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Reactions of 3-Methylbenzyne with 2-Substituted Furans.[1] Steric Effects

Melvin S. Newman* and R. Kannan[2]

Department of Chemistry, The Ohio State University, Columbus, Ohio 43210

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3-Methylbenzyne generated from two pairs of isomeric precursors, namely, 2-amino-3-methylbenzoic acid (1)–2-amino-6-methylbenzoic acid (2) and 2-fluoro-3-methylbromobenzene (3)–6-fluoro-2-methylbromobenzene (4), has been reacted with 2-methylfuran (5), 2-*tert*-butylfuran (6), 2-(1,3-dioxolan-2-yl)furan (7), and 2-carbomethoxyfuran (8). The proportions of isomeric adducts produced were the same (±2%) for each furan and are expressed as ratio of less hindered isomer (1,5-naphthalene derivative) to more hindered isomer (1,8-naphthalene derivative) as follows: for **5**, 58/42; **6**, 64/36; **7**, 61/39; **8**, 57/43. Thus the addition of an unsymmetrical benzyne to a furan seems very slightly affected by steric or polar effects. The results are interpreted as evidence supporting a true benzyne intermediate.

Benzyne reacts readily with furans to form 1,4-dihydro-1,4-epoxynaphthalenes which are of great synthetic interest because of their ready conversion to other types of compounds.[3,4] In order to increase the synthetic utility and understanding of this type of reaction, we have studied the reactions of 3-methylbenzyne prepared from two isomeric pairs of precursors with 2-substituted furans.

Although a fair amount of work has been done on the relative reactivities in Diels–Alder type reactions of benzynes (prepared from different precursors) with pairs of other reactants,[5,6] little is known about steric effects.[7] Conflicting steric results have been reported in the reaction of 3,5-di-*tert*-butylfuran[8] (in which the predominant adduct proved to be the more hindered 1,3,6,8-tetra-*tert*-butyl-1,4-dihydro-1,4-epoxynaphthalene) and with 2-benzyl-5-*tert*-butylfuran[9] (in which the ratio of the less hindered isomer to the more hindered isomer was 14/11).

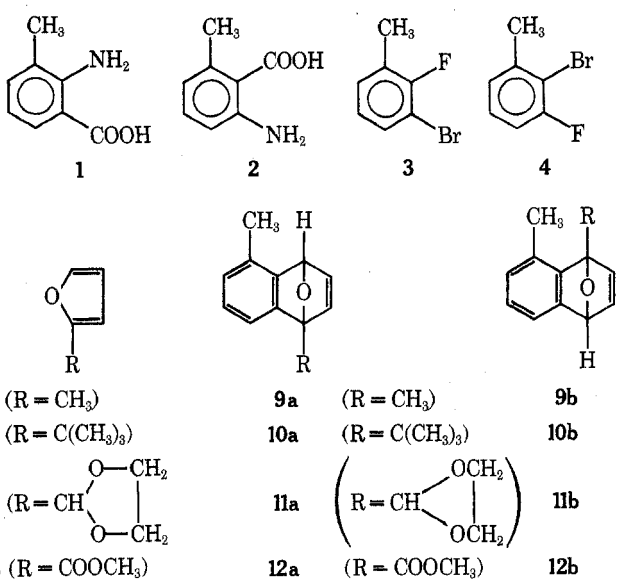
In the work reported herein we have determined the products formed when two pairs of isomeric compounds, 2-amino-3-methylbenzoic acid (**1**)–2-amino-6-methylbenzoic acid (**2**) and 2-fluoro-3-methylbromobenzene (**3**)–6-fluoro-2-methylbromobenzene (**4**), were treated to produce 3-methylbenzyne in the presence of 2-methylfuran (**5**), 2-*tert*-butylfuran (**6**), 2-(1,3-dioxolan-2-yl)furan (**7**), and 2-carbomethoxyfuran (**8**), to yield the isomeric adduct pairs (**9a, 9b**), (**10a, 10b**), (**11a, 11b**), and (**12a, 12b**). The results are summarized in Table I.

