100 ml. of ether prepared from 4.0 g. (0.0077 mole) of hexaphenyldisilane, was added over 25 minutes to a stirred solution of 5.24 g. (0.0184 mole) of recrystallized triphenylchloromethane in 50 ml. of ether. Each drop of the suspension as it was added caused a localized red color in the flask which rapidly disappeared, and at the end of the 25 minutes the flask contained a pale yellow suspension, due to the precipitation of a white solid. The reaction was stirred for an additional 2 hours, and a sample of the suspension failed to give a positive Color Test I. The reaction was hydrolyzed with water, and the solid filtered from the ether and water layers. The residue (0.45 g. or 11%) was recrystallized from pyridine and melted at 360–363°, and did not depress the mixed melting point with hexaphenyldisilane. During the filtration of this residue, a white flaky solid precipitated from the deep-yellow ether layers. The flask was allowed to stand in the air until precipitation ceased (overnight) and then the 5.5 g. of material melting 167–215° was filtered off. This solid was refluxed with 100 ml. of 1:1 ethanol–ethyl acetate and the hot suspension was filtered. The residue weighed 4.2 g. (88%), melted at 184–186°, and did not depress a mixed melting point with authentic bis-triphenylmethyl peroxide. The ether layer, from which this material precipitated, and the ethanol-ethyl acetate extract were worked up and from them a total of 4.9 g. (50%) of hexaphenyldisiloxane, m.p. 220–222° was recovered (mixed melting point), together with some gummy material which resisted purification.

A similar run in which the reaction flask was immersed in a Dry Ice–acetone-bath at about −30° behaved as above except that the red color formed on addition of the triphenylsilylpotassium persisted for some time. The products isolated were hexaphenyldisilane (16%), hexaphenyldisiloxane (53%), bis-triphenylmethyl peroxide (63%) and some gum.

AMES, IOWA

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

Small-Ring Compounds. XI. Some New Cyclobutane, Cyclobutene and Cyclobutanone Derivatives Derived from the Adduct of Phenylacetylene with 1,1-Difluoro-2,2-dichloroethylene

BY JOHN D. ROBERTS,[1] G. BRUCE KLINE AND HOWARD E. SIMMONS, JR.

RECEIVED MARCH 9, 1953

The adduct (I) of phenylacetylene and 1,1-difluoro-2,2-dichloroethylene (obtained in 76% yield in 2 hours at 130°) has been shown to be 1,1-difluoro-2,2-dichloro-3-phenylcyclobutene. Hydrogenation of I yielded 1,1-difluoro-3-phenylcyclobutane (II), while hydrolysis with concentrated sulfuric acid at 100° gave crystalline 2,2-dichloro-3-phenylcyclobutenone (III). The structure of III was firmly established by base-induced cleavage to 4,4-dichloro-3-phenyl-2-butenoic acid (IV) and by reduction to 3-phenylcyclobutanone. I was found to rearrange to 1,1-difluoro-2,4-dichloro-3-phenylcyclobutene (VIII) on heating with triethylamine. VIII on hydrolysis with concentrated sulfuric acid yielded 2,4-dichloro-3-phenylcyclobutenone (IX), the structure of which was established by reactions similar to those used for III and reduction to phenylcyclobutane. IX displayed no tendency to yield 1-acetoxy-2,4-dichloro-3-phenylcyclobutadiene with isopropenyl acetate and *p*-toluenesulfonic acid under conditions where other ketones are converted to enol acetates.

