The Reaction of 1-Tetralones with Palladium/Carbon[1]

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The dehydrogenation of 1-tetralone [3,4-dihydro-1(2*H*)-naphthalenone] and similar α,β-unsaturated ketones is generally thought to give predominantly phenolic products rather than arenes. Conditions (absence of solvent, 260°, and palladium/carbon catalyst) are described that provide the arene as the major product. Steric interference to palladium/carbon dehydrogenation was observed in 4,5-dimethyl derivatives.

Dehydrogenation of cyclic ketones may lead to arenes or, with retention of oxygen, to phenolic compounds or neutral oxygen-containing condensation products. The nature of the dehydrogenation product is governed by the structure and stereochemistry, the type of dehydrogenating agent, the reaction temperature, the presence of hydrogen acceptor and/or sulfur compounds, and the solvent (if any).[3]

Exclusive formation of phenolic compounds as contrasted to conversion to arenes has been reported for the following dehydrogenations: 1-tetralone with Se[4a] or S,[4b] 3-methyl-1-tetralone with Se[4c,d] or S,[4d] 6-methyl-1-tetralone with Pd/C,[4e] 7-methyl-1-tetralone with S[4f] or Pd/C,[4g] 5,7-dimethyl-1-tetralone with Se,[4h] and 5,8-dimethyl-1-tetralone with Se[4h] or S.[4f] Other studies using Pd/C catalyst in high-boiling solvents (*p*-cymene, triethylbenzene, and phenyl ether) gave good yields of phenolic materials from di- and trialkylcyclohexenones,[3e] 1-tetralone,[5a] and 2,6-dibenzylidenecyclohexanone.[5b] The formation of 1-naphthol from 1-tetralone (**1**) during catalytic dehydrogenation has been rationalized[5a] as proceeding through the enol. We have observed that 1-naphthol also is dehydrogenated to naphthalene.

Pd/C-catalyzed dehydrogenation of 1-tetralones in the absence of solvent may give the corresponding naphthalene. Examples include reaction of **1** (77% and 37% yields)[3a,5a] and 7-methyl-1-tetralone (34%)[5c] and our earlier[1] dehydrogenation of 2,5,8-trimethyl-1-tetralone (**8**), 3,5,8-trimethyl-1-tetralone (**9**), and 4,5,8-trimethyl-1-tetralone (**10**) to the corresponding naphthalenes.

As pointed out by Linstead and Michaelis,[5a] the direct conversion of 1-tetralones to naphthalenes could be a useful synthetic route since it bypasses two steps of the usual procedure

tetralone $\longrightarrow$ tetralol $\longrightarrow$ dihydronaphthalene $\longrightarrow$ naphthalene

With this in mind, **1** and a series of eleven methyl-substituted 1-tetralones were dehydrogenated under conditions conducive to loss of oxygen, *i.e.*, no solvent,[5a] high temperature,[5a] and a Pd/C catalyst, to determine the effect of methyl substitution on the stereochemistry and utility of the reaction. Exploration of a direct and efficient formation of arenes from 1-tetralones was of interest in our synthesis of hydrocarbons for the Standard Samples Program of the American Petroleum Institute.[6a]

The data of Table I show that the yields of naphthalenes from 1-tetralones are indeed influenced by methyl-group substitution but that significant hindrance to formation of arene results only from substituents concurrently present at positions 4 and 5 as illustrated by the decreased yields obtained from **10** and **11**. As has been pointed out, such substituents at positions 4 and 5 are believed to introduce sufficient steric crowding to cause conformational distortion of the substituted tetralone.[6c] Resistance of **10** and **11** to dehydrogenation under the conditions used is possibly due to inadequate contact with the catalyst surface or the inability of the incipient 4,5-dimethyl interaction to facilitate formation of the more planar enol form.

