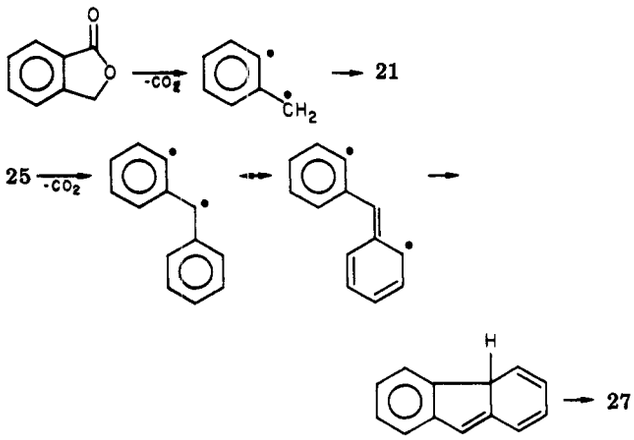

In summary, these plasma reactions demonstrate that extrusion of carbon monoxide or carbon dioxide can provide a direct route to benzocyclobutene or benzocyclopropene. The major reaction products are generally rationalizable in terms of schemes involving diradical intermediates as product precursors, but the mechanisms are in fact unknown.

Experimental Section

All reactants were commercial samples whose purity was ascertained by GC. Authentic samples of products were also commercially available except for **7**, **21**, **22**, and **28**.

Plasmolysis experiments were carried out in a double walled reactor tube (300 × 25 mm i.d.), which had dual reactant inlets as described previously.[3] Argon gas was added through one of those inlets. When the reaction was carried out without the addition of argon, one of the inlets was closed with a stopper. The dual inlets and an upper portion of the reactor were heated with heating tape to prevent condensation. The glow discharge was generated by a radiofrequency generator at 13.6 MHz (Tegal Model 100) with inductive coupling (copper coil, 10 turns in 100 mm) through a tunable Collins filter. The applied power (P) was measured with a built-in wattmeter, and in every case the circuit was balanced so that the reflected power was negligible. Flow rate (r) was calculated from the amount of material lost from the reactant reservoir and the elapsed time during plasmolysis. Except where noted in the text, experiments with reactants 1–6 employed a pumping system with a small diameter outlet from the cold trap. This restricted the pumping capacity as noted. Removal of this restriction led to a reduction in pressure in the plasma zone, especially when the total pressure was relatively high with argon as diluent gas. An accurate measure of this change was not made. After the plasmolysis, the inner wall of the reactor and the inlets were washed with 30–40 mL of acetone. Acetone solution was concentrated with a rotatory evaporator and then analyzed.

Analysis of products was generally carried out by GC, using an internal standard. The column was 10% silicon gum rubber SE-30 on Chromosorb W 80/100 mesh, 2 or 3 m, and dimethyl phthalate or acetophenone were standards. In the case of 1, NMR was also employed using *tert*-butyl chloride or diphenylmethane as internal standards, since **7** seemed to be decomposed through the GC column. Absorptions of a vinyl proton of **8** at δ 5.75, methylene protons of **1** at δ 3.54, methylene protons of **7** at δ 3.15, methyl protons of *tert*-butyl chloride at δ 1.62, and methylene protons of diphenylmethane at δ 3.94 were used for analysis. Identification of other products was achieved by GC by comparison with authentic samples and was confirmed by GC–MS. Benzocyclobutene (**7**) was isolated from the reaction of **1** by a distillation, and its ^{1}H and ^{13}C NMR spectra were consistent with published data:[4b,11] ^{1}H NMR ($CDCl_3$) δ 3.18 (s, 4), 7.11 (m, 4); ^{13}C NMR ($CDCl_3$) δ 29.8, 122.7, 126.8, 146.1.

Benzocyclopropene (**21**) and allene **22** were collected by GC and identified from comparison of their ^{1}H, ^{13}C NMR, and mass spectra with literature values. **21**: ^{1}H NMR ($CDCl_3$) δ 3.18 (s, 2 H), 7.22 (s, 4 H). **22**: ^{1}H NMR ($CDCl_3$) δ 5.30 (s, 2 H), 6.42 (s, 4 H).

