dropwise addition of 3 mL of H_2O, 4.1 mL of 3 M aqueous NaOH, and then 8 mL of H_2O. The suspension was filtered to remove the solid residue and the residue was thoroughly washed with CH_2Cl_2. The combined filtrates were concentrated in vacuo and then distilled to give 14 g (87%) of **3-d_2-OH**, bp 85 °C/10 mm, which was pure by GLC: ^{1}H NMR (CD_3COCD_3–D_2O, 50:50 v/v) δ 4.2 (s, 1 H, OH), 3.65–3.56 (m, 4 H, CH_2CH_2), 3.57 (s, 2 H, CH_2CD_2), 3.36 (s, 3 H, CH_3).

2-(2-Methoxyethoxy)ethyl Tosylate (3-OTs). The standard pyridine procedure[12] was followed to give **3-OTs** (in 36% yield) as a solid (from hexane at −80 °C) which melted below 0 °C when warmed. The structure of the tosylate was confirmed by ^{1}H NMR (CD_3Cl) spectroscopy: δ 7.78 (d, J = 8.0, 2 H, Ar H), 7.43 (d, J = 8.0, 2 H, Ar H), 4.10 (m, 2 H, CH_2OSO_2), 3.58 (m, 2 H, $CH_2CH_2OSO_2$), 3.39–3.50 (m, 4 H, $MeOCH_2CH_2$), 3.26 (s, 3 H, CH_3O), 2.44 (s, 3 H, CH_3Ar).

2-(2-Methoxyethoxy)ethyl-1,1-d_2 Tosylate (3-d_2-OTs). Using **3-d_2-OH**, the deuteriated tosylate was prepared and isolated from the cold (−80 °C) hexane solution (35.6% yield); it melted below 0 °C when warmed. Its structure was confirmed by ^{1}H NMR ($CDCl_3$) spectroscopy: δ 7.78 (d, J = 8.0, 2 H, ArH), 7.43 (d, J = 8.0, 2 H, Ar H), 3.58 (s, 2 H, CH_2CD_2), 3.39–3.50 (m, 4 H, $MeOCH_2CH_2$), 3.26 (s, 3 H, CH_3O), 2.44 (s, 3 H, CH_3Ar).

Kinetic Measurements. The conductivity of the appropriate solutions, which were 10^{-3} M each in substrate and 2,6-lutidine, was measured at specific times by means of a computer-actuated conductivity bridge.[11] First-order rate constants were calculated by using the LSKIN program. Multiple determinations were made for each concentration.

Acknowledgment is made to the U.S. Army Research Office (DAAL03-86-K-0026) and to the National Aeronautical and Space Administration (NAGW-812) for financial support.

Registry No. 3-OTS, 50586-80-6; 3-OH-d_2, 83326-05-0; 3-OTs-d_2, 111959-31-0.

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One-Pot Synthesis of 3-Chloro-1,1,2-trimethylindenes from Trifluoromethanesulfonic Acid Catalyzed Benzoylation of 2-Methyl-2-butene

Christian Roussel,* Harivelo G. Rajoharison, Lucien Bizzari, and Latifa Shaimi

ESIPSOI, UA CNRS 126, University Aix-Marseille III, Rue Normandie-Niemen, 13397 Marseille, Cedex 13, France

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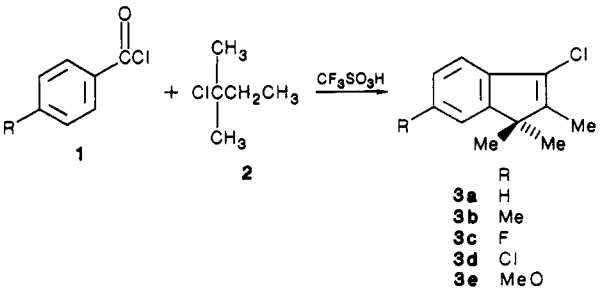
Acylation of alkenes, with aliphatic acyl halides, in the presence of Lewis acids or protonic acids is a versatile method to prepare various derivatives resulting from monoacylation,[1] diacylation[2,3] (pyrylium synthesis), triacylation,[3] and tetraacylation.[4]

Continuing our study on acylations catalyzed by sulfonic acids,[3b,5] we have found that acylation of alkenes (or alkenes precursors) with aromatic acylhalides, in the presence of 15% trifluoromethanesulfonic acid leads to an unprecedented one-pot synthesis of 3-chloroindenes.

