($CDCl_3$) 0.93, 0.92 (s, overlapping d, 6 H), 2.43 (s, 3 H), 7.27, 7.87, (dd, 4 H); IR (KBr) 3540, 1600, 1405, 1320, 1150 cm^{-1}. Anal. Calcd for $C_{20}H_{30}N_2O_3S$: C, 63.50; H, 7.93; N, 7.40; S, 8.47. Found: C, 63.46; H, 7.83; N, 7.52; S, 8.61.

***cis*-Hydrindenol 13a.** To a stirred solution of 189 mg (0.5 mmol) of *p*-toluenesulfonylhydrazone **18** and 4 mL of tetramethylethylenediamine in 3 mL of anhydrous ether at 0 °C under nitrogen was added dropwise 3 mL of a 1 M solution of methyllithium in diethyl ether. The reaction mixture was stirred overnight at room temperature. Then, 20 mL of water was carefully added, and the organic layer was separated, washed several times with water, and dried over anhydrous magnesium sulfate. Concentration afforded 94 mg of crude material which was subjected to preparative TLC (silica gel, 1:1 benzene/EtOAc) to give 74 mg (76%) of colorless oil: ^1H NMR ($CDCl_3$) 0.93 (s, 3 H), 1.08 (d, J = 6 Hz, 3 H), 3.22-3.77 (m, 2 H), 5.53 (br s, 2 H); IR (neat) 3340 (br), 1655, 1440, 1370, 1025 cm^{-1}; ^{13}C NMR (62.9 MHz, $CDCl_3$) 17.0, 22.2, 22.3, 28.7, 29.5, 33.9, 37.4, 41.4, 46.8, 49.0, 68.0, 125.1, 132.3.

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Registry No. (±)-**3a**, 79980-73-7; **3a**, 64190-56-3; **3c**, 79980-74-8; **4a**, 79918-60-8; *erythro*-**4b**, 79918-61-9; *threo*-**4b**, 79918-62-0; **7**, 55048-74-3; **8**, 79280-39-0; **9**, 79918-63-1; **10**, 79918-64-2; **11**, 79918-65-3; (±)-**13a**, 79980-75-9; **13a**, 79918-66-4; **13c**, 79980-76-0; **14**, 79918-67-5; **15**, 79918-68-6; **16a**, 79918-69-7; **16b**, 79918-70-0; **17**, 79918-71-1; **18**, 79918-72-2.

Synthesis of 4-*tert*-Butyl-1,1-dimethylindan and 7-*tert*-Butyl-3,3-dimethyl-1-indanone and a Comparison of Isomers

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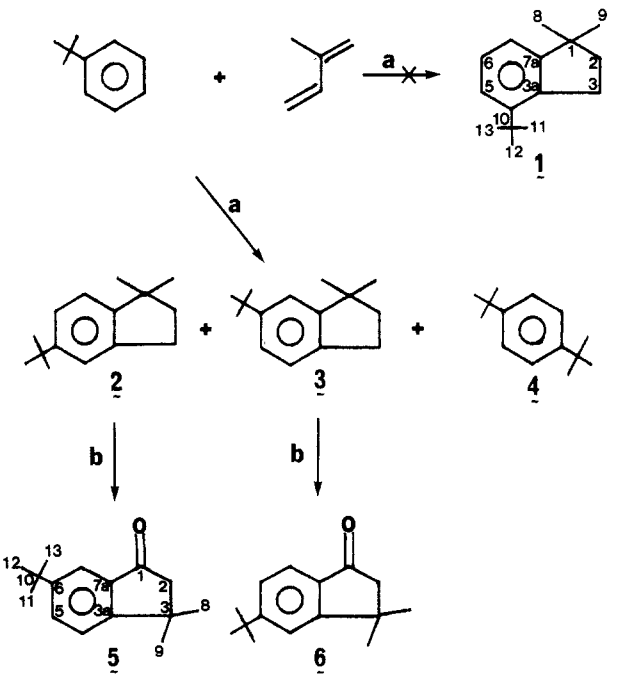
4-*tert*-Butyl-1,1-dimethylindan was synthesized to help establish the identity of products (5- and 6-*tert*-butyl-1,1-dimethylindan as minor and major products, respectively) from the sulfuric acid catalyzed condensation of *tert*-butylbenzene and isoprene. NMR (^1H and ^{13}C) studies of these hydrocarbons and their corresponding indanones, obtained through chromic acid oxidation, provided structural proof. Gated decoupling experiments were crucial to complete assignment.

It was earlier reported that the sulfuric acid catalyzed condensation of isoprene and *tert*-butylbenzene yields 6-*tert*-butyl-1,1-dimethylindan (**3**) as the major product.[2a,b,c] 1,4-Di-*tert*-butylbenzene (**4**) and what was assumed[2a] to be 4-*tert*-butyl-1,1-dimethylindan (**1**) were also reported. 5-*tert*-Butyl-1,1-dimethylidan (**2**) forms instead of **1** as shown in Scheme I. The emergence order and ratio of these cyclialkylation reaction products from a UC W-98 gas chromatography (GC) column were **4**/**3**/**2** (3:98:2). Conclusive identification of **2** as a minor reaction product of Scheme I became possible only through extensive fractional distillation[3a] and preparative GC[3b] which provided a pure sample of **2**. The infrared spectrum of **2** suggested 1,2,4 substitution rather than the 1,2,3 arrangement required for **1**.[2d,e] The evidence for the identity of **2** included chromic acid oxidation to 6-*tert*-butyl-3,3-dimethyl-1-indanone (**5**) and direct comparison with au-

Scheme I



[a] H_2SO_4. [b] CrO_3, HOAc.