Acknowledgment. This work was supported by the National Science Foundation and a NATO Cooperative Research Grant.

Registry No. **1**, 615-13-4; **2**, 530-93-8; **3**, 119-84-6; **4**, 91-64-5; **5**, 83-33-0; **6**, 529-34-0; **7**, 694-87-1; **8**, 100-42-5; **9**, 496-11-7; **10**, 95-13-6; **11**, 536-74-3; **12**, 496-16-2; **13**, 271-89-6; **15**, 108-88-3; **17**, 300-57-2; **21**, 4646-69-9; **22**, 27041-32-3; **23**, 100-52-7; **24**, 643-79-8; **25**, 87-41-2; **26**, 596-29-2; **27**, 86-73-7; **28**, 789-24-2; **29**, 486-25-9; C_6H_6, 71-43-2.

Electroreductive Elimination of Phenolic Hydroxyl Groups and a New Synthesis of Olivetol[1]

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Received June 5, 1979

The replacement of phenolic hydroxyl groups by hydrogen was achieved through the electrochemical reduction of aryl diethyl phosphates. The mechanism of the initiation step was proposed to be one-electron transfer into not the phosphate group but the aromatic nucleus. This new reduction was applied to the synthesis of olivetol.

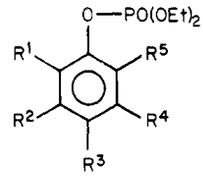
Organic synthesis often requires the elimination of hydroxyl groups from phenolic compounds, and two methods have already been exploited. One of them is based on the reduction of aryl ethers[2] or aryl phosphates[3] with alkali metals in ammonia and the other is the hydrogenolysis.[4]

(1) Electroorganic Chemistry. 39.

(2) (a) W. H. Pirkle and J. L. Zabriskie, *J. Org. Chem.*, **29**, 3124 (1964); (b) P. A. Sartoretto and F. J. Sowa, *J. Am. Chem. Soc.*, **59**, 603 (1937); (c) Y. K. Sawa, N. Tsuji, and S. Maeda, *Tetrahedron*, **15**, 144, 154 (1961).

0022-3263/79/1944-4508$01.00/0

Table I. Electrochemical Reduction of Aryl Diethyl Phosphates



run no.	$ArOPO(OEt)_2$[a]	mmol	$[Et_4NOTs]$, mmol	[DMF], mL	F/mol[b]	product[c] (%)
1	16, R^1 = OMe	3.3	17	30	5.7	anisole (61)
2	17, R^1 = *i*-Pr; R^4 = Me	10	40	65	5.6	*p*-cymene (44)
3	18, R^1 = OMe; R^3 = allyl	10	40	65	4.6	*m*-*n*-propylanisole (66)
4	19, R^1 = OMe; R^3 = 1-propenyl	3.3	17	30	6.7	*m*-*n*-propylanisole (73)
5	9, R^1 = OMe; R^3 = *n*-Pr	3.0	17	30	5.0	*m*-*n*-propylanisole (58)
6	20, R^1 = R^5 = OMe	3.3	17	30	6.7	*m*-dimethoxybenzene (54)
7	21, R^2 = R^4 = OMe	3.3	17	30	6.7	*m*-dimethoxybenzene (43)
8	22, β-naphthyl diethyl phosphate	3.3	17	30	7.4	tetralin (59)

[a] Groups other than hydrogen are shown in the table. [b] The amount of electricity passed. [c] Yields determined by GLC.

Although the former method has been believed to involve the reduction with solvated electrons, little attention has been paid to an electrochemical method in which the electron itself acts as a reducing agent.

