Experimental Section

General. Melting points were taken on a Yanagimoto micromelting point apparatus and are uncorrected. Infrared spectra were obtained on a Jasco IR-G or a Hitachi EPI-G3 spectrometer. ^1H NMR spectra were measured on a JEOL C-60HL or a JEOL 4H-100 instrument and are reported in parts per million downfield from internal Me_4Si. ^{13}C NMR spectra were recorded on a JEOL FX-60 pulsed Fourier transform nuclear magnetic resonance spectrometer operating at 15.030 MHz. Samples were observed in 10-mm o.d. tubes, at 0.1–0.2 M solutions in chloroform-*d* at 30 °C. Chemical shifts are given in parts per million downfield from Me_4Si as zero. Partial proton decoupling was used to distinguish between individual carbon atoms. Mass spectra were obtained on a JEOL 01SG-2 mass spectrometer.

General Procedure for Reaction of 1 with 2. A stirred solution of **1** (3 mmol) and **2** (6 mmol) in dry toluene (25 ml) was refluxed under nitrogen until **1** was consumed. The reaction was followed by NMR and TLC. Toluene was evaporated from the solution and the residue was recrystallized from ethanol to afford colorless crystals of **3** (Tables I and II).

General Procedure for Hydrolysis and Dilactonization of 3. The dimethyl ester **3** (4 mmol) in 95% aqueous dimethyl sulfoxide (150 ml) containing potassium hydroxide (0.8 g) was stirred at 80 °C in a water bath for 5 h. The reaction mixture was poured into ice–water (ca. 1.5 l.) and acidified carefully with dilute hydrochloric acid. The white solid formed was filtered and dried. Without further purification, the hydrolysis product was treated with excess bromine (6 mmol) in dichloromethane (20 ml) with stirring at room temperature for 7 h, and the solution was concentrated under reduced pressure. The residue was recrystallized from ethanol, forming colorless prisms of **5** (Tables III and IV).

General Procedure for Electrolysis of 4. The diacid **4** (1 mmol) was dissolved in a solution of 90% aqueous pyridine (50 ml) and triethylamine (0.7 ml). This stirred mixture was electrolyzed under nitrogen between two platinium plate electrodes at 100–200 V (dc) with a current of 0.5 A for 7 h, during which time the mixture was cooled with an ice water bath. The dark brown mixture was concentrated under reduced pressure. To the residue was added 10% aqueous solution of sodium hydrogen carbonate and the mixture was extracted with benzene and ether, washed with water, and then dried ($MgSO_4$). After evaporation of the solvents, the residue was crystallized from ethanol to yield **5** (Table III).

Acknowledgment. We are grateful to Professor Kazuhiro Maruyama (Faculty of Science, Kyoto University) for his interest and encouragement. This work has been supported in part by a Research Grant (to K.M. and T.U.) from the Ministry of Education, Japan.

Registry No.—**1a,** 26307-17-5; **1b,** 51932-77-5; **1c,** 61202-93-5; **2,** 1128-10-5; **4a,** 61202-94-6; **4b,** 61202-95-7; **4c,** 61202-96-8.

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1-Methyl-1-dihalomethylcyclohexane Derivatives[1]

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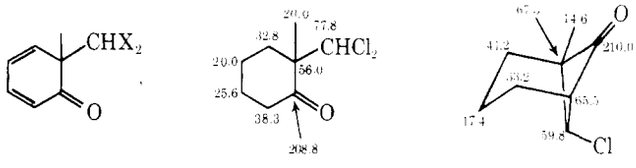
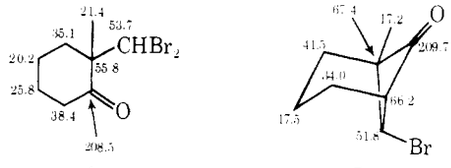
Two projects of terpene synthesis required the use of dihalomethylcyclohexadienones, derived from Reimer–Tiemann reactions of *o*- and *p*-cresols, as starting materials. In this connection it became important to determine the stereochemistry and conformation of the cyclohexanic substances encountered in early steps of the reaction sequences, a task accomplished in part by ^{13}C NMR spectroscopy.

