CH_3), 175 (M - CO_2H), 174 (M - CO_2H - H^+). Anal. Calcd for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32. Found: C, 70.67; H, 7.23.

2-Hydroxy-6,7,8,9-tetrahydro-5*H*-benzocycloheptene-7-carboxylic Acid (XIII). The procedure used was adapted from that of McOmie, Watts, and West.[10] To a stirred solution of methoxy acid XII (1.0 g, 0.0045 mol) in dichloromethane (200 mL) was added a 1.02 M solution of boron tribromide in dichloromethane (10.6 mL, 0.011 mol). The reaction mixture was stirred at 23 °C for 0.5 h in an argon atmosphere and water was added, and when the vigorous reaction had subsided, enough ethyl acetate was added so that the organic phase was less dense than water. The organic phase was separated, washed with water (3 × 20 mL) and once with brine, and dried (Na_2SO_4), and the solvent was removed in vacuo. The crude product was chromatographed on a 100-g silica gel dry column (2.5 × 30 cm) which was developed with ethyl acetate/Skelly B/methanol (33:66:0.7) to yield 0.55 g of XIII: mp 174–175 °C; ^1H NMR (acetone-d_6) δ 1.2–2.0 (4 H, m, C_6 and C_8H), 2.5 (1 H, m, C_7H), 2.6–3.0 (4 H, m, C_5 and C_9H), 6.4–6.7 (1 H, m, C_3H), 6.59 (2 H, brs, OH and CO_2H), 6.64 (1 H, s, C_1H), 6.85–7.05 (1 H, m, C_4H); IR (KBr) 3365, 3100, 2955, 2860, 1715, 1610 cm^{-1}; MS, *m/e* 206 (base peak, M^+), 161 (M - CO_2H), 160 (M - CO_2H - H^+). Anal. Calcd for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84. Found: C, 69.75; H, 6.89.

2-Hydroxy-7-(hydroxymethyl)-6,7,8,9-tetrahydro-5*H*-benzocycloheptene (XIV). A modification of the procedure of Cerny and Malek was used.[11] To a stirred, refluxing solution of phenolic acid XIII (0.24 g, 0.0012 mol) in dry benzene (10 mL) under argon was added dropwise over 1 h a 0.36 M solution of sodium bis(2-methoxyethoxy)aluminum hydride in benzene (Red-Al; 1.34 mL, 0.0036 mol). When the addition was complete, reflux was continued for 2 h, and after the mixture cooled, 9 N sulfuric acid was added until all salts dissolved. The reaction mixture was saturated with sodium chloride and extracted with ethyl acetate (4 × 10 mL). The combined organic phases were washed with sodium bicarbonate and with brine and dried (Na_2SO_4), and the solvent was removed to yield a semisolid which was chromatographed on a silica gel preparative thin-layer plate (2 mm × 20 cm × 20 cm) with 50% ethyl acetate in Skelly B as the eluent to yield 0.12 g (54%) of XIV: mp 138 °C; ^1H NMR (acetone-d_6) 0.7–2.2 (5 H, m, C_6, C_7, and C_8H), 2.6–2.88 (4 H, m, C_5 and C_9H), 3.35 (2 H, d, J = 5.5 Hz, CH_2OH), 3.4 (2 H, brs, OH), 6.38–6.7 (1 H, m, C_3H), 6.6 (1 H, s, C_1H), 6.75–7.05 (1 H, m, C_4H); IR (KBr) 3440, 3040, 2940, 2865, 1612 cm^{-1}; MS, *m/e* 192 (base peak, M^+), 174 (M - H_2O), 160 (M - H_2O - CH_2), 159 (M - H_2O - CH_2 - H^+). Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.77; H, 8.30.

Preparation of Potassium *tert*-Butoxide. A 0.011 M solution of potassium *tert*-butoxide in *tert*-butyl alcohol was prepared by heating at reflux under argon a mixture of potassium (0.215 g, 0.0055 mol) and dry *tert*-butyl alcohol (0.5 L) until all the potassium dissolved. The solution was stored in a sealed flask under argon.

