Experimental Section

IR spectra were recorded on a Beckman Acculab 3 spectrophotometer, ^1H NMR spectra on a Perkin-Elmer R-24B, and ^{13}C NMR spectra on a JEOL FX60Q instrument. Melting points are corrected and microanalyses were performed by the analytical Department, Bristol Laboratories, Syrause, NY.

General Acid-Catalyzed Transamination Procedure. The Transamination of α-Methylbenzylamine. To a solution of 1.12 g (5 mmol) of 9-fluorenone-1-carboxylic acid (1)[4] and 30 mL of glacial HOAc were added 0.606 g (5 mmol) of (−)-α-methylbenzylamine and 70 mL of toluene. The resultant solution was heated at reflux temperature for 23.5 h under a Soxhlet extraction apparatus filled with molecular sieves (4 Å). A precipitated solid was collected by filtration and recrystallized from either HOAc or methanol to afford essentially pure **3** in 72% yield: mp 255–280 °C dec; IR (Nujol) 3120 (NH_3^+), 1685 (CO_2H), 1590 cm^{-1} (CO_2^-); ^1H NMR (Me_2SO-d_6) δ 9.0 (br, carboxyl H), 7.4-8.3 (m, aromatic H), 5.64 (br, CHN), 1.89 (s, NH_2); ^{13}C NMR (Me_2SO-d_6) 167.71 (CO_2H), 120.64–142.46 (aromatic), 54.22 ppm ($CHNH_2$); mass spectrum (70 eV), *m/e* 225.1 (molecular ion). The acetate salt of **3** was identical with authentic[5] material with respect to its IR, melting point and mixture melting point.

The transamination of optically pure (either enantiomer) α-methylbenzylamine produced a sample of **3** whose optical rotation in several solvents was essentially zero.

After **3** was separated from the reaction mixture, the filtrate was diluted with water and the pH was adjusted from 3.0 to 8.5. The resultant aqueous solution was extracted with EtOAc and the organic extracts (EtOAc and toluene) were washed and dried. Removal of the solvent left an oily residue which contained essentially two components by TLC. The faster of these had an R_f value identical with that of acetophenone. The two components were separated by elution on a silica gel column, using 80% petroleum either (bp 30–60 °C) and 20% EtOAc. The first product eluted was identified as acetophenone (0.36 g, 60%) by its IR spectrum and 2,4-dinitrophenylhydrazone derivative.

Acidification of the above pH 8.5 aqueous solution resulted in the precipitation of 9-fluorenone-1-carboxylic acid (1) and starting material (0.32 g, 28% recovery).

Acid-Catalyzed Transamination of 9-Fluorenone and Benzylamine. To a solution of 0.9 g (5 mmol) of 9-fluorenone and 30 mL of glacial HOAc were added 50 mL of toluene and 0.54 g (5 mmol) of benzylamine. The mixture was heated at reflux temperature for 101 h, after which the volatile components were removed by distillation under reduced pressure. The residual oil crystallized from ethanol to afford 0.11 g (9.9%) of crystals of 9-acetamidofluorene: mp 267–268 °C (lit.[10,11] mp 245–246, 255, 260–261 °C); IR (Nujol) 3280 (NH), 1650 (C=O), 1550 cm^{-1} (amide II); ^1H NMR (Me_2SO-d_6) δ 8.4 (d, NH), 7.2–7.9 (m, aromatic H), 5.95 (d, CH), 1.95 (s, CH_3CO); ^{13}C NMR (Me_2SO-d_6) 170.05 (C=O), 144.86–120.05 (aromatic), 54.09 (CHN), 22.60 ppm (CH_3).

Anal. Calcd for $C_{15}H_{13}NO$: C, 80.69; H, 5.86; N, 6.27. Found: C, 80.44; H, 6.08; N, 6.31.

