nism for all ketene cycloadditions is probably not likely but rather the process is dependent upon the substrates involved.

Experimental Section

Diphenylketene was prepared by the dehydrochlorination of diphenylacetyl chloride with triethylamine.[11,12] The ketene was vacuum distilled prior to each kinetic run. Benzene, heptane, cumene, and THF were distilled from lithium aluminum hydride under a nitrogen atmosphere through a 30-plate Oldershaw column.

Apparatus.—A constant-temperature water bath was heated with an immersion heating element coupled to a Fisher proportional temperature controller that afforded a temperature control of ±0.02°. The rate of disappearance of dihydropyran was followed by vpc. An Aerograph AP-40 operating with a thermal conductivity detector was used with 10 ft × 0.25 in. columns packed with 15% Ucon and 2% Oronite on 30–60 mesh white Chromosorb. An oven temperature of 95° was employed. *n*-Heptane was used as an internal standard. Least-squares rate constants and activation parameters were calculated on an IBM 1620 computer.

Cycloaddition in Cumene.—To a solution of 4.57 g (0.0645 mole) of dihydropyran, 12 ml of cumene, and 2.5 ml of *n*-heptane, 3.77 g (0.0195 mole) of diphenylketene was added. The reaction was undisturbed for 24 hr. Obtained was 5.0 g of 8,8-diphenyl-2-oxabicyclo[4.0.2]octan-7-one which corresponds to a 93% yield, mp 154–156° (lit.[3] mp 154–155°). The nmr spectrum (Varian A-60) in $CDCl_3$ with internal TMS standard showed the following: multiplet at 7.75 (aromatic protons), doublet centered at 5.25 (methinyl hydrogen adjacent to ether linkage), multiplet centered at 3.95 (methinyl hydrogen adjacent to carbonyl), a multiplet centered at 3.5 (methylene adjacent to ether linkage), and a multiplet centered at 1.6 ppm (remaining two methylenes). These protons were in the ratio 10:1:1:2:4.

Solvent Effects.—The solvents employed in this study were DMF, *n*-butyronitrile, THF, and toluene. All of the solvents were refluxed and distilled from lithium aluminum hydride under a nitrogen atmosphere through a 30-plate Oldershaw column. The description of a typical run follows. A solution of 4.56 g (0.0545 mole) of dihydropyran, 2.5 ml of *n*-heptane, and 12.5 ml of dry tetrahydrofuran was placed in a 30-ml reaction vessel equipped with a rubber septum. The vessel was placed in a constant-temperature bath at 40 ± 0.02° and the contents were allowed to equilibrate. A 5.68-g (0.0293 mole) portion of diphenylketene was then added through a hypodermic syringe and the rate of disappearance of dihydropyran was followed by vpc.

Registry No.—Diphenylketene, 525-06-4; dihydropyran, 110-87-2.

Acknowledgment.—This work was supported by a Faculty Research Grant, North Texas State University.

(11) H. Staudinger, *Ber.*, **44**, 1619 (1911).

(12) In a private communication, Dr. J. C. Martin (Tennessee Eastman Co., Kingsport, Tenn.) suggested a modified procedure which employs benzene as a solvent. This was found to definitely be an improvement for obtaining pure diphenylketene.

The Anodic Oxidation of 3,3-Diphenylacrylic Acid and Diphenylacetylene

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Received October 4, 1966

The anodic oxidation of 3,3-diphenylacrylic acid in acetic acid at a carbon anode yields without rearrangement 4-phenylcoumarin, 2,2-diphenylvinyl acetate, and diphenylacetaldehyde, and with rearrangement benzil and related compounds which are also obtained from diphenylacetylene. A mechanism is proposed which involves the oxidation–rearrangement sequence 2,2-diphenylvinyl radical → 2,2-diphenylvinylcarbonium ion → 1,2-diphenylvinylcarbonium ion. Anodic oxidation of diphenylacetylene under the same conditions yields mainly benzoin acetate and a keto diacetate which is readily hydrolyzed or pyrolyzed to benzil.

We have reported previously[1] on the anodic oxidation of aliphatic carboxylic acids at carbon anodes. Olefins and esters were obtained *via* carbonium ion intermediates. The products were similar to those obtained by diazotization of the corresponding amines, also a carbonium ion process. Now we wish to report a similar study of an α,β-unsaturated acid, 3,3-diphenylacrylic acid. Again, data from the diazotization of the corresponding amine are available for comparison.