In our continuing study on the electroreductive cleavage of bonds between carbon and heteroatoms,[5] we have investigated the electrochemical reduction of aryl diethyl phosphates (**2**) to exploit a simple practical procedure of the replacement of phenolic hydroxyl groups by hydrogen (**1** → **3**) and an application of this method to the synthesis of olivetol, a key intermediate in the synthesis of cannabinoids.[6]

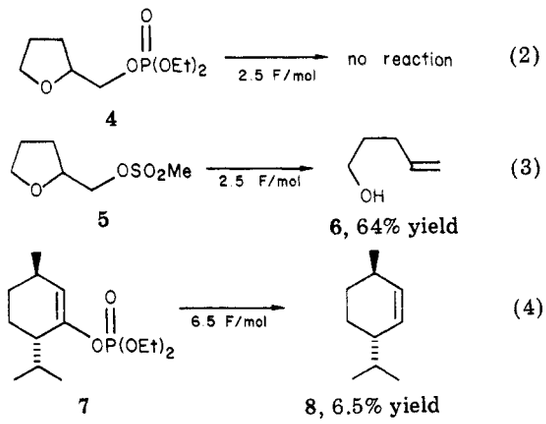
$$\underset{1}{ArOH} \rightarrow \underset{2}{ArOPO(OEt)_2} \rightarrow \underset{3}{ArH} \qquad (1)$$

Results and Discussion

Electroreduction of Aryl Diethyl Phosphates. Although cyclic voltammetric reduction peaks of **2** were not observed in the potential range more positive than −2.5 V vs. SCE,[7] the following reaction conditions were found to be satisfactory for the preparative electroreductive transformation of **2** to **3**. Thus, in a divided cell equipped with a lead cathode and a platinum anode, 4.6–7.4 F/mol of electricity was passed through a solution of **2** in dimethylformamide (DMF) containing tetraethylammonium *p*-toluenesulfonate (Et_4NOTs) at the cathode potential of −2.6 to −2.7 V vs. SCE. Working up the reaction mixture gave the products (**3**) in the yields shown in Table I.

Allylic and conjugated double bonds in aromatic side chains (runs 3 and 4 in Table I) and a half of the naphthalene nucleus (run 8 in Table I) were also hydrogenated under the conditions shown. Coupling products were not detected. The starting materials not reduced could be recovered from the reaction mixture.

Reaction Mechanism. Although the reaction mechanism is not yet conclusive, the initiation step is relatively clear. Namely, one electron seems to be transferred into not the phosphate group but the aromatic nucleus on the basis of the following evidence. (1) Tetrahydrofurfuryl diethyl phosphate (**4**) was completely inert (eq 2), whereas



tetrahydrofurfuryl methanesulfonate (**5**) was cathodically reducible to the ring opened alcohol (**6**) in a reasonable yield (eq 3).[8] (2) The reduction of enol diethyl phosphate (**7**) to the olefin (**8**) was barely perfomable in a yield of only 6.5% (eq 4). The difference of reactivity between aryl and enol diethyl phosphates may be due to the relative difficulty of the electron transfer to a simple olefinic bond rather than an aromatic nucleus.

The yields of the reduction of **18** and **19** are higher than that of **9**. Possibly, the electron transfer to **19** is easier than that to **9**, because in **19** the double bond conjugates with the aromatic nucleus. In the reduction of **18**, the isomerization of **18** to **19** was observed to a certain extent under the reduction conditions in which the reaction medium became basic during the electroreduction.

Proton Sources. Since preparative experiments were carried out using commercial DMF under atmospheric conditions, water existing in the reaction system can be the source of some 60% of the proton. This proposal is

(3) (a) G. W. Kenner and N. R. Williams, *J. Chem. Soc.*, 522 (1955); (b) S. W. Pelletier and D. M. Locke, *J. Org. Chem.*, **23**, 131 (1958); (c) R. A. Rossi and J. F. Bunnett, *J. Org. Chem.*, **38**, 2314 (1973); (d) S. J. Dominianni, C. W. Ryan, and C. W. DeArmitt, *J. Org. Chem.*, **42**, 344 (1977); (e) S. J. Shafer, W. D. Closson, J. M. F. van Dijk, O. Piepers, and H. M. Buck, *J. Am. Chem. Soc.*, **99**, 5118 (1977). (f) Recently, the reduction with titanium metal has been reported: S. C. Welch and M. E. Walters, *J. Org. Chem.*, **43**, 4797 (1978).

