tion of 2.73 molar equivalents of hydrogen by a mixture of 27.3 g. (0.1 mole) of hexachlorocyclopentadiene (I), 30 ml. of absolute ethanol and 0.100 g. of platinum dioxide was completed in 80 minutes. The reaction mixture was filtered and cooled with Dry Ice and the crystallized product was removed by filtration. Two crystallizations from petroleum ether (b.p. 35–37°) gave 10.0 g. (49%) of 1,2,3,4-tetrachlorocyclopentadiene (III), m.p. and mixed m.p. 60–62°.[2]

Catalytic Hydrogenation of 1,2,3,4,5-Pentachlorocyclopentadiene.—A mixture of 18.8 g. (0.079 mole) of 1,2,3,4,5-pentachlorocyclopentadiene, 35 ml. of absolute ethanol and 0.15 g. of platinum dioxide was hydrogenated until 0.086 mole of hydrogen was absorbed. The mixture was filtered and cooled with Dry Ice to yield 6.0 g. (38%) of 1,2,3,4-tetrachlorocyclopentadiene, m.p. and mixed m.p. 60–62.5°.

Catalytic Hydrogenation of Octachlorocyclopentene.—The hydrogenation of a mixture of 34.4 g. (0.1 mole) of octachlorocyclopentene, 100 ml. of absolute ethanol and 0.100 g. of platinum dioxide was stopped after one hundred minutes and absorption of 3.8 molar equivalents of hydrogen. The reaction mixture was filtered and cooled with Dry Ice to give 7.9 g. of 1,2,3,4-tetrachlorocyclopentadiene, m.p. and mixed m.p. 60–62°. An additional 2.0 g. of this product was obtained by distillation of the filtrate. The total yield was 49%.

Catalytic Hydrogenation of 1,2,3,4-Tetrachlorocyclopentadiene.—A mixture of 10.2 g. (0.05 mole) of 1,2,3,4-tetrachlorocyclopentadiene, 50 ml. of absolute ethanol and 0.161 g. of platinum dioxide was hydrogenated until 5.0 molar equivalents of hydrogen was absorbed. The resulting mixture was filtered and distilled to give 2.4 g. (69%) of liquid, b.p. 45–50°, $n^{20}D$ 1.4045. This material was washed with water, dried and distilled. The distillate gave an infrared spectrum identical with that of cyclopentane.[11]

Attempted Reduction of 1,2,3,4,5-Pentachlorocyclopentadiene with Lithium Aluminum Hydride.—1,2,3,4,5-Pentachlorocyclopentadiene (16.5 g., 0.0694 mole) in 100 ml. of anhydrous ether was treated with an ether solution of lithium aluminum hydride (0.165 mole) at −50°. A total of 1.789 liters (0.0718 mole) of gas was liberated. The reaction mixture was hydrolyzed by pouring it onto a mixture of crushed ice and concentrated hydrochloric acid. The organic product was extracted with ether and dried. The extract was distilled to give 12.5 g. of liquid distillate which completely dimerized to V, m.p. and mixed m.p. 215–218°. An additional 2.5 g. of V was recovered from the distillation residue (total recovery 94%).

1,4,5,6,7-Pentachlorobicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic Acid.—Maleic anhydride (3.44 g., 0.35 mole) and 6.5 g. (0.0262 mole) of 1,2,3,4,5-pentachlorocyclopentadiene were heated to 120° when a vigorous reaction occurred and the temperature of the mixture rose rapidly to 200°. The mixture was cooled and recrystallized from water to give 6.8 g. (69%) of colorless needles, m.p. 183–184.5°.

Anal. Calcd. for $C_9H_5Cl_5O_4$: C, 30.50; H, 1.42; neut. equiv., 177.2. Found: C, 30.19; H, 1.70; neut. equiv., 179.2

4,5,6,7,8-Pentachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene.—Cyclopentadiene (9.9 g., 0.15 mole) was added slowly to a refluxing solution of 35.7 g. (0.15 mole) of 1,2,3,-4,5-pentachlorocyclopentadiene (II) in 200 ml. of petroleum ether (b.p. 60–70°). The solvent was removed under reduced pressure and the residue was crystallized on cooling. This material (26.2 g., 57.5%) was crystallized twice from petroleum ether (b.p. 30–60°) to give colorless plates, m.p. 100–101°.

