thin layer chromatography on silica gel. The results are summarized in Table VI. The compounds were characterized by their NMR spectra (Table VII).

Spectroscopic Data. The infrared spectra were recorded in dilute solutions employing cells of different path length on a Perkin-Elmer Model 283 instrument.

The NMR spectra were recorded on the Chicago 350-MHz and the Bruker 270-MHz instruments. The low-temperature spectra were recorded reproducibly over the broad temperature ranges. In all these experiments, tetramethylsilane was employed as an internal standard to ensure that the line broadening observations were not the consequence of field inhomogeneity or solvent viscosity effects.

The rotation rate, k_r, and the rotational free-energy barriers were calculated in the customary way at the coalescence temperature.

Acknowledgment. This investigation was supported by Grant No. 1-R01-CA-20049 awarded by the National Cancer Institute, DHEW, and by the Illinois Division of the American Chemical Society. The research was also supported by the NMR Special Facility Grant, CA 14599.

Registry No. $C_6H_5NHCONH_2$, 64-10-8; $(CH_3)_2CHNHCONH_2$, 691-60-1; $(CH_3)_3CNHCONH_2$, 1118-12-3; c-$C_5H_{10}NCONH_2$, 2158-03-4; $C_6H_5NHCONHCH_3$, 1007-36-9; $CH_3NHCONHCH_2CH_3$, 28145-10-0; $CH_3NHCONHC(CH_3)_3$, 25347-94-8; $CH_3NHCONHCH(CH_3)_2$, 38014-53-8; $CH_3NHCONH(c\text{-}C_6H_{11})$, 39804-96-1; $CH_3NHCONHCH_2CH_2CH_3$, 38014-52-7; $CH_3NHCONHCH(CH_3)CH_2CH_3$, 38014-55-0; $CH_3NHCONHCH_2CH(CH_3)_2$, 38014-54-9; $CH_3NHCON(CH_3)_2$, 632-14-4; $CH_3NHCON(CH_2CH_3)_2$, 39499-81-5; $CH_3NHCON(CH(CH_3)_2)_2$, 57883-81-5; $CH_3NHCONC_5H_{10}$-c, 36879-48-8; $CH_3NHCONC_4H_8$-c, 36879-46-6; $CH_3NHCON(CH_2CH_2CH_2CH_3)_2$, 21260-54-8; $CH_3NHCON(CH_2CH_2CH_3)_2$, 36614-21-8; $CH_3NHCON(CH_2CH(CH_3)_2)_2$, 72479-12-0; $CH_3N(NO)CONH_2$, 684-93-5; $CH_3CH_2N(NO)CONH_2$, 759-73-9; $C_6H_5N(NO)CONH_2$, 6268-32-2; $CH_3N(NO)CONHCH_3$, 13256-32-1; $CH_3N(NO)CONHCH_2CH_3$, 72479-13-1; $CH_3N(NO)CONHC(CH_3)_3$, 72479-14-2; $CH_3N(NO)CONHCH(CH_3)_2$, 72479-15-3; $CH_3N(NO)CONH(c\text{-}C_6H_{11})$, 16813-38-0; $CH_3N(NO)CONHCH_2CH_2CH_3$, 72479-16-4; $CH_3N(NO)CONHCH(CH_3)CH_2CH_3$, 72479-17-5; $CH_3N(NO)CONHCH_2CH(CH_3)_2$, 72479-18-6; $CH_3N(NO)CONHC_6H_5$, 21561-99-9; $CH_3N(NO)CON(CH_3)_2$, 3475-63-6; $CH_3N(NO)CON(CH_2CH_3)_2$, 50285-72-8; $CH_3N(NO)CON(CH(CH_3)_2)_2$, 72479-19-7; $CH_3N(NO)CONC_5H_{10}$-c, 72479-20-0; $CH_3N(NO)CONC_4H_8$-c, 67084-42-8; $CH_3N(NO)CON(CH_2CH_2CH_2CH_3)_2$, 72479-21-1; $CH_3N(NO)CON(CH_2CH(CH_3)_2)_2$, 72479-22-2; $CH_3N(NO)CON(CH_2CH_2CH_3)_2$, 72479-19-7; $CH_3NHCON(NO)CH_2CH_3$, 72479-23-3; $CH_3NHCON(NO)CH_2CH_2CH_3$, 72479-24-4; $CH_3NHCON(NO)CH_2CH(CH_3)_2$, 72479-25-5; $(CH_3)_2CHN(NO)CONH_2$, 16830-14-1; methyl isocyanate, 624-83-9.