6,7,8,9-Tetrahydro-4a,7-methano-4a*H*-benzocyclohepten-2(5*H*)-one (I). The mesylate II was prepared by the procedure of Pazdernik.[12] A solution of the phenolic alcohol XIV (0.1 g, 0.00052 mol) in dry pyridine (2 mL) was cooled in an ice bath under argon; methanesulfonyl chloride was added, and the solution was stirred at 0 °C for 1.5 h. The reaction mixture was poured onto ice, and the aqueous phase was acidified with 6 N HCl, saturated with sodium chloride, and extracted with ethyl acetate (3 × 20 mL). The combined extracts were washed with 5% HCl and brine, dried (Na_2SO_4), and concentrated in vacuo.

The crude mesylate II was cyclized to the tricyclic dienone I as described by Masamune.[2] A solution of the mesylate II in 0.011 M potassium *tert*-butoxide in *tert*-butyl alcohol (52 mL, 0.000 55 mol) was refluxed under argon for 7 h, and the solvent was removed on a rotary evaporator to yield a dark solid. The crude reaction product was triturated with ethyl acetate (4 × 20 mL), and the combined extracts were dried (Na_2SO_4) and concentrated in vacuo to yield a viscous oil which was chromatographed on a preparative silica gel thin-layer plate (0.5 mm × 20 cm × 20 cm) with 33% ethyl acetate in Skelly B as the eluent to yield 0.052 g (57%) of I: ^1H NMR ($CDCl_3$) δ 1.35–2.0 (4 H, m, C_5 and C_8H), 1.75–2.0 (2 H, m, C_8 and methano H), 1.95–2.4 (1 H, m, C_7H), 2.35–2.75 (2 H, m, C_9H), 6.0 (1 H, brs, C_1 H), 6.25 (1 H, dd, J = 9.5, 2 Hz, C_3H), 6.7 (1 H, d, J = 9.5 Hz, C_4H); IR (neat) 1660, 1628, 1605 cm^{-1}; MS, *m/e* 174 (M^+), 146 (M - CH_2=CH_2), 145 (M - CH_2=CH_2 - H^+). Anal. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.72; H, 8.17.

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Registry No. I, 26315-72-0; II, 83561-50-6; III, 83561-51-7; IV, 83561-52-8; V, 83561-53-9; VI, 83561-54-0; VII, 83561-55-1; VIII, 83561-56-2; IX, 83561-57-3; X (isomer 1), 83561-58-4; X (isomer 2), 83561-63-1; XI, 83561-59-5; XII, 83561-60-8; XIII, 83561-61-9; XIV, 83561-62-0.

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Reactions of 2,6-Dimethylphenol and 2,6-Dimethylanisole with Electrophilic Allylating Agents[1]

Bernard Miller* and Michael P. McLaughlin

Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01003

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Electrophilic substitution reactions of phenols and phenyl ethers normally take place exclusively at positions ortho or para to the activating oxygen functions, providing such positions are available for attack. Even in reactions of 2,6-dialkylphenols and 2,6-dialkylphenyl ethers, in which the alkyl groups direct attack to meta positions, most electrophilic substitution reaction,[2] including Friedel–Crafts reactions with *tert*-butyl and isopropyl chloride,[3] have been shown to proceed solely at the para positions.

Friedel–Crafts benzylations are exceptions to this rule.[4] Benzylation of 2,6-dimethylphenol (2,6-DMP) with a variety of benzylating agents, solvents, and catalysts yields ca. 38% of meta-benzylation products, while benzylation of 2,6-dimethylanisole (2,6-DMA) and other 2,6-dialkylphenyl alkyl ethers yields predominately (ca. 70%) meta-substitution products.[4]

Allylation reactions would be expected to closely resemble benzylation reactions, but difficulties can arise due to the reactivity of the double bonds of allylic halides and alcohols. Thus, our attempts to react either 2,6-DMP or 2,6-DMA with allyl alcohol, catalyzed by sulfuric acid, resulted in formation of higher molecular weight products from the allyl alcohol but no reaction with the phenol or anisole. Similar results were obtained by employing either allyl chloride or allyl bromide with anhydrous zinc chloride as the catalyst.