(4) (a) W. J. Musliner and J. W. Gates, Jr., *J. Am. Chem. Soc.*, **88**, 4271 (1966); (b) V. K. Clauss and H. Jensen, *Angew. Chem.*, **85**, 981 (1973); (c) E. Vowinkel and C. Wolff, *Chem. Ber.*, **107**, 907 (1974); (d) E. Vowinkel and H. J. Baese, *ibid.*, **107**, 1213 (1974).

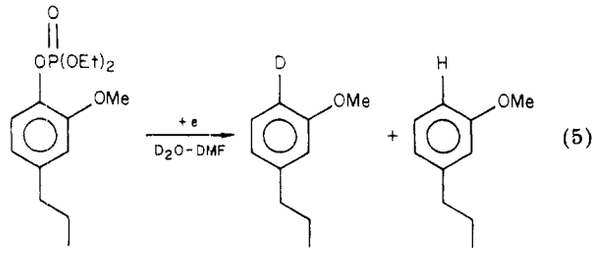
(5) (a) T. Shono, Y. Matsumura, and S. Kashimura, *Chem. Lett.*, 69 (1978); (b) T. Shono, Y. Matsumura, S. Kashimura, and H. Kyutoku, *Tetrahedron Lett.*, 2807 (1978).

(6) H. G. Krishnamurty and J. S. Prasad, *Tetrahedron Lett.*, 2511 (1975), and references cited therein.

(7) The measurement of the reduction potential of aryl diethyl phosphates was carried out under the following conditions: substrate, 0.1 M; solvent, DMF; supporting electrolyte, 0.05 M Et_4NCl; cathode, Pt; anode, Pt; scanning rate, 100 mV/s.

(8) T. Shono, Y. Matsumura, K. Tsubata, and Y. Sugihara, *Tetrahedron Lett.*, 2157 (1979).

supported by the following facts. Under an atmosphere of nitrogen, the electroreduction of **9** in the mixed solvent of thoroughly dried DMF and deuterium oxide containing tetrabutylammonium perchlorate (Bu_4NClO_4) as a supporting electrolyte resulted in the formation of **10** and **10′** in the total yield of 68% (eq 5).

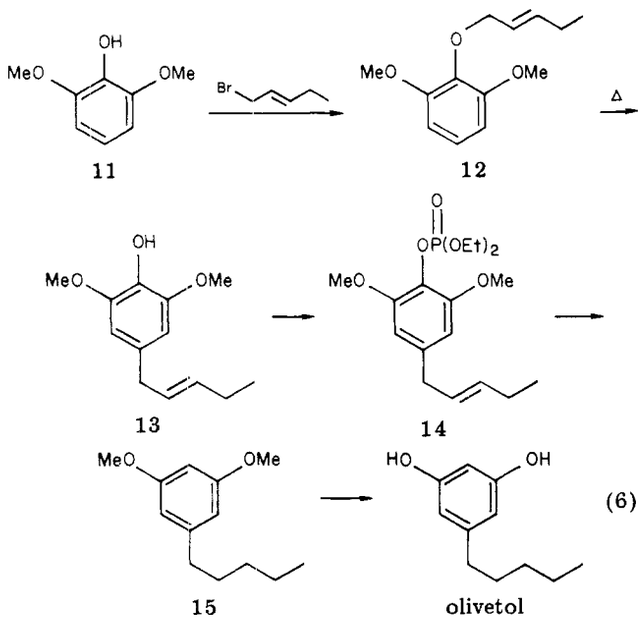


(5)

9 10 10′

The isotopic purity (**10**/**10** + **10′**) was 60 ± 10%. The same reduction in DMF-d_7 and D_2O containing anhydrous lithium perchlorate ($LiClO_4$)[9] gave almost the same isotopic purity, suggesting that DMF cannot be a source of proton or hydrogen. Although it is still quite uncertain, it is one possibility that about 40% of hydrogen came from the substrate itself.

Synthesis of Olivetol. The synthesis of olivetol was achieved according to the sequence shown in eq 6.



