Disproportionation of Tri-*t*-butylphenoxy.—When concentrated (*ca.* 20%) solutions of tri-*t*-butylphenoxy in petroleum ether were cooled to −70° (Dry Ice and acetone) blue crystals separated from the mixture. These crystals maintained their blue color for several weeks at room temperature, although they gradually turned yellow. On heating they decomposed vigorously at around 80°. A gas, having the characteristic odor of isobutylene, was evolved. Vacuum distillation of part of the decomposition product gave approximately a 50% yield of 2,4,6-tri-*t*-butylphenol, identified by its melting point and infrared spectrum. Careful fractional recrystallization of the decomposition product from methanol and water gave a yellow compound I, m.p. 148–149° in low yield. The infrared spectrum of this compound shows the absence of a hydroxyl group (no absorption in the region of 3300–3700 cm.$^{-1}$) and the presence of a conjugated carbonyl (strong absorption at about 1688 cm.$^{-1}$). The ultraviolet spectrum shows a maximum at 287 mμ, ϵ_{max} 3.7 × 10^3, similar to phenyl ethers (footnote *b* of Table I). *Anal.* Calcd. for $C_{32}H_{50}O_2$(I): C, 82.34; H, 10.80; mol. wt., 466.72. Found: C, 82.51; H, 10.53; mol. wt. (Rast, micro), 472.

In an attempt to simplify the separation problem, a reaction was run under conditions where the regenerated 2,4,6-tri-*t*-butylphenol would be reoxidized and converted to disproportionation product. In an apparatus equipped with a reflux condenser and mercury trap, a solution of 10 g. of the phenol in 50 ml. of benzene was stirred with a solution of 10 g. of potassium hydroxide and 50 g. of potassium ferricyanide in 150 ml. of water. The temperature was maintained at 70° for five days. At the end of this period the system had no detectable blue color. Evaporation of the benzene left an orange-yellow, viscous residue. Attempted recrystallizations from methanol and water produced a mixture of crystals which we were unable to satisfactorily separate. The infrared spectrum of this mixture indicated that it contained approximately 50% of dimer XI, that the other constituent(s) also had a carbonyl and that no hydroxyl group was present in the mixture. The carbon–hydrogen analysis of the mixture suggests that the other product is a dimer which has lost two *t*-butyl groups.

Anal. Calcd. for $C_{28}H_{41}O_2$: C, 82.10; H, 10.09. Found for the mixture: C, 82.19; H, 10.13.

Analytical.—All carbon–hydrogen analyses were performed by the Schwarzkopf Microanalytical Laboratory.

BURLINGTON, VERMONT

[CONTRIBUTION NO. 2029 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY]

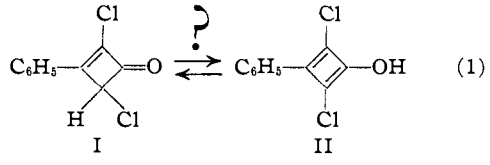
Small-Ring Compounds. XIII. The Mechanism of Racemization of Optically Active 2,4-Dichloro-3-phenylcyclobutenone[1]

BY ERWIN F. JENNY[2] AND JOHN D. ROBERTS

RECEIVED AUGUST 29, 1955

Racemization of optically active 2,4-dichloro-3-phenylcyclobutenone has been shown to involve reversible formation of (1-phenyl-2-chloroethenyl)-chloroketene. 2,4-Dichloro-3-phenyl-3-butenoic acid yields 2,4-dichloro-3-phenylcyclobutenone on treatment with acetic anhydride.

2,4-Dichloro-3-phenylcyclobutenone[3] (I) is of considerable theoretical interest since on enolization it would yield 2,4-dichloro-3-phenylcyclobutadienol (II).