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(2) (a) Eisenbraun, E. J.; Mattox, J. R.; Bansal, R. C.; Wilhelm, M. A.; Flanagan, P. W.; Carel, A. B.; Laramy, R. E.; Hamming, M. C. *J. Org. Chem.* **1968**, *33*, 2000. (b) This reaction was also carried out by Wood, T. F.; Angiolini, J. *Tetrahedron Lett.* **1963**, 1. (c) Indan **3** was synthesized and purified for the American Petroleum Institute Reference Materials program. Requests for **3** should be directed to A. J. Streiff, Carnegie-Mellon University, Schenley Park, Pittsburg, PA 15213. (d) We thank Dr. D. E. Boone for calling our attention to the incorrect assignment of structure for the minor component as **1**. Cf. Young, C. W.; DuVall, R. B.; Wright, N. (*Anal. Chem.* **1951**, *23*, 709) for use of IR spectroscopy in distinguishing 1,2,3, and 1,2,4 substitution of benzene. (e) Nakanishi, K. "Infrared Absorption Spectroscopy"; Holden Day: San Francisco, 1962; p 26.

(3) (a) We thank A. J. Streiff, API Project 58B, Carnegie-Mellon University, Pittsburgh, PA 15213, for the distillation fraction which provided **2**. (b) Preparative GC separations were made at 170 °C on a 4-in. × 10-ft column of 60-70-mesh Gas Pak W coated with 25% Carbowax 20-M. We thank R. E. Laramy, Continental Oil Co., for this purification of **2**. (c) Analytical GC studies were obtained with a 0.25-in. ×11-ft column of 80-100-mesh Chromosorb G, DMCS-treated and coated with 5% UC W-98 in a Hewlett-Packard 5750 FID GC apparatus and with a 0.25 mm × 20 m glass capillary column interior coated with SE-54 in a Vaian 3700 FID GC apparatus.

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Table I. ^{1}H NMR Spectroscopic Data

compd	δ [a,b] *gem*-CH_3	*t*-Bu	$ArCH_2CH_2$	$ArCH_2$	ArH
1	1.21	1.35	1.83	3.01	6.88-7.20
2	1.21	1.27	1.86	2.82	7.0-7.32
3	1.22	1.28	1.87	2.78	6.80-7.10
15 [c]	1.17		1.82	2.80	7.0
5	1.39	1.33	2.43		7.28-7.66
6	1.40	1.35	2.42		7.20-7.68
14	1.36	1.41	2.46		7.2-7.5
16 [c]	1.36		2.46		7.16-7.76

[a] (CCl_4) in parts per million from internal Me_4Si. [b] Numbering system provided with structures 1 and 5. [c] Compounds 15[7a] and 16[7a] were synthesized for this study.

Table II. ^{13}C NMR Spectroscopic Data

compd	δ [a,b] C-1 [c]	C-2 [d]	C-3	C-3a [c]	C-4 [e]	C-5 [e]	C-6 [e]	C-7 [e]	C-7a [c]	C-8, [f] C-9	C-10	C-11, [f] 12,13
1	42.6	41.3	31.7 [d]	139.6	146.0 [c]	123.0	126.3	119.6	153.2	28.5	35.4	30.4
2	43.5	41.7	30.2 [d]	142.3	121.2	149.0 [c,g]	123.4	121.3	149.3 [g]	28.5	34.4	31.7
3	44.0	41.8	29.5 [d]	139.7	123.9	123.3	149.4 [c]	118.6	152.2	28.7	34.6	31.7
15 [h]	43.8	41.4	29.5 [d]	142.1	124.2	125.9	126.1	121.6	152.0	29.6		
17	32.8	25.3	32.8	143.9	125.9	124.2	124.2	125.9	143.9			
18 [h]	39.4	34.7	31.4	143.3	124.0	125.9	125.9	122.8	148.2	19.8		
5	205.7	53.3	38.0 [c]	160.9	122.8	132.4	150.5 [c]	119.3	134.9	29.9	34.7	31.3
6	204.8	53.2	38.4 [c]	163.7	119.4	158.8 [c]	124.9	122.7	132.7	30.0	35.5	31.2
14	204.9	54.0	37.1 [c]	166.6	121.1	134.1	124.4	151.5 [c]	132.7	29.8	35.8	30.3
16 [h]	204.9	52.7	38.3 [c]	163.3	122.9 [g]	134.6	127.1	123.3 [g]	135.0	29.8		
19 [i]	206.2	36.0	25.6	154.9	127.0 [g]	134.3	126.6 [g]	123.3	136.9			

[a] ($CDCl_3$) in parts per million from internal Me_4Si. [b] Numbering systems provided with structures 1 and 5. [c] Singlet observed in off-resonance decoupled spectrum (ORDS). [d] Triplet observed (ORDS). [e] Doublet observed (ORDS) unless otherwise noted. [f] Quartet observed (ORDS). [g] Assignments may be interchanged. [h] Compounds 15,[7a] 16,[7a] and 18 were synthesized for this study. [i] Reference 4b.

Table III. Long-Range Carbon-Proton Coupling Data

compd	carbon	coupling [a] with protons on C-4	C-5	C-6	C-7
1	C-5			<0.8	6.5
	C-6		<0.8		0.8
	C-7		≃8.5	≃1.5	
2	C-4			8.0	2.2
	C-6	6.8			<0.8
	C-7	<0.8		<0.8	
3	C-4		2.2		2.2
	C-5	1.0			5.6
	C-7	<0.8	5.7		

[a] ($CDCl_3$) in hertz.

thentic 5.[4a] In addition, the ^{1}H and ^{13}C NMR values presented in Tables I and II and long-range carbon–proton coupling data in Table III as applied to select aromatic carbons also support this assignment to 2.

