temperature. After addition of a saturated ammonium chloride solution (30 mL), the organic layer was separated, the aqueous solution was extracted with CH_2Cl_2 (3 × 30 mL), and the combined organic layers were washed with a saturated sodium thiosulfate solution (50 mL), dried over magnesium sulfate, and concentrated. The residue was purified by chromatography on silica gel (ether) to give 580 mg (72% yield) of a mixture of diastereoisomers **4b** (91%) and **3b** (9%). The spectral data for **4b** follow. ^1H NMR (δ): 0.88 (3 H, t); 1.24–1.65 (14 H, m); 1.72 (1 H, dd, *J* = 8.4 Hz, *J'* = 1.5 Hz); 1.82 (1 H, m); 3.68–4.08 (5 H, m); 4.92 (1 H, s); 5.01 (1 H, s); 6.38 (2 H, m).

General Procedure for the Oxidation of Diols 3 and 4. To a stirred solution of the diol (1 mmol) in acetone (10 mL), kept at 0 °C, was added dropwise 1.5 mL of Jones reagent (prepared by dissolution of CrO_3 (2 g, 20 mmol) in water (11.5 mL) and concentrated H_2SO_4 (3.5 mL)). The reaction mixture was allowed to reach room temperature and stirred for 45 min (if necessary, a few drops of Jones reagent were added in order to obtain a persistent orange coloration). The excess of oxidant was then destroyed by addition of isopropyl alcohol. The solution was filtered. The filtrate was concentrated, and the residue was extracted with CH_2Cl_2 (10 mL). The solid was dissolved in water (15 mL), and the aqueous layers were extracted with CH_2Cl_2 (3 × 15 mL). The combined organic layers were washed with a saturated solution of sodium bicarbonate (30 mL) and water (30 mL). The organic layer was dried over magnesium sulfate and concentrated. The crude lactones were purified and separated from the minor diastereoisomer by chromatography on silica gel [R = CH₃, ether; R = C_4H_9, ether–hexane (80–20); R = C_8H_{17}, ether–hexane (60–40)].

(−)-(1R,2S,5R,6S,7S)-4,10-Dioxa-5-methyltricyclo-[5.2.1.0²,⁶]dec-8-en-3-one (5a). Yield, 63%; [α]²⁰_D −120° (CHCl₃, c 0.5). IR (neat): 3080 (w); 1770 (vs); 1200 (s); 1020 (s) cm⁻¹; CIMS (NH₃), *m/e* (relative intensity): 184 (MNH₄⁺, 5.8); 166 (M⁺, 0); *116* (100). ^1H NMR (δ): 1.44 (3 H, d, *J* = 6.5 Hz); 2.31 (1 H, dd, *J* = 7.8 Hz, *J'* = 3.4 Hz); 2.88 (1 H, d, *J* = 7.8 Hz); 4.50 (1 H, qd, *J* = 6.5 Hz, *J'* = 3.3 Hz); 5.00 (1 H, s); 5.26 (1 H, s); 6.44 (2 H, m). Anal. Calcd for C₉H₁₀O₃: C, 65.06; H, 6.02. Found: C, 65.08; H, 6.32.

(−)-(1R,2S,5R,6S,7S)-4,10-Dioxa-5-*n*-octyltricyclo-[5.2.1.0²,⁶]dec-8-en-3-one (5b). Yield, 38%; mp 55.5 °C; [α]²⁰_D −56° (CHCl₃, c 1). IR (CDCl₃): 3070 (w); 1770 (vs); 1190 (s) cm⁻¹. CIMS (NH₃), *m/e* (relative intensity): 282 (MNH₄⁺, 68.3); 265 (MH⁺, 0.4); 264 (M⁺, 0); *214* (100). ^1H NMR (δ): 0.89 (3 H, t); 1.23–1.78 (14 H, m); 2.33 (1 H, dd, *J* = 7.8 Hz, *J'* = 3.4 Hz); 2.83 (1 H, d, *J* = 7.8 Hz); 4.34 (1 H, m); 4.96 (1 H, s); 5.28 (1 H, s); 6.44 (2 H, m). Anal. Calcd for C₁₆H₂₄O₃: C, 72.73; H, 9.09. Found: C, 72.81; H, 9.30.

(−)-(1R,2S,5R,6S,7S)-4,10-Dioxa-5-*n*-butyltricyclo-[5.2.1.0²,⁶]dec-8-en-3-one (5c). Yield, 35%; [α]²⁰_D −69° (CHCl₃, c 0.5); IR (neat): 3090 (w); 1760 (vs); 1200 (s); 1020 (s) cm⁻¹. CIMS (NH₃), *m/e* (relative intensity): *226* (MNH₄⁺, 100); 209 (MH⁺, 8.5); 208 (M⁺, 0.3); *158* (100). ^1H NMR (δ): 0.92 (3 H, t); 1.25–1.50 (4 H, m); 1.60–1.77 (2 H, m); 2.32 (1 H, dd, *J* = 7.8 Hz, *J'* = 3.4 Hz; 2.83 (1 H, d, *J* = 7.8 Hz); 4.33 (1 H, m); 4.96 (1 H, s); 5.26 (1 H, s); 6.43 (2 H, m). Anal. Calcd for C₁₂H₁₆O₃: C, 69.23; H, 7.69. Found: C, 68.92; H, 8.01.

