87901-84-6; **6a**, 67411-86-3; **6b**, 87901-87-9; **6c**, 77028-91-2; **7a**, 87901-88-0; **7b**, 87901-89-1; **7c**, 87901-90-4; **8a**, 3697-24-3; **8b**, 77028-88-7; **8c**, 77028-91-2; **9**, 77029-19-7; **10**, 87901-91-5; **11**, 74206-63-6; **12**, 81851-67-4; 10-methoxy-5-carbomethoxychrysene, 87901-85-7.

Acyl Fluoride Friedel-Crafts Reactions. Regioselective Synthesis of 3-Acylacenaphthenes and 2-Acyl-6-alkylnaphthalenes

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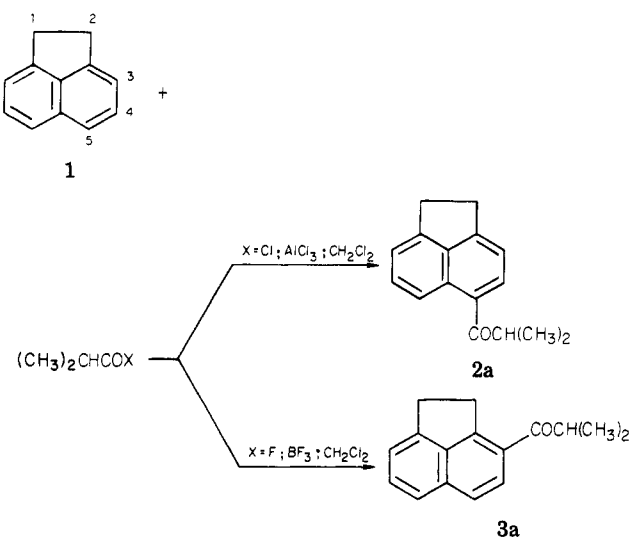
Received June 28, 1983

Several researchers have studied the acylation of simple benzenoid aromatics by acyl fluorides in the presence of catalysts.[1] Although these workers established some points of kinetic and mechanistic distinction for these reagents, it is generally assumed that acyl fluorides do not offer any preparative advantage over acyl chlorides.[2] We show that the acyl fluoride–BF_3 system exhibits exceptional regioselectivity in the acylation of certain polycyclic aromatic substrates.

Reactions of acenaphthene (**1**) with electrophiles usually give 5-substituted acenaphthenes; minor components include the 3-isomers, which are difficult to isolate.[3] Accordingly, we found that **1** reacted with isobutyryl chloride–$AlCl_3$ in CH_2Cl_2 to give an 80:20 mixture of 5-isobutyrylacenaphthene (**2a**) and 3-isobutyrylacenaphthene (**3a**) (Scheme I). It was surprising to observe that **1** reacted with isobutyryl fluoride–BF_3 in CH_2Cl_2 to give reverse regiochemistry. The ratio of **2a** to **3a** was 15:85, and pure **3a** was obtained in 65% yield by recrystallization. This 3-acylation of acenaphthene with the acyl fluoride–BF_3 system appears to be a general reaction; Table I gives typical examples. The substitution patterns were established by comparison of NMR spectra to that of the known compound **3c**. In each case, the 3-substituted acenaphthene was isolated in moderate yield by crystallization. Comparison reactions with the corresponding anhydrides or acyl chlorides and $AlCl_3$ gave the 3-isomers in only 10–25% (VPC) yield.

Acylation of 2-alkylnaphthalenes with acyl fluorides–BF_3 to 2-acyl-6-alkylnaphthalenes was also particularly clean. Thus, 2-methylnaphthalene (**4**) and isobutyryl chloride–$AlCl_3$ in CH_2Cl_2 gave a mixture consisting of four products [only 30% was 2-isobutyryl-6-methylnaphthalene (**5a**)], whereas isobutyryl fluoride–BF_3 in CH_2Cl_2 gave **5a** in 83% yield (isolated; Scheme II). Table II gives further examples of the 6-acylation of 2-methylnaphthalene by acyl fluorides–BF_3. Again, the substitution patterns were proved by NMR analysis based on the known **5c**. In each case, comparison reactions using acyl chlorides–$AlCl_3$ gave poor regioselectivity.

