was sublimed to give 1.44 g (71% yield) of **14**. The ether-soluble and alkali-insoluble fraction gave 0.23 g of solid 1,2-dihydro-1-phenanthrol (**16**): mp 115–116.5°, mass spectrum (70 eV) *m/e* 196 (M^+).

Anal. Calcd for $C_{14}H_{12}O$: C, 85.71; H, 6.12. Found: C, 85.52; H, 6.06.

Pd/C Dehydrogenation of 1,2,3,4-Tetrahydro-2,5,8-trimethyl-1-naphthol (17) and 1,2,3,4-Tetrahydro-3,5,8-trimethyl-1-naphthol (19) to 1,4,6-Trimethylnaphthalene (18).—The tetrahydronaphthols **17**, bp 95° (0.4 mm), mp 79–81°, and **19**, mp 76–77°, were prepared by $LiAlH_4$ reduction of **8** and **9**.[6f] Dehydrogenation of **17** and **19** with Pd/C at 270° was followed with glc studies and shown to be complete in about 8 hr. There was no evidence of naphthol formation. Both alcohols gave about 98% yield of **18**,[6f,9] bp 91° (0.9 mm).

The orange picrate of **18**, mp 134–135° [lit.[9] 133°], was prepared.

Pd/C Dehydrogenation of 1,2,3,4-Tetrahydro-4,5,8-trimethyl-1-naphthol (20) to 1,4,5-Trimethylnaphthalene (21).—The tetrahydronaphthol **20**, bp 110° (0.5 mm) [lit.[9] bp 106–107° (0.1 mm)], obtained by $LiAlH_4$ reduction of **10** was treated with Pd/C in the same procedure as was used for **17** and **19**. At the end of 8 hr, the glc analysis showed the presence of four peaks. The largest was due to unreacted **20** and the second major peak represented **21**. This peak increased with time and was approximately 35% of the total peak area at the end of 8 hr.

Registry No.—**1**, 529-34-0; **2**, 1590-08-5; **3**, 14944-23-1; **4**, 19832-98-5; **5**, 19550-57-3; **6**, 13621-25-5; **7**, 5037-63-8; **8**, 10468-59-4; **9**, 10468-60-7; **10**, 10468-61-8; **11**, 27410-97-5; **12**, 27310-98-6; **16**, 27410-99-7.

Acknowledgment.—We thank the American Petroleum Institute for partial support of this work through API Research Project 58A and the Research Foundation of Oklahoma State University for their assistance. Grateful acknowledgment is made also to the National Science Foundation and to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. We thank Dr. O. C. Dermer for having read the manuscript.

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[9] L. Ruzicka and L. Ehman, *Helv. Chim. Acta*, **15**, 140 (1932).

The Reaction of Formaldehyde with Deactivated Benzoic Acids. An Ester-Directed Electrophilic Aromatic Substitution Process[1]

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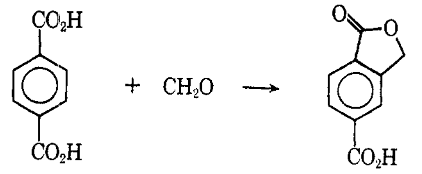
The reaction of formaldehyde with benzoic acids bearing electron-withdrawing groups has been shown to provide phthalide derivatives. The reaction media must contain sulfur trioxide. Evidence is presented to show that an intermediate is formed prior to the electrophilic attack which involves the carboxyl group. It is suggested that this intermediate is a methylene ester, stabilized by sulfur trioxide.

Terephthalic acid in strong acid media undergoes several electrophilic substitution reactions, such as nitration,[2] halogenation,[3] and mercuration.[4] The reaction of terephthalic acid and formaldehyde in sulfur trioxide-containing media to give 5-carboxyphthalide (**1**) has recently been reported.[5] 5-Carboxyphthalide can be nitrated and halogenated to yield 6-nitro- or 6-halo-5-carboxyphthalide. The $-CH_2O-$ substituent of 5-carboxyphthalide should activate the material toward electrophilic attack, relative to terephthalic acid.[6] But while terephthalic acid reacts easily with formaldehyde,[5] 5-carboxyphthalide does not, and only small amounts of the diadduct, **2**, can be detected from treatment of 5-carboxyphthalide with formaldehyde, even under forcing conditions.



