[Contribution No. 2084 from the Gates and Crellin Laboratories of Chemistry of the California Institute of Technology]

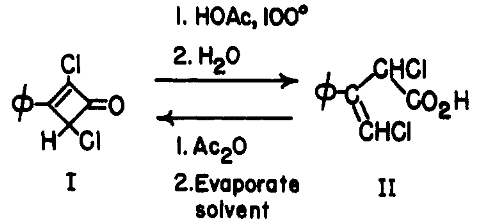
Small-Ring Compounds. XVI. The Structure of the Carboxylic Acid from Ring Opening of 2,4-Dichloro-3-phenylcyclobutenone[1]

By Ernest F. Silversmith[2] and John D. Roberts

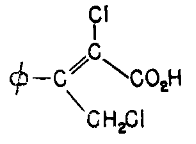
Received March 12, 1956

The structure 2,4-dichloro-3-phenyl-3-butenoic acid (II), previously proposed for the product of the base-induced ring opening of 2,4-dichloro-3-phenylcyclobutenone (I) is supported by nuclear magnetic resonance spectroscopy and demonstration of the presence of an asymmetric center by partial resolution.

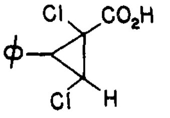
In previous research,[3] it was found that 2,4-dichloro-3-phenylcyclobutenone (I) and a carboxylic acid considered[4] to be 2,4-dichloro-3-phenyl-3-butenoic acid (II) were extraordinarily easily interconverted under mild conditions.



The carboxylic acid was first prepared[4] by a sodium hydroxide-induced ring opening of I. Structure II was assigned on the basis of the elemental analysis, hydrogenation to β-phenylbutyric acid, ozonization to phenacyl chloride and the ultraviolet absorption spectrum which showed no maximum between 260–270 $m\mu$. The carbon skeleton of the acid was considered to be established by the structure of the hydrogenation product while ozonization was taken to indicate that the two chlorine atoms were not located on the same carbon atom. The ultraviolet spectrum indicated that the double bond was not conjugated with the carboxyl function, as would be the case if the correct structure were 2,4-dichloro-3-phenyl-2-butenoic acid (III). It was expected that a compound having structure III would show an absorption maximum at 260–270 $m\mu$ like those observed for 4,4-dichloro-3-phenyl-2-butenoic acid (IV) and β-methylcinnamic acid.[4] Objections to the assigned structure II have been voiced on two counts. First, the infrared spectrum (Fig. 1) shows strong absorption at 6.90 μ, characteristic of a $-CH_2-$ group, as would be expected for III.



III



V

Second, the ultraviolet absorption spectrum[4] is hardly typical of a styryl derivative and it has been suggested that the carboxylic acid may actually be some sort of a dichlorophenylcyclopropanecarboxylic acid (perhaps V). Alternatively, a compound with structure III might have an abnormal ultraviolet absorption spectrum by virtue of steric hindrance to coplanarity of the phenyl and carboxyl groups with respect to the double bond. Consequently, we have reëvaluated the previous[4] structural assignment.

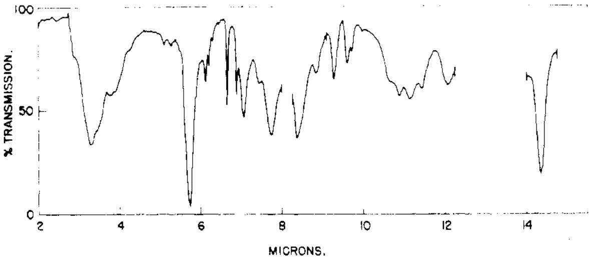
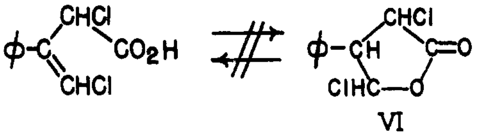


Fig. 1.—Infrared spectrum of 0.050 g. of 2,4-dichloro-3-phenyl-3-butenoic acid in 0.5 ml. of chloroform, 0.1 mm. NaCl cell, Perkin-Elmer Model 21 Recording Infrared Spectrometer. Blank regions correspond to strong solvent absorption.