Competitive [1,3]- and [3,3]-Sigmatropic Rearrangements

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Several cases of the oxy-Cope rearrangement, which typically prefers the [3,3]-sigmatropic route, are now known to occur in a [1,3]-sigmatropic fashion. By contrast, the symmetry-allowed thermal rearrangement of carbanions (or their enol derivatives; e.g., trialkylsilyl) derived from allylic esters occurs exclusively in a [3,3]-sigmatropic manner. However, the corresponding anions derived from benzyl esters, for which the [3,3]-sigmatropic path is energetically unfavorable, rearrange by a [1,3]-sigmatropic mechanism. We report the first two examples of this rearrangement.

The oxy-Cope isomerization, whose rate can be markedly affected by the experimental conditions employed,[1-3] proceeds, typically, via a [3,3]-sigmatropic rearrangement. However, in certain systems, and especially those involving medium-sized rings,[2] the reaction can occur, overwhelmingly, via a [1,3]-sigmatropic rearrangement.

In selected cases involving other reactions, substantial loss of π-electron delocalization, which is a requirement when cinnamyl systems undergo a [3,3]-sigmatropic rearrangement, can favor the [1,3] isomerization. For example, cinnamyl thiocyanate, when heated, is converted into cinnamyl isothiocyanate.[4]

By contrast, the large number of symmetry-allowed thermal rearrangements of allylic ester enolates which have been reported since the first examples were described over 30 years ago[5] occur exclusively in a [3,3]-sigmatropic manner. Even with the enolates derived from cinnamyl isobutyrate (**1a**), no [1,3]-sigmatropic shift is observed.[6] We have confirmed this result and, as expected, have demonstrated that the isomeric transformation **1b** → **2b** proceeds readily.

On the assumption that the transition state for the conversion **1** → **2** is more polar than **1**, we have explored a variety of experimental conditions designed to facilitate the process. During fixed intervals of time and temperature and by use of the lithium enolate, the silyloxy derivative,[7] or the corresponding enol diethyl phosphate, the amounts of **3a** and **3b** isolated fell within the range of 35–55%. However, under like conditions of time and temperature, the addition of moderate amounts of nitrobenzene (μ = 4.0) to the system resulted in yields of **3a** and **3b** of 75 and 71%, respectively.

It is, in fact, the dependable regiospecificity of the allylic ester enolate rearrangement that has made it such a valuable tool in the synthesis of complex natural products.[8,9]

(1) D. A. Evans and A. M. Golob, *J. Am. Chem. Soc.*, **97**, 4765 (1975).
(2) R. W. Thies and E. P. Seitz, *J. Org. Chem.*, **43**, 1050 (1978).
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(4) E. Bergmann, *J. Chem. Soc.*, 1361 (1935).
(5) R. T. Arnold and S. Searles, Jr., *J. Am. Chem. Soc.*, **71**, 1150 (1949). See G. Bennett, *Synthesis*, 589 (1977), for a review.
(6) R. Malzieu [*Bull. Soc. Chim. Fr.*, 879 (1976)] first reported the rearrangement of cinnamyl isobutyrate using sodium hydride in boiling toluene. Our sample was identical with one (mp 85–86 °C) graciously provided by R. R. Covington, Mead Johnson and Company, which he obtained by using lithium amide in dry toluene for the rearrangement.
(7) R. E. Ireland, R. H. Mueller, and A. K. Willard, *J. Org. Chem.*, **41**, 986 (1976).
(8) G. Fráter, *Helv. Chim. Acta*, **58**, 442 (1975).

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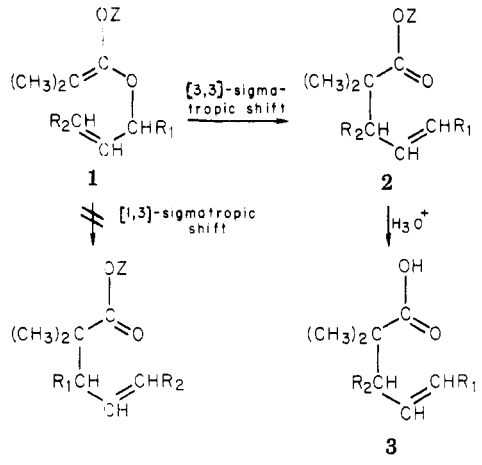
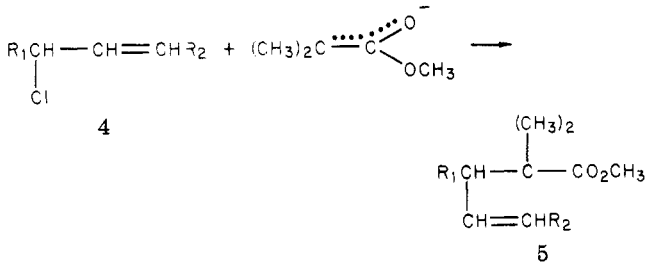