Scheme I



Scheme II

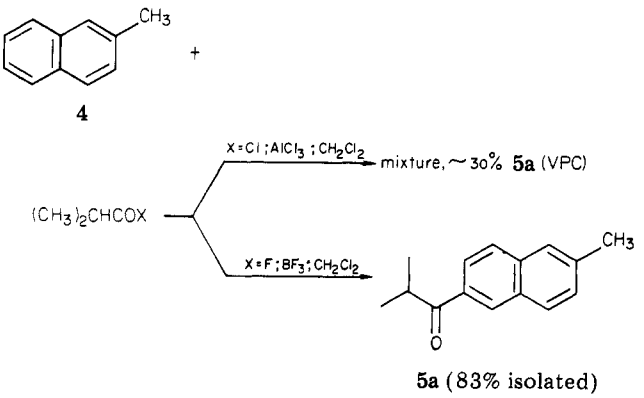


Table I. Acylations of Acenaphthene with Acyl Fluorides–BF_3[a]

entry	R in RCOF	product ratio (VPC): 3-isomer, 3	product ratio (VPC): 5-isomer, 2	yield of 3, %	mp (bp) of 3, °C
a	i-C_3H_7	85	15	65	75-76
b	n-C_9H_{19}	75	25	48	43-44
c	CH_3	51	49	31	103-105
d	p-$CH_3C_6H_4$	56	44	39	92-94

[a] Yields refer to isolated, purified products. See the Experimental Section for spectral properties and analyses.

Table II. Preparation of 2-Acyl-6-methylnaphthalenes 5 by Acylation with Acyl Fluorides–BF_3[a]

entry	R in RCOF	yield of 5, %	mp (bp) of 5, °C
a	$(CH_3)_2CH$	83	(140-150 (1.5 mm))
b	n-C_9H_{19}	81	54-56
c	CH_3	77	66-68
d	C_2H_5	70	60-62

[a] Yields refer to isolated, purified products. For spectra and analyses, see the Experimental Section.

Olah[1e] showed that toluene predominately gives para acylation with both acyl chlorides and acyl fluorides, and we observed that the simple substrates furan and 2-methylthiophene lead to the same products (2- and 2,5-substitution, respectively) with both acylating agents. It is only with polycyclic aromatic substrates that surprising

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0022-3263/84/1949-0384$01.50/0

results are obtained with acyl fluorides–BF_3.[4]

The unusual regioselectivity presented here is specific for the acyl fluoride–BF_3 system. Acyl fluorides–$AlCl_3$ gave product mixtures very similar to those obtained with acyl chlorides–$AlCl_3$, whereas acyl chlorides–BF_3 did not give any acylations. Even though the reasons for the selectivity are unclear, this chemistry offers, for the first time, a method by which a variety of 3-substituted acenaphthenes and 2,6-disubstituted naphthalenes can easily be made.[5,6] We recommend that use of the acyl fluoride–BF_3 reagent be considered whenever it is necessary to modify the isomer distribution of products from a Friedel–Crafts reaction.

Experimental Section

General Methods. Melting and boiling points are uncorrected. IR spectra were taken on a Perkin-Elmer Model 137 spectrophotometer. ^1H NMR spectra were obtained with Varian EM-360 and JEOLCO MH-100 spectrometers and are reported in parts per million (δ) from internal tetramethylsilane, and coupling constants (J) are given in hertz. Mass spectra were recorded with a VG ZAB mass spectrometer in the field-desorption mode. Acyl fluorides were prepared according to Olah and Kuhn.[7]

General Procedure for Acylations. The following procedure for 3-isobutyrylacenaphthene is typical of all the acylations reported in Tables I and II. A solution of 0.020 mol of 1 and 0.025 mol of isobutyryl fluoride[7] in 100 mL of CH_2Cl_2 was treated with dry BF_3 at 0–10 °C for 1 h, warmed to 25 °C, and quenched with water, and the organic phase was dried and stripped to give an oily 15:85 mixture of **2a** and **3a** (VPC). Recrystallization from hexane–ether gave 3.1 g (65%) pure **3a**: mp 75–76 °C; mass spectrum, m/e 224; NMR ($CDCl_3$) δ 7.95 (d, J = 8, 1 H), 7.3–7.75 (m, 4 H), 3.2–3.9 (m, 5 H), 1.25 (d, J = 7, 6 H). Anal. Calcd: C, 85.7; H, 7.19. Found: C, 85.5; H, 7.09.