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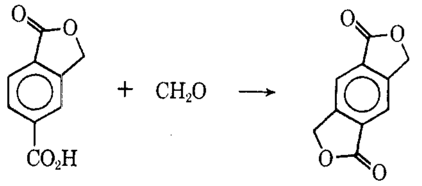

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These observations suggested that the reaction of terephthalic acid and formaldehyde may involve more than direct electrophilic substitution by a protonated or sulfated formaldehyde species and prompted our further investigation of the system. We have since studied the scope of the reaction and extended it to other deactivated aromatic substrates. In this paper we propose that the terephthalic acid reaction represents one example of a class of electrophilic aromatic substitutions involving deactivated benzoic acids. These reactions are characterized by an ortho-directing effect which results from an esterification occurring prior to ring attack.

Results

Electrophilic substitution reactions are generally sensitive to changes in acid strength. Therefore, a number of known Lewis acids were added to the formaldehyde–

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[1] Presented, in part, before the Division of Petroleum Chemistry, American Chemical Society, Houston Meeting, Feb 22–27, 1970.

[2] (a) G. A. Burkhardt, *Ber.*, **10**, 144 (1877); (b) R. Wegscheider, *Monatsh. Chem.*, **21**, 621 (1900).

[3] S. Akiyosi, M. Okamura, and S. Hashimoto, *J. Chem. Soc. Jap., Ind. Chem. Sect.*, **57**, 214 (1954); *Chem. Abstr.*, **49**, 2774*a* (1955).

[4] F. C. Whitmore and L. L. Isenhour, *J. Amer. Chem. Soc.*, **51**, 2785 (1929).

[5] L. S. Forney, *J. Org. Chem.*, **35**, 1695 (1970).

[6] The effect of a $-CH_2O-X$ group on the activation of aromatic systems toward electrophilic attack has not been reported. However, the σ_p^+ for phenylacetic acid toward nitration is −0.164 which means the $-CH_2CO_2H$ group is activating relative to H.[7] In contrast, the CH_3O-CH_2- group has been found to have a positive σ^* (0.64) relative to H (0.49).[8] Generally, it is thought that σ^* represents ground-state effects, and as a result the $-CH_2O-X$ is a moderate activator toward electrophilic aromatic substitution.

[7] H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, **80**, 4979 (1958).

[8] P. Ballinger and F. A. Long, *ibid.*, **82**, 795 (1960).

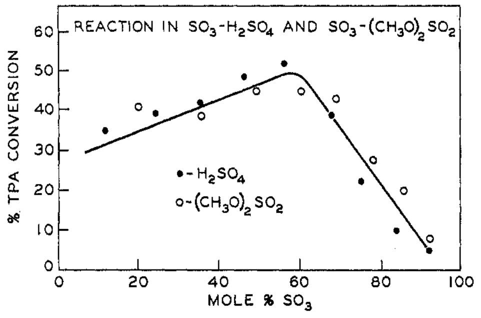

Figure 1.—Yield of 5-carboxyphthalide in sulfuric acid (black dots) and methyl sulfate (open circles) solutions containing varying amounts of SO_3. Conditions were: 1 *M* terephthalic acid and 1 *M* formaldehyde, reacted in sealed glass tubes for 1 hr at 150 ± 0.2°.

terephthalic acid reaction. The results are shown in Table I. Without added metal salts, a 61% conversion to 5-carboxyphthalide was achieved in 2 hr. Addition of Lewis acids gave lower conversions. The results with added Lewis acids are not in accord with a direct electrophilic substitution mechanism, *i.e.*, dependent upon the acid strength of the medium. Were such a system operative, the highest conversion would have been observed with SbF_5, contrary to the observed effect.