With the structure of 2 established, it became of interest to obtain a synthetic sample of 1 for spectral comparison, to determine its stability under acidic conditions, and to use it as a GC standard in studying the cyclialkylation of *tert*-butylbenzene with isoprene.

The reactions of Scheme II were used to prepare 1 and the corresponding indanone 14. The acids, 8a and 9a, were prepared through known procedures.[4a] The prearation of alcohol 10[5a] and chloride 11[5b] proceeded as expected. In the conversion of 11 to 1, there was considerable chloride elimination which resulted in a mixture of 1/12 (1:1.3).[3c] This mixture was partially separated by distillation and completely by preparative GC.[3b] Oxidation of the mixture of 1 and 12 with permanganate in benzene with phase-transfer oxidation,[6a] catalyzed by Aliquat 336, gave a mixture of 1/13 (1.6:1.0).[3c] This mixture was separated through use of Girard's reagent T.[6b] Hydrocarbon 1 was then oxidized to indanone 14 with CrO_3 in acetic acid.[7a,b] Chromic acid oxidation was extended to indans 2 and 3 (Scheme I) to provide 5 and 6 for comparison. These indanones (5, 6, and 14) and their derivatives played an important role in identifying hydrocarbons 1, 2, and 3.

We sought information about the influence of the *tert*-butyl group in 1, 2, and 3 vs. 1,1-dimethylindan (15) and 5, 6, and 14 vs. 3,3-dimethyl-1-indanone (16) in regard to its influence on chemical reactivity and in spectroscopic assignments. 7-*tert*-Butyl-3,3-dimethyl-1-indanone (14) does not form a semicarbazone. The remaining indanones (5, 6, and 16) form semicarbazones and all four readily yield 2,4-dinitrophenylhydrazones. Having 1 available made it possible to determine its stability under acidic conditions. The GC data clearly show that 1 is not present as a product from the reaction of *tert*-butylbenzene and isoprene in the presence of sulfuric acid. We considered that 1 may form, but steric effects introduced by ortho

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(5) (a) van Bekkum, H.; Nieuwstad, Th. J.; von Barneveld, J.; Klapwijk, P.; Wepster, B. M. *Recl. Trav. Chim. Pay-Bas.* **1969**, *88*, 1028. (b) Norris, J. F.; Olmsted, A. W. "Organic Syntheses", Collect. Vol. 1, 2nd ed.; Blatt, A. H., Ed.; Wiley: New York, 1948; pp 144–145.

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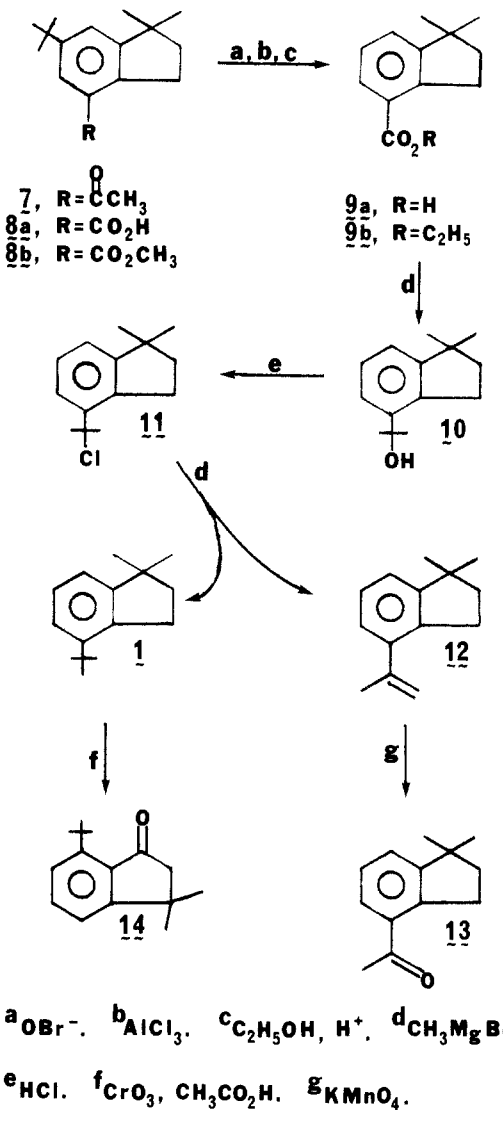
(7) (a) Harms, W. M.; Eisenbran, E. J. *Org. Prep. Proced., Int.* **1972**, *4*, 67. (b) Burnham, J. W.; Duncan, W. P.; Eisenbraun, E. J.; Keen, G. W.; Hamming, M. C. *J. Org. Chem.* **1974**, *39*, 1416. (c) Tashiro, M.; Fukata, G.; Yamato, T. *Org. Prep. Proced., Int.* **1976**, *8*, 263. (d) Eisenbraun, E. J.; Harms, W. M.; Burnham, J. W.; Dermer, O. C.; Laramy, R. E.; Hamming, M. C.; Keen, G. W.; Flanagan, P. W. *J. Org. Chem.* **1977**, *42*, 1967.

Scheme II



substitution of the *tert*-butyl group could promote rapid rearrangement of the *tert*-butyl group or dealkylation (loss of *tert*-butyl, ring cleavage, or complete loss of C-5 unit).