The principal obstacle to the elucidation of the chemistry of cyclobutane and its derivatives is the difficulty encountered in large-scale laboratory synthesis of four-membered carbocyclic rings. Perkin's classical malonic ester syntheses and their modifications[2] have been of considerable utility but are customarily limited by rather low yields and restriction to acyl- or carboxyl-substituted derivatives. Ideal syntheses of cyclobutane and cyclobutene would be afforded by addition of ethylene to ethylene or acetylene, respectively, but these reactions do not appear to have so far been achieved. Substituted ethylenes and ketenes have been converted to cyclobutane derivatives in thermal or photochemical reactions.[3] However, with few exceptions,[3,4] the yields are low or the products are not well-suited for further transformations. The fairly recent discovery that fluorinated ethylenes will often thermally dimerize[5] or add to other unsaturated compounds[6] to give high yields of cyclobutane derivatives provides an excellent synthetic route to a wide variety of fluorinated cyclobutanes, which unfortunately usually display the customary chemical inertness of the fluorine functions.[5b,7] In the present research we have utilized the activating influence of fluorine in the cycloaddition reaction and attempted to find useful processes by which the fluorine could be subsequently removed. The most interesting results so far obtained relate to the adduct from 1,1-difluoro-2,2-dichloroethylene and phenylacetylene and will be described in this paper.

1,1-Difluoro-2,2-dichloroethylene reacts smoothly with phenylacetylene at 130°, and, after 2 hours, a 76% yield of 1,1-difluoro-2,2-dichloro-3-phenylcyclobutene (I) may be obtained.[8] The structure

---

(1) Gates and Crellin Laboratories, California Institute of Technology, Pasadena 4, California.

(2) *Cf.* (a) R. C. Fuson in H. Gilman, "Organic Chemistry, An Advanced Treatise," John Wiley and Sons, Inc., New York, N. Y., Vol. I, 2nd Ed., Chap. 2; (b) E. R. Buchman, A. O. Reims, T. Skei and M. J. Schlatter, THIS JOURNAL, **64**, 2696, 2703 (1942); (c) H. M. Walborsky, *ibid.*, **71**, 2941 (1949); (d) J. Cason and C. F. Allen, *J. Org. Chem.*, **14**, 1036 (1949).

(3) (a) W. E. Hanford and J. C. Sauer in R. Adams, "Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., Vol. III, 1946, Chap. 3; (b) H. Staudinger and E. Suter, *Ber.*, **53**, 1092 (1920), and earlier papers; (c) L. I. Smith, C. L. Agre, R. M. Leekley and W. W. Prichard, THIS JOURNAL, **61**, 7 (1939); (d) E. C. Coyner and W. S. Hillman, *ibid.*, **71**, 324 (1949); (e) A. Mustafa, *Chem. Revs.*, **51**, 1 (1952).

(4) (a) B. T. Brooks and G. Wilbert, THIS JOURNAL, **63**, 870 (1941); (b) A. T. Blomquist and J. Kwiatek, *ibid.*, **73**, 2098 (1951).

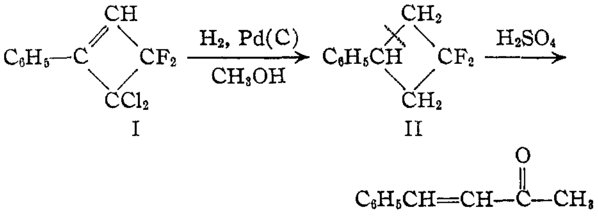
(5) (a) J. Harmon, U. S. Patent 2,404,374 (1946); (b) A. L. Henne and R. P. Ruh, THIS JOURNAL, **69**, 279 (1947); (c) P. L. Barrick, U. S. Patent 2,427,116 (1947); (d) P. L. Barrick and R. D. Cramer, U. S. Patent 2,441,128 (1948); (e) M. Prober and W. T. Miller, Jr., THIS JOURNAL, **71**, 598 (1949).

(6) (a) D. D. Coffman, P. L. Barrick, R. D. Cramer and M. S. Raasch, THIS JOURNAL, **71**, 490 (1949); (b) A. L. Barney and T. L. Cairns, *ibid.*, **72**, 3193 (1950).

(7) Some very interesting reactions of hexafluorocyclobutene have been described lately by K. E. Rapp, *ibid.*, **73**, 5901 (1951), and R. L. Pruett, C. T. Bahner and H. A. Smith, *ibid.*, **74**, 1633, 1638, 1642 (1952).

