The barrier to ring inversion for **1** is slightly smaller than those of 1,2-dithiane, 11.6 kcal/mol,[5] and 1,3-dithiane, 10.4 kcal/mol,[6] although it would hardly be tenable to draw very detailed conclusions concerning dithiane itself from the results for **1**. On the basis of the fluorine chemical-shift differences at −90°, which compare reasonably well with those for noninverting (or slowly inverting) *gem*-fluorocyclohexanes,[7] we have assumed that the preferred conformation of **1** is a chair—possibly strongly puckered as for 1,4-dithiane.[8]

Registry No.—**1**, 710-65-6.

Acknowledgment.—We are grateful to Mr. J. E. Leininger for assistance with the computing.

[5] C. Claesen, G. M. Androes, and M. Calvin, *J. Amer. Chem. Soc.*, **82**, 4428 (1960).

[6] H. Friebolin, S. Kabuss, W. Maier, and A. Luttringhaus, *Org. Magnetic Resonance*, **1**, 67 (1969).

[7] Cf. G. A. Yousif and J. D. Roberts, *ibid.*, **90**, 6428 (1968), and references cited therein.

[8] J. B. Lambert, *J. Amer. Chem. Soc.*, **89**, 1836 (1967); J. B. Lambert, R. E. Carhart, and P. W. R. Corfield, *ibid.*, **91**, 3567 (1969).

Observations Related to the Preparation of 2-Phenyliodoniobenzoate

GEOFFREY F. MORRISON AND JOHN HOOZ

Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada

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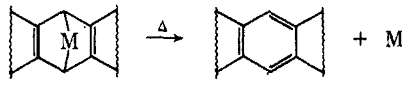
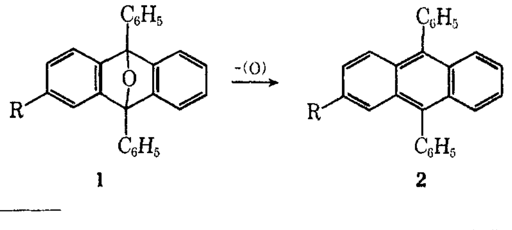
Several M-bridged polycyclic systems are known to undergo thermally induced extrusion of the bridging elements with concomitant formation of an aromatic system. When this operation is conducted in the presence of a reagent to trap M, it frequently constitutes a synthetically useful process.[1] With this notion in mind, we investigated the thermolysis of 9,10-epoxy-9,10-diphenyl-9,10-dihydroanthracene (**1**, R = H), a compound previously reported to undergo thermal decay, ostensibly in accord with the abovementioned principle, to produce 9,10-diphenylanthracene (**2**, R = H), although the fate of the oxygen bridge was not established.[2]

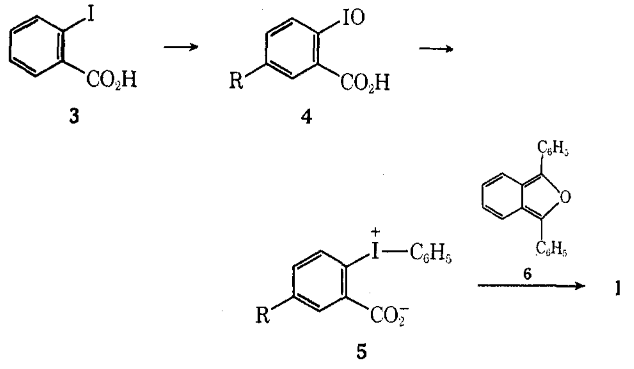




1 **2**

We reproduced the procedure (Scheme I) for the synthesis of **1** (R = H) from 2-phenyliodoniobenzoate (**5**) and 1,3-diphenylisobenzofuran (**6**), which involved:[2] oxidation (fuming nitric–sulfuric acid mixture) of *o*-iodobenzoic acid (**3**) to an *o*-iodosobenzoic acid (**4**); sulfuric acid-catalyzed condensation of **4** with benzene to produce betaine **5**, followed by thermal decomposition of the benzyne precursor **5** in the presence of **6**.

