mole) was stirred in 3 ml. of hydrochloric acid (2:1) and treated at 3° with 0.69 g. (0.0081 mole) of sodium nitrite dissolved in 1.4 ml. of water. After 5 min. of stirring 12.5 ml. of a 50% hypophosphorous acid solution (0°) was added. This mixture was stirred for 15 min., then permitted to stand overnight at 5°. The oily suspension was extracted with 40 ml. of ether and after drying and stripping the solvent 1.1 g. (90%) of a dark oil was isolated. Infrared analysis indicated 3,4-dichlorotoluene was present (3–4%), no 2,4-dichlorotoluene. No standard was available for the 3,4-dichlorotoluene.

Oxidation to dichlorotoluic acids. A suspension of 0.8 g. (0.0049 mole) of the crude dichlorotoluenes obtained above and 20 ml. of nitric acid (2:3) was placed in a sealed tube at 140° for 2 days. The mixture of solids resulting were treated with boiling water to extract the acids. The water yielded 0.33 g. (35%) of solid, m.p. 135–140°. An infrared analysis indicated the mixture contained approximately 85–90% 2,3-dichlorobenzoic acid and 10–15% 2,4-dichlorobenzoic acid.

NIAGARA FALLS, N. Y.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF DEPAUW UNIVERSITY]

Acid-Catalyzed Decarbonylation of 2,4,6-Trimethoxybenzaldehyde Accompanying Condensation Reactions

HOWARD BURKETT, FRED SCHULTZ, AND JOHN CASSADY

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At concentrations above approximately $1 \times 10^{-4}M$ 2,4,6-trimethoxybenzaldehyde, I, in mineral acid forms 2,4,6,2′,4′,6′,-2″,4″,6″-nonamethoxytriphenylmethane (II). Kinetic studies showed II to be formed from the condensation of I with 1,3,5-trimethoxybenzene (III) from the normal decarbonylation of I. 2,4,6,2′,4′,6′-Hexamethoxydiphenylcarbinol was obtained from the reaction of I and III in perchloric acid.

In connection with a study of the mechanism of the acid-catalyzed decarbonylation of 2,4,6-trimethoxybenzaldehyde[1] (I) experiments were carried out to identify the product (formic acid) which had its origin in the aldehyde group. For this purpose the concentration of I was necessarily of the order of 1.0×10^{-2} to $2.5 \times 10^{-3} M$, compared with concentrations of approximately 2.0 to 6.0 $\times\ 10^{-5}M$ used in all of the kinetic studies. In all of the experiments at the higher concentrations, a red solution, a red precipitate, and absorption at 520–560 mμ were observed. None of these occurred in the kinetic studies. By treatment of the red solid with water, a white solid was obtained. These results were not published pending further research. Nevertheless, we proposed that the white solid was probably 2,4,6,2′,4′,6′,2″,4″,6″-nonamethoxytriphenylmethane (II) resulting from reaction of I with the 1,3,5-trimethoxybenzene (III) formed by decarbonylation of I, and that the red compound was a complex between II and the mineral acid.

The proposed structures of these materials were based principally upon reports that, in acid, aromatic aldehydes reacted readily with 1,3,5-(or 1,2,4-)trimethoxybenzene to form substituted triarylmethanes, which were colored in the acid solution.[2] In one case the triarylmethane was obtained when only the aldehyde was used. Thus, 2,4,5,-2′,4′,5′,2″,4″,5″ - nonamethoxytriphenylmethane was prepared by heating 2,4,5-trimethoxybenzaldehyde with 25% hydrochloric acid.[2(b)]

Recently, W. M. Schubert, P. Myhre, and A. T. Nielsen[3] observed a colored precipitate in each case when certain 2,4,6-trisubstituted benzaldehydes were heated with mineral acid. They proposed and presented evidence that the red precipitate they obtained was an adduct of one or two moles of aldehyde with one mole of mineral acid. In certain cases they recovered the aldehyde from the complex but did not do so for the product from 2,4,6-trimethoxybenzaldehyde.

