[CONTRIBUTION FROM THE NICHOLS CHEMICAL LABORATORIES, NEW YORK UNIVERSITY, UNIVERSITY HEIGHTS]

The Action of Sulfuric Acid and Oleum on Carbamic Esters

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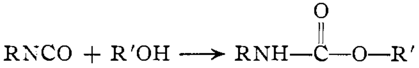
Cleavage of carbamic esters with 5% oleum leads to the formation of ammonium bisulfate or amine acid sulfates. It is concluded that these esters undergo alkyl–oxygen fission. Sulfamic acids are formed in increasing yields with the use of 30% and then 60% oleum. The formation of sulfamic acids is explained by N-sulfonation of the carbamic esters prior to their acidolysis. Sulfamic acid, methylsulfamic acid and ethylsulfamic acid are thus readily prepared by reaction of ethyl carbamate, ethyl N-methylcarbamate and ethyl N-ethylcarbamate, respectively, with 60% oleum. Ethyl N-phenylcarbamate is converted by oleum at moderate temperature to N-carbethoxysulfanilic acid; at elevated temperatures ester cleavage occurs and sulfanilic acid results.

Carbamic esters are obtainable by the addition of alcohols to organic isocyanates or to cyanic acid (R = H).



$$\mathrm{RNCO} + \mathrm{R'OH} \longrightarrow \mathrm{RNH{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}R'}$$

The possibility exists that under the influence of sulfuric acid and heat, if necessary, carbamic esters may suffer a cleavage which would essentially be a reversal of this addition reaction, and that sulfamic acids would ultimately be formed, since sulfamic acids are known to result from the reaction of organic isocyanates or cyanic acid with sulfuric acid.[2,3]

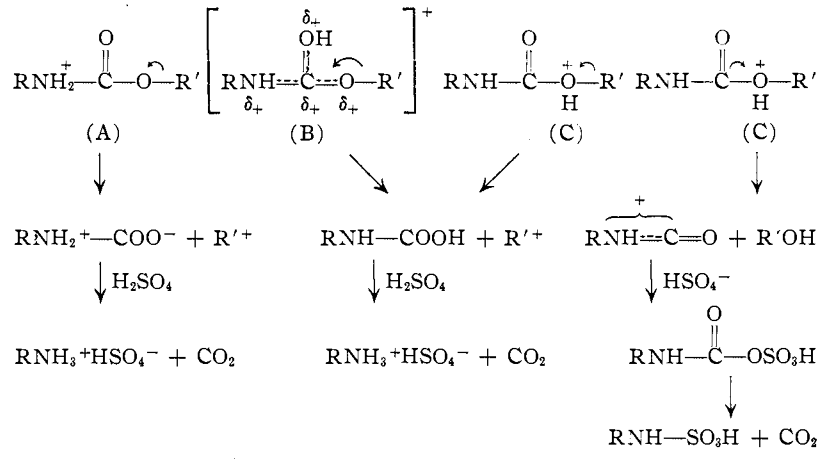
$$\mathrm{RNCO} + \mathrm{H_2SO_4} \longrightarrow \mathrm{RNH{-}SO_3H} + \mathrm{CO_2}$$

It is readily seen that the postulated cleavage of carbamic esters involves carbamyl–oxygen fission[4] as opposed to alkyl–oxygen fission.

The behavior of several unsubstituted carbamic esters (R = H; R′ = C_2H_5, *s*-C_4H_9, *n*-C_5H_{11}, $C_6H_5CH_2$) was first investigated. All these esters were subjected to the action of 5% oleum. With *s*-butyl carbamate and benzyl carbamate carbon dioxide was evolved at 0°, whereas with ethyl carbamate and *n*-amyl carbamate a temperature of nearly 90° was required for the release of carbon dioxide. The only N-containing product, however, was in each case ammonium bisulfate, sulfamic acid being completely absent. This result indicated that the esters were cleaved at the alkyl–oxygen bond and not at the carbamyl–oxygen bond.

Before cleavage occurs, carbamic esters are undoubtedly protonated by sulfuric acid with the formation of one or more of three species (A, B and C), which differ in the location of the additional proton. Alkyl–oxygen fission, which may take place with any of these forms, will yield ammonium bisulfate or amine acid sulfates, whereas carbamyl–oxygen fission, which appears possible with C only, will lead to sulfamic acids.