(6)

The alkylation of commercially available pyrogallol 1,3-dimethyl ether (**11**) with 1-bromo-2-pentene preferentially gave **12** in the yield of 88%. Claisen rearrangement of **12** followed by phosphorylation yielded **14** (73% yield from **12**). The electrochemical reduction of **14** resulted in the direct formation of olivetol dimethyl ether (**15**) (67% yield), of which conversion to olivetol has been reported.[6]

Experimental Section

General. Boiling and melting points are uncorrected. ^1H NMR spectra were recorded on a Varian EM-360 NMR spectrometer in CCl_4. The infrared spectra were determined with a Hitachi 215 infrared spectrophotometer. Gas chromatographic analyses were performed on a Yanaco GCG 550T gas chromatograph.

Preparation of Aryl Diethyl Phosphates. According to the conventional method,[3a] aryl diethyl phosphates (**9**, **14**, **16–22**) were synthesized as follows. A solution of 50 mmol of an aryl alcohol and 52 mmol of diethyl phosphite in 15 mL of CCl_4 was cooled in an ice bath with vigorous stirring, and 52 mmol of triethylamine was added dropwise. During the addition, the reaction temperature was kept between 0 and 5 °C. When the addition was completed, the reaction mixture was allowed to stand overnight at room temperature. The mixture was diluted with chloroform and washed with 20 mL of water, 20 mL of 10% hydrochloric acid, four 10-mL portions of 10% aqueous sodium hydroxide, and 20 mL of water, successively, and dried over anhydrous potassium carbonate. After the drying agent was filtered and the solvent was evaporated in vacuo, aryl diethyl phosphates were isolated by distillation or recrystallization. The syntheses of **4** and **7** were accomplished by the method of Ireland et al.[11]

Physical properties and spectroscopic data of the diethyl phosphates are discribed below.

2-Methoxyphenyl diethyl phosphate (16):[3a] bp 142 °C (1.1 mm); IR (neat) 3060, 1600, 1260, 1214, 1178, 1115, 1022, 755 cm^{-1}; NMR (CCl_4) δ 1.31 (t, 6 H), 3.80 (s, 3 H), 4.12 (2 q, 4 H), 6.60–7.30 (m, 4 H).

2-Isopropyl-5-methylphenyl diethyl phosphate (17): bp 118–119 °C (0.58 mm); IR (neat) 3030, 1618, 1270, 1155, 1020, 895, 820 cm^{-1}; NMR (CCl_4) δ 1.20 (d, 6 H), 1.32 (t, 6 H), 2.31 (s, 3 H), 3.27 (m, 1 H), 4.11 (2 q, 4 H), 6.67–7.17 (m, 3 H).

Anal. Calcd for $C_{14}H_{23}O_4P$: C, 58.73; H, 8.10; P, 10.82. Found: C, 59.03; H, 8.03; P, 10.58.

2-Methoxy-4-allylphenyl diethyl phosphate (18): bp 134–135 °C (0.27 mm); IR (neat) 3070, 1635, 1598, 1272, 1153, 1128, 1027, 895, 818 cm^{-1}; NMR (CCl_4) δ 1.31 (t, 6 H), 3.30 (d, 2 H), 3.81 (s, 3 H), 4.13 (2 q, 4 H), 4.77–5.21 (m, 2 H), 5.56–6.25 (m, 1 H), 6.49–7.23 (m, 3 H).

Anal. Calcd for $C_{14}H_{21}O_5P$: C, 55.99; H, 7.05; P, 10.32. Found: C, 55.73; H, 6.95; P, 10.09.

2-Methoxy-4-(1-propenyl)phenyl diethyl phosphate (19): bp 159 °C (0.51 mm); IR (neat) 3070, 1595, 1268, 1160, 1125, 1022, 900, 820 cm^{-1}; NMR (CCl_4) δ 1.32 (t, 6 H), 1.85 (m, 3 H), 3.82 (s, 3 H), 4.11 (2 q, 4 H), 5.41–6.44 (m, 2 H), 6.52–7.32 (m, 3 H).

Anal. Calcd for $C_{14}H_{21}O_5P$: C, 55.99; H, 7.05; P, 10.32. Found: C, 56.00; H, 6.89; P, 10.40.

