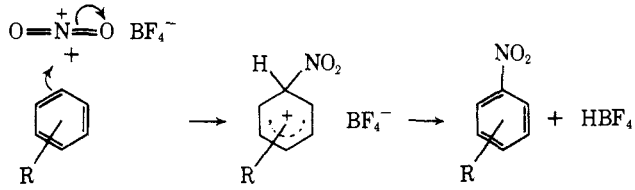

σ bond. Thus the higher reactivity and lower selectivity of the nitronium ion nitration can be explained.

Experimental Section

Materials. Nitromethane, boron trifluoride, methyl nitrate, benzene, alkylbenzenes, and their nitro derivatives are, except stated below, commercial materials. They were, whenever necessary, purified before use. Nitromethane was purified as described previously.[47] 2-Iodo-*p*-xylene and 2-fluoro-*p*-xylene were prepared by Sandmeyer and Schiemann reactions, respectively, from 2,5-dimethylaniline. Nitro-2-methoxy- and nitro-2-halo-*p*-xylenes were prepared from the corresponding nitro-2-amino-*p*-xylenes.[48] Nitro-1,2,3-trimethylbenzenes,[49] nitro-1,2,4-trimethylbenzenes,[49] nitrotetramethylbenzenes,[23a] and nitropentamethylbenzene[23a] were prepared according to the procedures reported. Chloro-, bromo-, and iododurenes were prepared by the method of Tohl.[50] Methoxydurene and fluorodurene were prepared from aminodurene, which was obtained by reduction of nitrodurene. 6-Nitro 3-substituted durenes were prepared by the nitration of the corresponding substituted durenes with the nitrating agent described by Olah and Lin.[23a]

Procedure for Competitive Nitration. In a typical experiment, 10 mmol of benzene, 10 mmol of toluene, and 1 mmol of methyl nitrate were mixed with 45 ml of nitromethane. Into this solution, 1.5 mmol of boron trifluoride in a 5-ml nitromethane solution was added. The reaction mixture was vigorously stirred and the temperature was kept constant at 25° during the reaction. The reaction time was generally 50 min. After that, the reaction solution was quenched with ice–water, extracted with ether, washed with 5% sodium bicarbonate solution, dried over magnesium sulfate, concentrated, and analyzed by gas–liquid chromatography.

Analytical Procedure. The analyses of all products were carried out by gas–liquid chromatography, using a Perkin-Elmer Model 900 gas chromatograph equipped with a hydrogen flame ionization detector and either open tubular capillary columns or packed column. Peak areas were obtained with an Infotronics Model CRS-100 electronic printing integrator. Relative response data were determined as described previously.

Characteristic retention times of the nitro compounds along with type of columns conditions are listed in Table V.

Acknowledgment. Support of our work by a grant of the U. S. Army Office of Research, Durham, N. C., is gratefully acknowledged.

(47) G. A. Olah, S. J. Kuhn, S. H. Flood, and B. A. Hardie, *J. Amer. Chem. Soc.*, **86**, 1039 (1964).
(48) R. van Helden, P. E. Verkade, and B. M. Wepster, *Recl. Trav. Chim. Pays-Bas*, 73, 39 (1954).
(49) M. Dolinsky, J. H. Jones, C. D. Ritchie, R. L. Yates, and M. A. Hall, *J. Ass. Offic. Anal. Chem.*, **42**, 709 (1959).
(50) A. Tohl, *Ber.*, **25**, 1521 (1892).

Synthesis of *trans*-3,4-Dihydroxy-3,4-dihydrobenzoic Acid[1]

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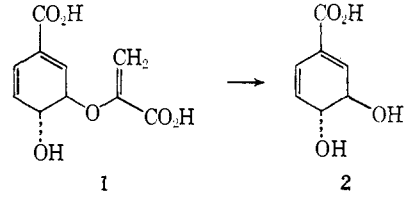
Abstract: The synthesis of racemic *trans*-3,4-dihydroxy-3,4-dihydrobenzoic acid (**2**) is described. Reaction of *trans*-1,2-dihydrophthalic acid (**3**) with excess peracid afforded **4** that was converted to the mono methyl ester **6** *via* anhydride **5**. Decarboxylation of **6** gave iodide **7**. Reaction of **7** with zinc dust afforded **8** as an unstable complex that, on treatment with triethylamine, was converted to **9**. Hydrolysis of **9** with aqueous potassium hydroxide and acidification gave racemic **2**. Monoepoxidation of **3** afforded **14** that reacted with hot methanol to give **16**.