Anal. Calcd. for $C_{10}H_7Cl_5$: C, 39.45; H, 2.32. Found: C, 39.69; H, 2.37.

Chlorine gas was passed through a mixture of 7.76 g. (0.0207 mole) of 4,5,6,7,8-pentachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene, 35 ml. of carbon tetrachloride and 0.2 g. of anhydrous aluminum chloride at room temperature for 160 minutes. After filtering the mixture, the solvent was removed and the residue was crystallized from petroleum ether (b.p. 30–60°) to give colorless plates, m.p. 150–151°.

Anal. Calcd. for $C_{10}H_6Cl_8$: C, 29.36; H, 1.46. Found: C, 29.50; H, 1.95.

Acknowledgments.—The authors wish to thank the Hooker Electrochemical Company for financial support of this work and to acknowledge the assistance of Dr. H. E. Ungnade.

LAFAYETTE, INDIANA

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[11] Catalog of Infrared Spectral Data, American Petroleum Institute Research Project 44, serial number 254.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF EMORY UNIVERSITY]

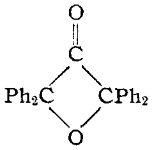
sym-Tetraphenylacetone. III. The Preparation of 2,2,4,4-Tetraphenyloxetanone

BY G. BROOKE HOEY,[1a,b] DOUGLAS O. DEAN[1a,c] AND CHAS. T. LESTER[2]

RECEIVED JULY 21, 1954

The autoöxidation of tetraphenylacetone under a variety of conditions, the presence of strong base excepted, produces a heterocyclic ketone, 2,2,4,4-tetraphenyloxetanone. The structure of the ketone has been established by its chemical reactions, its degradation products and the infrared spectrograms of the ketone and three alcohols produced from it.

In a previous publication[3] we reported that *sym*-tetraphenylacetone (I) was cleaved by oxygen in the presence of base to give an essentially quantitative yield of diphenylacetic acid and benzophenone. We wish now to report that the autoxidation of I in acetic acid gives a lesser amount of cleavage products and a substantial yield of a dioxo compound to which we have assigned the structure, 2,2,4,4-tetraphenyloxetanone (II).



II

This compound has appeared frequently in this Laboratory as a product of the prolonged treatment of I and its derivatives under a variety of reaction conditions.[4] Some examples of its synthesis are recorded in Table I.

II was described some years ago by Vorlander[5] as the product of the oxidation of tetraphenylallene. On the basis of its analysis and

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[1] (a) Taken in part from the Ph.D. Dissertations of G. B. Hoey, Emory University, 1954, and D. O. Dean, Emory University, 1950; (b) Tennessee Eastman Fellow, 1952–1953; (c) supported in part by a contract with the Office of Naval Research.

[2] Responsible co-author.

[3] D. O. Dean, W. B. Dickinson, G. B. Hoey and C. T. Lester, THIS JOURNAL, 76, 4988 (1954).

[4] II was first isolated in very small yield from a 0.001 *M* solution of α-bromo-*sym*-tetraphenylacetone in pyridine which had been heated for several weeks; W. B. Dickinson, M.S. thesis, Emory University, 1947.

[5] D. Vorlander and P. Winstein, *Ber.*, 56, 1122 (1923).