Diazotization of 2,2-diphenylvinylamine with nitrosyl chloride yielded diphenylacetylene and *cis*- and *trans*-α-chlorostilbene. These products were explained by means of a phenyl migration in a vinylcarbonium ion.[2] With isoamyl nitrite as the diazotizing agent, the only product was diphenylacetylene.

We expected diphenylacetylene from the electrolytic oxidation of 3,3-diphenylacrylic acid by an oxidation sequence analogous to that of the aliphatic acids. Because aromatic[3] and olefinic[4] hydrocarbons are acetoxylated under the electrolysis conditions used, the acetoxylation of diphenylacetylene was also studied.

(1) W. J. Koehl, Jr., *J. Am. Chem. Soc.*, **86**, 4686 (1964).

(2) D. Y. Curtin, J. A. Kampmeier, and B. R. O'Connor, *ibid.*, **87**, 863 (1965).

(3) S. D. Ross, M. Finkelstein, and R. C. Peterson, *ibid.*, **86**, 4139 (1964).

(4) F. D. Mango and W. A. Bonner, *J. Org. Chem.*, **29**, 1367 (1964).

Results

The principal products of the anodic oxidation of 3,3-diphenylacrylic acid are summarized in Table I, and those of diphenylacetylene and related compounds are listed in Table II. Carbon anodes were used in all experiments; acetic acid was the usual solvent. None of the expected diphenylacetylene was detected among the products of 3,3-diphenylacrylic acid, but compounds which are derived from diphenylacetylene under the same conditions were found.

Benzoin and benzoin acetate are primary products of the electrochemical reactions of both diphenylacetylene and the acid; that is, they are observed spectroscopically in the product mixture obtained by dilution of the electrolyte with water. Benzil is a secondary product. It is not detected spectroscopically in this mixture, but is readily formed from some component of it by hydrolysis or by pyrolysis on the gas chromatograph. In this discussion the term benzil is used to include any compounds which are detected as benzil on the gas chromatograph.

A sample of a benzil precursor was isolated by column chromatography from a diphenylacetylene product mixture. Of the acetates and keto acetates derivable from diphenylacetylene, the elemental analysis of

TABLE I

PRODUCTS OF 3,3-DIPHENYLACRYLIC ACID

Solvent	HOAc + H_2O	HOAc + Ac_2O	CH_3OH[a]	HOAc[b] + H_2O
Electricity[c]	6.4	2.4	2.2	6.8
Products[d]				
1,1-Diphenylpropene	2	15	...	Trace
Benzophenone	18	4	4	13
Diphenylacetaldehyde	8			9
Diphenylacetylene	...	...	...	9
Deoxybenzoin	2	5	...	2
Benzil	21	23	4	31
2,2-Diphenylvinyl acetate	3	3		
Benzoin	Trace	...	...	2
Benzoin acetate	17	3	...	17
4-Phenylcoumarin[e]	24	35	58	19

[a] Unlisted products: methyl 3,3-diphenylacrylate, 4%; unidentified, 30%. [b] 3,3-Diphenylacrylic acid + diphenylacetylene. [c] Total quantity passed in faradays per mole of 3,3-diphenylacrylic acid. [d] Per cent gas chromatographic peak area. [e] Includes an acetate derived from 4-phenylcoumarin.

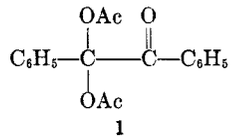
TABLE II

PRODUCTS OF DIPHENYLACETYLENE AND RELATED COMPOUNDS

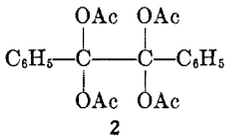
Reactant	Diphenylacetylene	Stilbenediol diacetate	Benzoin	Benzil
Electricity[a]	10[b]	4.0	10	2.7	2.7
Products[c]					
Benzaldehyde	...	...	...	21	9
Diphenylacetylene	68	67	...	...	...
Deoxybenzoin	...	...	...	5	Trace
Benzil	20	28	13	3	12
Benzoin	3	...	...	40	49
Benzoin acetate	9	4	19	28	25
α,α'-Stilbenediol diacetate	Trace	Trace	54	...	...