Chorismic acid (**1**) is the branch point intermediate in the biosynthesis of aromatic amino acids and growth factors in bacteria.[2-4] The importance of **1** in the biosynthesis of aromatic substances in other microorganisms and plants has become apparent.[2-5] One of the enzymic transformations of **1** is the cleavage of the enolpyruvyl group giving *trans*-3,4-dihydroxy-3,4-dihydrobenzoic acid (**2**).[4,6,7] The acid-catalyzed conversion of **1** to **2** has also been observed.[4]

The metabolic function of **2** is not clearly understood. It may play a part, directly or indirectly, in metal metabolism.[4] Attempts to demonstrate that **2** is a precursor of 3,4-dihydroxybenzoic acid in *Aerobacter aerogenes* have not been successful.[8]

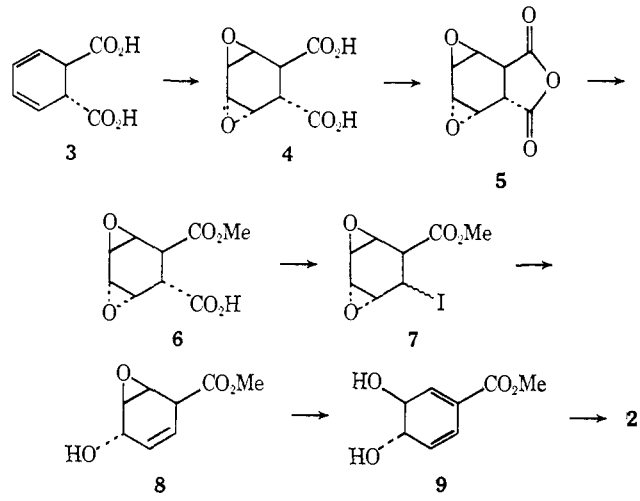
Scheme I



Because of our interest in the intermediates in the biosynthesis of aromatic amino acids and growth factors in microorganisms and plants, a synthesis of racemic **2** has been accomplished.[9] The synthetic sequence is outlined in Scheme II.

(1) Financial support from the National Institutes of Health, Grant No. 1R01-GM19103, and from Hoffmann-LaRoche, Inc., Nutley, N. J., is gratefully acknowledged.
(2) F. Gibson and J. Pittard, *Bacteriol. Rev.*, **32**, 465 (1968).
(3) F. Lingens, *Angew. Chem.*, 80, 384 (1968); *Angew. Chem., Int. Ed. Engl.*, 7, 350 (1968).
(4) I. G. Young, F. Gibson, and C. G. MacDonald, *Biochim. Biophys. Acta*, **192**, 62 (1969).
(5) R. G. H. Cotton and F. Gibson, *Biochim. Biophys. Acta*, **156**, 187 (1968).
(6) Reaction catalyzed by extracts from *Aerobacter aerogenes*. The absolute configuration of **1** and **2** is that shown in Scheme I.
(7) I. G. Young and F. Gibson, *Biochim. Biophys. Acta*, **177**, 182 (1969).
(8) 3,4-Dihydroxybenzoic acid is formed from dehydroshikimic acid rather than *via* the shikimic acid → **1** pathway: see ref 4 and references cited therein.
(9) The synthesis of racemic *trans*-2,3-dihydroxy-2,3-dihydrobenzoic acid has also been completed: R. M. DeMarinis, C. N. Filer, S. M. Waraszkiewicz, and G. A. Berchtold, *J. Amer. Chem. Soc.*, **96**, 1193 (1974).