The filtrate from above was concentrated in vacuo to an oil (1.36 g) which was dissolved in 25 mL of EtOAc and extracted with 3 N HCl (2 × 20 mL). The organic layer was washed with water, dried, and then concentrated on a rotary evaporator at reduced pressure to a partially crystalline oil (0.64 g). According to TLC (70% hexane, 30% benzene), this oil was composed of 9-fluorenone and benzaldehyde. Oxidation with Ag_2O produced 0.05 g of benzoic acid (which indicated an 8.2% yield of benzaldehyde) and 0.3 g of 9-fluorenone (33% recovery).

The aqueous HCl extract from above was adjusted to pH 8.0 with 3 N NaOH and was then extracted with EtOAc (2 × 30 mL). The EtOAc solution was washed and dried and the solvent was removed by distillation at reduced pressure. The residual solid (0.51 g, 56.3% 9-fluorenylamine) was crystallized from hexane: mp 62–63 °C; an *N*-acetyl derivative melted at 253–254 °C (lit.[10,11] mp 64–65 and 255 °C, respectively).

Transamination of 9-Fluorenone-1-carboxylic Acid (1) and L-Alanine in Aqueous Pyridine. A solution of 0.34 g (1.5 mmol) of 1, 0.13 g (1.5 mmol) of L-alanine in 7.5 mL of water, and 22.5 mL of pyridine was heated at reflux temperature for 3 h. A tan precipitate was collected by filtration (0.11 g), mp 217–221 °C. The spectral properties of this product and its *N*-acetate salt and the melting point of the latter (210–211 °C) were identical with those of authentic **3**. The yield was 32%.

The filtrate was diluted with 25 mL of water and the pH was adjusted to 9.0 with 3 N NaOH. This was extracted with EtOAc (2 × 25 mL) and the organic layer was washed with water, dried, and distilled under reduced pressure. The residual oil weighed 0.03 g but could not be identified. It showed only a zone at the origin after TLC using 80% C_6H_6, 15% EtOAc, and 5% HOAc.

The aqueous layer from the above extraction was adjusted to pH 2.0 with 6 N HCl and was then extracted with EtOAc (2 × 30 mL). The EtOAc solution was washed and dried, and the solvent was removed in vacuo to afford a red solid which weighed 0.22 g: mp 193–194 °C [(lit.[4] mp 191–193 °C (for 1)]; TLC, R_f identical with that of 1 (80% C_6H_6, 15% EtOAc, and 5% HOAc). The yield of recovered 9-fluorenone-1-carboxylic acid was 64.7%.

Acknowledgment is made for the generous assistance of Dr. N. E. Heimer, who obtained and helped interpret many of the NMR spectra. Gratitude is also extended to Bristol Laboratories, Syracuse, NY, for all of the microanalyses.

Registry No. 1, 1573-92-8; 2 (R = Ph; Y = H), 100-46-9; (±)-2 (R = Ph; Y = CH_3), 618-36-0; (−)-2 (R = Ph; Y = CH_3), 2627-86-3; 2 (R = $(CH_2)_2CH_3$; Y = H), 109-73-9; 2 (R = CH_2CH_3; Y = H), 107-10-8; 2 (R = Ph; Y = CO_2H), 875-74-1; 2 (R = $(CH_2)_2CO_2H$; Y = CO_2H), 56-86-0; 2 (R = CH_3; Y = CO_2H), 56-41-7; 2 (R = CH_2Ph; Y = CO_2H), 150-30-1; 3, 75031-63-9; 3-acetate salt, 75031-64-0; 4 (R = Ph; Y = H), 100-52-7; 4 (R = CH_3; Y = H), 98-86-2; 2-ethyl-2-hexenal, 645-62-5; 9-fluorenone, 486-25-9; 9-acetamidofluorene, 75031-65-1.

(10) Schmidt, J.; Stutzel, H. *Chem. Ber.* **1908**, *41*, 1243.
(11) Kuhn, R.; Jacob, P. *Chem. Ber.* **1925**, *58*, 1432.