(8) The reaction also has been carried out independently by E. T. McBee, H. M. Hill and G. B. Bachman, *Ind. Eng. Chem.*, **41**, 70 (1949), but other than the physical properties and analysis no evidence for the structure of the product was adduced.

of I was established by the following reactions. Hydrogenation gave 1,1-difluoro-3-phenylcyclobutane (II), which on hydrolysis with concentrated sulfuric acid yielded benzalacetone. If one assumes that the *gem*-difluoro group becomes the carbonyl group of the benzalacetone, then the phenyl group may be assigned to the 3-position with respect to the fluorines.



No detectable hydrolysis of I occurred after 12 hours at reflux with an acetone–water mixture. With concentrated sulfuric acid at 100°, hydrogen fluoride was evolved, and when the reaction mixture was poured into ice-water, crystalline 2,2-dichloro-3-phenylcyclobutenone (III) separated. The unusual character of this reaction prompted a thorough investigation of the structure of the reaction products. The infrared spectrum of III showed the characteristic 5.6 μ carbonyl absorption of cyclobutanones,[9] and the substance formed carbonyl derivatives. Vigorous oxidation gave benzoic acid showing the benzene ring was not altered in the hydrolysis reaction. III dissolved on warming with dilute sodium hydroxide solution and, on acidification, yielded solid 4,4-dichloro-3-phenyl-2-butenoic acid (IV). This reaction parallels the cleavage of α-halogen substituted ketones in the haloform reaction and probably has a similar mechanism.

Possible alternative structures such as 4,4-dichloro-3-phenyl 3-butenoic acid (V) or 2,2-dichloro-3-phenyl-3-butenoic acid (VI) were ruled out either by ozonization which gave α,α-dichloroacetophenone or the ultraviolet absorption spectrum (Fig. 1) which was very similar to that of β-methylcinnamic acid. The carbon skeleton of IV was established by hydrogenation to β-phenylbutyric acid.

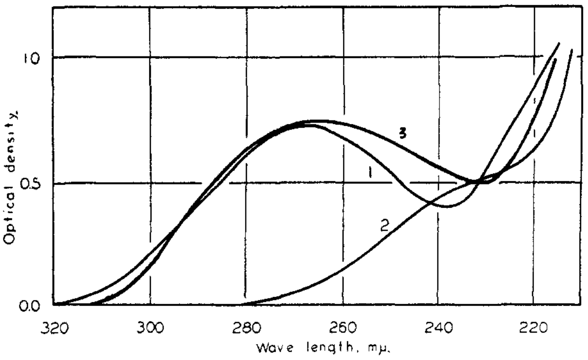
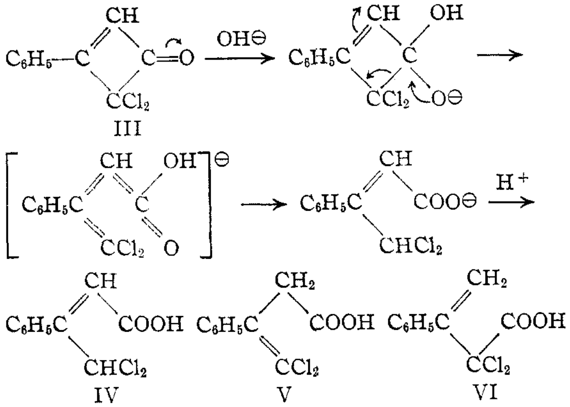
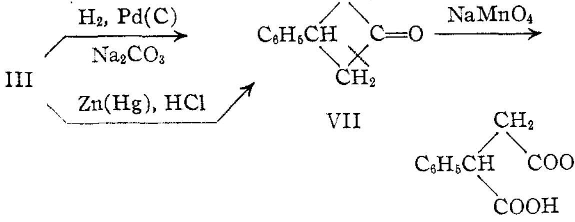


Fig. 1.—Ultraviolet spectra: Cary recording spectrophotometer, model 11MS, with 1-cm. quartz cell. The curves are for ethanol solutions, 10^{-4} *M* and are corrected for solvent absorption: 1, 4,4-dichloro-3-phenyl-2-butenoic acid; 2, 2,4-dichloro-3-phenyl-3-butenoic acid; 3, β-methylcinnamic acid.

