C_3), 23.1 (t, J_{FC} = 3.7 Hz, methyls on C_3), 21.3 (t, J_{FC} = 3.1 Hz, allylic CH_3 on C_2); IR 575, 770, 860, 925, 1070 (s), 1215, 1385, 1450, 1640 (w, C=C), 2960 cm^{-1}; MS, m/e 259.9882$_2$ ● 0.0027 (M^+, 0.1% of base, ±10.1 ppm), calcd for $C_7H_{11}F_2I$ m/e 259.9873$_6$ (deviation = 0.0008$_6$; +3.3 ppm); other major fragments 133 (71.3, $M^+ - I$), 128 (10.7), 127 (8.0), 113 (21.2), 97 (15.4), 91 (29.1), 85 (11.0), 83 (16.7), 77 (26.3), 73 (33.2), 70 (13.4), 69 (22.0), 67 (16.7), 65 (28.8), 61 (14.1), 57 (35.4), 55 (37.5), 53 (17.8), 51 (11.1), 43 (32.0), 41 (100), 39 (46.3), 29 (13.6), 28 (15.2), 27 (20.9).

Photolysis of CF_2I_2 and Ia without Hg. In the absence of mercury, a photolysis performed as described above showed only 40% conversion of CF_2I_2 and gave a similar product ratio.

Radical Addition of CF_2I_2 to 1-Hexene. Into a 10-mL round-bottomed flask were weighed 0.325 g of CF_2I_2 (1.07 mmol), 1.108 g of 1-hexene (13.2 mmol), and 10 mg of benzoyl peroxide. After refluxing the magnetically stirred solution for 10.5 h, excess olefin was removed by rotary evaporation, and the pale pink residue was purified by flash chromatography,[10] eluting with hexane, to yield 1,1-difluoro-1,3-diiodoheptane (**3**): 0.304 g (73%); ^1H NMR δ 0.95 (t, J = 6 Hz, 3 H), 1.2-3.1 (br m, 6 H), 2.8-3.6 (m, 2 H), 4.32 (quintet, J = 7 Hz, 1 H); ^{19}F NMR ϕ 36.18 (midpoint, AB, J_{AB} = 172 Hz, $\Delta\phi$ AB = 1.75 ppm; downfield F, dd, J_{HF} = 18, 10 Hz; upfield F, dd, J_{HF} = 17, 14 Hz); ^{13}C NMR δ 99.6 (t, J_{FC} = 316 Hz, C_1), 58.2 (t, J = 40 Hz, C_2), 39.2 (s), 31.5 (s), 25.3 (br s, C_3), 21.7 (s), 13.9 (s, C_7); IR 895 (s), 1060, 1165, 2870, 2880, 2930 (s), 2970 (s) cm^{-1}; MS, 388 (1.0, M^+), 261 (4.8, $M^+ - I$), 41 (100, C_3H_5 and many smaller fragments). The ^{19}F NMR showed the product to contain about 3% of the opposite regioadduct 2-(difluoroiodomethyl)-1-iodohexane: ϕ 38.1 (midpoint, AB of d, J_{AB} = 172 Hz, $\Delta\phi$ AB = 1.75, J_{HF} = 10 Hz).