[a] Total quantity passed in faradays per mole of reactant. [b] This reaction in acetic acid containing water; all others in anhydrous acid. [c] Per cent gas chromatographic peak area.

this sample fits the keto diacetate **1** most closely. The infrared spectrum of the sample supports this assignment. The band at 1715 cm^{-1} is consistent with an α-substituted aryl ketone, and the 1770-cm^{-1} band is in reasonable agreement with the 1761-cm^{-1} carbonyl band of the geminal diacetate, 1,1-diacetoxypropane.[5] The purity of this sample of the benzil precursor has not been ascertained. It may also contain some tetraacetate (**2**). Although neither of these compounds



1

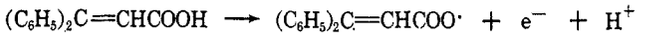


2

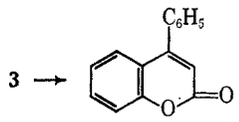
has been described in the literature, similar unstable acetates have been reported as products of the reaction of lead tetraacetate with a variety of acetylenic compounds.[6]

Discussion

3,3-Diphenylacrylic Acid.—The anodic oxidation of this acid commences in the usual Kolbe manner and has as its first intermediate the carboxy radical **3**.



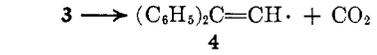
3



Evidence for this radical is the cyclization product, 4-phenylcoumarin (Table I). The cyclization has a precedent in the electrochemical formation of 4-phenyl-3,4-dihydrocoumarin from 3,3-diphenylpropanoic acid[7] and in the formation of 3,4-dimethylcoumarin by thermal decomposition of *t*-butyl *cis*-α,β-dimethylpercinnamate.[8] However, no phenyl 3-phenylcinnamate or phenyl phenylpropiolate, possible products of a 1,4-phenyl migration were detected as they were from 3,3-diphenylpropanoic acid.[7]

Under the reaction conditions 4-phenylcoumarin is acetoxylated to a small extent, but it is not converted to any of the other products listed in Table I.

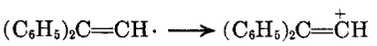
The carboxy radical (**3**) also undergoes decarboxylation to the vinyl radical (**4**). Evidence for this radical



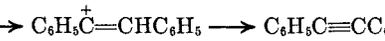
4

is the presence of 1,1-diphenylpropene, a sizable product in anhydrous acetic acid. This probably results from coupling of radical **4** with methyl radical produced by the concurrent Kolbe electrolysis of acetic acid.

2,2-Diphenylvinyl radical (**4**) can logically lose one electron in an anodic reaction to form 2,2-diphenylvinylcarbonium ion (**5**). There is precedence for rearrangement of this to 1,2-diphenylvinylcarbonium ion (**6**) and diphenylacetylene.[2] Although no diphenylacetylene has been found, the presence of benzil, benzoin, and benzoin acetate, which are formed from



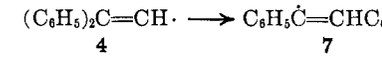
4 **5**



6

diphenylacetylene under the same reaction conditions, is taken as evidence that diphenylacetylene or the closely related species (**6**) has been formed *via* the expected phenyl shift.

Alternatively the carbonium ion (**6**) could result from a phenyl migration in the radical (**4**) followed by oxida-



4 **7**

tion of the rearranged radical (**7**) to **6**. Although such phenyl shifts are well known in alkyl radicals,[9] they have not been reported in vinyl radicals. The rearranged vinyl radical (**7**), like the unrearranged radical (**4**), should couple with a methyl radical to form 1,2-diphenylpropene. Its absence argues against a phenyl shift in the vinyl radical (**4**).

Furthermore the products in Table I provide evidence for the existence of 2,2-diphenylvinylcarbonium ion (**5**).

(5) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1958.