TABLE I

EFFECT OF ADDED SALTS ON THE REACTION OF FORMALDEHYDE AND TPA

Salt	% TPA	% 5-CP
None	39	61
$ZnBr_2$	19	55[a]
$FeCl_3$	47	53
$AlCl_3$[b]	46	54
$TiCl_4$	64	36
SbF_5	75	25
NaCl	42	58
LiF	40	60

[a] The products included 26% of a mixture of brominated carboxyphthalides, which was not characterized. [b] The $AlCl_3$ was not completely soluble at the concentration used (0.5 g/5 ml of mixture).

Addition of the neutral salts, NaCl and LiF, did not affect the conversion. Since the highly ionic nature of the oleum medium would be only slightly changed by additional neutral ionic species, no great effect on conversion was expected or observed.

The conversion was quite sensitive to the nature of the solvent used for the reaction. As shown by Table II, the conversions in 30% SO_3–H_2SO_4 and 30% SO_3–dimethyl sulfate were nearly equivalent and much greater than those observed in other media. A moderate conversion was found in 30% SO_3–HSO_3F. On the other hand, 100% HSO_3F, 98% H_2SO_4 (aqueous), HSO_3F–SbF_5 (the so-called "Magic Acid"[9]), and methanesulfonic acid gave uniformly poor results. If the condensation was facilitated by high acid strength, then the fastest rate, and presumably the greatest conversion in 2 hr, would have been observed in HSO_3F–SbF_5.

TABLE II

SOLVENT EFFECT ON THE REACTION OF FORMALDEHYDE AND TPA AT 150° FOR 2 HR

Run	Solvent	% conversion to 5-CP
1	30% SO_3–H_2SO_4	95
2	30% SO_3–dimethyl sulfate	92
3	30% SO_3–HSO_3F	20
4	HSO_3F	3
5	98% H_2SO_4 aqueous	1[a]
6	30% SO_3–methanesulfonic acid	0
7	SbF_5–HSO_3F (1:1)	0
8	100% SO_3	94[b]

[a] Product work-up indicated 12% terephthaloyloxyacetic acid (isolated as the dimethyl ester). [b] The reaction solution was more concentrated than in the other cases (about 6 *M* in TPA and formaldehyde). As a result, this run cannot be directly compared for conversion data.

The unifying features of the solvents listed in Table II seemed to be that relatively high conversions were observed in solvents characterized by their free SO_3 content, with the single exception of methanesulfonic acid. This implies that SO_3 is a critical factor for the condensation. This was confirmed by a reaction in 100% SO_3. The reactant concentration was not comparable with runs 1–7, since the use of 100% SO_3 required a more concentrated reaction medium to prevent a phase separation. However, these conditions provided an excellent conversion (>90%) to 5-carboxyphthalide.

A comparison of the formaldehyde–terephthalic acid condensation in sulfuric acid and dimethyl sulfate media with varying amounts of SO_3 is presented in Figure 1. Two features of the graph are apparent: in both media, equivalent conversions are found at any given SO_3 concentration, despite the great contrast in the nature of these media; the conversion in both solvents reaches a maximum at 60 mol % SO_3 content.

The dependence of the conversion on the SO_3 content of the media strongly suggests that the same mechanism is operative in both sulfuric acid and dimethyl sulfate. In view of the differences in the highly protic (sulfuric acid) and aprotic (dimethyl sulfate) media, this supports the assertion that the condensation is not a direct electrophilic substitution process by a protonated or sulfated formaldehyde species. It must be noted, however, that proton catalysis of the reaction cannot be excluded on the basis of these data, since even in the dimethyl sulfate media some protons were introduced by the dissociation of terephthalic acid in solution.