Scheme II

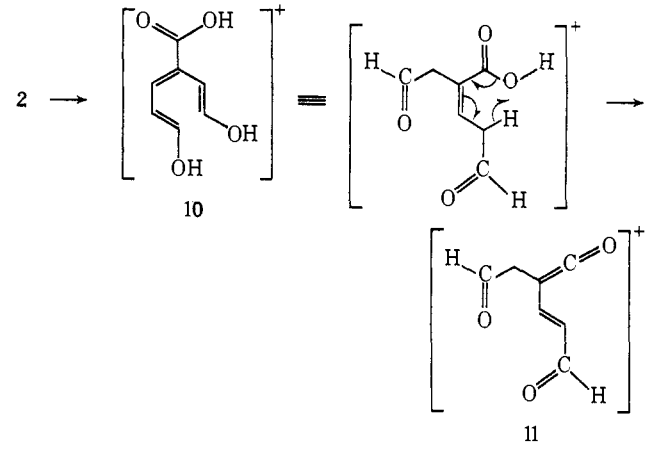


Epoxidation of *trans*-1,2-dihydrophthalic acid (**3**) with excess *m*-chloroperbenzoic acid in ethyl acetate gave, in 84% yield, a single, crystalline bis epoxide (**4**), the stereochemistry of which is discussed later. Trifluoroacetic anhydride smoothly converted **4** to anhydride **5**. That epimerization did not occur to form the cis anhydride was established by treatment of **5** with water to regenerate **4**. Reaction of **5** with methanol afforded **6** in quantitative yield.

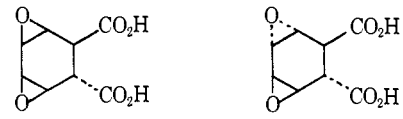
Decarboxylation of **6** to iodide **7** (stereochemistry undetermined) was effected by Barton's procedure[10] of irradiation after treatment with *tert*-butyl hypoiodite. The reaction presumably involves photolysis of the acyl hypoiodite to afford the acyloxy radical and subsequent loss of carbon dioxide to form the corresponding carbon radical that is captured by iodine. The carbon radical derived from **6** is apparently captured by iodine in preference to cleavage of the adjacent epoxy group to give **8**, a reaction known to occur with oxirylcarbinyl radicals.[11] Generation of the carbon radical by treatment of iodide **7** with tri-*n*-butyltin hydride and chromatography on silica gel did in fact give a mixture of **8** and **9**. When the reaction mixture was chromatographed on Florisil, a mixture of **9** and aromatic material was obtained. A more convenient procedure involved treatment of **7** with zinc dust in ether containing acetic acid to afford **8** as an unstable complex with zinc iodide. The complex was treated with triethylamine in ether at room temperature to give **9** in 51% yield from **7**. Hydrolysis of **9** with aqueous potassium hydroxide at room temperature and acidification afforded racemic **2** (74%) that was characterized by analysis and comparison of spectral data with that reported for **2** derived from **1**.[4]

The metastable peaks in the mass spectrum of **2** indicate two competing pathways of decomposition,[4] one of which involves initial loss of water to form the molecular ion of 3- or 4-hydroxybenzoic acid. The second pathway involves formation of an ion (*m/e* 138) by loss of water followed by three successive losses of 28 or 29 mass units to give ions of high intensity at *m/e* 110 (100%), 109 (28%), 82 (76%), 81 (83%), 54 (21%), and 53 (61%). The fragmentation pattern suggests electron impact causes cleavage of the C_3–C_4 bond and the formation of the 3,4-secodihydrobenzoic acid molecular ion, radical **10** (Scheme III), which readily loses water to form an ion such as **11** from which the successive loss of CO and CHO units would be expected.[12]

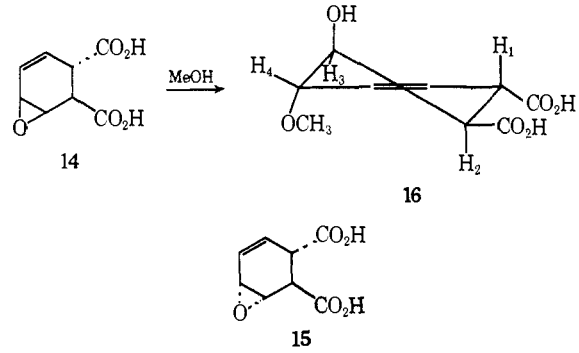
Scheme III



The assignment of stereochemistry to the product from bis epoxidation of **3** as that indicated by **4** rather than **12** or **13** was based on the following evidence. Reaction of **3** with singlet oxygen and thermal rearrangement of the endoperoxide afforded **12**, the