(−)-(1R,2S,5S,6S,7S)-4,10-Dioxa-5-methyltricyclo-[5.2.1.0²,⁶]dec-8-en-3-one (6a). Yield, 31%; mp 124 °C; [α]²⁰_D −132° (CHCl₃, c 0.5). ^1H NMR (δ): 1.49 (3 H, d, *J* = 6.5 Hz); 2.60 (1 H, dd, *J* = *J'* = 7.8 Hz); 2.91 (1 H, d, *J* = 7.8 Hz); 4.82 (1 H, dq, *J* = 7.8 Hz, *J'* = 6.5 Hz); 5.18 (1 H, s); 5.26 (1 H, s); 6.45 (2 H, m).

(−)-(1R,2S,5S,6S,7S)-4,10-Dioxa-5-*n*-octyltricyclo-[5.2.1.0²,⁶]dec-8-en-3-one (6b). Yield, 29%; mp 86.5 °C; [α]²⁰_D −121° (CHCl₃, c 0.975). ^1H NMR (δ): 0.87 (3 H, t); 1.17–1.75 (14 H, m); 2.58 (1 H, dd, *J* = *J'* = 7.8 Hz); 2.90 (1 H, d, *J* = 7.8 Hz); 4.58 (1 H, m); 5.16 (1 H, s); 5.26 (1 H, s); 6.44 (2 H, m).

General Procedure for the Thermolysis of Lactones 5 and 6. A solution of lactone (1 mmol) in toluene (3 mL) was heated under reflux (bath temperature: 120 °C) for 3 h. The solutions were directly chromatographed on silica gel (20 g) [ether–hexane (60–40)] affording butenolides (−)-(R)-**7(a–c)** and (+)-(S)-**7(a,b)** with 90–96% yields.

Spectal data of each butenolide are in good agreement with those given in the literature.⁵ᵇ,¹⁶

(+)-(R)-γ-Dodecanolactone (8). To a stirred suspension of 10 mg of 10% palladium on coal in ethanol (3 mL) under an hydrogen atmosphere was added 98 mg (0.5 mmol) of butenolide (−)-(R)-**7b** in ethanol (2 mL). When the required amount of hydrogen had been taken up (11.2 mL), the catalyst was removed by filtration. The filtrate was then concentrated, and the residue was purified by chromatography on silica gel [ether–hexane (50–50)] to yield 85 mg (86%) of lactone 8. [α]²⁰_D +37.8° (MeOH, c 1). IR (neat): 1780 (vs); 1180 (s); 1130 (m); 1020 (m) cm⁻¹. MS, *m/e* (relative intensity): 198 (M⁺, 0); 180 (M⁺ − H₂O, 0.8); *85* (100); 84 (24.6); 56 (10.2); 55 (14.0); 41 (11.8). ^1H NMR (δ): 0.90 (3 H, t); 1.20–1.95 (15 H, m); 2.24–2.42 (1 H, m); 2.55 (2 H, dd, *J* = 9.7 Hz, *J'* = 6.7 Hz); 4.51 (1 H, m).

(+)-(3S,4R)-3-Methyl-4-octanolide (9). To a stirred solution of lithium dimethylcuprate (2.5 mmol; prepared from addition of a solution of methyllithium (1.5 M) in ether (3.3 mL, 5 mmol) to CuI (525 mg, 2.5 mmol) at −20 °C) in ether (10 mL) was added dropwise a solution of (−)-(R)-**7c** (70 mg, 0.5 mmol) in ether (5 mL) at −60 °C. The reaction mixture was allowed to reach room temperature over a period of 2 h. Then the solution was hydrolyzed by addition of a 10% aqueous HCl solution (5 mL). The resulting mixture was filtered on Celite, and the aqueous phase was extracted with ether (2 × 10 mL). The combined organic layers were dried over magnesium sulfate and concentrated. The residue was purified by chromatography on silica gel [ether–hexane (50–50)] to yield 62 mg (80%) of 9. [α]²⁰_D +72.8° (MeOH, c 1). Spectral data are in good agreement with those given by Günther.¹⁵ᵃ

Preparation and Reactions of Trianions from the Dimethylphenols

Robert B. Bates,* Teruna J. Siahaan, Kessara Suvannachut, Stephen K. Vasey, and Kraig M. Yager

Department of Chemistry, University of Arizona, Tucson, Arizona 85721

Many aromatics containing primary alkyl groups are best prepared by two-step one-pot sequences consisting of (1) dimetalating readily available aromatics such as the xylenes¹ and the cresols² in the benzylic positions to give delocalized dianions such as **1** and **2** (Chart I) and (2) adding electrophiles or oxidizing agents; such aromatics cannot be readily prepared by Friedel–Crafts reactions due to carbonium ion rearrangements and orientation limitations. All three isomeric *trianions* **3** have also been prepared³⁻⁵ (the 1,3,5-isomer, with the largest resonance stabilization,⁵ in 86% yield), and we now wish to report efforts to prepare the corresponding trianions containing one and two oxygens, i.e., trianions **4** from the dimethylphenols and trianions **5** from the dihydroxytoluenes. While only the

(1) Bates, R. B.; Ogle, C. A. *J. Org. Chem.* 1982, *47*, 3949.
(2) Bates, R. B.; Siahaan, T. J. *J. Org. Chem.* 1986, *51*, 1432.
(3) Trimitsis, G. B.; Tuncay, A.; Beyer, R. D.; Ketterman, K. J. *J. Org. Chem.* 1973, *38*, 1491.
(4) Klein, J.; Medlik-Balan, A. *J. Am. Chem. Soc.* 1977, *99*, 1473.
(5) Bates, R. B.; Hess, B.; Ogle, C. A.; Schaad, L. *J. Am. Chem. Soc.*, 1982, *103*, 5052.

