intensively as *preassociation catalysis*.[7]

It is conceivable that the diffusional approach of BH to the tetrahedral adduct is the rate-limiting step. Since this is the fastest catalytic action possible for BH, it enables us to set a minimum lifetime for the tetrahedral intermediate, by use of the Jencks clock.[8] For the various phenols in Table II, k_{BH} averages around 2400 M^{-2} s^{-1}. We recall that $k_{BH} = k_a k'_{BH}/k_{-a}$ and that $k_a \sim 300$ M^{-1} s^{-1}: thus $(k'_{BH}/k_{-a}) \sim 8$ M^{-1}. Then if k'_{BH} had its maximum value of, say, 10^{9-10} M^{-1} s^{-1}, k_{-a} would have its maximum value of around 10^{8-9} s^{-1}. Of course k'_{BH} may by smaller (if events after diffusion together of BH and adduct limit the rate); then k_{-a} will be proportionally smaller. Therefore the tetrahedral adduct must have a characteristic lifetime of at least 1-10 ns.

Experimental Section

Materials. The substrate *m*-$NO_2C_6H_4N(CH_3)COCF_3$ was available from previous work.[3,5] *p*-Bromophenol and *p*-chlorophenol, both from Eastman Kodak, were recrystallized from petroleum ether (30-60 °C), *o*-chlorophenol and *p*-cresol were distilled at reduced pressure, and methyl *p*-hydroxybenzoate (Matheson, Coleman and Bell) was used as supplied. Methanol was purified by the method of Lund and Bjerrum[9] but gave identical results when used as supplied (Mallinckrodt reagent grade). Sodium methoxide solutions were prepared by dissolution of cleaned metallic sodium, stored in polyethylene, and standardized against potassium hydrogen phthalate with phenolphthalein. Buffers were prepared by dilution of weighed samples of phenol with appropriate volumes of methanol and sodium methoxide solutions.

Kinetics. Buffer solutions (2.5 mL) were thermostated in a 10-mm cuvet in the constant-temperature cell holder of a Cary 16 or Beckman DB spectrophotometer, at 25.0 ± 0.1 °C. To initiate reaction, 10 μL of a stock solution of substrate were injected with an Eppendorf pipet. Absorbances at 390 nm were collected to 80% reaction, the final absorbance was read after 10 half-life times, and first-order rate constants were calculated by a nonlinear least-squares method.

Appendix

Derivation of eq 2. See Scheme II for definitions of k_0 and i; then

$$k_0 - i = \frac{k_a M(k_e + k_{BH}RB)}{k_a + k_e + k_{BH}RB} - \frac{k_a k_e M}{k_a + k_e}$$

$$k_0 - i = \frac{k_a^2 k_{BH} MRB}{(k_a + k_e + k_{BH}RB)(k_a + k_e)}$$

$$k_0 - i = \left(\frac{k_a M}{k_a + k_e}\right)\left(\frac{k_a k_{BH}RB}{k_a + k_e + k_{BH}RB}\right)$$

$$\frac{1}{k_0 - i} = \left(\frac{k_a + k_e}{k_a M}\right)\left(\frac{k_a + k_e + k_{BH}RB}{k_a k_{BH}RB}\right)$$

$$\frac{1}{k_0 - i} = \left\{\frac{k_a + k_e}{k_a M}\right\}\left\{\left(\frac{k_a + k_e}{k_a k_{BH}R}\right)\left(\frac{1}{B}\right) + \frac{1}{k_a}\right\} \quad (2)$$

Registry No. *m*-$NO_2C_6H_4N(Me)COCF_3$, 32368-22-2.

(7) Jencks, W. P.; Salvesen, K. *J. Am. Chem. Soc.* **1971**, *93*, 1419. Jencks, W. P. *Acc. Chem. Res.* **1976**, *9*, 425.
(8) Jencks, W. P. *Acc. Chem. Res.* **1980**, *13*, 161.
(9) Lund, H.; Bjerrum, I. *Ber.* **1931**, *64*, 210.

Aluminum Chloride Catalyzed Reaction of Acetanilide with Pivalyl Chloride

Przemyslaw Maslak, Phillip E. Fanwick, and Robert D. Guthrie*

Department of Chemistry, University of Kentucky, Lexington, Kentucky 40506-0055

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Product development was studied in the aluminum chloride catalyzed reaction of acetanilide with pivalyl chloride. 3-*tert*-Butylacetanilide is the major product because of its relative resistance to dealkylation by reaction-produced HCl. At long reaction times all alkylation products are converted back to acetanilide with the only survivor being 2,2-dimethyl-5-*tert*-butyl-7-acetamidoindanone. The crystal structure of this compound was determined. It crystallized in the space group P_{nma} with cell constants a = 12.571 (3) Å, b = 7.302 (1) Å, c = 16.910 (3) Å, V = 1552.24 Å^3, z = 4. Refinement of the 1224 data with $F^2 \geq 3\sigma(F^2)$ resulted in discrepancy indices R_1 = 0.056 and R_2 = 0.074. A novel mechanism for formation of this indanone is proposed, involving nucleophilic attack by alkene on a protonated arene ring.