SCHEME I



The physical properties of compounds **4**, **5**, and **1** obtained by this route were in accord with those reported[2] for **4** (R = H), **5** (R = H), and **1** (R = H). However, **1** was recovered (91% yield) after being heated at reflux in triglyme solution.[3]

In view of the well-documented analogy between various thermolysis and electronolysis reactions,[4] the mass spectrum of **1** was investigated for an M − 16 ion. Although such fragmentation was not observed to be appreciable, the appearance of the molecular ion at *m/e* 391, consistent with the formulation $C_{26}H_{17}NO_3$, *requires reconstitution of* **1** (*R* = *H*), *prepared by this route, as* **1** (*R* = NO_2). Correspondingly, materials synthesized by this procedure are reassigned structures **4** (R = NO_2) and **5** (R = NO_2). All revised assignments are supported by correct compositional analyses, as well as corroborative ultraviolet, infrared, proton magnetic resonance, and mass spectroscopic evidence (*cf.* Experimental Section). Apparently the conditions selected for oxidation (ArI → ArIO) were adequate to effect electrophilic aromatic nitration as well.[5]

An authentic sample of **5** (R = H) was obtained by successively treating a mixture of **3** in concentrated sulfuric acid with potassium persulfate, benzene, then base, according to the method of LeGoff[6] and Fieser.[7] Compounds **5**-H and **5**-NO_2 were thereby readily distinguished; compounds **1**-H and **1**-NO_2 were also spectroscopically differentiated. Compound **1**-H was recovered (92% yield) after being heated at reflux in triglyme solution (2.5 hr),[3] and in 90% yield after a 2.25-hr reflux period in a diglyme solution containing cyclohexene.

Compound **5**-NO_2 serves as an effective "4-nitrobenzyne" precursor. Thermolysis of **5**-NO_2 in the

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[1] *Inter alia*, diimide (M = HNNH), E. J. Corey and W. L. Mock, *J. Amer. Chem. Soc.*, **84**, 685 (1962); dimethylsilylene [M = $Si(CH_3)_2$], H. Gilman, S. S. Cottis, and W. H. Atwell, *ibid.*, **86**, 1596 (1964); singlet oxgen, H. H. Wasserman, and J. R. Scheffer, *ibid.*, **89**, 3073 (1967); tetramethyldisilene, G. J. D. Peddle, D. N. Roark, A. M. Good, and S. G. McGeachin, *ibid.*, **91**, 2807 (1969). For a survey of other examples, see B. P. Stark and A. J. Duke, "Extrusion Reactions," Pergamon Press, New York, N. Y., 1967.

[2] F. M. Beringer and S. J. Huang, *J. Org. Chem.*, **29**, 445 (1964).

[3] Although this result differs from previous observations,[2] we cannot account for the discrepancy.

[4] A. Maccoll in "Modern Aspects of Mass Spectroscopy," R. I. Reed, Ed., Plenum Press, New York, N. Y., 1968, pp 143–168.

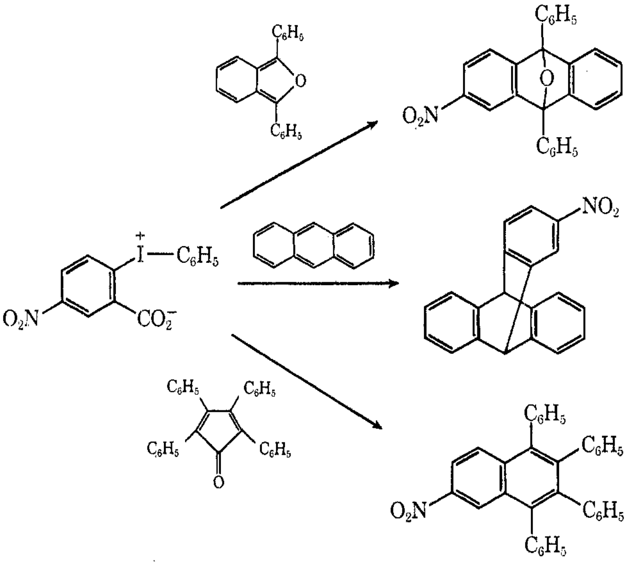
[5] This result is in accord with the observations of H. Goldstein and A. V. Grampoloff, *Helv. Chim. Acta*, **13**, 310 (1930).