The formaldehyde condensation was extended to *m*- and *p*-nitrobenzoic acids. The *m*-nitrobenzoic acid is the more reactive to direct electrophilic attack, since its 5 position is not as deactivated as reactive sites in *p*-nitrobenzoic acid.[10] However, no reaction occurred, and *m*-nitrobenzoic acid was recovered unchanged. Formaldehyde condensation with *p*-nitrobenzoic acid under analogous conditions gave a 47% yield of 5-nitrophthalide. This initially was unexpected, since all ring positions of *p*-nitrobenzoic acid are deactivated, as each position is either ortho to a carboxy or nitro group. Thus, the condensation with nitrobenzoic acids does not occur *via* a direct electrophilic attack.

Discussion

From the foregoing results, a mechanistic interpretation of the condensation of formaldehyde with highly

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[9] G. A. Olah and R. H. Schlosberg, *J. Amer. Chem. Soc.*, **90**, 2726 (1968).

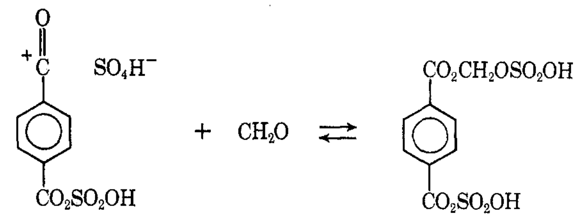
[10] E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., New York, N.Y., 1959, p 428.

deactivated aromatic substrates, such as terephthalic acid, must include the following features: (a) the same mechanism is operative in both oleum and dimethyl sulfate–SO_3 media; (b) the reaction of nitrobenzoic acids does not occur through attack by some free electrophilic formaldehyde species; (c) SO_3 must be intimately involved in the condensation in a role which cannot be played by other Lewis acids such as SbF_5 or $AlCl_3$, etc; and (d) reaction is retarded in fluorosulfonic acid and methanesulfonic acid.

These criteria can be satisfied by formation of an intermediate complex involving the carboxyl function prior to attack on the aromatic nucleus. A hydroxymethyl ester is proposed, formed *via* reaction of formaldehyde with a TPA species as shown in eq 1. Formaldehyde has been suggested to form hydroxymethyl esters with carboxylic acids. Although such products have not been isolated, their postulation aids in understanding the chemistry of formaldehyde in solution.[11] It is worth noting that the electrophilic metalations of benzoic acid and derivatives have been found to occur subsequent to interaction with the carboxyl group. Thus, the thallation of benzoic acid and its esters was recently suggested to occur by initial formation of a thallium–carbonyl complex, followed by intramolecular substitution of thallium into the ortho position of the acid.[12] Similarly, mercuration of terephthalic acid produces the mercurophthalide.[4]

The nature of the aromatic acid, formaldehyde, and proposed formaldehyde ester intermediate cannot be conclusively specified under our reaction conditions. However, acids and esters would certainly be rapidly sulfated in SO_3 media.[13] Indeed, since formaldehyde itself forms a stable complex with SO_3,[14] it is probable that the esterification is a result of a reaction between a formaldehyde–sulfur trioxide complex and the aromatic acid, present as the sulfate or corresponding acylium ion. The acid sulfate of acetic acid in sulfuric acid–SO_3 is converted to the acylium ion at 13–17% SO_3 content at 35°.[15] Under still more acidic conditions, such as SbF_5–HSO_3F mixtures, the diacylium ion of terephthalic acid can be prepared.[16] If the monoacylium ion of terephthalic acid is the reactive species for the esterification, then the rate increase up to 60 mol % SO_3 in either sulfuric acid or dimethyl sulfate may correspond to increasing acylium ion concentrations at higher SO_3 levels. As a consequence of eq 1, this would increase the concentration of the hydroxymethyl ester in solution, and the reaction rate would be enhanced, as shown in Figure 1.