properties of which differ from those of **4**.[14] Epoxidation of **3** with 1 equiv of *m*-chloroperbenzoic acid gave **14** (and not **15**) in high yield, and **14** was converted to **4** on further epoxidation. Epoxide **14** reacted with



methanol under reflux to give a crystalline methoxy alcohol assigned structure **16** on the basis of the nmr spectrum that showed $J_{H_1-H_2}$ = 10 Hz and $J_{H_2-H_3}$ = 2 Hz. The large coupling between H_1 and H_2 indicates they are quasiaxial; the small coupling between H_2 and H_3 indicates H_2 is quasiequatorial and the carboxyl group at C_2 and the hydroxyl group at C_3 are cis.

(10) D. H. R. Barton, H. P. Faro, E. P. Serebryakov, and N. F. Woolsey, *J. Chem. Soc.*, 2438 (1965).

(11) H. G. Kuivila, *Accounts Chem. Res.*, **1**, 299 (1968); S. K. Pradhan and V. M. Girijavallabhan, *Tetrahedron Lett.*, 3103 (1968); E. L. Stogryn and M. H. Gianni, *ibid.*, 3025 (1970); A. Suzuki, N. Miyaura, M. Itoh, H. C. Brown, G. W. Holland, and E. Negishi, *J. Amer. Chem. Soc.*, **93**, 2792 (1971).

(12) *trans*-2,3-Dihydroxy-2,3-dihydrobenzoic acid shows a similar fragmentation pattern.[9,13]

(13) I. G. Young, L. M. Jackman, and F. Gibson, *Biochim. Biophys. Acta*, 177, 381 (1969).

(14) J. S. Krouwer and G. A. Berchtold, unpublished results.

Consequently, the monoepoxide from which **16** is derived is assigned structure **14** and the bis epoxide is assigned structure **4**.

Experimental Section

Infrared spectra were taken on a Perkin-Elmer Model 237 spectrophotometer. Ultraviolet spectra were taken on a Cary Model 14 spectrophotometer. Proton nmr spectra were taken on a Varian Model T-60 spectrometer, and chemical shift data are reported in parts per million downfield from tetramethylsilane as an internal standard at 0.00. Mass spectra were run on a Hitachi Perkin-Elmer RMU-6D mass spectrometer with an ionizing potential of 70 eV and are expressed in per cent relative to the most intense peak. Except for the high mass region only the *m/e*'s of greater than 20% relative intensity are listed. The high resolution mass spectrum was obtained on a CEC-21-110B spectrometer.[15] Melting points were taken on a Thomas Hoover "Uni Melt" and are corrected. Gas chromatographic analyses were carried out with either a Hewlett-Packard Model 5750 gas chromatograph with thermal conductivity detectors or a Varian Aerograph Model 2100 gas chromatograph with flame ionization detectors in an all glass system. Microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn.

3α,8β-Dioxatricyclo[5.1.0.0^{2,4}]octane-5α,6β-dicarboxylic Acid (4). A solution of 6.00 g (35.7 mmol) of **3**[16] and 43.5 g (214 mmol) of 85% *m*-chloroperbenzoic acid in 1.5 l. of ethyl acetate was stirred at room temperature for 12 days. The solution was evaporated to dryness under vacuum and the white, crystalline residue was transferred to a sintered glass funnel. Repeated washings with $CHCl_3$ removed the aromatic acids and left 6.1 g (84%) of **4** as a white powder that required no further purification: mp 245° dec; ir (KBr) 3410, 3060, 1735, 1300, 1175, 865 cm^{-1}; nmr (acetone-d_6) δ 3.30 (s, 2 H), 3.59 ppm (s, 4 H); *m/e* 200 (5), 182 (5), 171 (7), 164 (15), 154 (18), 138 (34), 121 (23), 100 (26), 99 (26), 97 (30), 84 (44), 83 (21), 73 (69), 60 (22), 58 (23), 55 (39), 45 (28), 44 (98), 43 (100).