We tried using benzene and chlorobenzene as solvents to study the stability of 1 under acidic conditions simulating those used in the preparation of 3.[2a] However, with chlorobenzene and sulfuric acid 1 was stable for 3 h.

With benzene as a solvent, sulfuric acid caused 1 to form a reaction mixture consisting of *tert*-butylbenzene, **15**, **4**, **3**, **2**, and **1** in the ratio 48:27:1:3.3:5:1581 over a 3-h period. Increasing the concentration of sulfuric acid and the reaction time to 6 h gave the ratio 31:26:1:2.3:2.5:26.

Treatment of **2** and **3** in the absence of solvent with sulfuric acid gave product mixtures consisting of *tert*-butylbenzene, **15**, **4**, **3**, and **2** in the ratios 25:20:1:1.3:77 and 21:15:1:22:1.8 from **2** and **3**, respectively. Hydrocarbon **1** was not observed.

In addition, we attempted transalkylation of **15** with sulfuric acid using *tert*-butylbenzene as source of alkyl group. Only traces of 1,4-di-*tert*-butylbenzene, **2**, and **3** were observed during 24 h. Again **1** was not observed. However, transfer of *tert*-butyl group from 2,6-di-*tert*-butyl-*p*-cresol to **15** took place rapidly in nitromethane solvent, using $AlCl_3$ catalyst.[7c] These studies suggest that **2** is derived mainly from meta attack in the initial alkylation and that the **2**/**3** isomer ratio is established before cyclialkylation takes place.

We previously pointed out that polycyclialkylation of *tert*-butylbenzene may be minimized by limiting the isoprene component.[2a] Gas chromatographic analysis of the products from the reaction of **3** with isoprene in the presence of sulfuric acid showed a 4–5% yield of 1,1,6,6-tetramethyl-*as*-hydrindacene (**20**) believed to result from condensation of **3** with isoprene and subsequent loss of *tert*-butyl group. The identity of **20** was established through comparison with authentic material.[7d] High-resolution mass spectrometry studies verified the empirical formula of **20** and also showed that 4-*tert*-butyl-3,3,6,6-tetramethyl-*as*-hydrindacene as well as the two possible hexamethyltrindans[7d] are not products of this reaction. However, *m*/*e* 256 and 272 were observed. The latter value suggests formation of 6-*tert*-butyl-4-isopentyl-1,1-dimethylindan. Reduction of the isopentenyl side chain to the isopentyl group has been observed in similar cyclialkylation reactions.[7d]

As shown in Table I, **1** experiences deshielding of *tert*-butyl protons to δ 1.35 compared to δ 1.27 and 1.28 for **2** and **3**. A similar deshielding of *tert*-butyl protons to δ 1.41 is observed for **14**. In addition, an expected deshielding to δ 3.01 is observed for the benzylic protons of **1**. Other than these observations, the principal NMR support for the structural assignments of the compounds appearing in Schemes I and II is derived from ^{13}C data.

1,1-Dimethylindan (**15**) and 3,3-dimethyl-1-indanone (**16**) were selected as models for comparison and interpretation of ^{13}C data. The assignments shown for **15** and **16** are based in turn on those of indan (**17**), 1-methylindan (**18**), and 1-indanone (**19**).

Comparison of singlet peaks in the proton off-resonance decoupled ^{13}C spectra of indans (**1**, **2**, **3**) and indanones (**5**, **6**, **14**) with ^{13}C spectra of models **15** and **16** permitted direct identification of C-1, C-3a, C-7a for all of these compounds as well as C-3 of **5**, **6**, and **14** as shown in Table II.

Introduction of a *tert*-butyl group causes the extensive deshielding observed at 146.0, 149.0, 149.4, 150.5, 158.5, and 151.5 ppm at the substituted carbon for **1** (C-4), **2** (C-5), **3** (C-6), **5** (C-6), **6** (C-5), and **14** (C-7), respectively. In only one case, **2** at C-5 and at C-7a, is caution required since the absorptions are at 149.0 and 149.3 ppm. Off-resonance decoupled spectra (triplet observed) also permitted assignment at C-2 (**1**, **2**, **3**, **5**, **6**, **14**) and C-3 for **1**, **2**, and **3**. The position, intensity, and multiplicity of the off-resonance decoupled spectra allowed assignment of all methyl groups. The remaining peaks from aromatic carbons (C-4, C-5, C-6, C-7) were characterized through observation of a doublet in the off-resonance decoupled ^{13}C spectrum and their peak positions relative to the model compounds **15**, **16**, and **17** as presented in Table II.

The specific assignment of C-4 and C-7 in **2** and C-4 and C-5 in **3** was made possible only through analysis of their long-range carbon coupling with protons on the aromatic ring. Similarly the gated decoupling values for **1** are consistent with the assigned values and hence its structure. These long-range carbon–proton coupling constants, shown in Table III, were obtained by gated decoupling techniques which allowed a full coupling between carbons and protons. The fact that three-bond coupling ($^3J_{CCCH}$ usually between 5 and 8 Hz) is greater than two-bond or four-bond coupling ($^3J_{CCH}$ or $^4J_{CCCCH}$ less than 2 Hz) allows the assignment (Table II).[8]

The UV data for **1** in Table IV, in comparison to those of **2** and **3**, show a consistent decrease in ϵ at all values except at 214 nm.

(8) Weigert, F. J.; Roberts, J. D. *J. Am. Chem. Soc.* **1967**, *89*, 2967.