Table I. Products and Yields in Reactions of Dimethylphenols with Lochmann's Base Followed by Dimethyl or Diethyl Sulfate

starting Me$_2$PhOH	dialkyl sulfate	products (yield, %)			
		monoalkyltd	dialkyltd	trialkyltd	tetraalkyltd
2,3	Me	6, R = Me; 2,3 (46)	7, R = Me; 2-Et-3-Me (7)	8, R = Me; 2,3 (20)	10, R = Me; 2,3 (11) 11a (5)
			7, R = Me; 3-Et-2-Me (7)	9, R = Me; 3-Et-2-Me (4)	
2,4	Me	6, R = Me; 2,4 (29)	7, R = Me; 2-Et-4-Me (23)	8, R = Me; 2,4 (19)	10, R = Me; 2,4 (5)
			7, R = Me; 4-Et-2-Me (2)	9, R = Me; 4-Et-2-Me (4)	
2,5	Me	6, R = Me; 2,5 (12)	7, R = Me; 2-Et-5-Me (9)	8, R = Me; 2,5 (52)	10, R = Me; 3,6 (3)
			7, R = Me; 5-Et-2-Me (23)		
2,6	Me	6, R = Me 2,6 (20)	7, R = Me; 2-Et-6-Me (43)	8, R = Me; 2,6 (36)	
3,4	Me		7, R = Me; 4-Et-3-Me (28)	8, R = Me; 3,4 (44) 9, R = Me; 5-Et-4-Me (10) 9, R = Me; 4-Et-5-Me (2)	10, R = Me; 4,5 (13)
3,5	Me		7, R = Me; 3-Et-5-Me (3)	8, R = Me; 3,5 (80)	10, R = Me; 3,5 (7) 11b, R = Me (4) 11c, R = Me (1)
3,5	Et	6, R = Et; 3,5 (4)	7, R = Et; 3-Pr-5-Me (9)	8, R = Et; 3,5 (70)	10, R = Et; 3,5 (3) 11b, R = Et (2) 11c, R = Et (4)

Chart I
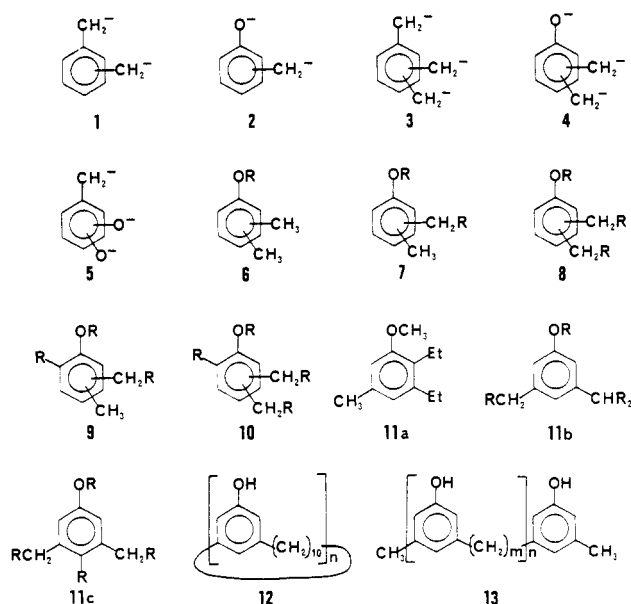
dianions were obtained from the isomers of the latter which we tried (the 2,5-, 2,6-, 3,4-, and 3,5-isomers; presumably their dianions are too stable to metalate further under our conditions), we herein describe the apparent preparation of all six trianions 4 and some of their reactions.

Trianions **4** were prepared by refluxing the corresponding dimethylphenols in heptane for 18 h with 4 equiv of KO-*t*-Bu and 4.5 equiv of *n*-BuLi and reacted with excess dimethyl sulfate to produce methylated products in yields indicated in Table I. In accordance with MO calculations which suggest the stability order for the hydrocarbon anions **3** to be $1,3,5 > 1,2,4 > 1,2,3$,[5] the yield of desired trialkylation product **8** is highest in the 3,5-case (80%), and underalkylation products **6** and **7** are very minor in this case (only 3%), more serious with the 2,4- (54%), 2,5- (44%), and 3,4-isomers (28%) and most serious with the 2,3- (60%) and 2,6-isomers (63%).