Whereas dichloromethylcyclohexadienones are common Reimer–Tiemann products, their dibromomethyl equivalents have been reported only rarely.[2,3] Treatment of *o*-cresol with bromoform and base yielded dienone **1b**, whose hydrogenation produced ketone **4**. Dehydrobromination of the latter with potassium *tert*-butoxide led to bicycle **5**. These three reactions parallel the earlier **1a** → **2** → **3** sequence[4] and have the same



1a, X = Cl
b, X = Br

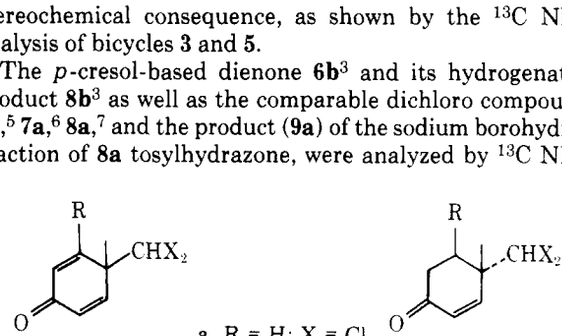
2 **3**



4 **5**

stereochemical consequence, as shown by the ^{13}C NMR analysis of bicycles **3** and **5**.

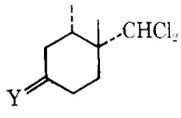
The *p*-cresol-based dienone **6b**[3] and its hydrogenation product **8b**[3] as well as the comparable dichloro compounds **6a**,[5] **7a**,[6] **8a**,[7] and the product (**9a**) of the sodium borohydride reaction of **8a** tosylhydrazone, were analyzed by ^{13}C NMR



6 **7**

a, R = H; X = Cl
b, R = H; X = Br
c, R = Me; X = Cl
d, R = Me; X = Br

8 **9**



10a, Y = O
b, Y = H_2

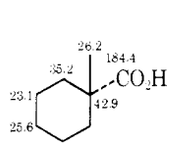
Table I. Carbon Shifts of 1-Methyl-1-dihalomethylcyclohexane Derivatives[a,e]

	6a[b]	6b	6c	7a	7c	7d	8a	8b	8c	8d	9a	9c	9d	10a	10b
C(1)	47.3	47.4	50.4	44.2	47.3	46.6	41.3	40.6	43.8	43.0	41.9	44.5	44.0	43.2	43.6
C(2)	148.3	149.1	157.5	30.2	33.6	34.4	33.3	34.0	36.3	36.7	34.4	35.8	36.5	38.2	34.8
C(3)	130.3	130.3	129.4	33.3	41.6	42.0	36.3	36.6	45.3	45.4	21.7	30.9	31.4[c]	44.8	29.7[d]
C(4)	184.3	184.5	184.7	197.4	197.5	197.5	209.9	209.7	209.5	209.4	25.7	25.6	25.7	209.8	19.5
C(5)	130.3	130.3	130.6	129.2	129.4	129.4	36.3	36.6	36.8	37.1	21.7	21.3	21.6	36.5	21.8[d]
C(6)	148.3	149.1	147.6	151.3	150.8	152.3	33.3	34.0	29.4	31.4	34.4	29.5	31.7[c]	29.9	29.3
1-Me	22.6	24.5	23.5	20.7	16.8	18.4	18.2	19.8	15.8	16.6	18.0	16.3	17.0	16.2	16.1
2-Me			18.7		14.8	15.1			15.2	15.8		15.1	15.1	14.7	13.7
X_2CH	76.4	49.9	75.8	79.8	78.7	55.4	82.0	59.0	81.5	59.4	84.0	83.5	63.2	81.6	83.6

[a] The δ values are in parts per million downfield from Me_4Si; $\delta(Me_4Si) = \delta(CDCl_3) + 76.9$ ppm. [b] Cf. R. Hollenstein and W. von Philipsborn, *Helv. Chim. Acta*, **55**, 2030 (1972). [c] Signals may be reversed. [d] Determined by deuteration of **10a**. [e] Registry no.: **6a**, 6611-78-5; **6b**, 17746-79-1; **6c**, 14789-74-3; **7a**, 38510-80-4; **7c**, 61279-00-3; **7d**, 61279-01-4; **8a**, 24463-33-0; **8b**, 49783-23-5; **8c**, 42374-15-2; **8d**, 61279-02-5; **9a**, 24147-13-5; **9c**, 61279-03-6; **9d**, 61279-04-7; **10a**, 42374-18-5; **10b**, 61279-05-8.

spectroscopy. The carbon shifts, listed in Table I, facilitated the general structure analysis of methylated derivatives of **6–9** (vide infra).