Anal. Calcd for $C_8H_8O_6$: C, 48.01; H, 4.03. Found: C, 47.87; H, 4.21.

3α,8β-Dioxatricyclo[5.1.0.0^{2,4}]octane-5α,6β-dicarboxylic Anhydride (5). A mixture of 2.00 g (10.0 mmol) of **4** and 40 ml of trifluoroacetic anhydride was stirred at room temperature in a stoppered flask. Within 0.5 hr all the solid had dissolved. Upon continued stirring a large amount of crystalline, white solid precipitated. After 1 hr the suspension was evaporated to dryness under vacuum. To the solid residue was added 60 ml of diethyl ether and 0.5 ml of water, and the mixture was stirred 5 min and evaporated to dryness under vacuum. To the resulting pale yellow solid was added 40 ml of trifluoroacetic anhydride, and the mixture was stirred at room temperature (1.5 hr). The mixture was evaporated to dryness under vacuum and was washed with 2 × 10 ml of ice-cold acetate to give 1.55 g (85%) of **5** as a slightly off-white solid that could be used without further purification. Recrystallization from ethyl acetate–pentane gave fine, white needles: mp 160–230° dec; ir ($CHCl_3$) 3010, 1878, 1802, 1595, 1360, 1268, 1188, 1170 cm^{-1}; nmr (acetone-d_6) δ 3.60 (m, 2 H), 3.80 (m, 2 H), 4.15 ppm (s, 2 H); *m/e* 164 (17), 154 (5), 138 (5), 136 (8), 120 (17), 110 (58), 81 (100), 55 (23), 53 (60), 39 (50).

Anal. Calcd for $C_8H_6O_5$: C, 52.75; H, 3.32. Found: C, 52.89; H, 3.21.

Methyl 5α-Carboxy-3α,8β-dioxatricyclo[5.1.0.0^{2,4}]octane-6β-carboxylate (6). A mixture of 908 mg (4.99 mmol) of **5** in 25 ml of absolute methanol was stirred at room temperature for 24 hr (**5** dissolved within 3 hr) and the solution was evaporated to dryness under vacuum to give a quantitative yield of **6** as a crystalline, white solid. Recrystallization from ethyl acetate–pentane gave 856 mg (80%) of **6** as clusters of white needles: mp 140–142°; ir ($CHCl_3$) 3500–2400, 1740, 1720, 1433, 1292, 1265, 1165, 1012, 982 cm^{-1}; nmr (acetone-d_6) δ 3.32 (s, 2 H), 3.57 (m, 4 H), 3.77 ppm (s, 3 H); *m/e* 186 (5), 185 (4), 183 (12), 170 (6), 168 (8), 167 (6) 164 (20), 142 (27), 139 (24), 137 (32), 136 (85), 126 (25), 125 (35), 114 (30), 113 (100), 111 (56), 110 (59), 109 (71), 108 (39), 99 (38), 98 (44), 97 (34), 95 (38), 85 (28), 84 (75), 83 (45), 82 (43), 81 (100), 53 (79), 45 (40), 44 (76), 43 (50), 41 (55), 39 (93).

Anal. Calcd for $C_9H_{10}O_6$: C, 50.47; H, 4.71. Found: C, 50.25; H, 4.89.

Methyl 5-Iodo-3α,8β-dioxatricyclo[5.1.0.0^{2,4}]octane-6β-carboxylate (7). A solution of *tert*-butyl hypoiodite in benzene prepared from 11.70 g of I_2 and 3.44 g of potassium *tert*-butoxide according to the procedure of Barton *et al.*[10] was added to 2.35 g (11.0 mmol) of **6** in 300 ml of benzene. The mixture was irradiated for 3 hr with two 300-W tungsten lamps, and the temperature was kept below 30°. After 3 hr the irradiation was stopped and the solution was washed with aqueous sodium thiosulfate solution until the I_2 color was gone, 200 ml of water, 3 × 200 ml of saturated aqueous sodium bicarbonate solution, and 200 ml of saturated sodium chloride solution. The benzene solution was dried (Na_2SO_4), filtered, and evaporated to give 2.99 (92%) of **7** as a yellow viscous oil: ir ($CHCl_3$) 1740, 1432, 1352, 1260, 1224, 1190 cm^{-1}; nmr (acetone-d_6) δ 4.5–5.0 (m, 1 H), 3.73 (s, 3 H), 3.3–3.9 ppm (m, 5 H). Iodide **7** was too unstable to permit distillation or chromatographic purification, so it was used in subsequent reactions without further purification.