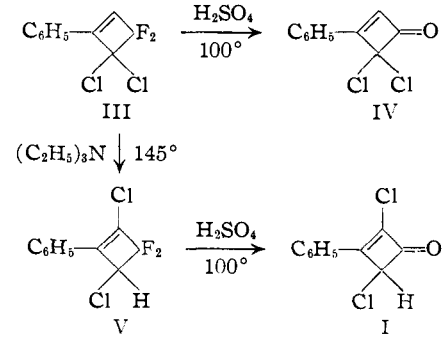
(1)

I II

Enolization of I does not occur readily. The compound gives no color with ferric chloride solution and shows no hydroxyl absorption in the infrared.[3] It dissolves in alkali, but acidification yields 2,4-dichloro-3-phenyl-3-butenoic acid and complex products.[3] No reaction was noted in an attempt to convert I to 1-acetoxy-2,4-dichloro-3-phenylcyclobutadiene with isopropenyl acetate in the presence of *p*-toluenesulfonic acid under conditions which have been used successfully to convert other ketones to their enol acetates.[3]

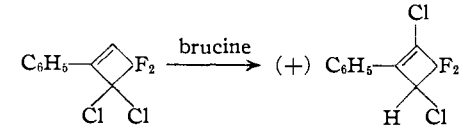
None of the foregoing observations strictly preclude interconversion of I and II, provided the equilibrium constant is suitably small. Formation of II could be definitely excluded if compound I were resolved (it has one asymmetric center) and found not to racemize under any of the conditions which are usually conducive to enolization. It has now been found that partial resolution of I is easily achieved but that loss of optical activity occurs rather readily on heating in several solvents. The mechanism of this racemization reaction is the subject of the present investigation.

Preparation of 1,1-difluoro-2,2-dichloro-3-phenylcyclobutene (III) from 1,1-difluoro-2,2-dichloroethylene and phenylacetylene has been described previously.[3] III was transformed to 2,2-dichloro-3-phenylcyclobutenone (IV), 1,1-difluoro-2,4-dichloro-3-phenylcyclobutene (V) and I as shown in the equations



III IV V I

Rearrangement of III with brucine in place of triethylamine gave optically active V possibly by way of a stereospecific and reversible Menschutkin reaction.



(1) Presented at the 14th National Organic Symposium of the American Chemical Society, Lafayette, Ind., June 14, 1955.

(2) Arthur Amos Noyes Fellow, 1954–1955.

(3) J. D. Roberts, G. B. Kline and H. E. Simmons, Jr., THIS JOURNAL, **75**, 4765 (1953).

Optically active V did not appear to racemize appreciably in 4.5 hours at 100°. However, on hydrolysis with sulfuric acid, optically active V afforded racemic I. It is not known to what extent racemization occurs during the actual hydrolysis reaction since the optically active ketone I racemized under the reaction conditions.

Racemic I was partially resolved by preferential destruction of one of the enantiomers with brucine in chloroform solution. Values of $[\alpha]^{25}D$ as high as 5.4° (c 0.2, chloroform) were observed. The optically active ketone racemized by kinetically first-order processes in chloroform, sulfuric acid or acetic acid solutions at 100°. The kinetic data for several typical racemization experiments are shown in Fig. 1. Rate constants are listed in Table I.

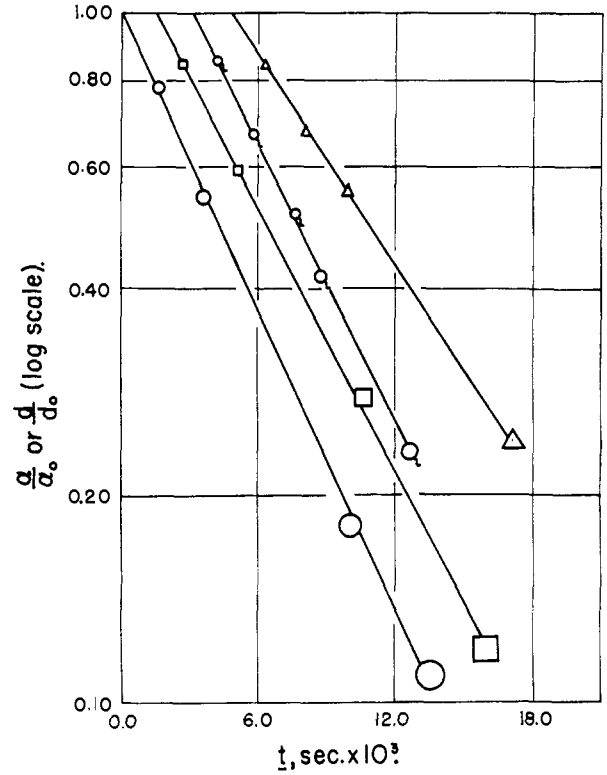


Fig. 1.—Rate data for racemization and ring-opening of 2,4-dichloro-3-phenylcyclobutenone. The abscissa is shifted 1.5–4.5 × 10^3 sec. for the three right-hand plots; O, racemization of 0.3 M ketone in chloroform; □, racemization of 0.3 M ketone in ethanol, t scale shifted 1.5 × 10^3 sec.; O_1, ring-opening of 1.0 × 10^{-3} M ketone in ethanol, t scale shifted 3.0 × 10^3 sec.; △, racemization of 0.3 M ketone in acetic acid, t scale shifted 4.5 × 10^3 sec. The size of the coördinate points represents approximate limit of observational error.

