of ethanol was heated under reflux for 2.5 hr. and the product isolated as described above. A 68% yield of III, b.p. 77–79° (1 mm.), was obtained. The infrared spectrum was identical with that of the material prepared from I; III was also prepared from II by the same procedure.

2-Ethoxy-3-phenyl-2-cyclobutenone (V).—Compound III (20.8 g.) was added to a well-stirred mixture of 30 ml. of concentrated sulfuric acid and 5 ml. of water which had been preheated on a steam-bath. The whole was heated and stirred for 3 min., and the resulting dark-brown solution was poured into an ice–water slurry. The mixture was extracted with two 75-ml. portions of ether and the combined extracts were dried over magnesium sulfate. The ether was removed and the product was fractionated through a 10-cm. Vigreux column. A total of 13.7 g. (74%) of V was collected as an orange oil at 110.7–113.0° (1.4 mm.). The color persisted when the material was redistilled. The infrared, ultraviolet and nuclear magnetic resonance spectra were in accord with the proposed structure.

The 2,4-dinitrophenylhydrazone of V was prepared and found to have m.p. 272.0–273.6°, after recrystallization from ethyl acetate.

Anal. Calcd. for $C_{18}H_{16}N_4O_4$: C, 58.70; H, 4.35. Found: C, 58.60; H, 4.41.

Five-gram samples of V were heated under reflux with (1) a mixture of 15 ml. of ethanol, 20 ml. of water and 3 ml. of concentrated sulfuric acid for 18 hr., and (2) 20 ml. of 48% hydriodic acid for 2 hr. After the stated reaction times, water was added and the product was extracted with ether. The extracts were washed with water, dried, and the ether distilled. The infrared spectra of the reaction products were identical with that of the starting material. The recovery from the hydriodic acid reaction was about 40%.

1,1-Difluoro-2-*t*-butoxy-3-phenyl-2-cyclobutene (VI).—1,1,2,-Trifluoro-2-chloro-3-phenylcyclobutane (I, 16 g., 0.073 mole) was added to a slurry of potassium *t*-butoxide from the reaction of 6 g. (0.154 g. atom) of potassium metal with 90 ml. of *t*-butyl alcohol and the mixture was heated under reflux for 14 hr. Water (500 ml.) was added and the whole extracted with three 100-ml. portions of ether. The combined extracts were washed with two 100-ml. portions of water, dried and the ether was removed by distillation. Fractionation of the residue yielded a small forerun of II and 13.0 g. (75%) of VI, b.p. 93–96° (1.6 mm.).

Anal. Calcd. for $C_{14}H_{16}OF_2$: C, 70.57; H, 6.77. Found: C, 70.49; H, 6.75.

2-Hydroxy-3-phenyl-2-cyclobutenone (VII).—1,1-Difluoro-2-*t*-butoxy-3-phenyl-2-cyclobutene (VI, 4.6 g.) was added at once to a stirred mixture of 3 ml. of water and 12 ml. of concentrated sulfuric acid that had been preheated on a steam-bath. The whole was heated and stirred for 2 min. and then poured into an ice–water slurry. The resulting yellow solid was separated by filtration and dried in a vacuum desiccator. The crude product was purified by dissolving it in a small amount of acetone, adding 60–70° ligroin, boiling off the acetone, and allowing the product to crystallize. In several runs the yield varied between 50 and 70%. The purest sample obtained had m.p. 155–165° dec.

Anal. Calcd. for $C_{10}H_8O_2$: C, 74.99; H, 5.03. Found: C, 75.36; H, 4.71.

The phenylurethan of VII was prepared and found to have m.p. 134.2–134.8° after recrystallization from 86–100° ligroin.

Anal. Calcd. for $C_{17}H_{13}O_3N$: C, 73.11; H, 4.69. Found: C, 73.21; H, 4.72.