Table IV. Ultraviolet Spectroscopic Data

compd	95% EtOH, λ_{max}, nm (ϵ)
1	214 (9600), 261 (370), 266 (470), 268 (400), 273 (480)[a]
2	213 (9400), 262 (840), 267 (1300), 270 (1220), 276 (1700)[a]
3	213 (8950), 262 (900), 267 (1320), 269 (1300), 275 (1720)[a]
15	207 (8570), 210 (8540), 214 (7200), 253 (670), 265 (1080), 272 (1290)[a]
5	247 (10 300), 297 (2400)[b]
6	254 (14 600), 289 (3100)[b]
14	252 (9100), 297 (2400)[b]
16	244 (12 000), 289 (2400)[b]

[a] 1×10^{-4} mol/L. [b] 4.5×10^{-5} mol/L.

Experimental Section[9]

Synthesis of 4-*tert*-Butyl-1,1-dimethylindan via 7, 8a, 8b, 9a, 9b, 10, 11. Hypobromite Oxidation of 4-Acetyl-6-*tert*-butyl-1,1-dimethylindan (7) to 6-*tert*-Butyl-1,1-dimethyl-4-indancarboxylic Acid (8a). A 480-g (2.0 mol) sample of **7** was oxidized with NaOBr in dioxane.[4a] The acidified product gave 453 g (93%) of crude **8a**. Recrystallization from petroleum ether (bp 60–68 °C) gave **8a**: mp 191–192 °C (lit.[4a] mp 190.5–192 °C); ^{1}H NMR (CCl_4, 60 MHz) δ 11.22 (s, 1, CO_2H), 7.84, 7.22 (d, 2, ArH), 3.23 (t, 2, $ArCH_2$), 1.93 (t, 2, $ArCH_2CH_2$), 1.36 (s, 9, *tert*-butyl), 1.25 (s, 6, *gem*-CH_3); IR (KBr) 1702 cm^{-1} (C=O).

A sample of **8a** was esterfied with diazomethane to give methyl 6-*tert*-butyl-1,1-dimethylindan-4-carboxylate (**8b**): ^{1}H NMR (CCl_4, 60 MHz) δ 7.67, 7.12 (d, 2, ArH), 3.80 (s, 3, $COOCH_3$), 3.13 (t, 2, $ArCH_2$), 1.89 (t, 2, $ArCH_2CH_2$), 1.32 (s, 9, *tert*-butyl), 1.23 (s, 6 *gem*-CH_3); IR (film) 1740 cm^{-1} (C=O).

Conversion of 8a to 1,1-Dimethylindan-4-carboxylic Acid (9a). A mixture of 326 g (1.32 mol) of crude **8a**, 2.7 L of toluene, and 720 g (5.5 mol) of $AlCl_3$ was stirred at room temperature for 19 h.[4a] The reaction mixture was decomposed by stirring with ice and hydrochloric acid and then extracted with petroleum ether (bp 60–68 °C). The organic layer was extracted with 2 L of 5% NaOH solution. Acidification and filtration yielded 232 g (92%) of crude product. Recrystallization from petroleum ether (bp 60–68 °C) gave **9a**: mp 145–146 °C (lit.[4a] mp 145–147.6 °C); ^{1}H NMR (CCl_4, 60 MHz) δ 12.43 (s, 1, COOH), 7.80 (m, 1, ArH), 7.80, 7.12 (s, 2, ArH), 3.29 (t, 2, $ArCH_2$), 1.93 (t, 2, $ArCH_2CH_2$), 1.26 (s, 6, *gem*-CH_3).

Ethyl 1,1-Dimethylindan-4-carboxylate (9b). A 130-g (0.68 mol) sample of **9a** was esterified with 95% ethanol (250 mL) in the presence of 10 mL of H_2SO_4 and 500 mL of benzene for 7 days, using a Dean–Stark separator to remove water. The reaction yielded 150 g of an orange oil. Distillation gave 147 g (98%) of **9b**: bp 115 °C (0.5 mm); ^{1}H NMR (CCl_4, 60 MH_z) δ 7.67 (center of m, 1, ArH), 7.12 (s, 1, ArH), 7.07 (center of m, 1, ArH), 4.23 (q, 2, CH_2CH_3), 3.20 (t, 2, $ArCH_2$), 1.88 (t, 2, $ArCH_2CH_2$), 1.35 (t, 3, CH_2CH_3), 1.22 (s, 6, *gem*-CH_3).

Anal. Calcd for $C_{14}H_{18}O$: C, 77.03; H, 8.31. Found: C, 76.89; H, 8.34.

1,1-Dimethyl-4-(1-hydroxy-1-methylethyl)indan (10). To 750 mL (2.1 mol) of methylmagnesium chloride in tetrahydrofuran (THF) was added a solution of 142 g (0.65) of **9b** in 400 mL of THF over 80 min. This rate maintained a reflux temperature. After 5 h of reflux and subsequent cooling, a saturated solution of NH_4Cl (400 mL) was added over 2 h. Ether extraction, drying, ($MgSO_4$), and concentration gave 132 g (99%) of waxy white solid. Recrystallization from petroleum ether (bp 60–68 °C) gave **10**: mp 80–81 °C; IR (KBr) 3100–3600 cm^{-1} (OH); ^{1}H NMR (CCl_4, 60 MHz) δ 7.01–6.80 (m, 3, ArH), 3.02 (t, 2, $ArCH_2$), 1.82 (t, 2, $ArCH_2CH_2$, center of triplet overlapping with OH), 1.82 (s, 1, OH), 1.48 (s, 6, $C(CH_3)_2OH$), 1.20 (s, 6, *gem*-CH_3).

Anal. Calcd for $C_{14}H_{20}O$: C, 82.30; H, 9.87. Found: C, 82.16; H, 10.04.