The interesting possibility mentioned earlier that the racemization of ketone I might be due to slow equilibration with the corresponding enol II, eq. 1, was completely ruled out on the basis of the following observations. Racemization of optically active I in deuterosulfuric acid or deuteroacetic acid yielded the racemic compound with no detectable formation of the α-deuteroketone VI.

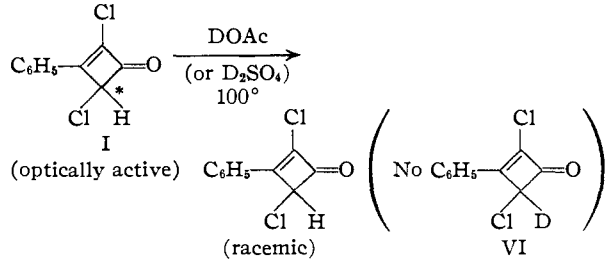
Unequivocal evidence that the breaking of the carbon–hydrogen bond was not involved in the rate-determining step of the racemization was obtained by a comparison of the rate constants for the racemization of optically active ketones I and VI. The latter compound was prepared from deuterophenylacetylene in the usual manner. The assigned location of the deuterium was confirmed by infrared analysis of the C–H stretching vibrations using a spectrometer with a LiF prism. The infrared spectrum indicated that VI contained 20–30% of its protium analog I. The rates of racemization of the deuterated ketone VI were followed polarimetrically in acetic acid and chloroform and were found to be less than 10% slower than the corresponding racemization rates for the hydrogen compound I (see Table I).

TABLE I

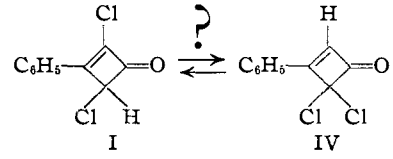
RATE CONSTANTS FOR RACEMIZATION AND RING-OPENING REACTIONS AT 100° OF 2,4-DICHLORO-3-PHENYLCYCLOBUTENONE (I)

Solvent	Addend, M	Ketone, M	Racemization rate constant,[a] sec.$^{-1}$ × 10^4	Ketone, M × 10^3	Ring-opening rate constant,[b] sec.$^{-1}$ × 10^4
$CHCl_3$	.....	0.3	1.7	..	..
$CHCl_3$	.....	.2	1.8	..	..
$CHCl_3$	.....	.3 (2-D)[c]	1.8	..	..
$CHCl_3$	0.05 $C_6H_5N(CH_3)_2Cl$	.3	2.1[d]	..	..
HOAc	.....	.3	1.1	1.0	0.14
HOAc	.....	.3 (2-D)[c]	1.1	..	..
HOAc	.05 LiCl	.3	1.1	..	..
HOAc	.01 TsOH[e]	.3	1.2	..	..
HOAc	.05 NaOAc	.3	1.2	1.0	.73
HOAc	.10 NaOAc	..	..	1.0	.89
HOAc	.24 NaOAc	..	..	1.0	1.1
C_2H_5OH	.....	.3	1.4	1.0	1.6
C_2H_5OH	.....	.3 (2-D)[c]	1.3	1.0	1.3
C_2H_5OH	.05 LiCl	.3	1.5	1.0	1.5
C_2H_5OH	.0012 TsOH[e]	.3	1.5	..	..
C_2H_5OH	.25 LiCl .005 TsOH[e]	.3	1.5	..	..
C_2H_5OH	.05 LiCl .0010 TsOH[e]	..	..	1.0	1.4

[a] Determined from measurements of α_D at 25°. Standard deviations in ethanol ±3–5% and ±5–10% in chloroform or acetic acid. [b] Determined from measurements of light absorption at 298 mμ. Standard deviations ±2–3% in ethanol or acetic acid. [c] Rate run with 2,4-dichloro-3-phenylcyclobutenone-2-^{2}H. [d] The solution darkened so that the rate could only be followed to 32% reaction, the rate constant is probably good to ±10–15%. [e] p-Toluenesulfonic acid.

