XI and resulted in a 72% yield of XIII, b.p. 84–85° (50 mm.), n^{25}D 1.4310.

Anal. Calcd. for $C_9H_{16}O_2$: C, 69.19; H, 10.33. Found: C, 69.24; H, 10.30.

Acid Hydrolysis of 3-Methylenecyclobutanone Ethylene Ketal.—A heterogeneous mixture of 3.6 g. (0.018 mole) of XII and 5 ml. of 0.24 *M* perchloric acid solution was shaken mechanically for 13 hours at room temperature. The hydrolysis was followed by infrared spectroscopy using small aliquots of the organic phase and, after 13 hours, the line at 1770 cm.$^{-1}$ assigned to the conjugated ketone XIV was found to be increasing in intensity faster than the line at 1807 cm.$^{-1}$ assigned to I. The spectra indicated that the hydrolysis was far from complete. The purple organic layer was separated. The aqueous phase was saturated with sodium chloride and extracted with three 15-ml. portions of methylene chloride. The organic phases were combined and dried over anhydrous magnesium sulfate overnight in a refrigerator. The drying agent was removed by filtration and the now orange solution was fractionated under reduced pressure using an efficient concentric-tube column to remove the solvent, b.p. −3° (100 mm.). The residue was transferred to a micro concentric-tube column and was fractionated at reduced pressure. Two fractions were obtained of about 0.1 ml. each, b.p. 20° (10 mm.), both of which were mixtures of I, XIV and a hydroxylic component (presumably water) with I predominating as shown by the infrared spectra. A total of 2.3 g. (64%) of starting material was recovered by short-path reduced-pressure distillation.

In another experiment with 0.1 g. of XII and 1 ml. of acid solution, the mixture gave a 2,4-dinitrophenylhydrazone derivative which was very difficult to recrystallize, but after three recrystallizations from a benzene–hexane mixture was yellow and had m.p. 138–140°.

Anal. Calcd. for $C_{11}H_{10}O_4N_4$: C, 50.38; H, 3.84. Found: C, 51.41; H, 4.02.

Attempts to repeat this preparation were unsuccessful.

Acid Hydrolysis of 3-Methylene-1,1-diethoxycyclobutane (XIII).—A mixture of 1.0 g. (0.0064 mole) of XIII and 1.5 g. (0.064 mole of water) of 0.11 *M* perchloric acid was shaken mechanically for about 12 hr. at which time the n.m.r. spectrum of the organic phase indicated that about 50% of the starting material had hydrolyzed. The mixture was saturated with sodium chloride and the top yellow layer was removed and fractionated at 10 mm. using a semi-micro concentric-tube column. About 0.4 ml. of distillate was obtained which from its infrared, ultraviolet and n.m.r. spectra appeared to contain about 50% ethanol. The product gave a **2,4-dinitrophenylhydrazone**, m.p. 82–85°, which consisted of red and orange particles. Five recrystallizations from *n*-hexane yielded about 9 mg. of yellow needles, m.p. 116.4–116.8°.

Anal. Calcd. for $C_{11}H_{10}O_4N_4$: C, 50.38; H, 3.84. Found: C, 50.03; H, 4.47.

3-Methylcyclobutanone (XVI). A. From 1-Methylene-3,3-diethoxycyclobutane (XIII).—A solution of 2.5 g. of XIII in 20 ml. of absolute ethanol was hydrogenated over 0.1 g. of platinum dioxide in a low-pressure apparatus. The catalyst was centrifuged and the ethanol was mostly distilled at atmospheric pressure through a 30-cm. spiral-wire packed column. The concentrated residue containing XV was shaken mechanically with 4 ml. of 0.15 *M* perchloric acid. Hydrolysis was complete in 2 hr. and the resulting homogeneous solution was saturated with sodium chloride and extracted with three 5-ml. portions of ether. The combined extracts were dried over anhydrous magnesium sulfate and the ether removed by fractionational distillation through a 30-cm. spiral-wire packed column. The residue was distilled at atmospheric pressure through a micro distillation apparatus and yielded four fractions of which only the last two, about 0.2 g., b.p. *ca.* 110°, were free from ether although still apparently contaminated with ethanol and water. The crude product gave a **2,4-dinitrophenylhydrazone** which was recrystallized five times from *n*-hexane and gave orange needles of m.p. 108.5–109.5° (uncor.).

Anal. Calcd. for $C_{11}H_{12}O_4N_4$: C, 50.00; H, 4.58. Found: C, 50.06; H, 4.68.

In a second preparation from XIII, the hydrogenation was performed in the absence of solvent. The small amount of ethanol encountered as a by-product was removed by fractionation through a micro concentric-tube column. About a 50% yield of XVI was obtained; b.p. 112–113° (atm.), 71.5–72° (200 mm.) and n^{25}D 1.4140. The ultraviolet spectrum had λ_{max} 280.5 mμ (ϵ 15.2 in 95% ethanol).

Anal. Calcd. for C_5H_8O: C, 71.39; H, 9.58. Found: C, 71.19; H, 9.72.

B. From the 3-Methylenecyclobutanone (I)–3-Methylcyclobutanone (XIV) Mixture.—The first fraction of the ketonic mixture obtained from the acid hydrolysis of XII described above was dissolved in 1 ml. of 95% ethanol and was hydrogenated over platinum dioxide at low pressure. After removal of the catalyst by centrifugation, the solution was treated with aqueous 2,4-dinitrophenylhydrazine reagent and afforded 0.1 g. of a solid with m.p. 108–109°, after 3 recrystallizations from *n*-hexane. The m.p. was not depressed on admixture with the derivative obtained from procedure A above.