Recovery of the aldehyde is, in itself, not conclusive evidence that the product is a simple adduct since similarly substituted diarylcarbinols upon treatment with acid may yield the corresponding triarylmethane and aldehyde in good yield.[2(a,c,e)]

The present work was undertaken to learn the nature of the product and the mode of its formation when 2,4,6-trimethoxybenzaldehyde in greater than $10^{-4}\ M$ concentration was treated with strong hydrochloric acid and perchloric acid.

Two different materials were obtained upon treatment of I with perchloric acid. The first, a light red solid, was obtained if the reaction mixture was cooled a few minutes after mixing. The second, a dark red solid, separated after a longer reaction time. Only the dark red solid could be isolated from the hydrochloric acid experiments.

Since there was no assurance that the first product was pure, no more work was done on it at that time. A planned more extensive study of aldehyde-mineral acid adducts of a number of aromatic aldehydes will include this compound.

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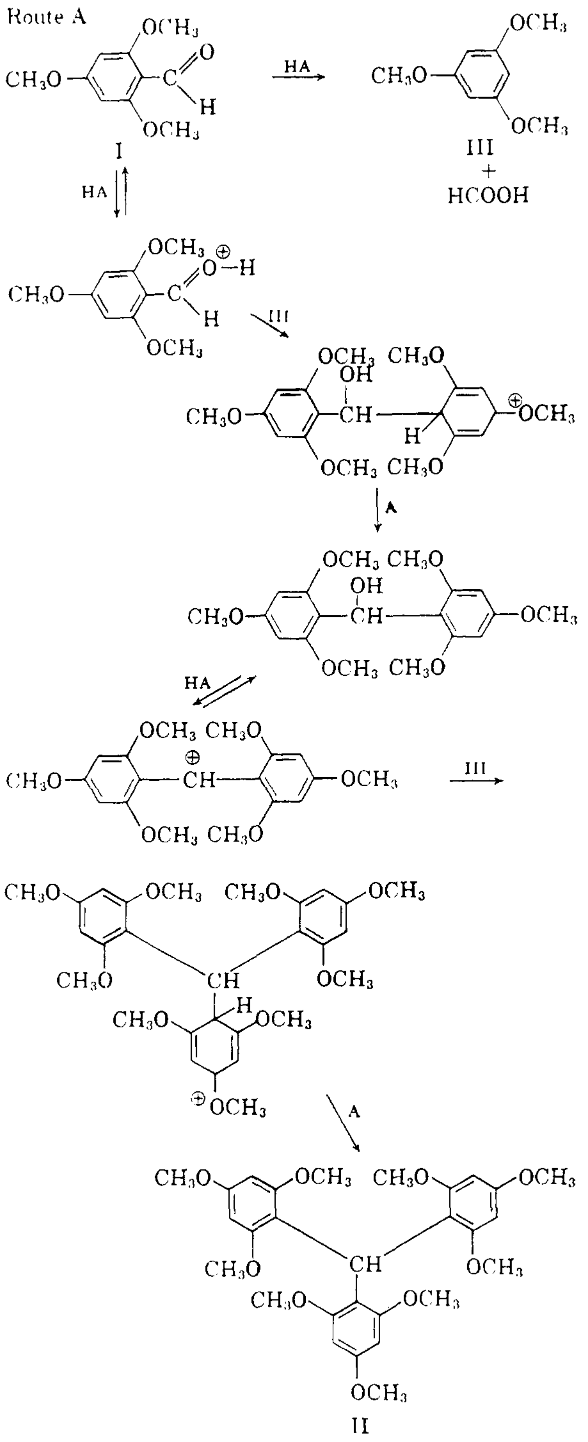
(1) H. Burkett, W. M. Schubert, F. Schultz, R. B. Murphy, and R. Talbott, *J. Am. Chem. Soc.*, **81**, 3923 (1959).

(2) (a) St. v. Kostanecki and V. Lampe, *Ber.*, **39**, 4018 (1906); (b) R. Fabinyi and T. Szeki, *Ber.*, **43**, 2676 (1910); (c) T. Szeki, *Ber.*, **44**, 1478 (1911); (d) T. Szeki, *Ber.*, **62**, 1374 (1929); (e) J. Kenyon and R. F. Mason, *J. Chem. Soc.*, 4964 (1952); (f) I. Lifschitz, *Rec. trav. chim.*, **53**, 191 (1934).