Addition of CF_2I_2 to Methyl Propenoate. A mixture of 1.02 g of methyl propenoate (11.8 mmol, MCB, freshly distilled from phenothiazene onto molecular sieves), 2.15 g of CF_2I_2 (7.07 mmol), about 4 mL of benzene, and 0.1 g of benzoyl peroxide (0.1 mmol) were allowed to react similarly for 19 h at 90-106 °C to yield 36% of unreacted CF_2I_2 plus 1.29 g (47%) of methyl 4,4-difluoro-2,4-diiodobutanoate (**4**): ^1H NMR (100 MHz) δ 4.55 (dd, J = 10, 3.8 Hz, 1 H), 2.84-3.95 (m, 2 H), 3.77 (s, 3 H); ^{19}F NMR ϕ 40.1 (midpoint, AB, J_{AB} = 176 Hz, $\Delta\phi$ AB = 0.3 ppm, J_{HF} = 15 Hz); IR 900, 1075, 1120, 1170, 1195, 1255, 1315 (w), 1360 (w), 1415 (w), 1435 (w), 1735 (s), 2960 (w) cm^{-1}; ^{13}C NMR δ 170.3 (s, C=O), 97.0 (t, J_{FC} = 315 Hz, CF_2I), 54.5 (t, J_{FC} = 21 Hz, CH_2) 53.3 (s, CH_3), 7.8 (t, J_{FC} = 2.4 Hz, CHI); MS, 359 (1.3, M - OCH_3), 331 (0.3, M - CO_2CH_3), 263 (20.8, M - I), 254 (0.8, I_2), 136 (100, M - I), 127 (24.5, I), 77 (27.7, $C_3H_3F_2$), 64 (3.0, $C_2H_2F_2$), 59 (17.3, CO_2CH_3), 31 (13.9, OCH_3 and other fragments), no M^+ observed.

Addition of CF_2I_2 to *trans*-4-Octene. A mixture of 0.70 g of CF_2I_2 (2.3 mmol), 0.81 g of *trans*-4-octene (7.2 mmol), and 0.10 g benzoyl peroxide was allowed to react similarly, yielding a 1:1 mixture of the two possible diasterioisomeric 4-(difluoroidomethyl)-5-iodoctanes **5**: 84%; ^{19}F NMR ϕ 36.6 (midpoint, AB of d, $\Delta\phi$ AB = 3.02 ppm, J_{AB} = 187 Hz; downfield F, d, J_{HF} = 14 Hz; upfield F, d, J_{HF} = 17.5 Hz), 37.5 (midpoint, AB of d, $\Delta\phi$ AB = 3.17 ppm, J_{AB} = 188 Hz; downfield F, d, J_{HF} = 13.5 Hz; upfield F, d, J_{HF} = 15 Hz); ^1H NMR of reaction mixture shows the hydrogens on C_5 at δ 4.45 (multiplets).

Radical Addition of CF_2I_2 to Cyclohexene. A mixture of 1.00 g of CF_2I_2 (3.3 mmol), 1.20 g of cyclohexene (14.6 mmol), and 0.03 g of benzoyl peroxide (0.1 mmol) was allowed to react at 90-97 °C for 20 h to yield 61% of a mixture consisting of 65% *trans*-1-(difluoroiodomethyl)-2-iodocyclohexane (**6**), 28% *cis*-1-(difluoroiodomethyl)-2-iodocyclohexane (**7**), 4% unreacted CF_2I_2, and 3% of an unidentified product (ϕ 42, midpoint, AB, $J \simeq 10$ Hz, $\Delta\phi \simeq 1$ ppm). The major diastereomeric products were isolated by preparative GLC (20% OV-210 on Chromasorb WHP 60/80, 10 ft × $^1/_4$ in., 150 °C: retention times, trans, 27 min; cis, 33 min, some slight decomposition under these GC conditions). **6**: ^{19}F NMR ϕ 34.5 (d, J = 10.3 Hz); ^1H NMR δ 4.27 (ddd, J_{trans} = 8.5 Hz, J'_{trans} = 7.0 Hz, J_{cis} = 4.5 Hz, 1 H, HCI), 1.1-2.5 (complex multiplets, 9 H); ^{13}C NMR δ 108.0 (t, J = 319 Hz, CF_2I), 57.3 (t, J = 16.5 Hz, C_1), 38.3 (s), 27.9 (s), 27.5 (dd, J = 3.6, 2.5 Hz), 26.2 (s), 22.7. **7**: ^{19}F NMR ϕ 42.4 (midpoint, AB, J_{AB} = 172 Hz, $\Delta\phi$ = 5.12; downfield F, d, J_{HF} = 13.6 Hz; upfield F, d, J_{HF} = 12.8 Hz); ^1H NMR δ 4.75 (br s, 1 H, H-CI), 1.1-2.3 (complex multiplets, 9 H); ^{13}C NMR δ 105.7 (dd, J = 321, 320 Hz, CF_2I), 57.5 (t, J = 9.8 Hz, C_1), 37.2 (s), 32.1 (dd, J = 3.7, 2.4 Hz, C_6), 24.8 (s), 23.6 (t, J = 2.4 Hz, C_2), 22.2 (s).