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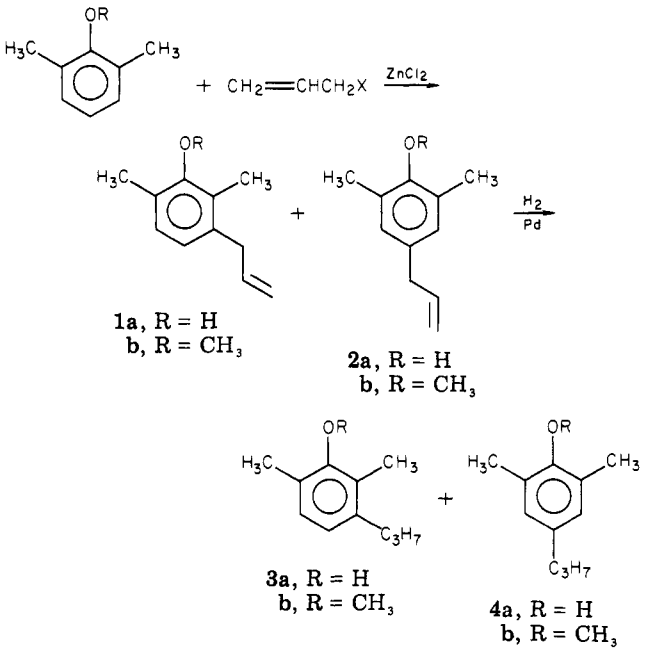
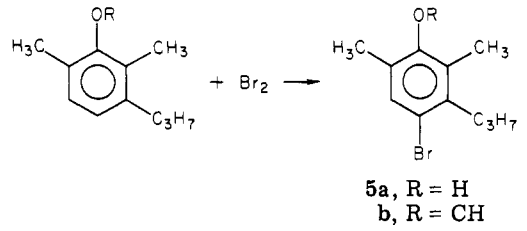
For minimization of these side reactions, dilute solutions of allyl bromide and allyl chloride were added very slowly to refluxing solutions of 2,6-DMP (present in ca. 5 molar excess to minimize diallylation) in the presence of zinc chloride. Even under these conditions, reaction with allyl bromide gave a complex mixture, apparently resulting from further reaction of the initial products. In contrast, reaction with allyl chloride usually gave very clean reaction mixtures, whose VPC traces showed, in addition to unreacted 2,6-DMP, two overlapping peaks with appropriate retention times for allyldimethylphenols. The NMR spectrum of these products (isolated together by preparative VPC) corresponded to that expected of a mixture of 3-allyl-2,6-dimethylphenol (**1a**) and 4-allyl-2,6-dimethylphenol (**2a**) (see Experimental Section), although the percentages of the two isomers in the mixture could not be established with any accuracy.





When the mixture of allylation products was hydrogenated at low pressure, the product showed two separate VPC peaks, in the area ratio 76:24. (In a second reaction, the products were present in an area ratio of 77:23.) However, separation of the two components on a preparative scale was still not possible. Sufficient bromine was therefore added to the hydrogenation products to react with the minor component, which was assumed to be the *m*-propyl isomer **3a**. After bromination, the smaller peak in the VPC trace had disappeared to be replaced by a peak at much higher retention time, and the doublet of doublets in the aromatic region of the NMR spectrum had been replaced by a singlet at lower field. The components of the reaction mixture were isolated by preparative VPC and identified by their spectra and by comparison with synthetic samples as 2,6-dimethyl-4-propylphenol (**4a**) and 4-bromo-2,6-dimethyl-3-propylphenol (**5a**).

Reaction of excess 2,6-DMA with allyl chloride under the conditions employed for reaction with 2,6-DMP followed by catalytic hydrogenation similarly yielded two products in a 60:40 ratio (VPC). The IR and NMR spectra and VPC retention times of the mixture were identical with those of a mixture containing 60% of 2,6-dimethyl-3-propylanisole (**3b**) and 40% 2,6-dimethyl-4-propylanisole (**4b**) (prepared by methylation of the corresponding phenols).