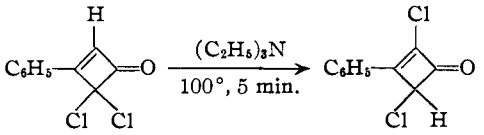


Another possible mechanism for the racemization of the optically-active ketone I would involve equilibration with the symmetrical ketone IV.



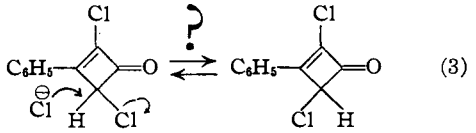
(2)

The equilibrium constant for a rearrangement of this type was shown to be very much on the side of I by the fact that the symmetrical ketone IV rearranged completely to I on heating with a trace of triethylamine at 100° for 5 minutes.



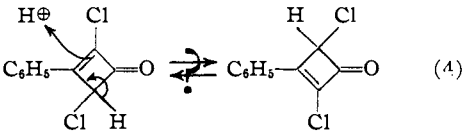
However, eq. 2 cannot account for the racemization of the optically active ketone because IV does not rearrange in chloroform (in the absence of tertiary amines) or acetic acid at 100° under the conditions of the racemization experiments.

Consideration was also given to racemization of the optically active ketone I by an SN2-type displacement of the α-chlorine of I by external chloride ion.



(3)

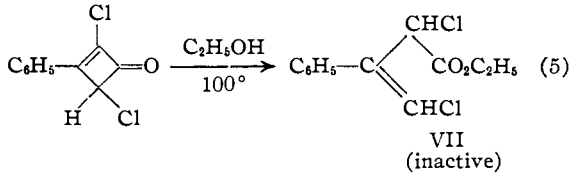
This mechanism was eliminated by the finding that racemization in either chloroform or acetic acid was not accelerated by added chloride ion (Table I). Another possible mechanism would involve external hydrogen ions and a shift of the double bond as shown in eq. 4.



(4)

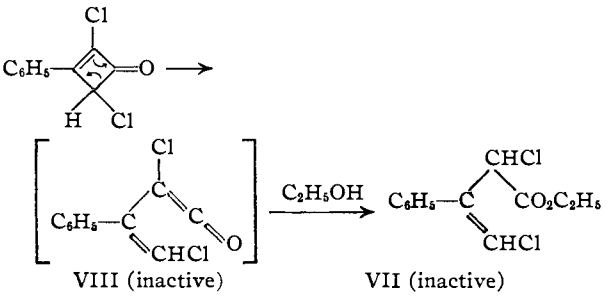
This formulation is inconsistent with the fact that the reaction rate in acetic acid is not increased by added toluenesulfonic acid (Table I) and is also controverted by the lack of significant H–D exchange when the protonated optically active ketone I is racemized in deuteroacetic acid or deuterosulfuric acid as described above.

The key to the mechanistic problem presented by the racemization of the optically active ketone I was provided by the observation (see Fig. 1) that the rate of loss of optical activity in absolute ethanol at 100° was equal to the rate of ring opening to give ethyl 2,4-dichloro-3-phenyl-3-butenoate (VII).[4]



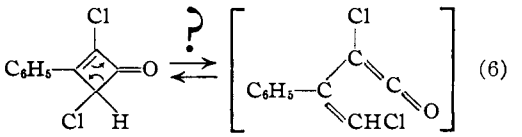
(5)

The rates of neither of the processes were affected by 0.005 *M* toluenesulfonic acid or 0.25 *M* lithium chloride and were slowed by less than 10% by D-substitution at the 2-position (Table I). The equivalence of the reaction rates for racemization and ring opening suggests a common intermediate. A very reasonable slow step would be a thermal ring opening of the optically active ketone I to give optically inactive (1-phenyl-2-chloroethenyl)-chloroketene (VIII). This substance would be expected to react rapidly with ethanol to yield the optically inactive ester VII.