The ultraviolet, infrared and nuclear magnetic resonance spectra of VII were in agreement with the proposed structure. Even pure samples underwent fairly rapid decomposition in air or under vacuum—the initially white crystals become brown within two weeks; VII was found to give a dark-green color with ferric chloride solution.

A mixture of 1.00 g. of VII, 0.25 g. of sodium hydroxide, 25 ml. of ethanol, 5 ml. of water and 10 ml. of ethyl iodide was heated under reflux for 15.5 hr. Water (200 ml.) was added and the mixture was extracted with ether. The extracts were washed with water, dried, and the ether was removed. The infrared spectrum of the residue was identical with that of the ethoxyketone V.

Compound VII (5 g.) was reduced with zinc amalgam and hydrochloric acid by the procedure used for 2,4-dichloro-3-phenylcyclobutenone,[3] except that the mixture was heated for 13.5 hr. instead of 2 hr. Fractionation of the product gave 0.33 g. of phenylcyclobutane, b.p. 46–47° (2.3 mm.), $n^{25}D$ 1.5243 (lit.[18] b.p. 101–102° (41 mm.), $n^{20}D$ 1.5277). The infrared spectrum was indistinguishable from that of authentic phenylcyclobutane.[3,19]

The dissociation constant of VII was measured as follows. A solution of 0.02 g. of VII in 180 ml. of boiled water was titrated with approximately 0.02 *N* carbonate-free[20] sodium hydroxide solution. The *p*H of the solution was measured at intervals with the aid of a Beckman model G *p*H meter with Beckman calomel and type E glass electrodes. A stream of nitrogen was bubbled through the solution during the titration. Two determinations were made, and the average pK_A (*p*H at the half-neutralization point[18]) was 6.25 ± 0.05 (28°).

(18) F. H. Case, THIS JOURNAL, **56**, 715 (1934).

(19) E. J. Smutny and J. D. Roberts, *ibid.*, **77**, 3420 (1955).

(20) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Co., New York, N. Y., 1952, pp. 526–528.

PASADENA, CALIFORNIA

[CONTRIBUTION NO. 2296 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY]

Small-Ring Compounds. XVIII. Alkali-induced Ring Opening of Some Phenylcyclobutenone Derivatives[1]

BY L. SKATTEBØL AND JOHN D. ROBERTS

RECEIVED JANUARY 9, 1958

Phenylcyclobutenedione (I) has been found to decompose by the action of alkali to benzylidenepyruvic acid (X) and benzaldehyde. Similarly 2-hydroxy-3-phenyl-2-cyclobutenone (V) yields benzylpyruvic acid (VII), and 4-hydroxy-3-phenylcyclobutenedione (XI) gives phenylpyruvic acid (XII) and 1,3-diphenylpropene (XIII). Possible reaction mechanisms for the formation of these substances are proposed.

Preparations of phenylcyclobutenedione (phenylcyclobutadienoquinone, I) and several of its substitution products have been reported recently.[2] A number of reactions of these unusual substances have been investigated[3] and one of the most interesting is the conversion of I by hot alkali to benzaldehyde, 33% yield.[4] The object of the present research was to clarify the mechanism of this

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

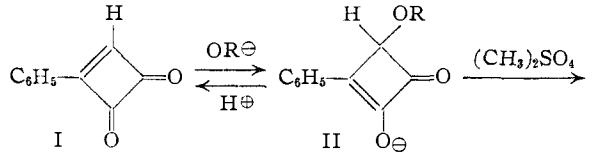
(2) J. D. Roberts and E. J. Smutny, THIS JOURNAL, **77**, 3420 (1955).

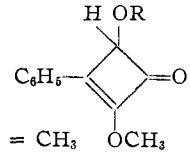
(3) J. D. Roberts, *Rec. Chem. Progr.*, **17**, 95 (1956), and unpublished results in this Laboratory.

(4) First observed by Dr. E. J. Smutny.

reaction. To this end, the initial phases of the reaction of I with alkali were investigated.