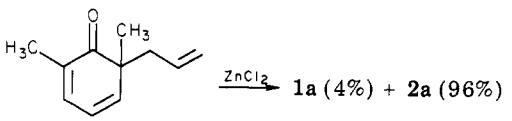
Slow addition of a dilute solution of allyl bromide to excess 2,6-DMA in the presence of zinc chloride not only gave products with VPC peaks for **1b** and **2b** but also gave products with larger retention times. These products, isolated as a mixture by preparative VPC, were found to contain bromine and to lack vinyl peaks in their NMR spectra. They presumably arose by addition of HBr to the double bonds of **1b** and **2b**, either before or after migration of the double bonds into conjugation with the ring.

Dehydrohalogenation of the crude reaction products with potassium *tert*-butoxide in *tert*-butyl alcohol resulted in disappearance of the high retention time peaks and enhancement of the peaks for **1b** and **2b**. After hydrogenation of the mixture, the product contained two components in a 60:40 ratio. The spectra and VPC retention times of this mixture were identical with those of a mixture of **3b** and **4b**. Addition of sufficient bromine to react with the major component and isolation of the two resulting products by preparative VPC showed the products to be **4b** and 4-bromo-2,6-dimethyl-3-propylanisole (**5b**), identified by comparison with synthetic samples.

Friedel–Crafts allylations of 2,6-DMP and 2,6-DMA thus yield high percentages of meta-substitution products. If it is assumed that ρ values for electrophilic allylation are similar to those for benzylation,[5] then the percentage of meta attack is nearly 1 order of magnitude greater than would be expected on theoretical grounds,[4] even if steric effects of the methyl groups, which would be expected to inhibit attack at meta positions, are neglected.

Formation of meta-allylation products, like formation of meta-benzylation products,[4] does not appear to result from rearrangements of products or intermediates formed by initial attack at the ortho or para positions of 2,6-DMP or 2,6-DMA. We observed, for instance, that the composition of a mixture of **1a** and **2a** containing ca. 96% **2a** was unchanged after prolonged solution in refluxing chloroform containing zinc chloride and allyl chloride. Furthermore, allylation of 2,6-DMP-*4-d* gave a mixture of **1a** and **2a** in precisely the same ratio as was obtained from the undeuterated phenol. The absence of a measurable deuterium isotope effect strongly argues against formation of the meta-allylated product by migration of an allyl group in the σ complex formed by initial attack at the para position.

To test the possibility that allylation initially occurs at an ortho position of 2,6-DMP to yield cyclohexadienone **6**, we subjected **6** to the conditions employed for Friedel–Crafts reactions of 2,6-DMP. It was rapidly converted to a mixture of phenols under these conditions, although no rearrangement occurred under the same conditions in the absence of the Lewis acid catalyst. Hydrogenation of the rearrangement product gave a mixture containing ca. 96% of the *p*-*n*-propyl isomer **4a** and 4% of **3a**. Clearly,



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any ortho allylation of 2,6-DMP would have resulted in an increase in the yield of para-allylated product and a *decrease* in the yield of meta-allylated product. The fact that allylation reactions, particularly of 2,6-DMP, give somewhat higher percentages of para-substitution products than do the corresponding benzylation reactions[4] may be due to some initial ipso attack by allylating agents at positions ortho to the oxygen functions, but this possibility cannot be confirmed at present.

At present, we can offer no convincing explanation for the high percentages of meta-allylation (and benzylation) products of 2,6-dialkylphenols and -anisoles.

Experimental Section

Unless otherwise indicated, all reagents and solvents were reagent grade or were purified before use by standard methods.

All melting points and boiling points are uncorrected. ^{1}H NMR spectra were recorded on a Perkin-Elmer Model R12A spectrometer in deuteriochloroform solution with Me_4Si as an internal standard. Vapor-phase chromatographic analyses were carried out on column A (a 5 ft × $^1/_8$ in. 5% Apiezon L on Chromosorb W column) or on column B (a 6 ft × $^1/_8$ in. 3% Silar column). Preparative VPC runs were carried out by employing a 5 ft × 0.25 in. 5% Apiezon column. Elemental analyses were carried out by the University of Massachusetts Microanalytical Laboratory, Amherst, MA.