Once formed, the formaldehyde–ester may undergo protonation and loss of water to provide a primary carbonium ion stabilized by association with SO_3, as shown in eq 2 and 3.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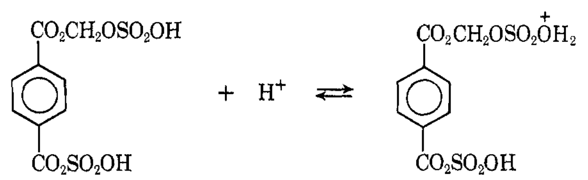
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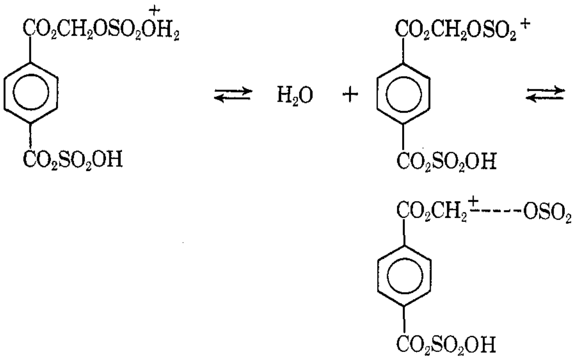
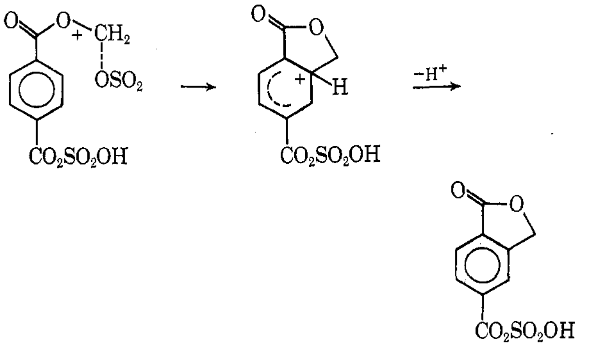

(3)


(4)

Primary carbonium ions are extremely reactive. Therefore, reversal of the stabilized ester species formed in eq 3 to re-form an acylium ion and formaldehyde must be a major reaction pathway. However, proximity to the nucleophilic oxygen of SO_3 should stabilize this primary oxycarbonium ion. Lewis acids lacking nucleophilic oxygens would not be expected to facilitate the reaction because they cannot stabilize this positively charged ester. This is in accord with our results of Table II. Indeed, primary oxycarbonium ions have been found to possess greatly enchanced stabilities, relative to primary carbonium ions in the hydrocarbon series.[17]

Alternative explanations[18] for the lack of catalytic effect from added Lewis acids cannot be ruled out from the experimental data. Thus, the added acid may preferentially form a complex with formaldehyde, decreasing its availability. Or, the Lewis acid may complex with the carboxyl group para to the site of formaldehyde esterification, deactivating the aromatic nucleus toward electrophilic attack. However, we prefer the argument based on the absence of oxygen in the Lewis acids, as noted above. This reasoning is in accord with the decreased reactivity in fluorosulfonic acid and methanesulfonic acid media.

The SO_3 stabilization of the primary oxycarbonium ion allows it to participate in a second reaction pathway,

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(11) J. F. Walker, "Formaldehyde," ACS Monograph Series, No. 159, American Chemical Society, Washington, D. C., 1964.

(12) E. C. Taylor, F. Kiezle, R. L. Robey, and A. McKillop, *J. Amer. Chem. Soc.*, **92**, 2175 (1970).

(13) E. E. Gilbert, *Chem. Rev.*, **62**, 575 (1962).

(14) E. E. Gilbert, "Sulfonation and Related Reactions," Interscience, New York, N. Y., 1965, p 370.

(15) N. C. Deno, C. U. Pittman, Jr., and M. J. Wisotsky, *J. Amer. Chem. Soc.*, **86**, 4370 (1964).

(16) G. A. Olah and M. B. Comisarow, *ibid.*, **88**, 3313 (1966).

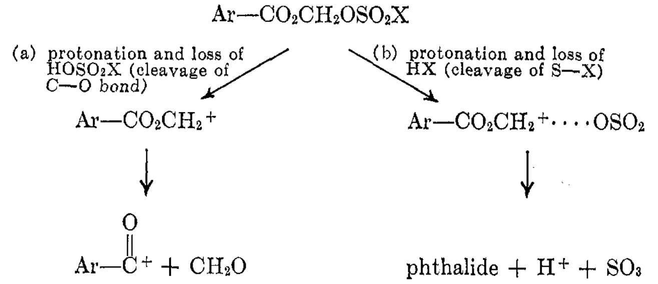
(17) B. G. Ramsey and R. W. Taft, *ibid.*, **88**, 3058 (1966).