The ultraviolet absorption spectrum of I in alkaline solution shows a strong bathochromic shift, $\Delta\lambda$, of 49 mμ. On addition of acid, I is regenerated. This behavior can be explained by the formation of II through operation of the following equilibrium (R = H). In order to demonstrate



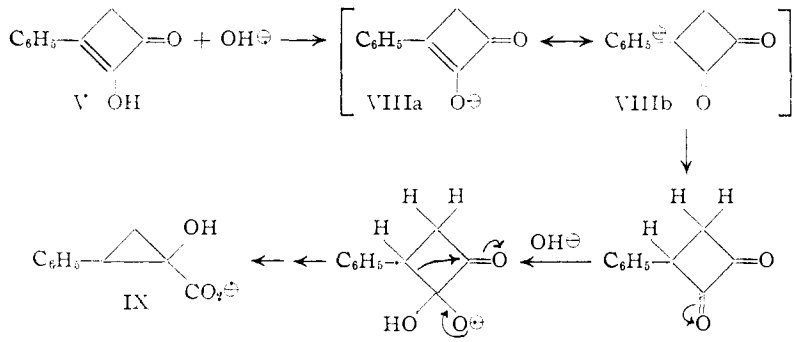


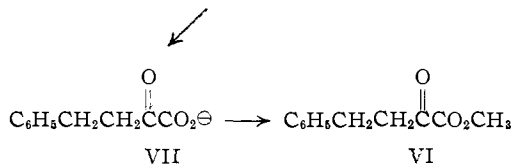
III, R = CH_3

the presence of species like II in alkaline media, the quinone I was treated with sodium methoxide in methanol and the resulting anion II (R = CH_3) was methylated with dimethyl sulfate. A small yield of the expected dimethoxy compound (III, R = CH_3) was obtained; III has been prepared previously by the methanolysis of I[5] and its structure established from its nuclear magnetic resonance spectrum and by its hydrolysis to I.

Treatment of I with 0.5 *N* sodium hydroxide in boiling methanol yielded, besides benzaldehyde, a small yield of an acidic substance which, on esterification with methanol and sulfuric acid, afforded a crystalline ester which proved to be identical in all respects with an authentic sample of methyl benzylidenepyruvate (IV).[6] To aid in the elucidation of the course of this ring-opening reaction, which did not seem easily predictable on the basis of II (R = H) as an intermediate, it was decided to investigate the corresponding reaction of 2-hydroxy-3-phenyl-2-cyclobutenone (V).[7] This compound possesses the enolized 1,2-cyclobutanedione system, as in II, and may be expected to undergo a similar ring-opening reaction in the presence of alkali. The 308.5 mμ ultraviolet absorption maximum of V in ethanol showed a strong bathochromic shift ($\Delta\lambda$ 41.5 mμ) on the addition of alkali,[8] but the alkali-induced decomposition of V gave no benzaldehyde; an acidic product was obtained which was converted to a methyl ester (VI) in 50% over-all yield; VI readily formed a 2,4-dinitrophenylhydrazone and reduced Tollens reagent. Hydrogen peroxide oxidation of VI yielded β-phenylpropionic acid. These data suggest that VI is methyl benzylpyruvate. This inference was confirmed by comparison with an authentic sample.[9]

In the absence of phenyl migration, or other deep-seated rearrangements, there seems little doubt that the ring-opening of V to benzylpyruvic acid (VII) must involve cleavage of the 2,3-ring bond. This presents a mechanistic problem since consideration of the conventional resonance forms (VIIIa,b), for the enolate anion of V indicates that the 2,3-bond should have the highest bond order of any of the cyclobutane ring bonds. The following mechanistic scheme provides a more or less plausible route for the formation of VII from V with alkali. The role of the base is here visualized





VII VI

to cause a benzilic acid-type rearrangement which is then followed by a ring opening of the resulting cyclopropanol derivative IX (as occurs with cyclopropanol itself)[10] to generate a carbonyl group.