PASADENA, CALIF.

[CONTRIBUTION NO. 2350 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY]

Small Ring Compounds. XXII. Ring Opening of Halogenated 3-Phenylcyclobutenones in Acetic Acid and Aqueous Sodium Hydroxide[1a]

BY ERNEST F. SILVERSMITH,[1b] YOSHIO KITAHARA,[1c] MARJORIE C. CASERIO AND JOHN D. ROBERTS

RECEIVED MAY 22, 1958

Ring-opening reactions of a number of halogen-substituted 3-phenylcyclobutenones in acetic acid and in aqueous sodium hydroxide have been investigated and the resulting carboxylic acids identified. The course of reaction in acetic acid can be rationalized by a mechanism involving vinylketene intermediates. The base-induced ring-opening reaction appears to follow a course dependent on the number and location of the halogen atoms but is generally similar to the haloform reaction.

In earlier work,[2,3] alkali-induced ring-opening reactions of two chlorine-substituted 3-phenylcyclobutenones were studied as an aid to the structure proof of the starting materials. It was found that 2,4-dichloro-3-phenylcyclobutenone (I) and 2,2-dichloro-3-phenylcyclobutenone (II) react with aqueous sodium hydroxide to yield 2,4-dichloro-3-phenyl-3-butenoic acid (III) and 4,4-dichloro-3-phenyl-2-butenoic acid (IV), respectively.

It was suggested[2] that these base-induced ring-openings proceed by a mechanism resembling that of the cleavage step of the haloform reaction,[4] although no explanation was presented for the ex-

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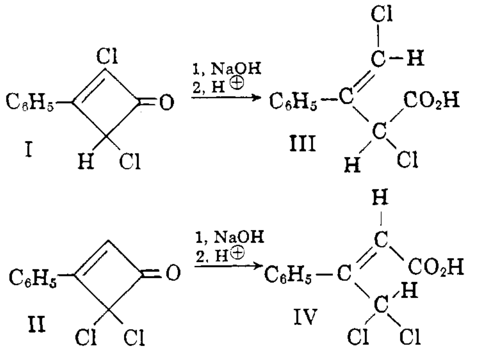
[1] (a) Supported in part by a grant from the National Science Foundation; (b) National Science Foundation Postdoctoral Fellow, 1955–1956; (c) Arthur A. Noyes Fellow, 1956–1957. Fulbright travel grantee. Present address: Chemical Research Institute for Non-Aqueous Solutions, Tohoku University, Sendai, Japan.

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

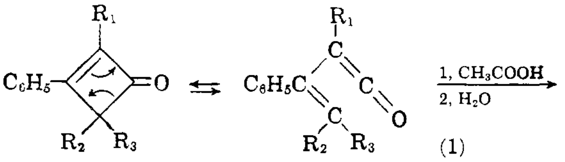
[3] E. F. Silversmith and J. D. Roberts, *ibid.*, **78**, 4023 (1956).

[4] J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, p. 295.

clusive formation of the β,γ-unsaturated acid III from I and the α,β-unsaturated acid IV from II.

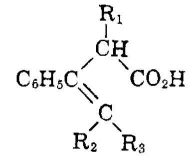


Subsequently, ring opening of the 2,4-dichloroketone I in acetic acid, and in ethanol, was shown to afford the mixed anhydride (with acetic acid) and the ethyl ester of III, respectively.[5] Strong evidence was presented in support of a vinylketene intermediate for these reactions (eq. 1).



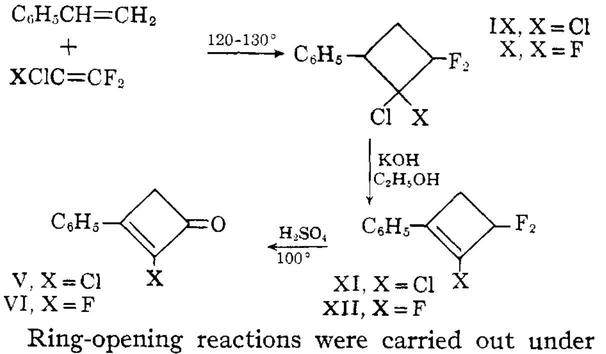
(1)

I, $R_1 = R_2 = Cl, R_3 = H$
II, $R_1 = H, R_2 = R_3 = Cl$
V, $R_1 = Cl, R_2 = R_3 = H$



III, $R_1 = R_2 = Cl, R_3 = H$
IIIa, R_3 and α-H = ^2H;
IIIb, α-H = ^2H;
IIIc, $R_3 = {}^2H$
VII, $R_1 = H, R_2 = R_3 = Cl$
VIII, $R_1 = Cl, R_2 = R_3 = H$

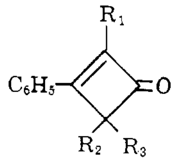
In the present research, the ring-opening reactions of I and II and other halogen-substituted 3-phenylcyclobutenones were investigated further in order to better understand the mechanisms involved. The additional compounds studied, 2-chloro-3-phenyl-2-cyclobutenone (V) and 2-fluoro-3-phenyl-2-cyclobutenone (VI), were synthesized as summarized.



