Anal. Calcd for $C_{18}H_{11}IO_3$: C, 45.61; H, 3.21; I, 37.13. Found: C, 45.37; H, 3.12; I, 37.12.

9,10-Epoxy-9,10-diphenyl-9,10-dihydroanthracene (1, R = H).—1,3-Diphenylisobenzofuran (4.0 g, 15 mmol) was reacted with 2-phenyliodoniobenzoate (5.5 g, 16 mmol) according to the method of Fieser.[7] 9,10-Epoxy-9,10-diphenyl-9,10-dihydroanthracene was obtained as colorless crystals: mp 190–192° (lit.[13] mp 188–188.5°); 87% yield. Recrystallization (benzene–ether–methanol) caused no change in melting point: uv max (petroleum ether) 220 mμ (ε 38,000); nmr τ 2.02 (m, 4), 2.54 (m, 10), 3.01 (m, 4); mass spectrum *m/e* 346 (35), 330 (4), 269 (15), 268 (15), 241 (20), 239 (24), 134 (11), 119 (10), 106 (12), 105 (100), 77 (49), 51 (13).

Anal. Calcd for $C_{26}H_{18}O$: C, 90.14; H, 5.24. Found: C, 90.25: H, 5.11.

A portion of the product was reduced by refluxing with zinc dust in glacial acetic acid for 20 min.[13] 9,10-Diphenylanthracene was obtained as pale yellow crystals, mp 246–249° (lit.[2] mp 246–247°), in 68% yield, and exhibited an infrared spectrum identical with that of an authentic sample.

Thermal Behavior of 9,10-Epoxy-9,10-diphenyl-9,10-dihydroanthracene (1, R = H).—The epoxy compound (200 mg) was dissolved in triglyme (5 ml). The solution was heated at reflux (*ca.* 225°) for 2.5 hr under nitrogen, then cooled to 90°, and ethanol (3 ml) was added. The solution was reheated to boiling and water was added dropwise until a faint, permanent precipitate was formed. On cooling, there was obtained 186 mg of colorless crystals, mp 190–192°. The absence of 9,10-diphenylanthracene was confirmed (tlc), and the product was recrystallized (cyclohexane) to give colorless crystals, mp 191–192°.

Anal. Calcd for $C_{26}H_{18}O$: C, 90.14; H, 5.24. Found: C, 89.86; H, 5.33.

Thermal Behavior of 2-Nitro-9,10-Epoxy-9,10-Diphenyl-9,10-Dihydroanthracene (1, R = NO_2).—The nitroepoxy compound (200 mg) was treated as described above for the unnitrated derivative. Pale yellow crystals, mp 187–189° (182 mg), were recovered and recrystallized (benzene–methanol, 1:2 by volume) to give starting material, mp 190–190.5°.

Anal. Calcd for $C_{26}H_{17}NO_3$: C, 79.78; H, 4.38; N, 3.58. Found: C, 79.88; H, 4.45; N, 3.46.

Thermal Behavior of 9,10-Epoxy-9,10-diphenyl-9,10-dihydroanthracene (1, R = H) in Presence of Cyclohexene.—Cyclohexene (0.82 g; 10 mmol) and diglyme (10 ml) were placed in a 50-ml 3-necked flask, fitted with a gas inlet tube and condenser; the latter was connected to a cold finger filled with Dry Ice–acetone. Nitrogen was bubbled through the solution prior to and for a few minutes after the addition of 9,10-epoxy-9,10-diphenyl-9,10-dihydroanthracene (0.35 g, 1 mmol). The mixture was then heated to reflux (146°) under nitrogen for 2.25 hr.

Analysis by glpc (10% Squalane, 100°) showed almost complete recovery of cyclohexene (>98%) and no other visible volatile products.

The clear, colorless solution was distilled to *ca.* half volume and then ethanol (5 ml) was added. The solution was reheated to boiling and water added dropwise until a faint, permanent precipitate was formed. The solution was cooled to afford colorless crystals, mp 188–190° (0.315 g). The product was recrystallized (cyclohexane) to give colorless crystals, mp 191–192°.

Anal. Calcd for $C_{26}H_{18}O$: C, 90.14; H, 5.24. Found: C, 90.02; H, 5.23.

Registry No.—**1**, R = NO_2, 23367-37-5; **1**, R = H, 19061-38-2; **4**, R = NO_2, 23330-00-9; **5**, R = NO_2, 23330-01-0; **5**, R = H, 1488-42-2; 6-nitro-1,2,3,4-tetraphenylnaphthalene, 23330-03-2; 2-nitrotriptycene, 4628-55-1.

Acknowledgment.—We wish to thank the National Research Council of Canada for financial support of this work and the University of Alberta for an Intersession Bursay (G. F. M.).