With phenylcyclobutenedione (I), operation of a similar mechanism, as outlined below, might be expected to give benzylidenepyruvic acid (X). Only a small amount of X appeared to be present in the reaction mixture. However, this is not unreasonable since X is known to undergo a reverse aldol reaction in alkaline solution to give benzaldehyde,[11]

(5) F. B. Mallory, Ph.D. Thesis, Calif. Institute of Technology, 1957.

(6) M. Reimer, THIS JOURNAL, **46**, 783 (1924). We are grateful to Dr. Emma Stecher for an authentic sample of the corresponding acid.

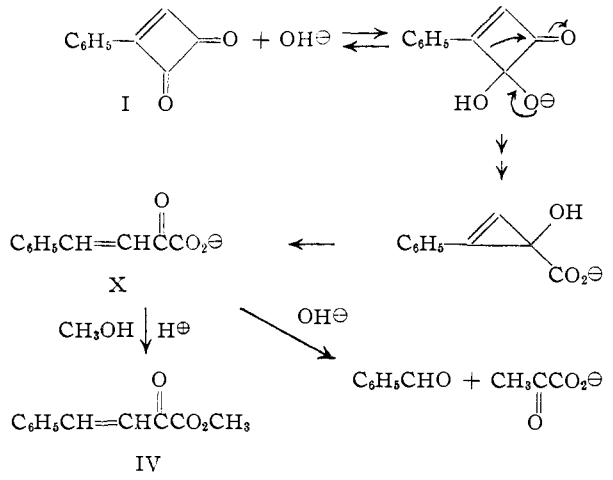
(7) E. F. Silversmith and J. D. Roberts, *ibid.*, **80**, 4083 (1958).

(8) A similar shift, $\Delta\lambda$ 43.5 mμ, has been recorded for 2-hydroxy-3-methylcyclohex-2-enone in alkaline solution by H. S. French and M. E. T. Holden, THIS JOURNAL, **67**, 1239 (1945).

(9) W. Wislicenus and M. Münzesheimer, *Ber.*, **31**, 554 (1898); W. Wislicenus, *ibid.*, **31**, 3133 (1898); *Ann.*, **246**, 315 (1888).

(10) J. K. Magrane and D. L. Cottle, THIS JOURNAL, **64**, 484 (1942); G. W. Stahl and D. L. Cottle, *ibid.*, **65**, 1782 (1943).

(11) E. Erlenmeyer, Jr., *Ber.*, **36**, 2527 (1903).

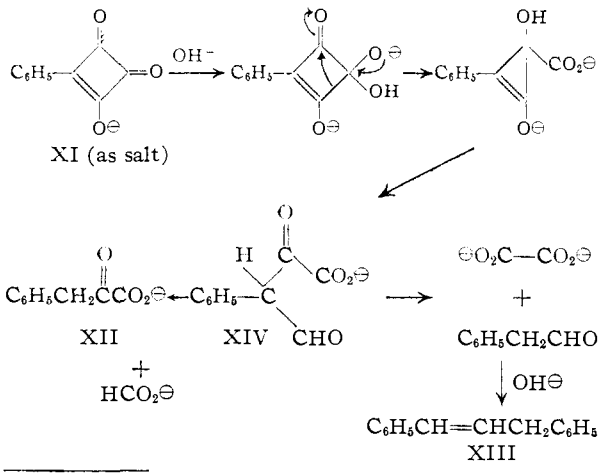


the principal observed reaction product. The role of the anion II (R = H) in this ring-opening reaction is uncertain, although X can be visualized as being formed from II (by a path similar to that written for the ring opening of V) *via* β-hydroxy-β-benzylpyruvic acid.

As expected for the operation of a mechanism such as that above, I with sodium deuteroxide in deuterium oxide affords α-deuterobenzaldehyde, C_6H_5CDO. Deuterium is presumably incorporated during the ring opening of the proposed cyclopropene intermediate.