Ring-opening reactions were carried out under basic conditions (aqueous sodium hydroxide) and acidic conditions (acetic acid). In the latter instance, the first-formed mixed anhydrides were not isolated as such but were hydrolyzed to the corresponding acids. The structures of the acidic products obtained from these experiments were separately established by elemental analyses, neutralization equivalents, ozonization and hydrogenation products, and infrared, ultraviolet and nuclear magnetic resonance spectra. In some ring-opening experiments, deuterated reagents were used in order to determine the origin of certain hydrogen atoms in the products; the positions occupied by deuterium were determined from the nuclear magnetic resonance spectra of these products. Table I lists the carboxylic acids obtained as products from the ring openings of all the halogenated 3-phenylcyclobutenones so far investigated under the different reaction conditions employed.

TABLE I

PRODUCTS FROM RING-OPENING REACTIONS OF HALOGENATED 3-PHENYLCYCLOBUTENONES



Compound	R_1	R_2	R_3	Conditions[a]	Product
I	Cl	Cl	H	A	2,4-Dichloro-3-phenyl-3-butenoic acid (III)
				B	2,4-Dichloro-3-phenyl-3-butenoic acid (III)
				C	2,4-Dichloro-3-phenyl-3-butenoic acid-2,4-$^2H_2$[b] (IIIa)
				D	2,4-Dichloro-3-phenyl-3-butenoic acid-2-^2H[b] (IIIb)
Ia	Cl	Cl	^2H	B	IIIb[c]
II	H	Cl	Cl	A	4,4-Dichloro-3-phenyl-3-butenoic acid (VII)
				B	4,4-Dichloro-3-phenyl-2-butenoic acid (IV)
V	Cl	H	H	A	2-Chloro-3-phenyl-3-butenoic acid (VIII)
				B	4-Chloro-3-phenyl-3-butenoic acid (XVI)
				C	4-Chloro-3-phenyl-3-butenoic acid-2,4-$^2H_2$[b] (XVIa)
VI	F	H	H	A	α-Fluoro-β-methylcinnamic acid (XIII)
				B	4-Fluoro-3-phenyl-3-butenoic acid (XVII)

[a] A, ketone heated in acetic acid and the mixed anhydride hydrolyzed by addition of water; B, ketone heated with sodium hydroxide solution and the mixture acidified; C, as in B, except for use of sodium deuteroxide–deuterium oxide, followed by acidification; D, as in A, except with use of deuterioacetic acid and deuterium oxide. [b] The carboxyl deuterium was usually lost in the purification steps, *cf.* ref. 3. [c] Not completely deuterated at 2-position; see discussion part.

The acidic products isolated from the ring-opening reactions in acetic acid clearly show that cleavage occurs universally between the ketonic and methylene ring-carbons. However, the products do not all have the same skeletal structure. Thus, while the 2,4-dichloroketone I, the 2,2-dichloroketone II and the 4-chloroketone V gave β,γ-unsaturated acids, the 4-fluoroketone VI gave an α,β-unsaturated acid. A plausible explanation of the difference in products from VI and the other ketones is suggested by models of the vinylketene intermediate corresponding to each ketone. The size of the phenyl and chlorine substituents for the ketenes from chloroketones I, II and V indicates that coplanarity, and hence conjugation, of the vinyl and ketene groupings can be achieved only by forcing the phenyl group out of coplanarity

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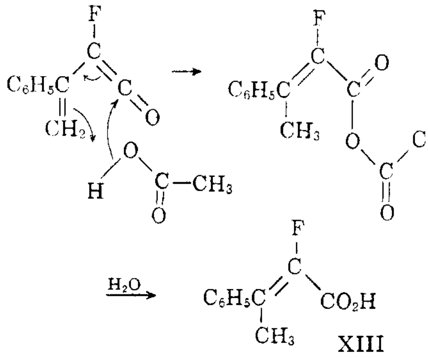
[5] E. F. Jenny and J. D. Roberts, THIS JOURNAL, 78, 2005 (1956).

with the vinyl group. This would result in a loss of resonance energy as the styrene-type conjugation is destroyed. More likely, this type of conjugation is preserved and the "isolated" ketene system reacts by 1,2-addition of acetic acid to give the mixed anhydride of a β,γ-unsaturated acid (eq. 1). However, the vinylketene intermediate from the fluoroketone VI might more easily attain the completely planar configuration owing to the smaller size of the fluorine atom. This configuration has the unsaturated centers in full conjugation, and formation of a mixed anhydride of an α,β-unsaturated acid could result from 1,4-addition of acetic acid to this intermediate (eq. 2).

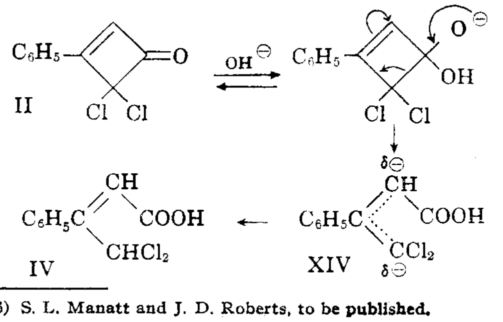


(2)

This reasoning is further supported by the observed formation of β-methylcinnamic acid from the ring opening of 3-phenyl-2-cyclobutenone in acetic acid.[6]

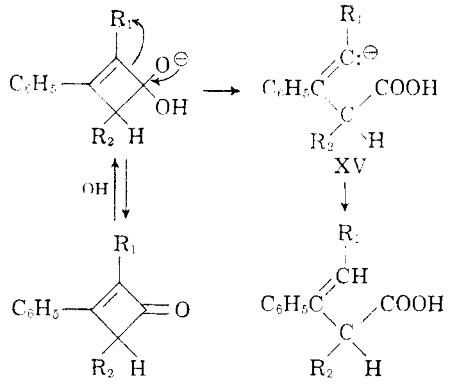
It was observed previously[3] that reaction of I with deuterioacetic acid gave 2,4-dichloro-3-phenyl-3-butenoic-2-^{2}H acid (IIIb). The position of deuterium is that expected from the mechanism of ring opening outlined in eq. 1. The relatively low sensitivity of the ring-opening rate of I to the nature of the solvent[5] indicates vinylketene formation to be an uncatalyzed thermal reaction. It is of practical synthetic importance that the ring opening of 2,2-dichloro-3-phenylcyclobutenone (II) in acetic acid affords the β,γ-unsaturated isomer of 4,4-dichloro-3-phenylbutenoic acid, while the α,β-unsaturated isomer is available from the alkali-induced reaction.