3-Decanoylacenaphthene (3b) was obtained in 48% yield by fractional crystallization (ethanol) of the crude acenaphthene–decanoyl fluoride product and had the following: mp 43–44 °C; IR (melt) 5.95, 6.82, 7.49, 11.93, 13.2 μm; NMR ($CDCl_3$) δ 7.95 (d, J = 8, 1 H), 7.3–7.8 (m, 4 H), 2.8–3.8 (m, 6 H), 0.8–2.2 (m, 17 H); mass spectrum, m/e 308 (calcd 308). Anal. Calcd. for $C_{22}H_{28}O$: C, 85.7; H, 9.14. Found: C, 85.7; H, 9.24.

3-Acetylacenaphthene (3c) was purified by recrystallization from methanol and had the following: mp 103–105 °C (lit.[3d] mp 103–104 °C); NMR ($CDCl_3$) δ 7.9 (d, J = 8, 1 H), 7.2–7.7 (m, 4 H), 3.2–3.7 (m, 4 H), 2.67 (s, 3 H); mass spectrum m/e 196 (calcd 196).

3-(*p*-Toluyl)acenaphthene (3d): mp 92–94 °C (CH_3OH); IR (mull) 6.00, 6.19, 7.76, 7.88, 8.42, 8.61, 11.71, 13.16 μm; NMR ($CDCl_3$) δ 7.8 (d, J = 8, 1 H), 7.3–7.6 (m, 8 H), 3.4–3.7 (m, 4 H), 2.52 (s, 3 H); mass spectrum, m/e 272 (calcd 272). Anal. Calcd for $C_{20}H_{16}O$: C, 88.2; H, 5.92. Found: C, 88.1; H, 5.87.

2-Isobutyryl-6-methylnaphthalene (5a): bp 140–150 °C (1.5 mm); IR (neat film) 5.93, 6.10, 7.20, 8.13, 8.34, 8.61, 8.86, 10.08, 12.40 μm; NMR ($CDCl_3$) δ 8.43 (br s, 1 H), 7.2–8.0 (m, 5 H), 3.66 (septet, J = 7, 1 H), 2.60 (s, 3 H), 1.27 (d, J = 7, 6 H); mass spectrum, m/e 212 (calcd 212). Anal. Calcd for $C_{15}H_{16}O$: C, 84.8; H, 7.58. Found: C, 84.6; H, 7.60.

2-Decanoyl-6-methylnaphthalene (5b): mp 54–56 °C (ethanol); IR (mull) 5.96, 8.40, 11.29, 12.12, 13.47, 13.90 μm; NMR ($CDCl_3$) δ 8.44 (br s, 1 H), 7.16–8.1 (m, 5 H), 3.10 (t, J = 7, 2 H), 2.56 (s, 3 H), 0.8–2.1 (m, 17 H); mass spectrum m/e 296 (calcd 296). Anal. Calcd for $C_{21}H_{28}O$: C, 85.1; H, 9.51. Found: C, 84.8; H, 9.61.

2-Acetyl-6-methylnaphthalene (5c): mp 66–68 °C (ethanol–hexane) (lit.[8] mp 66.5 °C); NMR ($CDCl_3$) δ 8.41 (br s, 1 H), 7.2–8.1 (m, 5 H), 2.70 (s, 3 H), 2.52 (s, 3 H).

2-Propionyl-6-methylnaphthalene (5d): mp 60–62 °C (hexane); IR (mull) 5.91, 8.38, 8.83, 10.5, 11.1, 12.2 μm; NMR ($CDCl_3$) δ 8.40 (br s, 1 H), 7.2–8.1 (m, 5 H), 3.00 (q, J = 6.5, 2 H), 2.41 (s, 3 H), 1.19 (t, J = 6.5, 3 H); mass spectrum, m/e 198 (calcd 198). Anal. Calcd for $C_{14}H_{14}O$: C, 84.8; H, 7.11. Found: C, 84.5; H, 7.03.