The reaction of dienone **6a** with lithium dimethylcuprate produced a methylated enone of unknown stereochemistry. Its hydrogenation product had to be either **8c** or **10a** and was identical with the minor component of the ca. 4:1 isomer mixture from a hydrogenation of dienone **6c**.[8] Treatment of **6b** with lithium dimethylcuprate, followed by hydrogenation, led to an enone and anone, respectively, with stereochemical features identical with the products of the two-reaction sequence emanating from **6a**, as evidenced by ^{13}C NMR analysis. In order to determine the relative configuration of the various chloro compounds, they were converted into 1,2-dimethylcyclohexanecarboxylic acids of known constitution. Sodium borohydride reduction of the tosylhydrazone of the **6a**-derived cyclohexanone gave a 1-dichloromethyl-1,2-dimethylcyclohexane whose treatment with sodio ethyleneglycolate,[7] followed by acid hydrolysis of the resultant ethylene acetal and chromic acid oxidation,[7] yielded a carboxylic acid identical with the product of the Diels–Alder reaction of butadiene and tiglic acid followed by hydrogenation.[9] In view of the structure of the latter product being **12** the methylation



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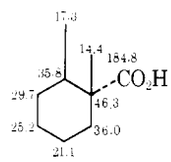

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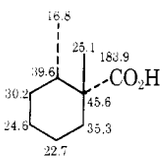

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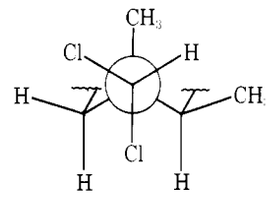
products of **6a** and **6b** are **7c** and **7d**, respectively, their dihydro derivatives **8c** and **8d**, respectively, and the deoxo compounds **9c** and **9d**, respectively. Furthermore, the major product of the hydrogenation of **6c** possesses structure **10a**.

Both cyclohexanone **8a** and the mixture of ketones **8c** and **10a** could be deoxygenated by successive treatments with tosylhydrazine and sodium borohydride and the resultant 1-dichloromethyl-1-methylcyclohexane (**9a**)[7] and the mixture of cyclohexanes **9c** and **10b**, respectively, were transformed into 1-methylcyclohexanecarboxylic acid (**11**) and the mixture of acids **12** and **13**, respectively, for ^{13}C NMR analysis (cf. shifts portrayed on formulas **11**, **12**, and **13**). The acid **13** was identical with the product of the reaction of 1,2-dimethylcyclohexanol with formic and sulfuric acids.[10,11]

The chemical shifts of the carbons β to the carbonyl group in the cyclohexanones **8c** and **10a** (cf. Table I) are interpreted most readily on the basis of the presence of equatorial dichloromethyl groups with preferred rotamer populations **14** and **15**, respectively. The same conformations appear to predominate in the cyclohexanes **9c** and **10b**, respectively.[12] The



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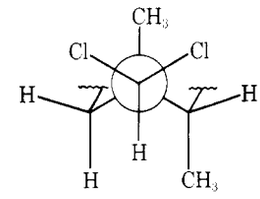

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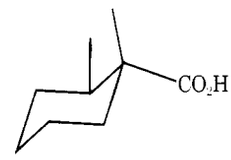

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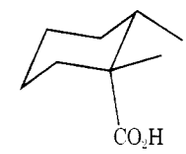

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1-methyl shifts of the acids **12** and **13** reveal these compounds to possess conformations **16** and **17**, respectively.