In the course of our research we found it necessary to prepare ring-substituted pivalophenones. The literature indicates that Friedel-Crafts acylation with pivalyl chloride (PC) is successful when promoted by electron-donating substituents but gives *tert*-butyl substitution with unactivated aromatic compounds. Benzene, for example, gives 4-*tert*-butylpivalophenone and *tert*-butylbenzene but no unsubstituted pivalophenone.[1] Anisole gives 4-methoxypivalophenone, but acetanilide is reported to react with PC in chloroform to give 4-*tert*-butylacetanilide (4-BA) in 55% yield along with recovered acetanilide and no ketonic products.[2] Hoping to redirect this latter reaction by changing the conditions, we studied the reaction of acetanilide with PC and $AlCl_3$ in both CH_2Cl_2 and CS_2. No pivalylation product was formed and, the ortho-para-directing reputation of the acetamido group not withstanding, the major product turned out to be 3-*tert*-butylacetanilide (3-BA). We also isolated a ketone, but this was not 4-pivalylacetanilide. We became sufficiently interested to follow product development and to identify the ketonic compound.

(1) Pearson, D. E. *J. Am. Chem. Soc.* **1950**, *72*, 4169.
(2) Rothstein, E.; Saville, R. W. *J. Chem. Soc.* **1949**, 1950.

Results

The product distribution for the $AlCl_3$-promoted reaction of PC with acetanilide was followed as a function of added PC and time. The results are displayed in Table I. It may be seen that although the acetanilide recovery

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Table I. Products of the Reaction of Pivalyl Chloride (PC) with Acetanilide

rctn time, min	products, % yield[a] acetanilide	3-BA	4-BA	DBA	1	comments
			In CS_2			
20	18	40	20	20		1 equiv of PC added
40	8	38	18	33		2 equiv of PC added
60	9	31	20	35	1	3.2 equiv of PC added
95	13	30	19	20	5	stirred at 25 °C
120	55	25	3	1	7	refluxing
140	59	17	3	1	13	refluxing
			In CH_2Cl_2			
40	45	30	13	2		1 equiv of PC added
70	38	35	16	3	2	2 equiv of PC added
115	28	35	20	6	6	3.2 equiv of PC added
220	70	7	3	1	8	stirred at ca. 25 °C
1295	66		1	2	14	at ca. 25 °C

[a] ±5% of measured value.

Table II. Induced Chemical Shift of 4

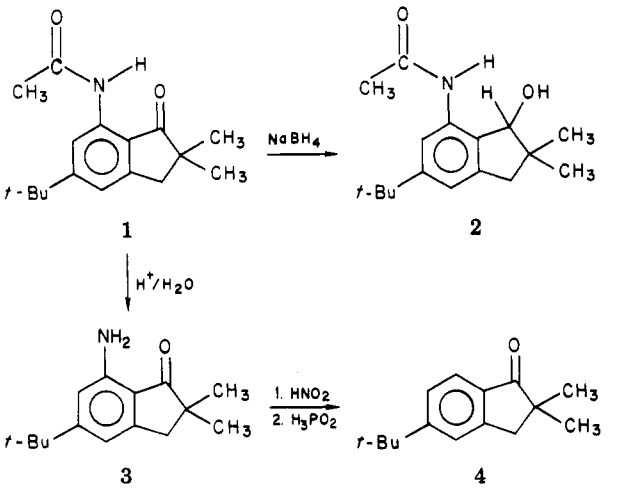
$Eu(thd)_3$, mg	$Eu(thd)_3/4$	H_7[b] δ	H_7[b] Δδ[a]	H_4[c] δ	H_4[c] Δδ[a]	H_6[d] δ	H_6[d] Δδ[a]
0.0		7.66		7.40		7.40	
3.2	0.17	7.88	+0.22	7.49	+0.09	7.29	−0.11
5.1	0.27	8.16	+0.50	7.61	+0.21	7.22	−0.18
14.1	0.76	8.93	+1.27	7.99	+0.59	7.04	−0.36

[a] Δδ = difference between chemical shift and induced chemical shift (in ppm). Plus sign indicates downfield shift. [b] Doublet, J = 9 Hz. [c] Singlet. [d] Doublet, J = 9 Hz.

is reduced by adding a greater excess of PC, acetanilide is regenerated with the passage of time, showing that some, and possibly all, of the products are generated reversibly. The data also suggest the likelihood that 4-BA is a kinetic product that is readily dealkylated under the reaction conditions and supplanted by the more persistent 3-BA and 3,5-di-*tert*-butylacetanilide (DBA). Interestingly, even the direct alkylation of acetanilide with *tert*-butyl chloride gives 3-BA as the major product. Bubbling CO gas through this latter reaction mixture (sweeping out HCl) results in 4-BA becoming the major product, whereas bubbling with a CO–HCl mixture does not have this effect.