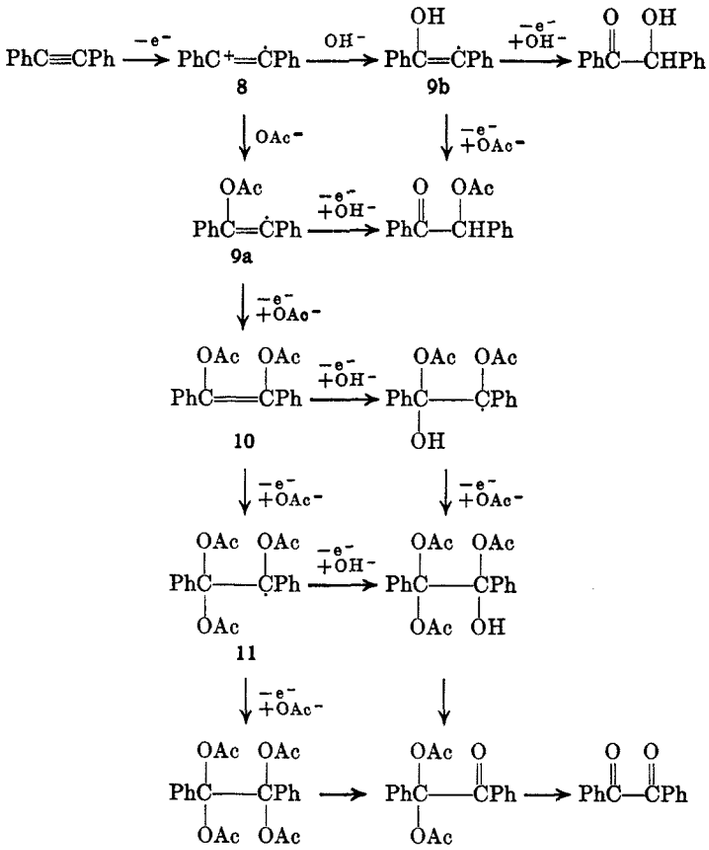
(6) J. Jadot and M. Neuray, *Bull. Soc. Roy. Sci. Liege*, **30**, 34, 52, 431 (1961); **31**, 247 (1962).

(7) W. A. Bonner and F. D. Mango, *J. Org. Chem.*, **29**, 430 (1964).

(8) J. A. Kampmeier and R. M. Fantazier, *J. Am. Chem. Soc.*, **88**, 1959 (1966).

(9) *E.g.*, in the decarbonylation of 3-arylaldehydes: D. Y. Curtin, and M. J. Hurwitz, *ibid.*, **74**, 5381 (1952).

SCHEME I



This ion could combine with acetate ion to form 2,2-diphenylvinyl acetate or with hydroxide ion to form diphenylacetaldehyde. Both of these compounds have been detected among the products.

One remaining product in Table I is benzophenone. Diphenylacetaldehyde is reported[10] to be oxidized by air to benzophenone, and indeed when it is exposed to air in the electrolyte solution, benzophenone is formed. When 2,2-diphenylvinyl acetate is subjected to the electrochemical oxidation in aqueous acetic acid, both benzophenone and diphenylacetaldehyde are formed.

Table I shows that the proportion of 4-phenylcoumarin in the products is about twice as large when the reaction solvent is methanol as when it is acetic acid. Hence solvent plays an important role in determining the relative rates of cyclization and decarboxylation of the carboxy radical (**3**), possibly in a complex in which acetic acid promotes a concerted decarboxylation and phenyl migration.

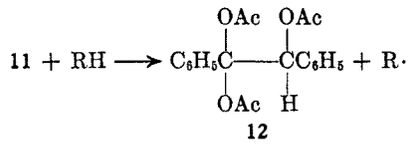
Diphenylacetylene.—The experimental evidence and mechanistic rationale above take the anodic reaction of 3,3-diphenylacrylic acid by sequential intermediates **4** and **5** to **6**. The 1,2-diphenylvinylcarbonium ion (**6**) is a logical precursor for diphenylacetylene, which is not found, and benzil, benzoin acetate, etc., which are. Because diphenylacetylene is found in the related diazonium reaction,[2] is relatively unstable under the experimental conditions and gives the types of products formed, its anodic reactions were also studied.

The products of diphenylacetylene (Table II) can be explained by Scheme I. Diphenylacetylene is shown as being oxidized in a one-electron-transfer process to a radical cation (**8**). The electrophilic species (**8**) combines with a nucleophile such as acetate or hydroxide ion. The resulting vinyl radical (**9**) suffers the loss of another electron, and a nucleophile then reacts with the cationic species produced. An unsaturated compound results, which if it has a free hydroxyl group undergoes an enol–keto transformation and yields benzoin or benzoin acetate. Both have been found. Benzoin acetate is neither oxidized further nor hydrolyzed in control experiments under the acetoxylation conditions. Benzoin can make only a small contribution to the final product, benzil, since as shown in Table I, very little benzil is formed from benzoin under the reaction conditions. Therefore, at this stage of the oxidation α,α'-stilbenediol diacetate (**10**) is the only compound capable of being oxidized further to benzil. The description of the reaction sequence in Scheme I in terms of discrete steps and simple intermediates is not meant to preclude concerted processes or reactions of complexes, nor is the writing of radical cations (*e.g.*, **8**) meant to preclude dications analogous to those proposed in the anodic acetoxylation of aromatic hydrocarbons and olefins.[11]