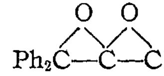
TABLE I

SYNTHESIS OF OXETANONE FROM $Ph_2CACOCHPh_2$

A, g.	Other reagents	Time, days	Temp., °C.	Yield G.	Yield %
H, 5[a]	91% HOAc	2	107–110	3.2	61.5
H, 5[b]	91% HOAc	2.2	107–110	0	0
H, 200[c,d]	91% HOAc	105	80–100	98.5	47.3
H, 36	Br_2, H_2O, CCl_4	43	25–50	14	37.5
H, 3.6	93% pyridine	42	50	1.1	30[f]
Br, 36	Pyridine	22	50	4.4	10
HO, 5	Br_2 in CCl_4	0.7	75–80	2.5	50

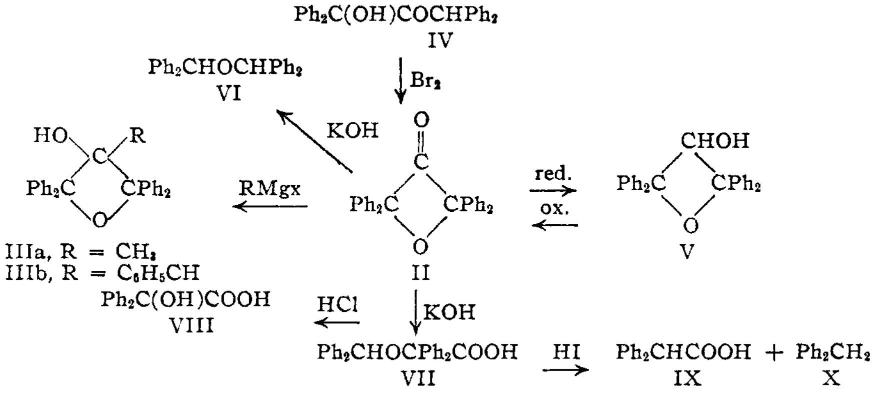
[a] Oxygen gas was bubbled through the solution for the entire reaction period. [b] Nitrogen gas was bubbled through the solution. [c] The flask was heated by a battery of light bulbs. [d] A 33% yield of benzophenone, a 9.1% yield of diphenylacetic acid and 18 g. of unidentified polymeric material were also isolated from this reaction. This experiment started as a light-catalyzed bromination of I. After water accidentally entered the flask it was allowed to stand for six weeks before working up. [f] A large amount of unreacted ketone was recovered. [g] The principal product was a polymeric material.

method of synthesis he assigned it a diepoxide structure,



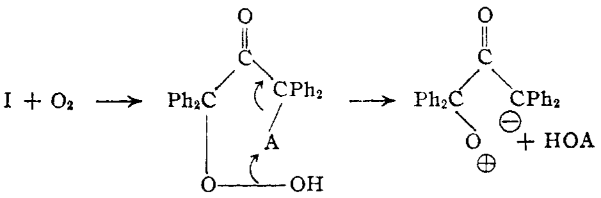
$Ph_2C{-}C{-}CPh_2$ (O O)

[6] We have assigned the oxetanone structure to II for the following reasons: (a) the chemical transformations indicated by the equations



(b) Infrared spectrograms of II, IIIa, IIIb and V: II showed a strong absorption at 5.5 μ, strikingly similar to the carbonyl group in β-propiolactone.[7,8] We are not prepared to assign any particular absorptions to the ring,[9,10] but II showed strong absorption at 6.9 μ, 8.9, 10.3 and 10.4 μ; IIIa, IIIb and V each show absorptions at 6.7–6.9 μ, 8.7–8.9 μ and 10.0–10.2 μ.[11] A strong absorption in the region of 10 μ has been described as characteristic of oxetane rings.[9] (c) Finally, II shows a half-wave potential consistent with a ketone structure when subjected to polarographic reduction.[12]

Except for No. 7 in Table I we assume that the oxetanone is formed *via* a hydroperoxide intermediate, XI. In strong base,[3] XI is cleaved as previously postulated,[13] but in acid or weak base the reaction may proceed in an alternative manner[14]



A = H, Br XI XII (ionic equiv. of II)

Experimental[15]