Reaction of Ethyl Cyclopropanecarboxylate with Base[1a]

Harold W. Pinnick,* Yeong-Ho Chang, Scott C. Foster,[1b] and Meledath Govindan

Department of Chemistry, University of Georgia, Athens, Georgia 30602

Received October 26, 1979

Ethyl cyclopropanecarboxylate reacts with strong base to give a self-condensation product involving 3 mol of the ester. Some chemistry of this new compound is described.

The carbonyl group renders α hydrogens acidic.[2] Deprotonation with a strong base gives a carbanion which allows the formation of bonds by alkylation, acylation, and condensation.[2] We here report our results in attempting to functionalize the α position of ethyl cyclopropanecarboxylate as the initial step in a convergent synthesis of pyrrolizidine alkaloids.[3]

Methyl cyclopropanecarboxylate reportedly is deprotonated by lithium diisopropylamide (LDA) in tetrahydrofuran (THF) at −78 °C to give a mixture of *O*- and *C*-trimethylsilyl derivatives in 10% and 40% yields, respectively, after quenching with chlorotrimethylsilane (Me_3SiCl).[4] Nevertheless, sequential mixing of LDA, ethyl

(1) (a) Presented at the 31st Southeastern Regional Meeting of the American Chemical Society, Oct 24–26, 1979, Roanoke, VA. (b) Undergraduate research participant.
(2) House, H. O. "Modern Synthetic Reactions", 2nd ed.; W. A. Benjamin: Menlo Park, CA; 1972, Chapter 9.
(3) Pinnick, H. W.; Chang, Y.-H. *Tetrahedron Lett.* **1979**, 837.
(4) (a) Ainsworth, C.; Chen, F.; Kuo, Y.-N. *J. Organomet. Chem.* **1972**, *46*, 59. (b) Ainsworth reported a 50% yield of distilled Me_3Si derivatives of the ester. Under their conditions, we obtained a nearly 1:1 mixture of Me_3Si compounds and the new material. The latter will not distill, so its presence could have been overlooked very easily.

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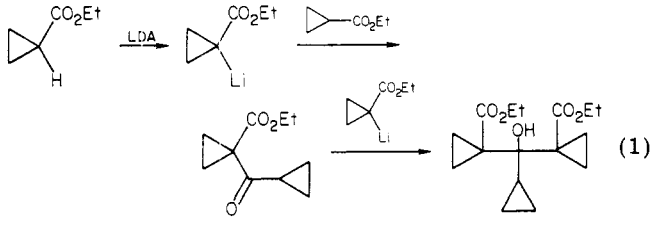
cyclopropanecarboxylate, and Me_3SiCl at −78 °C followed by quenching at −78 °C resulted in no Me_3Si incorporation. Instead, a new compound is formed. If these reagents are mixed at −78 °C and then allowed to warm to room temperature before the workup,[4a] the same new product is obtained as well as the Me_3Si derivatives.[4b] The new compound is formed by either of these procedures if the Me_3SiCl is left out.

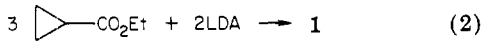
On the basis of elemental analysis and spectral data (see Experimental Section), the new compound is assigned structure 1. It apparently is formed by the two-step Claisen–aldol sequence shown in eq 1. The yield is 87%



(1)

1

(60% of analytically pure material) and is the same if 1.0 or 0.7 equiv of LDA is used; however, 1/3 equiv of LDA gives a 47% yield (90% conversion) of the diester 1. Since lithium ethoxide has no effect on ethyl cyclopropanecarboxylate, the stoichiometry of the reaction is confirmed as that shown in eq 2 and is consistent with the sequence