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Synthesis of Esters of Acid-Unstable Alcohols by Means of *n*-Butyllithium[1]

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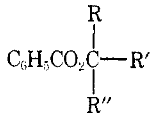
Esters are most conveniently prepared by the action of acid chlorides on alcohols. However, the by-product in such reactions, hydrogen chloride, usually precludes substantial ester formation when the alcohol can form relatively stable carbonium ions. For example, the reaction of phenylacetyl chloride with *t*-butyl alcohol affords predominately phenylacetic acid and isobutylene rather than the desired *t*-butyl phenylacetate. Esters of tertiary alcohols can be prepared, though, in the presence of tertiary amines like pyridine and N,N-dimethylaniline,[3] or magnesium metal[4] where such bases react with the hydrogen chloride as it is formed.

This report describes a convenient synthesis of esters derived from tertiary alcohols, and from other alcohols which readily undergo acid-catalyzed rearrangements. The synthesis simply involves conversion of alcohols into their lithium alkoxide salts by means of *n*-butyllithium in tetrahydrofuran (THF)–hexane, followed by the addition of an equivalent of an appropriate acid halide, and heating for 1 hr (eq 1).

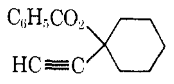
$$\mathrm{ROH} \xrightarrow[\text{THF–hexane}]{n\text{-}C_4H_9Li} \mathrm{ROLi} \xrightarrow[1\text{ hr}]{R'COCl} \mathrm{R'COOR} + \mathrm{LiCl} \qquad (1)$$

The results are summarized in Table I. This Table shows that benzoate esters **1a–e** and **2–5**, pivalate esters **6a** and **6b**, cinnamate ester **7**, and hydrocinnamate



$$C_6H_5CO_2\overset{R}{\underset{R''}{C}}\text{—}R'$$

1a, R = R′ = R″ = CH_3
b, R = CH_3; R′ = R″ = C_2H_5
c, R = R′ = R″ = C_2H_5
d, R = H; R′ = CH_3; R″ = *t*-C_4H_9
e, R = R′ = H; R″ = *t*-C_4H_9



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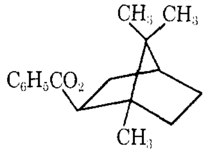

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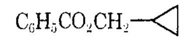

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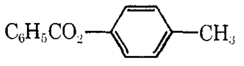

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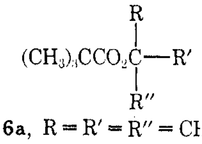

$$(CH_3)_3CCO_2\overset{R}{\underset{R''}{C}}\text{—}R'$$

6a, R = R′ = R″ = CH_3
b, R = R′ = R″ = C_2H_5

$C_6H_5CH{=}CHCO_2C(CH_3)_3$
7

$C_6H_5CH_2CH_2CO_2C(CH_3)_3$
8

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[2] Undergraduate research participant.

[3] J. F. Norris and G. W. Rigby, *J. Amer. Chem. Soc.*, **54**, 2088 (1932).

[4] A. Spassow, "Organic Syntheses," Coll. Vol. III, John Wiley & Sons, Inc., New York, N. Y., 1955, p 144.

TABLE I

SUMMARY OF ESTERS PREPARED FROM LITHIUM ALKOXIDES AND ACID CHLORIDES

Ester	Yield, %	Bp (mm) or mp, °C	Lit bp (mm) or mp, °C	Nmr, δ
1a	89	88–90 (3)	96 (2)[a]	7.06 (m, 5, ArH), 0.93 (s, 9, CH_3)
1b	87	106–108 (3)	89 (1.5)[b]	7.16 (m, 5, ArH), 1.1 (q, 4, CH_2), 0.48 (t, 6, CH_3), 0.375 (s, 3, CH_3)
1c	94	95–97 (2.5)		7.2 (m, 5, ArH), 2.5 (q, 6, CH_2), 0.4 (t, 9, CH_3)
1d	76	98–100 (3)	105–106 (5)[c]	7.16 (m, 5, ArH), 4.42 (q, 1, OCH), 0.65 (d, 3, $HCCH_3$), 0.38 (s, 9, CH_3)
1e	78	73–75 (1.2)	110 (10)[d]	7.46 (m, 5, ArH), 3.65 (s, 2, CH_2), 0.65 (s, 9, CH_3)
2	70	54–55	54–55[e]	7.65 (m, 5, ArH), 2.43 (s, 1, $\equiv CH$), 2.1, 1.5 (m, 10, CH_2)
3	69	152 (2.5)	25.5[f]	7.72 (m, 5, ArH), 5.0 (m, 1, OCH), 1.7 (m, 16, CH_2CH_3)
4	91	98.5–100 (7.5)		7.8 (m, 5, ArH), 4.2 (d, 2, CH_2), 0.9 (m, 5, Δ)
5	94	71–72	71–72[g]	7.73 (m, 9, ArH), 2.35 (s, 3, CH_3)
6a	64	78–80 (105)	134–5 (760)[h]	1.21 (s, 9, CH_3), 0.91 (s, 9, CH_3)
6b	75	32 (0.5)		1.88 (q, 6, CH_2), 1.16 (s, 9, CH_3), 0.8 (t, 9, CH_3)
7	88	75–77 (0.3)	144 (3)[i]	7.3 (m, 5, ArH), 6.83 (q, 2, $C{=}CH$), 1.47 (s, 9, CH_3)
8	72	120–122 (7)	119–121 (10)[j]	7.0 (s, 5, ArH), 2.5 (m, 4, CH_2), 1.23 (s, 9, CH_3)