Examination of the results in Table I reveals that the ratio of products obtained from isomeric 3-methylbenzyne precursors is the same, within experimental error, for each of the

Table I. Reactions of Isomeric 3-Methylbenzyne Precursors with 2-Substituted Furans[a]

Benzyne precursor	Yield, %,[b,c] and ratio[d] of adducts for R = CH_3 9a/9b	$C(CH_3)_3$ 10a/10b	11a/11b	$COOCH_3$ 12a/12b
1[e]	(50)[b] 58/42	(51)[b] 64/36	(81)[b] 61/39	(82)[c] 57/43
1[f]	(70)[b] 58/42	(59)[b] 65/35	(50)[b] 59/41	(54)[b] 57/43
2[e]	(44)[b] 58/42	(53)[b] 62/38	(75)[c] 61/39	(75)[c] 58/42
3[g]	(74)[b] 58/42	(73)[b] 64/36	(81)[c] 61/39	*h*
4[g]	(76)[b] 58/42	(74)[b] 62/38	(76)[c] 61/39	*h*

[a] In all experiments the quantity of THF was the same and the ratio of benzyne precursor to furan was one. [b] Isolated yield of mixture of adducts; see Experimental Section. [c] Yield estimated after column chromatography of reaction mixture; see Experimental Section. [d] Ratios reported represent the average of a number of runs in which the results generally checked to within ±1% of the average. [e] Diazotization and decomposition as described.[10]. [f] Diazotization and decomposition as described.[11] [g] Pure sublimed magnesium was used under conditions similar to those described.[4,12] [h] Reaction not carried out.



substituted furans studied. These facts support the concept that 3-methylbenzyne is the true reactant and not some partly reacted intermediate. Thus the results of the present work support the ideas of Huisgen and co-workers,[6] who studied the competitive reactions of symmetrical benzyne with different benzyneophiles. In addition our studies indicate that there is very little effect of a polar or steric nature in the Diels–Alder type reactions involved.

Experimental Section[13]

2-Amino-3-methylbenzoic Acid (1). In a 4-l. beaker equipped with a mechanical stirrer and thermometer were placed 90 g (0.54 mol) of chloral hydrate, 453 g of Na_2SO_4, and 1.5 l. of water. A solution of 51.5 g (0.48 mol) of freshly distilled *o*-toluidine and 410 g (2.5 mol) of hydroxylamine sulfate in 500 ml of water containing 50 ml of concentrated HCl was added rapidly and the stirred mixture was heated to 45 °C during 1.5 h to 52 °C in 45 min, and then to 65 °C for 1 h. On cooling there was obtained 78.5 g (91.6%) of 2-hydroxyiminoacet-*o*-toluidide, mp 119–120 °C (lit.[14] mp 121 °C, 63%), suitable for the next step after drying in air. To 800 ml of anhydrous HF[15] in a 2-l. polyethylene bottle was added 100 g of the above *o*-toluidide in portions during 45 min. After the HF was allowed to evaporate (2–3 days), the residue was triturated with a solution at 60 °C of 50 ml of H_2SO_4 and 400 ml of water. The crude isatin was collected by filtration of the cooled suspension, washed with water, and dissolved in 700 ml of hot 5% NaOH. After filtration through Celite (filter aid, J. T. Baker Chemical Co.) the filtrate was acidified with concentrated HCl to yield 93.7 g (100%) of orange-red 7-methylisatin, mp 270–271 °C (lit.[16] mp 266 °C). To a solution of 80.0 g of 7-methylisatin in 20 g of NaOH, 80 g of KCl, and 900 ml of water at 8–10 °C was added 88 g of cooled 30% H_2O_2 during 1.5 h. After an additional 45 min at 20 °C, the addition of 180 ml of acetic acid caused precipitation of an almost colorless solid, **1**, mp 166–168 °C, in almost quantitative yield. Pure **1**, mp 174–176 °C (lit.[17] mp 172 °C), was obtained in 83% yield by recrystallization from water. Only pure **1** was used in the generation of 3-methylbenzyne.

