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° ($\sim$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° ($\sim$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]

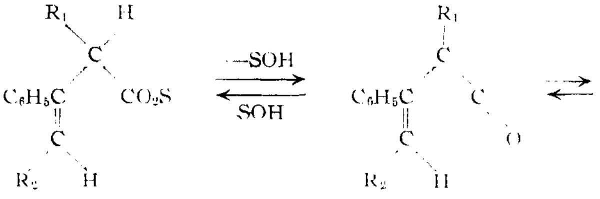
Small-Ring Compounds. XIX. On the Synthesis of Cyclobutenones *via* Vinylketenes[1]

By Ernest F. Silversmith,[2a] Yoshio Kitahara[2b] and John D. Roberts

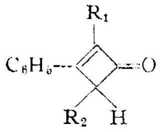
Received February 24, 1958

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.



III, $R_1 = R_2 = Cl$, S = H
IV, $R_1 = Cl$, $R_2 = H$, S = H
II, $R_1 = R_2 = Cl$



I, $R_1 = R_2 = Cl$
V, $R_1 = Cl$, $R_2 = H$
VI, $R_1 = F$, $R_2 = H$

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-

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[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.

butenoic acid,[6] 2- and 4-chloro-3-phenyl-3-butenoic acids[4] and 2-phenyl-3-butenoic acid[7]) with acetic anhydride and with thionyl chloride, (3) the reaction of an α,β-unsaturated acid chloride (crotonyl chloride) with triethylamine,[8] (4) reactions of β,γ-unsaturated acid chlorides (4-phenyl-3-butenoyl chloride, vinylacetyl chloride[9] and 2-chloro-3-phenyl-3-butenoyl chloride) with triethylamine,[8] and (5) a silver oxide-catalyzed rearrangement of a vinyldiazoketone[8] (diazomethyl α-styryl ketone, obtained from the reaction of atropyl chloride[10] and diazomethane).

Experimental

2-Chloro-3-phenyl-2-cyclobutenone.—A solution of 0.4 g. of 2-chloro-3-phenyl-3-butenoic acid (IV) in 4.0 ml. of acetic anhydride was refluxed for 30 min. The reaction mixture was poured into 5% sodium bicarbonate solution containing crushed ice and stirred at room temperature for 3 hr. Extraction with ether, evaporation, sublimation and recrystallization from cyclohexane gave 0.08 g. of the ketone V, m.p. 63–65°, which was identified by its m.p., mixed m.p. and infrared spectrum.

The following experiment is reasonably typical of many of the attempted ring closures. A solution of 0.3 g. of α-fluoro-β-methylcinnamic acid[4] (VII) in 3 ml. of acetic anhydride was refluxed for 30 min. The reaction mixture was poured into 5% sodium bicarbonate solution and extracted with ether. Acidification of the sodium bicarbonate solution gave 0.20 g. of unchanged VII, m.p. and mixed m.p. 128–129.5°. The ethereal solution was dried over magnesium sulfate, filtered and the ether evaporated. The infrared spectrum of the residue indicated it to be a mixture of anhydrides. The mixture was dissolved in sodium bicarbonate solution and subsequent acidification gave 0.04 g. of the starting acid, m.p. and mixed m.p. 129–130°, which was also identified by its infrared spectrum.

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[9] Prepared from thionyl chloride and vinylacetic acid in the usual manner. For the preparation of the acid, see L. Talaise and R. Frognier, *Bull. Soc. Chim. Belg.*, **42**, 427 (1933).

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

Mechanisms of Decomposition of Neutral Sulfonium Salts in Solution. I. Trimethyl- and Tribenzyl-sulfonium Salts[1–3]

BY C. GARDNER SWAIN AND LAURA E. KAISER

RECEIVED MARCH 3, 1958

The decomposition of trimethyl- and tribenzyl-sulfonium salts in 90% acetone–10% water solution at 50–100° in the absence of strong bases involves neither carbonium ion formation nor solvolysis in the rate-determining step, but instead a reaction with the anion. The kinetics appears first order only because of exactly compensating salt effects. When a relatively inert anion (perchlorate) is used, no reaction occurs under the same conditions.

The decomposition of tri-*n*-alkylsulfonium salts in solution in the absence of strong bases has been found to be a first-order reaction. Halban studied the decomposition of triethylsulfonium bromide into ethyl bromide and diethyl sulfide by following the disappearance of bromide ion by a Volhard titration.[4] He found that the reaction was first order in 17 different solvents and solvent mixtures, including tetrachloroethane (studied from 18–70°), nitrobenzene (18–70°), acetone (30–60°), 90% acetone–10% water (70–90°), acetic acid and five alcohols. Essex and Gelormini[5] and Corran[6] also found first-order kinetics for this compound in various solvents. Gleave, Hughes and Ingold studied the decomposition of trimethylsulfonium salts in water, 60, 80 and 100% ethanol at 100°.[7] The chloride, bromide and carbonate gave constant and identical first-order rate constants in 100% ethanol within experimental error (7.3 × 10^{-5}, 7.8 × 10^{-5} and 7.4 × 10^{-5} sec.$^{-1}$, respectively, by Volhard titration for chloride and bromide ions and acid titration for carbonate ion), whereas calculated second-order rate constants varied by more than a factor of two in the course of a run. Added carbonate ion (as tetraethylammonium carbonate) did not alter the rate of decomposition of trimethylsulfonium carbonate. It was concluded that the reaction was unimolecular, with

$$(CH_3)_3S^{\oplus} \longrightarrow CH_3^{\oplus} + (CH_3)_2S \qquad (1)$$

as the rate-determining step.

On the other hand, the strongly basic sulfonium salts, trimethylsulfonium phenoxide and hydroxide, gave second-order kinetics.[7] The appreciable effect of ionic strength was noted, and rate constants were compared at concentrations in the neighborhood of 0.1 M (0.013 M^{-1} sec.$^{-1}$ for phenoxide and 0.74 M^{-1} sec.$^{-1}$ for hydroxide in 100% ethanol). The reaction with hydroxide was 20,000 times faster in 100% ethanol than in water, but the kinetics was second-order in both solvents. The reactions with phenoxide and hydroxide ions were interpreted by a single-stage bimolecular mechanism

$$RO^{\ominus} + (CH_3)_3S^{\oplus} \longrightarrow ROCH_3 + (CH_3)_2S \qquad (2a)$$

The authors concluded that they had observed a "point of mechanistic change" between the carbonate and phenoxide ions.

Since a methyl cation is an especially high-energy carbonium ion, three possibilities in addition

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[1] Supported by the Office of Naval Research. Reproduction permitted for any purpose of the United States Government.

[2] *Cf.* Paper II, C. G. Swain, L. E. Kaiser and T. E. C. Knee, THIS JOURNAL, **80**, 4092 (1958).

[3] For complete experimental details, *cf.* L. E. Kaiser, Ph.D. Thesis, M. I. T., February, 1954.

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