Experimental Section

Melting points were determined on a Reichert micro hot stage and are uncorrected. Infrared spectra were obtained on a Perkin-Elmer 167 spectrophotometer. ^1H NMR spectra of $CDCl_3$ solutions (Me_4Si, δ 0 ppm) were recorded on a Varian A-56/60A spectrometer, while the ^{13}C NMR spectra were produced on a Varian XL-100-15 spectrometer operating at 25.2 MHz in the Fourier transform mode. The δ values denoted on formulas **2**, **3**, **4**, **5**, **11**, **12**, and **13** refer to $CDCl_3$ solutions.

6-Dibromomethyl-6-methyl-2,4-cyclohexadienone (1b). A solution of 200 g of NaOH in 500 ml of H_2O was added dropwise over a 1.5-h period to a vigorously stirring solution of 233 g of freshly distilled *o*-cresol in 546 g of $CHBr_3$ and the stirring continued at room temperature for 48 h. The mixture was diluted with 2 l. of H_2O, the layers separated, and the aqueous phase extracted with 1 l. of pentane. The extract was dried (Na_2SO_4), evaporated to 250 ml, and combined with the $CHBr_3$ phase. The organic solution was washed with H_2O (500 ml), cold Claisen alkali (360 ml), H_2O (300 ml) again, and saturated brine solution. It then was dried (Na_2SO_4) and evaporated (30 °C, 1 Torr). The residue, 38.4 g, was chromatographed on alumina (activity 1) and eluted with chloroform, yielding 35 g of dienone **1b**: mp 51–52 °C; IR ($CHCl_3$) C=O 6.03 (s), C=C 6.10 μ (s); ^1H NMR δ 1.30 (s, 3, Me), 5.95 (s, 1, BrCH), 6.08 (dd, 1, J = 10, 2 Hz, H-2), 6.42 (dd, 1, J = 10, 6 Hz, H-4), 6.73 (ddd, 1, J = 10, 2, 1 Hz, H-5), 7.07 (ddd, 1, J = 10, 6, 2 Hz, H-3).

Anal. Calcd for $C_8H_8OBr_2$: C, 34.32; H, 2.88. Found: C, 34.12; H, 2.95.

2-Dibromomethyl-2-methylcyclohexanone (4). A mixture of 12.05 g of **1b** and 1.20 g of 10% Pd/C in 90 ml of EtOH was hydrogenated at room temperature and atmospheric pressure for 6 h. It then was filtered and the filtrate concentrated to 30 ml, diluted with 150 ml of H_2O, and extracted with 200 ml of hexane. The extract was dried (Na_2SO_4) and evaporated. The residue, 11 g, was chromatographed on SiO_2 and eluted with 30:1 hexane–ether, yielding 8.85 g of oily ketone **4**: IR ($CHCl_3$) C=O 5.84 μ (s); ^1H NMR δ 1.27 (s, 3, Me), 6.28 (s, 1, BrCH).

Anal. Calcd for $C_8H_{12}OBr_2$: C, 33.83; H, 4.26. Found: C, 33.98; H, 4.23.

***syn*-7-Bromo-1-methylbicyclo[3.1.1]heptan-6-one (5).** A solution of 7.0 g of **4** in 35 ml of dry Me_3COH was added dropwise over a 2-h period to a solution of 7 g of $KOCMe_3$ in 100 ml of Me_3COH under nitrogen at room temperature and the mixture then stirred at 65 °C for 3 h. It was concentrated to 75 ml, 120 ml of 5% aqueous $NaHCO_3$ solution added, and the mixture extracted with 200 ml of hexane. The extract was washed with H_2O (160 ml), dried (Na_2SO_4), and evaporated. Chromatography of the residue, 4.83 g, on SiO_2 and elution with hexane gave 220 mg of an exo–endo mixture of *tert*-butyl 1-methylbicyclo[3.1.0]hexane carboxylates. Elution with 30:1 hexane–ether gave 2.2 g of liquid ketone **5**: IR ($CHCl_3$) C=O 5.60 μ (s); ^{1}H NMR δ 1.18 (s, 3, Me), 3.38 (t, 1, J = 3 Hz, COCH), 4.20 (s, 1, BrCH).

Anal. Calcd for $C_8H_{11}OBr$: C, 47.31; H, 5.46. Found: C, 47.45; H, 5.28.