Some minor byproducts **9** and **10** have had alkyl groups added to the ring ortho to the oxygen function. These may be arising from competing ring metalation ortho to O^{-}[6] or during the quench by the well-known ortho metalation of aryl alkyl ethers.[7,8] To determine the facility of ortho

(6) Posner, G. H.; Canella, K. A. *J. Am. Chem. Soc.* **1985**, *107*, 2571.

metalation of ethers under these conditions, we tried them on anisole, obtaining a quantitative yield of a mixture of four ring-alkylated products (40% 2-methylanisole, 35% 2,6-dimethylanisole, 18% 2,5-dimethylanisole, and 6% 2-ethylanisole). When treated similarly, phenol gave anisole in 63% yield, along with 18% of 2-methylanisole, 8% of 2,5-dimethylanisole, and 5% of 2,6-dimethylanisole. The much lower yields of ortho-metalation products with phenol than with anisole may indicate that ethers are the main species being ortho-metalated in the above cases.

An attempted preparation of 4-hydroxy[10,10]metacyclophane (**12**, $n = 1$) by simultaneous addition of a suspension of trianion 3,5-**4** and a solution of 1,8-dibromooctane to THF gave the desired product in 3% yield; much more cyclic dimer **12** ($n = 2$) was found (50%), along with 5% of bis(phenol) **13** ($m = 10$, $n = 1$).

Attempted preparations of 4,4'-dihydroxy[2,2]metacyclophane by oxidation of trianion 3,5-**4** gave none of this product. When iodine (which gave the best yield without the hydroxyl groups[1]) was the oxidant, intractable iodinated products were formed. When cuprous bromide was used, **13** ($m = 2$, $n = 1$) (40%) and **13** ($m = 2$, $n = 2$) (35%) were identified as the major oxidation products.

These reactions provide ready access to many new phenolics bearing primary alkyl substituents.

Experimental Section

For general techniques, see ref 2.

Trianions 4. Heptane (130 mL) in a 250-mL round-bottom flask was deoxygenated with argon for 15 min, and KO-*t*-Bu (4.48 g, 40 mmol, Aldrich) and 29.0 mL of 1.55 M (45 mmol) *n*-BuLi in hexane (Aldrich) were added. After the mixture was stirred 15 min, dimethylphenol (1.22 g, 10 mmol) was added, and the solution was refluxed 18 h. The initial and final colors after adding the phenols were as follows: 2,3, yellow → dark brown; 2,4, dark yellow → brown; 2,5, orange → yellowish brown; 2,6, bright yellow → reddish brown; 3,4 orange → dark brown; 3,5 yellow → reddish brown. After cooling to 0 °C, the mixture was filtered (Schlenk), the solid was washed with 50 mL of pentane, and residual pentane was blown off with argon. For reactions, this trianion salt was

(7) Beak, P.; Snieckus, V. *Acc. Chem. Res.* **1982**, *15*, 306.

(8) In one case in which a *gel* was quenched with diethyl sulfate, four extra products were obtained (each in <4% yield), at least two of which resulted from intermolecular exchange during the quench, since one of their aryl protons had been replaced by a *sec*-butyl group (no doubt via the sequence ethylation, metalation, ethylation). When this reaction was repeated with enough added solvent to break up the gel, none of these products were observed.

(9) Insignificant differences in yields were observed when inverse addition was used.

suspended by stirring at 0 °C in 150 mL of THF.

Reactions of Trianions 4 with Dimethyl Sulfate. After injecting dimethyl sulfate (7.6 mL, 80 mmol) into the trianion suspension and stirring for 18 h, KOH (5.09 g, 91 mmol) and 75 mL of MeOH were added, and the solution was refluxed for 2 h to destroy excess dimethyl sulfate.[10] Water (20 mL) was added, followed by 5 N HCl to acidify the solution, which was then extracted with 3 × 200 mL of pentane. After drying (MgSO$_4$), filtration, evaporation, and vacuum-distillation, the products were separated by GC on SE-30 silicone oil, Ucon LB-550x, or Carbowax 20M. Yields estimated from the GC information and the NMR spectrum of the crude product after adding 100 µL of CH$_2$Cl$_2$ as an internal standard are given in Table I. Compounds **6** have been previously described, but the other compounds are apparently new. Satisfactory elemental analyses were obtained on the desired products **8**; all compounds were characterized via their ^{1}H NMR parameters (CDCl$_3$, TMS), which are given below.

2-Ethyl-3-methylanisole (7, R = Me; 2-Et-3-Me): δ 7.10 (t, J = 7.8 Hz, H-5), 6.81 (d, J = 7.8 Hz, H-4), 6.75 (d, J = 7.8 Hz, H-6), 3.84 (s, OMe), 2.70 (q, J = 7.5 Hz, CH$_2$), 2.34 (s, 3-Me), 1.13 (t, J = 7.5 Hz, 2-Me).

3-Ethyl-2-methylanisole (7, R = Me; 3-Et-2-Me): δ 7.13 (t, J = 7.9 Hz, H-5), 6.82 (d, J = 7.9 Hz, H-4), 6.74 (d, J = 7.9 Hz, H-6), 3.83 (s, OMe), 2.69 (q, J = 7.5 Hz, CH$_2$), 2.19 (s, 2-Me), 1.21 (t, J = 7.5 Hz, 3-Me).