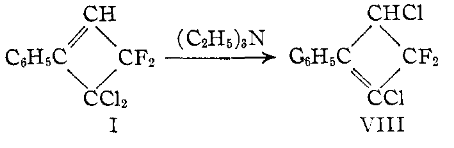


Production of α,α-dichloroacetophenone from IV proves the existence of a *gem*-dichloro grouping in III at a position adjacent to the carbon carrying the benzene ring. The 1,3-relation of the carbonyl and phenyl groups in III is confirmed by the carbon skeleton of IV.

The existence of a cyclobutane ring in III was established by hydrogenation or mild chemical reduction to 3-phenylcyclobutanone (VII). The structure of VII (which has not been previously prepared) was confirmed by permanganate oxidation to phenylsuccinic acid.



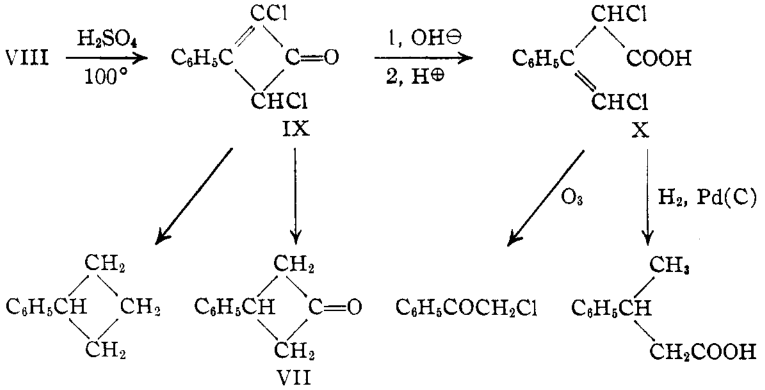
In some of the earlier preparations of I, the reaction of phenylacetylene and 1,1-difluoro-2,2-dichloroethylene was carried out at 150–170° and, in order to diminish the possibility of acid-induced polymerization, a small amount of triethylamine was added to the reaction mixture. The desired result was achieved, but the reaction took a different course in that 1,1-difluoro-2,4-dichloro-3-phenylcyclobutene (VIII) was formed instead of I. It was subsequently found that I is readily converted to VIII by heating with triethylamine. The over-all process is an anionotropic rearrangement, such as is common in simpler systems, although not previously reported to be catalyzed by triethylamine.



The structure of VIII was established by sulfuric acid hydrolysis to 2,4-dichloro-3-phenylcyclobutenone (IX) and conversion of IX with base to 2,4-dichloro-3-phenyl-3-butenoic acid (X). X has the same carbon skeleton as its isomer IV, since hydrogenation gave β-phenylbutyric acid. However, the double bond was apparently in a different position since the ultraviolet spectrum of X was different from IV or β-methylcinnamic acid (Fig. 1). Ozonization of X gave α-chloroacetophenone show-

---

[9] (a) J. D. Roberts and C. W. Sauer, This Journal, **71**, 3925 (1949); (b) J. D. Roberts and W. F. Gorham, *ibid.*, **74**, 2278 (1952).



ing that VIII had a different arrangement of chlorine atoms than I. Reduction of ketone IX gave phenylcyclobutane and 3-phenylcyclobutanone confirming the presence of a four-membered ring in VIII and IX.

IX is interesting since, on enolization, it would be converted to 1-hydroxy-2,4-dichloro-3-phenylcyclobutadiene. The compound displays no enolic properties; it does not give a color with ferric chloride solution and shows no hydroxyl absorption in the infrared. It dissolves in basic solution, but acidification yields X and complex products. In an attempt to convert IX to 1-acetoxy-2,4-dichloro-3-phenylcyclobutadiene with isopropenyl acetate and *p*-toluenesulfonic acid, no reaction was noted. The reaction conditions have been successfully employed to convert other ketones to their enol acetates.[10]

Further research on the cyclobutane compounds described in this paper is in progress.