In contrast to the ring openings in acetic acid, the products formed under alkaline conditions from the several halogenated 3-phenylcyclobutenones indicate that the ring can be cleaved in two different ways. Cleavage of 2,2-dichloroketone II occurs between the carbonyl carbon and the dichloromethylene group probably by way of the reaction sequence (eq. 3).



(3)

On the other hand, the nature of the products shows that the alkali-induced openings of the 4-chloroketone V and the 4-fluoroketone VI clearly proceed with the breaking of the bond between the carbonyl group and halovinyl group, possibly as in eq. 4.



(4)

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

III, $R_1 = R_2 = Cl$
XVI, $R_1 = Cl, R_2 = H$
(XVIa, 2,4-H = ^{2}H)
XVII, $R_1 = F, R_2 = H$

The assignment of the *cis* configuration of R_1 and phenyl group in III, and hence in XVI and XVII, is supported by ultraviolet spectral data which will be discussed below. If the configurations are correct, the intermediate vinyl anion XV must preserve its stereochemical configuration in the interval between the time it is generated and takes on a proton.[7] Vinyl anions previously have been proposed as reaction intermediates in a number of related processes.[8] The only alternative to having a vinyl anion which does not undergo rapid stereochemical inversion is to have some sort of front-side electrophilic attack of a proton simultaneously with the breaking of the C–C bond.

With the 2,4-dichloroketone I, ring opening by either eq. 3 or 4 would lead to the *same* product provided the resulting carbanion of 2,4-dichloro-3-phenylbutenoic acid (isomeric with XIV) were to add a proton only so as to yield the unconjugated acid III. The more economical explanation is to have I, like 4-chloroketone V and 4-fluoroketone VI, yield the unconjugated acid by the route of eq. 4. In contrast, with the 2,2-dichloroketone II, the *gem*-dichloro group next to the carbonyl group (and the absence of an electron-attracting halogen on the double bond) would tend to favor ring cleavage by way of anion XIV and give the conjugated acid IV.

In an effort to determine whether or not I opens with alkali in accord with eq. 4, the reaction was carried out in deuterium oxide solution. If eq. 4 were correct, the hydrogen on the 4-position of the acid carbon chain would be supplied by the solvent and the product would be 2,4-dichloro-3-phenyl-3-

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[6] S. L. Manatt and J. D. Roberts, to be published.

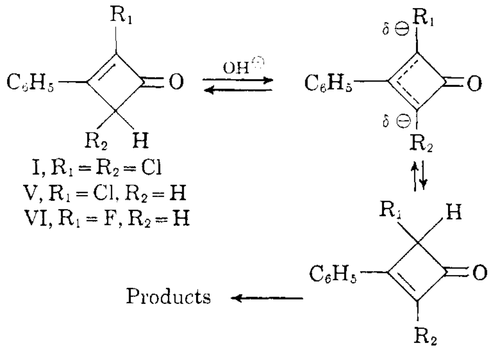
[7] Stereoisomeric vinyllithium derivatives have been studied extensively by D. Y. Curtin. See D. Y. Curtin and E. E. Harris, THIS JOURNAL, **73**, 2716, 4519 (1951); D. Y. Curtin, H. W. Johnson, Jr., and E. G. Steiner, *ibid.*, **77**, 4566 (1955); D. Y. Curtin and J. W. Crump, *ibid.*, **80**, 1922 (1958).

[8] (a) A. A. Bothner-By, *ibid.*, **77**, 3293 (1955); (b) S. I. Miller and R. M. Noyes, *ibid.*, **74**, 629 (1952); (c) T. L. Jacobs and W. R. Scott, Jr., *ibid.*, **75**, 5497 (1953); (d) S. I. Miller and G. Shkapenko, *ibid.*, **77**, 5038 (1955); (e) W. E. Truce, J. A. Simms and M. M. Boudakian, *ibid.*, **78**, 695 (1956).

butenoic-4-^{2}H acid (IIIc). On the other hand, a reaction path similar to eq. 3 would afford 2,4-dichloro-3-phenyl-3-butenoic-2-^{2}H acid (IIIb). Ketone V was run as a control since it clearly reacts by eq. 4. The products actually obtained from the ring openings of I and V in sodium deuteroxide–deuterium oxide solution were identified as 2,4-dichloro-3-phenyl-3-butenoic-2,4-$^2H_2$ acid (IIIa) and 4-chloro-3-phenyl-3-butenoic-2,4-$^2H_2$ acid (XVIa), respectively, as evidenced by their respective n.m.r. spectra. Moreover, on treating the undeuterated acids III and XVI with sodium deuteroxide in deuterium oxide under the same conditions as employed in the ring-opening experiments of I and V, the recovered acids were deuterated in the 2-position. Thus deuterium at the 4-position of III confirms that I undergoes a reaction with base by the same mechanism as V (eq. 4), while deuterium at the 2-position of III is evidently incorporated by exchange with the deuterium from the solvent.