2-Amino-6-methylbenzoic Acid (2). The nitration of acet-*o*-toluidide was carried out as described[18] on a 2-mol scale. The alkaline method of separation (ref 18, footnote 8) was used to obtain 237 g (61% based on *o*-toluidine) of 2-methyl-6-nitroacetanilide, mp 155–157 °C, which was then hydrolyzed almost quantitatively to 2-methyl-6-nitroaniline, mp 92–94 °C, essentially as described.[17] This amine (47.3 g) was converted into 42.7 g (83%) of 2-methyl-6-nitrobenzonitrile, mp 107–108 °C (lit.[19] mp 109–110 °C, 63%) as described.[17] Hydrolysis to recrystallized 2-methyl-6-nitrobenzamide, mp 158–159 °C (lit.[17] mp 158 °C, 71%) in 72% yield was accomplished by heating the nitrile (83.7 g) with a solution of 330 ml of concentrated H_2SO_4 and 175 ml of water at 110–115 °C for 1 h. The amide in the sulfuric acid filtrate was diazotized with sodium nitrite to yield 21 g (22%) of 2-methyl-6-nitrobenzoic acid, mp 151–153 °C. Diazotization of the solid amide[17] yielded additional acid, mp 151–153 °C, the overall yield from nitrile being 76%. Reduction to 2-amino-6-methylbenzoic acid (**2**), mp 125–126 °C (lit.[17] mp 125–126 °C), was accomplished by treating a hot solution of 69.0 g of 2-methyl-6-nitrobenzoic acid in 80 ml of 29% ammonia with a suspension of 680 g of $FeSO_4$ in 2 l. of ammonium hydroxide. After heating for several hours to allow ammonia to escape the mixture was acidified with acetic acid to yield 33.0 g (57%) of **2**.

3-Bromo-2-fluorotoluene* (3). Nitration of *m*-toluic acid to 2-nitro-3-methylbenzoic acid, mp 218–220 °C, was accomplished in 50% yield as described.[19] To a stirred suspension of 107.0 g of the nitro acid in 900 ml of concentrated H_2SO_4 at −5 to 0 °C was added 42.2 g of sodium azide. The suspension became blue violet. On warming toward 60 °C (final temperature) the color changed to pink, gas evolution occurred continuously, and a clear solution was obtained. This was poured on ice and the mixture was made alkaline with ammonium hydroxide. The crude solid was collected and recrystallized from benzene–cyclohexane to yield 74.4 g (83%) of orange-yellow 2-nitro-3-methylaniline, mp 104–106 °C (lit.[20] mp 108 °C). This amine was converted into 3-bromo-2-nitrotoluene, bp 152–156 °C (35 mm), pure by GLC, in 82% yield as described.[20] Reduction to 2-bromo-6-methylaniline, bp 140–144 °C (40 mm), was accomplished in 86% yield as described.[21] Replacement of the amino group by fluorine was accomplished as described[22] to yield GLC pure **3** as a colorless oil, bp 185–186 °C, in 70% yield. Before use in generating 3-methylbenzyne, benzene solutions of **3** and **4** were washed with concentrated H_2SO_4 in the cold until the acid layer was colorless. The halides were then recovered and distilled.

2-Bromo-3-fluorotoluene* (4). A suspension of 100 g of 2-methyl-6-nitroaniline (prepared by nitration of acet-*o*-toluidide as described[18]) in 150 ml of 48% HBr and 200 ml of water was converted[23] into 94 g (60%) of 2-bromo-3-nitrotoluene, bp 166–170 °C (45 mm) [lit.[23] bp 135–136 °C (8 mm)]. Reduction to 2-bromo-3-methylaniline,* bp 145–148 °C (45 mm), was accomplished in 95% yield as described for a similar case.[21] Conversion of this bromo amine into **4**, bp 184–187 °C, was effected in 50% yield essentially as described for a similar case.[22] Pure **4**, bp 187 °C, was obtained by fractionation in a small column.

2-*tert*-Butylfuran (6). A mixture of 37.8 g of methyl 2-furoate and 28.0 g of *tert*-butyl chloride was added dropwise during 40 min to an ice–salt cooled suspension of 60 g of $AlCl_3$ in 300 ml of CS_2. After a

further 3 h at this temperature the mixture was poured on ice. After the usual workup the residue yielded 51.1 g (93.6%) of GLC pure methyl 5-*tert*-butyl-2-furoate, bp 112–114 °C (20 mm).[24] After alkaline hydrolysis there was obtained 47 g of 5-*tert*-butyl-2-furoic acid, mp 98–100 °C (lit.[25] mp 103.5–104.5 °C). After decarboxylation as described[25] there was obtained **6**, bp 119–120 °C, in 51% yield. There was some loss of product in the forerun. The use of an efficient fractionation column is recommended for future work.