Steric inhibition to dehydrogenation of the monomethyl-1-tetralones **2**, **3**, and **4** appears to be absent; indeed, the presence of a methyl group actually improves the combined yield of steam-volatile dehydrogenation products for **2** and **3**. In particular, the 44% yield of 2-methylnaphthalene and the 35% yield of 2-methyl-1-naphthol from **2** shown in Table I provide an interesting contrast to the 0 and 47% yields of these products from the action of molten KOH–NaOH on **2**.[6b]

As seen from Table I, a nonsteam-volatile residue was obtained in significant yield in many cases. Attempts to identify the dimeric products existing in the tar fraction from **1** have been inconclusive. The glc analysis

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[1] E. J. Eisenbraun and C. W. Hinman, *Amer. Chem. Soc., Div. Petrol. Chem., Prepr.*, **10**, No. 1, 33 (1965).

[2] (a) American Petroleum Institute Graduate Research Assistantship 1965–1967; (b) NSF Graduate Trainee 1967–1968; (c) American Chemical Society Petroleum Research Fund Fellow, GF 395, 1968–1969; (d) API GRA, 1962–1965; (e) deceased.

[3] (a) P. N. Rylander and D. R. Steele, *Engelhard Ind. Tech. Bull.*, **9**, 50 (1968); (b) R. P. Linstead, K. O. A. Michaelis, and S. L. S. Thomas, *J. Chem. Soc.*, 1139 (1940); (c) R. P. Linstead, *Ann. Rep.*, **33**, 294 (1936); (d) H. Adkins, L. M. Richards, and J. W. Davis, *J. Amer. Chem. Soc.*, **63**, 1320 (1941); (e) E. C. Horning, M. G. Horning, and G. N. Walker, *ibid.*, **71**, 169 (1949); (f) E. C. Horning and M. G. Horning, *ibid.*, **69**, 1359 (1947); (g) L. M. Jackman, *Advan. Org. Chem.*, **2**, 352 (1960).

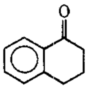
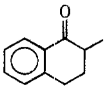
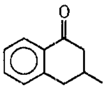
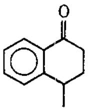
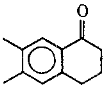
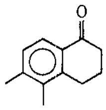
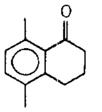
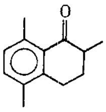
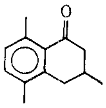
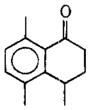
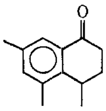
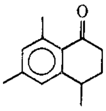
[4] (a) N. N. Vorozhtsov and V. A. Koptyug, *Zh. Obshch. Khim.*, **28**, 98 (1958); (b) G. Darzens and G. Levy, *C. R. Acad. Sci.*, **194**, 181 (1932); (c) P. P. T. Sah, *Z. Vitamin-, Hormon- Fermentforsch.*, **3**, 324 (1950); (d) M. Tishler, L. F. Fieser, and N. L. Wendler, *J. Amer. Chem. Soc.*, **62**, 2866 (1940); (e) G. Di Modica and S. Tira, *Ann. Chim. (Rome)*, **46**, 838 (1956); *Chem. Abstr.*, **51**, 6578*c* (1957); (f) L. Ruzicka and H. Waldmann, *Helv. Chim. Acta*, **15**, 907 (1932); (g) L. Ruzicka and E. Morgeli, *ibid.*, **19**, 377 (1936); (h) W. Cocker, B. E. Cross, J. T. Edward, D. S. Jenkinson, and J. McCormick, *J. Chem. Soc.*, 2355 (1953).

[5] (a) R. P. Linstead and K. O. A. Michaelis, *ibid.*, 1134 (1940); (b) E. C. Horning, *J. Org. Chem.*, **10**, 263 (1945); (c) J. A. Corran and W. B. Whalley, *J. Chem. Soc.*, 4719 (1958).

