the reported m.p. of the substance prepared by chlorosulfonation of ethyl N-phenylcarbamate is 103°.[13] A mixed m.p. of the products prepared by the two methods showed no depression.

When a reaction mixture of ethyl N-phenylcarbamate and 15% oleum was heated to higher temperatures than previously, evolution of carbon dioxide started at 75° and became vigorous at 90°. Sulfanilic acid precipitated when the reaction mixture was poured on ice.

NEW YORK, N. Y.

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(13) R. Adams, P. H. Long and A. J. Johanson, THIS JOURNAL, **61**, 2342 (1939).

[CONTRIBUTION NO. 109 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TENNESSEE]

Reactions of Carboxylic Acids in Sulfuric Acid

BY CLARK M. WELCH AND HILTON A. SMITH

RECEIVED SEPTEMBER 25, 1952

The reactions of several organic acids in sulfuric acid have been investigated. The "*i*" factors have been determined by cryoscopic methods, the evolution of carbon monoxide studied, and the carbonium ions present when the acids are dissolved in sulfuric acid have been allowed to react with various reagents. The influence of certain substituents on the stability of the carbonium ions also has been investigated.

An interesting and peculiar preparation of stable triphenylcarbonium ions is by the reaction of triphenylacetic acid with sulfuric acid. Carbon monoxide is quantitatively evolved.

$$(C_6H_5)_3COOOH + H_2SO_4 \longrightarrow (C_6H_5)_3C^+ + CO + H_3O^+ + 2HSO_4^-$$

If the deeply colored solution is subsequently poured into water, triphenylcarbinol is precipitated,[1] or if the solution is poured into an alcohol the corresponding ether is obtained.[2] The well known decomposition of formic acid in sulfuric acid is similar to this reaction.

The behavior of other carboxylic acids in 100% sulfuric acid has been studied in order to determine how generally the loss of carbon monoxide occurs in this medium. Several methods were used to determine the course of the reaction in each case. The van't Hoff *i* factors were determined cryoscopically. The principal constituent of any gas evolved was identified and the total volume determined. The organic products obtained by pouring the reaction mixture into various reagents were determined in several instances. A portion of the results appears in Table I, the remainder following in the discussion of the individual compounds.

Diarylacetic Acids.—The value of *i* that should theoretically be obtained after the loss of carbon monoxide has taken place is 4.0, since the carbon monoxide formed does not remain in the solution. The van't Hoff factors actually observed for diphenylacetic acid increased rapidly with time owing to the occurrence of sulfonation and are inconclusive. The low yield of carbon monoxide indicates that competing reactions predominated.

When the colored solution was poured into water, a 15% yield of bis-(diphenylmethyl) ether was obtained. Alternatively, when the solution was poured into glacial acetic acid and the product saponified, a 10% yield of diphenylcarbinol was obtained. These reactions are characteristic of diphenylcarbonium ions, which have been shown to be stable in 100% sulfuric acid.[3] It is clear that a reaction analogous to that of triphenylacetic acid did occur to a minor extent.

TABLE I

THE VAN'T HOFF FACTORS AND YIELDS OF CARBON MONOXIDE FROM CARBOXYLIC ACIDS IN 100% SULFURIC ACID AT 25°

Organic acid	Color of solution	i^a	t, min.	Yield of CO, %^{c}
Diphenylacetic	Yellow-orange	4.0	10^b	40
		4.9	180	
Bis-(*p*-chlorophenyl)-acetic	Orange	3.3	50	98
		3.5	100^b	
		3.7	1200	
Bis-(*p*-nitrophenyl)-acetic	Pale yellow	1.7	20	0
		2.3	1400	
Benzilic	Red	5.4	30^b	15^d
		5.8	1300	
4,4′-Dichlorobenzilic	Red	3.7	15	0
		4.8	80	
Isobutyric	Colorless	2.0	15	0
		2.0	1400	
Dicyclohexylacetic	Colorless	2.0	20	15
	Yellow	3.0	250	52
	Red-brown	6.3	900	65^e
2,4,6-Trimethylcyclohexanecarboxylic	Colorless		10	5
			130	44
	Red-brown		1100	72^e