Formation of 4-*tert*-Butyl-1,1-dimethylindan (1) as a Mixture with 4-Isopropenyl-1,1-dimethylindan (12). A mixture of 1.5 L of concentrated hydrochloric acid and 61 g of **11** was stirred overnight with an E-1 Vibromixer at room temperature. This mixture was extracted with 3 L of ether in two portions. The extract was washed with water, 5% NaOH solution, and saturated brine and then concentrated. One liter of THF was added and the volume was reduced to 500 mL. This solution was dried (Na_2SO_4). A portion containing **11** was concentrated under reduced pressure to remove THF: ^{1}H NMR (CCl_4, 60 MHz) δ 7.10–6.88 (m, 3, ArH), 3.12 (t, 2, $ArCH_2$), 1.97 (s, 6, $C(CH_3)_2Cl$, overlap with the following triplet), 1.88 (t, 2, $ArCH_2CH_2$), 1.23 (s, 6, *gem*-CH_3). There was no vinyl proton absorption.

The dried crude alkyl chloride **11** in THF was used directly by adding it to a stirred and refluxing solution of 310 mL (0.9 mol) of methylmagnesium chloride in THF over 2 h. Reflux was continued for 18 h. The ether extract of the product was dried ($MgSO_4$) and concentrated to 58 g of a yellow oil. Distillation at 62–72 °C (0.2 mm) gave 45 g of a colorless mixture which showed three components in the GC trace **12/1/unknown** (25:19:1) in the order of GC[3c] elution.

Phase-Transfer-Catalyzed Permanganate Oxidation of a Mixture of 1 and 12 to a Mixture of 1 and 4-Acetyl-1,1-dimethylindan (13). A mixture of 33 g of **1** and **12** and 20 mL of benzene was added over 2 h to a stirred mixture of 30 mL of benzene, 42 g of Aliquat 336, 94 g of $KMnO_4$ in 75 mL of H_2O held at 40–55 °C.[6a] Close attention is required during addition since there appears to be a time lag in temperature rise. After being stirred at 60 °C for 3 h, the reaction mixture was filtered through Dicalite to remove MnO_2. This cake was rinsed with petroleum ether (bp 60–68 °C). The organic phase of the filtrate was dried ($MgSO_4$) and concentrted to 31 g of a red oil shown by GC to contain **1/13/unknown** in the ratio 12:7:1 in the order of GC[3c] elution. The water layer of the filtrate was acidified and extracted with ether, but the extract gave negligible residue.

Separation of 1 and 4-Acetyl-1,1-dimethylindan (13) by Girard's Procedure.[6b] A 15-g mixture of crude **1/13** (1.0:1.3), 15 g of Girard's T reagent, 15 mL of acetic acid, and 150 mL of 95% ethanol was stirred at reflux temperature for 12 h. The reaction mixture was cooled, added to 1 L of water, and then extracted with three 400-mL portions of petroleum ether (bp 60–68 °C). The extract was dried ($MgSO_4$), filtered, and concentrated to 6.2 g of a yellow oil. Distillation gave 4 g of **1**: bp 60–61 °C (0.1 mm); GC[3c] analysis at 229 °C showed a single peak with 4.4-min retention time.

Anal. Calcd for $C_{15}H_{22}$: C, 89.04; H, 10.96. Found: C, 89,24; H, 11.06.

The aqueous layer was mixed with 50 mL of concentrated HCl and heated on the steam bath under a reflux condenser for 4 h. The reaction mixture was cooled and extracted with petroleum ether (bp 60–68 °C), and the extract was dried ($MgSO_4$), filtered, and concentrated to a yellow oil. Distillation gave 2.1 g of **13**: bp 82 °C (0.15 mm); IR (film) 1680 cm^{-1} (C=O); ^{1}H NMR (CCl_4, 60 MHz) δ 7.48 (m, 1, ArH), 7.13 (s, 1, ArH), 7.01 (m, 1, ArH), 3.16 (t, 2, $ArCH_2$), 2.46 (s, 3, $COCH_3$), 1.87 (t, 2, $ArCH_2CH_2$), 1.22 (s, 6, *gem*-CH_3); GC[3c] single peak at 229 °C with 5.3-min retention time.

Anal. Calcd for $C_{13}H_{16}O$: C, 82.93; H, 8.57. Found: C, 82.86; H, 8.64.

The orange 2,4-DNPH of **13** was prepared[10] and recrystallized from $CHCl_3$: mp 162–164 °C; ^{1}H NMR ($CDCl_3$, 100 MHz) δ 9.12 (d, 1, ArH), 8.33 (d of d, 1, ArH), 7.98 (d, 1, ArH), 7.50–7.05 (m, 3, ArH), 3.20 (t, 2, $ArCH_2$), 2.46 (s, 3, $COCH_3$), 1.98 (t, 2, $ArCH_2CH_2$), 1.30 (s, 6, *gem*-CH_3); mass spectrum, *m/e* (relative intensity) 368 (M^+, 22), 338 (17), 333 (22), 306 (17), 276 (23), 261 (31), 246 (16), 186 (69), 172 (100), 156 (72), 129 (44).

Anal. Calcd for $C_{19}H_{20}N_4O_4$: C, 61.94; H, 5.47; N, 15.29. Found: C, 61.66; H, 5.54; N, 14.92.