Acknowledgment.—We are indebted to Dr. M. Tsutsui and Mr. David Knutson for help with some of the experimental work.

Experimental

1,1-Difluoro-2,2-dichloro-3-phenylcyclobutene (I).—The following conditions were found to give the most satisfactory results. Phenylacetylene (18.4 g., 0.18 mole), 1,1-difluoro-2,2-dichloroethylene[11] (24.0 g., 0.18 mole) and about 0.1 g. of hydroquinone were heated in a sealed glass tube at 130° for 2 hours. The crude product was distilled away from some polymeric material under reduced pressure and then fractionated through a 10-cm. Vigreux column. The yield of 1,1-difluoro-2,2-dichloro-3-phenylcyclobutene was 30.1 g. (71%), b.p. 109–111° (5 mm.), $n^{25}\text{D}$ 1.5435 (lit.[8] b.p. 135°, 15 mm.).

Anal. Calcd. for $C_{10}H_6Cl_2F_2$: C, 51.10; H, 2.57. Found: C, 51.58; H, 2.98.

1,1-Difluoro-3-phenylcyclobutane (II).—1,1-Difluoro-2,2-dichloro-3-phenylcyclobutene (35 g.) was hydrogenated at atmospheric pressure in 175 ml. of methanol over 7% palladium-on-charcoal. The catalyst was separated by filtration, the methanol was removed under reduced pressure, and the residue taken up in ether and washed with water. The ethereal solution was dried over magnesium sulfate and fractionally distilled. After the ether was removed, a non-chlorine containing fraction, b.p. 88–90° (20 mm.), amounting to 9 g. (36%) was collected. The remainder of the product was an unresolved mixture of chlorofluorohydrocarbons, b.p. 90–125° (20 mm.), $n^{25}\text{D}$ 1.4892–1.5089, which was not further investigated. The low, boiling material was redistilled and afforded 5.4 g. (22%) of pure 1,1-difluoro-3-phenylcyclobutane, b.p. 88.1–88.3° (20 mm.)- $n^{25}\text{D}$ 1.4828.

Anal. Calcd. for $C_{10}H_{10}F_2$: C, 71.41; H, 5.99. Found: C, 71.26; H, 6.17.

Hydrolysis of 1,1-Difluoro-3-phenylcyclobutane.—Concentrated sulfuric acid (15 g.) was heated on a steam-cone in a flask equipped with mechanical stirrer and 5 g. of 1,1-difluoro-3-phenylcyclobutane added quickly. Hydrogen fluoride was evolved, and after 15 minutes the mixture was poured cautiously into excess ice cold 10% sodium hydroxide solution. The products were extracted with ether, the extract washed with water, dried and distilled. The yield of crude benzalacetone was 0.8 g. (18%). The product was identified by its infrared spectrum and conversion to the 2,4-dinitrophenylhydrazone, m.p. 223–225°, which did not depress the m.p. of an authentic sample.

2,2-Dichloro-3-phenylcyclobutenone (III).—Concentrated sulfuric acid (40 g.) was heated on a steam-cone in a flask equipped with a mechanical stirrer, and then 20 g. of 1,1-difluoro-2,2-dichloro-3-phenylcyclobutene was added quickly. Hydrogen fluoride evolution began at once. The mixture was heated and stirred for 11 minutes and then immediately poured into a stirred slush of ice and water. The precipitate was collected by filtration, washed with water and recrystallized from alcohol–water. The yield of 2,2-dichloro-3-phenylcyclobutenone as light tan crystals was 15 g. (82%), m.p. 73.5–77°. Further crystallizations from ethanol gave an analytical sample as white needles, m.p. 79.5–80.5°.

Anal. Calcd. for $C_{10}H_6OCl_2$: C, 56.37; H, 2.84; Cl, 33.28. Found: C, 56.42; H, 2.87; Cl, 32.76.

The 2,4-dinitrophenylhydrazone of III was obtained as yellow needles, m.p. 232–234° (dec.) after recrystallization from ethyl acetate.