[6] (a) Correspondence regarding samples of the hydrocarbons mentioned in this paper should be directed to A. J. Strieff, API Samples office, Carnegie-Mellon University, Schenley Park, Pittsburgh, Pa.; (b) J. M. Springer, C. W. Hinman, E. J. Eisenbraun, P. W. K. Flanagan, and M. C. Hamming, *J. Org. Chem.*, **35**, 1260 (1970); (c) G. D. Johnson, S. Searles, and W. C. Lin, *ibid.*, **27**, 4031 (1962); (d) E. Mosettig and H. M. Duvall, *J. Amer. Chem. Soc.*, **59**, 367 (1937); (e) R. D. Haworth, *J. Chem. Soc.*, 1125 (1932); (f) E. J. Eisenbraun, C. W. Hinman, J. M. Springer, J. W. Burnham, T. S. Chou, P. W. Flanagan, and M. C. Hamming, *J. Org. Chem.*, in press.

TABLE I

THE REACTION OF 1-TETRALONES WITH Pd/C

Structure number	Structure	Corresponding naphthalene,[a] %	Corresponding naphthol,[b] %	Nonsteam-volatile material,[c] %	Glc product ratio[d]
1		37	18	27	14
2		44	35	10	14
3		46	47	4	12
4		35	22	34	33
5		46	7	43	11
6		29	11	52	13
7		48	*e*	28	3
8		43	*e*	33	5
9		44	*e*	34	17
10		<4	*f*	7	0.05
11		13	*f*	33	0.24
12		51	*f*	28	4

[a] Determined by comparison of glc peak areas with those obtained from standard solutions. Yields are independent of unreacted tetralones (*cf.* last column of this table). [b] Yield determined gravimetrically except as noted. [c] Yield of nonsteam-volatile material determined gravimetrically after steam distillation. [d] Ratio of glc peak areas of corresponding naphthalene and the accompanying tetralone. The relative peak area of the tetralone is taken as 1. [e] The corresponding naphthol was shown to be present by glc but it was not extracted by 10% NaOH. [f] Glc studies indicated the corresponding naphthol was not present.

indicates three components represented by two minor peaks of similar retention time and a major peak several minutes removed. The mass spectrum shows a major molecular ion at m/e 268 ($C_{20}H_{12}O$) and a minor one at m/e 254 ($C_{20}H_{14}$). Finally, the glc retention times of the minor components are similar to those of authentic samples of binaphthyls (mol wt 254, $C_{20}H_{14}$). Thus, the evidence indicates the presence of such structures. The mass spectra of dimeric products from **1**, **5**, **9**, and **11** are given in Table II.

TABLE II

MASS SPECTRAL CORRELATION OF DIMERIC RESIDUES FROM Pd/C DEHYDROGENATIONS

Starting material	Molecular ion peak of product	Fragmentation peaks[a]
1	268[b]	269 (23), 268 (100), 254 (64), 252 (19), 239 (18)
5	326	326 (67), 156 (40), 45 (39), 31 (100), 18 (65)
9	352	352 (79), 337 (100), 176 (98), 168.5 (58), 161 (42)
11	366[c]	367 (32), 366 (100), 365 (81), 353 (43), 352 (42)

[a] 70 eV m/e (rel intensity). [b] Also m/e 254. [c] Also m/e 338.

The Pd/C dehydrogenation studies were extended to 2-tetralone, 3,4-dihydro-1(2*H*)-phenanthrenone (**13**), 1,2,3,4-tetrahydro-2,5,8-trimethyl-1-naphthol (**17**), 1,2,-3,4-tetrahydro-3,5,8-trimethyl-1-naphthol (**19**), and 1,-2,3,4-tetrahydro-4,5,8-trimethyl-1-naphthol (**20**) as shown in Schemes I and II, respectively.

The dehydrogenation (Pd/C) of 2-tetralone gave naphthalene (54%) and 2-naphthol (26%).