(9) Mass spectra were obtained with a CEC Model 21-110 B high-resolution instrument. Proton and ^{13}C NMR (fully proton-decoupled and off-resonance spectra) were recorded on Varian Associates HR-60 and XL-100 NMR spectrometers. Gated decoupling experiments to obtain long-range C–H coupling constants were performed on a Varian CFT 20 instrument. Chemical shifts are reported in parts per million downfield from Me_4Si as an internal standard and coupling constants are in hertz. Carbon spectra were obtained in approximately 30% $CDCl_3$ containing 5% Me_4Si.

(10) Shriner, R. L; Fuson, R. C.; Curtin, D. Y.; Morrill, T. C. "The Systematic Identification of Organic Compounds", 6th ed.; Wiley: New York, 1980; p 179.

Chromic Acid Oxidation of 1 to 6-*tert*-Butyl-3,3-dimethyl-1-indanone (14), 2 to 6-*tert*-Butyl-3,3-dimethyl-1-indanone (5), and 3 to 5-*tert*-Butyl-3,3-dimethyl-1-indanone (6). To a stirred 1.0-g (0.005 mol) sample of 1 dissolved in 1 L of acetic acid at room temperature was added a mixture of 2.5 g of CrO_3 dissolved in 25 mL of water.[7a,b] After the mixture was stirred overnight, 3 L of water was added and the reaction mixture was then extracted twice with 600 mL of petroleum ether (bp 60–68 °C). The extract was dried ($MgSO_4$), filtered, concentrated, and distilled to give 0.92 g (86%) of 14: bp 75 °C (0.1 mm); IR (film) 1707 cm^{-1} (C=O); mass spectrum, *m/e* (relative intensity) 216 (M^+, 28), 201 (41), 174 (34), 159 (41), 91 (11), 57 (29), 54 (100).

Anal. Calcd for $C_{15}H_{20}O$: C, 83.28; H, 9.32. Found: C, 83.25; H, 9.30.

The usual method of preparing a semicarbazone[10] failed to give a derivative of 14. To this reaction mixture was added an acidic, alcoholic solution of 2,4-dinitrophenylhydrazine.[10] The 2,4-DNPH precipitated immediately and was filtered, washed with water, and then recrystallized from 95% ethanol and again from a mixture of $CHCl_3$ and petroleum ether (bp 60–68 °C) to give the red, crystalline 2,4-DNPH of 14: mp 210–212 °C; ^1H NMr ($CDCl_3$, 100 MHz) δ 13.84 (s, 1, NH), 9.15 (d, 1, ArH), 8.37 (d of d, 1, ArH), 8.10 (d, 1, ArH), 7.60–7.10 (m, 3, ArH), 2.84 (s, 2, CH_2), 1.63 (s, 9, *tert*-butyl), 1.42 (s, 6, *gem*-CH_3); mass spectrum, *m/e* (relative intensity) 396 (M^+, 12), 215 (35), 200 (100), 159 (28), 144 (22), 57 (10).

Anal. Calcd for $C_{21}H_{24}N_4O_4$: C, 63.62; H, 6.10; N, 14.14. Found: C, 63.62; H, 6.10; N, 14.00.

Oxidation of 2 with CrO_3 gave 5: mp 50–51 °C (lit.[4] mp 50–51 °C). The semicarbazone of 5 was prepared[10] and then recrystallized from 95% ethanol: mp 202–204 °C (lit.[11] mp 198–199 °C); ^1H NMR ($CDCl_3$, 100 MHz) δ 8.76 (s, 1, NNH), 7.63 (d, 1, ArH), 7.40 (d of d, 1, ArH), 7.18 (d, 1, ArH), 6.00 (br s, 2, $CONH_2$), 2.67 (s, 2, CH_2), 1.35 (s, 6, *gem*-CH_3), 1.33 (s, 9, *tert*-butyl); mass spectrum, *m/e* (relative intensity) 273 (M^+, 58), 258 (28), 241 (22), 215 (100), 200 (28), 198 (22), 185 (25), 57 (28).

Anal. Calcd for $C_{16}H_{23}N_3O$: C, 70.29; H, 8.48. Found: C, 70.39; H, 8.52.

The orange 2,4-DNPH of 5 was prepared[10] and then recrystallized from a mixture of $CHCl_3$ and petroleum ether (bp 60–68 °C); mp 241–242 °C (lit.[11] mp 238–239 °C); ^1H NMR ($CDCl_3$, 100 MHz) δ 9.15 (d, 1, ArH), 8.37 (d of d, 1, ArH), 8.15 (d, 1, ArH), 7.82 (d, 1, ArH), 7.55 (d of d, 1, ArH), 7.29 (d, 1, ArH), 2.83 (s, 2, CH_2), 1.43 (s, 6, *gem*-CH_3), 1.39 (s, 9, *tert*-butyl).

Oxidation of 1.0 g of 3 gave 0.96 g (90%) of 6: mp 49–51 °C (lit.[7a] mp 49–51 °C). The semicarbazone was prepared and recrystallized from 95% ethanol to give colorless crystals: mp 213–215 °C; ^1H NMR ($CDCl_3$, 100 MHz) δ 8.84 (s, 1, NNH), 7.55 (d, 1, ArH), 7.32 (d, 1, ArH, 7.24 (s, 1, ArH), 6.00 (br s, 2, $CONH_2$), 2.66 (s, 2, CH_2), 1.35 (s, 6, *gem*-CH_3), 1.32 (s, 9, *tert*-butyl).

Anal. Calcd for $C_{16}H_{23}N_3O$: C, 70.29; H, 8.48; N, 15.45. Found: C, 70.32; H, 8.61; N, 15.25.