(3) Private communication.

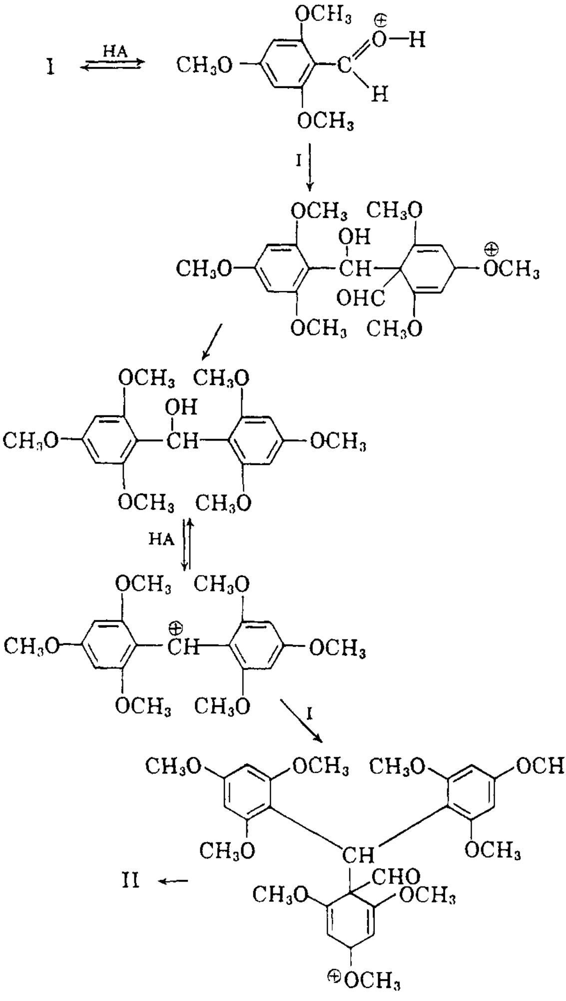
Route A



The dark red product obtained upon longer treatment with acid was more stable than the first. This product from the perchloric acid could be recrystallized from acetic acid and kept indefinitely. The product from hydrochloric acid on standing in a vacuum desiccator gradually lost hydrogen chloride and became white. Treatment of the material from either acid with water or with aqueous alkali also yielded the same white solid, which was identical with that obtained in the earlier experiment. The elemental analysis, molecular weight, and infrared spectrum of this compound were consistent with the proposed structure (II). Titration of the dark red solid with alkali indicated it to be a 1:1 molar adduct of II and the mineral acid.

For the mode of formation of II, two general routes were considered. One route involved the decarbonylation of I followed by condensation of two molecules of this decarbonylation product (III) with one molecule of I. Plausible reactions are shown in Route A. The other route involved condensation prior to, or simultaneous with, the loss of the aldehyde group in two steps by a sequence of reactions such as those in Route B.

Route B



That II is formed at the higher concentrations and not at the lower ones would undoubtedly depend upon the higher concentration of III for Route A or I for Route B so that the rate of condensation (in either case) may compete favorably with the decarbonylation. Therefore, addition of III to the reaction mixture with I at low concentration should increase the rate of disappearance of I and give the red compound if the reaction proceeds by Route A but should have no effect if it goes by Route B.

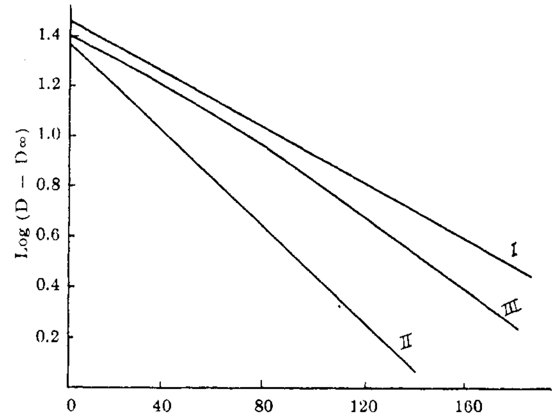


Fig. 1. Rate of disappearance of 2,4,6-trimethoxybenzaldehyde. I. With $2.5 \times 10^{-5} M$ aldehyde. II. With aldehyde at same concentration plus $1.3 \times 10^{-3} M$ 1,3,5-trimethoxybenzene. III. With $1.0 \times 10^{-3} M$ aldehyde.