2-Methoxy-4-(*n*-propyl)phenyl diethyl phosphate (9): bp 152 °C (0.68 mm); IR (neat) 1600, 1590, 1272, 1213, 1155, 1125, 1030, 920, 817 cm^{-1}; NMR (CCl_4) δ 0.94 (t, 3 H), 1.31 (t, 6 H), 1.64 (m, 2 H), 2.54 (t, 2 H), 3.80 (s, 3 H), 4.12 (2 q, 4 H), 6.43–7.24 (m, 3 H).

Anal. Calcd for $C_{14}H_{23}O_5P$: C, 55.62; H, 7.67; P, 10.25. Found: C, 55.42; H, 7.46; P, 10.30.

2,6-Dimethoxyphenyl diethyl phosphate (20): mp 74 °C (from ethyl acetate); IR (KBr) 3010, 1605, 1262, 1110, 1025, 773, 739 cm^{-1}; NMR (CCl_4) δ 1.35 (t, 6 H), 3.77 (s, 6 H), 4.15 (2 q, 4 H), 6.30–7.04 (m, 3 H).

Anal. Calcd for $C_{12}H_{19}O_6P$: C, 49.65; H, 6.60; P, 10.67. Found: C, 49.81; H, 6.73; P, 10.56.

3,5-Dimethoxyphenyl diethyl phosphate (21): bp 148–149 °C (0.40 mm); IR (neat) 1600, 1273, 1148, 1020, 860, 680 cm^{-1}; NMR (CCl_4) δ 1.31 (t, 6 H), 3.69 (s, 6 H), 4.10 (2 q, 4 H), 6.04–6.34 (m, 3 H).

Anal. Calcd for $C_{12}H_{19}O_6P$: C, 49.65; H, 6.60; P, 10.67. Found: C, 49.78; H, 6.58; P, 11.08.

β-Naphthyl diethyl phosphate (22):[3a] bp 147–148 °C (0.30 mm); IR (neat) 3050, 1630, 1596, 1280, 1162, 1027 cm^{-1}; NMR (CCl_4) δ 1.30 (t, 6 H), 4.10 (2 q, 4 H), 7.03–7.84 (m, 7 H).

Tetrahydrofurfuryl diethyl phosphate (4): 31% yield; bp 116–118 °C (1.2 mm); IR (neat) 1270, 1168 cm^{-1}; NMR (CCl_4) δ 1.33 (t, 6 H), 1.87 (m, 4 H), 3.57–4.30 (m, 9 H).

Anal. Calcd for $C_9H_{19}O_5P$: C, 45.38; H, 8.04; P, 13.00. Found: C, 45.20; H, 7.86; P, 12.74.

(9) This salt was used instead of Bu_4NClO_4 since tetraalkylammonium salts have been known to be efficient proton donors.[10]

(10) A. J. Fry and R. G. Reed, *J. Am. Chem. Soc.*, **93**, 553 (1971).

(11) R. E. Ireland, D. C. Muchmore, and U. Hengartner, *J. Am. Chem. Soc.*, **94**, 5098 (1972).

3-Methyl-6-isopropylcyclohexen-1-yl diethyl phosphate (7): 40% yield; bp 103–108 °C (1.0 mm); IR (neat) 1664, 1290, 1270, 1000, 838 cm^{-1}; NMR (CCl_4) δ 0.65–1.15 (m 10 H), 1.32 (t, 6 H), 1.54–2.54 (m, 6 H), 4.02 (2 q, 4 H), 5.28 (m, 1 H).

Anal. Calcd for $C_{14}H_{27}O_4P$: C, 57.92; H, 9.37; P 10.67. Found: C, 57.67; H, 9.28; P, 9.96.

2,6-Dimethoxy-4-(2-pentenyl)phenyl diethyl phosphate (14): 97% yield; bp 180–182 °C (0.55 mm); IR (neat) 1598, 1275, 1220, 1163, 1130, 1028, 818 cm^{-1}; NMR (CCl_4) δ 0.97 (t, 3 H), 1.32 (t, 6 H), 2.00 (m, 2 H), 3.17 (m, 2 H), 3.71 (s, 6 H), 4.10 (2 q, 4 H), 5.39 (m, 2 H), 6.20 (s, 2 H).