Which nucleophile reacts with the various cationic species in Scheme I depends on the water concentration of the reaction medium. Thus, benzoin is found only in the aqueous runs. However, benzoin acetate is found under both aqueous and anhydrous conditions. A reaction path not involving water must also be available for its formation. Hydrogen abstraction by the triacetate radical (**11**) may provide the additional path. The triacetate (**12**) would then be converted to benzoin acetate either in the reaction medium or in the work-up and analysis.

(10) J. W. Huffman and R. P. Elliott, *Chem. Ind.* (London), 650 (1963).

(11) L. Eberson and K. Nyberg, *J. Am. Chem. Soc.*, **88**, 1686 (1966).



12

Stilbenediol diacetate (**10**) is shown in Scheme I as the key intermediate on the path leading to benzil; yet only traces of the diacetate are found in the products. The pure diacetate under the same conditions as diphenylacetylene is converted to the same products, but at about one-third the rate of diphenylacetylene. Thus it seems that the diacetate should accumulate as a product if it is formed at all. This paradox may be explained by competition among the reactants for adsorption on the anode as well as competition among the oxidation reactions of the adsorbed species.

A mechanism for the acetoxylation of diphenylacetylene can be written which involves direct attack of an acetoxy radical on diphenylacetylene, but this seems unlikely for two reasons: (1) the lifetime of the acetoxy radical is estimated to be too short for reaction outside the solvent cage in which it is formed,[12] and (2) in the anodic acetoxylation of aromatic hydrocarbons and olefins, oxidation of the unsaturated substrate to a cationic species followed by reaction of this with acetate has been demonstrated.[11]

Finally, when a mixture of diphenylacetylene and 3,3-diphenylacrylic acid was electrolyzed, diphenylacetylene was consumed about three times as fast as the acid. The proportion of products derivable from diphenylacetylene increased somewhat, and that of 4-phenylcoumarin decreased (Table I). This experiment does not establish diphenylacetylene as an intermediate, but it may explain why none is detected.

Benzoin and benzil were also examined independently under the acetoxylation conditions. Benzoin is partially acetylated to benzoin acetate in a nonelectrochemical reaction. Some reduction to deoxybenzoin occurs, and quite a lot of benzaldehyde is formed. Benzil is reduced, presumably at the cathode, to benzoin from which the additional products are derived.[13] The absence of benzaldehyde in the diphenylacetylene products is a further indication that there is not much free benzoin or benzil present. The benzaldehyde forming reaction has not been studied.

Experimental Section

Apparatus.—The electrochemical cell consisted of a cylindrical vessel 5 cm in diameter and 15 cm in height fitted with a reflux condenser, a thermometer, and a magnetic stirrer. The cathode was a platinum gauze cylinder 3.5 cm in diameter and 5 cm in height. The anode was a 0.25-in. diameter carbon rod mounted on the axis of the cathode cylinder. The area of the working surface of the anode was approximately 11 cm. The anodes were National Carbon Co. graphite AGKSP spectroscopic electrodes. They were used with no pretreatment.

Materials.—All the chemicals used were commercially available materials except the following compounds which were prepared. 3,3-Diphenylacrylic acid was prepared from 1,1-diphenylethylene and oxalyl chloride;[14a] it has mp 161–162°[14b] (lit.[14a] mp 167°). 4-Phenylcoumarin was prepared from 1-*o*-methoxyphenyl-1-phenylethylene and oxalyl chloride.[14a] Benzoin acetate was prepared by acetylation of benzoin[15] and α,α'-stilbenediol diacetate was prepared by reductive acetylation of benzil.[16] 1,1-Diphenylpropene was prepared *via* a Grignard reaction[17] and 1,2-diphenylpropene was obtained by a modification of the preceeding method using benzylmagnesium chloride[18] and acetophenone. 2,2-Diphenylvinyl acetate was prepared from diphenylacetaldehyde and acetic anhydride.[19]