Cyclohexenones 7c and 7d. A solution of 1.44 g of dienone **6a** in 15 ml of dry ether was added over a 20-min period to a freshly prepared 0.22 M ethereal $LiCuMe_2$ solution (50 ml) kept under N_2 at −5 °C and the mixture stirred at −5 °C for 3 h. It then was poured into 120 ml of 2 N HCl and extracted with ether (250 ml). The extract was washed with H_2O and saturated $NaHCO_3$ and NaCl solutions, decolorized (activated charcoal), dried ($MgSO_4$), and evaporated. Crystallization of the residual solid (1.57 g) from hexane gave colorless crystals of ketone **7c**: mp 62–64 °C; IR (CCl_4) C=O 5.92 (s), C=C 6.04 μ (m); ^{1}H NMR δ 1.00 (d, 3, J = 7 Hz, 5-Me), 1.24 (s, 3, 4-Me), 5.91 (s, 1, ClCH), 6.08 (d, 1, J = 10 Hz, H-2), 7.08 (d, 1, J = 10 Hz, H-3).

Anal. Calcd for $C_9H_{12}OCl_2$: C, 52.20; H, 5.84; Cl, 34.24. Found; C, 52.39, H, 5.94; Cl, 34.08.

A like reaction between dienone **6b** (1.01 g in 10 ml of ether) and $LiCuMe_2$ (50 ml of 0.10 M ethereal solution) led to 0.98 g of solid whose crystallization from hexane yielded crystalline ketone **7d**: mp 72–74 °C; IR (CCl_4) C=O 5.94 (s), C=C 6.04 μ (m); ^{1}H NMR δ 1.01 (d, 3, J = 7 Hz, 5-Me), 1.32 (s, 3, 4-Me), 6.06 (s, 1, BrCH), 6.25 (d, 1, J = 10 Hz, H-2), 7.26 (d, 1, J = 10 Hz, H-3).

Anal. Calcd for $C_9H_{12}OBr_2$: C, 36.52; H, 4.09. Found: C, 36.76; H, 4.14.

Cyclohexanones 8c, 8d, and 10a. A mixture of 630 mg of **7c** and 100 mg of 10% Pd/C in 100 ml of EtOAc was hydrogenated at room temperature and atmospheric pressure and then filtered. Evaporation of the filtrate yielded 620 mg of ketone **8c**: IR (CCl_4) C=O 5.82 μ (s); ^{1}H NMR δ 0.93 (d, 3, J = 6 Hz, 3-Me), 1.22 (s, 3, 4-Me), 5.97 (s, 1, ClCH); spectral properties identical with literature values.[8]

Similar hydrogenation of **7d** (150 mg of **7d**, 20 mg of 10% Pd/C, and 20 ml of EtOAc) yielded ketone **8d** (150 mg): mp 88–91 °C; IR (CCl_4) C=O 5.78 μ (s); ^{1}H NMR δ 0.94 (d, 3, J = 7 Hz, 3-Me), 1.08 (s, 3, 4-Me), 6.14 (s, 1, BrCH); *m/e* (calcd for $C_9H_{14}OBr_2$; 295.941) 295.931.

Repetition of the hydrogenation of dienone **6c** according to the literature procedure[8] as well as in EtOAc as above gave a 41:9 mixture of **10a** and **8c**, respectively, with spectral properties identical with those recorded.[8]

Cyclohexanes 9a, 9c, 9d, and 10b. A solution of 1.00 g of **8a** and 1.86 g of *p*-toluenesulfonylhydrazine in 100 ml of MeOH was refluxed for 2 h, whereupon it was cooled, 1.90 g of $NaBH_4$ added in small portions, and the mixture refluxed for 4 h.[13] It then was poured into 150 ml of H_2O and extracted with 300 ml of pentane. The extract was washed with H_2O and saturated NaCl solution, dried (Na_2SO_4), and evaporated. A pentane solution of the residue was filtered through an alumina column and evaporated, yielding 0.77 g of liquid dichloride **9a**, identical in all respects with an authentic sample.[7]

A Caglioti reduction of **8c** under the above conditions (595 mg of **8c**, 970 mg of $TsNHNH_2$, and 65 ml of MeOH; 1.1 g of $NaBH_4$) led to 455 mg of liquid dichloride **9c** [^{1}H NMR δ 0.85 (d, 3, J = 7 Hz, 2-Me), 1.00 (s, 3, 1-Me), 5.88 (s, 1, ClCH)] which was used without purification in the acetalation–oxidation (vide infra).