[a] The average of several determinations. [b] The time at which gas evolution had become sufficiently slow so as not to interfere with the freezing point determinations. [c] Assuming the gas to be pure carbon monoxide (see Experimental). [d] For the most dilute solution used (0.011 *M* in benzilic acid). [e] The gas was contaminated with SO_2.

$$(C_6H_5)_2CHCOOH + H_2SO_4 \longrightarrow (C_6H_5)_2CH^+ + CO + H_3O^+ + 2HSO_4^-$$

The same reaction was probably observed by Bistrzycki and Siemiradzki,[4] who isolated bis-(diphenylmethyl) ether from the reaction of fuming sulfuric acid with diphenylacetic acid. The quantitative conversion of α,α-diarylpropionic acids to 1,1-diarylethylenes by treatment with sulfuric acid and then with water[5] undoubtedly proceeds by conversion of the acids to stable methyldiarylcarbonium ions. This type of ion reacts with water to form an olefin[6] rather than a carbinol.

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(1) A. Bistrzycki and E. Reintke, *Ber.*, **38**, 839 (1905).

(2) H. A. Smith and R. J. Smith, THIS JOURNAL, **70**, 2401 (1948).

(3) C. M. Welch and H. A. Smith, *ibid.*, **72**, 4748 (1950).

(4) A. Bistrzycki and B. v. Siemiradzki, *Ber.*, **39**, 51 (1906); **41**, 1665 (1908).

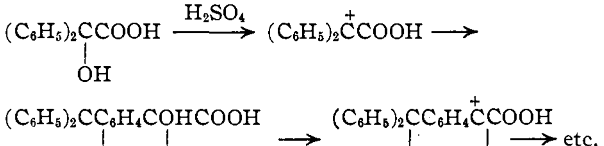
(5) A. Bistrzycki and E. Reintke, *ibid.*, **38**, 840 (1905).

(6) M. S. Newman and N. C. Deno, THIS JOURNAL, **73**, 3644 (1951).

A striking example of the carbonium ion formation is afforded by bis-(*p*-chlorophenyl)-acetic acid. The van't Hoff factor was 3.5 and the yield of carbon monoxide was nearly quantitative. Addition of the colored reaction mixture to water resulted in an 88% yield of bis-(*p*,*p*'-dichlorodiphenylmethyl) ether. Addition of the reaction mixture to acetic acid and saponification resulted in a 52% yield of bis-(*p*-chlorophenyl)-carbinol. These reactions are characteristic of stable bis-(*p*-chlorophenyl)-carbonium ions.[6]

By contrast, bis-(*p*-nitrophenyl)-acetic acid underwent no loss of carbon monoxide whatever. Its van't Hoff factor places it with di- and trichloroacetic acid[7] as a very weak proton acceptor, after allowance is made for the partial protonation of the nitro groups such as occurs in nitrobenzene.[8] The opposite effects that *p*-chloro and *p*-nitro groups have on the reaction of diphenylacetic acid in sulfuric acid are the ones that would be predicted on the basis of the resonance effects of these groups.

Benzilic Acids.—The intense and characteristic color which benzilic acids exhibit in sulfuric acid could be the result of two modes of reaction, one involving the α-hydroxyl group or one involving the carboxyl group. The observed van't Hoff factors are inconclusive owing to the occurrence of extensive sulfonation and polymerization. The yields of carbon monoxide were found to vary considerably with the proportions of benzilic acid and sulfuric acid used. In 0.011 *M* solution, the yield was 15% while in 0.44 *M* solution it rose to 39%. The same trend was observed using 96% sulfuric acid. This is in contradiction to the statement of Klinger and Standke[9] that the reaction is characterized by exactly a 50% yield of carbon monoxide. The increase in yield with increasing concentration of benzilic acid can be accounted for if the α-hydroxyl group is preferentially attacked to give a carbonium ion which initiates polymerization.



$$(C_6H_5)_2\underset{\substack{|\\ \mathrm{OH}}}{C}COOH \xrightarrow{H_2SO_4} (C_6H_5)_2\overset{+}{C}COOH \longrightarrow$$