The Pd/C dehydrogenation of **13** (Scheme I) gave 18% of **14** and a trace of **15**. In the presence of naphthalene, Pd/C caused dehydrogenation to a mixture of 71% of **14** and 11% of **16** but **15** was not found. Dehydrogenation of **16** with Pd/C using naphthalene as solvent gave 83% of **14**. The improved yield of **14** when naphthalene was used confirms an earlier report.[6d]

The tetrahydrotrimethylnaphthols **17** and **19** are completely dehydrogenated to 1,4,6-trimethylnaphthalene (**18**) in 8 hr (Scheme II). However, **20**, with its 4,5-dimethyl substitution, is considerably more resistant to dehydrogenation to 1,4,5-trimethylnaphthalene (**21**); only 35% conversion took place in 8 hr. There was no evidence that the corresponding naphthols were formed during the dehydrogenation of **17**, **19**, or **20**.

Experimental Section[7]

The tetralones used in the study were either purchased from commercial sources or prepared as described.[6b,f] 3,4-Dihydro-1(2*H*)-phenanthrenone (**13**) was prepared by Friedel-Crafts reaction of naphthalene and succinic anhydride.[6d,e] The Pd/C catalysts were purchased from Engelhard Industries.

Naphthalene, 1-methylnaphthalene, 2-methylnaphthalene, 2,3-dimethylnaphthalene, and 1,4-dimethylnaphthalene were commercially available. The other naphthalenes necessary for the preparation of standard solutions for glc analyses were prepared from the corresponding 1-tetralones by Clemmensen reduction and subsequent Pd/C dehydrogenation to 1,4,5- and 1,4,6-trimethylnaphthalene; Pd/C catalytic hydrogenation to the tetralin and subsequent dehydrogenation to give 1,3,5- and 1,3,8-trimethylnaphthalene; and Pd/C dehydrogenation of 5,7-

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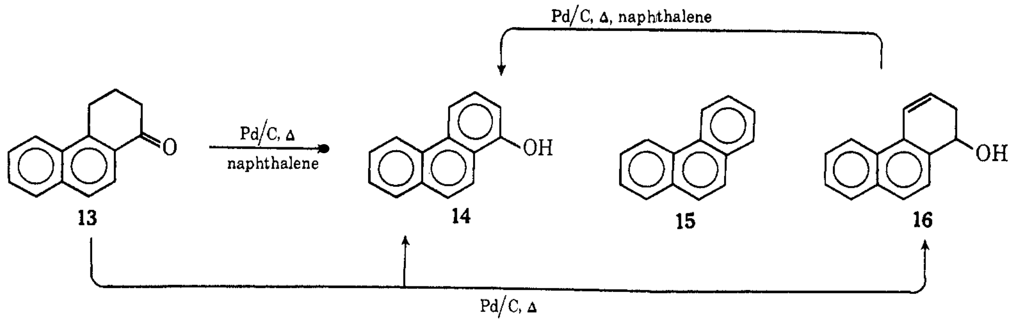
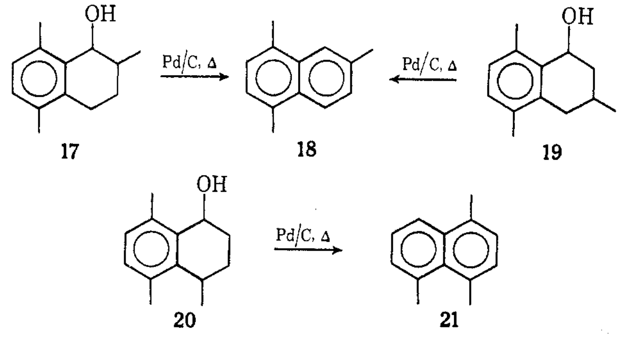
[7] Elemental analyses were determined by Galbraith Laboratories, Knoxville, Tenn. Nmr spectra were determined on Varian HR-60 and A-60 spectrometers. Mass spectrometric data were compiled using a Consolidated Electrodynamics Corp. Model 21-103C mass spectrometer. Ir and uv spectra were obtained on Beckman IR-5A and Cary 14 spectrophotometers, respectively. Melting points are corrected. Glc studies were carried out on a 0.25-in. × 4-ft column of SE-30 on Chromosorb P and/or a 0.25-in. × 6-ft column of 5% silicone rubber on acid-washed, DMCS-treated Chromosorb W. Glc separations were done on a 10-ft × 0.25-in. column of 25% Carbowax 20M on acid-washed Chromosorb W.