Preparation of II. (a) From I, Reaction 3, Table I.—A solution of 200 g. of I in 1800 ml. of 91% acetic acid was heated under reflux for 42 days. Heat was supplied by eight 200-watt bulbs.[16] Two hundred ml. of acetic acid was removed by distillation and the crystals separating from the residue were isolated by filtering the hot solution (60–80°). This prevents unreacted I from separating from the solution. The filtrate was reheated for 28 days. A repetition of the above precedure was followed by a final heating of 35 days. At this time the reaction mixture was cooled to room temperature and the final batch of crystals removed by filtration. The combined crystalline products were purified by crystallization from acetone, yielding 98 g. (47%) of II, m.p., 199–201°. *Anal.* Calcd. for $C_{27}H_{20}O_2$: C, 86.17; H, 5.32. Found: C, 86.17; H, 5.50. The final filtrate above was concentrated by distillation to 300 ml. This was made basic with 10% aqueous sodium hydroxide and the basic solution steam distilled. From the distillate was recovered 32.2 g. (32.1%) of benzophenone identified as semicarbazone, m.p. 165–167°; reported 165°.[17] An insoluble, polymeric residue, 18.0 g., was removed from the basic solution above. This solution on boiling with Norite, acidifying and filtering gave 10.6 g. (9.1%) of diphenylacetic acid, m.p. and mixture m.p., 146–148°. Reactions 1 and 2 in Table I were processed in essentially the same manner (however, the product was not isolated in batches) except that no effort was made to find any product other than II and I. In reaction 2, 4.8 g.

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[6] The assumption that allenes would yield diepoxides is not supported by later work on allene oxidation. *Cf.* Q. Z. Bouis, *Bull. soc. chim. France*, [4] **51**, 1177 (1932); J. Boeseken, *Rec. trav. chim.*, **54**, 657 (1935); F. B. LaForge and F. Acree, Jr., *J. Org. Chem.*, **6**, 208 (1941). Hydroxyketones are the usual products. We have made several unsuccessful attempts to isolate hydroxytetraphenylacetone (IV) from the oxidation of tetraphenylallene. However, we have been able to show that II can be made by the oxidation of IV.

[7] S. Searles, M. Tamres and G. M. Barrow, THIS JOURNAL, **75**, 71 (1953).

[8] We are indebted to Dr. T. L. Gresham of the B. F. Goodrich Co. for a complete spectrogram of β-propiolactone.

[9] S. Searles and G. M. Barrow, THIS JOURNAL, **75**, 1175 (1953).

[10] The possibility of ring strain imparted by the carbonyl group could conceivably modify the absorption characteristics of the ring.

[11] The spectrograms of mulls of IIIa, IIIb and V failed to show hydroxyl absorption. However, carbon tetrachloride solutions of IIIa and V showed a moderate adsorption at 2.81μ (hydroxyl). Presumably these high-melting compounds are very strongly hydrogen bonded. II failed to show any hydroxyl absorption as a mull or as a solution.

[12] The details of this reduction will be reported by Dr. R. A. Day of this Laboratory.

[13] W. von E. Doering and R. M. Haines, THIS JOURNAL, **76**, 482 (1954).

[14] Reaction 4 in Table I could proceed: ketone → bromoketone → IV → II, IV reacting as in reaction 7. No effort was made to isolate IV in reaction 4 or XI in any of the preparations of II.

[15] All m.p.'s are uncorrected. The infrared spectrograms of the mulls were prepared by Samuel P. Sadtler and Sons, Inc., Philadelphia, Pa.; those of the carbon tetrachloride solutions by Mr. J. E. Baudean, Perkin–Elmer Corp., New Orleans, La. Active hydrogen determinations were done in the usual manner, using methylmagnesium iodide in dibutyl ether.

[16] At the time this experiment was run it was felt that visible light was an important adjunct. Subsequent experiments do not support our original impression; *viz.*, run 1 in Table I.

[17] S. M. McElvain, "The Characterization of Organic Compounds," The Macmillan Co., New York, N. Y., 1947, p. 241.

of I was recovered. Reactions 4, 5 and 6 are not satisfactory procedures and no details are given.