(18) Private communication with Min-Hon Rei.

in addition to reversion to reactants. This pathway involves attack on the aromatic ring and leads to phthalide formation (eq 4) by electrophilic attack of the stabilized oxycarbonium ion.

The mechanism described above will reconcile the solvent effects noted in Table I. Formation of the SO_3-stabilized primary carbonium ion (eq 2 and 3) can be generalized to include other solvents as shown below (Scheme I). When X = CH or OCH_3, protonation of these groups followed by their loss as neutral species competes favorably with protonation and loss of $HOSO_2X$ (regeneration of starting materials). Since protonation of F with loss of HF is relatively less likely, the rate of phthalide formation would be expected to decrease in fluorosulfonic acid. Cleavage of the SX bond seems quite unlikely when X = methyl, and as a consequence, little if any phthalide formation is anticipated in methanesulfonic acid.

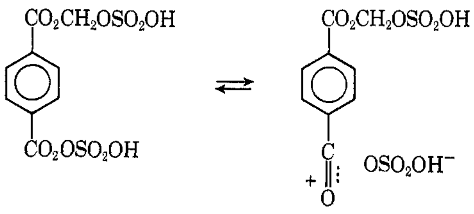
SCHEME I



X = OH in SO_3, H_2SO_4 media
X = OCH_3 in $(CH_3O)_2SO_2$
X = F in HSO_3F
X = CH_3 in HSO_3CH_3

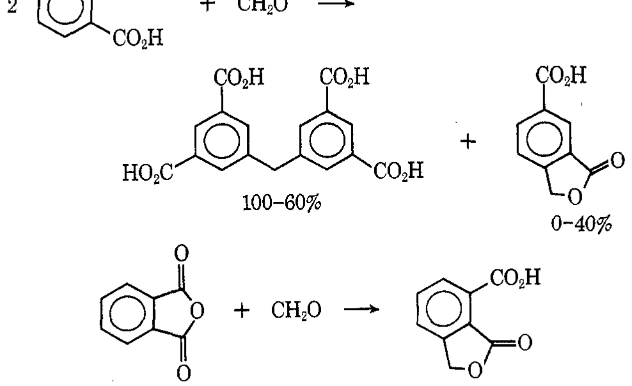
The nitrobenzoic acid condensations can also be understood in terms of a mechanism in which an electrophilic attack on the aromatic ring is preceded by esterification. The carboxyl group must now control the course of the reaction, so that attack occurs only at the 2 and 6 positions. Since a *m*-NO_2 substituent strongly deactivates both these positions, electrophilic attack from an intermediate ester or carboxyl complex should be decreased or prevented in the case of *m*-nitrobenzoic acid. On the other hand, the 2 and 6 positions of *p*-nitrobenzoic acid are less deactivated by the nitro group, relative to the meta isomer. Hence, electrophilic attack on *p*-nitrobenzoic acid by a complex of formaldehyde and a carboxyl group is more likely to occur than attack by the equivalent complex formed from *m*-nitrobenzoic acid. Had the reaction of nitrobenzoic acids not proceeded through a preliminary esterification, the meta isomer should have been the more reactive. Furthermore, the expected product would have been 3,3′-dicarboxy-5,5′-dinitrodiphenylmethane, by analogy of the formaldehyde condensations with benzoic acid to provide 3,3′-dicarboxydiphenylmethane,[19] and with isophthalic acid to provide 3,3′,5,5′-tetracarboxydiphenylmethane.[20]

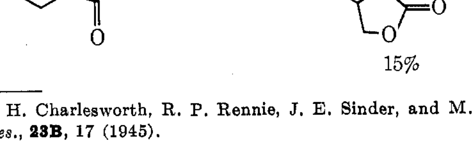
The decreased conversion at SO_3 levels greater than 60 mol %, as shown in Figure 1, can be explained by the formation of an acylium ion of the formaldehyde–ester. Such a reaction will powerfully deactivate the aromatic nucleus toward an electrophilic attack according to eq 4, since this would require an intermediate aromatic dicarbonium ion. Thus the conversion decreases at SO_3 concentrations above 60 mol %.