2-Ethyl-4-methylanisole (7, R = Me; 2-Et-4-Me): δ 6.95 (m, H-3,5), 6.73 (d, J = 8.8 Hz, H-6), 3.80 (s, OMe), 2.66 (q, J = 7.5 Hz, CH$_2$), 2.27 (s, 4-Me), 1.18 (t, J = 7.5 Hz, 2-Me).

4-Ethyl-2-methylanisole (7, R = Me; 4-Et-2-Me): δ 6.95 (m, H-3,5), 6.73 (d, J = 8.8 Hz, H-6), 3.81 (s, OMe), 2.56 (q, J = 7.6 Hz, CH$_2$), 2.20 (s, 2-Me), 1.20 (t, J = 7.6 Hz, 4-Me).

2-Ethyl-5-methylanisole (7, R = Me; 2-Et-5-Me): δ 7.03 (d, J = 7.5 Hz, H-3), 6.71 (d, J = 7.5 Hz, H-4), 6.68 (s, H-6), 3.81 (s, OMe), 2.59 (q, J = 7.6 Hz, CH$_2$), 2.38 (s, 5-Me), 1.17 (t, J = 7.6 Hz, 2-Me).

5-Ethyl-2-methylanisole (7, R = Me; 5-Et-2-Me): δ 7.04 (d, J = 7.5 Hz, H-3), 6.71 (d, J = 7.5 Hz, H-4), 6.68 (s, H-6), 3.83 (s, OMe), 2.62 (q, J = 7.6 Hz, CH$_2$), 2.18 (s, 2-Me), 1.23 (t, J = 7.6 Hz, 5-Me).

2-Ethyl-6-methylanisole (7, R = Me; 2-Et-6-Me): δ 7.02 (m, H-3,5), 6.97 (t, J = 7.5 Hz, H-4), 3.74 (s, OMe), 2.68 (q, J = 7.6 Hz, CH$_2$), 2.30 (s, 6-Me), 1.23 (t, J = 7.6 Hz, 2-Me).

4-Ethyl-3-methylanisole (7, R = Me; 4-Et-3-Me): δ 7.04 (d, J = 8.2 Hz, H-5), 6.73 (d, J = 2.7 Hz, H-2), 6.65 (dd, J = 8.2, 2.7 Hz, H-6), 3.78 (s, OMe), 2.59 (q, J = 7.6 Hz, CH$_2$), 2.23 (s, 3-Me), 1.20 (t, J = 7.6 Hz, 4-Me). The possibility that this was 3-ethyl-4-methylanisole was ruled out by the observation of a strong NOE between the 2-proton and the ring methyl protons.

3-Ethyl-5-methylanisole (7, R = Me; 3-Et-5-Me): δ 6.63 (br s, H-4), 6.58 (br s, H-2, H-6), 3.78 (s, OMe), 2.59 (q, J = 7.6 Hz, CH$_2$), 2.31 (s, 5-Me), 1.22 (t, J = 7.6 Hz, 3-Me).

2,3-Diethylanisole (8, R = Me; 2,3): δ 7.13 (t, J = 7.9 Hz, H-5), 6.82 (d, J = 7.9 Hz, H-4), 6.74 (d, J = 7.9 Hz, H-6), 3.83 (s, OMe), 2.69 (q, J = 7.5 Hz, 3-CH$_2$), 2.67 (q, J = 7.5 Hz, 2-CH$_2$), 1.23 (t, J = 7.5 Hz, 3-Me), 1.13 (t, J = 7.5 Hz, 2-Me).

2,4-Diethylanisole (8, R = Me; 2,4): δ 6.99 (d, J = 8.9 Hz, H-5), 6.98 (s, H-3), 6.77 (d, J = 8.9 Hz, H-6), 3.80 (s, OMe), 2.62 (q, J = 7.5 Hz, 2-CH$_2$), 2.58 (q, J = 7.5 Hz, 4-CH$_2$), 1.21 (t, J = 7.5 Hz, 2-Me), 1.19 (t, J = 7.5 Hz, 4-Me).

2,5-Diethylanisole (8, R = Me; 2,5): δ 7.06 (t, J = 7.5 Hz, H-3), 6.74 (d, J = 7.5 Hz, H-4), 6.69 (s, H-6), 3.82 (s, OMe), 2.63 (q, J = 7.6 Hz, 5-CH$_2$), 2.60 (q, J = 7.6 Hz, 2-CH$_2$), 1.24 (t, J = 7.6 Hz, 5-Me), 1.18 (t, J = 7.6 Hz, 2-Me).

2,6-Diethylanisole (8, R = Me; 2,6): δ 7.05 (m, Ar H), 3.74 (s, OMe), 2.68 (q, J = 7.6 Hz, CH$_2$), 1.24 (t, J = 7.6 Hz, 2-Me).

3,4-Diethylanisole (8, R = Me; 3,4): δ 7.08 (d, J = 8.2 Hz, H-5), 6.74 (d, J = 2.7 Hz, H-2), 6.70 (dd, J = 8.2, 2.7 Hz, H-6), 3.79 (s, OMe), 2.63 (q, J = 7.6 Hz, 3-CH$_2$), 2.59 (q, J = 7.6 Hz, 4-CH$_2$), 1.22 (t, J = 7.6 Hz, 3-Me), 1.19 (t, J = 7.6 Hz, 4-Me).