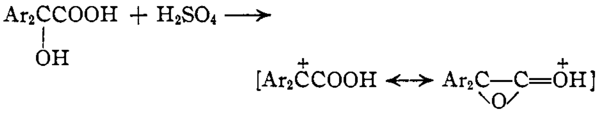
$$(C_6H_5)_2\underset{\substack{|\\ \mathrm{COOH}}}{C}C_6H_4\underset{\substack{|\\ C_6H_5}}{C}OHCOOH \longrightarrow (C_6H_5)_2\underset{\substack{|\\ \mathrm{COOH}}}{C}C_6H_4\underset{\substack{|\\ C_6H_5}}{\overset{+}{C}}COOH \longrightarrow \text{etc.}$$

The polymers thus formed would be poly-(triarylacetic) acids which would readily lose carbon monoxide to yield highly colored polymeric ions. The polymerization (and carbon monoxide evolution) would be favored by increasing concentrations of benzilic acid.

If, on the contrary, the carboxyl group of benzilic acid were preferentially attacked by the sulfuric acid, the yield of carbon monoxide should decrease slightly with increasing concentration of organic solute (and decreased strength of sulfuric acid). A slight decrease was actually observed with diphenylacetic acid.

In 4,4'-dichlorobenzilic acid, the probability of polymerization by the sulfuric acid is reduced owing to the deactivation of the benzene rings. No carbon monoxide whatever was evolved. This result is confirmation that the α-hydroxyl group is attacked. It is opposite to the effect observed in the diarylacetic acids, in which the resonance effect of the chlorine atoms facilitated the loss of carbon monoxide.

The van't Hoff factors observed for 4,4'-dichlorobenzilic acid increased rapidly with time, indicating that the highly colored solute was undergoing rapid secondary reactions. When the reaction mixture was allowed to stand just long enough to reach its most intense coloration before it was poured into water, most of the original compound could be recovered. The highly colored solute initially formed was probably a resonance hybrid of carbonium and oxonium ion structures.



$$Ar_2\underset{\substack{|\\ \mathrm{OH}}}{C}COOH + H_2SO_4 \longrightarrow [Ar_2\overset{+}{C}COOH \longleftrightarrow Ar_2C\underset{\diagdown O \diagup}{—}C{=}\overset{+}{O}H]$$

The acid-catalyzed condensation of benzilic acid with benzene derivatives to yield triarylacetic acids[10] very probably proceeds *via* the formation of such ions as the reactive intermediates.

Aliphatic Acids.—The evolution of carbon monoxide from such acids as dicyclohexylacetic acid and 2,4,6-trimethylcyclohexanecarboxylic acid when these were dissolved in 100% sulfuric acid was unexpected. Trimethylacetic acid is known to undergo this reaction at elevated temperatures[11] but is stable in 100% sulfuric acid at room temperature.[8] Isobutyric acid is also stable, its van't Hoff factor of 2.0 indicating the carboxyl group to be protonated. It is evident that branching at the β-carbon atom of the carboxylic acid is as important as branching at the α-carbon in promoting the loss of carbon monoxide. Attempts to isolate and identify the organic products of the reaction were unsuccessful.

Synthesis of 4,4'-Dichlorobenzilic Acid.—Montagne[12] has described the rearrangement of 4,4'-dichlorobenzil to 4,4'-dichlorobenzilic acid and the conversion of the crude acid to its silver salt, which can be recrystallized readily, in contrast to the crude acid. The acid obtained from the purified silver salt in this Laboratory was rather impure, probably due to a slow decomposition of the silver salt observed to occur when that compound was in solution.

Another method of synthesis was developed in which bis-(*p*-chlorophenyl)-acetic acid was converted to its acid chloride, chlorinated under irradiation and the resulting bis-(*p*-chlorophenyl)-α-chloroacetyl chloride was hydrolyzed in aqueous sodium carbonate. The acid prepared in this way was readily purified without being converted to its silver salt. The over-all yield was 48%. The starting material is available from the alkaline hydrolysis of DDT.[13] This synthesis is the first re-

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(7) *Cf.* L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 46.

(8) H. P. Treffers and L. P. Hammett, THIS JOURNAL. **59**, 1708 (1937).