The mechanistic pathway presented in the foregoing section accounts for the experimental observations on the condensation of formaldehyde with highly deactivated substrates. However, a direct electrophilic substitution reaction of formaldehyde is sufficient to explain diarylmethane formation from benzoic or isophthalic acids, or phthalide formation from activated benzoic acids.[21] Given that a choice of reaction pathways exists for reaction of formaldehyde with more or less deactivated benzoic acids, it should be possible to find intermediate cases where a competition between these reaction pathways can be observed. In this event, some diarylmethane derivatives should be formed by attack of a free electrophilic formaldehyde species, along with some phthalide derivatives derived from a formaldehyde–ester species. Therefore, we reinvestigated the reaction of phthalic and isophthalic acids with formaldehyde.

The reaction of isophthalic acid and formaldehyde was reported to yield only tetracarboxydiphenylmethane.[20] However, we found that with suitable control of conditions, 6-carboxyphthalide was also formed in yields up to 40%. We believe that this substrate represents an intermediate case which can form products by either a "direct" electrophilic substitution reaction (leading to a diarylmethane) or by a substitution reaction involving carboxyl participation (leading to phthalide). As would be expected in such intermediate cases, the partitioning of material between the two reaction pathways is sensitive to experimental conditions. The formaldehyde condensation with phthalic anhydride may represent yet another such intermediate case, as a





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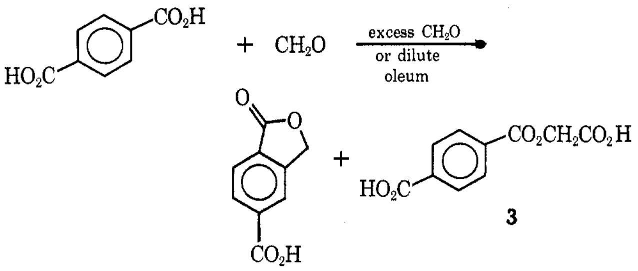
[19] R. W. Beattie and R. H. Manske, *Can. J. Chem.*, **42**, 223 (1964).

[20] J. R. LeBlanc, D. B. Sharp, and J. G. Murray, *J. Org. Chem.*, **26**, 4731 (1961).

[21] E. H. Charlesworth, R. P. Rennie, J. E. Sinder, and M. M. Yan, *Can. J. Res.*, **23B**, 17 (1945).

15% yield of 7-carboxyphthalide results from this reaction.

When the 5-carboxyphthalide synthesis is run with a large excess of formaldehyde, or in dilute oleum mixtures, terephthaloyloxyacetic acid (**3**) appears as a product of the reaction. The isolation of terephthaloyloxyacetic acid under conditions similar to those which provide 5-carboxyphthalide strongly suggest that terephthalic acid is undergoing esterification during the reaction. The formation of **3** indicates that some of the formaldehyde was oxidized to carbon monoxide under



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the reaction conditions. Two reaction pathways involving CO can be envisaged which would lead to terephthaloyloxyacetic acid, as shown below.

$$\begin{tikzcd}
 & & \mathrm{ArCO_2CH_2CO_2H} \\
\mathrm{CH_2O + CO} \arrow[r, shift left, "\mathrm{H^+}"] & \mathrm{HOCH_2COOH} \arrow[l, shift left] \arrow[r, shift left, "\mathrm{ArCO_2H},\ \mathrm{SO_3}"] & \mathrm{ArCO_2CH_2CO_2SO_2OH} \arrow[u, "\mathrm{H_2O}"'] \arrow[l, shift left, "\mathrm{-ArCO_2H},\ \mathrm{-SO_3}"] \arrow[d, shift right, "\mathrm{-CO}"'] \\
 & \mathrm{ArCO_2H + CH_2O + SO_3} \arrow[r, shift left] & \mathrm{ArCO_2CH_2OSO_2OH} \arrow[l, shift left] \arrow[u, shift right, "\mathrm{CO}"'] \arrow[d, "\mathrm{SO_3}"] \\
 & & \text{phthalide}
\end{tikzcd}$$