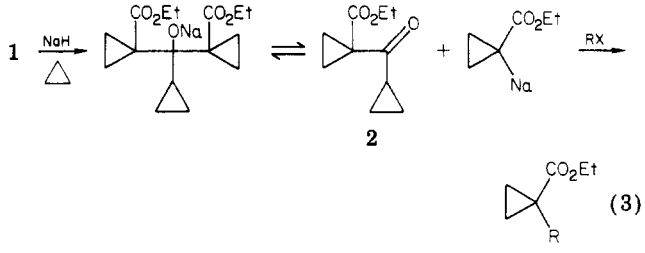


(2)

proposed in eq 1. These results indicate that the anion of ethyl cyclopropanecarboxylate is formed by the action of LDA on the cyclopropyl ester but that the anion is very reactive. This makes sense because of the low acidity of a cyclopropyl methine adjacent to a carbonyl.[5-8]

Other bases also fail to generate a useful concentration of the anion of ethyl cyclopropanecarboxylate.[9] Tritylithium has been used for anion generation where LDA has failed,[10] but when tritylithium and the cyclopropyl ester were combined, only the diester 1 was obtained after quenching with acetic acid-d_1. Another base which has been used to generate even aldehyde enolates without condensation is potassium hydride.[11] Even though gas was evolved and a yellow-brown color developed when ethyl cyclopropanecarboxylate was added to potassium hydride in THF, the resulting reaction mixture gave neither the self-condensation product 1 nor the expected trapping product when quenched with Me_3SiCl, acetic acid-d_1, methyl iodide, benzyl bromide, allyl bromide, benzaldehyde, or methyl benzoate.

One final attempt to trap the anion of ethyl cyclopropanecarboxylate was made by stirring the diester 1 with sodium hydride in the presence of methyl iodide, allyl bromide, or benzyl bromide. It was hoped that the elusive anion would be formed reversibly and then trapped irreversibly (eq 3). Unfortunately, only the keto ester 2 and ethyl cyclopropanecarboxylate were isolated in addition to recovered diester 1.



(3)

Carboxylic acids have been functionalized at the α position via the corresponding dianions.[12] Consequently, cyclopropanecarboxylic acid was allowed to stir with 2.2 equiv of LDA in THF. A variety of trapping agents (acetic acid-d_1, deuterium oxide, benzyl bromide, and methyl iodide) failed to react.[13]

Another synthetic equivalent of the desired ester anion is the anion of cyclopropanecarbonitrile. Walborsky has reported successful H–D exchange as well as methylation of 2,2-diphenylcyclopropanecarbonitrile.[14] When stirred with potassium hydride in THF, cyclopropanecarbonitrile gives a bright yellow solution and gas evolution; however, allyl bromide, benzaldehyde, and methyl benzoate fail to give any of the expected trapping product.[15]

With the diester 1 in hand, we explored some of its chemistry. The hydroxyl group is very unreactive. Attempted acetylation with acetic anhydride and triethylamine even in the presence of 4-(dimethylamino)pyridine[16] in either refluxing THF or benzene for 2 days failed (no reaction). Base-catalyzed ether formation was tried without success (eq 3), and reaction with excess ethanol and catalytic *p*-toluenesulfonic acid in refluxing benzene, toluene, or xylene also failed to convert the alcohol 1 into an ether. When the diester 1 was stirred in THF with excess lithium aluminum hydride (LAH) for 5 days, the expected triol 3 was formed in 94% yield (eq 4). Saponification occurred after 2 days with refluxing aqueous potassium hydroxide (eq 5). The resulting diacid 4 would

(5) The rate of H–D exchange in isopropyl ketones is much greater than that in analogous cyclopropyl ketones: (a) Rappe, C.; Sachs, W. H. *Tetrahedron* **1968**, *24*, 6287; (b) Amburn, H. W.; Kauffman, K. C.; Shechter, H. *J. Am. Chem. Soc.* **1969**, *91*, 530.

(6) Calculations show that there is a significant barrier to inversion in cyclopropyl anions, so resonance stabilization by an adjacent carbonyl is low: (a) Clark, D. T.; Armstrong, D. R. *J. Chem. Soc. D* **1969**, 850; (b) Tyrrell, J.; Kolb, V. M.; Meyers, C. Y. *J. Am. Chem. Soc.* **1979**, *101*, 3497.