(9) H. Klinger and O. Standke, *Ber.*, **22**, 1214 (1889).

(10) For examples, see A. Bistrzycki and L. Mauron, *ibid.*, **40**, 4060 (1907); A. Bistrzycki and W. Niederberger, *Helv. Chim. Acta*, **11**, 263 (1928).

(11) A. Bistrzycki and L. Mauron, *Ber.*, **40**, 4370 (1907).

(12) P. J. Montagne, *Rec. trav. chim.*, **21**, 19 (1902).

(13) O. Grummitt, A. Buck and R. Egan, *Org. Syntheses*, **26**, 21 (1946).

ported conversion of a diarylacetic acid to the corresponding benzilic acid. The intermediate bis-(*p*-chlorophenyl)-α-chloroacetyl chloride is a new compound.

Experimental

Freezing Point Measurements.—The apparatus, technique and solvent have been described elsewhere.[3] The freezing point depressions measured in duplicate runs checked within 3% of the total magnitude of the depression. Eastman Kodak Co. diphenylacetic acid was recrystallized from benzene prior to use. It then melted at 147.4–148.4°. Eastman benzilic acid was used without further purification. Eastman isobutyric acid was redistilled prior to use. Bis-(*p*-chlorophenyl)-acetic acid, m.p. 167.2–168.2°, was prepared from DDT.[13] It was recrystallized from benzene. Bis-(*p*-nitrophenyl)-acetic acid, m.p. 172.3–173.3°, with decomposition, was prepared by nitrating methyl diphenylacetate.[14] Dicyclohexylacetic acid, m.p. 139.4–140.0°, was prepared by the hydrogenation of diphenylacetic acid over Adams platinum catalyst in acetic acid.[15] It was recrystallized from ethanol-water. 2,4,6-Trimethylcyclohexanecarboxylic acid, m.p. 105.0–106.0°, was prepared by the hydrogenation of 2,4,6-trimethylbenzoic acid over Adams platinum catalyst.[16] It was recrystallized from petroleum ether. The preparation of 4,4′-dichlorobenzilic acid will be described separately. The above melting points are corrected.

Analysis of the Gases Evolved.—The gas evolved from the given compound in 100% sulfuric acid was collected and a lighted splint was introduced into the gas. If the gas was observed to burn with a visible flame, it was considered to be chiefly carbon monoxide, since other gases which could be evolved would not be combustible. This behavior was actually observed in all cases in which a gas was evolved.

The volume of gas evolved was determined in an apparatus similar to that used in the Tschugaeff–Zerewitinoff method for determining active hydrogen, the gas being collected over mercury. Check runs were made using sodium formate as the solute, since this is known to react with sulfuric acid to give quantitative yields of carbon monoxide.[17] Apparent yields of 101–102% were obtained in collecting 3.5–19.0 ml. of gas. With two of the compounds studied, sulfur dioxide was detected by its odor.

The Conversion of Diphenylacetic Acid to Bis-(diphenylmethyl) Ether.—A 1.00-g. quantity of diphenylacetic acid was added to 40 ml. of 100% sulfuric acid with stirring. After the solution had been stirred for 5 minutes, it was poured into 300 ml. of ice-water. The orange color of the solution disappeared immediately. The mixture was shaken with two 40-ml. portions of carbon tetrachloride. The combined carbon tetrachloride layers were shaken with 50 ml. of 5% aqueous sodium hydroxide, were separated and evaporated to dryness. There was obtained 0.12 g. of a solid melting at 95–104°.

The product was dissolved in methanol and the hot solution was treated with Norite A, which was found to remove an uncolored impurity. After filtration the solution was concentrated and the solid was allowed to crystallize. After an additional recrystallization, it melted at 108.9–109.4°. A mixture of this with an authentic sample of bis-(diphenylmethyl) ether[18] showed the same melting point. The authentic sample melted at 109.1–109.6°.

The Conversion of Diphenylacetic Acid to Diphenylcarbinol.—The solution prepared from diphenylacetic acid and sulfuric acid as above was poured after 5 minutes into 50 ml. of glacial acetic acid which had been cooled almost to its freezing temperature. The reaction temperature was kept below 35° during the additions of the sulfuric acid solution. The mixture was stirred and was poured into 200 ml. of water.