The above conclusion was verified further by the results of the ring opening of 2,4-dichloro-3-phenylcyclobutenone-2-^{2}H[5] (Ia) in sodium hydroxide and water. The n.m.r. spectrum of the product showed the 2-position of the butenoic acid chain to be partially deuterated but indicated no deuteration at the 4-position. This result accords with the ring cleavage of I by the mechanism in eq. 4. Ring cleavage by eq. 3 would have positioned deuterium on the 4-carbon of the acid chain. That the 2-position is not wholly deuterated arises from the facile exchange of hydrogen from the 2-carbon as explained above.

An alternative mechanism for the ring openings of I, V and VI is shown in eq. 5. Hydroxide ion first acts to initiate a prototropic rearrangement, the product of which may then undergo ring opening as per eq. 3 to give the observed products. This mechanism is considered improbable on the basis of the experiment with 2,4-dichloro-3-phenylcyclobutenone-2-^{2}H (Ia) which gave 2,4-dichloro-3-phenyl-3-butenoic-2-^{2}H acid (IIIb). No deuterium should have been found in the product if the mechanism in eq. 5 were correct.



(5)

Ultraviolet spectral data for the acids produced by ring opening of the halo-ketones, and certain pertinent reference compounds, are listed in Table II. Acids IV and XIII adsorb essentially at the same wave lengths as β-methylcinnamic acid—which is consistent with the α,β-unsaturated structure assigned them—whereas, the β,γ-unsaturated acids III, VII, VIII, XVI and XVII absorb at lower wave lengths. However, the spectra of these latter acids are not comparable with the spectra of styrene[9] and β-chlorostyrene[9] (*cis* or *trans*). There is a pronounced shift to lower wave lengths and smaller extinction coefficients (particularly for III) which may be attributed in part to steric inhibition of conjugation between the double bond and attached phenyl group by the acetic acid or chloroacetic acid moieties. Further, the 2,4-dichloro acid III is tentatively assigned the *cis* configuration of 3-phenyl- and 4-chloro- substituents on the evidence that λ_{max} is shifted to *lower* wave lengths and the extinction coefficient is *smaller* than that of the 2-chloro acid VIII. It was mentioned previously that formation of *cis*-III from the base-induced ring opening of I necessarily implies that the proposed vinyl anion XV adds on a proton in a stereospecific manner. Thus, by analogy with III, the 4-chloro acid XVI and the 4-fluoro acid XVII are also tentatively assigned the respective *cis* configurations since the mode of their formation is the same as that of III.

TABLE II

ULTRAVIOLET SPECTRAL DATA FOR HALOGENATED 3-PHENYLBUTENOIC ACIDS[a]

Compound	λ_{max}	ϵ_{max}
IV[b]	268	7,450
β-Methylcinnamic acid[b]	266	7,500
III[b]	233	5,000
XVI	236	7,280
VIII	239	7,870
VII	228	8,300
XVII	237	10,700
	242	10,200
	252	5,170
XIII	264	13,200
β-Chlorostyrene		
(Mostly *trans*)[c]	254	18,920
(*cis*)	254	16,575
Styrene[c]	246	13,500

[a] Cary recording spectrometer, model 11 M, with 1-cm. quartz cells in 95% ethanol as solvent. [b] Ref. 2. [c] Ref. 9.

Experimental

1,1-Difluoro-2,2-dichloro-3-phenylcyclobutane (IX).—A mixture of 32 g. (0.307 mole) of styrene, 41 g. (0.309 mole) of 1,1-difluoro-2,2-dichloroethylene and 0.5 g. of hydroquinone was heated in a sealed tube at 130° for 3 hr. The mixture was fractionated through a 30-cm. Vigreux column. The main fraction (42 g., 58% yield) boiled at 73.8–74.2° (1 mm.) and had $n^{25}D$ 1.5103.

Anal. Calcd. for $C_{10}H_8Cl_2F_2$: C, 50.66; H, 3.40. Found: C, 50.59; H, 3.51.

1,1-Difluoro-2-chloro-3-phenyl-2-cyclobutene (XI).—To a solution of 3.2 g. (0.049 mole) of 85% potassium hydroxide in 60 ml. of absolute ethanol was added 9.5 g. (0.040 mole) of IX. A precipitate of potassium chloride formed immediately. The mixture was heated at reflux for 1 hr. and cooled to room temperature. The solid was removed by filtration and the filtrate was concentrated to *ca.* 20 ml. Water (70 ml.) was added and the mixture was extracted with three 50-ml. portions of ether. The combined ether extracts were washed with water (70 ml.) and dried, and the ether was removed by distillation. The product (6.3 g., 78%) had b.p. 66–67° (1 mm.) and $n^{25}D$ 1.5390.

Anal. Calcd. for $C_{10}H_7ClF_2$: C, 59.87; H, 3.52. Found: C, 59.83; H, 3.63.

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[9] A. C. Cope and M. Burg, THIS JOURNAL, **74**, 168 (1952).

2-Chloro-3-phenyl-2-cyclobutenone (V).—Concentrated sulfuric acid (10 ml.) was heated in a large test-tube with mechanical stirring on a steam-bath and 6.0 g. (0.030 mole) of XI was added. The mixture became dark brown and vigorous gas evolution occurred. Heating and stirring were continued for 15 min. and the mixture was poured into an ice-water slurry. The yellow solid was collected by filtration, washed and dried; 3.0 g. (56%). Recrystallization from 60–70° ligroin gave colorless needles, m.p. 67.2–68.2°. The ultraviolet spectrum was very similar to that of I[2] and the infrared and nuclear magnetic resonance spectra were also in agreement with the assigned structure.