Scheme I



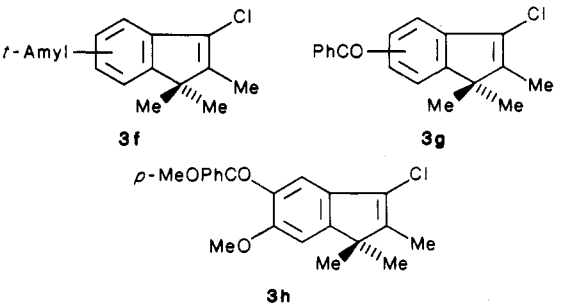
Results and Discussion

The acylations were performed by benzoyl chloride or various para-substituted benzoyl chlorides and trifluoromethanesulfonic acid on 2-chloro-2-methylbutane, according to Scheme I.

In a typical run, the alkyl halide and the aroyl chloride are put together at 0 °C, and CF_3SO_3H is added dropwise (5 min). The reaction mixture is then warmed at 80 °C for 24 h. After cooling, treatment of the crude reaction medium with dry pentane affords a substituted benzoic acid in large amount and traces of pyrylium salts, which were not further analyzed. The reaction medium is then treated with a 10% NaOH solution in order to eliminate the sulfonic acid and to hydrolyze unreacted benzoyl chloride. Dichloromethane extraction, drying, and evaporation afford an oil, which is submitted to bulb-to-bulb distillation followed by flash chromatography of the volatile fraction to give 3-chloroindene derivatives. Table I reports the experimental conditions and the yields in chloroindenes isolated in pure state according to the general procedure. All the 3-chloroindenes were identified by conventional methods (GC/MS, IR, ^{1}H and ^{13}C NMR).

Results given in Table I indicate that the experimental conditions and the substituent on the aromatic ring are of importance in the course of the reaction.

Benzoyl chloride and *p*-methoxybenzoyl chloride give low yields of chloroindene **3a** (run 1) and chloroindene **3e** (run 8), respectively. In both cases, the reaction does not stop after the formation of the initial chloroindene and chloroindenes **3f**, **3g**, and **3h**, resulting from further alkylation or further acylation were isolated in larger amount than **3a** and **3e** (Table I).[6] This is often the case in Friedel–Crafts chemistry when the obtained products are still reactive.



It was found impossible to have more than 50% yield when stoichiometric amounts of alkyl halide and benzoyl chloride were used. The reaction should proceed according to Scheme II. It involves the formation of 2-methyl-2-

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(5) Rajoharison, H. G.; Roussel, C. *Bull. Soc. Chim. Fr.* **1986**, 307.

(6) The multiplicity pattern of coupling constants in the aromatic region of the ^{1}H NMR spectra and coupling constants in ^{13}C NMR spectra indicate that the substituent is situated in position 5 or 6 and not in position 4 or 7 in **3f**, **3g**, and **3h**.