The aqueous mixture was shaken with 100 ml. of ether. The ether layer was washed with two 50-ml. portions of 6% aqueous sodium hydroxide, 50 ml. of ether being added prior to the second washing. The ether solution was dried over anhydrous magnesium sulfate, filtered and evaporated to dryness. There was obtained 0.15 g. of a liquid residue.

This product was treated with a solution prepared from 1 g. of sodium and 30 ml. of 95% ethanol. The mixture was refluxed for two hours. It was poured into 100 ml. of water and shaken with 50 ml. of ether. The ether layer was separated and dried over anhydrous magnesium sulfate. The solution was filtered and evaporated to dryness. The residue weighed 0.09 g. and melted at 62–64°.

The solid was dissolved in methanol. The hot solution was treated with Norite A and then filtered. The filtrate was evaporated to dryness. The product melted at 64.5–66.1°. A mixture of this with diphenylcarbinol melted at 64.9–66.1°. The known sample of diphenylcarbinol melted at 65.3–66.2°.

The Conversion of Bis-(*p*-chlorophenyl)-acetic Acid to Bis-(*p*,*p*′-dichlorodiphenylmethyl) Ether.—A 0.300-g. quantity of bis-(*p*-chlorophenyl)-acetic acid was added to 20 ml. of 100% sulfuric acid. The mixture was stirred for 40 minutes and then poured onto 100 g. of crushed ice. The mixture was treated in the same manner as for diphenylacetic acid.

A transparent gum was obtained which crystallized when stirred with 1 ml. of methanol for 5 minutes. The yield of solid was 0.23 g., melting at 121–125°. It was recrystallized three times from methanol, after which it melted at 129.2–129.9°. An authentic sample of the ether[19] melted at 129.4–129.9°. A mixture of the two melted at 129.4–129.9°.

The Conversion of Bis-(*p*-chlorophenyl)-acetic Acid to Bis-(*p*-chlorophenyl)-carbinol.—The solution prepared as above was poured after 40 minutes into 50 ml. of glacial acetic acid which had been cooled to its freezing point. The reaction was carried out and the crude ester saponified in the same way as for diphenylacetic acid. There was obtained 0.143 g. of a solid melting at 89.2–92.6°. After two recrystallizations from ligroin, it melted at 92.8–93.3°. An authentic sample of bis-(*p*-chlorophenyl)-carbinol[20] melted at 92.5–93.3°. A mixture of the two melted at 92.8–93.4°.

The Behavior of 4,4′-Dichlorobenzilic Acid in 100% Sulfuric Acid.—A 0.497-g. quantity of the compound was added to 30 ml. of 100% sulfuric acid with vigorous stirring. Solution was completed very quickly, resulting in an intense red color. The solution was stirred for one minute and then was poured into 200 ml. of ice-water. The color disappeared instantly. The mixture was stirred and was then shaken with 100 ml. of ether. The ether layer was separated and was dried over anhydrous sodium sulfate after which it was filtered and evaporated to dryness. The weight of the residue was 0.497 g. indicating no sulfonation had occurred during the short period of reaction with the sulfuric acid.

The product was stirred with two 75-ml. portions of hot 60–90° ligroin. After these portions were decanted a small amount of gummy solid remained. The combined ligroin solutions were evaporated to a volume of 2 ml., most of the organic product separating from solution. The mixture was stirred with 75 ml. of hot ligroin, which was again decanted from a small amount of gummy material. The ligroin was concentrated to 2 ml. The cycle was repeated with 30 ml. of ligroin and then with 15 ml. of ligroin. This method of purification is based on the fact that the gummy impurity dissolved in ligroin more slowly than did the main product.

The ligroin solution finally obtained was seeded with 4,4′-dichlorobenzilic acid and allowed to evaporate at room temperature with occasional stirring. The residue solidified completely after one week. The yield was 0.473 g. of material melting at 87.5–94.0°. The product did not depress the melting point of 4,4′-dichlorobenzilic acid when mixed with the latter. Its neutral equivalent was 330. Assuming it to be 4,4′-dichlorobenzilic acid contaminated with an impurity of very high neutral equivalent, its purity was 90%. The extent of recovery of 4,4′-dichlorobenzilic acid was therefore about 85%. Since the sulfuric acid solution had reached its full intensity of coloration during the one-minute reaction period, it appears that the highly col-

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(14) L. Haskelburg and D. Lavie, THIS JOURNAL, **71**, 2580 (1949).