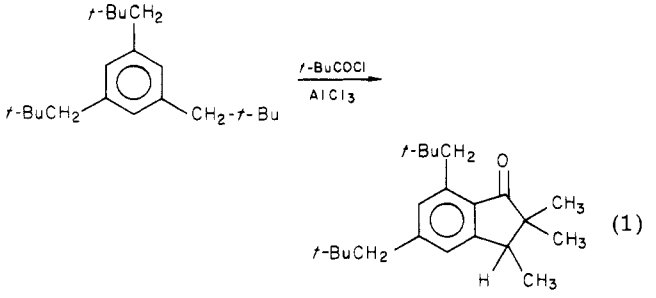
When the initial products start to disappear, the ketonic product appears. It is clear from elemental analysis and spectral data that this compound is a dimethyl-*tert*-butylacetamidoindanone (1). The ^1H NMR spectrum of this compound shows seven singlets with the amido hydrogen appearing at unusually high chemical shift (10.3 ppm). The spectrum also displays one unusually deshielded aromatic hydrogen (8.5 ppm). Borohydride reduction of 1 gives an alcohol 2 (Scheme I). The singlet observed for the hydrogen introduced in this reduction indicates clearly that 1 is a 2,2-dimethylindanone. The two methyl groups and the two benzylic hydrogens show the expected nonequivalence in 2. Hydrolysis of 1 produced an aminoindanone, 3, in which the downfield aromatic hydrogen present in 1 and 2 returns to normal range. Hydrodeamination of 3 gave 4. With the help of some literature precedent,[3] an induced chemical shift study on 4 showed the presence of hydrogen in positions 6 and 7 (see Table II). The identity of 4 was thus established as 2,2-dimethyl-5-*tert*-butylindanone. The position of the acetamido group in 1 is indicated by the downfield location of its N–H resonance, suggesting a hydrogen-bonding interaction with the indanone carbonyl. We concluded that 1 was 2,2-dimethyl-5-*tert*-butyl-7-acetamidoindanone. Residual uncertainty regarding the structure of 1 was removed by X-ray crystallographic analysis.

Scheme I



Discussion

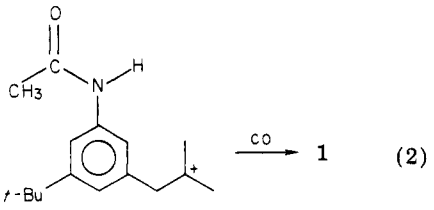
Indanone formation is not without some precedent when aromatic compounds react with CO under Friedel–Crafts conditions. The mechanisms that have been suggested for these reaction do not fit very well with the observations of the present study, however. For example, PC and 1,3,5-trineopentylbenzene react as shown in eq 1.[4] The



(1)

(3) Hofer, O. *Monatsh. Chem.* **1979**, *110*, 745.

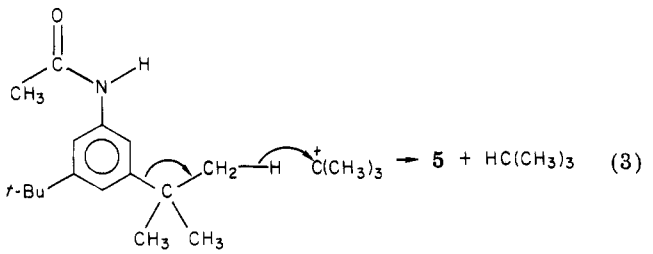
simple mechanism involving benzylic hydrogen abstraction followed by methyl migration and reaction of the resultant tertiary cation with CO was rejected by the authors on the basis of their observation that 1,3,5-trineopentylbenzene did not rearrange on treatment with $AlCl_3$ in the absence of PC.[5] It will be noted that the mechanism actually proposed to explain this case would predict a 3,3-dimethylindanone derivative as the product of our reaction and this is not observed. Moreover, a sequence leading to the observed products from a cation such as **5** (eq 2) is both logical and precedented.[6]



(2)

5

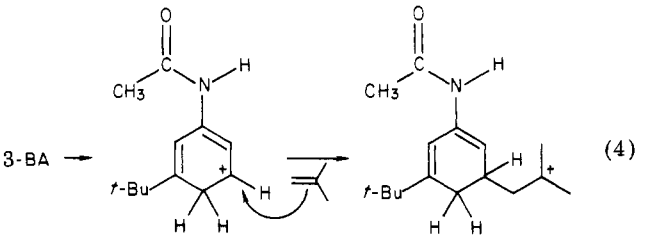
Such a sequence seems by far the most reasonable explanation for formation of **1** provided that a route can be suggested to generate **5** from components of the reaction mixture. Two possible routes occur to us. The first is hydride removal from a methyl group in DBA. Phenyl migration would be concerted with this process and would lead to the required cation as shown in eq 3. Hydride



(3)

removal from a *tert*-butylarene has been suggested by Barclay and co-workers[6] as a critical step in the $AlCl_3$-promoted formation of 1,1,4,4,5,5,8,8-octamethyloctahydroanthracene from benzene and *tert*-butyl chloride. This would actually seem a more attractive interpretation of our reaction than that studied by Barclay because the product structure in his case demands that nucleophilic attack by 2-methylpropene occurs at the CH_2 group. Barclay argues for a phenonium ion intermediate that is attacked at the least hindered site. It is well-established,[7] however, that incipient neophyl cations give only rearranged products even with more reactive nucleophiles than those present under Friedel–Crafts conditions.