Radical Addition of CF_2I_2 to 2,3-Dimethyl-2-butene. Refluxing 0.56 g of CF_2I_2 (1.8 mmol), 0.86 g of 2,3-dimethyl-2-butene (10 mmol), and 0.02 g of benzoyl peroxide (0.08 mmol) for 24 h gave **2** as the only F-containing product. More than half of the CF_2I_2 was recovered unchanged. The yield was 95% based on converted CF_2I_2 and ^{19}f NMR integration.

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Registry No. 1, 823-25-6; 2, 87970-47-6; 3, 87970-48-7; 4, 87970-49-8; (*R**,*R**)-5, 87970-50-1; (*R**,*S**)-5, 87970-51-2; 6, 87970-52-3; 7, 87970-53-4; CF_2I_2, 1184-76-5; CI_4, 507-25-5; HgF_2, 7783-39-3; 2,3-dimethyl-2-butene, 563-79-1; 1-hexene, 592-41-6; methyl propenoate, 96-33-3; *trans*-4-octene, 14850-23-8; cyclohexene, 110-83-8.

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A Convenient, Mild Method for the Cyclization of 3- and 4-Arylalkanoic Acids via Their Trifluoromethanesulfonic Anhydride Derivatives

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The cyclization reaction of 3- and 4-arylalkanoic acids to the corresponding cyclic ketones has been the subject of intense study for many years.[1] In particular, considerable attention has been focused on the synthesis of 1-tetralone analogues (**3**, n = 2) from 4-arylbutanoic acids in connection with the synthesis of the dihydrodiol and diol epoxide metabolites of carcinogenic polycyclic aromatic hydrocarbons.[2] The cyclization is generally effected either directly by using strong acids such as HF, methanesulfonic acid, and polyphosphoric acid or via the acid chloride, promoted by metal halides such as $AlCl_3$ and $ZnBr_2$.[1-3]

In recent years, activation of certain electrophiles as their trifluoromethanesulfonate (or triflate) derivatives has found widespread application owing to their pronounced leaving-group capabilities.[4] While this triflate activation has been extensively explored in the intermolecular Friedel-Crafts acylation of aromatic coumounds by Effenberger and his co-workers,[5] its intramolecular version has not been reported. In the following, we describe a highly efficient and mild one-pot procedure for the cyclization of 3- and 4-arylalkanoic acids to the corresponding cyclic ketones via their triflic anhydride derivatives **2** (Scheme I).

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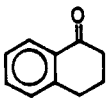
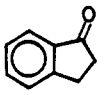
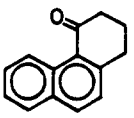
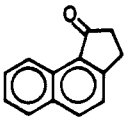
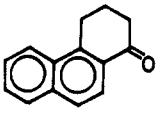
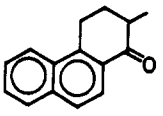
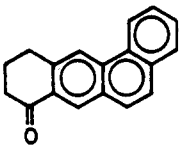
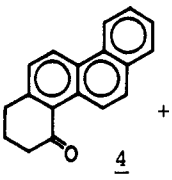
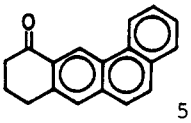
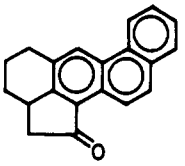
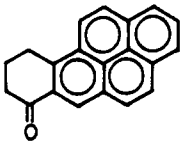
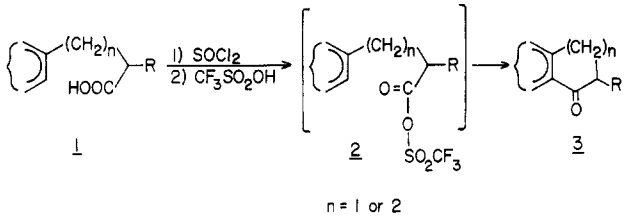
Table I. Products from the Cyclization of 3- and 4-Arylalkanoic Acids via Triflic Anhydride Derivatives