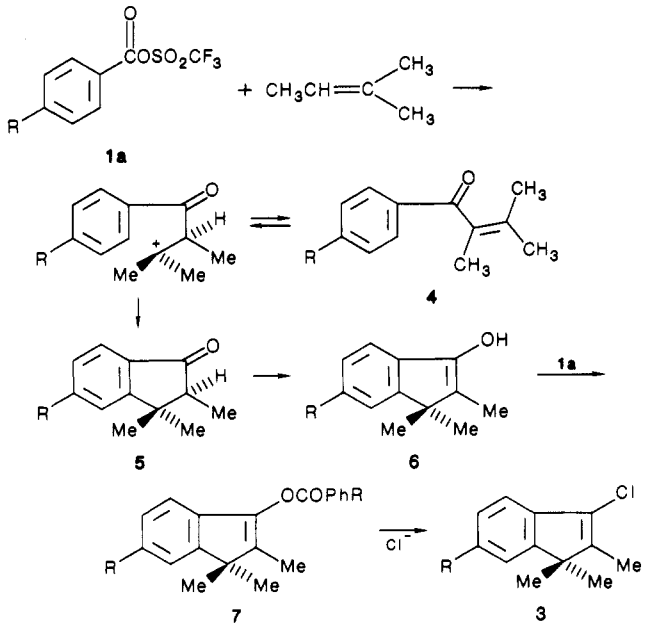
0022-3263/88/1953-0683$01.50/0

Table I

R	runs	molar equiv 1	molar equiv 2	T, °C	reactn time, h	molar equiv of CF_3SO_3H	product, yield[a]
H	1	1	1	80	4	0.3	**3a**, 14% (**3f**, 19%; **3g**, 19%)
H	2	1	1	40	4	0.3	no reaction
H	3	1	1	80	24	0.03	**3a**, 9% (**3f**, 1.5%; **3g**, 0.9%)
Me	4	1	1	80	24	0.15	**3b**, 36%
Me	5	2	1	80	24	0.15	**3b**, 61%
F	6	2	1	80	24	0.15	**3c**, 62%
Cl	7	2	1	80	24	0.15	**3d**, 76%
MeO	8	2	1	80	24	0.15	**3e**, 10%[b] (**3h**, 15%)

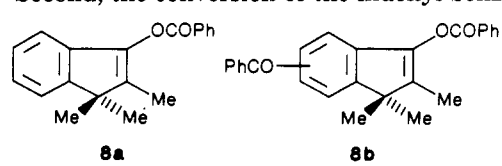
[a] Pure isolated compounds. [b] In the presence of 1,2-dichloroethane.

Scheme II



butene from the alkyl halide and a mixed anhydride derived from trifluoromethanesulfonic acid and aroyl chloride as acylating agent.[7] The use of trifluoromethanesulfonic acid as catalyst appears to promote the formation of indenol **6**, which is further acylated to give the corresponding benzoate **7** which is displaced by the free chloride ion to give **3** (Scheme II).[8]

The proposed reaction scheme is supported by the following experiments. First, we checked that indenyl benzoates **7** are obtained in the absence of chloride ion sources. Thus we reacted 2-methyl-2-butanol and an excess of benzoyl anhydride in the presence of methanesulfonic acid. Benzoates **8a** and **8b** were obtained (total yields 42% in isolated compounds from 2-methyl-2-butanol).[9] Second, the conversion of the indenyl benzoate **7** to the chloroindene from displacement of the chloride ion was established by treating indenyl benzoate **8b** with benzoyl chloride and trifluoromethanesulfonic acid according to run 1 experimental conditions: chloroindene **3g** was obtained.[10]



Our results are in sharp contrast with what has been reported on acylation of 2-methyl-2-butene with benzoyl chloride catalyzed by Lewis acid.[11,12] These acylations were performed with a large amount of catalyst (100–200%) as it is usual in Friedel–Crafts acylation reactions and the reaction stops after the first acylation step leading to ketoalkene **4** (using $SnCl_4$) or indanone **5** (using $AlCl_3$). In the case of 100% Lewis acid catalyzed acylation reaction, it is well-known that complexation of the resulting ketone occurs. Such a complexation should prevent the next reaction steps which readily proceed using sulfonic acid catalyst.

Experimental Section

General Procedures. Trifluoromethanesulfonic acid (Fluka) was used without further purification. All the substituted benzoyl chlorides are commercially available. Analysis of the reaction mixture by GLC were performed on an Intersmat IGC 16 (FID), equipped with a 1.5 m × 1/8 in. i.d. stainless steel column packed with Chromosorb PAW 80–100 mesh, 10% SE 30. A temperature range 140–300 °C was programmed to increase at 8 °C/min. Nitrogen pressure was 2.2 bars. GLC/MS were obtained on a Ribermag R-10-10. NMR spectra were run on a VARIAN XL 200 in deuteriochloroform.