A mechanism that appears not to have been previously considered includes nucleophilic attack on a ring-protonated species. The critical step in our case is shown in eq 4. A variety of sequences for conversion of **6** to **1** are possible. The process of eq 4 is very likely an endergonic one, but this is not objectionable when stable



(4)

6

products are eventually formed.

Proving involvement of the step shown in eq 4 will not be easy. The standard isotopic labeling approaches to such problems would undoubtedly fail because of the ready reversibility of all of the reactions preceding indanone formation.[8]

Experimental Section

Aluminum Chloride Catalyzed Reaction between Pivalyl Chloride (PC) and Acetanilide. Pivalyl chloride (34.2 g, 0.284 mol) in 60 mL of CS_2 was added portionwise to a vigorously stirred mixture of acetanilide (10.9 g, 0.080 mol) and $AlCl_3$ (40 g, 0.30 mol) in 140 mL of CS_2. After addition was completed the reaction mixture was stirred for 20 min at ca. 25 °C and then refluxed for 45 min. After cooling the mixture was poured on ice (ca. 500 g) with stirring. The organic layer was separated and washed with water. The water layer was extracted with $CHCl_3$ (200 mL) and the extract combined with the organic layer. The solution was dried over Na_2SO_4 and the solvent was removed under reduced pressure, giving 37.5 g of a brown oil. A part of the mixture (15.2 g) was chromatographed on an alumina column, using hexane/$CHCl_3$ as an eluant. The following fractions were collected: A (hexane), 3.36 g of yellow oil, mixture of at least five products as indicated by GC, none containing aromatic protons, as indicated by NMR; B (hexane), 2.67 g, oily solid, mixture of aliphatic components similar to fraction A but also containing some aromatic compounds; C (hexane/$CHCl_3$ 10%), 1.56 g, solid mp 152–160 °C; D (hexane/$CHCl_3$ 20%), 2.45 g, solid mp 90–95 °C; E (hexane/$CHCl_3$ 30%), 0.59 g, solid mp 98–106 °C; F (hexane/$CHCl_3$ 60%), 3.22 g, white solid mp 113–116 °C, identified as acetanilide.

Fraction A was analyzed by GC. At least five components were detected. NMR analysis indicated no aromatic protons. It is believed that this is a mixture of decomposition products of PC. No attempt was made to separate and identify the components.

Fraction B was recrystallized from hexane, giving 0.5 g of white crystals, mp 162–164 °C. Fraction C after recrystallization from hexane yielded 0.4 g of identical white solid: mp 163–164 °C; ^1H NMR (90 MHz, $CDCl_3$) δ 10.31 (br s, 1 H, slowly exchangeable with D_2O), 8.49 (s, 1 H), 7.02 (s, 1 H), 2.92 (s, 2 H), 2.23 (s, 3 H), 1.31 (s, 9 H), 1.21 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 212 (s), 169 (s), 161 (s), 152 (s), 139 (s), 119 (s), 117 (d, J_{C-H} = 157 Hz), 114 (d, J_{C-H} = 164 Hz), 46 (s), 42 (t, J_{C-H} = 125 Hz), 36 (s), 31 (q, J_{C-H} = 120 Hz), 25 (q, J_{C-H} = 120 Hz); IR ($CDCl_3$) 3300, 2880, 1681, 1622, 1601, 1543, 1427, 1271, 920 cm^{-1}; MS, *m/e* 273, 258, *231*, 216, 189, 145, 57, 44.

Anal. Calcd for $C_{17}H_{23}NO_2$: C, 74.69; H, 8.48; N, 5.12. Found C, 74.66; H, 8.54; N, 4.54.

With help of a chemical degradation (see below) this compound was identified as 2,2-dimethyl-5-*tert*-butyl-7-acetamidoindanone (**1**). The identification of **1** was confirmed by single-crystal X-ray structure determination. The mother liquor from recrystallization of fraction B was composed mostly of products of decomposition of PC as indicated by NMR and was not further investigated. The mother liquor from recrystallization of fraction C contained still more **1** but mostly 3-*tert*-butylacetanilide (3-BA). 3-BA was

(4) Dahlberg, E.; Martinson, P.; Olsson, K. *Acta Chem. Scand., Ser. B* **1974**, *28*, 1136, 1143.

(5) It should be recognized that such control experiments never exactly duplicate the reaction conditions. In this particular case the decomposition of pivalyl chloride produces HCl at much higher concentration than would be present in its absence. In our own example a mixture of CO and HCl produced only a trace of indanone.