2-(1,3-Dioxolan-2-yl)furan (7). This compound, bp 74–76 °C (1 mm), was obtained essentially as described.[26]

Reactions of 3-Methylbenzyne Precursors with Furans. The general procedure (footnote *e*, Table I) adopted for **1** and **2** was as follows. A solution of 3.0 g (0.02 mol) of **1** (or **2**) in 20 ml of THF was added dropwise from a pressure equalizing addition funnel during 2–2.5 h to a stirred solution at 50 °C of 0.02 mol of **5, 6, 7,** or **8** and 3.4 ml (2.96 g, 0.025 mol) of freshly distilled amyl nitrite in 20 ml of THF. After another 1 h the THF was removed under vacuum and the residue was taken up in 200 ml of ether and worked up as usual. The crude product obtained after removal of ether was analyzed (three duplicate injections) by GLC[27] to give the ratios reported in Table I (footnote *d*). The yields of adduct obtained by vacuum distillation of these products are represented by footnote *b* in Table I. In a few cases, footnote *c* in Table I, the crude products were chromatographed on alumina (treated with ethyl acetate before use) to afford the yields recorded. The ratios, *d*, obtained by this procedure starting from **1** were the same as those obtained when procedure *f*, Table I, was used. Procedure *f* was as follows. To a magnetically stirred solution of 3.0 g of **1** and 150 mg of trichloroacetic acid in 20 ml of THF in a 100-ml beaker cooled with ice water was added 3.2 ml (2.79 g) of freshly distilled amyl nitrite, the temperature rising as high as 20 °C. After stirring for 1–1.5 h, the buff precipitate was collected, washed with THF until the washings were colorless, and used directly while wet with solvent in the reactions with the furans. On an air-dried basis the yields of betaines were 95–99%, but because of danger in handling the dry materials, only solvent-wet products were used. We found it advantageous to use slightly larger amounts of CCl_3COOH than recommended[11] because the yields of adducts with the furans were somewhat higher when betaines thus made were used. The solvent-wet betaines were then added to a solution of 1 equiv of furan in THF and the mixture (total volume 40 ml) was heated at 50 °C until gas evolution was complete (2–3 h). After removal of solvent, isolation and analysis of the adduct mixture were similar to those described above.

The general procedure for generating and reacting **3** and **4** was as follows. In a flamed 100-ml three-necked flask fitted with a reflux condenser, stirrer, and pressure-equalizing dropping funnel were placed 20 ml of THF freshly distilled over $LiAlH_4$, 0.02 mol of substituted furan, and 0.022 g-atom of pure sublimed magnesium.[28] While a slow stream of nitrogen was flowing, a solution of 0.02 mol of freshly distilled bromofluorotoluene, **3** or **4**, in 20 ml of THF was added during 30 min to the contents of the flask held at reflux. After the addition was completed the contents were held at reflux for 2 h, cooled, and treated with 20 ml of saturated NH_4Cl solution. After the usual workup, the solvents were removed and the residue analyzed by GLC.[27] The yields reported in Table I were obtained by distillation of the crude products or by chromatography as indicated by footnotes *b* and *c*, Table I.

Proof of Structure, 1,4-Dihydro-1,5-dimethyl-1,4-epoxynaphthalene (9a) and 1,4-Dihydro-1,8-dimethyl-1,4-epoxynaphthalene (9b). A vacuum distilled sample (0.60 g) of a mixture of **9a** and **9b** (63:37 by GLC analysis, not the same as the 58:42 ratio of total product because of slight fractionation during distillation) was hydrogenated in methanol over 5% Pd/C (50 mg) for 30 min at 45 psi of hydrogen. After removal of the catalyst by filtration and the solvent by distillation the residue was held at reflux for 1 h in ethanol saturated with dry HCl. The aromatized product (500 mg) had two components by GLC (column B, 63:37). The minor component was shown to be 1,8-dimethylnaphthalene by peak enhancement of the minor peak (retention time 2.5 min of column B[13] at 145 °C with synthetic pure 1,8-dimethylnaphthalene.[29] In another experiment similar to the above, chromatography (over silicic acid using 40–50 °C petroleum ether) of the aromatic dimethylnaphthalene fraction followed by recrystallization from methanol of the fraction rich in the major component yielded some pure 1,5-dimethylnaphthalene,[30] mp 78–80 °C, *m/e* 156.[31]