Anal. Calcd. for $C_{10}H_7OCl$: C, 67.24; H, 3.95. Found: C, 67.30; H, 4.02.

Ketone V (5 g.) was hydrogenated by the procedure previously employed for I.[2] Distillation of the product yielded 2.5 g. of a colorless liquid, b.p. 90–92° (2.0 mm.) (lit.[2] b.p. 93–95°, 1.5 mm.), which had an infrared spectrum identical with that of 3-phenylcyclobutanone.[2] The 2,4-dinitrophenylhydrazone of this ketone had m.p. 151.0–152.2° (lit.[1] m.p. 148.5–150°) and did not depress the m.p. of an authentic sample.[2] The semicarbazone had m.p. 210.2–212.0° (lit.[2] m.p. 210.5–212°).

1,1,2-Trifluoro-2-chloro-3-phenylcyclobutane (X).—A mixture of 35 g. (0.336 mole) of styrene, 45 g. (0.386 mole) of trifluorochloroethylene and 0.5 g. of hydroquinone was heated in a sealed tube at 120° for 23 hr. The hydroquinone was removed from the cooled mixture by filtration and the filtrate was fractionated through a 30-cm. Vigreux column. The product X (53.2 g., 71%) was collected at 60.0–61.5° (0.5 mm.).

Anal. Calcd. for $C_{10}H_8ClF_3$: C, 54.44; H, 3.65. Found: C, 54.69; H, 3.32.

1,1,2-Trifluoro-3-phenyl-2-cyclobutene (XII).—A solution of 7.52 g. (0.114 mole) of potassium hydroxide (85.3% pure) in 150 ml. of absolute ethanol was added, with shaking, to 25.24 g. (0.114 mole) of X. It is important that equivalent amounts of X and potassium hydroxide be used and the temperature kept below 35°, since an excess of base and/or higher temperatures result in the formation of 1,1-difluoro-2 ethoxy-3-phenyl-2-cyclobutene.[10] The mixture was kept at room temperature for 2.5 hr., 500 ml. of water was added and the mixture was extracted four times with 150-ml. portions of ether. The combined extracts were washed with water (two 100-ml. portions), dried, and the ether was removed. The distilled product, b.p. 64.0–65.5° (1.2 mm.), amounted to 17.1 g. (81%).

Anal. Calcd. for $C_{10}H_7F_3$: C, 65.22; H, 3.83. Found: C, 65.29; H, 3.81.

2-Fluoro-3-phenyl-2-cyclobutenone (VI).—Concentrated sulfuric acid (15 ml.) was stirred and heated on the steam-bath. Compound XII (7 g.) was added, and heating and stirring were continued for 8 min. Gas was evolved and the reaction mixture darkened. The material was poured into an ice–water slurry and the yellow solid (5.7 g., 92%) was removed by filtration. Recrystallization of the crude product from aqueous ethanol gave VI as colorless needles, m.p. 82.0–83.0°. The ultraviolet, infrared and nuclear magnetic resonance spectra were in accord with the proposed structure.

Anal. Calcd. for $C_{10}H_7OF$: C, 74.07; H, 4.35. Found: C, 74.16; H, 4.42.

Reaction of V with Aqueous Sodium Hydroxide.—To 50 ml. of 1.5 *M* sodium hydroxide solution, heated on a steam-bath, there was added 5.0 g. of V. The mixture was heated with good shaking and, after 10 min., most of the organic material had gone into solution. The mixture was cooled and acidified with 1.5 *M* hydrochloric acid. The aqueous solution was separated from the resulting red-brown oil by decantation. The oil was shaken with dilute sodium bicarbonate solution; most of the organic material dissolved and a solid precipitate formed. The resulting mixture was filtered by suction and the filtrate acidified. A brown oil was obtained which solidified on cooling to 0°. The solid was collected, dried (2.9 g., 53%) and recrystallized from 60–70° ligroin to yield XVI as white plates of m.p. 81.0–82.2°.

Anal. Calcd. for $C_{10}H_9O_2Cl$: C, 61.08; H, 4.61; neut. equiv., 196.6. Found: C, 61.19; H, 4.79; neut. equiv., 198.8.

The infrared spectrum of XVI had the characteristic absorptions of the carboxyl group (3 to 4 μ and 5.83 μ), carbon–carbon double bond (6.12 μ) and phenyl group (6.23, 6.32 and 6.67 μ). From the ultraviolet spectrum of XVI (Table II), it is clear that the double bond is not conjugated with the carboxyl group. The nuclear magnetic resonance spectrum had four peaks approximately in the ratio 1:5:1:2 which were in appropriate positions to be ascribed to the carboxyl, phenyl, vinyl and alkyl hydrogens, respectively.