Methyl 5α-Hydroxy-7-oxabicyclo[4.1.0]hept-3-ene-2-carboxylate (8). To a solution of 666 mg (2.25 mmol) of **7** in 20 ml of diethyl ether was added 1 ml of glacial acetic acid and 0.94 g of activated Zn dust.[17] The mixture was stirred at room temperature (45 min), filtered, and evaporated to give 700 mg of a mixture of zinc iodide and **8** as a viscous, yellow oil: nmr (acetone-d_6) δ 5.75 (m, 2 H), 4.40 (m, 2 H), 3.77 (s, 3 H), 3.3–3.9 ppm (m, 3 H). Pure **8** could not be obtained from the unstable complex, so it was used in subsequent steps without further purification.

Methyl *trans*-3,4-Dihydroxy-3,4-dihydrobenzoate (9). To a solution of crude **8** prepared from 556 mg (1.88 mmol) of **7** in 50 ml of diethyl ether was added 6 ml of triethylamine, and the mixture was stirred at room temperature (20 min). A viscous oil formed on the bottom of the flask. The ether solution was separated from the oil, and the oil was washed repeatedly with ether. The original ether solution and the extracts were evaporated to give 320 mg of a brown oil. Preparative tlc on a 20 × 20 cm plate of silica gel (2000 μ) provided 163 mg (51%) of **9** as a pale yellow oil: R_f 0.3 (ether); ir ($CHCl_3$) 3400, 1713, 1638, 1602, 1435, 1250 cm^{-1}; nmr (acetone-d_6) δ 6.86 (m, 1 H), 6.26 (d of m, 1 H, J = 10 Hz), 5.95 (d of m, 1 H, J = 10 Hz), 4.50 (m, 4 H), 3.79 ppm (s, 3 H); *m/e* 170 (49), 168 (25), 155 (9), 153 (12), 152 (69), 137 (50), 124 (35), 121 (100), 110 (60), 109 (42), 93 (45), 85 (32), 83 (50), 82 (45), 81 (68), 65 (50), 59 (23), 55 (28), 53 (63), 41 (23), 39 (73).

Anal. (Molecular ion) Calcd for $C_7H_{10}O_4$: 170.05791. Found: 170.05994.

***trans*-3,4-Dihydroxy-3,4-dihydrobenzoic Acid (2).** One pellet of potassium hydroxide was added to a solution of 337 mg of **9** in 15 ml of water. The solution was stirred at room temperature (3 hr), acidified to pH 1 with dilute aqueous HCl, and extracted with 8 × 10 ml of diethyl ether. The acidified aqueous solution was then continuously extracted with diethyl ether (4 days) to afford 230 mg (74%) of racemic **2** as a pale yellow solid from the ether extract. Recrystallization from acetone–pentane gave analytically pure racemic **2**: mp 150–151° dec, the mp of **2** derived from 1 is 170° dec.[4] The ir, uv, nmr, and mass spectra and analysis of racemic **2** were in agreement with those reported for **2** derived from **1**.

7β-Oxabicyclo[4.1.0]hept-4-ene-2β,3α-dicarboxylic Acid (14). A solution of 2.00 g (11.9 mmol) of **3** and 2.85 g (14.0 mmol) of *m*-chloroperbenzoic acid in 400 ml of ethyl acetate was stirred at room temperature (24 hr). The solution was evaporated to dryness under vacuum, and the white crystalline residue was transferred to a sintered glass funnel. The product was washed with 5 × 20 ml of chloroform to remove aromatic acids and give 2.06 g (94%) of **14** as a white crystalline powder that required no further purification: mp 140° dec; ir (KBr) 3500–2400, 1705, 1620, 1395, 1275, 1165 cm^{-1}; nmr (acetone-d_6) δ 3.00–3.95 (m, 4 H), 6.15 ppm (m, 2 H); *m/e* 156 (6), 139 (5), 122 (12), 105 (14), 78 (47), 44 (100), 43 (71).