3,5-Diethylanisole (8, R = Me; 3,5): δ 6.65 (br s, H-4), 6.58 (br s, H-2), 3.79 (s, OMe), 2.62 (q, J = 7.6 Hz, CH$_2$), 1.23 (t, J = 7.6 Hz, 3-Me).

3-Ethyl-2,6-dimethylanisole (9, R = Me; 3-Et-2-Me): δ 6.94 (d, J = 7.6 Hz, H-5), 6.85 (d, J = 7.6 Hz, H-4), 3.75 (s, OMe), 2.69 (q, J = 7.5 Hz, CH$_2$), 2.30 (s, 6-Me), 2.28 (s, 2-Me), 1.21 (t, J = 7.5 Hz, 3-Me).

4-Ethyl-2,6-dimethylanisole (9, R = Me; 4-Et-2-Me): δ 6.84 (s, H-3), 3.71 (s, OMe), 2.63 (q, J = 7.6 Hz, CH$_2$), 2.26 (s, 2-Me), 1.22 (t, J = 7.6 Hz, 4-Me).

5-Ethyl-2,4-dimethylanisole (9, R = Me; 5-Et-4-Me): δ 6.90 (s, H-3), 6.64 (s, H-6), 3.81 (s, OMe), 2.63 (q, J = 7.6 Hz, CH$_2$), 2.21 (s, 2-Me), 2.16 (s, 4-Me), 1.23 (t, J = 7.6 Hz, 5-Me).

4-Ethyl-2,5-dimethylanisole (9, R = Me; 4-Et-5-Me): δ 6.90 (s, H-3), 6.64 (s, H-6), 3.80 (s, OMe), 2.59 (q, J = 7.6 Hz, CH$_2$), 2.27 (s, 5-Me), 2.21 (s, 2-Me), 1.20 (t, J = 7.6 Hz, 4-Me).

2,3-Diethyl-6-methylanisole (10, R = Me; 2,3): δ 6.99 (d, J = 7.7 Hz, H-5), 6.88 (d, J = 7.7 Hz, H-4), 3.76 (s, OMe), 2.69 (q, J = 7.5 Hz, 3-CH$_2$), 2.64 (q, J = 7.5 Hz, 2-CH$_2$), 2.28 (s, 6-Me), 1.22 (t, J = 7.5 Hz, 3-Me), 1.17 (t, J = 7.5 Hz, 2-Me).

2,4-Diethyl-6-methylanisole (10, R = Me; 2,4): δ 6.86 (br s, Ar H), 3.71 (s, OMe), 2.65 (q, J = 7.6 Hz, 4-CH$_2$), 2.65 (q, J = 7.6 Hz, 2-CH$_2$), 2.27 (s, 6-Me), 1.23 (t, J = 7.6 Hz, 4-Me), 1.21 (t, J = 7.6 Hz, 2-Me).

3,6-Diethyl-2-methylanisole (10, R = Me; 3,6): δ 7.01 (d, J = 7.8 Hz, H-5), 6.91 (d, J = 7.8 Hz, H-4), 3.71 (s, OMe), 2.66 (q, J = 7.6 Hz, 3-CH$_2$), 2.65 (q, J = 7.6 Hz, 6-CH$_2$), 2.24 (s, 2-Me), 1.22 (t, J = 7.6 Hz, 3-Me), 1.20 (t, J = 7.6 Hz, 6-Me).

4,5-Diethyl-2-methylanisole (10, R = Me; 4,5): δ 6.92 (s, H-3), 6.64 (s, H-6), 3.81 (s, OMe), 2.62 (q, J = 7.6 Hz, 5-CH$_2$), 2.56 (q, J = 7.6 Hz, 4-CH$_2$), 2.17 (s, 2-Me), 1.21 (t, J = 7.6 Hz, 5-Me), 1.18 (t, J = 7.6 Hz, 4-Me).

3,5-Diethyl-2-methylanisole (10, R = Me; 3,5): δ 6.64 (s, H-3), 6.57 (s, H-6), 3.81 (s, OMe), 2.61 (q, J = 7.6 Hz, 5-CH$_2$), 2.60 (q, J = 7.6 Hz, 3-CH$_2$), 2.14 (s, 6-Me), 1.24 (t, J = 7.6 Hz, 5-Me), 1.18 (t, J = 7.6 Hz, 3-Me).

2,3-Diethyl-5-methylanisole (11a): δ 6.63 (s, H-4), 6.55 (s, H-6), 3.80 (s, OMe), 2.63 (q, J = 7.5 Hz, 3-CH$_2$), 2.61 (q, J = 7.5 Hz, 2-CH$_2$), 2.31 (s, 6-Me), 1.21 (t, J = 7.5 Hz, 3-Me), 1.10 (t, J = 7.5 Hz, 2-Me).

5-Ethyl-3-isopropylanisole (11b, R = Me): δ 6.67 (s, H-4), 6.61 (s, H-2), 6.58 (s, H-6), 3.80 (s, OMe), 2.86 (heptet, J = 6.9 Hz, 3-CH), 2.60 (q, J = 7.6 Hz, CH$_2$), 1.24 (t, J = 7.6 Hz, 5-Me; d, J = 6.9 Hz, 3-Me).