Synthesis Procedures. (a) 3-Chloroindenes 3a–h. To a mixture of 10.6 g (0.1 mol) of 2-chloro-2-methylbutane and 0.1 mol (or 0.2 mol) of acylating agent (benzoyl chloride, 4-methoxybenzoyl chloride, 4-fluorobenzoyl chloride, 4-chlorobenzoyl chloride, or 4-methylbenzoyl chloride) was added 2.25 g (0.015 mol) of CF_3SO_3H dropwise under cooling and stirring (0 °C). The colorless mixture rapidly turned brownish. At the end of the addition, the reaction was warmed to the desired temperature (80 °C) for 24 h. After cooling, the crude reaction mixture was treated with 100 mL of dry pentane to precipitate the substituted benzoic acid which formed and traces of pyrylium salts. After filtration, the pentane was evaporated, and the resulting oil was treated with 50 mL of 10% NaOH solution for 1 h at 60 °C. After cooling, the organic layer was extracted with 2 × 50 mL of dichloromethane and dried with $MgSO_4$. Filtration and evaporation yielded a brownish oil, which was further handled according to the following specific treatments.

(7) The formation of mixed anhydrides between sulfonic acid and acid chloride, as powerful acylating agent is well documented: (a) Effenberger, F.; Sohn, E.; Epple, g. *Chem. Ber.* **1983**, *116*, 1195. (b) Effenberger, F.; Epple, G.; Eberhard, J. K.; Bühler, U.; Sohn, E. *Chem. Ber.* **1983**, *116*, 1183. (c) Hulin, B.; Koreeda, M. *J. Org. Chem.* **1984**, *49*, 207. (d) Martens, H.; Janssens, F.; Hoornaert, G. *Tetrahedron* **1975**, *31*, 177. (e) Shastin, A. V.; Gavrishova, T. N.; Balenkova, E. S. *Zh. Org. Khim.* **1985**, *21*, 1862; *J. Org. Chem. USSR (Engl. Transl.)* **1985**, *21*, 1704. (f) Effenberger, F. *Angew. Chem.,, Int. Ed. Engl.* **1980**, *19*, 151. (g) Roberts, R. M. G.; Wells, A. S. *Inorg. Chim. Acta* **1986**, *112*, 167.

(8) Benzoyl trifluoromethanesulfonate is a mild reagent for the benzoylation of hydroxyl groups. Brown, L.; Koreeda, M. *J. Org. Chem.* **1984**, *49*, 3875.

(9) The formation of indenyl benzoates **7** from indanones **5** is very similar to the already reported formation of 1-(isobutyroyloxy)-1-aryl-2,2-dimethylethylenes during acylation of aromatics with *i*-$PrCOSO_3CF_3$. This reaction proceeds through the acylation of the enol form of the intermediate aryl isopropyl ketone.[7a]

(10) Indenyl benzoate **8b** was chosen instead of **8a** to avoid complication arising from further benzoylation.

(11) Colonge, J.; Chambion, J. *Bull. Soc. Chim. Fr.* **1947**, 999.

(12) (a) El-Khawaga, A. M.; Abdelwahab, A. M.; El-Zohry, M. F.; Khalaf, A. A. *Rev. Roum. Chim.* **1985**, *30*, 599. (b) Khalaf, A. A.; Abdel-Wahab, A. M. A.; El-Khawaga, A. M.; El-Zohry, M. F. *Bull. Soc. Chim. Fr.* **1984**, *7–8*, 285. (c) Khalaf, A. A.; El-Khawaga, A. M. *Rev. Roum. Chim.* **1981**, *26*, 5, 739.

3-Chloro-1,1,2-trimethyl-2-indene[13] **(3a)**: colorless oil; 100 °C (5 mbar) [bulb-to-bulb distillation], obtained in pure state from a mixture of **3a**, **3f**, and **3g**; ^{1}H NMR ($CDCl_3$) δ 1.25 (6 H, s), 1.98 (3 H, s), 7.40 (4 H, s); ^{13}C NMR ($CDCl_3$) δ 9.84 (2-Me), 23.70 (1-Me), 49.13 (1-C), 118.45 (CH), 120.88 (CH), 125.45 (CH), 126.77 (CH); MS (70 eV), *m/e* (relative intensity) 194 (14), 192 (41), 179 (6.3), 177 (23), 165 (13), 163 (40), 158 (14), 157 (100), 142 (39), 141 (21), 129 (23), 128 (59), 127 (44), 126 (13), 115 (18), 105 (16), 101 (6), 77 (17), 71 (18), 70 (23), 63 (15), 55 (13)), 51 (19), 39 (11), 29 (18), 27 (25).