Anal. Calcd. for $C_{16}H_{10}O_4N_4Cl_2$: C, 48.87; H, 2.56. Found: C, 48.56; H, 2.76.

Oxidation of 0.5 g. of III by heating under reflux for 20 minutes with 1.4 g. of sodium permanganate trihydrate and 4 ml. of 6 *N* sodium hydroxide in 20 ml. of water gave after separation of the manganese dioxide, destruction of the excess permanganate with sodium bisulfite and acidification, 0.034 g. (12%) of benzoic acid which was identified by m.p. and mixed m.p. with an authentic sample.

4,4-Dichloro-3-phenyl-2-butenoic Acid (IV).—A mixture of powdered 2,2-dichloro-3-phenylcyclobutenone (5 g.) with 50 ml. of 1.5 *N* sodium hydroxide solution was stirred vigorously and heated gently on a steam-cone until solution was complete. The mixture was then immediately cooled and acidified with hydrochloric acid.[12] The resulting solid was collected, dissolved in cold dilute alkali and extracted with two 50-ml. portions of ether. Acidification of the alkaline solution gave 4.3 g. (80%) of 4,4-dichloro-3-phenyl-2-butenoic acid, m.p. 118–122°. Recrystallization from hexane gave an analytical sample of m.p. 124.5–125°. The ultraviolet spectrum is given in Fig. 1.

Anal. Calcd. for $C_{10}H_8O_2Cl_2$: C, 51.97; H, 3.49; Cl, 30.69. Found: C, 52.00; H, 3.50; Cl, 30.93.

The methyl ester of IV was obtained by way of the reaction of IV with excess diazomethane in ether and after recrystallization from acetic acid–water had m.p. 51–52°.

Anal. Calcd. for $C_{11}H_{10}O_2Cl_2$: C, 53.90; H, 4.11. Found: C, 53.86; H, 4.30.

Treatment of 1.4 g. of IV with a 100% excess of ozonized oxygen at 0° in ethyl acetate solution following by a 1-hour reflux period with 50 ml. of 35% hydrogen peroxide and 10 ml. of acetic acid gave, after removal of the solvent, crude α,α-dichloroacetophenone, which was identified by conversion to D,L-mandelic acid, m.p. 118–120° (no depression on admixture with an authentic sample) according to Houben and Fischer,[13] and conversion to a red 2,4-dinitrophenyl-

---

[10] H. J. Hagemeyer, Jr., and D. C. Hull, *Ind. Eng. Chem.*, **41**, 2920 (1949).

[11] In the early work, this material was prepared from commercial 1,1-difluorotetrachloroethane as described by A. L. Henne and E. G. Wiest, THIS JOURNAL, **62**, 2051 (1950). The later preparations employed a commercial product, "Genetron 170," supplied by the General Chemical Co.

[12] The success of the preparation is markedly dependent on the speed with which the foregoing operations are carried out. Prolonged contact with alkali tends to give complex non-chlorine containing products.

[13] J. Houben and W. Fischer, *Ber.*, **64**, 2636 (1931).

hydrazone, m.p. 296° (dec.) after crystallization from nitromethane. The hydrazone, which was also obtained from an authentic sample of α,α-dichloroacetophenone under the same conditions, was actually the bis-2,4-dinitrophenylhydrazone of phenylglyoxal.

4,4-Dichloro-3-phenyl-2-butenoic acid (IV) (0.60 g.) absorbed 98% of three moles of hydrogen per mole of substrate at atmospheric pressure in methanol over a 7% palladium-on-carbon catalyst. The solvent was evaporated, the residue boiled 3 minutes with 2 *N* sodium hydroxide. acidified and extracted with ether. Evaporation of the ether left an oil which was refluxed with excess thionyl chloride for 15 minutes and then poured cautiously into cold concentrated ammonia solution. The solid was collected and recrystallized from water. The product, 3-phenylbutyramide, had m.p. 105.5–107° and did not depress the m.p. of an authentic sample.