(6) Barclay, L. R. C.; Hilchie, J. W.; Gray, A. H.; Hall, N. D. *Can. J. Chem.* **1960**, *38*, 94.

(7) Lancelot, C. J.; Cram, D. J.; Schleyer, P. v. R. In "Carbonium Ions"; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley-Interscience: New York, 1972; Vol. III, pp 1387–1394.

(8) The advantage of this new model is that hydrogen removal from a nonactivated position in the manner of eq 3 is avoided. Once the protonated aromatic has been attached to an alkene, the ring could be protonated again and serve as a nucleofuge. Such a process could explain the rearranged alicyclic system in Barclay's octamethyloctahydroanthracene.

isolated from this mixture by GC and identified by comparison of its physical and spectral properties with those of an authentic sample.

Fraction D was recrystallized from hexane/benzene (10:1, v/v), giving 1.33 g of white crystals, mp 98–99 °C, identified as 3-BA (lit.[9] mp 99 °C): ^{1}H NMR (90 MHz, $CDCl_3$) δ 7.25 (m, 5 H), 2.21 (s, 3 H), 1.27 (s, 9 H); MS, *m/e* 191, 176, *150*, 134, 106, 94, 91, 77, 65, 57, 43. The mother liquor from recrystallization of fraction D contained more 3-BA and also small amounts of two additional products. These products were collected from GC and analysed by NMR and MS. The first one (mp 170–171.5 °C) was identified as 4-*tert*-butylacetanilide (4-BA) by comparison with an authentic sample (for preparation of 4-BA, see below): ^{1}H NMR (90 MHz, $CDCl_3$) δ 7.82 (br s, 1 H, slowly exchangeable with D_2O), 7.34 (d, 2 H, J = 8.5 Hz), 7.23 (d, 2 H, J = 8.5 Hz), 2.11 (s, 3 H), 1.24 (s, 9 H); MS, *m/e* 191, 176, *134*, 70, 57, 55. The second product (mp 144–146 °C) was identified as 3,5-di-*tert*-butylacetanilide (DBA) (lit.[10] mp 145–146 °C) by its spectral properties and comparison with an authentic sample (undepressed mixture melting point): ^{1}H NMR (90 MHz, $CDCl_3$) δ 7.49 (br s, 1 H, slowly exchangeable with D_2O, partially overlapping with broad singlet at 7.38), 7.38 (br s, 2 H), 7.18 (m, 1 H), 2.17 (s, 3 H), 1.28 (s, 9 H); MS, *m/e* 247, *232*, 205, 190, 176, 147, 134, 83, 57.

Fraction E was composed of 3-BA (minor component) and acetanilide (major component) as indicated by GC analysis. Fraction F was identified as pure acetanilide.

The second part of the reaction mixture (12.3 g) was tested by NMR. The presence of characteristic peaks at 10.31 and 8.49 ppm confirmed the presence of 1 in the crude mixture. To this mixture a standard was added (2,4-dinitrochlorobenzene). GC analysis allowed calculation of the following yields (recalculated for total mixture; isolated yield in parentheses): acetanilide 58% (53%), 3-BA 19% (16%), 4-BA 3%, DTBA 1%, 1 (12% (7%). Substitution of CH_2Cl_2 for CS_2 as a solvent in the above procedure did not produce any significant change in the observed products or their yields.

Acidic Hydrolysis of 1. Compound 1 (0.40 g, 1.5 mmol) was added to a mixture of 20 mL of methanol and 20 mL of 1 N aqueous HCl. The mixture was refluxed for 5 h. After cooling to room temperature, the solution was made alkaline with 10 mL of ca. 10% aqueous NaOH and extracted with CH_2Cl_2 (100 mL). The extract was dried over Na_2SO_4 and the solvent was evaporated, leaving 0.38 g of yellow oil. Recrystallization from hexane gave white crystals, mp 83–85 °C (0.34 g, 97%), tentatively identified as 2,2-dimethyl-5-*tert*-butyl-7-aminoindanone (**3**): ^{1}H NMR (90 MHz, $CDCl_3$) δ 6.63 (m, 1 H), 6.47 (m, 1 H), 5.50 (br s, exchangeable with D_2O, 2 H), 2.82 (s, 2 H), 1.31 (s, 9 H), 1.21 (s, 6 H); IR (KBr) 3460, 3340, 2980, 2880, 1662, 1608, 1432, 1269, 1215, 982, 868, 70 cm^{-1}; MS, *m/e* *231*, 216, 189, 160, 146, 130, 115, 77, 57.