The decomposition of protonated carbamic esters is represented as a unimolecular process in the diagram, but a bimolecular displacement mechanism, in which bisulfate ion would have to attack the alkyl group (R′) in case of alkyl–oxygen fission and the carbon atom of the carbonyl group in case of carbamyl–oxygen fission, must be equally considered. The reactivity differences exhibited by the various unsubstituted carbamic esters in their alkyl–oxygen fission are of interest in this connection. The high reactivity of benzyl carbamate is to be anticipated, regardless of whether benzyl–oxygen fission is unimolecular or bimolecular,[5] and thus need not be further discussed. The fact that *s*-butyl carbamate is cleaved much more readily than ethyl carbamate and *n*-amyl carbamate supports a unimolecular alkyl–oxygen fission for these three esters with the conditional assumption being made that they all react by an identical mechanism. The opposite result would have been obtained if all three esters had suffered a bimolecular alkyl–oxygen cleavage. Should the above assumption not hold, then it may be predicted from a consideration of energetics and of steric factors that a bimolecular mechanism would apply to ethyl carbamate and *n*-amyl carbamate and a unimolecular mechanism to *s*-butyl carbamate. The reverse situation would be theoretically untenable. It is thus possible to conclude that at least *s*-butyl carbamate undergoes a unimolecular alkyl–oxygen cleavage.



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[2] T. I. Bieber, THIS JOURNAL, **75**, 1405 (1953).

[3] M. Linhard, *Ann.*, **535**, 267 (1938).

[4] Since the carbamyl group of carbamic esters corresponds to the acyl group of ordinary carboxylic esters, carbamyl–oxygen fission is analogous to acyl–oxygen fission.

[5] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 154; E. D. Hughes, *Trans. Faraday Soc.*, **37**, 627 (1941); A. G. Evans, *ibid.*, **42**, 719 (1946); E. R. Alexander, "Ionic Organic Reactions," John Wiley & Sons, Inc,, New York, N. Y., 1950, p. 91.

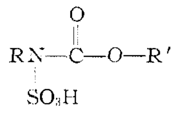
The use of 5% oleum, rather than of 100% sulfuric acid, in these cleavage reactions deserves some comment. Had 100% sulfuric acid been employed, then one could have argued that a carbamyl-oxygen fission may actually have occurred, and that water, resulting from the action of sulfuric acid on the alcohol R'OH, caused hydrolysis of the carbamyl ion or of carbamylsulfuric acid to ammonium bisulfate and carbon dioxide. The non-occurrence of sulfamic acid, however, when 5% oleum is used, clearly excludes the possibility of carbamyl–oxygen fission.

No special effort to determine the final fate of the R' groups was made, since, regardless of the findings, no additional information pertinent to the cleavage mechanism could have been gained. In the case of benzyl carbamate a polymer of the polybenzyl type $(-C_6H_4CH_2-)_n$ was formed.[6]

s-Butyl carbamate and benzyl carbamate were also rapidly cleaved by concentrated sulfuric acid in the cold, while cleavage of ethyl carbamate and *n*-amyl carbamate by the same reagent required a temperature of 90–100°. This fact is of some practical significance for the Curtius amine synthesis. The acid azide decomposition is frequently performed in the presence of an alcohol, and the carbamic ester, which forms as a result, is finally hydrolyzed to the amine. The use of alcohols such as *s*-butyl alcohol or benzyl alcohol is to be recommended, since the *s*-butyl or benzyl carbamates will be readily cleaved by cold concentrated sulfuric acid. The benzyl group appears again as a polybenzyl polymer. The rapid conversion of dibenzyl 2,5-pyrazinedicarbamate to 2,5-diaminopyrazine by cold concentrated sulfuric acid has recently been reported[7]; the corresponding diethyl ester is resistant to cleavage by the same reagent.[8]

When ethyl carbamate and *s*-butyl carbamate were subjected to the action of 30 and 60% oleum, the product was found to contain sulfamic acid together with ammonium bisulfate. The reaction of ethyl carbamate with 30% oleum produced a 23% yield of sulfamic acid; with 60% oleum sulfamic acid was obtained in 51–69% yield (a greater oleum to ester ratio favors a higher yield). The cleavage temperature with 60% oleum was 20–30° lower than that with 5% oleum. The reaction of *s*-butyl carbamate with 30% oleum, which proceeded vigorously in the cold, gave a 12% yield of sulfamic acid; the use of 60% oleum led to a 22% yield. It is evident that under similar conditions much higher yields of sulfamic acid are obtainable from ethyl carbamate than from *s*-butyl carbamate.