Compound XVI (0.3 g.) was hydrogenated by the method previously used for III.[2] The hydrogenation product was converted to 3-phenylbutyramide as before.[2] This latter substance had m.p. 103.6–104.6° (lit.[2] m.p. 104–106°) and did not depress the m.p. of an authentic sample.[2]

Compound XVI (0.95 g.) was dissolved in 50 ml. of ethyl acetate and treated with an excess of ozone at 0°. The solvent was removed and the residual oil was poured into 50 ml. of hot water and allowed to stand for 10 min. Concentrated sulfuric acid (2 ml.) was added and the mixture was heated at reflux for 5 min. The mixture was cooled and extracted with two 40-ml. portions of methylene chloride. The combined extracts were washed with water, dried, and the solvent was removed. The residue was a mixture of a neutral and an acidic component; these were separated by taking the mixture up in sodium bicarbonate solution, extracting with ether, acidifying the aqueous layer, and extracting the acidic component with ether. The acidic material was shown (by infrared spectrum and mixed m.p.) to be benzoic acid.[11] The neutral product was converted to the 2,4-dinitrophenylhydrazone which, after recrystallization from ethyl acetate, had m.p. 238–241° (reported[12] for acetophenone 2,4-dinitrophenylhydrazone, m.p. 239–240°) and did not depress the m.p. of an authentic sample.[13]

Reaction of V with Acetic Acid.—A solution of 2.0 g. of V in 30 ml. of acetic acid was heated under reflux for 19 hr. Water (10 ml.) was added and refluxing was continued for 1 hr. The solvent was removed in a stream of air and the residue was shaken with sodium bicarbonate solution. The mixture was filtered and acidified and the resulting oil was extracted with ether. Evaporation of the ether followed by recrystallization of the product from ligroin afforded 2-chloro-3-phenyl-3-butenoic acid (VIII) as white prisms, m.p. 85.2–86.3°.

Anal. Calcd. for $C_{10}H_9O_2Cl$: C, 61.08; H, 4.61; neut. equiv., 196.6. Found: C, 61.02; H, 4.59; neut. equiv., 196.7.

Ozonolysis of VIII by the method used for XVI (omitting the addition of sulfuric acid) gave a product which yielded a 2,4-dinitrophenylhydrazone of m.p. 213.0–215.0° dec. after recrystallization from ethyl acetate (lit.[14] m.p. 212° for phenacyl chloride 2,4-dinitrophenylhydrazone) and did not depress the m.p. of an authentic sample.

The infrared spectrum of VIII possessed absorptions characteristic of carboxyl (3–4 and 5.78 μ), carbon–carbon double bond (6.12 μ) and phenyl (6.23, 6.33 and 6.67 μ). The ultraviolet spectrum (Table II) clearly showed that the double bond is not conjugated with the carboxyl group.

The nuclear magnetic resonance spectrum at 40 mc. of a 50% solution of VIII in acetone showed four peaks at −184, −86.0, −15.5 and −12.3 c.p.s. (ref. H_2O) with areas approximately in the ratio of 1:5:2:1, respectively. In conjunction with the ultraviolet and ozonolysis data, these peaks are assigned to carboxyl, phenyl, vinyl and allylic hydrogens, respectively. Accordingly, the structure of VIII is 2-chloro-3-phenyl-3-butenoic acid.

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(10) E. F. Silversmith and J. D. Roberts, This Journal, **80**, 4083 (1958).

(11) The cleavage of benzoylacetic acid, the probable initial product of the ozonolysis, can yield benzoic acid as well as acetophenone; see W. H. Perkin, *J. Chem. Soc.*, **45**, 170 (1884), and A. Baeyer and W. H. Perkin, *Ber.*, **17**, 59 (1884).

(12) R. Huisgen and W. Rapp, *ibid.*, **85**, 826 (1952).

(13) Most workers have reported a melting point of around 250° for the 2,4-dinitrophenylhydrazone of acetophenone; see, for example, J. H. Ross, *Anal. Chem.*, **25**, 1288 (1953). However, some workers have reported melting points around 239° (*e.g.*, ref. 12) and this can be attributed to the possibility of geometrical isomerism (F. Ramirez and A. F. Kirby, This Journal, **76**, 1037 (1954)). Obtaining an authentic sample of the lower-melting isomer proved to be quite difficult; a sample was isolated from the mother liquors of a recrystallization of authentic acetophenone 2,4-dinitrophenylhydrazone from ethyl acetate.

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

Reaction of II with Acetic Acid.—A solution of 3.0 g. of II in 30 ml. of acetic acid was heated at reflux for 16 hr. The product was hydrolyzed and isolated by the method described above for the acetolysis of V. Recrystallization from ligroin yielded 46% of 4,4-dichloro-3-phenyl-3-butenoic acid (VII) as white plates, m.p. 127.8–128.4°.

Anal. Calcd. for $C_{10}H_8O_2Cl_2$: C, 51.97; H, 3.49; neut. equiv., 231.1. Found: C, 52.01; H, 3.46; neut. equiv., 233.6.

The infrared spectrum of VII showed absorptions at 3–4 μ and 5.83 μ characteristic of carboxyl, at 6.18 μ for the carbon–carbon double bond, and 6.88 μ for the phenyl group. From the ultraviolet spectrum (Table II) it is evident that the double bond is not conjugated with the carboxyl group. The nuclear magnetic resonance spectrum had peaks corresponding to carboxyl, phenyl and alkyl hydrogens with areas in the ratio 1:5:2. No absorption due to vinyl hydrogen was observed. The evidence accords with the structure 4,4-dichloro-3-phenyl-3-butenoic acid. An attempt was made to ozonize this acid by the same procedure used for VIII and XVI; however, only starting material could be isolated from the reaction mixture.

Reaction of VI with Aqueous Sodium Hydroxide.—The 4-fluoroketone VI (2.5 g.) was heated with 1.5 *M* sodium hydroxide solution using the procedure described for V, except that the time of heating was reduced to 5 min. The product was isolated as before, and recrystallization from ligroin gave 4-fluoro-3-phenyl-3-butenoic acid (XVII) as white needles, m.p. 64.2–65.4°, in 33% yield.