3,5-Diethyl-4-methylanisole (11c, R = Me): δ 6.60 (s, Ar H), 3.79 (s, OMe), 2.63 (q, J = 7.5 Hz, CH$_2$), 2.16 (s, 4-Me), 1.20 (t, J = 7.5 Hz, 3-Me).

Reaction of Trianion 3,5-4 with Diethyl Sulfate. This reaction was run similarly, with the results given in Table I.

5-Methyl-3-propylphenetole (7, R = Et; 5-Me-3-Pr): δ 6.59 (br s, H-4), 6.54 (br s, H-2, H-6), 4.01 (q, J = 7.0 Hz, OCH$_2$), 2.51 (t, J = 7.4 Hz, ArCH$_2$), 2.29 (s, 5-Me), 1.62 (sextet, J = 7.4 Hz, 3-CH$_2$Me), 1.39 (t, J = 7.0 Hz, 1-Me), 0.93 (t, J = 7.4 Hz, 3-Me).

3,5-Dipropylphenetole (8, R = Me; 3,5): δ 6.59 (br s, H-4), 6.55 (br s, H-2), 4.01 (q, J = 7.0 Hz, OCH$_2$), 2.52 (t, J = 7.4 Hz, ArCH$_2$), 1.62 (sextet, J = 7.4 Hz, 3-CH$_2$Me), 1.40 (t, J = 7.0 Hz, 1-Me), 0.93 (t, J = 7.4 Hz, 3-Me).

3,5-Dipropyl-2-ethylphenetole (10, R = Et; 3,5): δ 6.58 (d, J = 1.4 Hz, H-4), 6.52 (d, J = 1.4 Hz, H-6), 4.01 (q, J = 7.0 Hz, OCH$_2$), 2.63 (q, J = 7.4 Hz, 2-CH$_2$), 2.51 (t, J = 7.3 Hz, 3,5-ArCH$_2$), 1.62 (sextet, J = 7.3, 5-CH$_2$Me), 1.59 (sextet, J = 7.3, 3-CH$_2$Me), 1.40 (t, J = 7.0 Hz, 1-Me), 1.10 (t, J = 7.4 Hz, 2-Me), 0.98 (t, J = 7.3 Hz, 3-Me), 0.94 (t, J = 7.3 Hz, 5-Me).

5-Propyl-3-(1-ethylpropyl)phenetole (11b, R = Et): δ 6.54 (s, H-2,H-6), 6.50 (s, H-4), 4.01 (q, J = 7.0 Hz, OCH$_2$), 2.53 (t, J = 7.3 Hz, 3-ArCH$_2$), 2.25 (m, CH), 1.61 (sextet, J = 7.3 Hz, 5-CH$_2$Me), 1.57 (m, 3-CH$_2$), 1.40 (t, J = 7.0 Hz, 1-Me), 0.92 (t, J = 7.3 Hz, 5-Me), 0.77 (t, J = 7.3 Hz, 3-Me).

3,5-Dipropyl-4-ethylphenetole (11c, R = Et): δ 6.57 (s, Ar H), 4.00 (q, J = 7.0 Hz, OCH$_2$), 2.59 (q, J = 7.5 Hz, 4-CH$_2$), 2.56 (q, J = 7.4 Hz, 3-ArCH$_2$), 1.61 (sextet, J = 7.4 Hz, 3-CH$_2$Me), 1.39 (t, J = 7.0, 1-Me), 1.10 (t, J = 7.5 Hz, 4-Me), 1.00 (t, J = 7.4 Hz, 3-Me).

Reaction of Trianion 3,5-4 with 1,8-Dibromooctane. A suspension of trianion 3,5-4 and a solution of 2.71 g (9.97 mmol) 1,8-dibromooctane in 20 mL THF were simultaneously added via dropping funnel over 15 min to 200 mL of stirred THF. Stirring 18 h and working up as above gave a crude product, which was separated by MPLC on silica gel to give **12** (n = 1) (3%), **12** (n = 2) (50%), and **13** (m = 10, n = 1) (5%).

4-Hydroxy[10]metacyclophane (12, n = 1): δ 6.72 (s, H-4), 6.47 (s, H-2), 4.71 (s, OH), 2.61 (~t, J = 6.2 Hz, α-CH$_2$), 1.66 (m, β-CH$_2$), 1.19 (m, γ-CH$_2$), 1.12 (m, δ-CH$_2$), 0.96 (m, ε-CH$_2$); these

methylene shifts closely parallel those observed for the cyclophane lacking the hydroxyl group.[1]

4,4′-Dihydroxy[10,10]metacyclophane (12, *n* = 2): δ 6.57 (s, H-4), 6.47 (s, H-2), 4.77 (s, OH), 2.51 (t, *J* = 7.5 Hz, α-CH₂), 1.57 (m, *J* = 7.5 Hz, β-CH₂), 1.25 (br s, other CH₂'s).

1,10-Bis(3-hydroxy-5-methylphenyl)decane (13, *m* = 10, *n* = 1): δ 6.57 (s, H-2,4), 6.47 (s, H-6), 4.78 (s, OH), 2.50 (t, *J* = 7.3 Hz, α-CH₂), 2.27 (s, Me), 1.57 (m, *J* = 7.3, β-CH₂), 1.27 (br s, other CH₂'s).