2,6-Dimethyl-3-propylanisole (3b). 2,6-Dimethyl-3-propylphenol[6] (0.40 g, 2.4 mmol) was dissolved in 20 mL of *tert*-butyl alcohol, and potassium *tert*-butoxide (0.29 g, 2.5 mmol) was added. The mixture was shaken until the solid had dissolved, and methyl iodide (1.0 mL) was then added. The mixture was shaken briefly, allowed to stand for 10 min, poured into 100 mL of water, and extracted with methylene chloride. The methylene chloride layer was washed four times with water, dried over magnesium sulfate, and filtered, and the solvent was evaporated. The residue was chromatographed on alumina, eluting with petroleum ether, to yield 0.21 g (1.2 mmol, 50%) of 2,6-dimethyl-3-propylanisole (**3b**) as a colorless liquid: ^{1}H NMR δ 0.80 (t, J = 8 Hz, 3 H) 1.20–1.85 (m, 2 H), 2.20 (s, 3 H), 2.30 (s, 3 H), 2.54 (t, J = 8 Hz, 2 H), 3.65 (s, 3 H), 6.65 (d, J = 7 Hz, 1 H), 6.98 (d, J = 7 Hz, 1 H). Anal. Calcd for $C_{12}H_{18}O$: C, 80.83; H, 10.2. Found: C, 80.77; H, 9.47.

2,6-Dimethyl-4-propylanisole (4b). To a mixture of zinc (20 mesh, 25 g) amalgamated with 0.8 g of mercury(II) chloride in 50 mL of 50% aqueous hydrochloric acid was added a solution of 3,5-dimethyl-4-methoxypropiophenone (4.4 g, 0.023 mol) in 60 mL of hot 2-propanol. The reaction mixture was heated at reflux with stirring for 20.5 h. An additional 50 mL of 50% aqueous hydrochloric acid was then added and heating continued for an additional 47 h. The reaction mixture was then cooled, the solvent was evaporated under vacuum, and the residue was extracted with petroleum ether. The organic layer was washed with saturated sodium chloride solution, extracted with Claisen's alkali, and washed again with saturated ammonium chloride solution. The solution was dried over magnesium sulfate and filtered, and the solvent was evaporated to give 5 g of a yellow oil, which appeared to consist of 80% of the desired product (by VPC and NMR analysis). Distillation through a 3-in. column packed with nichrome gauze gave 2,6-dimethyl-4-propylanisole:[6] 0.44 g (11%); colorless liquid; bp 133 °C (27 torr); ^{1}H NMR δ 0.80 (t, J = 8 Hz, 3 H), 1.15–2.0 (m, 2 H), 2.25 (s, 6 H), 2.45 (t, J = 7 Hz, 2 H), 3.65 (s, 3 H), 6.80 (s, 2 H).

2,6-Dimethyl-3-propyl-4-bromophenol (5a). A solution of bromine (4.05 g, 0.0253 mol) in 50 mL of chloroform was added drop by drop to a solution of 2,6-dimethyl-3-propylphenol (4.17 g, 0.0254 mol) in 80 mL of chloroform. The mixture was allowed to stand at room temperature for 1.5 h, washed with sodium sulfite solution and then with ammonium chloride solution, dried over sodium sulfate, and filtered, and the solvent was evaporated. The dark purple product was twice recrystallized from carbon tetrachloride to give **5a** as a white solid: mp 90.5–91.5 °C; ^{1}H NMR δ 1.0 (t, J = 7 Hz, 3 H), 1.2–1.8 (m, 2 H), 2.15 s, 3 H), 2.20 (s, 3 H), 2.72 (t, J = 8 Hz, 2 H), 4.55 (s, 1 H), 7.15 (s, 1 H). Anal. Calcd for $C_{11}H_{15}OBr$: C, 54.10; H, 6.61; Br, 32.73. Found: C, 54.11; H, 6.91; Br, 32.44.