Sulfamic acid formation with oleum of considerable strength is best explained by N-sulfonation of the carbamic ester and subsequent alkyl–oxygen fission of the sulfonated ester (R = H; R' = C_2H_5, *s*-C_4H_9).



$$R\underset{SO_3H}{N}-\overset{O}{\overset{\|}{C}}-O-R'$$

As more concentrated oleum is used, N-sulfonation prior to ester cleavage competes more successfully with direct ester cleavage, and the conversion to sulfamic acid increases accordingly. The low yields of sulfamic acid from *s*-butyl carbamate as compared to those from ethyl carbamate are a consequence of the fact that *s*-butyl carbamate undergoes ester cleavage far more readily than ethyl carbamate, so that the chances for N-sulfonation prior to ester cleavage are much slimmer for the former ester.

A somewhat related mechanism for the formation of sulfamic acid would involve sulfonation of the ammonia being liberated as a consequence of the alkyl–oxygen cleavage of ethyl carbamate or *s*-butyl carbamate; this sulfonation must obviously compete with protonation which leads to ammonium bisulfate.[9] However, the differences in the yields of sulfamic acid resulting from ethyl carbamate and *s*-butyl carbamate find no ready explanation if this mechanism is accepted.

Another possibility, the conversion of ammonium bisulfate to sulfamic acid by the action of oleum

$$NH_4HSO_4 + SO_3 \longrightarrow H_2N-SO_3H + H_2SO_4$$

was ruled out by a demonstration that treatment of ammonium bisulfate with 60% oleum under conditions resembling closely those of the ethyl carbamate–60% oleum reaction produced no sulfamic acid whatsoever.

Two N-alkylcarbamic esters (R = CH_3, C_2H_5; R' = C_2H_5) were allowed to react with oleum. On reaction of ethyl N-ethylcarbamate with 5% oleum evolution of carbon dioxide occurred at about 90°. Ethylamine acid sulfate, the major product, was accompanied by a 6% yield of ethylsulfamic acid. The yield of the latter increased sharply as more concentrated oleum was employed; it was 85% with 30% oleum and 93% with 60% oleum. The cleavage temperature was about 60°, when 60% oleum was used. The reaction of ethyl N-methylcarbamate with 60% oleum produced methylsulfamic acid in 94% yield. Methylsulfamic acid and ethylsulfamic acid may thus be conveniently synthesized; these acids are precipitated as crystalline solids on pouring the reaction mixtures into ether.

The behavior of alkyl N-alkylcarbamates toward oleum clearly resembles that of alkyl carbamates and is subject to the same interpretation. The yields of alkylsulfamic acids from ethyl N-alkylcarbamates are, however, considerably higher than those of sulfamic acid from ethyl carbamate for any given oleum concentration and a similar mole ratio of reactants. As no appreciable differences appear to exist in the ease of ester cleavage of the various ethyl esters, it can be inferred from a yield comparison that ethyl N-alkylcarbamates are more readily N-sulfonated than ethyl carbamate. This follows from the fact that N-sulfonation prior to ester cleavage must rival the direct ester cleavage with greater success if higher yields of sulfamic acids are to be obtained.

The action of oleum on ethyl N-phenylcarbam-

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[6] *Cf.* R. L. Shriner and A. Berger, *J. Org. Chem.*, **6**, 305 (1941).

[7] D. M. Sharefkin and P. E. Spoerri, THIS JOURNAL, **73**, 1637 (1951).

[8] P. E. Spoerri and A. Erickson, *ibid.*, **60**, 402 (1938).