3-Chloro-1,1,2,6-tetramethyl-2-indene[14] **(3b)**: colorless oil; 95 °C (5 mbar) [bulb-to-bulb distillation]; ^{1}H NMR ($CDCl_3$) δ 1.22 (6 H, s), 1.93 (3 H, s), 2.38 (3 H, s), 7.06 (1 H, d, J_{AB} = 7.5 Hz), 7.11 (1 H, s), 7.2 (1 H, d, J_{AB} = 7.5 Hz); ^{13}C nmr ($CDCl_3$) δ 9.73 (2-Me), 21.52 (*p*-Me), 23.83 (1-Me), 49.32 (1-C), 118.24 (CH), 121.90 (CH), 127.48 (CH), 127.27 (CCl), 135.28 (2-C), 137.71 (MeC), 145.75 (3a-C), 151.54 (7a-C); MS (70 eV), *m/e* (relative intensity) 208 (7), 206 (24), 179 (12), 177 (39), 170 (13), 171 (100), 157 (22), 156 (33), 142 (47), 141 (56), 139 (13), 128 (15), 127 (12), 115 (42), 91 (3), 77 (9), 76 (8), 63 (18), 51 (15).

3-Chloro-6-fluoro-1,1,2-trimethyl-2-indene (3c): colorless oil, 110 °C (4.5 mbar) [bulb-to-bulb distillation]; ^{1}H NMR ($CDCl_3$) δ 1.21 (6 H, s), 1.92 (3 H, s), 6.90–7.03 (2 H, m), 7.22 (1 H, dd); ^{13}C NMR ($CDCl_3$) δ 9.78 (2-Me), 23.58 (1-Me), 49.62 (1-C), 108.95 (CH, J = 24 Hz), 113.45 (CH, J = 23 Hz), 119.25 (CH, J = 8 Hz), 124 (CCl), 136.0 (2-C), 146.46 (3a-C), 153.42 (7a-C), 162.0 (CF, J = 244 Hz); MS (70 eV), *m/e* (relative intensity) 212 (11), 210 (34), 195 (10.5), 176 (14), 175 (100), 106 (62), 159 (41), 157 (10), 147 (16), 133 (26), 125 (2), 107 (2), 79 (4), 69 (6), 51 (4), 39 (8), 27 (5).

3,6-Dichloro-1,1,2-trimethyl-2-indene (3d): colorless oil; 110–115 °C (4.5 mbar) [bulb-to-bulb distillation]; ^{1}H NMR ($CDCl_3$) δ 1.16 (6 H, s), 1.89 (3 H, s), 7.19 (1 H, d), 7.20 (1 H, s), 7.24 (1 H, d); ^{13}C NMR ($CDCl_3$) δ 9.75 (2-Me), 23.36 (1-Me), 49.55 (1-C), 119.31 (C-H), 121.55 (CH), 124.23 (CCl), 126.89 (CH), 131.60 (ClC_{aryl}), 135.57 (2-C), 147.25 (3a-C), 152.77 (7a-C); MS (70 eV), *m/e* (relative intensity) 228 (26), 226 (41), 213 (7), 211 (12), 193 (40), 192 (17), 191 (100), 178 (11), 177 (11), 176 (36), 163 (8), 156 (41), 155 (11), 141 (37), 139 (32), 115 (19), 99 (4), 77 (9), 76 (12), 75 (12), 63 (20), 51 (13).

3-Chloro-6-methoxy-1,1,2-trimethyl-2-indene (3e): colorless oil isolated by liquid chromatography on silica (eluent heptane/dichloromethane, 70:30) (R_f 0.44) from the 130 °C (4 mbar) fraction of the bulb-to-bulb distillation; ^{1}H NMR ($CDCl_3$) δ 1.28 (6 H, s), 1.92 (3 H, s), 3.75 (3 H, s), 6.69 (1 H, d), 6.82 (1 H, s), 7.12 (1 H, d); ^{13}C NMR ($CDCl_3$) δ 9.79 (2-Me), 23.94 (1-Me), 49.39 (1-C), 55.48 (MeO), 108.28 (CH), 111.31 (CH), 118.93 (CH), 124.37 (CCl), 133.27 (2-C), 144.50 (3a-C), 152.98 (7a-C), 158.62 (MeOC); MS (70 eV), *m/e* (relative intensity) 224 (26), 222 (75), 209 (11), 207 (34), 188 (23), 187 (100), 172 (65), 157 (11), 141 (9), 128 (30), 115 (10), 93 (3), 77 (6), 63 (8), 51 (8).