(15) H. A. Smith, D. M. Alderman and F. W. Nadig, *ibid.*, **67**, 273 (1945).

(16) H. A. Smith and J. A. Stanfield, *ibid.*, **71**, 82 (1949).

(17) E. R. Shierz, *ibid.*, **45**, 447 (1923); M. Wegner, *Z. anal. Chem.*, **42**, 427 (1903).

(18) Prepared by the method of A. M. Ward, *J. Chem. Soc.*, 2291 (1927).

(19) Prepared by the method of O. Grummitt and A. C. Buck, THIS JOURNAL, **67**, 693 (1945).

(20) Prepared by the method of J. F. Norris and D. M. Tibbetts, *ibid.*, **42**, 2091 (1920).

ored solute formed in the sulfuric acid reacted with water subsequently to regenerate 4,4′-dichlorobenzilic acid. The color was of an intensity characteristic of stable aryl-substituted carbonium ions.

The Synthesis of Bis-(*p*-chlorophenyl)-α-chloroacetyl Chloride.—A 5.00-g. quantity (0.0178 mole) of bis-(*p*-chlorophenyl)-acetic acid obtained as described earlier was treated with 10 ml. of thionyl chloride. The mixture was kept at reflux temperature for 90 minutes. Most of the thionyl chloride was then removed by evaporation on a steam-plate. The crude acid chloride was dissolved in 20 ml. of dry carbon tetrachloride to which was added 1 ml. of phosphorus trichloride. The solution was transferred to an 8-inch Pyrex test-tube. The original container was washed with 10 ml. of carbon tetrachloride which was then added to that in the test-tube. The test-tube was fitted with a reflux condenser and a fritted glass bubbler tube, these being held in place by a two-hole rubber stopper. A 300-watt bulb was mounted next to the test-tube, which was warmed by a water-bath. As soon as reflux temperature was reached, chlorine was bubbled vigorously through the irradiated solution.

After four to five hours the chlorination was stopped. The solvent was evaporated by being warmed under suction. Then 10 ml. of low boiling petroleum ether was added. The solution was decanted from a small amount of solid impurities. Evaporation of the solvent then gave a crude product which crystallized on being chilled and stirred. The material was recrystallized three times from 6–8 ml. portions of low boiling petroleum ether, the process being facilitated by seeding. Additional solid was obtained by concentrating the mother liquors and recrystallizing the recovered material. The product melted at 60.4–61.4°. The yield was 3.91 g. (66%). After an additional recrystallization it melted at 60.7–61.7°.

Anal.[21] Calcd. for $C_{14}H_8OCl_4$: C, 50.34; H, 2.41. Found: C, 50.38; H, 2.54.

4,4′-Dichlorobenzilic Acid.—A 1.00-g. quantity (0.00299 mole) of the bis-(*p*-chlorophenyl)-α-chloroacetyl chloride was added to a solution of 2.0 g. of sodium carbonate in 25 ml. of water. The mixture was heated to reflux temperature for one hour, during which most of the organic material went into solution. After the mixture had been allowed to cool, it was poured into 200 ml. of water. The solution was filtered and the filtrate was acidified by adding a mixture of 2 ml. of concentrated sulfuric acid in 15 ml. of water. The mixture was shaken with 100 ml. of ether The ether layer was separated, and was evaporated to dryness by gentle warming. The residue was a viscous sirup which solidified after standing for three days with occasional stirring.

It was dissolved in 150 ml. of hot 60–90° ligroin and the solution was decanted from a small quantity of insoluble material. The solution was evaporated to a volume of 50 ml., seeded and allowed to cool slowly with stirring. Crystallization occurred readily. The cooled mixture was filtered under suction. The solid was dried at 45° under suction. There was obtained 0.65 g. of a product melting at 91.9–92.7°. The yield was 73% of the theoretical value based on the α-chloroacetyl chloride. The product gave a neutral equivalent of 296.9. The theoretical value for 4,4′-dichlorobenzilic acid is 297.1.