Oxidation of Trianion 3,5-4 with Cuprous Bromide. Anhydrous cuprous bromide (5.74 g, 20 mmol) was added to a suspension of trianion 3,5-4 in THF, giving a black color. After the mixture was stirred 18 h, water (20 mL) was added, giving a green color which changed to violet on acidification with 5 N HCl. Workup as above gave 13 (*m* = 2, *n* = 1) (40%) and 13 (*m* = 2, *n* = 2) (35%).

1,2-Bis(3-hydroxy-5-methylphenyl)ethane (13, *m* = 2, *n* = 1): δ 6.61 (s, H-4), 6.50 (br s, H-2,6), 4.63 (s, OH), 2.80 (s, CH₂), 2.29 (s, Me).

3,5-Bis(2-(3-hydroxy-5-methylphenyl)ethyl)phenol (13, *m* = 2, *n* = 2): δ (acetone-*d₆*) 8.15 (s, central OH), 8.13 (s, other OH's), 6.58 (s, central H), 6.55 (s, H-6), 6.53 (s, H-2,4), 6.49 (s, other H's on central ring), 2.74 (s, CH₂), 2.21 (s, Me).

Short-Lived Intermediates. 9. Polar Alkene Photochemistry and the Perpendicular Alkene Question[1]

James E. Gano* and Stanley E. Rowan

Bowman-Oddy Laboratories, Department of Chemistry, University of Toledo, Toledo, Ohio 43606

The synthesis of alkenes with twisted double bonds has attracted much attention[2] particularly since the isolation of stable Bredt's rule violators.[3] All known examples have introduced twist by locating the double bond in a ring, e.g. 1,[4] or attaching bulky substituents, e.g. 2.[5] Ab initio calculations have shown that 90°-twisted double bonds might be stabilized by suitable selection of substituents, e.g. 3.[6a] This prediction has never been experimentally addressed.[6,7]

In our continuing pursuit of highly twisted alkenes, the photochemistry of 2-(dicyanomethylene)-1,3-dioxacyclopentane (4), a push–pull substituted alkene, was undertaken to test the ab initio prediction and to initiate a study of the photochemistry of push–pull substituted alkenes.[8] Thermal equilibration of the singlet excited state of 4 in a polar environment, on the basis of Salem's report,[6a] was expected to lead to a twisted geometry, twist angle ~75°. That twisted excited state was expected to drop to the ground state energy surface onto an energy maximum on opposite sides of which were the planar ground state and the 90°-twisted ground-state conformations. Some of the relaxing hot molecules were expected to partition into the 90°-twisted conformation, which would be stable at 10 K.

Push–pull substituted alkene 4 was readily prepared[9] and deposited, via vacuum sublimation, or codeposited with diluents onto a cryostat window at low temperatures (10–20 K). Extra care was necessary to insure that highly polar 4 was not associated in the matrices.[10] Although stable to 300-nm light, 4 readily reacted, giving similar results, when exposed to 254-nm (mercury) or 229-nm (cadmium) light.

Irradiation (229 nm) of 4, matrix-isolated in argon, produced species with IR absorptions at 2172 (m), 1727 (w), 1601 (s), 1452 (w), and 1155 (m, sh) cm⁻¹ (Figure 1). The UV spectrum showed a new, broad absorption (~265 nm) red-shifted from the absorption of 4 at 232 nm (isospestic point 254 nm). Simultaneous IR/UV monitoring linked all new bands to the same primary products. Warming for ¹/₂ h (35 K) had no significant effect on the

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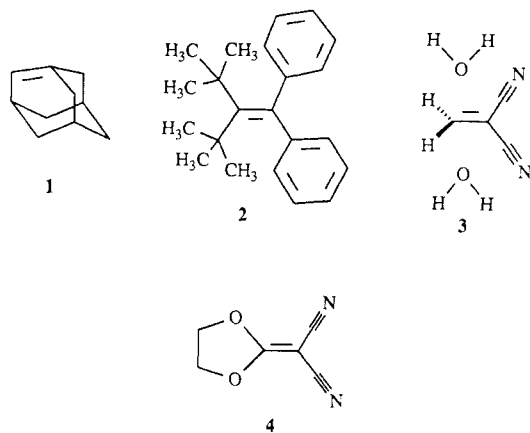
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(9) Contrary to the literature report that 4 was an unstable, pink solid, mp 115–116.5 °C, vacuum sublimation gave a colorless solid, mp 119–120 °C. See: (a) Dickson, C. L.; Melby, L. R. *Organic Syntheses*; Wiley: New York, 1963; Collect. Vol. IV, p 276. (b) Careful inspection of the literature revealed the reported structural assignment for 4 to be ambiguous since the mechanistically less likely but accessible isomer 4a was not ruled out. Since 4 was found to show four signals in its ¹³C NMR spectrum, this uncertainty was removed.
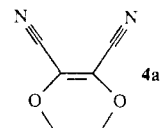
(10) Aggregation of this very polar alkene was clearly evident in the heptane matrix by the appearance of a new C=C stretching band at 1615 cm⁻¹ at the expense of the sharp monomer band at 1635 cm⁻¹ when the matrix was heated to 35 K.