Proof of Structure, 1-*tert*-Butyl-1,4-dihydro-1,4-epoxy-5-methylnaphthalene (10a) and 1-*tert*-Butyl-1,4-dihydro-1,4-epoxy-8-methylnaphthalene (10b). These compounds were obtained by reactions similar to those described above. Analyses as to compounds were made by GLC, column A.[27] The identity of the two components was assigned by NMR analysis. There were two singlets corresponding to $ArCH_3$, a major (2.20 ppm) and a minor (2.41 ppm). In the case of 5,7-di-*tert*-butyl-1,4-dimethylnaphthalene,[8b] the less hindered 1-methyl group resonates at 2.61 ppm and the more hindered 4-methyl group at 2.77 ppm. This fact led us to assign the structure **10a** to the compound whose $ArCH_3$ group was at 2.20 and 10b having $ArCH_3$ at 2.41. In keeping with these assignments the $ArCH_3$ in 1-*tert*-butyl-1,4-epoxy-5-methyl-1,2,3,4-tetrahydronaphthalene (obtained by reduction over Pd/C), the major component, resonates at 2.30 ppm while the $ArCH_3$ resonance in the minor component, 1-*tert*-butyl-1,4-epoxy-8-methyl-1,2,3,4-tetrahydronaphthalene, was at 2.50 ppm. Confirmation of the above assignments was obtained by considering the resonances of the hydrogens on the peri positions involving the 1,4-epoxy linkage. In **10a** (the major component), this hydrogen (on C_4) resonated at 5.53 ppm whereas in **10b** the value was 5.36 ppm. In the tetrahydro compounds, obtained by reduction of the mixture of **10a** and **10b** over Pd/C, the corresponding values were 5.26 (multiplet in major component) and 5.13 ppm (m in minor). Attempts to aromatize the tetrahydro compound mixture with acid led to mixtures in which some loss of *tert*-butyl groups had occurred.

Proof of Structure, 1,4-Dihydro-1-(1,3-dioxolan-2-yl)-1,4-epoxy-5-methylnaphthalene* (11a) and 1,4-Dihydro-1-(1,3-dioxolan-2-yl)-1,4-epoxy-8-methylnaphthalene* (11b). Mixtures of **11a** and **11b** obtained in the addition reactions were combined and chromatographed over silica gel (100–200 mesh, 100 g/g of mixture) using 20% ethyl acetate in benzene as eluent. The material in the first fraction proved to be the major component and was further recrystallized thrice from ethyl acetate–hexane to fairly pure **11a**, mp 91.0–92.5 °C, *m/e* 230.[31] The analytical sample of **11a**, mp 94.8–95.1 °C, NMR ($CDCl_3$) 2.26 (3, s, $ArCH_3$), 5.56 [1, s, $CH(-O-)_2$], 5.78 ppm (1, s, C_4 H), was obtained by further recrystallization. From the second fraction in a similar way was isolated a small amount of the minor component, **11b** mp 109–110 °C. The analytical sample of **11b**, mp 111.8–112.0 °C, *m/e* 230, NMR ($CDCl_3$) 2.38 (3, s, $ArCH_3$), 5.66 (1, s, C_4 H), 5.96 ppm [1, s, $CH(-O-)_2$], was obtained by further recrystallization. The assignment of **11a** and **11b** was made because the hydrogen on the carbon (C_4) in **11a** containing the epoxy link was further downfield (δ 5.78) when sterically hindered by the peri methyl group than in the isomer (δ 5.66) where this hydrogen is next to a peri hydrogen.[8b]

In addition to the NMR evidence, samples of **11a** and **11b** were catalytically reduced (Pd/C) in 80% yields to 1-(1,3-dioxolan-2-yl)-1,4-epoxy-5-methyl-1,2,3,4-tetrahydronaphthalene,* mp 80–81 °C, *m/e* 232, and 1-(1,3-dioxolan-2-yl)-1,4-epoxy-8-methyl-1,2,3,4-tetrahydronaphthalene,* mp 91.5–92.0 °C respectively. The dihydro adduct above, mp 80–81 °C (40 mg), was heated with 2 ml of 98% formic acid on a steam bath for 30 min. The aromatic aldehyde thus obtained was immediately oxidized by heating with aqueous sodium hydroxide and the freshly prepared Ag_2O from 200 mg of $AgNO_3$ to yield 24 mg (67%) of 5-methyl-1-naphthoic acid, mp 184–186 °C (lit.[32] mp 188–189 °C).