entry	product(s)	% yield[a]	mp,[b] °C
1		87	
2		89	
3		91	69-70 (69-70)[d]
4		71	101-103 (102-104)[e]
5		89	93-95 (94-96)[f]
6		82	73-75 (74-75)[g]
7		75	178-180 (179-180)[h]
8[c]	 +  4 5	70 (4/5 = 5/1)[i]	
9	4 + 5	82 (4/5 = 1/1.2)[i]	
10		95	192-194 (192-193)[j]
11		81	173-174 (173-175)[h]

[a] Yields of the distilled or recrystallized material. [b] Reported melting points are given in parentheses. [c] The reaction was stopped after 6 h at −78 °C. [d] Reference 6. [e] Reference 7. [f] Reference 8. [g] Reference 9. [h] Reference 10. [i] The product ratio was determined by 360-MHz NMR. See also ref 3a. [j] Reference 11. [k] Reference 12.

Scheme I



Triflic anhydrides **2** were conveniently generated in situ from the acid chlorides of the starting carboxylic acids **1**. The highly reactive triflic anhydrides smoothly produced cyclic ketones in excellent yields (Table I). While the cyclization of 4-arylbutanoic acids was virtually complete within 3–4 h at −78 °C, that of 3-arylpropanoic acids required temperatures near 0 °C for several hours in order to reach completion. We recommend, however, for the sake of operational convenience, that the reaction mixture be gradually warmed up to room temperature, except for the cases where regioisomeric ketone formation becomes a problem. For example, the cyclization of 4-(2-phenanthryl)butanoic acid was shown to be highly temperature dependent (see entries 8 and 9 in Table I). Thus, cyclization at −78 °C for 6 h provided predominantly 1,2-dihydrochrysen-4(3*H*)-one (**4**), whereas at higher temperatures formation of the isomeric 7,8-dihydrobenz[*a*]-anthracen-5(6*H*)-one (**5**) becomes more favored.

In conclusion, the method described herein employing triflate activation offers a convenient, mild one-pot synthesis of 1-indanone and 1-tetralone systems and should find useful applications in the synthesis of their acid-sensitive and temperature-sensitive analogues.

Experimental Section

General Procedure for the Triflic Anhydride Mediated Cyclizations of 3- and 4-Arylalkanoic Acids. The mixture of the carboxylic acid **1** (5 mmol) and thionyl chloride (10 mmol) was heated at reflux in dry benzene (10 mL) for 1 h. The solvent was removed in vacuo and fresh dry benzene (5 mL) was introduced and again removed in vacuo. The same procedure was repeated again with 5 mL of dry methylene chloride. The crude acid chloride was then dissolved in 15 mL of dry methylene chloride and the solution was cooled to −78 °C and was treated with trifluoromethanesulfonic acid (5 mmol). The reaction mixture was allowed to warm up to room temperature over a period of 3 h and kept at that temperature overnight. The solution was poured into ice water, and the two layers were separated. The aqueous layer was extracted once with methylene chloride, and the combined organic layers were washed successively with 5% $NaHCO_3$, water, and brine and dried over sodium sulfate. The organic solvent was removed in vacuo and the product purified either by recrystallization or by Kugelrohr distillation (entries 1 and 2 in Table I). The characterization of the products was made through direct comparison (IR, 360-MHz ^1H and 90.56-MHz ^{13}C NMR, and/or mixture melting point measurements) with the authentic samples made by literature methods.