[a] Reference 3. [b] British Patent 932,773 (July 31, 1963); *Chem. Abstr.*, **59**, 11167*f* (1965). [c] P. G. Stevens, *J. Amer. Chem. Soc.*, **55**, 4237 (1933). [d] Tissier, *Ann. Chim. Phys.*, **29**, 371; Beilstein, **9**, 113 (1926). [e] I. N. Nazarov, R. I. Kruglikova, and G. M. Nikolaev, *Zh. Obshch. Khim*, **29**, 1859 (1959). [f] M. A. Haller, *Comp. Rend.*, **109**, 31 (1889). [g] A. Behal and E. Choary, *Bull. Soc. Chim Fr.*, **11**, 603 (1894). [h] A. Butlerow, *Justus Liebigs Ann. Chem.*, **173**, 372 (1874). [i] B. Abramovitch, J. C. Shivers, B. E. Hudson, and C. R. Hauser, *J. Amer. Chem. Soc.*, **65**, 986 (1943). [j] W. von E. Doering and R. M. Haines, *ibid.*, **76**, 1859 (1959).

TABLE II

INFRARED AND ANALYTICAL DATA FOR NEW ESTERS

Ester	Ir, μ	Calcd, % C	Calcd, % H	Found, % C	Found, % H
1c	5.89, 7.82, 8.95, 9.7, 11.1, 14.0	76.36	9.09	76.13	9.16
4	6.05, 7.1, 7.6, 7.8, 8.0, 9.1, 9.9, 14.1	75.56	6.67	75.23	6.62
6b	5.7, 6.0, 7.0, 7.9, 8.6, 9.0, 11.0, 11.6, 13.0	72.00	12.00	71.89	12.13

ester **8** were prepared from appropriate lithium alkoxides and the respective acid chlorides in yields of 64–94%.

The structures of the esters were supported by comparison of their physical properties with literature values, and by nmr spectroscopy (Table I). Elemental analyses and infrared spectra were also obtained for esters **1c**, **4**, and **6b**, which appear to be new (Table II).

Incidentally, certain steroidal alcohols have been similarly esterified by means of their bromomagnesium salts. However, a wide range of yields below 70% were realized in these reactions and the corresponding lithium and sodium alkoxides were reported not to be so effective as magnesium.[5] Also, it has recently been shown that thallium salts of phenols react nearly quantitatively with certain acid halides but this metallic cation has apparently not yet been utilized in the synthesis of esters derived from tertiary alcohols.[6]

The current method seems to be applicable to any alcohol, but it may be limited to acid chlorides without labile α hydrogens, or at least to those halides whose corresponding ketenes are not volatile or do not dimerize readily.

Experimental Section[7]

General Preparation of Esters by Means of *n*-Butyllithium.—To a solution of 0.05 mol of the appropriate alcohol (Table I) in 75 ml of anhydrous THF, was added under nitrogen during several minutes, 35.0 ml (0.055 mol) of 1.6 *M* *n*-butyllithium in hexane.[8] After 30 min, the resulting solution was treated during 5 min by the dropwise addition of a solution of 0.055 mol of the acid chloride (Table I) in 50 ml of THF. The resulting solution was brought to reflux for 1 hr, cooled to 0° by an ice bath, and hydrolyzed by the addition of 100 ml of water. The aqueous phase was extracted with three 50-ml portions of ethyl ether, and the combined organic phases were dried ($CaSO_4$ or $MgSO_4$), and concentrated. The crude product was purified by vacuum distillation or by recrystallization (Table I). Infrared and nmr spectra were determined for each ester and were in agreement with the assigned structures.

Registry No.—*n*-Butyllithium, 109-72-8; **1a**, 774-65-2; **1b**, 23293-73-4; **1c**, 23293-74-5; **1d**, 23293-75-6; **1e**, 23581-70-2; **2**, 23293-77-8; **3**, 20279-54-3; **4**, 23293-79-0; **5**, 614-34-6; **6a**, 16474-43-4; **6b**, 23293-82-5; **7**, 14990-09-1; **8**, 16537-10-3.

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(5) D. D. Evans, D. E. Evans, G. S. Lewis, P. J. Palmer, and D. J. Weyell, *J. Chem. Soc.*, 3578 (1963).

(6) E. C. Taylor, G. W. McLay, and A. McKillop, *J. Amer. Chem. Soc.*, **90**, 2422 (1968).

(7) Boiling points and melting points are uncorrected. Infrared spectra were obtained on a Perkin-Elmer Model 137 spectrometer either neat or as Nujol mulls. Nmr spectra were determined on a Varian Associates A-60 spectrometer. Analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

(8) Supplied by the Foote Mineral Co., Exton, Pa.