(7) Numerous examples show that cyclopropyl esters avoid anion formation. For example, methyl *cis*-bicyclo[6.1.0]nona-2,4,6-triene-*anti*-9-carboxylate loses the proton at C-1 when reacted with LDA: Boche, G.; Martens, D. *Chem. Ber.* **1979**, *112*, 175. Ethyl 2-methyl-2-nitrocyclopropanecarboxylate gives ethyl 2-methylenecyclopropanecarboxylate when treated with sodium hydride: Russell, G. A.; Makosza M.; Hershberger, J. *J. Org. Chem.* **1979**, *44*, 1195. In addition, a sugar derivative containing an ethyl cyclopropanecarboxylate moiety could not be methylated: Fitzsimmons, B. J.; Fraser-Reid, B. *J. Am. Chem. Soc.* **1979**, *101*, 6123.

(8) Cyclopropanecarboxaldehyde gives only Cannizzaro reaction products when allowed to react with base. Cyclobutanecarboxaldehyde undergoes base-catalyzed aldol condensation followed by other reactions. This difference reflects the low acidity of cyclopropanecarboxaldehyde relative to the cyclobutyl analogue. See: Van der Maeden, F. P. B.; Steinberg, H.; DeBoer, T. J. *Recl. Trav. Chim. Pays-Bas* **1972**, *91*, 221; *Tetrahedron Lett.* **1967**, 4521.

(9) Ethyl cyclopropanecarboxylate reacts with sodium amide or tritylsodium to give products derived from 1,2-addition: Piehl, F. J.; Brown, W. G. *J. Am. Chem. Soc.* **1953**, *75*, 5023.

(10) For example, in the methylation of (carbomethoxy)cyclopentene: Cargill, R. L.; Bushney, D. F.; Good, J. J. *J. Org. Chem.* **1979**, *44*, 300.

(11) Groenewegen, P.; Kallenberg, H.; van der Gen, A. *Tetrahedron Lett.* **1978**, 491.

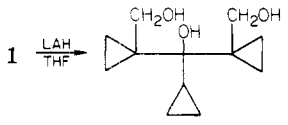
(12) (a) Creger, P. L. *J. Org. Chem.* **1972**, *37*, 1907 and references cited therein. (b) Krapcho, A. P.; Cashdan, D. S.; Jahngen, E. G. E. *Ibid.* **1977**, *42*, 1189; (c) Ada, W.; Encarnacion, L. A.; Fick, H.-H. *Synthesis* **1978**, 828.

(13) Me_3SiCl reportedly traps the dianion of cyclopropanecarboxylic acid at 0 °C: Ainsworth, C.; Kuo, Y. N. *J. Organomet. Chem.* **1973**, *47*, 73.

(14) (a) Walborsky, H. M.; Motes, J. M. *J. Am. Chem. Soc.* **1970**, *92*, 2445. (b) Walborsky, H. M.; Hornyak, F. M. *Ibid.* **1955**, *77*, 6026.

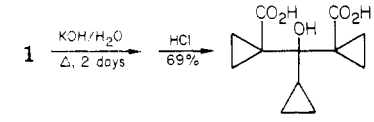
(15) Addition of cyclopropanecarbonitrile to LDA in THF at −78 °C followed by allyl bromide gave, after the mixture warmed to room temperature, the expected allyl nitrile. We are currently examining the reactivity of this anion.

(16) (a) Hassner, A.; Krepski, A.; Alexanian, V. *Tetrahedron* **1978**, *34*, 2069. (b) Hofle, G.; Steglich, W.; Vorbruggen, H. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 569.



(4)

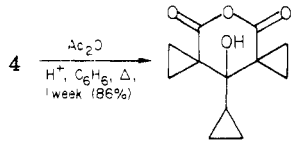
3



(5)

4

not yield the corresponding anhydride by azeotropic removal of water (catalytic *p*-toluenesulfonic acid in refluxing benzene); however, acetic anhydride in refluxing benzene with acid catalysis for 1 week sucessfully gave the desired anhydride **5** (eq 6).