Reduction of 1 with Sodium Borohydride. To a solution of 1 (0.40 g, 1.5 mmol) in 30 mL of methanol was added $NaBH_4$ (0.7 g, 18 mmol). The resulting mixture was not homogeneous initially, but everything dissolved after ca. 0.5 h. The mixture was stirred for 1 h at room temperature and then poured into 200 mL of water and extracted with CH_2Cl_2 (100 mL). The extract was dried over Na_2SO_4 and the solvent was evaporated, leaving 0.40 g (100% yield) of slightly pink solid, mp 216–219 °C. This solid was recrystallized from $CHCl_3$/hexane, giving white crystals, mp 218–219 °C. This compound was tentatively identified as 2,2-dimethyl-5-*tert*-butyl-7-acetamidoindanol (**2**): ^{1}H NMR (90 MHz, $CDCl_3$) δ 8.42 (br s, 1 H), 8.00 (s, 1 H), 6.95 (s, 1 H), 4.81 (d, 1 H, J = 6.5 Hz), 2.81 (d, 1 H, J = 7.5 Hz), 2.69 (d, 1 H, J = 7.5 Hz), 2.60 (d, 1 H, J = 6.5 Hz, partially overlapping with signal at 2.69), 2.20 (s, 3 H), 1.31 (s, 9 H), 1.22 (s, 3 H), 1.15 (s, 3 H); ^{1}H NMR (90 MHz, $CDCl_3$ + D_2O) δ 4.80 (s, 1 H), 4.60 (s, H_2O), and no peak at 2.60; IR (KBr) 3240 (br), 3020, 2948, 2882, 1642, 1548, 1480, 1368, 1322, 1291, 1042, 999 cm^{-1}; MS, *m/e* 275, 257, 242, 231, 216, *201*, 175, 70, 57, 43.

Hydrodeamination of 3. Compound **3** (0.37 g, 1.6 mmol) was treated with 4 mL of concentrated HCl in 20 mL of water and heated (ca. 80 °C) for 15 min until the mixture was homogeneous. The solution was cooled to 0 °C and treated with 0.2 g (2.9 mmol) of sodium nitrite in 4 mL of water with stirring. The resultant solution was stirred for 10 min at 0 °C and then treated with 4.4 mL of 50% H_3PO_2 precooled to 0 °C. The reaction mixture was stirred for 2 h at 0 °C and then kept at ca. 5 °C for 17 h. The resultant mixture was extracted with CH_2Cl_2 (100 mL). The extract was dried over Na_2SO_4 and the solvent was evaporated, leaving 0.25 mg of a brown-red oil. The oil was purified by alumina chromatography, using pentane/$CHCl_3$ (10:1 v/v) as eluant. The second 100-mL fraction produced 0.13 g (38% yield) of a slightly yellow oil, which was identified as 2,2-dimethyl-5-*tert*-butylindanone (**4**). Spectral data were obtained for a sample purified by GC separation: ^{1}H NMR (90 MHz, $CDCl_3$) δ 7.66 (d, 1 H, J = 9 Hz), 7.40 (m, 2 H), 2.93 (s, 2 H), 1.31 (s, 9 H), 1.19 (s, 6 H); IR (neat) 2944, 2848, 1702, 1601, 1320, 1215, 1078, 990, 702 cm^{-1}; MS, *m/e* 216, 201, 186, 173, 159, 145, 141, 131, 129, 128, 115, 91, 77, 57, 41. The structure of **4** was confirmed by the following NMR shift reagent technique. To **4** (ca. 5.7 mg, 0.026 mmol) in $CDCl_3$ (ca. 0.5 mL) were added increasing amounts of tris(2,2,6,6-tetramethyl-3,5-heptanedionato)europium [Eu(thd)$_3$], and the chemical shifts of aromatic protons were recorded. The results are presented in Table II.

Aluminum Chloride Catalyzed Reaction of Acetanilide and *tert*-Butyl Chloride in the Presence of Carbon Monoxide. To a mixture of $AlCl_3$ (6.7 g, 0.05 mol) and acetanilide (5.4 g, 0.040 mol) in 50 mL of CS_2 was added dropwise *tert*-butyl chloride (4.1 g, 0.044 mol) in 20 mL of CS_2 over 1.5 h with stirring. At the same time a stream of CO was slowly passed through the reaction mixture. A sample was withdrawn after ca. 2 h, worked up, and tested by GC. The following products were detected (relative amounts): acetanilide (1.0), 3-BA (1.2), 4-BA 4.6), DBA (1.6). No 1 was detected. The reaction mixture was then refluxed for 50 min during which time CO was bubbled through the mixture. GC analysis did not indicate any changes in relative amounts of the products. No 1 was detected. The reaction mixture was poured into ice (500 mL) and extracted with CH_2Cl_2 (100 mL). The extract after drying and solvent evaporation gave 8.77 g of white solid. The recrystallization of the product from benzene/hexane (1:5, v/v) gave 2.3 g (30% yield) of 4-*tert*-butylacetanilide (4-BA), which after additional recrystallization from methanol had mp 170–172 °C (lit.[2] mp 171–172 °C). The rest of the mixture was separated on an alumina colum, using hexane–$CHCl_3$ (1:1, v/v) as an eluant. The first fraction gave 0.9 g (9% yield) of a white solid, mp 145–146 °C, which was identified as DBA (lit.[10] mp 145–146 °C) by spectral properties and acidic hydrolysis to 3,5-di-*tert*-butylaniline, crystals from methanol mp 53–55 °C (lit.[10] mp 50.5–53 °C): ^{1}H NMR (90 MHz, $CDCl_3$) δ 6.88 (t, 1 H, J = 1.5 Hz), 6.52 (d, 2 H, J = 1.5 Hz), 3.53 (br s, 2 H, exchangeable with D_2O), 1.47 (s, 18 H).