The rate of disappearance of I at $2.5 \times 10^{-5} M$ concentration was measured with no III, and with III at two concentrations. The rates were faster in the presence of III as shown in Table I and Fig. 1. Moreover, the reaction mixtures containing III were colored and showed absorption at 520–560 mμ typical for II. That II was formed at high dilution of I if sufficient III was present supports Route A. The increase in rate upon adding III indicates that I disappeared by two routes—decarbonylation and condensation with III.

The rate of disappearance of I was also measured at $1 \times 10^{-3}M$ concentration. The rate during the first forty minutes was the same as for the $2.5 \times 10^{-5}M$ run but increased gradually to a rate 1.3 times the initial rate as noted in Table I and Fig. 1. The proposed Route A would predict such a result since the build-up in the concentration of III would cause an increase in rate as the reaction progressed.

TABLE I

KINETIC RESULTS

2,4,6-Trimethoxybenzaldehyde, *M*	1,3,5-Trimethoxybenzene, *M*	$k \times 10^{-3}$, sec.$^{-1}$
2.5×10^{-5}	0	0.215, 0.215, 0.218
2.5×10^{-5}	1.3×10^{-4}	0.225, 0.224, 0.229
2.5×10^{-5}	1.3×10^{-3}	0.361, 0.348, 0.391
1.0×10^{-3a}	0	0.208, 0.215, 0.205
1.0×10^{-3b}	0	0.269, 0.271, 0.266

[a] 0–40 min. [b] 80–160 min.

Since Route A proposes 2,4,6,2′,4′,6′-hexamethoxydiphenylcarbinol (IV) as an intermediate, attempts were made to isolate it. IV was not obtained starting with I alone, but heating a mixture of I and III in 40–45% perchloric acid for a limited time yielded a red solid from which IV was obtained by treating with water and alkali. The red solid had a correct analysis for 2,4,6,2′,4′,6′-hexamethoxydiphenylcarbinyl perchlorate.

Prolonged heating of I, II, and IV with strong mineral acid yielded III. Thus it would appear that the reactions by which II is formed are reversible to the starting materials.

EXPERIMENTAL

Materials. The perchloric acid and hydrochloric acid solutions were prepared from concentrated analytical reagent grade solutions suitably diluted with distilled water. The final concentrations were checked by titration with standard alkali. The acetic acid was glacial reagent grade of stated purity greater than 99.5%.

Published methods were used for the preparation of 1,3,5-trimethoxybenzene,[4] m.p. 52–53°, and 2,4,6-trimethoxybenzaldehyde,[2e] m.p. 117.5–118°. These compounds were recrystallized from petroleum ether (b.p. 35–60°) and alcohol, respectively, until the melting point was unchanged, then recrystallized two more times.

Initial experiments. Samples of approximately 0.05 g. of 2,4,6-trimethoxybenzaldehyde in 14 drops of 25% hydrochloric acid were heated on the steam bath for the stated length of time. After cooling in ice the precipitate, if any, was observed, filtered, and boiled with water, resulting in a white or off-white solid. This "final solid" was washed with water and/or alcohol and the melting point taken. With no heating before cooling in ice no precipitate was obtained within 1 hr., even though the solution became red. With a 1-min. heating period, the original precipitate was red and the final solid melted at 182–186°. Heating for 5 min. gave a similar result except the m.p. was 207–210°. Heating for 25 min. and 3.5 hr. gave an orange-brown powder. The melting point of the final solid was *ca.* 50°. After recrystallization from petroleum ether, the melting point was 52–53° and gave no depression upon mixing with 1,3,5-trimethoxybenzene.