(6)

5

In conclusion, the base-catalyzed condensation of ethyl cyclopropanecarboxylate allows simple entry into tricyclopropyl compounds. The difficulty in generating the anion of cyclopropyl esters, acids, and nitriles can be attributed to lower acidity as well as abnormally high reactivity of the anion[17] because of little resonance stabilization.[18]

Experimental Section

Melting points were determined on a Thomas-Hoover apparatus and are uncorrected. All reactions involving strong bases (LDA, trityllithium, or KH) were run under nitrogen in glassware which was flamed out. Tetrahydrofuran was distilled from potassium. Microanalyses were performed by Atlantic Microlab. Infrared spectra were obtained on Perkin-Elmer Models 237B, 257, and 297 spectrometers. Proton NMR spectra were determined on a Varian T-60 and EM-390 spectrometers. Hydrogen-decoupled ^{13}C NMR spectra were recorded on a JEOL PFT-100 spectrometer. Mass spectra were obtained on a Hewlett-Packard Model 5992-B GC/MS.

Preparation of Diester 1. Diisopropylamine (14.6 mL, 104 mmol) was dissolved in 60 mL of THF and the solution cooled to 0 °C. A solution of *n*-butyllithium/hexane (38.3 mL of 2.5 M solution, 96 mmol) was added, and the reaction mixture was stirred for 30 min and cooled to −78 °C. Ethyl cyclopropanecarboxylate (18.2 g, 160 mmol) in 30 mL of THF was added dropwise over 15 min, and the resulting solution was stirred for 30 min at −78 °C and allowed to warm to room temperature over 1 h. The reaction mixture was poured into 100 mL of saturated aqueous NaCl, and this was extracted with three 50-mL portions of ether which were combined, dried over $MgSO_4$, and concentrated to give 13.8 g (87%) of crude product. Recrystallization from hexane gave 9.5 g (60%) of pure crystals: mp 36–37 °C; ^1H NMR (CCl_4) 0.2–0.6 (m, 5 H), 0.6–1.6 (m, 8 H), 1.25 (t, J = 7 Hz, 6 H), 2.1 (s, 1 H), 4.2 (q, J = 7 Hz, 4 H); ^{13}C NMR ($CDCl_3$)[19] δ −0.67 (t, CH_2), 11.64 (t, CH_2), 14.08 (q, CH_3), 14.26 (d, CH), 32.80 (s, C), 60.60 (t, CH_2), 69.86 (s, C), 174.28 (s, C); IR (KBr) 3420, 3100, 3000, 1710, 1360, 1295, 1130, 1000 cm^{-1}; mass spectrum, *m/e* 280, 265, 251, 223, 197, 177.

Anal. Calcd for $C_{16}H_{24}O_5$: C, 64.84; H, 8.16. Found: C, 64.88; H, 8.20.

Reduction of Diester 1 to Triol 3. Lithium aluminum hydride (0.23 g, 6.0 mmol) was added to 50 mL of THF under N_2 at −78 °C, and 1.48 g (5.00 mmol) of diester **1** in 10 mL of THF was added dropwise. The reaction mixture was allowed to warm to room temperature and to stir for 5 days. Excess hydride reagent was quenched with methanol, and 1 mL of saturated aqueous Na_2SO_4 was added. This mixture was stirred for 10 min, anhydrous $MgSO_4$ was added, and the crude triol was isolated after filtration and concentration. Recrystallization from hexane/ether gave 1.00 g (94%) of the triol after drying under vacuum; mp 69–70 °C.

Anal. Calcd for $C_{12}H_{20}O_3$: C, 67.89; H, 9.50. Found: C, 65.20; H, 9.05. Calcd for $C_{12}H_{20}O_3 \cdot {}^1/_2H_2O$: C, 65.10; H, 9.57.