3-Chloro-5(6)-*tert*-amyl-1,1,2-trimethyl-2-indene (3f): colorless oil obtained together with **3a** in the 110 °C/(1 mbar) [bulb-to-bulb distillation] fraction and purified by preparative GLC; ^{1}H NMR ($CDCl_3$) δ 0.68 (3 H, t), 1.25 (6 H, s), 1.31 (6 H, s), 1.60 (2 H, q), 1.96 (3 H, s), 7.40 (3 H, s); ^{13}C NMR ($CDCl_3$) δ 9.72 (2-Me), 23.85 (1-Me), 28.33, 28.40, 28.55, 36.80, 49.44 (1-C), 51.97, 117.78 (CH), 118.58 (CH), 124.38 (CH), 126.94 (CCl), 137.56 (2-C), 146.05 (3a-C), 147.29 (5-C or 6-C), 151.07 (7a-C); MS (70 eV), *m/e* (relative intensity) 264 (5), 262 (14.5), 247 (4), 235 (35), 233 (100), 218 (10), 205 (3), 198 (3), 183 (4), 165 (6), 155 (5), 141 (6), 128 (3), 115 (4), 99 (3), 77 (4), 71 (3).

5(6)-Benzoyl-3-chloro-1,1,2-trimethyl-2-indene (3g): white solid (mp 88 °C); obtained together with part of **3f** in the 120–160 °C (0.5–0.3 mbar) fraction during bulb-to-bulb distillation and purified by preparative TLC (eluent heptane/dichloromethane, 50:50); ^{1}H NMR ($CDCl_3$) δ 1.3 (6 H, s), 2.01 (3 H, s), 7.3–7.96 (8 H, complex); ^{13}C NMR ($CDCl_3$) δ 10.25 (2-Me), 23.49 (1-Me), 49.92 (1-C), 117.97 (CH), 122.33 (CH), 124.92 (CCl), 128.23 (CH), 129.34 (CH), 130.44 (CH), 132.06 (CH), 134.9 (5- or 6-C), 138.40 (2-C), 144.51 (3a-C), 151.35 (7a-C), 196.57 (C=O); MS (70 eV), *m/e* (relative intensity) 298 (11), 296 (34), 281 (3), 262 (13), 261 (67), 141 (10), 105 (100), 77 (55), 63 (4), 51 (12).

3-Chloro-6-methoxy-5-(*p*-methoxybenzoyl)-1,1,2-trimethyl-2-indene (3h). White solid (mp 132 °C) isolated by liquid chromatography of the bulb-to-bulb distillation residue yielding **3e** (eluent benzene/methyl *tert*-butyl ether, 70:30) (R_f 0.28); ^{1}H NMR ($CDCl_3$) δ 1.28 (6 H, s), 1.95 (3 H, s), 3.76 (3 H, s), 3.85 (3 H, s), 6.90 (2 H, d), 6.98 (1 H, s), 7.26 (1 H, s), 7.82 (2 H, d); ^{13}C NMR ($CDCl_3$) δ 9.84 (2-Me), 23.89 (1-Me), 49.93 (1-C), 105.79 (CH), 113.56 (CH), 119.05 (CH), 124.19 (CCl), 128, 131, 132.29 (CH), 133.07 (2-C), 145.57 (3a-C), 154.98 (7a-C), 156.54, 163.6, 195.09 (C=O); MS (70 eV), *m/e* (relative intensity) 356 (18), 341 (2), 339 (2), 321 (9), 189 (66), 135 (100), 77 (55); IR 1640 (C=O), 1590 cm^{-1} (C=C).