Acknowledgment. We are grateful to the National Cancer Institute, NIH (Grant No. CA-25185) for the sup-

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port of this research and to the National Science Foundation for its contribution to the purchase of a Bruker 360-MHz NMR spectrometer.

Registry No. 4, 66267-06-9; 5, 60968-15-2; benzenebutanoic acid, 1821-12-1; benzenepropanoic acid, 501-52-0; 2-naphthalenebutanoic acid, 782-28-5; 2-naphthalenepropanoic acid, 21658-35-5; 1-naphthalenebutanoic acid, 781-74-8; α-methyl-1-naphthalenebutanoic acid, 7498-80-8; 3-phenanthrenebutanoic acid, 13728-56-8; 2-phenanthrenebutanoic acid, 77520-30-0; 8,9,10,11-tetrahydro-8-benz[a]anthraceneacetic acid, 6299-45-2; 1-pyrenebutanoic acid, 3443-45-6; 1-tetralone, 529-34-0; 1-indanone, 83-33-0; 2,3-dihydro-4(1*H*)-phenanthrenone, 778-48-3; 2,3-dihydro-1*H*-benzinden-1-one, 6342-87-6; 3,4-dihydro-1-(2*H*)-phenanthrenone, 573-22-8; 3,4-dihydro-2-methyl-1(2*H*)-phenanthrenone, 3580-60-7; 10,11-dihydrobenz[a]anthracen-8-(9*H*)-one, 5472-20-8; 2a,3,4,5-tetrahydrobenz[j]aceanthrylen-1-(2*H*)-one, 87883-45-2; 9,10-dihydrobenzo[a]pyren-7(8*H*)-one, 3331-46-2; benzenebutanoyl chloride, 18496-54-3; benzenepropanoyl chloride, 645-45-4; 2-naphthalenebutanoyl chloride, 87883-46-3; 2-naphthalenepropanoyl chloride, 27673-99-0; 1-naphthalenebutanoyl chloride, 87883-47-4; α-methyl-1-naphthalenebutanoyl chloride, 87883-48-5; 3-phenanthrenebutanoyl chloride, 87883-49-6; 2-phenanthrenebutanoyl chloride, 87883-50-9; 8,9,10,11-tetrahydro-8-benz[a]anthraceneacetyl chloride, 87901-08-4; 1-pyrenebutanoyl chloride, 63549-37-1; trifluoromethanesulfonic acid, 1493-13-6.

Reaction of *n*-, *sec*-, and *tert*-Butyllithium with Dimethoxyethane (DME): A Correction

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Two recent communications report on kinetic and spectral evidence for the formation of a complex between metalating agent and substrate prior to deprotonation.[1,2] The second account[2] describes results obtained in the attempted metalation of formamidines with *t*-BuLi in dimethoxyethane (DME). The lack of D incorporation in these experiments was rationalized on the basis of a rather *stable complex* between substrate, metalating agent, and the bidentate solvent (DME). Furthermore, upon addition of benzaldehyde, benzyl alcohol and benzyl benzoate were isolated, the products of an apparent Cannizzarro reaction. We have evidence that the interpretation of these results[2] with DME is incorrect.

Dimethoxyethane has only rarely been used as a solvent in metalation reactions. Our own previous negative experience with this solvent and the peculiar results of the recent report[2] called for a more careful investigation of the stability of DME toward alkyllithiums. In several experiments we have shown that DME has a very limited stability toward butyllithium. With *t*-BuLi in particular, DME is readily deprotonated and undergoes β-elimination characteristic of several 1,2-diheterosubstituted ethanes. Thus, in contrast to the behavior of tetramethylethylenediamine (TMEDA), DME does not form a stable complex with *t*-BuLi. As illustrated in Scheme I, it is assumed that after coordination with one of the two oxygen