Electrolysis of Diphenylacetylene.—In a typical experiment diphenylacetylene (4.9 g, 0.028 mole), anhydrous sodium acetate (15 g), acetic acid (100 ml), and water (40 ml) were charged to the cell. The electrolysis was run for 18.5 hr with a constant current of 0.40 amp (0.036 amp/cm^2, 0.28 faraday) as the applied voltage was increased from 5.0 to 14.3 v and the temperature was increased from 25 to 44°. The reaction mixture was diluted with water (500 ml) and extracted with ether. A very viscous, orange product mixture (5.5 g) was obtained.

For reactions in an anhydrous medium the mixture consisted of diphenylacetylene (4.9 g), potassium acetate (20 g), acetic acid (80 ml), and acetic anhydride (40 ml). In a typical run an applied voltage of 10.2 to 13.4 v maintained a constant current of 0.50 amp (0.045 amp/cm^2, 0.12 faraday) at 24 to 26° for 6.5 hr. Electrolyses were also run with benzoin (5.0 g), benzil (5.0 g), benzoin acetate (2.8 g), and α,α'-stilbenediol diacetate (0.55 g), under conditions otherwise identical with those for diphenylacetylene in anhydrous solution.

Gas chromatographic analyses of the product mixtures from these reactions are summarized in Table II, with the exception of the benzoin acetate run from which benzoin acetate was recovered unchanged. The analyses were obtained on a programmed-temperature gas chromatograph using columns of 20% silicone rubber SE-30 on 60–80 Diatoport P (2 ft × 0.25 in. and 10 ft × 0.25 in.) and 10% Carbowax 20 M on 60–80 Chromosorb W (2 ft × 0.25 in.). Product identities were established by comparing retention times with those of authentic samples both separately and in mixtures on both kinds of columns.

Identities were confirmed by isolation of the compounds whenever possible. Benzoin acetate was isolated by gas chromatography. Its infrared spectrum was identical with that of an authentic sample. It could be detected in the infrared spectrum of the mixture when its concentration was high enough. Benzoin was isolated by gas chromatography from several product mixtures and by crystallization from one in which its concentration was quite high. Its identity was confirmed by its infrared spectrum.

Benzil was isolated by gas chromatography and identified by its infrared spectrum, but it could not be detected in the infrared spectrum of the product mixture. After the product mixture (1.0 g) was boiled for 20 min in 95% ethanol (10 ml) containing a few drops of hydrochloric acid, benzil was detected in the infrared spectrum. It was isolated by gas chromatography and crystallization. A sample of the benzil precursor was obtained by chromatography of the mixture on silica gel. It was eluted with methanol after other components had been eluted with benzene and chloroform. This sample had the infrared spectrum predicted by subtraction of the spectra of the identified components from that of the mixture. It yielded benzil under the same conditions as the mixture, and was hydrolyzed even on standing in the air. Its infrared spectrum had bands in the carbonyl region at 1715 and 1770 cm^{-1} determined on a Perkin-Elmer Model 237 infrared spectrophotometer. Further purification of the sample was not attempted because of its hydrolytic instability.

Anal. Calcd for $C_{18}H_{16}O_5$ (1): C, 69.3; H, 5.1. Found: C, 68.8; H, 5.5.

There were some unidentified minor components (less than 1%) in the product mixture. 1,2-Diphenylpropene was sought by gas chromatography but was not detected.

3,3-Diphenylacrylic Acid Electrolyses.—In a typical experiment a mixture of 3,3-diphenylacrylic acid (11.2 g, 0.05 mole),

(12) L. Herk, M. Feld, and M. Swarc, *J. Am. Chem. Soc.*, **83**, 2998 (1961).

(13) These cathodic reductions could have been prevented by using a divided cell. However these were the only reductions detected, and their contribution to the products of the reactions of 3,3-diphenylacrylic acid and diphenylacetylene was small. Therefore, it did not seem desirable to sacrifice the experimental simplicity of the single-compartment cell.

(14) (a) F. Bergmann, M. Weizmann, E. Dimant, J. Patai, and J. Szmuskuowicz, *J. Am. Chem. Soc.*, **70**, 1612 (1948); (b) melting points are uncorrected.

(15) N. Zinin, *Ann.*, **104**, 120 (1857).