The acid was at first prepared by the method of Montagne.[12] It was obtained in a low melting form (72–76°) which was difficult to purify. On standing overnight in ligroin solution, it deposited crystals melting at 88–90°. The low melting form did not depress the melting point of these crystals. The latter did not depress the melting point of the product obtained by hydrolyzing bis-(*p*-chlorophenyl)-α-chloroacetyl chloride. Montagne reported a melting point of 101.75° for his product, which he may have obtained in still a third crystalline modification.

1,1-Dichloro-2,2-bis-(*p*-chlorophenyl)-ethylene.—Incidental to the above research, the preparation of this olefin was carried out as described by Grummitt, Buck and Egan.[22] The product was at first obtained in a form not previously reported. It melted at 74.5–75.3°. Oxidation with boiling 70% nitric acid for 40 minutes converted it to *p*,*p*′-dichlorobenzophenenone, m.p. 147.0–148.0.[23]

After one month a sample of the olefin was recrystallized, yielding the stable form, m.p. 88.4–89.1°. A saturated solution of the low melting form seeded with the high melting form and cooled gave only the latter form. A mixture of the two forms melted at 88.4–89.1°.

KNOXVILLE, TENNESSEE

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[21] Galbraith Microanalytical Laboratories, Box 32, Knoxville, Tennessee.

[22] O. Grummitt, A. Buck and R. Egan, *Org. Syntheses*, **26**, 22 (1946).

[23] *Cf.* J. F. Norris and W. C. Twieg, *Am. Chem. J.*, **26**, 497 (1901).

[CONTRIBUTION FROM THE CHEMISTRY LABORATORIES, TEMPLE UNIVERSITY, AND THE PITMAN–DUNN LABORATORIES, FRANKFORD ARSENAL]

Autoxidation of the Saturated Aliphatic Diesters[1]

BY M. WESLEY RIGG AND HENRY GISSER

RECEIVED SEPTEMBER 24, 1952

This report describes an investigation of the thermal oxidation of the saturated esters of adipic acid. The preparation and physical properties of esters from alcohols having 5 and 6 carbon atoms are given. The esters were oxidized both by continuous passage of air through the esters and by oxidation in an apparatus which recorded rate of oxygen consumption. It was found that the distance of a tertiary carbon atom from the ester group exerts a considerable effect on oxidation rate, the rate decreasing as the distance is decreased. This effect is attributed to resonance of the ester group which results in an inductive effect along the carbon chain lowering the availability of electrons at the carbon in which oxidation is taking place. In general, esters from the *n*-alcohols oxidize at a lower rate than esters from the branched-chain alcohols. Activation energies for autoxidation of several esters were determined. The values reflect the effect of alcohol structure with respect to distance of the tertiary carbon from the ester group.

Kinetics of di-(3-methylbutyl) adipate autoxidation was studied in diethyl adipate solutions. In the early stages of oxidation (before appreciable hydroperoxide decomposition takes place) the rate of oxygen consumption, calculated per mole of ester, is proportional to the square of the ester concentration. As oxidation proceeds the rate of oxidation increases and becomes constant. At this stage, the rate of oxygen consumption is proportional to the square root of the ester concentration (when extent of oxidation is still small so that the concentration of ester has changed very little from the original). It is proposed that the oxidation mechanism involves chain branching due to hydroperoxide decomposition and this mechanism is found to explain the observed kinetics. Data are presented to show that the concentration of peroxide is independent of ester concentration.

In the autoxidation of saturated hydrocarbons the preponderance of evidence indicates that oxidation takes place preferentially at a tertiary C–H bond.[2] Secondary C–H bonds are attacked less readily and primary C–H bonds are still more stable

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[1] From the Ph.D. Thesis of H. Gisser.

[2] (a) A. D. Walsh, *Trans. Faraday Soc.*, **42**, 269 (1946); (b) A. D. Walsh, *ibid.*, **43**, 297 (1947); (c) A. W. Burwell, *Ind. Eng. Chem.*, **26**, 204 (1934).