SCHEME I



SCHEME II



dimethyl-1-tetralone to 1,3-dimethylnaphthalene. The physical and spectral properties of some of these naphthalenes and their tetrahydro derivatives will be published subsequently.[6f]

General Procedure for Pd/C Reactions. A. Apparatus and Procedure.—A 25-ml, three-necked, round-bottomed flask fitted with reflux condenser and a gas-inlet tube serves as the reaction vessel. Tygon tubing is attached to gas-inlet and gas-exit ports. A 5-g sample of tetralone and 0.5 g of Pd/C are used. A fast flow of helium is used initially to sweep out the system, and the helium flow then is lessened to maintain a slight positive pressure. The flask is lowered into a Wood's metal bath preheated to 70° and the bath temperature (by pyrometer and thermocouple probe as a safety measure) is raised rapidly (15-20°/min) to 260° and held stationary. After being heated for 4 hr, the reaction mixture is allowed to cool under helium atmosphere. Severe bumping due to water formed in the reaction can be lessened or eliminated by submerging the reaction flask into the bath far enough that the level of the molten metal is approximately 0.5 in. above that of the liquid in the flask.

B. Work-up for Tetralones 1, 2, 3, and 5 (Table III[8]).—The cooled reaction mixture is extracted successively with ether and chloroform and the solution is filtered through Dicalite. The filtrate is washed thoroughly with 10% NaOH solution. The alkaline wash then is back-extracted with ether and the ether solutions are combined. The alkaline solution is acidified with concentrated hydrochloric acid and extracted with ether. The extract is washed with water, dried ($MgSO_4$), filtered, and concentrated to give the phenolic material. The naphthol is purified by recrystallization from petroleum ether (bp 60-68°) and/or sublimation.

TABLE III

PROPERTIES OF NAPHTHOLS[a] PRODUCED IN Pd/C DEHYDROGENATION OF 1-TETRALONES

	Mp, °C	Mass spectrum[b]
1-Naphthol	95-96.5[c]	144 (100), 116 (42), 115 (94), 89 (12), 39 (13)
2-methyl-	62-63.5[d]	158 (100), 157 (23), 129 (38), 128 (36), 115 (21)
3-methyl-	90.5-93.5[e]	158 (100), 157 (23), 129 (29), 128 (28), 115 (22)
4-methyl-	75-78[f]	158 (100), 157 (46), 144 (35), 115 (40), 128 (30)
5,7-dimethyl-	55-59[g,h]	172 (100), 157 (30), 129 (24), 128 (22), 115 (14)
6,7-dimethyl-	138.5-140[i]	172 (100), 171 (13), 157 (27), 129 (23), 128 (22)

[a] Isolated by extraction of Pd/C dehydrogenation reaction mixtures with 10% NaOH. [b] 70 eV *m/e* (rel intensity). [c] Lit.[8a] 94°. [d] Lit.[8b] 64-65°. [e] Lit.[8c] 92.5-93.5°. [f] *Anal.* Calcd for $C_{11}H_{10}O$: C, 83.51; H, 6.37. Found: C, 83.44; H, 6.47. Lit.[8b] 84-85°. [g] Monohydrate, lit.[4h] 58-59°. [h] Lit.[8a] 79-80°. [i] Lit.[8d] 140°.

The main ethereal filtrate is washed with water, dried ($MgSO_4$), filtered, and concentrated to 50 ml by distillation. Percentage yields are determined using standard solutions as described for the KOH-NaOH reactions.[6f]

The concentrate then is thoroughly steam distilled and the nonvolatile residue dissolved in ether. The ether solution is dried ($MgSO_4$), filtered, and concentrated to yield the tar residue.

C. Modification Used for 4, 6, and 7.—Part B is modified by subjecting the alkali-washed extract to thorough steam distillation. The resulting residue is treated as before. The steam distillate is extracted with ether and the ether extract is dried ($MgSO_4$), filtered, and concentrated to 50 ml by distilling. The percentage yield of the naphthalene is determined as before.