Similar experiments were made using 12 drops of 42% perchloric acid and 10 drops of acetic acid. With no heating the solution became yellow (not red). Heating for 1 or 2 min. gave a light red precipitate and melting point of the final solid of 114–120°. Recrystallization of the latter gave a white solid, m.p. 117–118°, which gave no depression of the melting point on mixing with 2,4,6-trimethoxybenzaldehyde. Heating 5, 7, and 20 min. gave a dark red precipitate and a melting point of the final solid of about 204–207°. Nearly the same results were obtained using 14 drops of 42% perchloric acid without the acetic acid but the aldehyde did not dissolve readily in this acid. Allowing the aldehyde to stand at room temperature for 3 hr. with the same acid mixture then cooling gave only the light red solid, final solid melting point about 100°. Using 0.04 g. of 2,4,6-trimethoxybenzaldehyde and 0.04 g. of 1,3,5-trimethoxybenzene in the same solvent at room temperature gave a dark red precipitate in 7 min., which increased in amount then gradually dissolved followed by the formation of a dark red precipitate again. The final solid from the latter melted at 205–208°.

2,4,6,2′,4′,6′,2″,4″,6″-Nonamethoxytriphenylmethane. A mixture of 1.5 g. of 2,4,6-trimethoxybenzaldehyde and 4.5 ml. of 25.0% hydrochloric acid was heated for 5 min. on the steam bath. The mixture was cooled in ice and the resulting red solid was filtered. Warming the red solid with water, washing with hot alcohol, and recrystallizing twice from benzene-petroleum ether yielded 0.7 g. of a white solid, m.p. 208–210°.

Anal. Calcd. for $C_{28}H_{34}O_9$: C, 65.34; H, 6.67; mol. wt., 514.6. Found: C, 64.98; H, 6.62; mol. wt. (Rast), 526.

The infrared spectrum, especially the absence of any absorption typical for hydroxyl or carbonyl groups, was consistent with the proposed structure for this compound.

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(4) J. W. Clark-Lewis, *Australian J. Chem.*, **10**, **505** (1957).

The same compound was similarly prepared by heating the aldehyde for 13 min. with 36.0% perchloric acid and decomposing the resulting red solid by boiling with aqueous sodium hydroxide.

A sample of the red solid from the perchloric acid was recrystallized from glacial acetic acid giving beautiful red crystals with gold faces, m.p. 167–172°.

Anal. Calcd. for $C_{28}H_{34}O_9 \cdot HClO_4$: C, 54.6; H, 5.73; mol. wt., 615.1. Found: C, 54.07; H, 5.68; mol. wt. (titration with alkali), 607.

2,4,6,2′,4′,6′-Hexamethoxydiphenylcarbinol. To a solution of 0.2 g. of 2,4,6-trimethoxybenzaldehyde and 0.4 g. of 1,3,5-trimethoxybenzene in 30 ml. of glacial acetic acid was added 3.0 ml. of 42.0% perchloric acid. Heating for 9 min. on the steam bath followed by cooling in ice and recrystallizing from glacial acetic acid produced brown-red crystals (with gold-green faces) of 2,4,6,2′,4′,6′-hexamethoxydiphenylcarbinyl perchlorate, m.p. 190–192° dec.

Anal. Calcd. for $C_{19}H_{23}O_{10}Cl$: C, 51.2; H, 5.18; mol. wt., 446.9. Found: C, 51.07; H, 5.18; mol. wt. (titration with alkali), 441, 447, 443.

Heating an identical reaction mixture for 20 min. gave only the 2,4,6,2′,4′,6′,2″,4″,6″-nonamethoxytriphenylmethane-perchloric acid adduct.

The brown-red solid was warmed with 25% aqueous sodium hydroxide. The resulting yellow solid was recrystallized three times from alcohol-water to yield a white solid, m.p. 150–152°.

Anal. Calcd. for $C_{19}H_{24}O_7$: C, 62.6; H, 6.57; mol. wt., 364.4. Found: C, 62.21; H, 6.41; mol. wt. (Rast), 371.

In addition to other expected spectral features, strong absorption at 3610 cm.$^{-1}$, typical for the alcohol group, was observed.