Anal. Calcd for $C_8H_8O_5$: C, 52.18; H, 4.38. Found: C, 52.02; H, 4.41.

***trans*-2-Carboxy-*trans*-3-hydroxy-*cis*-4-methoxycyclohex-5-enecarboxylic Acid (16).** A solution of 323 mg (1.75) mmol) of **14** in 15 ml of absolute methanol was stirred under reflux for 3.5 hr, cooled, and evaporated under vacuum to give 340 mg (90%) of **16** as a viscous oil that crystallized upon trituration with pentane. Recrystallization from acetone–pentane gave clusters of white needles: mp 166° dec; ir (KBr) 3600–2400, 1705, 1410, 1280, 1187,

(15) The high resolution mass spectrum was provided by the Facility supported by National Institutes of Health Grant PRO0317 (Principal Investigator Professor K. Biemann) from the Biotechnology Resources Branch, Division of Research Resources.

(16) R. N. McDonald and C. E. Reineke, *Org. Syn.*, 50, 50 (1970).

(17) K. Tsuda, E. Ohki, and S. Nozoe, *J. Org. Chem.*, 28, 783 (1963).

1075, 955 cm^{-1}; nmr (acetone-d_6) δ 3.08 (d of d, 1 H, J = 10, 2 Hz), 3.44 (s, 3 H), 3.70 (d of m, 1 H, J = 10 Hz), 3.62 (m, 1 H), 4.47 (m, 1 H), 5.99 (m, 2 H), 7.4 ppm (very broad, 3 H), irradiation of the multiplet at 4.47 ppm caused collapse of the signal at 3.08 ppm to a clean doublet (J = 10 Hz); *m/e* 198 (8), 180 (10), 170 (7), 168 (7), 166 (7), 154 (21), 153 (22), 128 (100), 122 (25), 109 (42), 105 (22), 97 (32), 96 (81), 81 (29), 74 (48), 71 (24), 68 (49), 65 (25), 45 (37), 41 (42), 39 (51).

Anal. Calcd for $C_9H_{12}O_6$: C, 50.00; H, 5.60. Found: C, 49.90; H, 5.68.

Conformational Effects in the Mass Spectra of Long Chain Ethers of *p*- and *m*-Hydroxybenzoic Acid

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Abstract: Long chain ethers of *m*- and *p*-hydroxybenzoic acid, and their methyl esters, show ions in their mass spectra which are due to hydrogen abstraction from the hydrocarbon chain by the remote, ionized carboxy group. These ions appear at *m/e* 139 and 153, one mass unit greater than those of the intense ions due to phenyl ether rearrangement. The *m/e* 139/138 and 153/152 ratios increase with chain length. Kinetic arguments support hydrogen abstraction as rate determining, although the possibility of a change in the rate-determining step at low voltage with increase in chain length is discussed. Probability considerations are introduced as a step toward understanding in detail the effects of the conformational mobility of a hydrocarbon chain in mass spectral reactions leading to hydrogen abstraction. These ideas are compared with an internal solvation model recently proposed by Meyerson.

There are many examples in mass spectrometry of interaction, leading to hydrogen transfer, between two functional groups separated by a hydrocarbon chain.[1] Hydrogen transfer is an important process in long range interactions between a functional group and the chain itself,[2] and the effect of ring size on the hydrogen abstraction reaction has been noted.[1g,2d] Hydrogen abstraction can be activated by methyl or phenyl substitution on the chain,[3] leading to selective, but not specific, hydrogen abstraction. Chain coiling has been invoked by a number of authors[4] to explain these phenomena, which require that two groups, apparently separated by a flexible chain, be brought into spatial proximity during the lifetime of the molecular ion.