Scheme I

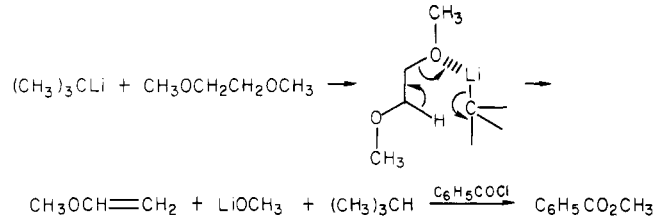

Table I

	$t_{1/2}$, min	
	−20 °C	−70 °C
DME/*n*-BuLi[a]	111 ± 5	
DME/*sec*-BuLi[b]	~2 ± 1	120 ± 5
DME/*t*-BuLi[c]	<<2	11 ± 2

[a] *n*-BuLi, 2.6 M/hexane, Alfa Products; 0.5 M solution in DME (12 mMol). [b] *sec*-BuLi, 1.4 M/hexane, Alfa Products; 0.25 M solution in DME (14 mMol). [c] *t*-BuLi, 2.3 M/pentane, Alfa Products; 0.5 M solution in DME (11.5 mMol).

atoms, a proton in the β-position is abstracted in a fast reaction (higher acidity than in TMEDA) followed by β-elimination and formation of methyl vinyl ether and lithium methoxide. By reproducing the reported[2] conditions (*t*-BuLi/pentane, 0.5 M solution in DME,[3] −20 °C/20 min), the expected white precipitate was indeed formed. Titration (1 M *sec*-BuOH/xylene) using either phenanthroline, as reported,[2] or the more reliable 2,2′-biquinoline[4] as an indicator gave no evidence of any remaining *t*-BuLi. When the addition of *t*-BuLi was carried out at −70 °C, followed by a 20-min reaction time at −20 °C, a clear yellow solution developed initially followed by the white precipitate. Titration with the two indicators showed less than 8% and 9%, respectively, of *t*-BuLi to be present under these conditions. After 20 min at −70 °C, 45% (phenanthroline) and 28% (2,2′-biquinoline) of *t*-BuLi was still detectable by titration with the two indicators. A control experiment under identical conditions (−70 °C, 20 min) using freshly distilled benzaldehyde as substrate, rather than a titration, led to a mixture consisting of 60% unreacted benzaldehyde, 25% *tert*-butylphenylcarbinol, and several unidentified impurities. This result is in good agreement with the titration value (28%) obtained by using the 2,2′-biquinoline indicator.

Chemical proof for the formation of lithium methoxide was obtained by treatment of the white precipitate (formed after 20 min/−20 °C) with an equimolar amount of benzoyl chloride. After a reaction time of 20 min at −20 °C, the mixture was quenched (−20 °C) with NaH_2PO_4 buffer. After workup, the product mixture (92% recovery) consisted of methyl benzoate (84%) and unreacted benzoyl chloride (Scheme I). The approximate half-lives of *n*-BuLi, *sec*-BuLi, and *t*-BuLi in DME were determined by using the 2,2′-biquinoline titration technique and are listed in Table I. The reactivity of the various butyllithiums with DME thus decreases in the order of *t*-BuLi > *sec*-BuLi ≫ *n*-BuLi.

In summary, our results indicate that DME has a rather limited stability toward butyllithiums and is cleaved extremely rapidly by *t*-BuLi. Furthermore, the reported

(1) Al-Aseer, M.; Beak, P.; Hay, D.; Kempf, D. J.; Mills, S.; Smith, S. G. *J. Am. Chem. Soc.* **1983**, *105*, 2080.
(2) Meyers, A. I.; Rieker, W. F.; Fuentes, L. M. *J. Am. Chem. Soc.* **1983**, *105*, 2082.
(3) Dimethoxyethane (DME): Baker, analyzed reagent, less than 0.1% H_2O.
(4) 2,2′-Biquinoline produces a sharper and clearer color change. Cf.: Gschwend, H. W.; Rodriguez, H. R. *Org. React. (N.Y.)* **26**, 1 (1979). Watson, S. C.; Eastham, J. F. *J. Organomet. Chem.* **1967**, *9*, 165.

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