The chemical and physical properties of the compound in question are as expected for a carboxylic acid. The infrared spectrum (Fig. 1) shows the typical OH and $C=O$ functions of the carboxyl group. Any possibility that the ultraviolet spectrum of the acid might be accounted for by a solvent-dependent and more or less dynamic equilibrium with the γ-lactone (VI) seems ruled out by the previous finding[3] of similar spectral properties for the acid and its ethyl ester. A cyclopropane structure like V is at variance with the unsaturated character of the molecule as evidenced by reactions with permanganate solution, ozone and hydrogen over palladium at atmospheric pressure. Furthermore, the infrared spectrum has a strong band at 6.12 μ as would be expected with an unsymmetrically substituted carbon–carbon double bond. Structure III is more difficult to eliminate and, as pointed out before, is actually favored by the infrared absorption band at 6.9 μ.



VI

The nuclear magnetic resonance spectrum (decreasing magnetic field from left to right) of the

---

(1) Supported in part by a grant from the National Science Foundation.

(2) National Science Foundation Postdoctoral Fellow, 1955–1956.

(3) E. F. Jenny and J. D. Roberts, This Journal, **78**, 2005 (1956).

(4) J. D. Roberts, G. B. Kline and H. E. Simmons, Jr., *ibid.*, **75**, 4765 (1953).

carboxylic acid in acetone solution (Fig. 2) shows four peaks approximately in the weight 1:1:5:1, besides the strong absorption due to the solvent. The far right-hand peak is typical of a carboxyl group and the two small left-hand peaks are in about the correct positions for hydrogens located on a carbon carrying a chlorine and double bonds. The relative weights of the carboxyl and C–H peaks indicate that only one hydrogen is located on the carbon carrying the chlorine as at the 2-position of structure II. With III the C–H resonance absorption of the hydrogens at the 4-position would be expected to be twice the carboxyl absorption. It was expected from previous work,[3] if II is formed by ring-opening of I, that the hydrogen at the 2-position would come from the solvent. This has been shown to be the case by opening I to II in deuteroacetic acid. The reaction product showed only faint proton resonance absorption for the –CHCl– position (Fig. 2). Further decisive evidence that the carboxylic acid is not III was provided by its resolution into optically active forms through crystallization of the brucine salt. A sample of the acid with $[\alpha]^{23}D$ $-46.2°$ (*c* 4.06, acetone) was obtained having an infrared absorption spectrum identical with that given in Fig. 1.

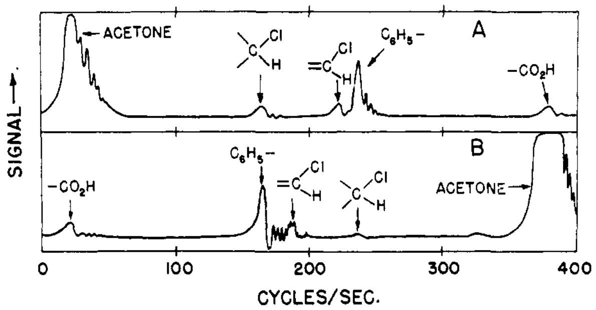


Fig. 2.—Nuclear magnetic resonance spectra of 5-mm. diameter samples at 40 mc. and 9040 gauss (12-sec. sweep) taken with Varian Associates Model V-4300 High Resolution Spectrometer: A, 50% solution of 2,4-dichloro-3-phenyl-3-butenoic acid in acetone solution, reverse sweep with higher magnetic field at the left; B, 50% solution of 2,4-dichloro-3-phenyl-3-butenoic-2-^{2}H acid in acetone, normal sweep with lower magnetic field at the left.

Experimental

2,4-Dichloro-3-phenyl-butenoic acid was prepared as described previously,[4] m.p. 111.8–113.0°.