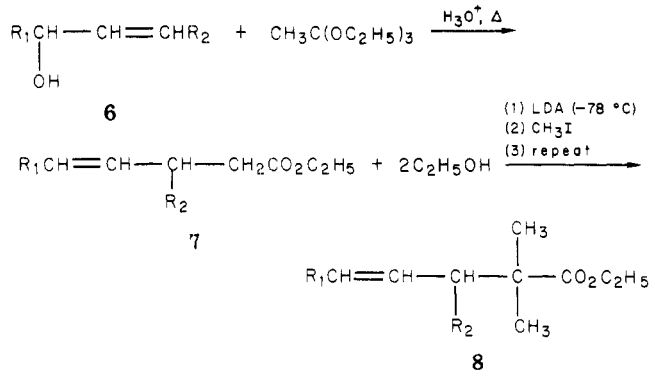
a, R_1 = H; R_2 = C_6H_5
b, R_1 = C_6H_5; R_2 = H
Z = (-), $Si(CH_3)_3$, or $OP(O)(OC_2H_5)_2$

As we earlier anticipated,[10] it is not possible to prepare, in pure form, the esters corresponding to **3a** and **3b** by classical alkylation reactions. For example, the direct alkylation of the carbanion derived from methyl isobutyrate with either of the allylic chlorides **4a** or **4b** leads to **5a** as the sole product.



a, R_1 = H; R_2 = C_6H_5
b, R_1 = C_6H_5; R_2 = H

The structures assigned to **3a** and **3b** are based on their NMR spectra. Independent confirmation came from a comparison of these with the spectra of the corresponding ethyl esters **8a** and **8b** which were synthesized by methylating the intermediates **7a** and **7b** derived from the olefinic ketal Claisen rearrangement.[11]

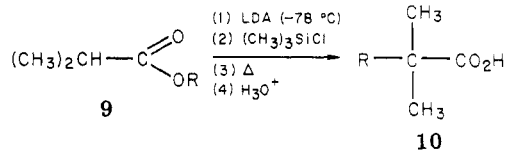


a, R_1 = H; R_2 = C_6H_5
b, R_1 = C_6H_5; R_2 = H

In discussions of nucleophilic substitution, allylic and benzylic derivatives are usually placed in the same general category. In reactions involving [3,3]-sigmatropic rearrangements, however, the two groups behave quite differently because of the reluctance of the benzyl moiety to undergo such transformations.

Enolates derived from hindered benzyl esters, which cannot undergo a facile Claisen condensation, should, therefore, either be relatively stable or undergo a [1,3]-sigmatropic rearrangement.

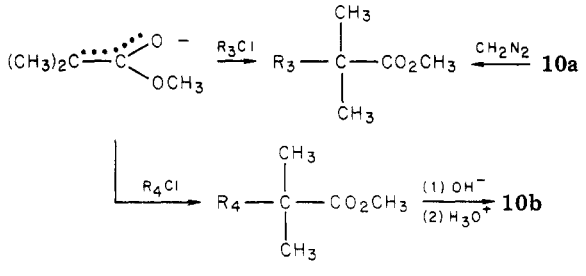
We report here the first two examples of the latter type. Under experimental conditions which lead solely to [3,3]-sigmatropic rearrangements with allylic esters, benzyl isobutyrate (**9a**) and 1-naphthylmethyl isobutyrate (**9b**) rearrange in a [1,3]-sigmatropic fashion to form (after acidification) the carboxylic acids **10a** and **10b**, respectively.



a, R = $C_6H_5CH_2$
b, R = 1-$C_{10}H_7CH_2$

The transformation **9b** → **10b** seems particularly significant, because the increased double bond character at the 1,2 position in the naphthalene moiety should allow for increased delocalization and favor some [3,3]-sigmatropic rearrangement. No such products, however, were observed.

The structures of **10a** and **10b**, assigned on the basis of their NMR spectra, were confirmed chemically as shown below.



R_3 = $C_6H_5CH_2$
R_4 = 1-$C_{10}H_7CH_2$

If these [1,3]-sigmatropic rearrangements are concerted, they should proceed with inversion of configuration at the benzyl carbon atom.[12] If, however, rearrangement occurs by way of dissociation to an ion pair followed by recombination,[13] extensive racemization of an appropriately substituted chiral molecule would be anticipated. Studies directed to this problem are under investigation.