Several attempts to prepare this compound by treatment of 2,4,6-trimethoxybenzaldehyde alone in either hydrochloric or perchloric acid for different lengths of time resulted in recovering the starting aldehyde, in isolating 2,4,6,2′,4′,6′,2″,4″,6″-nonamethoxytriphenylmethane and/or in isolating 1,3,5-trimethoxybenzene.

1,3,5-Trimethoxybenzene. A mixture of 0.2 g. of 2,4,6,2′,4′,6′,2″,4″,6″-nonamethoxytriphenylmethane and 1 ml. of 25% hydrochloric acid was heated for 20 min. on the steam bath. After cooling the reaction mixture, the resulting tan solid was filtered and recrystallized from petroleum ether, yielding white needles, m.p. 52–53°. A mixture of this compound with authentic 1,3,5-trimethoxybenzene melted at 52–53°. Treatment of 2,4,6,2′,4′,6′-hexamethoxydiphenylcarbinol in the same way gave the same product.

Kinetic experiments. The reactions were run in a thermostated bath placed in the light path of the Beckmann DU Spectrophotometer. The solvent acid for all determinations was taken from a stock solution made by mixing one volume of glacial acetic acid and two volumes of 70–72% perchloric acid. The temperature was controlled at 60° to ±0.05°. The rate of disappearance of the 2,4,6-trimethoxybenzaldehyde was followed by observing the decrease in the absorption in the region of 318 mμ. In each case data were obtained at three or more wave lengths and at least two separate runs were made. The reactions were followed for at least three half-lives. The plot of log $(D - D_\infty)$ *vs.* time was linear within ±0.01 log unit except for an occasional stray point and except for the one experiment in which the curvature of the plot was the significant observation.

Three plots are shown in Fig. 1. The results are summarized in Table I.

Acknowledgment. This research was supported by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of said fund. Some of the analyses were done by Clark Microanalytical Laboratory.

GREENCASTLE, IND.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF CREIGHTON UNIVERSITY]

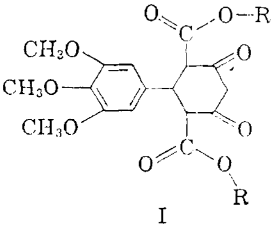
Synthesis of 5-(2′,3′,4′-Trimethoxyphenyl)-4,6-dicarbethoxycyclohexanedione-1,3 and Derivatives

PHILIPPOS E. PAPADAKIS AND WAYNE BOAND

Received August 8, 1960

The synthesis of 2,3,4-trimethoxybenzaldehyde (III) from trimethoxybenzene, *N*-methylformanilide and phosphorus oxychloride has been described. Ethyl 2,3,4-trimethoxybenzylidenemalonate (IV) and 5-(2′,3′,4′-trimethoxyphenyl)-4,6-dicarbethoxycyclohexanedione-1,3 (V) were prepared. The syntheses of the following derivatives of III and V are described: 2,4-dinitrophenylhydrazone of III; bisdiphenylhydrazone of V; 2,2-(vanillydene)-bis[5-(2′,3′,4′-trimethoxyphenyl)-4,6-dicarbethoxycyclohexanedione-1,3] (IX) and *N,N′*-bis{2-[5-(2′,3′,4′-trimethoxyphenyl)-4,6-dicarbethoxycyclohexane-1,3]}-*p,p′*-bisazodiphenyl (X).

The preparation of 5-(1′,2′,3′-trimethoxyphenyl)-4,6-dicarbethoxycyclohexanedione-1,3 (I) was reported in a previous publication.[1] The syntheses involved the conversion of 3,4,5-trimethoxybenzoylchloride to 3,4,5-trimethoxybenzaldehyde by the Sonn and Muller method[2] and further the preparation of I according to the method previously described.[3]



I

Mathiesen tried to prepare trimethoxybenzaldehyde directly from 3,4,5-trimethoxybenzoylchloride using the Rosemund's reduction method. He

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[1] P. E. Papadakis and R. Mathiesen, *J. Org. Chem.*, **21**, 593 (1956).

[2] Sonn and Muller, *Ber.*, **52**, 1934 (1919).

[3] P. E. Papadakis, *J. Am. Chem. Soc.*, **67**, 1799 (1945).