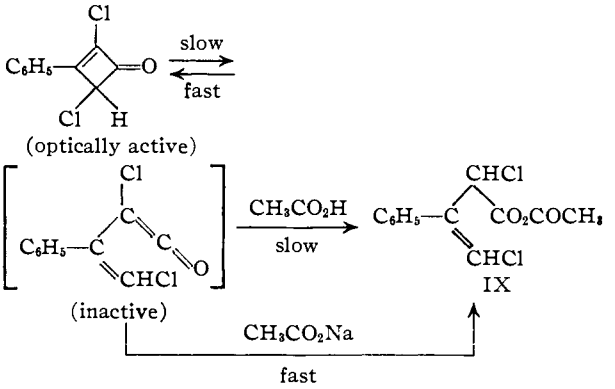
VIII (inactive) VII (inactive)

The racemization of optically active I in chloroform or acetic acid could occur with the ketene VIII as an intermediate if the ring-opening step were reversible.



(6)

The postulated reaction scheme requires that the ketene VIII undergo ring closure to I faster than it reacts with acetic acid to form a mixed anhydride IX.



The rate of ring opening of I in acetic acid can be followed spectroscopically and was found to be very much slower than racemization (Table I). Strong evidence that the racemization and ring-opening reactions involve a common intermediate was provided by the finding that sodium acetate greatly accelerates ring opening while only slightly increasing the rate of racemization (Table I). At high acetate concentrations, the ring-opening reaction is almost as fast as racemization. Sodium acetate must function to trap the intermediate ketene VIII and convert it to the anhydride IX. In the limiting circumstance, the rate of formation of IX will equal the rate of formation of the ketene.

The reversibility of the ring-opening reactions was demonstrated by the following experiment.

(4) The assigned structure, rather than ethyl 2,4-dichloro-3-phenyl-2-butenoate, was taken following the arguments used previously for the corresponding carboxylic acid.[4] However, steric inhibition of resonance associated with the bulky chlorine substituents might prevent the conjugated acid or ester from having the customary strong ultraviolet absorption characteristic of cinnamic acid derivatives. In the sequel, we shall continue to use the unconjugated structure VII although there is a distinct possibility that further structural evidence now being collected may necessitate some revision.

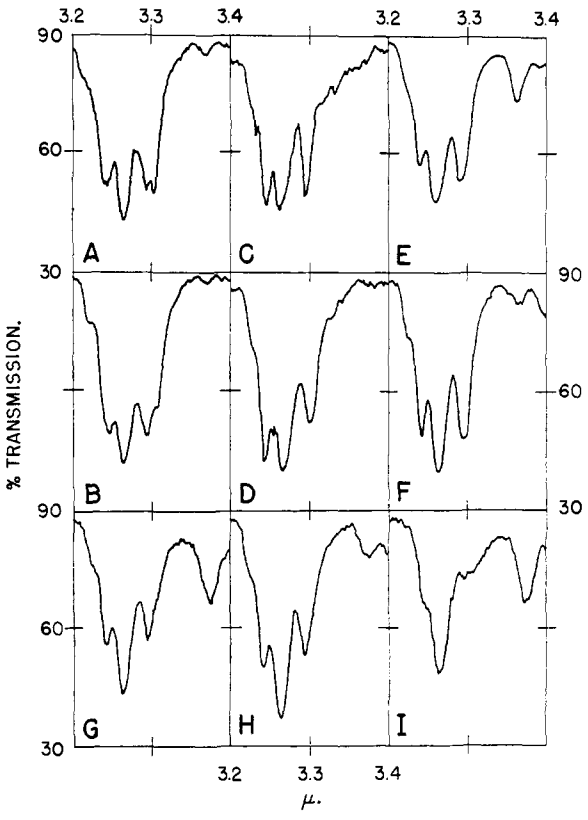
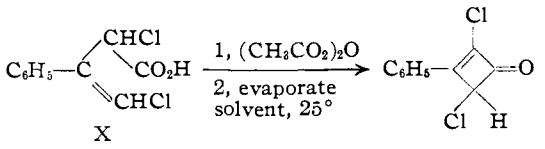