Anal. Calcd. for $C_{10}H_9O_2F$: C, 66.66; H, 5.03. Found: 66.72; H, 5.12.

The infrared spectrum of XVII had absorptions at 3–4 and 5.83 μ (carboxyl group) and 6.00 μ (carbon–carbon double bond). The ultraviolet absorption spectrum (Table II) indicates that the double bond is not conjugated with the carboxyl group. The n.m.r. spectrum showed four peaks of areas approximately in the ratio 1:5:1:2 and in the proper positions to be ascribed respectively to carboxyl, phenyl, vinyl and alkyl hydrogens. The structure of XVII was therefore assigned as 4-fluoro-3-phenyl-3-butenoic acid.

Reaction of VI with Acetic Acid.—A solution of 4.4 g. of VI in 50 ml. of acetic acid was heated at reflux for 19 hr., and the product was hydrolyzed and isolated as described above for V. Recrystallization from ligroin yielded 1.4 g. (29%) of α-fluoro-β-methylcinnamic acid (XIII) as white plates, m.p. 129.0–130.2°.

Anal. Calcd. for $C_{10}H_9O_2F$: C, 66.66; H, 5.03. Found: C, 66.69; H, 5.08.

The ultraviolet spectrum of XIII (Table II) is similar to that of β-methylcinnamic acid. The infrared spectrum showed an absorption at 5.88 μ which corresponds to the carbonyl group of an α,β-unsaturated carboxylic acid. The n.m.r. spectrum of XIII possessed three proton absorptions in the weights 5:3:1, identified from their positions as the phenyl, methyl and carboxyl proton resonances, respectively.

A solution of XIII (0.5 g.) in 25 ml. of ethyl acetate was treated with an excess of ozone at 0°. After removal of the solvent, 25 ml. of hot water was added to the residual oil. The mixture was heated on a steam-cone for 1 hr., then cooled and extracted with ether. The ether extracts were washed with sodium bicarbonate solution, dried over magnesium sulfate, and the solvent evaporated. The oily residue was converted to a 2,4-dinitrophenylhydrazone which, after recrystallization from ethyl acetate, gave material of m.p. 248–249°. The m.p. of this material was not depressed on admixture with an authentic sample of acetophenone 2,4-dinitrophenylhydrazone, m.p. 248.4–249.2°.

Reactions Involving Deuterated Reagents.—The reaction of I with deuterioacetic acid has been described elsewhere.[3] The reactions of I and V with deuterium oxide–sodium deuteroxide were carried out by the methods used in the reactions of I[2] and V with aqueous sodium hydroxide. The acids III and XVI were tested for deuterium exchange by heating them in deuterium oxide–sodium deuteroxide under the conditions of the ring-opening reactions by which they were prepared.

The reaction of 2,4-dichloro-3-phenylcyclobutenone-2-^{2}H[5] with aqueous sodium hydroxide was carried out as described previously for the undeuterated ketone.[2]

The deuterated positions in the resulting carboxylic acids were established with the aid of n.m.r. spectra.

PASADENA, CALIF.

[CONTRIBUTION FROM THE INSTITUTE OF ORGANIC CHEMISTRY, THE UNIVERSITY OF CHICAGO]

A New Method for the Epoxidation of α,β-Unsaturated Ketones

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t-Butyl hydroperoxide reacts with α,β-unsaturated ketones in benzene solution in the presence of a few mole per cent. of Triton-B to form the corresponding epoxides. By this method mesityl oxide, methyl vinyl ketone, methyl isopropenyl ketone, cyclohexenone and chalcone were converted to their epoxides. The steric requirements of this epoxidizing agent were indicated by its failure to react with isophorone and 4-cholesten-3-one. This selectivity was demonstrated by the conversion in high yield of 16-dehydroprogesterone to 16α,17α-epoxy-4-pregnen-3,20-dione. Alternately, the base-catalyzed reaction of *t*-butyl hydroperoxide with acrylonitrile or with methyl acrylate leads to the Michael addition product.

Introduction.—Although the thermal, free radical and acid-catalyzed reactions of hydroperoxides have been studied by several groups,[1] the base-catalyzed reactions have received relatively little attention. Kharasch[2] studied the decomposition of tertiary hydroperoxides in alkaline media and suggested the interaction of a hydroperoxide anion with a neutral hydroperoxide molecule to explain the products. The alkaline decomposition of secondary and primary hydroperoxides has been discussed by Kornblum,[3] who suggested a mechanism in which the removal of a hydrogen atom alpha to the hydroperoxy group occurs as the first step.

The Michael addition of hydroperoxides to olefins bearing a *meta*-directing group attached to one of the doubly-bound carbon atoms has been reported in the patent literature.[4] However, since the products described in this disclosure seemed to be inadequately characterized, and since the Michael reaction appeared to be a promising route to substituted peroxides which might themselves

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[1] For recent discussion and references, see: (a) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957; (b) A. V. Tobolsky and R. B. Mesrobian, "Organic Peroxides," Interscience Publishers, Inc., New York, N. Y., 1954.

[2] M. S. Kharasch, A. Fono, W. Nudenberg and B. Bischof, *J. Org. Chem.*, **17**, 207 (1952).

[3] N. Kornblum and H. E. De La Mare, THIS JOURNAL, **73**, 880 (1951).

[4] D. Harman, U. S. Patent 2,508,256.