The dihydro adduct above, mp 91.5–92.0 °C (250 mg), was similarly heated with 98% formic acid to yield a mixture which was not readily oxidized by Ag_2O. Chromatography afforded 70 mg of 8-methyl-1-naphthaldehyde, mp 65–67 °C, which proved identical with an authentic sample, mp 70–71 °C, prepared as described[33] (lit.[33] mp 71.5–72.0 °C) from 1,8-dimethylnaphthalene, by GLC, TLC, and ir measurements.

Proof of Structure, Methyl 1,4-Dihydro-1,4-epoxy-5-methyl-1-naphthoate* (12a) and Methyl 1,4-Dihydro-1,4-epoxy-8-methyl-1-naphthoate* (12b). About 2 g of a mixture of **12a** and **12b** was subjected to preparative TLC on silica gel. Only one broad band was obtained but this was separated into upper and lower halves. On extraction of the upper half 900 mg of product was obtained. Crystallization from ether–hexane afforded 500 mg of product, mp 95–97 °C, which proved to be **12a.** The analytical sample melted at 96.5–97.0 °C. Similarly from the lower half there was isolated a sample of **12b**, mp 55–56 °C.

On catalytic hydrogenation in methanol over Pd/C, 500 mg of **12a** afforded 420 mg of methyl 1,4-epoxy-5-methyl-1,2,3,4-tetrahydro-1-naphthoate,* mp 69–70 °C, ir (KBr) 1750 cm^{-1}, which, on heating with methanolic HCl for 2 h, afforded methyl 5-methyl-1-naphthoate. Aqueous alkaline hydrolysis afforded 5-methyl-1-naphthoic acid,[32] mp 186–188 °C, identical with the acid formed (see above) by oxidation of 5-methyl-1-naphthaldehyde by melting point and mixture melting point. In a similar way the adduct **12b** was hydrogenated and the crude product aromatized by heating with methanolic HCl to methyl 8-methyl-1-naphthoate, ir (neat) 1725 cm^{-1}. After heating in aqueous methanolic KOH for 16 h, the acid obtained by the usual

method (some ester, ca. 30% still remained) melted at 154.0–154.5 °C (lit.[34] mp 153 °C), ir (KBr) 1688 cm^{-1}, identical by mixture melting point with a sample obtained by oxidation of 8-methyl-1-naphthaldehyde (see above).

Registry No.—**1,** 4389-45-1; **2,** 4389-50-8; **3,** 59907-12-9; **4,** 59907-13-0; **5,** 534-22-5; **6,** 7040-43-9; **7,** 1708-41-4; **8,** 611-13-2; **9a,** 59907-14-1; **9b,** 59907-15-2; **10a,** 59907-16-3; **10b,** 59907-17-4; **11a,** 59907-18-5; **11b,** 59907-19-6; **12a,** 59907-20-9; **12b,** 59907-21-0; *o*-toluidine, 95-53-4; hydroxylamine sulfate, 13973-61-0; 2-hydroxyiminoacet-*o*-toluidide, 1132-03-2; 7-methylisatin, 1127-59-9; acet-*o*-toluidide, 120-66-1; 2-methyl-6-nitroacetanilide, 59907-22-1; 2-methyl-6-nitroaniline, 570-24-1; 2-methyl-6-nitrobenzonitrile, 1885-76-3; 2-methyl-6-nitrobenzamide, 40637-78-3; 2-methyl-6-nitrobenzoic acid, 13506-76-8; *m*-toluic acid, 99-04-7; 2-nitro-3-methylbenzoic acid, 5437-38-7; 2-nitro-3-methylaniline, 601-87-6; 3-bromo-2-nitrotoluene, 52414-97-8; 2-bromo-6-methylaniline, 53848-17-2; 2-bromo-3-nitrotoluene, 41085-43-2; 2-bromo-3-methylaniline, 54879-20-8; *tert*-butyl chloride, 507-20-0; methyl 5-*tert*-butyl-2-furoate, 59907-23-2; 5-*tert*-butyl-2-furoic acid, 56311-39-8; 1-(1,3-dioxolan-2-yl)-1,4-epoxy-5-methyl-1,2,3,4-tetrahydronaphthalene, 59907-24-3; 1-(1,3-dioxolan-2-yl)-1,4-epoxy-8-methyl-1,2,3,4-tetrahydronaphthalene, 59907-25-4; methyl 1,4-epoxy-5-methyl-1,2,3,4-tetrahydro-1-naphthoate, 59907-26-5; methyl 8-methyl-1-naphthoate, 15724-49-9; 8-methyl-1-naphthaldehyde, 6549-57-1.

References and Notes

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