Anal. Calcd for $C_{17}H_{27}O_6P$: C, 56.98; H, 7.59; P, 8.64. Found: C, 56.89; H, 7.74; P, 8.38.

Electroreduction of Diethyl Phosphates (4, 7, 9, 14, 16-22). A solution of 3.3 mmol of a phosphate in 30 mL of commercial DMF containing 5 g of Et_4NOTs was electrochemically reduced at the cathode potential of −2.6 to −2.7 V vs. SCE in a divided cell equipped with a platinum anode and a lead cathode. During the reaction, the solution was stirred with a magnetic stirrer and cooled with running water. After the amount of electricity listed in Table I was passed, the reaction mixture was poured into 100 mL of cold 3% aqueous hydrochloric acid, and organic products were extracted with three 50-mL portions of ether. The combined ethereal solution was dried over anhydrous magnesium sulfate, filtered, and evaporated to give the products in the yields shown in Table I. Products other than *m-n*-propylanisole, **8**, and **15** were identified by their physical and spectroscopic comparison with those of commercially available authentic samples. Product **8** was identified spectroscopically by comparison with the authentic sample.[12] The spectroscopic data of **15** were completely identical with those in the literature.[13] An analytical sample of *m-n*-propylanisole was collected by preparative GLC: IR (neat) 3060, 3030, 3000, 1610, 1585, 1262, 1045, 875, 775, 695 cm^{-1}; NMR (CCl_4) δ 0.91 (t, 3 H), 1.62 (m 2 H), 2.51 (t, 2 H), 3.69 (s, 3 H), 6.37–6.70 (m 3 H), 6.83–7.17 (m, 1 H); MS, *m/e* 150 (M^+).

Electroreduction of 9 in (a) a Dry DMF–D_2O System and (b) a DMF-d_7–D_2O System. (a) Commercial DMF was dried over calcium hydride, and the upper layer (300 mL) was decanted into a distillation flask containing D_2O (2 mL) and dry benzene (50 mL). The solution was distilled under a dry nitrogen stream at reduced pressure. DMF was distilled at the boiling point of 30–40 °C (1–5 mm), whereas D_2O and benzene were collected as a first fraction in a trap cooled with dry ice–acetone. This procedure was repeated twice. A solution of 0.25 mmol of **9** in 1 mL of dry DMF containing 0.15 g of anhydrous Bu_4NClO_4 and 6 μL of D_2O was electrochemically reduced in a divided cell equipped with a platinum anode and a lead cathode under a dry nitrogen stream. After 8 F/mol of electricity was passed, the usual workup yielded a mixture of **10** and **10′**. The isotopic purity (60 ± 10%) was calculated from NMR spectra of the product. (b) The electrolysis using commercial DMF-d_7 (99% grade) and anhydrous $LiClO_4$ was performed in a similar way as above.

2,6-Dimethoxyphenyl 2-Pentenyl Ether (12). A solution of 11.68 g (75 mmol) of pyrogallol 1,3-dimethyl ether and 13.3 g (89 mmol) of 1-bromo-2-pentene in 50 mL of acetone containing 13.5 g (97.5 mmol) of potassium carbonate was refluxed for 10.5 h. To the cooled solution was added 100 mL of water, and the solution was extracted with four 25-mL portions of ether. The ethereal solution was washed with two 50-mL portions of 10% sodium hydroxide solution and 30 mL of saturated brine and dried over calcium chloride; the solvent was evaporated. Distillation of the residual oil gave 14.58 g (88%) of compound **12**: bp 112–115 °C (1.0 mm); IR (neat) 3000, 1595, 1115, 970, 775, 732 cm^{-1}; NMR (CCl_4) δ 0.98 (t, 3 H), 2.00 (m, 2 H), 3.73 (s, 6 H), 4.27 (m, 2 H), 5.60 (m, 2 H), 6.3–6.9 (m, 3 H).