Fig. 2.—Infrared spectra: Perkin–Elmer model 21 infrared spectrophotometer with LiF prism; all compounds, 50 mg. in 1.0 ml. of CCl_4; 1.0-mm. NaCl cells. A, 1,1-difluoro-2,2-dichloro-3-phenylcyclobutene; B, 1,1-difluoro-2,2-dichloro-3-phenylcyclobutene-4-^{2}H, note weakening of absorption at 3.305 μ as compared to A; C, 2,2-dichloro-3-phenylcyclobutenone; D, 2,2-dichloro-3-phenylcyclobutenone-4-^{2}H; E, 1,1-difluoro-2,4-dichloro-3-phenylcyclobutene, note absorption by the aliphatic hydrogen at the 2-position at 3.365 μ; F, 1,1-difluoro-2,4-dichloro-3-phenylcyclobutene-2-^{2}H, note weakening of 3.365 μ band as compared to E; G, 2,4-dichloro-3-phenylcyclobutenone showing aliphatic C–H absorption at 3.365 μ; H, 2,4-dichloro-3-phenylcyclobutenone-2-^{2}H, note weakening of 3.365 μ absorption compared to G; I, 2,4-dichloro-3-phenylcyclobutenone from D_2SO_4 hydrolysis of 1,1-difluoro-2,4-dichloro-3-phenylcyclobutene, note unchanged magnitude of 3.365 μ absorption and loss of bands at 3.240 and 3.295 μ because of deuteration of aromatic ring.

Ketone I was heated in acetic acid at 100° for 50 hours and, at the end of this time, the ultraviolet spectrum indicated that ring-opening had occurred to the extent of 90%. However, when the solvent was evaporated under reduced pressure at 25°, a mixture containing approximately equal parts of the original ketone I and 2,4-dichloro-3-phenyl-3-butenoic acid (X) was obtained. Apparently, the anhydride IX which was formed in the initial ring-opening reaction lost acetic acid when the solvent was evaporated and partially reverted to the ketone I by way of the ketene VIII. Ring closure was also achieved by heating briefly a sample of X with acetic anhydride and evaporation of the solvent at room temperature. In these circumstances, ketone I was formed containing none of the acid X.



The possibility that cyclobutenone derivatives might be generally obtainable from vinylketenes or suitable precursors is currently being investigated.

Experimental Part

Optically Active 1,1-Difluoro-2,4-dichloro-3-phenylcyclobutene (V).—A solution of 53 g. of 1,1-difluoro-2,2-dichloro-3-phenylcyclobutene (III) and 10 g. of brucine in 50 ml. of chloroform was heated on a steam-cone and the solvent allowed to evaporate. The residue was heated on the steam-cone for 4 hours. The volatile material was removed at 0.1 mm. with the aid of an infrared lamp and collected in a Dry Ice-cooled trap. The contents of the trap were redistilled and afforded 48 g. (90%) of optically active V, b.p. 70–71.5° (~ 0.1 mm.), $n^{25}D$ 1.5499, $\alpha^{25}D$ (neat, 1 dm.) 1.25 ±0.02°. The infrared spectrum of the product indicated that the rearrangement was complete.

Deuterosulfuric Acid.—Deuterium oxide (15.0 ml., 99.9%) was placed in a flask immersed in a Dry Ice–acetone-bath and 31.5 ml. of Sulfan B (stabilized liquid sulfur trioxide, General Chemical Co.) was added dropwise. The rate of addition could be increased toward the end. After the addition was complete, the contents of the flask were allowed to warm to room temperature and some crystalline sulfur trioxide above the surface of the liquid was dissolved by shaking the flask. The deuterosulfuric acid prepared in this manner (calculated to be 100%) was used directly in the following preparation.

Hydrolysis of Optically Active 1,1-Difluoro-2,4-dichloro-3-phenylcyclobutene with Deuterosulfuric Acid.—Deuterosulfuric acid (75 g., about 100%) was heated on a steam-cone and optically active V (12.5 g.) was added all at once to the hot stirred acid. Hydrogen fluoride was evolved; after 25 minutes, the mixture was poured onto crushed ice. The precipitate was collected, washed with water and dried. The yield of crude I was 11.5 g. (100%), m.p. 74–76°, $[\alpha]^{25}D$ 0.00 ± 0.01° (*c* 0.30, chloroform). A small portion of the crude product was recrystallized from aqueous ethanol and petroleum ether (60–70°), m.p. 75–76°. The infrared spectrum of the product was taken with a Perkin–Elmer model 21 spectrophotometer equipped with a lithium fluoride prism and indicated that the phenyl group had become somewhat deuterated during the hydrolysis reaction; however, no deuterium appeared to be present in the four-membered ring (Fig. 2).