[6] E. LeGoff, *J. Amer. Chem. Soc.*, **84**, 3786 (1962).

[7] L. F. Fieser, "Organic Experiments," D. C. Heath and Co., Boston, Mass., 1964, pp 311–313; L. F. Fieser and M. J. Haddadin, *Org. Syn.*, **46**, 107 (1966).

presence of tetraphenylcyclopentadienone, anthracene, and 1,3-diphenylisobenzofuran, respectively (Scheme II), produced the corresponding adducts in isolated yields of 86, 43,[8] and 54%.

SCHEME II



Experimental Section[9]

5-Nitro-2-iodosobenzoic Acid (4, R = NO_2) and 3-Nitro-2-iodobenzoic Acid.—2-Iodobenzoic acid (4.96 g; 20 mmol) was heated at 100° for 1 hr in a mixture of concentrated sulfuric acid (6.7 ml) and fuming nitric acid[2] (3.3 ml). After cooling, the mixture was poured into ice–water and the resultant precipitate was filtered, washed with water, and dried to give pale yellow crystals (5.28 g). Fractional crystallization from water afforded two components, the first of which was 5-nitro-2-iodosobenzoic acid (3.32 g) as colorless crystals: mp 229–229.5° dec; 54% yield; uv max (H_2O) 207 mμ (ϵ 23,400), 272 (7080); ir (Nujol) 1616 (C=O of a 2-iodosobenzoic acid),[10] 1523 and 1348 cm^{-1} (NO_2); nmr (DMSO-d_6) AMX system, τ 1.24, 1.38, and 1.85, J_{MX} = 0.5 Hz, J_{AX} = 9 Hz, and J_{AM} = 2.5 Hz; mass spectrum *m/e* (rel intensity) 309 (1), 293 (100), 248 (39), 83 (47), 71 (53), 69 (62) 57 (94), 55 (75), 43 (87), 41 (58).

Anal. Calcd for $C_7H_4NIO_5$: C, 27.18; H, 1.30; N, 4.53; I, 41.08. Found: C, 27.11; H, 1.31; N, 4.37; I, 41.38.

The molecular weight was determined by the iodometric titration method of Twiss and Heinzelmann[11] as 311.6 (calcd for $C_7H_4NIO_5$: 309.0).

The second crop of crystals was identified as 3-nitro-2-iodobenzoic acid and was obtained as pale yellow crystals (0.90 g), mp 174–207° dec (lit.[12] 204–205.5°), in 15% yield: ir (Nujol) 1710 (C=O of acid), 1540 and 1374 cm^{-1} (NO_2); nmr (DMSO-d_6) AMX system, τ 2.09, 2.19, and 2.35, J_{AM} = 2 Hz, J_{AX} = 7 Hz, and J_{MX} = 8 Hz; ir and nmr spectra were essentially identical with those of a sample independently synthesized by a known procedure.[12]

Anal. Calcd for $C_7H_4NIO_4$: C, 28.69; H, 1.37; N, 4.77; I, 43.31. Found: C, 28.67; H, 1.55; N, 4.69; I, 43.43.

5-Nitro-2-Phenyliodoniobenzoate (5, R = NO_2).—5-Nitro-2-iodosobenzoic acid (3.32 g; 10.7 mmol) was dissolved in concentrated sulfuric acid (10 ml) at 0–5° and successively processed with benzene (10 ml), saturated potassium iodide solution (4 ml), and 10 ml of 5 *N* sodium hydroxide solution,[2] to afford a tan precipitate. This was filtered, washed with water, dried, and recrystallized (chloroform–methanol; 30:70 by volume), to afford colorless crystals: mp 220–221° dec; 68% yield; uv max (H_2O) 205 mμ (log ϵ 4.24), 266 (log ϵ 4.02); ir (KBr) 3100 (w), 3050 (w), 1625 (s), 1522 (s), 1400 (m), 1342 (s), 1338 (s), 1005 (m), 990 (m), 817 (m), 735 (s), 721 (s), and 685 cm^{-1} (m); nmr (DMSO-d_6) fine structure for ring hydrogens from τ 1.34 to 3.06; mass spectrum *m/e* 369 (0.2), 205 (7), 204 (100), 78 (5), 77 (84), 76 (6), 75 (6), 74 (7), 51 (29) [lit.[2] uv max (H_2O) 205 mμ (log ϵ 4.43), 266 (log ϵ 4.02); ir (KBr) 3005 (w) 1630 (s), 1524 (s), 1400 (m), 1335 (s), 1005 (w), 995 (w), 817 (m), 738 (s), 720 (s) and 685 cm^{-1} (m); nmr fine structure for ring hydrogens from τ 1.46 to 3.28].