D. Modification Used for 8, 9, 10, 11, and 12.—More chloroform than usual is needed to dissolve the reaction products from the trimethyl-1-tetralones. In order to avoid chloroform as the solvent for standard and unknown solutions, it is removed by steam distillation of the ether-chloroform filtrate. The nonvolatile residue and the steam distillate are treated as before. Washing with 10% NaOH solution does not remove the naphthol in these cases.

Pd/C Dehydrogenation of 2-Tetralone to Naphthalene and 2-Naphthol.—Dehydrogenation of 3 g of 2-tetralone for 11 hr at 250-282° gave 2.22 g of residue and a steam-volatile fraction which did not contain 2-tetralone but showed 2:1 ratio of glc peaks corresponding to naphthalene and 2-naphthol.

Deoxygenation of 1-Naphthol.—Naphthol (8.57 g) was treated with Pd/C (0.86 g) for 4 hr at 265° under He. Naphthalene was isolated by steam distillation and extraction of the steam distillate. The nonvolatile residue (5.85 g) of brown oil was recrystallized from 1:3 benzene-ethanol to yield a yellow powder: mp 165-175°; mass spectrum (70 eV) *m/e* (rel intensity) 268 (11), 255 (21), 254 (100), 252 (29), and 28 (44).

Pd/C Dehydrogenation of 3,4-Dihydro-1(2*H*)-phenanthrenone (13).—A 2-g sample of **13** was dehydrogenated with 0.067 g of 5% Pd/C at 220-225° for 24 hr. The products were isolated (*cf.* part B above) and yielded 0.36 g (18% yield) of 1-phenanthrol (**14**): mp 154.5-156° [lit.[6d] 153-154°]; mass spectrum (70 eV) *m/e* (rel intensity) 194 (95), 165 (78), 43 (100), 29 (24), 28 (26), and 15 (37). The material extracted from the basic solution gave 0.56 g of a mixture of **13** and **15**. This mixture was identified by glc on a 0.25-in. × 4-ft column of SE 30 on Chromosorb P at 190°. Considerable tar remained in the sublimation tube.

Pd/C Dehydrogenation of 3,4-Dihydro-1(2*H*)-phenanthrenone (13) in the Presence of Naphthalene.—A 2-g sample of **13**, 20 g of naphthalene, and 0.067 g of 5% Pd/C were treated as described in the previous experiment except that the filtered product was steam distilled to remove naphthalene. The base-soluble product

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[8] (a) "Dictionary of Organic Compounds," 4th ed, I. Heilbron, Ed. Oxford University Press, New York, N. Y., 1965, p 2378; (b) J. W. Cornforth, R. H. Cornforth, and R. Robinson, *J. Chem. Soc.*, 168 (1943); (c) B. R. Baker and G. H. Carlson, *J. Amer. Chem. Soc.*, **64**, 2657 (1942); (d) E. A. Coulson, *J. Chem. Soc.*, 1305 (1938).

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.

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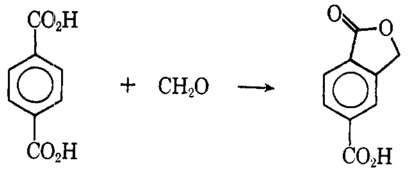
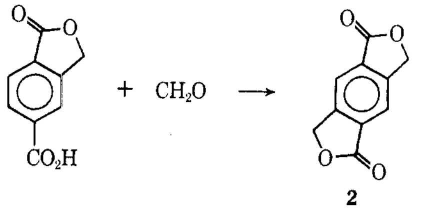
The reaction of formaldehyde with benzoic acids bearing electron-withdrawing groups has been shown to provide phthalide derivatives. The reaction media must contain sulfur trioxide. Evidence is presented to show that an intermediate is formed prior to the electrophilic attack which involves the carboxyl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



1



2

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 $\sigma_p{}^+$ 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).