(16) L. F. Fieser, "Experiments in Organic Chemistry," 3rd ed, D. C. Heath and Co., Boston, Mass., 1957, p 177.

(17) M. S. Kharasch and D. C. Sayles, *J. Am. Chem. Soc.*, **64**, 2972 (1942).

(18) F. S. Prout, R. J. Hartman, E. P.-Y. Huang, C. J. Korpics, and G. R. Tichelaar, "Organic Syntheses," Coll. Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1963, p 94.

(19) N. M. Micovic, M. M. Rogic, and M. F. Mihailovic, *Tetrahedron*, **1**, 340 (1957).

anhydrous sodium acetate (15 g), acetic acid (100 ml), and water (40 ml) was electrolyzed for 17 hr. The current was held at 0.50 amp (0.045 amp/cm², 0.32 faraday) by an applied voltage of 5.0 to 24.7 v. The temperature was held at 20 to 28°. The neutral product mixture (1.65 g) was a very viscous, orange liquid. For runs in anhydrous solution the acid (8.0 g), potassium acetate (20 g), acetic acid (80 ml), and acetic anhydride (40 ml) were used. The neutral product amounted to 4.8 g. A reaction in the absence of acetate was run with 3,3-diphenylacrylic acid (11.2 g, 0.05 mole), potassium hydroxide (1.3 g, 0.02 mole), methanol (110 ml), and water (15 ml). An applied voltage of 10 to 21 v was needed to maintain a current of 0.50 amp (0.045 amp/cm², 0.10 faraday) for 5.4 hr. The temperature increased from 30 to 56°. The neutral product amounted to 6.6 g. An electrolysis was also run with both diphenylacetylene (0.66 g) and 3,3-diphenylacrylic acid (9.0 g) under conditions otherwise identical with those of the run in acetic acid plus water, and 2.6 g of neutral product was obtained. Quantitative gas chromatographic analysis showed that only 12% of the diphenylacetylene remained in the product mixture. 2,2-Diphenylvinyl acetate (5.0 g) was electrolyzed under the same conditions.

Product distributions from typical expriments are summarized in Table I. These data were obtained in the same way as those in Table II. 1,1-Diphenylpropene and benzophenone were isolated by gas chromatography and identified by their infrared spectra. The benzophenone carbonyl band was detected in the infrared spectra of some of the mixtures. Benzil was isolated by gas chromatography and by the same hydrolysis procedure as in the case of diphenylacetylene, but it could not be detected in the infrared spectra of the mixtures. The benzil precursor obtained from diphenylacetylene was evident in the infrared spectra of the product mixtures obtained from 3,3-diphenylacrylic acid in acetic acid, but not in those from methanol. Benzoin acetate was isolated by gas chromatography and its identity was confirmed by its infrared spectrum. It was also detected in the infrared spectra of some of the mixtures. Both diphenylacetaldehyde and 2,2-diphenylvinylacetate were isolated by gas chromatography and identified by infrared spectra.

4-Phenylcoumarin was isolated by crystallization and by gas chromatography its identity being confirmed by comparison of its melting point (90–91°) and its infrared spectrum with those of an authentic sample.[13] Furthermore its mass spectrum agreed with the published spectrum.[20] The 4-phenylcoumarin value in Table II is a composite value for 4-phenylcoumarin and a compound which was also obtained when pure 4-phenylcoumarin was subjected to the same electrolysis conditions. This derivative has a band in the carbonyl region at 1775 and a band at 1210 cm^{-1}. These bands are consistent with an aryl acetate[5] structure. This 4-phenylcoumarin derivative was not detected when the electrolysis was carried out in methanol. No diphenylacetylene derivatives were obtained from 4-phenylcoumarin.

In addition to the products listed in Table I there were the following. Methyl 3,3-diphenylacrylate (3%) was found among the products of the run in methanol. 1,1-Diphenylethylene (<3%) was obtained from some runs. Stilbene may have been a product in methanol and 1,2-diphenylpropene may also have been a product in anhydrous acetic acid, but in each case the peak corresponding to these compounds was too small for conclusive identification by gas chromatography. There were some other unidentified minor products.

Registry No.—3,3-Diphenylacrylic acid, 606-84-8; diphenylacetylene, 501-65-5; α,α'-stilbenediol diacetate, 6316-81-0; benzoin, 119-53-9; benzil, 134-81-6.