This reaction was repeated with use of the same conditions with exception of the mode of CO introduction. The mixture of acetanilide and $AlCl_3$ in CS_2 was presaturated with CO and then *tert*-butyl chloride was added dropwise under a CO atmosphere. The sample withdrawn after addition of all of the *tert*-butyl chloride as well as the sample taken after 50 min of refluxing of the mixture was analyzed by GC and indicated the presence (relative amounts) of acetanilide (1.0), 3-BA (2.3), 4-BA (1.1), and DBA (0.6), but no **1** was detected.

Finally, the reaction was carried out by adding a dilute solution of *tert*-butyl chloride (15 g, 0.16 mol) in 70 mL of CH_2Cl_2 to a solution of acetanilide (5.44 g, 0.040 mol), and $AlCl_3$ (20 g, 0.15 mol) in 70 mL of CH_2Cl_2 was added dropwise over 20 h at room temperature with stirring. A very slow stream of CO was bubbled through the mixture. The reaction mixture was worked up in the usual way, and the components were separated on an alumina column. No pure **1** could be obtained; however, GC showed its presence in one of the fractions (<1%). The compound was collected from GC and its identity confirmed by MS analysis.

Aluminum Chloride Catalyzed Reaction of Acetanilide and *tert*-Butyl Chloride in the Presence of Carbon Monoxide and Hydrogen Chloride. The reaction was carried out in exactly the same way as described in the first part of the preceding section, the only exception being introduction of gaseous HCl together with CO. A sample taken from the reaction mixture before heating indicated the presence of acetanilide (1.0), 3-BA (3.2), 4-BA (0.9), and DBA (0.2) but no **1**. After refluxing for 50 min, acetanilide

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(1.0) became the major product. Small amounts of 3-BA (0.3), 4-BA (0.1), and other unidentified products were detected. No 1 could be detected.

Reaction of Acetanilide with *tert*-Butyl Chloride. To acetanilide (5.4 g, 0.040 mol) and $AlCl_3$ (6.7 g, 0.050 mol) in 80 mL of CS_2 was added portionwise *tert*-butyl chloride (4.1 g, 0.044 mol) in 20 mL of CS_2 during a 1-h period. The mixture was stirred and refluxed for 45 min. The reaction was quenched by pouring into ice (500 g) and then the mixture was extracted with CH_2Cl_2 (100 mL). The extract after drying and solvent evaporation gave 6.6 g of a white solid. GC analysis indicated the presence of the following components (relative amounts): acetanilide (1.0), 3-BA (1.6), 4-BA (0.8), and DBA (0.5). The crude reaction mixture was dissolved in ca. 10 mL of hot benzene. To this solution was added cold hexane. The precipitated solid was filtered off, giving 1.4 g (18% yield) of white plates, mp 97–99 °C. This material was identified as 3-BA (lit.[9] mp 99 °C). The solvent from the filtrate and the residue evaporated was dissolved in hot hexane (20 mL). Cooling produced a white precipitate, which after filtration and recrystallization from ethanol gave 4-BA (1.1 g, 14% yield), mp 171–172 °C (lit.[2] mp 171–172 °C).

X-ray Crystallographic Structure Determination for 2,2-Dimethyl-5-*tert*-butyl-7-acetamidoindanone. The compound crystallized in space group P_{nma}. The cell constants were a = 12.571 (3) Å, b = 7.302 (12) Å, c = 16.910 (3) Å, V = 1552.29 Å^3, and Z = 4. The density was 1.17 g cm^{-3} (calcd) and 1.16 g cm^{-3} (measd). The radiation was Mo Kα with a scan technique of ω–2θ with scan width = 0.8 + 0.035 tan θ deg and max 2θ = 50°. With a cutoff for observed reflections of $3\sigma(F^2)$, there were 1476 measured reflections and 1224 observed reflections. The structure was phased by using MULTAN77 and refined well. The final residuals were R_1 = 0.056, R_2 = 0.074. Positional parameters and the ORTEP drawing are available as supplementary data.

Registry No. 1, 88057-11-8; 2, 88057-12-9; 3, 88057-13-0; 4, 88057-14-1; 3-BA, 38382-35-3; 4-BA, 20330-45-4; DBA, 37055-54-2; pivalyl chloride, 3282-30-2; acetanilide, 103-84-4; *tert*-butyl chloride, 507-20-0.

Supplementary Material Available: Tables listing the positional parameters for and the ORTEP drawing of 2,2-dimethyl-5-*tert*-butyl-7-acetamidoindanone (8 pages). Ordering information is given on any current masthead page.