2,4-Dichloro-3-phenyl-3-butenoic-2-^{2}H Acid.—A solution of 400 mg. of 2,4-dichloro-3-phenylcyclobutenone in 6.2 ml. of deuteroacetic acid (prepared by hydrolysis of acetic anhydride with deuterium oxide) was heated for 64 hours at 100°. One ml. of deuterium oxide was added and the mixture refluxed for an hour. An additional ml. of deuterium oxide was then added and the solvent removed in a stream of dry nitrogen at room temperature. The residue was crystallized from chloroform–hexane and yielded the deuterium-substituted acid with m.p. 111.8–113.2°. In the over-all purification process including the crystallization from chloroform containing the usual ordinary ethanol as a preservative, the carboxyl hydrogen underwent extensive exchange as shown by the *n-m-r* spectrum (Fig. 2).

Resolution of 2,4-Dichloro-3-phenyl-3-butenoic Acid.—The carboxylic acid (3.9 g.) and 6.7 g. of dry brucine were dissolved in 20 ml. of boiling, dry acetone. The resulting solution was kept in a refrigerator and after three days a considerable white precipitate separated. The mother liquor was decanted and the residual solid recrystallized from acetone. The resulting brucine salt was shaken with 100 ml. of ether and 100 ml. of 1.5 *M* hydrochloric acid. The ether layer was removed and washed successively with 75 ml. of 1.5 *M* hydrochloric acid, water and concentrated sodium chloride solution. The ether was then removed and the residual white solid recrystallized three times from chloroform–hexane. The final product had m.p. 113.0–114.0° and $[\alpha]^{23}D$ $-46.2°$ (*c* 4.06, acetone). Its infrared spectrum was indistinguishable from that of the optically inactive starting material (Fig. 1).

Anal. Calcd. $C_{10}H_8O_2Cl_2$: C, 51.97; H, 3.49. Found: C, 52.35; H, 3.63.

Pasadena 4, California

[Contribution from Coates Laboratories, Louisiana State University]

Ring Size and Reactivity of Cyclic Olefins: Complexation with Aqueous Silver Ion[1,2]

By James G. Traynham and Merle F. Sehnert[3]

Received February 27, 1956

Equilibrium constants for complex formation between aqueous silver ion and some cyclic olefins have been determined by a distribution method. The orders of equilibrium constants found were cyclopentene > cycloheptene > cyclohexene and bicycloheptene > bicyclooctene. For the monocyclic olefins, thermodynamic functions for the reactions have been evaluated. The inference is made that the relative reactivity of the olefin as an electron donor in π-complex formation is a function of ring strain: strain in a cyclic olefin facilitates complex formation.

Several recent investigations have provided correlations of ring size and reactivity among cycloalkane derivatives in displacement and carbonyl reactions.[4] Little systematic work with cyclic olefins has been described, however. Reported here are the results of an initial study of the effects of ring size on the reactivity of cyclic olefins.

Olefin complexes have been studied extensively,[5] but seldom have cyclic olefins been included. The complexes with aqueous silver ion are well known and have been studied quantitatively by Lucas and co-workers.[6] The equilibrium reaction for the formation in solution of the easily dissociable 1:1 complexes[6a] may be represented by equation 1

$$\text{olefin} + Ag^{\oplus} \rightleftarrows \text{complex}^{\oplus} \qquad (1)$$

---

[1] Taken in part from the M.S. thesis submitted by M.F.S., January, 1956.

[2] Presented at the 11th Southwest Regional Meeting of the A.C.S., Houston, Texas, December 1, 1955.

[3] Frederick Gardner Cottrell research assistant, 1954–1955.

[4] H. C. Brown, J. H. Brewster and H. Shechter, This Journal, **76**, 467 (1954), and references cited there.

[5] A recent review, with many leading references, is found in Chap. 8, by J. Chatt, and Chap. 9, by G. Salomon, "Cationic Polymerization and Related Complexes," P. H. Plesch, Ed., Academic Press, Inc., New York, N. Y., 1953.

[6] (a) S. Winstein and H. J. Lucas, This Journal, **60**, 836 (1938); (b) H. J. Lucas, R. S. Moore and D. Pressman, *ibid.*, **65**, 227 (1943).