(b) **From IV, Reaction 7, Table I.**—A solution of 2 g. of bromine and 5 g. of IV in 100 ml. of carbon tetrachloride was placed in a Vycor flask and irradiated at 75–80° by four 8-watt ultraviolet tubes for 17 hours. The solvent and unreacted bromine were removed at the water pump and the residue taken up in boiling dibutyl ether. This gave, on cooling and filtering, 2.55 g. (50%) of II, m.p. and mixture m.p. 199–201°.

(c) **From Tetraphenylallene.**—The oxidation of 2 g. of tetraphenylallene by the procedure of Vorlander[5] gave 1.1 g. of II, m.p. and mixture m.p. 199–201°. Several attempts to isolate IV from this reaction were unsuccessful. However, a 30-second treatment of 2 g. of IV by Vorlander's oxidation procedure yielded 0.1 g. of II, m.p. and mixture m.p. 198–201°. An active hydrogen determination of II showed 0% enolization and 98% addition.

Reduction of II. (a) By Lithium Aluminum Hydride.—In the usual manner[18] 10 g. of II was reduced by 3 g. of lithium aluminum hydride to give 5.7 g. (57%) of V, m.p. 239–240°. *Anal.* Calcd. for $C_{27}H_{22}O_2$: C, 85.71; H, 5.82. Found: C, 85.41; H, 5.99.

(b) **By Isopropylmagnesium Bromide.**[19]—In the usual type of Grignard apparatus 10 g. of II reacted with 0.3 mole of isopropylmagnesium bromide[19] to produce 5.7 g. (57%) of V, m.p. and mixture m.p. 239–240°. The unsaturated nature of the effluent gas was demonstrated by its reaction with dilute aqueous potassium permanganate.

(c) **By Sodium Methoxide.**—A solution of 15 g. of II and 2.2 g. of sodium methoxide in 100 ml. of dioxane was heated at reflux for 2 hours. The solution was cooled and to it added 3 ml. of acetic acid and 150 ml. of water. The crystals separating were filtered and recrystallized from acetone–ethanol. This gave 14 g. (93%) of V, m.p. and mixture m.p. 239–240°.[20] Oxidation of 1 g. of V using 0.75 g. of chromic anhydride in 50 ml. of boiling acetic acid gave 0.56 g. (56%) of II, m.p. and mixture m.p. 199–201°. An active hydrogen determination of V showed 0.93 hydrogen per molecule.

Preparation of IIIa and IIIb.—Both compounds were prepared in the usual manner.[19] An excess of Grignard reagents was used in each case. The results are as follows: IIIa, 8.38 g. (89% yield) from 9.0 g. of II, m.p. 226–228°. *Anal.* Calcd. for $C_{28}H_{24}O_2$: C, 85.71; H, 6.38. Found: C, 85.76; H, 6.18. IIIb, 8.8 g. (70% yield) from 10.0 g. of II, m.p. 203–205°, mixture m.p. with II 175–185°. *Anal.* Calcd. for $C_{34}H_{28}O_2$: C, 87.15; H, 6.02. Found: C, 87.19; H, 6.36.

Ring Opening of II. (a) By Potassium Hydroxide in Dioxane.—A solution of 10 g. of II and 4 g. of potassium hydroxide in 100 ml. of 90% aqueous dioxane was heated at reflux with stirring for 3 hours. After the addition of 150 ml. of water and removal of 100 ml. of solvent at the water pump, the residue was extracted with benzene. The aqueous solution was boiled with Norite, filtered, cooled and acidified. The precipitate after filtering and drying was crystallized from benzene–petroleum ether. The product, O-benzhydrylbenzilic acid (VII), 7 g., has no definite m.p., but decomposes over the range 100–110°. *Anal.* Calcd. for $C_{27}H_{22}O_3$: C, 82.23; H, 5.58; neut. equiv., 394. Found: C, 82.60; H, 5.81; neut. equiv., 399. On heating with an aqueous acetic acid solution of hydrogen iodide, 2 g. of VII was cleaved to give 1 g. of IX, m.p. and mixture m.p. 144–146°, and 0.32 g. of X, m.p. 26°. Similarly 4 g. of VII was cleaved by hydrogen chloride to give 1.1 g. of VIII, m.p. and mixture m.p. 147–148°. The non-acidic fraction of this cleavage was not isolated.