3-Phenylcyclobutanone. A.—2,2-Dichloro-3-phenylcyclobutenone (III, 5.0 g.) was dissolved in 75 ml. of methanol and 5 ml. of water, 5 g. of sodium carbonate and 2.5 g. of 7% palladium-on-charcoal were added. On hydrogenation at room temperature and atmospheric pressure, 93% of three moles of hydrogen per mole of III was absorbed. The catalyst was separated by filtration, 100 ml. of water added and the mixture extracted well with ether. The combined ethereal extracts were washed with three portions of water and dried over magnesium sulfate. The ether was removed and the residue was distilled through a short Vigreux column under reduced pressure. The yield of reduction product of b.p. 109–118° (10 mm.) was 2.0 g. (59%). The infrared spectrum showed some carbonyl absorption besides that at 5.6 μ characteristic of cyclobutanones, so the material was purified through the **semicarbazone** (m.p. 210.5–212°, after recrystallization from aqueous alcohol). Regeneration of the ketone from 2.0 g. of the semicarbazone by steam distillation from oxalic acid gave 0.8 g. of 3-phenylcyclobutanone, b.p. 93–95° (1.5 mm.), $n^{25}D$ 1.5423. The infrared spectrum showed strong carbonyl absorption only at 5.6 μ.

Anal. (semicarbazone). Calcd. for $C_{11}H_{13}ON_3$: C, 65.00; H, 6.45. Found: C, 65.27; H, 6.57.

The **2,4-dinitrophenylhydrazone of VII** had m.p. 148.5–150° after recrystallization from ethyl acetate.

Anal. Calcd. for $C_{16}H_{14}O_4N_4$: C, 58.89; H, 4.32. Found: C, 58.98; H, 4.25.

B.—Amalgamated zinc was prepared by successive treatments of 50 g. of zinc dust with dilute hydrochloric acid, water and a solution of 5 g. of mercuric chloride in 100 ml. of water. The amalgam was washed with water, then placed with 5.5 g. of III and 25 ml. of water in a flask equipped with a mechanical stirrer, dropping funnel and reflux condenser. The stirrer was started and 50 ml. of concd. hydrochloric acid added over 20 minutes without external cooling. The mixture was allowed to stand for 1 hour, and the supernatant liquid was decanted. The solid residue was washed well with ether and the washings used to extract the liquid part of the reaction mixture. The combined ethereal extracts were washed with water, bicarbonate solution, water and dried over magnesium sulfate. The ether was removed and reduced pressure distillation gave 1.5 g. (40%) of 3-phenylcyclobutanone, b.p. 72–77° (0.3 mm.). The infrared spectrum of this material was the same as that of the 3-phenylcyclobutanone regenerated from the semicarbazone, and the 2,4-dinitrophenylhydrazone and semicarbazone derivatives melted at the same temperatures as those prepared by the hydrogenation reaction.

1,1-Difluoro-2,4-dichloro-3-phenylcyclobutene (VIII).—1,1-Difluoro-2,2-dichloro-3-phenylcyclobutene (I, 5.0 g.) was heated with 0.2 ml. of triethylamine and a few crystals of hydroquinone at 145° for 24 hours. The mixture was taken up in ether, washed with dilute hydrochloric acid and water and then dried over anhydrous calcium chloride. On distillation, an essentially quantitative yield of 1,1-difluoro-2,4-dichloro-3-phenylcyclobutene was obtained, b.p. 88–90° (0.4 mm.), $n^{25}D$ 1.5499.

Anal. Calcd. for $C_{10}H_6Cl_2F_2$: C, 51.10; H, 2.57. Found: C, 51.38; H, 2.72.

2,4-Dichloro-3-phenylcyclobutenone (IX).—Concentrated sulfuric acid (80 g.) was heated in a three-necked flask equipped with a mechanical stirrer on a steam-cone. The stirrer was started and 1,1-difluoro-2,4-dichloro-3-phenylcyclobutene (40 g., 0.17 mole) was added quickly. Hydrogen fluoride was evolved and after 25 minutes the mixture was immediately poured into a well-stirred slush of ice and water. The precipitate was collected, washed with water and recrystallized from 30% aqueous ethanol. The yield of 3-phenyl-2,4-dichlorocyclobutenone (IX) was 31 g. (86%), m.p. 74–77°. An analytical sample had m.p. 78–80° after several crystallizations from ethanol.