Anal. Calcd for $C_{13}H_8NIO_4$: C, 42.29; H, 2.18; N, 3.80; I, 34.37. Found: C, 42.39; H, 2.22; N, 3.76; I, 34.24.

2-Nitro-9,10-epoxy-9,10-diphenyl-9,10-dihydroanthracene (1, R = NO_2).—To a solution of 1,3-diphenylisobenzofuran (1.35 g; 5 mmol) in refluxing triglyme (38 ml) under nitrogen, was added 5-nitro-2-phenyliodoniobenzoate (3.16 g; 9 mmol) in small portions. After the addition (*ca.* 12 min) the mixture was maintained at reflux for a further 3 min. The majority of the solvent was then removed under reduced pressure (1 mm). Addition of water caused precipitation of a solid (2.80 g), which was chromatographed over Florisil using petroleum ether as eluant to give 2-nitro-9,10-epoxy-9,10-diphenyl-9,10-dihydroanthracene. Recrystallization (benzene–methanol) afforded very pale yellow crystals: mp 189–190°; 54% yield; uv max (95% EtOH) 216 mμ (ϵ 22,900), 244 (9300), 290 (4170); ir (Nujol) 1522 and 1340 cm^{-1} (NO_2); nmr τ 1.94 (d, 1, *J* = 2 Hz), 2.15 (m, 5), 2.60 (m, 9), 3.03 (m, 2); mass spectrum *m/e* 391 (80), 375 (8), 374 (27), 344 (20), 315 (12), 314 (13), 313 (16), 267 (12), 239 (24), 105 (100), 77 (47).

Anal. Calcd for $C_{26}H_{17}NO_3$: C, 79.78; H, 4.38; N, 3.58. Found: C, 79.99; H, 4.34; N, 3.70.

6-Nitro-1,2,3,4-tetraphenylnaphthalene was prepared in 86% yield from 2,3,4,5-tetraphenylcyclopentadienone and 5-nitro-2-phenyliodoniobenzoate by a method analogous to that of Fieser.[7] Recrystallization (chloroform–methanol) yielded yellow crystals: mp 275–277°; uv max (95% EtOH) 208 mμ (ϵ 53,500), 231 (38,000), 279 (29,500); ir (Nujol) 1522 and 1339 cm^{-1} (NO_2); nmr τ 1.35 (d of d, 1, *J* = 0.5, 2.5 Hz), 1.87 (d of d, 1, *J* = 2.5, 8.5 Hz), 2.22 (d of d, 1, *J* = 0.5, 8.5 Hz), 2.75 (m, 10), 3.13 (m, 10); mass spectrum *m/e* 477 (30), 447 (7), 78 (100), 77 (16), 52 (17), 51 (16), 50 (13).

Anal. Calcd for $C_{34}H_{23}NO_2$: C, 85.51; H, 4.85; N, 2.93. Found: C, 85.34; H, 5.10; N, 2.80.

2-Nitrotriptycene.—5-Nitro-2-phenyliodoniobenzoate (1.85 g, 5 mmol) was added to a refluxing solution of anthracene (0.89 g, 5 mmol) in triglyme (10 ml). After 3 min, excess anthracene was removed by addition of maleic anhydride (0.49 g, 5 mmol), refluxing for 5 min, and then adding ethanolic potassium hydroxide. The crystals which appeared upon cooling in an ice bath were filtered, washed with aqueous methanol, and dried to give 2-nitrotriptycene: 43% yield; mp 277–279° (methylene chloride–methanol) (lit.[8] mp 270–271°); ir (Nujol) 1517 and 1340 cm^{-1} (NO_2); nmr τ 1.80 (d, 1, *J* = 2.5 Hz), 2.08 (d of d, 1, *J* = 2.5, 8.5 Hz), 2.57 (m, 5), 2.92 (m, 4), 4.48 (s, 2); mass spectrum *m/e* 299 (100), 282 (18), 254 (11), 253 (60), 252 (100), 251 (17), 250 (27), 127 (12), 126 (24), 124 (16), 113 (13).