Racemization of Optically Active I in Sulfuric Acid.—A solution of 0.55 g. of optically active I ($[\alpha]^{25}D$ 5.23°, *c* 0.30, chloroform) in 2 ml. of concentrated sulfuric acid was heated on a steam-cone for ten minutes. The mixture was poured onto crushed ice. The resulting precipitate was collected, washed with water and recrystallized from aqueous ethanol. The product had m.p. 74–76°, $[\alpha]^{25}D$ 2.0° (*c* 0.30, chloroform).

Optically Active 2,4-Dichloro-3-phenylcyclobutenone (I).—A solution of 5 g. of racemic I and 5 g. of brucine in 30 ml. of chloroform was heated on a steam-cone for two hours. The chloroform was removed under reduced pressure and the residue shaken with water and ether in a separatory funnel. The ethereal layer was washed three times with 20 ml. of 2 *N* hydrochloric acid and three times with water. The ethereal solution was dried over sodium sulfate and the ether evaporated. The residue was recrystallized from aqueous ethanol and yielded 2.6 g. (52%), m.p. 77–78°, $[\alpha]^{25}D$ 5.20° (*c* 0.3, chloroform). The infrared spectrum of the optically-active I was identical with that of the racemic starting material.

Rearrangement of 2,2-Dichloro-3-phenylcyclobutenone (IV) to 2,4-Dichloro-3-phenylcyclobutenone (I).—A mixture of 5.0 g. of 2,2-dichloro-3-phenylcyclobutenone and 0.4 ml. of triethylamine was heated in a sealed tube on a steam-cone for five minutes. The mixture liquefied and turned dark brown but solidified when cooled. A sample was recrystallized from aqueous ethanol and yielded nearly colorless crystals of m.p. 76–78°, mixed m.p. with the starting ketone IV was below 50°, the mixed m.p. with 2,4-dichloro-3-phen-

ylcyclobutenone (I) was 76–78°. The infrared spectrum of the product indicated that the rearrangement was complete.

1,1-Difluoro-2,2-dichloro-3-phenylcyclobutene-4-^{2}H.—Phenylacetylene (102 g., 1.0 mole) was added in one portion to a solution of methylmagnesium iodide (prepared from 170 g. of methyl iodide and 30.5 g. of magnesium turnings) in 750 ml. of ether. The reaction mixture was heated for 22 hours and, during this time, 24.5 l. of methane was evolved. The mixture was cooled in an ice-bath and stirred vigorously while 70 ml. of deuteroacetic acid in 150 ml. of absolute ether was added slowly. The precipitate was removed by filtration and the ether distilled from the filtrate through a short fractionating column. The dark brown residue was distilled at atmospheric pressure and yielded 60 g. of crude product, b.p. 122–138°, which was shown by its infrared spectrum to contain phenylacetylene and deuterophenylacetylene approximately in the ratio 1:3.5 along with an unidentified contaminant. Although a mixture of phenylacetylene and deuterophenylacetylene could be separated from the crude product by careful fractional distillation, it was more economical of deuterium to use the unpurified preparation in the subsequent reactions.

Three 20-g. portions of the above crude preparation of deuterophenylacetylene were each mixed with 26 g. of 1,1-difluoro-2,2-dichloroethylene and heated in a sealed glass tube at 130° for 2.5 hours. The contents of the tubes were united and distilled under reduced pressure. After a small forerun at 42° (18 mm.), 62 g. was obtained of 1,1-difluoro-2,2-dichloro-3-phenylcyclobutene-4-^{2}H, b.p. 132–134° (18 mm.). The infrared spectrum of the product is shown in Fig. 2.

2,2-Dichloro-3-phenylcyclobutenone-4-^{2}H was prepared by hydrolysis of the corresponding 1,1-difluoro compound as described previously.[3] The product had m.p. 76–77° which was depressed by admixture with the 2,4-dichloro isomer. The infrared spectrum of the product is shown in Fig. 2.

1,1-Difluoro-2,4-dichloro-3-phenylcyclobutene-4-^{2}H was obtained by rearrangement of the corresponding 2,2-dichloro isomer by triethylamine at 145°.[3] The product had b.p. 93–95° (0.5 mm.) and its infrared spectrum is shown in Fig. 2.