[9] Free ammonia is not believed to be formed in the cleavage, so that protonation or sulfonation would have to occur concurrently with the heterolytic cleavage of the N–C bond in $H_3N^+-COO^-$, for example.

ate, a typical N-arylcarbamic ester, was finally investigated. With 15% oleum at 60° sulfonation occurred in the para position, the carbamic ester group remaining unaffected. The para sulfonation was proved by hydrolyzing the N-carbethoxysulfanilic acid to sulfanilic acid and converting the latter to *p*-chlorobenzenesulfonamide. N-Carbethoxysulfanilic acid was formerly synthesized by reaction of sulfanilic acid with ethyl chlorocarbonate in pyridine.[10]

When the reaction mixture of ethyl N-phenylcarbamate with 15% oleum was heated to 80–90°, carbon dioxide was evolved and sulfanilic acid was obtained. Ester cleavage of N-carbethoxysulfanilic acid had obviously taken place. It is possible that the ester cleavage was preceded to some extent by N-sulfonation and that, as a result, some N-sulfosulfanilic acid was formed; the latter, being an arylsulfamic acid, would be readily hydrolyzed to sulfanilic acid and sulfuric acid on dilution of the reaction mixture with water.

It is worth noting that according to a recent report on the chlorosulfonation of ethyl N-phenylcarbamate (using chlorosulfonic acid) the temperature in that reaction should not exceed 60°, since sulfanilic acid is formed at higher temperatures.[11]

Experimental

General Procedure for the Reaction of Carbamic and N-Alkylcarbamic Esters with Oleum.—The ester was added gradually to ice-cooled and mechanically stirred oleum. The mixture was then slowly heated on a water-bath until vigorous evolution of carbon dioxide occurred, except when the cleavage reaction occurred in the cold. After cessation of gas evolution, the reaction mixture was ice-cooled and poured on ice. The sulfamic acid or alkylsulfamic acid content of the resulting aqueous solution was then determined as described previously.[2] The data are summarized in Table I. Ammonium bisulfate or amine acid sulfates, whose presence could be readily demonstrated, make up the balance of N-containing product.

TABLE I

Reactants							
RNHCOOR′			Oleum		Reaction	RNHSO₃H	
R	R′	g.	Wt. % free SO₃	g.	temp., °C.	R	Yield, %
H	C_2H_5	5.0	5	20.0	80–90	H	0
H	C_2H_5	5.0	30	23.0	70–80	H	23
H	C_2H_5	5.0	60	22.6	60–70	H	51
H	C_2H_5	5.0	60	50.0	60–70	H	69
H	n-C_5H_{11}	7.4	5	20.0	80–90	H	0
H	s-C_4H_9	6.6	5	20.0	0–10	H	0
H	s-C_4H_9	6.6	30	23.4	0–10	H	12
H	s-C_4H_9	6.6	60	26.4	0–10	H	22
H	$C_6H_5CH_2$	8.4	5	40.0	0–10	H	0
C_2H_5	C_2H_5	6.6	5	20.0	90	C_2H_5	6
C_2H_5	C_2H_5	6.6	30	23.0	70	C_2H_5	85
C_2H_5	C_2H_5	6.6	60	25.5	60	C_2H_5	93
CH_3	C_2H_5	5.8	60	26.4	60	CH_3	94

Several product isolations of preparative significance will next be described.

Sulfamic Acid.—When 5.0 g. of ethyl carbamate was allowed to react with 26 ml. (about 50 g.) of 60% oleum at 60–70°, some sulfamic acid precipitated in the course of the reaction. Impure sulfamic acid could be obtained by filtration of the cold reaction mixture on a sintered-glass funnel. It was preferable, however, to pour the reaction mixture on a limited quantity of ice (the solubility of sulfamic acid is low in fairly concentrated sulfuric acid). The product, which was collected on a sintered-glass funnel, was practically pure after being washed with methanol and ether. It weighed 3.4 g. (63%) and did not give a sulfate test; m.p. 197–203° dec., reported m.p. 205° dec.

Anal. Calcd. for H_3NO_3S: N, 14.43. Found: N, 14.67.