Anal. Calcd for $C_{20}H_{13}NO_2$: C, 80.25; H, 4.38; N, 4.68. Found: C, 80.04; H, 4.32; N, 4.93.

2-Phenyliodoniobenzoate (5, R = H).—2-Iodobenzoic acid (10.0 g; 40 mmol) was converted into 2-phenyliodoniobenzoate by the method of Fieser and Haddadin.[7] The betaine was obtained as colorless crystals: mp 226–227° dec (lit.[7] mp 219–220° dec); 78% yield; uv max (H_2O) 207 mμ (ϵ 24,000), 226 (shoulder); ir (KBr) 1610 and 1347 cm^{-1} (C=O of carboxylate anion); nmr (DMSO-d_6) τ 1.86 (m, 3), 2.46 (m, 5), 3.32 (m, 1).

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(8) A synthesis of 2-nitrotriptycene (6.5% yield) *via* a 4-nitrobenzyne-route utilizing the reaction of anthracene and diazotized 4-nitroanthranilic acid, has been previously recorded: C. J. Paget and A. Burger, *J. Org. Chem.*, **30**, 1329 (1965).

(9) Melting points were determined with a Fisher-Johns apparatus and are uncorrected. Infrared spectra were measured on a Perkin-Elmer grating spectrophotometer Model 421. Ultraviolet spectra were recorded using a Perkin-Elmer ultraviolet-visible spectrophotometer Model 202. Nmr spectra were obtained with a Varian A-60 or HR-100 spectrometer. Mass spectra were measured with an AEI MS9 mass spectrometer at an ionizing energy of 70 eV. The microanalyses were performed by the Microanalytical Laboratory, Department of Chemistry, University of Alberta, Alberta, Canada, and by Galbraith Laboratories, Inc., Knoxville, Tenn.

(10) R. Bell and K. J. Morgan, *J. Chem. Soc.*, 1209 (1960).

(11) D. Twiss and R. V. Heinzelmann, *J. Org. Chem.*, **15**, 496 (1950); A. I. Vogel, "Quantitative Inorganic Analysis," John Wiley & Sons, Inc., New York, N. Y., 1961.

(12) P. J. Culhane, in "Organic Syntheses," Coll. Vol. I, A. H. Blatt, Ed., John Wiley & Sons, Inc., New York, N. Y., 1941, p 125.

Anal. Calcd for $C_{13}H_{11}IO_3$: 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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[13] G. Wittig, E. Knauss and K. Niethammer, *Justus Liebigs Ann. Chem.*, **630**, 16 (1960).

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

Edwin M. Kaiser and Robert A. Woodruff[2]

Department of Chemistry, University of Missouri, Columbia, Missouri 65201

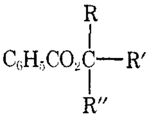
Received July 24, 1969

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).

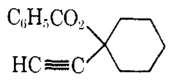
$$\mathrm{ROH} \xrightarrow[\text{THF–hexane}]{n\text{-}C_4H_9Li} \mathrm{ROLi} \xrightarrow[\text{1 hr}]{\text{R'COCl}} \mathrm{R'COOR} + \mathrm{LiCl} \qquad (1)$$

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



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

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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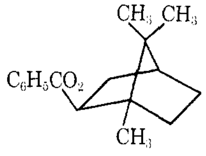

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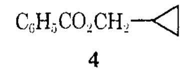

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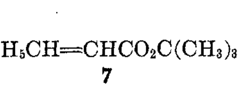

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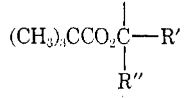

$$(CH_3)_3CCO_2\overset{\displaystyle R}{\underset{\displaystyle R''}{C}}—R'$$

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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[1] Supported by the Petroleum Research Fund, administered by the American Chemical Society, on Grant 959-G.

[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.