Hydroxyphenylcyclobutenedione (XI)[2] with boiling 10% aqueous sodium hydroxide gave a solid acidic and a liquid neutral product. The acid, m.p. 154–157°, was shown to be phenylpyruvic acid (XII) by comparison with an authentic sample.[12] The neutral substance (XIII), which was the main product of the reaction, had infrared and n.m.r. spectra resembling those of propenylbenzene. The compound readily formed a dibromide of m.p. 109–110°, which had the composition $C_{15}H_{14}Br_2$. This information indicates that XIII is 1,3-diphenylpropene, and the structural assignment was substantiated by comparison with an authentic sample.[13]

The possibility that phenylpyruvic acid XII is intermediate to the formation of 1,3-diphenylpropene XIII was ruled out by the absence of XIII on treating XII independently with alkali. It is probable that XII is formed along with XIII by a competing reaction.



The following mechanistic scheme for the formation of the observed products is closely related to those discussed earlier.

Evidence for the proposed route for formation of 1,3-diphenylpropene was obtained by isolation of oxalic acid as calcium oxalate from the reaction mixture. Phenylacetaldehyde is known to yield 1,3-diphenylpropene with alkali.[13] No carbon monoxide appeared to be evolved during the reaction.

The literature records the action of alkali on two compounds similar to XIV. Acetopyruvic acid is cleaved to acetone and oxalic acid[14] and ethyl benzoylpyruvate[15] gives acetophenone and oxalic acid.

Experimental

2,4-Dimethoxy-3-phenylcyclobutenone (III).—A solution of 3.2 g. of phenylcyclobutenedione (I) in sodium methoxide, prepared from 0.5 g. of sodium and 200 ml. of methanol, was left at room temperature for 24 hr. The methanol was then distilled under reduced pressure and the residue was immediately dissolved in 50 ml. of water. The solution was stirred and cooled in an ice-bath while 2.5 g. of dimethyl sulfate was added dropwise. After 2 hr. at room temperature, the product was extracted with ether, the extract washed with water and dried. Distillation yielded 0.30 g. of 2,4-dimethoxy-3-phenylcyclobutenone (III) as a viscous oil, b.p. (bath temperature) 130–140° (~1 mm.), $n^{23.5}D$ 1.5922. The product solidified on cooling and crystallized from pentane as pale yellow needles, m.p. 37–39°.

Anal. Calcd. for $C_{12}H_{12}O_3$: C, 70.57; H, 5.92; OCH_3, 30.39. Found: C, 70.78; H, 6.10; OCH_3, 30.24.

Phenylcyclobutenedione (I) **with Sodium Hydroxide.**—A solution of 1.6 g. of the quinone I in methanolic sodium hydroxide (50 ml., 0.5 *N*) was heated under reflux for 3 hr. Some of the methanol was removed under reduced pressure and water was added. The neutral reaction product, benzaldehyde, was extracted with ether, and the aqueous layer was acidified with sulfuric acid. A total of 1.25 g. of the starting material was removed by filtration and the filtrate was extracted with ether. The ethereal extract was dried and the ether evaporated. The sticky brown residue subsequently was esterified with methanolic sulfuric acid. The product was extracted with ether, the extract washed thoroughly with sodium bicarbonate solution and dried. Short-path, reduced-pressure distillation gave a small amount of a partly crystalline product which after several recrystallizations from petroleum ether gave IV as light yellow needles, m.p. 70–72°; IV showed λ_{max} 311 mμ, (ε 14,600) in methanol. Its melting point was not depressed on admixture with an authentic sample of methyl benzylideneepyruvate of m.p. 70–72°.[6]

Phenylcyclobutenedione with Sodium Deuteroxide.—The quinone I (700 mg.) was dissolved in a solution made from 400 mg. of sodium and 20 ml. of deuterium oxide. The benzaldehyde which formed was distilled with the deuterium oxide and separated by extraction with ether. Distillation of the extract yielded α-deuterobenzaldehyde. The n.m.r. spectrum of the product showed no proton resonance line at low magnetic field strengths of the type characteristic of an aldehydic hydrogen. The infrared spectrum showed two bands of medium intensity of 2050 and 2100 cm.$^{-1}$ representing C–D stretching vibrations, while the band at 2700–2800 cm.$^{-1}$, typical of an aldehydic hydrogen, was absent.