Acknowledgment. We are grateful to Prof. J. Dunogues, CNRS, France, for supplying representative NMR spectra of substituted acenaphthenes and to Profs. J. S. Swenton, The Ohio State University, and D. C. Baker, University of Alabama, for high-field NMR spectra.

Registry No. 2a, 87969-65-1; **3a**, 87969-66-2; **3b**, 87969-67-3; **3c**, 7434-96-0; **3d**, 87969-68-4; **4**, 91-57-6; **5a**, 73652-97-8; **5b**, 87969-69-5; **5c**, 5156-83-2; **5d**, 69750-34-1; acenaphthene, 83-32-9; isobutyryl fluoride, 430-92-2; decanoyl fluoride, 334-47-4; acetyl fluoride, 557-99-3; *p*-toluyl fluoride, 350-42-5; propionyl fluoride, 430-71-7; phenanthrene, 85-01-8; isobutyrylphenanthrene, 87969-64-0; anthracene, 120-12-7; 9-isobutyrylanthracene, 73633-41-7; 1-isobutyryulanthracene, 87969-70-8; 2-isobutyrylanthracene, 76868-33-2; 5-decanoylacenaphthene, 87969-71-9; 5-acetylacenaphthene, 10047-18-4; 5-*p*-toluylacenaphthene, 87969-72-0.

Supplementary Material Available: NMR spectra of compounds in Tables I and II (10 pages). Ordering information is given on any current masthead page.

(4) Reactions of acyl fluorides–BF_3 with some other polycyclic aromatic compounds were briefly examined. Phenanthrene reacted with isobutyryl fluoride–BF_3 to give two products (VPC, 67:33 ratio); a comparison reaction using isobutyryl chloride–$AlCl_3$ gave four of the five possible products (VPC 2:24:57:16; the last two identical with those from the fluoride reaction; VPC–MS showed that only monoacyl phenanthrenes were present). With anthracene as the substrate, isobutyryl chloride–$AlCl_3$ gave a single product, whereas isobutyryl fluoride–BF_3 suprisingly led to a mixture of all three possible products (VPC 8:30:62). In these cases, isomer separation and regiochemical assignments were not undertaken.

(5) Good regiochemistry can also be achieved by reacting acyl chlorides with anhydrous HF to generate acyl fluorides in situ, followed by the addition of BF_3 and an aromatic substrate. In the case of 2-methylnaphthalene with isobutyryl chloride in HF, followed by BF_3 addition, **5a** was obtained in 80% yield.

(6) Control experiments showed that the reaction products do not isomerize under the reaction conditions.

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Homoallylic Substitution Reactions of 1-Cyclopropyl-1-haloethane: Reaction with Lithium Dialkylcuprates[1]

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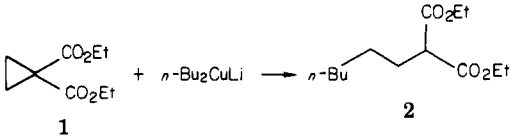
Received July 21, 1983

Cationic ring opening reactions of cyclopropane derivatives have been the focus of many studies,[2] but noncationic ring opening by nucleophiles has received only cursory attention. The latter process would be attractive since acid-sensitive substrates and nucleophiles, particularly carbanionic nucleophiles, could be utilized. An example that has found synthetic use involves attack by cuprates or amines on diethyl 1,1-cyclopropanedicarboxylate derivatives, **1**, to give products such as **2**.[3]



1 2

(1) Presented, in part, at the following: the 12th Northeast Regional Meeting of the American Chemical Society, Burlington, VT, June 1982, ORGN 186 (Hrubiec, R. T.; Smith, M. B.); the 13th Northeast Regional Meeting of the American Chemical Society, Hartford, CT, June 1983, ORGN 149 (Hrubiec, R. T.; Smith, M. B.).

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