(b) **By Potassium Hydroxide in Ethylene Glycol.**—A solution of 7.5 g. of II and 28 g. of potassium hydroxide in 125 ml. of 75% ethylene glycol was heated with distillation of water to 195° over a one-hour period. After standing several days at room temperature, the solution was poured onto cracked ice. The solid separating was filtered and recrystallized from ethanol. It proved to be VI, 0.5 g., m.p. and mixture m.p. with prepared sample[21] 109–110°. The odor of X was quite pronounced, but no effort was made to isolate it or its accompanying product, benzophenone.[22]

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[18] R. F. Nystrom and W. G. Brown, THIS JOURNAL, **69**, 2548 (1947).

[19] In all the Grignard reactions it was necessary to use either toluene or dibutyl ether as a solvent because of the low solubility of II in diethyl ether.

[20] The ease with which II undergoes a Ponndorff reduction is consistent with our unsuccessful efforts to convert V to II by an Oppenauer oxidation. Treating V in boiling toluene for 3 hours with aluminum *t*-butoxide and a 15 molar excess of cyclohexanone resulted in a quantitative recovery of V.

[21] R. S. Tipson, M. A. Clapp and L. H. Cretcher, *J. Org. Chem.*, **12**, 133 (1947).

[22] D. Y. Curtin and S. Leskowitz, THIS JOURNAL, **73**, 2630 (1951), report that dibenzhydryl ether (VI) is readily cleaved by strong base into X and benzophenone.

EMORY UNIVERSITY, GEORGIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Aminoalcohols Containing the 8-Oxa-3-azabicyclo[3.2.1]octane Ring System and Their Benzoates

BY ARTHUR C. COPE AND WARREN N. BAXTER

RECEIVED JULY 28, 1954

cis-2,5-Bis-(hydroxymethyl)-tetrahydrofuran (III), prepared by reduction of 5-hydroxymethylfurfural or dimethyl tetrahydrofuran-*cis*-2,5-dicarboxylate, has been converted through the ditosylate II into a series of aminoalcohols containing the 8-oxa-3-azabicyclo[3.2.1]octane ring system (V–XI, Table I). The aminoalcohols were prepared from the ditosylate II and aminoalcohols containing a primary amino group. Benzoate hydrochlorides (Table II) and one tropate hydrochloride have been prepared from the bicyclic aminoalcohols and tested for pharmacological activity. Evidence confirming the structure of the aminoalcohols was obtained by synthesis of an identical authentic sample of N-(2-hydroxyethyl)-8-oxa-2-azabicyclo[3.2.1]octane (V) from 8-oxa-3-azabicyclo[3.2.1]octane (I) and ethylene oxide. The structure of I was verified by degradation through reaction of its N-benzoyl derivative XIII with phosphorus pentachloride to *cis*-2,5-bis-(chloromethyl)-tetrahydrofuran (XIV).

Newth and Wiggins[1] have shown that the bicyclic secondary amine, 8-oxa-3-azabicyclo[3.2.1]octane (I), is formed by reaction of the 2,5-bis-(hydroxymethyl)-tetrahydrofuran ditosylate with m.p. 127.5–128° (which accordingly is the *cis* isomer) with ammonia in methanol. We have prepared a series of aminoalcohols containing the ring system present in I by reaction of the ditosylate II with seven aminoalcohols containing a primary amino group. It was of interest to determine the pharmacological activity of esters of these aminoalcohols, which have some features of structural similarity to scopolamine, the tropic acid ester of an aminoalcohol (scopine) which contains an ethylene oxide grouping.

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[1] F. H. Newth and L. F. Wiggins, *J. Chem. Soc.*, 155 (1948).