3-Phenyl-2-hydroxy-2-cyclobutenone (V) **with Sodium Hydroxide.**—A solution of 2.0 g. of V in methanolic sodium hydroxide (50 ml., 2 *N*) was heated under reflux for 7 hr. and left overnight at room temperature. Some of the methanol was removed under reduced pressure and then water was added. The solution was acidified with sulfuric

(12) E. Erlenmeyer, Jr., and E. Arbenz, *Ann.*, **333**, 228 (1904).
(13) R. Stoermer, C. Tier and E. Laage, *Ber.*, **58**, 2607 (1925).
(14) O. Mumm and C. Bergell, *ibid.*, **45**, 3040 (1912).
(15) C. Beyer and L. Claisen, *ibid.*, **20**, 2182 (1887).

acid and extracted with ether. The acidic product was separated from the ethereal solution by extraction with sodium bicarbonate solution. The bicarbonate layer was acidified and extracted with ether; the ether was then removed and the residue esterified with methanolic sulfuric acid in the usual way. Subsequent distillation of the esterification product afforded 1.0 g. (42%) of methyl benzylpyruvate (VI), b.p. 109–110° (~2 mm.), $n^{25}D$ 1.4968. The infrared spectrum was identical with that of an authentic sample.[9]

The 2,4-dinitrophenylhydrazone of VI was obtained as yellow needles, m.p. 153.5°, from methanol. The melting point of this derivative was not depressed by admixture with a sample prepared from authentic VI.

Anal. Calcd. for $C_{17}H_{16}O_6N_4$: C, 54.85; H, 4.33; N, 15.05. Found: C, 54.88; H, 4.23; N, 15.09.

Oxidation of 300 mg. of the acid VII in 1 ml. of glacial acetic acid with hydrogen peroxide (0.3 ml., 85%) yielded β-phenylpropionic acid identified by m.p. and mixed m.p. with an authentic sample.

Hydroxyphenylcyclobutenedione (XI) with Sodium Hydroxide.—A solution of 2.0 g. of the enol XI in 100 ml. of 10% aqueous sodium hydroxide was heated under reflux for 18 hr. The neutral products were extracted with ether. The aqueous layer was acidified with sulfuric acid and extracted with ether. The extracts were washed with water and dried over magnesium sulfate. Evaporation of the ethereal extract of the acidic reaction product gave a solid residue, which was recrystallized from benzene and afforded 100 mg. (8%) of phenylpyruvic acid (XII), m.p. 154–157°. XII showed an ultraviolet absorption maximum in ethanol at 287.5 mμ (ε 19,200) and its melting point was not depressed on admixture with an authentic sample.[12] Distillation of the ethereal extract of the neutral reaction products yielded 450 mg. (40%) of 1,3-diphenylpropene (XIII), b.p. 98–102° (~1 mm.), $n^{25}D$ 1.6002, with ultraviolet absorption maxima in ethanol at 251, 283.5 and 292.5 mμ (ε 22,300, 1890 and 1330, respectively). The infrared and ultraviolet spectra were identical with those of an authentic sample.[13] Compound XIII (250 mg.) reacted with bromine in glacial acetic acid at room temperature to yield a crystalline dibromide, m.p. 109–110°. The m.p. of this material was not depressed on admixture with the dibromide prepared from an authentic sample of XIII.

One alkaline cleavage of the hydroxyquinone XI was carried out under nitrogen and the yields obtained were 7 and 39% of XII and XIII, respectively. In another run, the aqueous layer, after the extraction of XIII, was acidified and treated with calcium chloride solution. The white precipitate which formed was identified as calcium oxalate.