4-Bromo-2,6-dimethyl-3-propylanisole (5b). Anhydrous potassium carbonate (0.40 g, 3.0 mmol) and dimethyl sulfate (0.40 g, 3.2 mmol) were added to a solution of 2,6-dimethyl-3-propyl-4-bromophenol (0.66 g, 2.7 mmol) in 20 mL of acetone. The mixture was stirred and heated to reflux for 18 h. It was then cooled, the solvent was evaporated under vacuum, and the residue was extracted with petroleum ether and washed with water, with Claisen's alkali, and with saturated sodium chloride solution. The solution was dried over magnesium sulfate and the solvent evaporated to give essentially pure (VPC) **5b**: 0.65 g (94%); pale yellow liquid; ^{1}H NMR (taken on a sample isolated by preparative VPC) δ 1.0 (t, 3 H, J = 8 Hz), 1.2–1.8 (m, 2 H), 2.20 (s, 3 H), 2.72 (t, J = 7 Hz, 2 H), 3.65 (s, 3 H), 7.22 (s, 1 H).

3-Bromo-2,6-dimethyl-4-propylanisole. A solution of bromine (0.23 g, 1.4 mmol) in 2 mL of glacial acetic acid was added drop by drop to a solution of 2,6-dimethyl-4-propylanisole (0.159 g, 0.892 mmol) in 10 mL of acetic acid. The reaction mixture was kept in the dark at room temperature for 18 h to give a nearly colorless solution. The mixture was added to aqueous sodium sulfite solution and extracted with petroleum ether, and the petroleum ether layer was washed with water, potassium hydroxide solution, and saturated ammonium chloride solution. It was then dried over magnesium sulfate and the solvent evaporated to give 0.18 g of a yellow liquid. VPC analysis (column A, 170 °C) showed peaks at 1.7 (2,6-dimethyl-4-propylanisole) and 5.9 min in an area ratio of 1:10. The major component was isolated by preparative VPC and identified as 3-bromo-2,6-dimethyl-4-propylanisole: ^{1}H NMR δ 0.95 (t, J = 8 Hz, 3 H), 1.3–1.9 (m, 2 H), 2.20 (s, 3 H), 2.35 (s, 3 H), 2.64 (t, J = 7.5 Hz, 2 H), 3.65 (s, 3 H), 6.90 (s, 1 H).

Reaction of Excess 2,6-Dimethylphenol with Allyl Chloride. A solution of allyl chloride (1.0 g, 0.013 mol) in 15 mL of chloroform was added very slowly to a refluxing mixture of 2,6-DMP (8.0 g, 0.066 mol) and zinc chloride (0.3 g) in 30 mL of chloroform. When the addition was complete (4 h), the mixture was cooled, washed with water, dried over magnesium sulfate, and filtered, and the solvent was evaporated. VPC analysis of the product (column A, 140 °C) showed a peak at 3.5 min (2,6-DMP) and overlapping peaks at 11.5 and 11.8 min. A sample was collected by preparative VPC at 200 °C. The aromatic region of its ^{1}H NMR spectrum showed peaks at δ 6.81 (br s), 6.67 (d, J = 8 Hz), and 6.9 (d, partially obscured by the s at 6.81). The remaining reaction product was dissolved in 50 mL of benzene, 0.5 g of 5% Pd/C added, and the mixture stirred overnight under 1 atm of hydrogen. The mixture was filtered and evaporated. The NMR spectrum of the product showed no vinyl absorptions. VPC analysis (column A, 140 °C) showed peaks at 11.7 and 12.6 min in an area ratio of 76:24. (A second reaction carried out in the same manner showed peaks in an ratio of 77:23.) Coinjection with authentic samples showed the lower retention time peak to have the same retention time as 2,6-dimethyl-4-propylphenol and the higher retention time peak to have the same retention time as 2,6-dimethyl-4-propylphenol.

The combined product from two runs (17.1 g) was distilled at 8 torr to remove unreacted 2,6-DMP. The residue (3.9 g) contained ca. 21% residual 2,6-DMP. A solution of bromine (3.4 g, 0.02 mol) in 10 mL of chloroform was added to the residue dissolved in 20 mL of chloroform. After 3 min, the solution was washed with sodium sulfite solution and with water, dried, and filtered, and the solvent was evaporated to yield 4.7 g of brown oil. VPC analysis (column A, 190 °C) showed the presence of three components which were isolated by preparative VPC and identified as **4-bromo-2,6-dimethylphenol**, **2,6-dimethyl-4-propylphenol**, and **4-bromo-2,6-dimethyl-3-propylphenol**.

When the reaction was carried out as above with **2,6-dimethylphenol-*4*-*d*** (0.80 g) and 0.20 g of allyl chloride, the ratio of products after hydrogenation was 76:24.