(b) Indenyl Benzoates 8a and 8b. Methanesulfonic acid (19.5 mL, 0.3 mol) was added rapidly to 271.2 g (1.2 mol) of benzoyl anhydride warmed at 60 °C. The temperature increased to 70 °C, and the mixure became brownish. The mixture was warmed to 115 °C for 30 min and then cooled to 75 °C. 2-Methyl-2-butanol (10.8 mL, 0.1 mol) was added dropwise for 30 min. The mixture became thick, and it was warmed to 100 °C for 18 h. On cooling, the mixture became very thick. It was dissolved into 300 mL of diethyl ether, and 100 mL of water was added. The ethereal layer yielded, after standing one night at 0 °C, a pink precipitate (11.3 g) which gave, after recrystallization in acetone, 9.8 g of 5(6)-benzoyl-3-indenyl benzoate (**8b**) (25% yield from 2-methyl-2-butanol) (mp 190–192 °C). The filtrate was neutralized with 200 mL of aqueous ammonia and extracted with dichloromethane. Liquid chromatography on silica (eluent pentane/dichloromethane, 80:20) yielded 4.8 g of 3-indenyl benzoate **8a** (17% yield from 2-methyl-2-butanol).

1,1,2-Trimethyl-3-indenyl benzoate (8a): pale yellow oil; ^{1}H NMR ($CDCl_3$) δ 1.30 (6 H, s), 1.80 (3 H, s), 7.0–8.3 (9 H, complex figure); ^{13}C NMR ($CDCl_3$) δ 8.30 (2-Me), 23.79 (1-Me), 47.24 (1-C), 117.56, 121.2, 125.11, 126.46, 128.64, 130.23, and 133.56 (CH), 129.31 (CCO_2), 142.29 (2-C), 137.46 (3a-C), 151.16 (7a-C), 163.94 (ester); MS (70 eV), *m/e* (relative intensity) 278 (1), 106 (6), 105 (100), 77 (22), 51 (5); IR 1730 cm^{-1} (C=O).

5(6)-Benzoyl-1,1,2-trimethyl-3-indenyl benzoate (8b): pink crystals; mp 190–192 °C; ^{1}H NMR ($CDCl_3$) δ 1.35 (6 H, s), 1.90 (3 H, s), 7.0–8.20 (15 H, complex figure); ^{13}C NMR ($CDCl_3$) δ 8.74 (2-Me), 23.56 (1-Me), 47.67 (1-C), 117.12, 122.7, 128.2, 128.75, 129.94, 130.25, 132.01, 133.91, and 134.4 (CH) and 128.95 (CCO_2), 138.4, 141.95 (1-C), 142.35 (2-C), 142.09 (3a-C), 151.24 (7a-C), 163.94 (ester), 196.81 (C=O); MS (70 eV), *m/e* (relative intensity) 382 (7), 106 (8), 105 (100), 77 (23), 51 (4); IR 1730 and 1640 cm^{-1} (C=O).

Registry No. 1 (R = H), 98-88-4; 1 (R = Me), 874-60-2; 1 (R = F), 403-43-0; 1 (R = Cl), 122-01-0; 1 (R = MeO), 100-07-2; **2**, 594-36-5; **3a**, 111976-94-4; **3b**, 111976-95-5; **3c**, 111976-96-6; **3d**, 111976-97-7; **3e**, 111976-98-8; **3f**, 111977-01-6; **3g**, 111977-02-7; **3h**, 111976-99-9; **8a**, 111977-00-5; **8b**, 111977-03-8; benzoyl anhydride, 93-97-0; 2-methyl-2-butanol, 75-85-4.

(13) Isomeric 2-chloro-1,1,3-trimethyl indene has been reported recently: Anke, L.; Weyerstahl, P. *Chem. Ber.* **1985**, *118*, 613.
(14) Quoted in: Neth. Appl. 7802, 38, 1979; *Chem. Abstr.* **1979**, *90*, 71951e.

Transition-State Geometry of [3,3]-Sigmatropic Rearrangements of Iminium Ions[1]

Robert J. Doedens, Guy P. Meier,[2] and Larry E. Overman*

Department of Chemistry, University of California, Irvine, California 92717

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The tandem 2-aza-Cope rearrangement–Mannich cyclization reaction (eq 1) has been demonstrated to provide

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(2) (a) NIH Postdoctoral Fellow (GM 08155), 1981–1983. (b) Current address: Department of Medicinal Chemistry, University of Washington, Seattle, WA 98195.

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