The sample was dried at 60 °C under vacuum overnight: mp 82–83 °C; ^1H NMR ($CDCl_3$, 90 MHz) δ 0.1–0.6 (m, 8 H), 0.7–1.4 (m, 5 H), 2.4 (br s, 3 H), 3.4 (d, J = 12 Hz, 2 H), 4.0 (d, J = 12 Hz, 2 H); IR (KBr) 3300, 3000, 1420, 1020, 990, 930 cm^{-1}.

Anal. Calcd for $C_{12}H_{20}O_3$: C, 67.89; H, 9.50. Found: C, 67.91; H, 9.52.

Preparation of Diacid 4. The diester **1** (1.48 g, 5.00 mmol) and potassium hydroxide (2.0 g, 36 mmol) in 45 mL of water were refluxed for 24 h and then cooled. Dilute HCl was added until the pH was 3, and the mixture was filtered. The crude solid was recrystallized from acetone/hexane to give 0.85 g (71%) of crystalline product: mp 160–163 °C; ^1H NMR (acetone-d_6, 90 MHz) −0.5–0.0 (m, 3 H), 0.1–1.0 (m, 10 H), 6.0 (br s, 3 H); IR (KBr) 3500, 2400–3300, 1680, 1420, 1310, 1195, 1030 cm^{-1}.

This diacid (72 mg, 0.30 mmol) was stirred with 38 mg (1.0 mmol) of LAH in 25 mL of THF for 2 days at room temperature. Workup as usual for the LAH reductions gave 50 mg (0.23 mmol, 77%) of material identical by ^1H NMR and TLC with the triol **3**.

Preparation of Anhydride 5. The diacid **4** (0.400 g, 1.67 mmol) was combined with acetic anhydride (0.51 g, 5.0 mmol) and *p*-toluenesulfonic acid (20 mg) in 50 mL of benzene, and the resulting solution was refluxed for 24 h and then cooled. Ammonia was bubbled through the reaction mixture until no more precipitate was formed. This was filtered, and the filtrate was concentrated to give 0.32 g (86%) of crystalline product: mp 84–88 °C; ^1H NMR (acetone-d_6) 0.4–0.7 (m, 5 H), 1.2–1.7 (m, 8 H), 3.7 (s, 1 H); IR (KBr) 3420, 3000, 1780, 1735, 1380, 1340, 1260, 1085, 1065, 1010 cm^{-1}.

Acknowledgment. We thank Dr. Stanford Smith and W. J. Layton for their assistance with the ^{13}C NMR spectra.

Registry No. **1**, 74808-31-4; **3**, 74808-32-5; **4**, 74808-33-6; **5**, 74824-37-6; ethyl cyclopropanecarboxylate, 4606-07-9; acetic anhydride, 108-24-7.

(17) Ester enolates are known to undergo self-condensation at room temperature: Sullivan, D. F.; Woodbury, R. P.; Rathke, M. W. *J. Org. Chem.* **1977**, *42*, 2038.

(18) The *tert*-butyl ester of cyclopropanecarboxylic acid was allowed to react with LDA (1.1 equiv) at −78 °C, quenched with allyl bromide (2.5 equiv), and allowed to warm to room temperature. No alkylation was observed, and the starting material was recovered.

(19) Multiplicities were determined from an off-resonance-decoupled (ORD) spectrum.

Synthesis of 8-Fluoro- and 10-Fluoro-3-methylcholanthrenes. Observations on the Elbs Reaction[1]

Melvin S. Newman* and Vinod K. Khanna[2]

Department of Chemistry, The Ohio State University, Columbus, Ohio 43210

Received May 6, 1980

The carcinogenic hydrocarbon 3-methylcholanthrene, **1**, has best been synthesized by means of the Elbs reaction,[3] a ring closure reaction which involves pyrolysis of 7-methyl-4-(1-naphthoyl)hydrindene, **2**, at temperatures near 400 °C. Recently we have become interested in

(1) This work was supported by Grant No. CA07394 from the NCI, department of HEW.

(2) Postdoctoral research associate.

(3) See Fieser, L. F. *Org. React.* **1942**, *1*, 129.

0022-3263/80/1945-4507$01.00/0