A Caglioti reduction of the mixture of ketones **8c** and **10a** under the aforementioned conditions (1.64 g of **8c** and **10a**, 2.68 g of $TsNHNH_2$, and 140 ml of MeOH; 3.03 g of $NaBH_4$) yielded 1.05 g of a 41:9 mixture of dichlorides **10b** [^{1}H NMR δ 0.99 (d, 3, J = 7 Hz, 2-Me), 1.21 (s, 3, 1-Me), 5.68 (s, 1, ClCH)] and **9c**, respectively, which was utilized without further purification in the acetalation–oxidation (vide infra).

A Caglioti reduction of **8d** under the above conditions (98 mg of **8d**, 120 mg of $TsNHNH_2$, and 10 ml of MeOH; 150 mg of $NaBH_4$) yielded 52 mg of liquid dibromide **9d**: ^{1}H NMR δ 0.80 (d, 3, J = 7 Hz, 2-Me), 1.04 (s, 3, 1-Me), 6.10 (s, 1, BrCH); *m/e* (calcd for $C_9H_{16}Br_2$, 281.962) 281.944.

1,2-Dimethyl-1-cyclohexanecarboxylic Acids 12 and 13. A mixture of 455 mg of **9c** and sodium ethyleneglycolate (from 1.20 g of Na) in 20 ml of distilled ethylene glycol was refluxed under N_2 for 26 h.[7,14] It then was poured into 50 ml of H_2O and extracted with 150 ml of pentane. The extract was washed with H_2O and saturated NaCl solution, dried (Na_2SO_4), and evaporated. A mixture of the residue, 425 mg of ethylene acetal [^{1}H NMR δ 0.85 (s, 3, 1-Me), 0.85 (d, 3, J = 6 Hz, 2-Me), 3.83 (s, 4, OCH_2), 4.68 (s, 1, O_2CH)], and 15 ml of 10% H_2SO_4 in 1.5 ml of EtOH was stirred at room temperature for 12 h. Water (50 ml) was added and the mixture extracted with pentane. The extract was washed with H_2O and saturated NaCl solution, dried (Na_2SO_4), and evaporated. A solution of the residual aldehyde [^{1}H NMR δ 0.76 (d, 3, J = 7 Hz, 2-Me), 0.88 (s, 3, 1-Me), 9.37 (s, 1, CHO)] in 20 ml of acetone was treated at 0 °C with enough Jones reagent (26 g of CrO_3, 23 ml of concentrated H_2SO_4, and 100 ml of H_2O) to produce a persistent brown color, whereupon it was permitted to warm to room temperature. After the addition of H_2O the mixture was extracted with ether. The extract was washed with H_2O and saturated brine and extracted with 10% KOH solution. The aqueous extract was acidified with 2 M H_2SO_4 and reextracted into ether. The organic solution was washed with H_2O and brine, dried, and evaporated, yielding 250 mg of acid **12**, identical in all respects with an authentic sample.[9]

The same three-reaction sequence on the dichloride mixture **9c** and **10b** (582 mg of dichlorides, 1.3 g of Na, and 20 ml of ethylene glycol) led successively to a 23:27 mixture (215 mg) of acetals [^{1}H NMR δ (**10b** derived) 4.75 (s, 1, O_2CH)] (corresponding to a 100 and 25% acetalation of **9c** and **10b**, respectively), aldehydes [^{1}H NMR δ (**10b** derived) 1.07 (s, 3, 1-Me), 9.71 (s, 1, CHO)] and acids (115 mg) **12** and **13**, identical in all respects with authentic samples.[9,10]

Registry No.—**1b**, 61279-06-9; **4**, 61279-07-0; **5**, 61279-08-1; **9c** ethylene acetal, 61279-09-2; **9c** aldehyde, 13036-68-5; **10b** ethylene acetal, 61279-10-5; **10b** aldehyde, 23668-50-0: **12**, 13277-92-4; **13**, 61279-11-6; *o*-cresol, 95-48-7.

References and Notes

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