Acknowledgment.—Valuable discussions with Dr. R. D. Offenhauer and the technical assistance of Mr. C. R. Manzoni are gratefully acknowledged.

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Effects of Solvents on the Reactions of Trichloromethanesulfinyl Radicals

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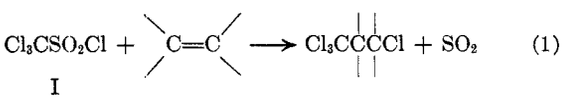
Received September 27, 1966

The relative rate of free-radical addition with respect to the rate of allylic halogenation of cyclohexene by trichloromethanesulfonyl chloride (Cl_3CSO_2Cl) suggests that trichloromethanesulfinyl radicals ($Cl_3CSO_2\cdot$) are complexed by alkenes. A reaction of the complexed radical with another molecule of the alkene is responsible for the addition of the trichloromethyl moiety to the alkene. Effective complexing of the trichloromethanesulfinyl radical by chlorobenzene, *t*-butylbenzene, and pyridine was also found. Competitive chlorinations of cyclohexane and toluene in the presence of pyridine show that only noncomplexed trichloromethanesulfinyl radicals are involved in hydrogen-abstraction reactions.

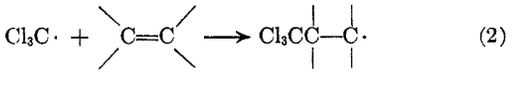
The free-radical reactions of trichloromethanesulfonyl chloride (I) with alkenes yield sulfur dioxide and addition products the same as those obtained from the free-radical addition of carbon tetrachloride to alkenes.[1] The formation of such addition products has led to the suggestion that the mechanism for this



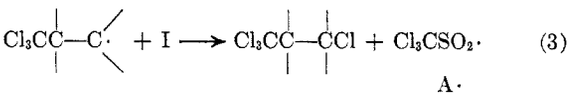
$$Cl_3CSO_2Cl + \text{>C=C<} \longrightarrow Cl_3CC\text{-}C\text{-}Cl + SO_2 \qquad (1)$$

I

reaction involves addition to the alkene of a trichloromethyl radical which is produced in the decomposition of the trichloromethanesulfinyl radical (A·) formed in the chain sequence shown in eq 2–4.[2] Free-radical



$$Cl_3C\cdot + \text{>C=C<} \longrightarrow Cl_3CC\text{-}C\cdot \qquad (2)$$

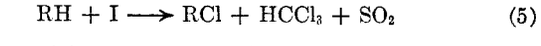


$$Cl_3CC\text{-}C\cdot + I \longrightarrow Cl_3CC\text{-}CCl + Cl_3CSO_2\cdot \qquad (3)$$

A·

$$A\cdot \longrightarrow Cl_3C\cdot + SO_2 \qquad (4)$$

reactions of Cl_3CSO_2Cl with alkanes yield halogenated alkanes, chloroform, and sulfur dioxide.[3] Investigations of this reaction showed that $Cl_3C\cdot$ was not the hydrogen-abstracting radical in the chain sequence



$$RH + I \longrightarrow RCl + HCCl_3 + SO_2 \qquad (5)$$

since competition reactions of various alkanes toward chlorination by I showed that I involved a more reactive hydrogen-abstracting radical than $Cl_3C\cdot$,[3b,c] the hydrogen atom abstracting species involved in halogenations of alkanes with $BrCCl_3$.[4] A chain sequence

(1) E. C. Ladd and L. Y. Kiley, U. S. Patent 2,606,213 (1952).

(2) H. Goldwhite, M. S. Gibson, and C. Harris, *Tetrahedron*, **30**, 1613 (1964).

(3) (a) E. S. Huyser, *J. Am. Chem. Soc.*, **82**, 5246 (1960); (b) E. S. Huyser and B. Giddings, *J. Org. Chem.*, **27**, 3391 (1962); (c) E. S. Huyser H. Schimke, and R. L. Burham, *ibid.*, **28**, 2141 (1963).

(4) E. C. Kooyman and G. C. Vegter, *Tetrahedron*, **4**, 382 (1958); E. S. Huyser, *J. Am. Chem. Soc.*, **82**, 391 (1960); G. A. Russell, C. DeBoer, and K. M. Desmond, *ibid.*, **85**, 365 (1963).