2,4-Dichloro-3-Phenylcyclobutenone-2-^{2}H (VI) was obtained by hydrolysis of 1,1-difluoro-2,4-dichloro-3-phenylcyclobutene-2-^{2}H with sulfuric acid as described above. The deuteroketone was recrystallized from water–ethanol and hexane; m.p. 75–77°, m.p. on admixture with 2,2-dichloro-3-phenylcyclobutenone-2-^{2}H <60°.

VI was partially resolved as described for the protium analog. The product had $[\alpha]^{25}D$ 2.35° (*c* 0.30, chloroform).

Racemization Reaction Rates.—Solutions of the optically active ketone (usually 0.3 *M*) in reagent grade solvents were sealed in ampules and heated at 100° in a vapor thermostat. In almost all experiments, the reactions were followed to at least 80% completion. The rotations were measured in 1-dm. tubes in a Winkel–Zeiss polarimeter. The uncertainty in reading the rotations was generally less than 2% except near the end of the reaction.

Ring-opening Reaction Rates.—Solutions of ketone I (1.0×10^{-3} *M*) were allowed to react at 100° as described above. The rate of the ring-opening reaction was followed by the change in optical density at about 298 mμ using 1.0-mm. silica cells and a Cary recording spectrophotometer, model 11M. Each reaction was followed to at least 80% completion and 6 to 10 points were taken. The rate constants are summarized in Table I.

Racemization of Optically Active 2,4-Dichloro-3-phenylcyclobutenone in Deuteroacetic Acid.—A solution of 200 mg. of the optically-active ketone and 5.0 ml. of deuteroacetic acid was heated at 95° for 5.5 hours. The optical rotation of this solution showed that racemization had occurred to the extent of 84%. The reaction mixture was frozen in Dry Ice and the acetic acid lyophilized under reduced pressure. The residue was recrystallized from hexane and had m.p. 77–78°. The infrared spectrum of this material and the starting ketone were virtually identical with no trace of absorption due to C–D bonds.

2,4-Dichloro-3-phenylcyclobutenone with Ethanol.—A solution of 2.45 g. of I in 15.0 ml. of absolute ethanol was heated in a sealed glass tube at 100° for 22 hours. The solvent was removed *in vacuo* and the oily product crystallized from 95% ethanol. Ethyl 2,4-dichloro-3-phenyl-3-butenoate (VII) was obtained as colorless needles, m.p. 59–60°. The ultraviolet and infrared spectra indicated that the double bond was not conjugated with the carbonyl group.[4]

Anal. Calcd. for $C_{12}H_{12}O_2Cl_2$: C, 55.62; H, 4.67; Cl, 27.36. Found: C, 55.61; H, 4.64; Cl, 27.30.

2,4-Dichloro-3-phenylcyclobutenone with Acetic Acid.—A solution of 65 mg. of optically active I in 1.0 ml. of glacial acetic acid was heated at 100° for 8.5 hours. The solvent was removed at room temperature in a stream of dry nitrogen and the crystalline residue dried under reduced pressure. The infrared spectrum of the product in chloroform showed it to be almost pure I.

A solution of 400 mg. of racemic I in 6.2 ml. of acetic acid was heated at 100° for 50 hours. At the end of this time the optical density at 298 mμ was less than 10% of the original value. The solvent was removed in a stream of dry nitrogen at room temperature and the infrared spectrum of the residue indicated it to consist of 2,4-dichloro-3-phenyl-3-butenoic acid (X) and I in the ratio of about 1:1. The mixture was separated by extraction with sodium carbonate solution and yielded 140 mg. of I, m.p. 74–75° and 140 mg. of acid X, m.p. 108–110° (reported m.p. 112–113°).

2,4-Dichloro-3-phenyl-3-butenoic Acid (X) to 2,4-Dichloro-3-phenylcyclobutenone with Acetic Anhydride.—A solution of 1.0 g. of X in 10 ml. of acetic anhydride was heated at 140° for ten minutes, then cooled to room temperature and the solvent removed in a stream of dry nitrogen. The residue was dried under reduced pressure and its infrared spectrum indicated the presence of substantial amounts of I, which could be isolated by crystallization from aqueous ethanol. The purified product (95 mg., 11%) had an infrared spectrum identical with that of an authentic specimen of I.

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