Anal. Calcd for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16. Found: C, 70.47; H, 8.11.

5-(2-Pentenyl)pyrogallol 1,3-Dimethyl Ether (13). The conversion of **12** to **13** was carried out by the method of Hahn and Wassmuth:[14] 75% yield; bp 126–135 °C (0.6 mm); IR (neat) 3500, 3025, 3000, 1615, 1115, 970, 835 cm^{-1}; NMR (CCl_4) δ 0.99 (t, 3 H), 2.06 (m, 2 H), 3.16 (m, 2 H), 3.79 (s, 6 H), 4.96 (s br, 1 H), 5.42 (m, 2 H), 6.21 (s, 2 H).

Anal. Calcd for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16. Found: C, 70.02; H, 8.22.

Olivetol was obtained from **15** by the known methods.[6]

Registry No. **4**, 71774-92-0; **7**, 71774-93-1; **9**, 71774-94-2; **10**, 71786-23-7; **10′**, 62103-69-9; **11**, 91-10-1; **12**, 71774-95-3; **13**, 71774-96-4; **14**, 71774-97-5; **15**, 22976-40-5; **16**, 16463-00-6; **17**, 67951-84-2; **18**, 26057-16-9; **19**, 71774-98-6; **20**, 67951-87-5; **21**, 71774-99-7; **22**, 16519-26-9; anisole, 100-66-3; *p*-cymene, 99-87-6; *m*-dimethoxybenzene, 151-10-0; tetralin, 119-64-2; tetrahydro-2-furanmethanol, 97-99-4; *trans*-3-methyl-6-isopropylcyclohex-1-en-1-ol, 71775-00-3; 2-methoxy-4-propylphenol, 2785-87-7; 2-methoxyphenol, 90-05-1; 2-isopropyl-5-methylphenol, 89-83-8; 2-methoxy-4-(2-propenyl)-phenol, 97-53-0; 2-methoxy-4-(1-propenyl)phenol, 97-54-1; 3,5-dimethoxyphenol, 500-99-2; 2-naphthol, 135-19-3; diethyl phosphate, 762-04-9; 1-bromo-2-pentene, 20599-27-3; olivetol, 500-66-3.

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Oxidation of Nitrosamines. 1. Formation of *N*-Nitrosoimminium Ions through the Oxidative Decarboxylation of *N*-Nitrosoproline, *N*-Nitrosopipecolic Acid, and *N*-Nitrososarcosine

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Received June 4, 1979

α-Acetoxy-*N*-nitrosopyrrolidine (**3**), α-acetoxy-*N*-nitrosopiperidine (**7**), and *N*-(α-acetoxymethylene)-*N*-methylnitrosamine (**15**), model compounds important in the study of nitrosamine metabolism, were synthesized from the corresponding nitrosamino acids. The nitrosamino acids were decarboxylated with lead tetraacetate to nitrosamino radicals, which were then oxidized to nitrosoimminium ions. Decarboxylation of nitrosoproline gave the solvolysis product **3** exclusively; nitrososarcosine gave the expected α-acetoxy compound, but dimethylnitrosamine was also obtained. Nitrosopipecolic acid gave the following compounds, with the relative yields in parentheses: *N*-nitroso-1,2,3,4-tetrahydropyridine (**8**, 10.6%), *N*-nitroso-1,2,3,6-tetrahydropyridine (**9**, 5.7%), *N*-nitroso-α-acetoxypiperidine (**7**, 33%), *N*-nitroso-*cis*-2,3-diacetoxypiperidine (**10**, 22%), *N*-nitroso-*trans*-2,3-diacetoxypiperidine (**11**, 28%), *N*-nitroso-4-acetoxy-1,2,3,4-tetrahydropyridine (**13**, <1%). The product distribution from the decarboxylation experiments is attributed to the stability of the nitrosoimminium ions.

The metabolic activation of nitrosamines to proximate carcinogens through α-hydroxylation has received much attention.[1] It is suggested that the highly reactive hydroxylated nitrosamine breaks down to a hydroxyazo in-

0022-3263/79/1944-4511$01.00/0