Meyerson and Leitch[5] proposed a model for such interactions in their discussion of the mass spectra of ω-phenylalkanols in which they envisaged the chain coiled in the gas phase. Their data are also compatible with a freely flexible chain. Since vapor phase coiling of hydrocarbon chains has been called into question,[6] this defines the nature of the problem: to understand the contribution of the conformational requirements of the chains to the interaction of groups separated by a linear hydrocarbon. We omit from our consideration reactions which involve the interaction of two heteroatom-containing functional groups. These are dominated by highly specific interactions to the exclusion of chain length effects.[1,7] We devote our attention to the effects of hydrocarbon chain conformation on the hydrogen abstraction reaction. The nonspecificity in abstraction from unactivated hydrocarbon chains[8] and the enhanced specificity in cases of local chemical activation[3b,5] suggest that conformational properties of the chain play an important role in determining the extent and stereochemistry of the hydrogen abstraction process.

An approach to this problem is to gather data in the proper form for comparison with calculations of hydrocarbon conformational statistics.[9] Such calculations, in principle, would allow one to separate the purely conformational contributions from the van der Waals and ion-induced dipole effects. These, in turn, could then be incorporated into conformational calculations. We have taken this approach, choosing to examine the interaction in the mass spectrometer between a hydrocarbon chain and a remote functional group, which can be presented and interpreted in terms of the reversible cyclization probability of the chain.

(1) (a) J. A. McCloskey and M. J. McClelland, *J. Amer. Chem. Soc.*, **87**, 5090 (1965); (b) R. E. Wolff, M. Greff, and J. A. McCloskey, *Advan. Mass. Spectrom.*, **4**, 193 (1968); (c) R. Brandt and C. Djerassi, *Helv. Chim. Acta*, **51**, 1750 (1968); (d) G. H. Draffan, R. N. Stillwell, and J. A. McCloskey, *Org. Mass. Spectrom.*, **1**, 669 (1968); (e) A. Casper, G. Teller, and R. E. Wolff, *ibid.*, **3**, 1351 (1970); (f) C. Wolff, R. E. Wolff, and J. A. McCloskey, *Tetrahedron Lett.*, 4335 (1966); (g) P. Brown, A. H. Albert, and G. R. Pettit, *J. Amer. Chem. Soc.*, **92**, 3212 (1970).

(2) (a) R. Ryhage and E. Stenhagen, "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press, New York, N. Y., 1963; (b) L. Dolejš, P. Beran, and J. Hradec, *Org. Mass. Spectrom.*, **1**, 563 (1968); (c) S. Meyerson, I. Puskas, and E. K. Fields, *Chem. Ind. (London)*, 1845 (1968); (d) G. Eadon and C. Djerassi, *J. Amer. Chem. Soc.*, **91**, 2724 (1969).

(3) (a) R. Ryhage and E. Stenhagen, *Ark. Kemi*, **15**, 291 (1959); (b) S. Meyerson and L. C. Leitch, *J. Amer. Chem. Soc.*, **88**, 56 (1966).

(4) (a) R. Ryhage and E. Stenhagen, *J. Lipid Res.*, **1**, 361 (1960); (b) P. Bommer and K. Biemann, *Annu. Rev. Phys. Chem.*, **16**, 492 (1965); (c) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, San Francisco, Calif., 1967, p 179.

(5) S. Meyerson and L. C. Leitch, *J. Amer. Chem. Soc.*, **93**, 2244 (1971).

(6) E. F. Meyer and K. S. Stec, *J. Amer. Chem. Soc.*, **93**, 5451 (1971).

(7) E. White, V. S. Tsuboyama, and J. A. McCloskey, *J. Amer. Chem. Soc.*, **93**, 6340 (1971); I. Dzidic and J. A. McCloskey, *ibid.*, **93**, 4955 (1971).

(8) (a) J. Cable and C. Djerassi, *J. Amer. Chem. Soc.*, **93**, 3905 (1971); (b) S. Meyerson, I. Puskas, and E. K. Fields, *ibid.*, **95**, 6056 (1973).

(9) (a) P. J. Flory, "Statistical Mechanics of Chain Molecules," Interscience, New York, N. Y., 1969; (b) M. Lal, *Brit. Polym. J.*, **3**, 240 (1971); (c) M. Sisido, *Macromolecules*, **4**, 737 (1971); (d) R. P. Smith and E. M. Mortensen, *J. Chem. Phys.*, **35**, 714 (1961).