No distinction can be made at this time between a reaction involving CO attack on the hydroxymethyl ester and a reaction involving esterification with hydroxyacetic acid formed previously by attack of CO and CH_2O under the reaction conditions. The latter process is similar to the synthesis of hydroxyacetic acid by the acid-catalyzed carbonylation of formaldehyde.[22] Although much higher temperatures and CO pressures are required in that process than we observe during 5-carboxyphthalide synthesis, the yields of terephthaloyloxyacetic acid are improved by reaction under CO pressure.

Recently, cyclohexanecarboxylic acid was shown to undergo decarbonylation in fuming sulfuric acid at 25°.[23] This agrees with our observation that hydroxyacetic acid reacts with terephthalic acid in fuming sulfuric acid to give a small yield of 5-carboxyphthalide. Since this reaction could only occur with decarbonylation, it indicates that the carbonylation of the terephthalic acid–formaldehyde ester is reversible, as indicated.

Experimental Section

Materials.—Aromatic substrates, formaldehyde (trioxane), cosolvents, and sulfur trioxide (Sulfan-B) were commercial products of the highest purity attainable.

The sulfur trioxide was stored in a vessel jacketed in boiling pentane (36°) to prevent crystallization catalyzed by traces of water.

Methods.—The preparation of phthalides from phthalic acids and nitrobenzoic acids was carried out according to the method described for the reaction with terephthalic acid.[5]

The effect of added salts on the 5-carboxyphthalide synthesis (Table I) was obtained from reactions conducted in sealed glass tubes. Solutions (5 ml) of 30% oleum, containing 1 *M* terephthalic acid and 1 *M* formaldehyde, and 0.5 g of salts were placed in a bath at 150 ± 0.2° for 2 hr. The products were converted to methyl esters and analyzed by gas chromatography. Material balances based on aromatics were all above 76%, and in most cases, 86–94%.

The experiments in various solvents (Table II) also were conducted for 2 hr at 150 ± 0.2°, in sealed glass tubes. Except as noted, the solutions were 1 *M* in terephthalic acid and 3 *M* in formaldehyde and were worked up as described above. Material balances, based on aromatics, were 79–90%.

Effect of CO on Preparation of Terephthaloyloxyacetic Acid (3).—Terephthalic acid (8.3 g, 0.05 mol) and formaldehyde (4.5 g, 0.30 mol of Trioxane) in 50 ml of 98% sulfuric acid were placed under 1000 psi of CO in a glass-lined pressure vessel.

After heating to 150° for 2 hr the contents of the vessel were poured into ice water, converted to methyl esters (MeOH–BF_3), and analyzed by gas chromatography. The product mixture contained 94% dimethyl terephthalate and 5% dimethyl terephthaloyloxyacetic acid. When this procedure was carried out in the absence of CO, only dimethyl terephthalate could be isolated.

Registry No.—Formaldehyde, 50-00-0; terephthalic acid, 100-21-0; **1**, 4792-29-4; **2**, 16776-76-4.

Acknowledgments.—The authors thank Mobil Chemical Company for permission to present this work, Mr. Ronald J. Gustafson for his technical assistance, and Professors O. L. Chapman and D. S. Noyce for valuable discussions while this work was in progress.

(22) D. J. Loder, U. S. Patent 2,152,852 (1939).

(23) M. I. Vinnik, R. S. Ryabova, and V. I. Ganina, *Zh. Fiz. Khim.*, **42**, 2916 (1968); *Chem. Abstr.*, **70**, 46570 (1969).