Alkylsulfamic Acids.—After reaction of 6.6 g. of ethyl N-ethylcarbamate with 39.0 g. of 60% oleum at 60°, the clear ice-cooled reaction mixture was poured slowly into 250 ml. of ether, which was shaken and cooled in an ice-bath. The precipitated ethylsulfamic acid was collected on a sintered-glass funnel and washed with 200 ml. of ether, whereupon it gave only a very faint sulfate test; it weighed 4.9 g. (70%). For further purification the solid was dissolved in a little methanol and reprecipitated by the addition of a much larger volume of ether. The sulfate-free material melted at 171–172°.

Anal. Calcd. for $C_2H_7NO_3S$: N, 11.19. Found: N, 10.92.

A small quantity of red viscous oil, that could not be induced to solidify, separated from the combined ether filtrate and washings used in the original isolation. This oil contained the very hygroscopic ethylamine acid sulfate. It is advisable to use a limited quantity of ether for precipitation of ethylsulfamic acid from the reaction mixture, in order to prevent serious contamination by ethylamine acid sulfate, which separates out on greater dilution; the yield of ethylsulfamic acid is, however, thereby reduced somewhat.

Methylsulfamic acid, formed by reaction of 5.8 g. of ethyl N-methylcarbamate with 32.3 g. of 60% oleum at 60°, was isolated and purified in practically identical fashion. The quantity of ether used in the separation of methylsulfamic acid was limited to 200 ml. so as to avoid contamination by methylamine acid sulfate, which appeared as an oil on greater dilution. The recrystallized substance melted at 179°.

Anal. Calcd. for CH_5NO_3S: N, 12.61. Found: N, 12.27.

Reaction of Ethyl N-Phenylcarbamate with 15% Oleum.—To 66.5 g. of ice-cooled and stirred 15% oleum was slowly added 12.0 g. of ethyl N-phenylcarbamate. No gas evolution occurred as the solution was heated to 60° and held there for 15 minutes. The reaction mixture was then ice-cooled and poured on 140 g. of ice, whereupon N-carbethoxysulfanilic acid precipitated as a white solid. The substance is readily water-soluble, but its solubility in strongly acidic solutions is low. After being collected on a sintered-glass funnel, the solid was dissolved in 55 ml. of water and reprecipitated by the addition of 100 ml. of concentrated hydrochloric acid with ice-cooling. The purified solid, collected on a sintered-glass funnel and dried over calcium chloride (at ordinary pressure), was shown by analysis to be the monohydrate. It weighed 15.0 g. (79%) and liquefied temporarily at 199–201° with evolution of a gas (the solid, which then formed, turned gradually brown on further heating).

Anal. Calcd. for $C_9H_{11}NO_5S$ (anhydrous form): C, 44.07; H, 4.50; N, 5.71; S, 13.07; neut. equiv., 245. Calcd. for $C_9H_{13}NO_6S$ (monohydrate): C, 41.06; H, 4.98; N, 5.32; S, 12.18; neut. equiv., 263. Found: C, 41.07; H, 4.86; N, 5.39; S, 12.01; neut. equiv., 263, 263.[12]

In order to prove that sulfonation had occurred in the para position, the substance was hydrolyzed to sulfanilic acid, which was then converted to *p*-chlorobenzenesulfonamide by a previously described procedure.[2] The hydrolysis was carried out in a sodium hydroxide solution that was refluxed for two hours, at least three moles of sodium hydroxide being required per mole of N-carbethoxysulfanilic acid; on acidification with hydrochloric acid carbon dioxide was evolved with foaming and sulfanilic acid precipitated.

N-Carbethoxysulfanilic acid monohydrate could also be converted in 94% yield to N-carbethoxysulfanilyl chloride by the action of a large excess of chlorosulfonic acid, first with ice-cooling and then at 50°. The product crystallized when the reaction mixture was poured on ice. After recrystallization from benzene it melted at 101–101.5°;

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[10] L. Raffa, *Farm. sci. e tec.* (*Pavia*), **3**, 35 (1948); *C. A.*, **42**, 4163e (1948).

[11] L. S. Solodar and Z. N. Shevchenko, *Zhur. Priklad. Khim.* (*J. Applied Chem.*), **22**, 508 (1949); *C. A.*, **44**, 2468e (1950).

[12] The substance reported by Raffa (ref. 10), m.p. 195° dec., appeared to be the anhydrous form (Found: N, 5.86; S, 13.00; no other analytical data given).

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

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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).