Anal. Calcd. for $C_{10}H_6OCl_2$: C, 56.37; H, 2.83; Cl, 33.28. Found: C, 56.17; H, 2.89; Cl, 33.13.

The orange **2,4-dinitrophenylhydrazone of IX** had m.p. 234.5–235° dec. after recrystallization from ethyl acetate.

Anal. Calcd. for $C_{16}H_{10}O_4N_4Cl_2$: C, 48.87; H, 2.56. Found: C, 48.99; H, 2.67.

Reduction of 10 g. of IX according to the hydrogenation procedure used for the isomeric dichloro ketone III yielded 5.2 g. of crude 3-phenylcyclobutanone which on conversion to the semicarbazone afforded 1.7 g. of the pure derivative, m.p. 211.5–212.5°. This semicarbazone did not depress the m.p. of an authentic sample prepared from III.

2,4-Dichloro-3-phenylcyclobutenone (0.50 g.) was refluxed with 0.24 g. of isopropenyl acetate and 0.10 g. of toluenesulfonic acid for 2 hours. No acetone was formed in the reaction and, on distillation of the isopropenyl acetate, the starting ketone was recovered.

2,4-Dichloro-3-phenyl-3-butenoic Acid (X).—2,4-Dichloro-3-phenylcyclobutenone (5.0 g., 0.024 mole) was heated and shaken with 50 ml. of 1.5 *N* sodium hydroxide solution on a steam-cone until all of the solid dissolved. The mixture was immediately cooled in an ice-bath and acidified with 1.5 *N* hydrochloric acid.[12] The resulting solid was collected and successively washed with water, dissolved in dilute sodium bicarbonate solution, filtered, reprecipitated with acid, dried and recrystallized from chloroform–hexane. The yield of 2,4-dichloro-3-phenyl-3-butenoic acid (X) was 3.0 g. (56%), m.p. 112–113°. The ultraviolet spectrum of X is given in Fig. 1.

Anal. Calcd. for $C_{10}H_8O_2Cl_2$: C, 51.97; H, 3.49; Cl, 30.69. Found: C, 51.95; H, 3.56; Cl, 30.50.

Ozonization of 0.50 g. of X by the procedure used for IV gave crude phenacyl chloride which was characterized as the 2,4-dinitrophenylhydrazone, m.p. 213–214° dec. (lit.[14] m.p. 212°).

On hydrogenation of 0.30 g. of X by the procedure used for IV, 105% of three moles of hydrogen per mole of X was absorbed and the reduction product yielded β-phenylbutyramide, m.p. 104–106°, which did not depress the m.p. of an authentic sample.

Phenylcyclobutane.—2,4-Dichloro-3-phenylcyclobutenone (IX, 4 g.) was stirred and heated to reflux with 50 g. of amalgamated zinc and 50 ml. of water. Concentrated hydrochloric acid (50 ml.) was added over 17 minutes and the mixture then heated and stirred for 2 hours.

The supernatant liquid was decanted, the zinc residue washed with ether, and the washings used to extract the aqueous portion of the reaction mixture. The combined extracts were washed with water, dried and the ether removed. Fractionation of the residue through a short Vigreux column gave 0.45 g. of phenylcyclobutane, b.p. 45° (1 mm.), $n^{25}D$ 1.5281 (lit.[15] 101–102° (41 mm.), $n^{20}D$ 1.5277). The product contained some unsaturated material (reaction with permanganate), but the infrared spectrum was essentially identical with that of a sample prepared by decarboxylation of α-phenylcyclobutanecarboxylic acid.[15]

CAMBRIDGE 39, MASSACHUSETTS

---

[14] C. H. F. Allen and J. H. Richmond, *J. Org. Chem.*, **2**, 222 (1937).

[15] F. H. Case, THIS JOURNAL, **56**, 715 (1934).