PASADENA, CALIFORNIA

[CONTRIBUTION NO. 2311 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY OF THE CALIFORNIA INSTITUTE OF TECHNOLOGY]

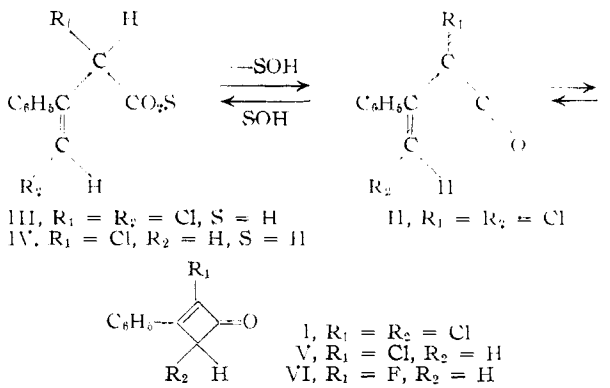
Small-Ring Compounds. XIX. On the Synthesis of Cyclobutenones *via* Vinylketenes[1]

BY ERNEST F. SILVERSMITH,[2a] YOSHIO KITAHARA[2b] AND JOHN D. ROBERTS

RECEIVED FEBRUARY 24, 1958

The previously reported preparation of 2,4-dichloro-3-phenylcyclobutenone from 2,4-dichloro-3-phenyl-3-butenoic acid (presumably by way of a vinylketene intermediate) does not appear to represent an example of a general synthetic route to cyclobutenones. 2-Chloro-3-phenylcyclobutenone is preparable by this method, but no success was achieved in attempted syntheses of a number of related compounds.

2,4-Dichloro-3-phenylcyclobutenone (I) has been shown to undergo ring opening in a variety of solvents to give the short-lived (1-phenyl-2-chloroethenyl)-chloroketene (II).[3] This vinylketene then cyclizes to regenerate I, or (as with hydroxylic solvents such as acetic acid and ethanol) reacts with the solvent to give open-chain products. It was further found that 2,4-dichloro-3-phenyl-3-butenoic acid (III) loses water when heated with acetic anhydride and yields I, presumably by way of II. The discovery of this reaction was hoped to lead to a possible general synthesis of cyclobutenones by ring closure of vinylketenes. However, this hope so far has not been realized.



2-Chloro-3-phenyl-3-butenoic acid (IV)[4] with acetic anhydride forms 2-chloro-3-phenyl-2-cyclobutenone (V) to the extent of 20–30%. However, a corresponding attempted ring closure of a closely related conjugated acid (α-fluoro-β-methylcinnamic acid (VII) from treatment of 2-fluoro-3-phenyl-2-cyclobutenone (VI) with acetic acid[4]) yielded only a mixture of acid anhydrides.

A number of other reactions, expected to yield intermediate vinylketenes, were carried out, but none appeared to result with significant cyclization to cyclobutenones. The reaction products were tested for cyclobutenones with 2,4-dinitrophenylhydrazine reagent and infrared absorption at or near 5.7 μ (characteristic of cyclobutenones).

The unsuccessful syntheses involved attempted vinylketene formation and cyclization by several types of reactions. These included (1) treatment of an α,β-unsaturated acid (γ-bromocrotonic acid) with acetic anhydride and thionyl chloride,[5] (2) treatment of β,γ-unsaturated acids (4-phenyl-3-

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

(2) (a) National Science Foundation Postdoctoral Fellow, 1955–1956; (b) Arthur Amos Noyes Fellow, 1956–1957. Fulbright Travel Grantee. Present address: Chemical Research Institute, Tohoku University, Sendai, Japan.

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

(4) E. F. Silversmith, Y. Kitahara and J. D. Roberts, *ibid.*, in press.

(5) In unpublished experiments, Dr. E. F. Jenny obtained I from III while trying to prepare the acid chloride with thionyl chloride.