hydroxide solution. The organic layer was separated, washed with two 300-ml. portions of water and dried over anhydrous sodium sulfate. After filtering, the solvent was removed at the water-pump and the residue was recrystallized from acetone and petroleum ether. The yield of II was 53 g., 82%, m.p. 108–109°. *Anal.* Calcd. for $C_{27}H_{21}OBr$: Br, 18.1; mol. wt., 441. Found: Br, 18.5; mol. wt., 442 (cryoscopic in benzene).

Many unsuccessful attempts to prepare the α,α′-dibromo derivative have been made, starting with both I and II.[14,15] An active hydrogen determination of II showed 103% enolization and 106% addition. On working up the reaction, however, a 93.5% yield of I was the only product which could be found.

Preparation of III, IV and V.—Either III or IV may be prepared in essentially quantitative yield by dissolving II in the appropriate alcohol, refluxing for 5–6 hours, removing excess solvent at the water-pump, cooling and filtering. III is a white crystalline compound, m.p. 73–74°. *Anal.* Calcd. for $C_{28}H_{24}O_2$: C, 85.71; H, 6.38. Found: C, 85.43; H, 6.20. The infrared spectrogram of III shows a strong absorption at 5.85 μ, characteristic of a carbonyl compound. IV is a white crystalline compound, m.p. 78–79°. *Anal.* Calcd. for $C_{29}H_{26}O_2$: C, 85.71; H, 6.40. Found: C, 85.79; H, 6.33. Heating II with isobutyl alcohol or *n*-amyl alcohol resulted in a quantitative recovery of II.[15]

A solution of 23.75 g. of II dissolved in 300 ml. of acetone was added to a solution of 15 g. of sodium carbonate in 200 ml. of water. The mixture was heated under reflux for 12 hr. The acetone was removed by distillation. After solidification the residue was filtered and recrystallized from ethanol, giving 18.2 g., 90%, of V, m.p. 118–119°. *Anal.* Calcd. for $C_{27}H_{22}O_2$: C, 85.66; H, 5.82. Found: C, 85.79; H, 5.88. The infrared spectrogram of V showed strong absorption at 2.92 μ (hydroxyl) and at 5.85 μ (carbonyl). Heating 1 g. of V with aqueous 50% hydrogen iodide converted it quantitatively into I, m.p. and mixture m.p. 133–134°. An active hydrogen determination showed 1.93 active hydrogens per molecule of V. A solution of 3.5 g. of V in 50 ml. of acetic anhydride was heated under reflux for 25 hours. After removal of 25 ml. of solvent at the water-pump, the residue was poured onto ice and filtered. The resulting solid was crystallized from ethanol, yielding 2.74 g., 70%, of α-acetoxy-*sym*-tetraphenylacetone, m.p. 165–167°. *Anal.* Calcd. for $C_{29}H_{24}O_3$: C, 82.86; H, 5.71. Found: C, 82.68; H, 5.73.

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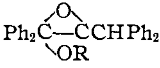
[8] The ease of formation of IV from II led Vorlander, ref. 4, to report the m.p. of II, recrystallized from ethanol, as 78°. This is in fact the m.p. of IV.

[9] This evidence precludes the possibility of structures of the type,  sometimes formed by the solvolysis of α-haloketones; *cf.* C. L. Stevens, W. Malik and R. Platt, THIS JOURNAL, **72**, 4758 (1950). While the spectrogram of IV was not prepared, there is no reason to suppose that ethanol would react any differently from methanol.

[10] A. Löwenbein and L. Schuster, *Ann.*, **481**, 106 (1930), have reported a similar reaction: $Ph_2CBrCOPh + 2PhMgBr \rightarrow (Ph_2CCOPh)MgBr + PhPh + MgBr_2$.

[11] All m.p.'s are uncorrected. Active hydrogens were determined in the usual manner, using methylmagnesium iodide in dibutyl ether. Microanalyses for carbon and hydrogen were performed by Drs. G. Weiler and F. B. Strauss, Oxford, England. The infrared spectrograms were prepared on Nujol mulls by Samuel P. Sadtler and Sons, Inc., Philadelphia, Pa.

[12] J. J. Ritter and M. J. Lover, THIS JOURNAL, **74**, 5576 (1952).

[13] R. F. Nystrom and W. G. Brown, *ibid.*, 2548 (1947).

[14] R. A. Day, M.S. Thesis, Emory University, 1937.

[15] M. R. Bush, M.S. Thesis, Emory University, 1938.

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Nucleophilic Displacement Reactions of Duryl Halophenyl Ketones

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The method developed earlier for making methoxy derivatives[2] of hindered diaryl ketones has now

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[2] R. C. Fuson and W. C. Hammann, THIS JOURNAL, **73**, 1851 (1951).