Rearrangement of 6-Allyl-2,6-dimethylcyclohexa-2,4-dien-1-one in the Presence of Zinc Chloride. Zinc chloride (0.3 g) was added to a solution of 6-allyl-2,6-dimethylcyclohexa-2,4-dien-1-one[7] (0.50 g) and allyl chloride (0.1 g) in 20 mL of

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(7) Miller, B. *J. Am. Chem. Soc.* **1965**, *87*, 5115.

chloroform. The solution was heated quickly to reflux and retained at reflux for a total contact time of 10 min. It was then cooled, washed with water, and dried over magnesium sulfate, and the solvent was evaporated. IR analysis showed the carbonyl peak to have disappeared. The product was dissolved in 20 mL of benzene, Pd/C (5%, 0.2 g) was added, and the mixture was stirred under an atmosphere of hydrogen for 3 h and then filtered. VPC analysis (column B, 140 °C) showed peaks with retention times of 11.8 and 12.7 min in an area ratio of 96.5:3.5.

A second run was carried out by stirring the reaction mixture overnight at room temperature. After hydrogenation, VPC analysis showed peaks at t_R = 11.7 and 12.6 min in an area ratio of 94:6.

Reaction of Excess 2,6-Dimethylanisole with Allyl Chloride. Allyl chloride (0.75 g, 0.010 mol) was added to a mixture of 2,6-DMA (8.60 g, 0.0631 mol) and anhydrous zinc chloride (0.52 g, 0.038 mol) in 40 mL of chloroform. The mixture was heated at reflux for 18.5 h and cooled, and the solvent was evaporated. The residue was extracted with 1:1 benzene–petroleum ether, and the extract was washed twice with saturated sodium chloride solution and dried over anhydrous magnesium sulfate. The solvent and excess 2,6-DMA were distilled off under vacuum to yield 0.30 g of a brown oily residue. VPC analysis on column A at 170 °C showed two peaks (t_R = 2.6 and 6.2 min) in an area ratio of 3.8:1. The major component was isolated by preparative VPC. Its NMR spectrum showed peaks at ca. δ 2.2 (4 peaks, 6 H), 3.1–3.4 (m, 2 H, allylic methylenes), 3.6 (s, 3 H, methoxy), and 4.7–5.3 (m, 2 H, terminal vinyl peaks), 5.5–6.3 (m, 1 H, secondary vinyl) and a 3-H signal consisting of a singlet at δ 6.85 overlapping doublets (J = 8 Hz) at δ 6.69 and 7.00. The spectrum corresponded to that expected of a mixture of 2-allyl- and 3-allyl-2,6-dimethylanisoles, but the ratio of isomers could not be determined.

In each of two later runs, the crude reaction product showed overlapping peaks at δ 5.8 and 6.2 (column B, 110 °C) but no products with higher retention times. The mixture in each case was dissolved in 10 mL of benzene and stirred under an atmosphere of hydrogen in the presence of 5% Pd/C (0.23 g) for 18 h. Filtration of the solution and evaporation of the solvent left a yellow oil whose NMR spectrum corresponded to that of a mixture of 3-propyl- and 4-propyl-2,6-dimethylanisoles. VPC analysis (column B, 100 °C) showed peaks (t_R = 5.5 and 6.8 min) in an area ratio of 40:60 in each run. Comparison with synthetic samples indicated the principal isomer to be 3-propyl-2,6-dimethylanisole.

Reaction of Excess 2,6-Dimethylanisole with Allyl Bromide. Allyl bromide (1.26 g, 0.104 mol) was added to a mixture of 2,6-DMA (7.34 g, 0.0539 mol) and anhydrous zinc chloride (1.04 g, 7.63 mmol) in 40 mL of chloroform. The mixture was heated at reflux for 19 h and worked up as described for the reaction with allyl chloride to yield 0.74 g of a yellow oil. VPC analysis (column A, 170 °C) showed peaks with retention times of 2.5 (corresponding to that expected for allyl dimethylanisoles), 5.0, 6.1, and 9.5 min. Isolation of the mixture of products with retention times of 5–6 min and of the product with the retention time of 9.5 min showed complex spectra lacking any vinyl peaks.