Acid-Catalyzed Rearrangement of [*m*.*n*.2]Propellanones

Kiyomi Kakiuchi,* Kazuo Itoga, Toshinori Tsugaru, Yukinori Hato, Yoshito Tobe, and Yoshinobu Odaira

Department of Applied Fine Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565, Japan

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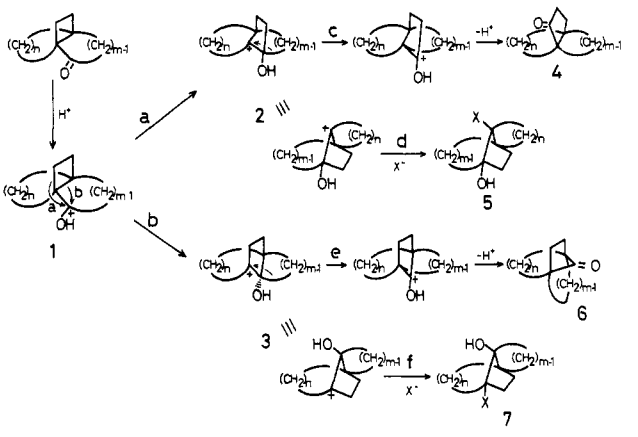
The acid-catalyzed rearrangement of [*m*.*n*.2]propellanones (m = 3–5, n = 3, 4) was studied to ascertain the effect of ring size on the mode of rearrangement. Propellanones **9** and **10**, containing a five-membered cycloalkanone ring, did not rearrange. Propellanones containing a six- or seven-membered cycloalkanone ring (**11**–**14**) rearranged smoothly to cyclopentanones **17a**, **18**, and **19** in a nonnucleophilic medium. In the presence of a nucleophile, the course of the rearrangement depended on whether the third cycloalkane ring contained three, four, or five carbon atoms. Thus propellanones **11** and **14** rearranged to (1*S**,5*R**,6*S**)-tricyclo[4.3.2.0^{1,5}]undecane derivatives **20a,b** and (1*S**,6*R**,7*S**)-tricyclo[5.3.2.0^{1,6}]dodecane derivatives **22a** and **23** by an unusual 1,2 alkyl shift of the central propellane bond followed by nucleophilic attack. The structures of **20a,b**, **22a**, and **23** were established by chemical transformations (Scheme II). The stereochemistry of methyl substituents on the cyclobutane ring of dimethyl[5.3.2]propellanones **15** and **16** influenced the course of rearrangement in the presence of a nucleophile.

As part of a study of the rearrangement of [*m*.*n*.2]propellanes ($m \geq 3$, $n \geq 2$)[1] triggered by strain release of one or two cyclobutane rings, we recently reported a novel acid-catalyzed rearrangement of [4̄.3.2]propellanone (**11**)[1f,2] and [5̄.3.2]propellanone (**14**)[3] to tricyclo[4.3.2.0^{1,5}]undecanes **20a,b** and tricyclo[5.3.2.0^{1,6}]dodecanes **22a** and **23**, respectively.[4]

In general, two modes of migration are available for this rearrangement as shown in Scheme I. One involves a 1,2 alkyl shift of the external cyclobutane bond to afford cation **2** (path a), which undergoes a further 1,2 alkyl shift to give [(m – 1).n.3̄]propellanone **4** (path c)[5] or is trapped by a nucleophile (X^-) to furnish the tricyclic alcohol **5** (path d).[1a] The other mode involves the 1,2 alkyl shift of the central propellane bond (path b) to give either [(m – 1).n.2.1]-

Scheme I



(1) For [*m*.3.2]propellanes ($m \geq 3$): (a) Tobe, Y.; Hayauchi, Y.; Odaira, Y. *J. Org. Chem.* **1981**, *46*, 5219 and reference 3 cited therein. For [*m*.2.2]propellanes ($m \geq 3$): (b) Sakai, Y.; Terashima, K.; Tobe, Y.; Odaira, Y. *Bull. Soc. Chem. Jpn.* **1981**, *54*, 2229 and ref 4 cited therein. (c) Tobe, Y.; Yonezawa, T.; Kakiuchi, K.; Odaira, Y. *Ibid.* **1982**, *55*, 3262. (d) Tobe, Y.; Kishimura, T.; Kakiuchi, K.; Odaira, Y. *J. Org. Chem.* **1983**, *48*, 551. (e) Tobe, Y.; Kakiuchi, K.; Odaira, Y.; Hosaki, T.; Kai, Y.; Kasai, N. *J. Am. Chem. Soc.* **1983**, *105*, 1376. For [*m*.*n*.2]propellalactones ($m \geq 4$, $n \geq 3$): (f) Kakiuchi, K.; Tsugaru, T.; Tobe, Y.; Odaira, Y. *J. Org. Chem.* **1981**, *46*, 4204 and ref 2 cited therein.

(2) Tricyclo[4.3.2.0^{1,6}]undecan-2-one. In the propellane nomenclature the bridge number of the carbonyl-bearing ring is indicated by a bar; in all compounds in this paper the carbonyl group is adjacent to the 0 bridge.

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