The red 2,4-DNPH of 6[10] was recrystallized from a mixture of $CHCl_3$ and petroleum ether: bp 60–68 °C; mp 239–240 °C; ^1H NMR ($CDCl_3$, 100 MHz) δ 9.10 (d, 1, ArH), 8.33 (d of d, 1, ArH), 8.08 (d, 1, ArH), 7.73 (d, 1, ArH), 7.34 (t, 2, ArH), 2.82 (s, 2, CH_2), 1.44 (s, 6, *gem*-CH_3), 1.38 (s, 9, *tert*-butyl).

Anal. Calcd for $C_{21}H_{24}N_4O_4$: C, 63.62; H, 6.10. Found: C, 63.71; H, 6.19.

Sulfuric Acid Catalyzed Isomerization of 4-*tert*-Butyl-1,1-dimethylindan (1). A. In Benzene. A 0.5-g (2.47 mmol) sample of pure 4-*tert*-butyl-1,1-dimethylindan (1) was added to a rapidly stirred (Teflon-covered magnetic bar) mixture of 0.12 g (1.24 mmol) of 97% sulfuric acid and 1.35 g (17.3 mmol) of benzene at 22 °C. At intervals over 3 h, stirring was stopped, and 0.3-mL samples of the reaction mixture were withdrawn. These samples were neutralized with 10% NaOH, washed with two 1-mL portions of H_2O, and dried ($MgSO_4$). GC analysis[3c] showed *tert*-butylbenzene/15/4/3/2/1 formed in the ratio 48:27:1:3.3:5:1581.

With a higher concentration of sulfuric acid (0.3 g of 1, 4.0 g of H_2SO_4, and 6.1 g of benzene), 1 reacted after 6 h to give the ratio 31:26:1:2.3:2.5:26. In similar experiments using this ratio of starting materials, 2 and 3 were treated for 14 h. The ratios of products (*tert*-butylbenzene, 15, 4, 3, 2) formed from 2 and 3 were 25:20:1:1.3:77 and 21:15:1:22:1.8. Indan 1 was not observed.

B. In Chlorobenzene. The initial experiment described in A was carried out in chlorobenzene instead of benzene. After 3 h, 1 was recovered unchanged. Identical experiments with 2 and 3 showed these indans were also stable to the reaction conditions.

***tert*-Butylation of 1,1-Dimethylindan. A. With *tert*-Butylbenzene and Sulfuric Acid.** To a magnetically stirred mixture of 2.0 g (13.7 mmol) of 1 and 9.2 g (68.5 mmol) of *tert*-butylbenzene, at 10 °C, was added dropwise 2.72 g (27.4 mmol) of 93% sulfuric acid. At intervals (0.1, 0.5, 1.0, 2.0, 22, and 24 h), 0.5-mL samples were withdrawn, quenched with 1 mL of 20% sodium hydroxide, washed twice with 1 mL of H_2O, and then dried ($MgSO_4$). The first four samples were run at 15 °C and then at 24 °C. GC analysis[3c] showed no transalkylation to 1,1-dimethylindan took place in 2 h. However, a trace of 1,4-di-*tert*-butylbenzene was observed. The later samples also showed traces of 2 and 3.

B. With 2,6-Di-*tert*-butyl-*p*-cresol, $AlCl_3$ and CH_3NO_2. To a solution of 2.0 g (0.01 mol) of 2,6-di-*tert*-butyl-*p*-cresol, 5 mL of nitromethane, and 7.3 g (0.05 mol) of pure 1,1-dimethylindan was added a mixture of 2.0 g (0.015 mol) of aluminum chloride in 5 mL of nitromethane.[7c] At intervals, samples (about 0.3 mL) were withdrawn and quenched in 1 mL of water. The organic layer was washed with 1 mL of 10% NaOH, two portions of 2 mL of H_2O, and dried ($MgSO_4$). GC analysis[3c] showed that, at 1, 2, 3, and 4 min, the ratios of 2/3 were 52:48, 55:45, 56:44, and 58:42, respectively. 4-*tert*-Butyl-1,1-dimethylindan (1) was not observed.

Treatment of 6-*tert*-Butyl-1,1-dimethylindan (3) with Isoprene in the Presence of Sulfuric Acid. 6-*tert*-Butyl-1,1-dimethylindan (3; 10 g, 0.049 mol) and 4.5 mL of 93% of sulfuric acid were combined and cooled in an ice–salt bath. To the vigorously stirred mixture was slowly added a cold homogeneous mixture of 10 g of 3 and 6.7 g (0.096 mol) of isoprene at 5–10 °C. Stirring was continued for 15 min. The reaction product was isolated as described[2a] and vacuum distilled to give 80% recovered 3 and 4.5% of 1,1,6,6-tetramethyl-*as*-hydrindacene (20)[7d] as shown by GC analysis.

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Registry No. 1, 16204-73-2; 2, 38393-97-4; 3, 3605-31-0; 4, 1012-72-2; 5, 38393-94-1; 5 semicarbazone, 79899-50-6; 5 2,4-DNPH, 79899-51-7; 6, 38393-93-0; 6 semicarbazone, 79899-52-8; 6 2,4-DNPH, 79899-53-9; 7, 13171-00-1; 8a, 61813-34-1; 8b, 79899-54-0; 9a, 55712-38-4; 9b, 55591-12-3; 10, 55591-13-4; 11, 79899-55-1; 12, 79899-56-2; 13, 55591-10-1; 13 2,4-DNPH, 79899-57-3; 14, 56298-78-3; 14 2,4-DNPH, 79899-58-4; 15, 4912-92-9; 16, 26465-81-6; 17, 496-11-7; 18, 767-58-8; 20, 5696-85-5.

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