Part of the crude product (0.47 g) was dissolved in 20 mL of *tert*-butyl alcohol, and potassium *tert*-butoxide (0.54 g, 4.8 mmol) was added. The solution was heated at reflux for 21 h and cooled to room temperature, and petroleum ether was added. The mixture was washed twice with saturated ammonium chloride solution and dried over magnesium sulfate, and the solvent evaporated to yield 0.35 g of a yellow oil. VPC analysis (column A, 170 °C) showed two peaks (t_R = 2.9 and 3.2 min). The high retention time peaks previously present had essentially disappeared. The dehydrohalogenation product was dissolved in 15 mL of methanol, 0.2 g of 5% Pd/C was added, and the mixture was stirred at room temperature under an atmosphere of hydrogen for 8 days. It was then filtered, and the solvent was evaporated under vacuum to give 0.29 g of a pale yellow oil, whose NMR spectrum indicated the absence of vinyl peaks. VPC analysis (column B, 108 °C) showed two peaks with retention times of 5.9 and 7.0 min in an area ratio of 40:60. The hydrogenation product was dissolved in 10 mL of glacial acetic acid, and a solution of bromine (0.13 g, 0.81 mmol) in 5 mL of glacial acetic acid was added drop by drop. The resulting mixture was shaken for 5 min, and sodium sulfite solution was added. The mixture was extracted with petroleum ether, and the organic layer was separated and then washed with distilled water, 5% potassium hydroxide solution, and saturated ammonium chloride solution. It was then dried over magnesium sulfate and filtered, and the solvent was evaporated to yield 0.23 g of a yellow oil, which showed two major peaks (t_R = 1.18 and 7.1 min at 170 °C). These components were isolated by preparative VPC and identified as **2,6-dimethyl-4-propylanisole** and **4-bromo-2,6-dimethyl-3-propylanisole**.

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Registry No. **3a**, 83547-48-2; **3b**, 83547-44-8; **4a**, 13037-82-6; **4b**, 83547-45-9; **5a**, 83547-46-0; **5b**, 83547-47-1; **6**, 20700-88-3; 2,6-DMP, 576-26-1; 2,6-DMA, 1004-66-6; $ZnCl_2$, 7646-85-7; 3,5-dimethyl-4-methoxypropiophenone, 5384-11-2; 3-bromo-2,6-dimethyl-4-propylanisole, 83547-49-3; allyl chloride, 107-05-1; allyl bromide, 106-95-6; 2,6-dimethylphenol-*4-d*, 22100-63-6; 4-bromo-2,6-dimethylphenol, 2374-05-2.

On the Selectivity–Selectivity Relationship in the Solvolysis Reactions of Alkyl Halides

Zvi Rappoport* and Rachel Ta-Shma

Department of Organic Chemistry, The Hebrew University, Jerusalem 91904, Israel

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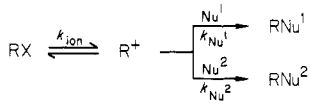
A recent common method for studying carbenium ion reactions and the nature of the solvolysis intermediates involves reactivity–selectivity plots.[1-7] The selectivities S are usually obtained from the product distributions in a competitive reaction of a cationoid species R^+ (which may be a free ion or an ion pair) with two nucleophiles Nu^1 and Nu^2 (eq 1), by application of eq 2.



(1)

$$S = k_{Nu^1}/k_{Nu^2} = [RNu^1][Nu^2]/[RNu^2][Nu^1] \quad (2)$$

Two common pairs of nucleophiles Nu^1 and Nu^2 which give reactivity–selectivity plots are N_3^- and H_2O[2,3] and H_2O and EtOH.[4-6,7a] Sneen and co-workers[2] and Schleyer and co-workers[3] found that a plot of log k_{solv}, where k_{solv} is the solvolysis rate constant of an alkyl chloride in 80% acetone, against the corresponding log S_N = log ($k_{N_3^-}/k_{H_2O}$) for many alkyl chlorides is linear. This is a reactivity–selectivity relationship since k_{solv} is presumably proportional to the stability of the ion R^+ in its reactions with nucleophiles.

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