Experimental Section

General Procedures. Tetrahydrofuran, nitrobenzene, and diisopropylamine were purified by standard methods and stored over appropriate drying agents. Trimethylsilyl chloride (Matheson, Coleman and Bell) was distilled and stored over molecular sieves. Diethyl chlorophosphate (Aldrich), benzyl isobutyrate (Matheson, Coleman and Bell), 1-chloromethylnaphthalene, and *n*-BuLi (1.6 M solution in hexane; Aldrich) were used without further purification. Lithium diisopropylamide[14] and cinnamyl isobutyrate[15] were prepared by standard methods. 1-Phenyl-2-

(9) W. C. Still and M. J. Schneider, *J. Am. Chem. Soc.*, **99**, 948 (1977).
(10) S. T. Kulenović and R. T. Arnold, *Croat. Chem. Acta*, **52**, 299 (1979).
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propenyl isobutyrate was prepared by the reaction of 1-phenyl-2-propen-1-ol with *n*-BuLi followed by addition of isobutyryl chloride.[10] Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. NMR spectra were recorded on a Varian A-56/60 spectrometer, and all chemical shifts are given in parts per million downfield from tetramethylsilane (δ scale). IR spectra were recorded as liquid films on sodium chloride plates with a Beckman IR-5A spectrophotometer.

2,2-Dimethyl-3-phenyl-4-pentenoic Acid (3a). A solution of cinnamyl isobutyrate (2.04 g, 10 mmol) in THF (5 mL) was added, dropwise and with stirring, to a solution of lithium diisopropylamide (12 mmol) in THF (2.8 mL) at −78 °C and under argon. The reaction mixture was stirred for 30–40 min at −78 °C. Nitrobenzene (15 mL) was added, and the stirred solution was allowed to warm to 70 °C over a period of 45 min and maintained at this temperature for 2 h. The solution was cooled to 25 °C, cold sodium hydroxide (50 mL, 5%) was added, and the layers were separated. The aqueous layer was extracted with ether (2 × 20 mL), cooled to 0 °C, and acidified with HCl (2 M). The acidic mixture was extracted with ether (3 × 30 mL) and dried ($MgSO_4$) and the solvent removed on a rotary evaporator to give a light-brown crystalline product (1.53 g, 75%) whose NMR was indistinguishable from the pure acid (1.4 g, 68.6%) obtained by recrystallization from ligroin: mp 85–86 °C (lit.[6] 88 °C); NMR ($CDCl_3$) δ 1.15 (d, 6 H), 3.62 (d, 1 H), 5.01 (m, 1 H), 5.25 (m, 1 H), 6.27 (m, 1 H), 7.24 (s, broad, 5 H), and 11.54 (s, 1 H).

When nitrobenzene was eliminated in the above experiment, only 0.7 g (34%) of **3a** was obtained plus 0.8 g of unreacted ester. When the intermediate carbanion **1a** was converted to its trimethylsilyloxy or diethyl phosphate derivative before rearrangement, the amounts of **3a** (plus some unreacted ester) isolated were 0.71 g (35%) and 0.72 g (36%), respectively.

2,2-Dimethyl-5-phenyl-4-pentenoic Acid (3b). In a manner similar to that described for **3a**, 1-phenyl-2-propenyl isobutyrate[10] (1.02 g, 5 mmol) in dry THF (3 mL) was added, dropwise and with stirring, to a solution of lithium diisopropylamide (6 mmol) in THF (1.4 mL) at −78 °C and under argon. The solution was stirred for 30–40 min at −78 °C, nitrobenzene (10 mL) was added, and the mixture was allowed to warm to 70 °C over a period of 45 min. Heating at 70 °C was continued for 3 h, and the light-brown crystalline acid **3b** isolated as described for **3a** (0.72 g, 71%). Its NMR was indistinguishable from that of the pure acid. Recrystallization from ligroin gave the pure, white acid (0.65 g, 64%): mp 103–104 °C (lit.[16] 104 °C); NMR ($CDCl_3$) δ 1.23 (s, 6 H), 2.44 (d, 2 H), 6.20 (m, 2 H), 7.23 (m, 5 H), and 11.79 (s, 1 H).

When nitrobenzene was eliminated from the above experiment, only 0.56 g (55%) of **3b** was obtained. When the intermediate carbanion ion **1b** was converted to its trimethylsilyloxy or diethyl phosphate derivative prior to rearrangement, the amounts of **3b** (plus some unreacted ester) isolated were 0.5 g (49%) and 0.49 g (48%), respectively.

Ethyl 3-Phenyl-4-pentenoate (7a). A solution of cinnamyl alcohol (13.42 g, 100 mmol), triethyl orthoacetate (113.6 g, 700 mmol), and propionic acid (0.05 g, 6.7 mmol) was stirred for 6 h at 138 °C with continuous distillative removal of ethanol. The reaction mixture was cooled and the solvent evaporated under reduced pressure (vacuum pump, 1 mm) to give a light-yellow crude product (19.81 g, 97%) whose NMR spectrum was indistinguishable from that of the pure product. Distillation gave the pure colorless ester (18.40 g, 90.1%): bp 84 °C (0.75 mm); IR (neat film) (cm^{-1}) 1735 (C=O), 1638 and 1603 (C=C), 1494, 1452, and 1372 (C=C, aromatic), 1257 and 1165 (C—O), 1033 (trans CH=CH), 919 (CH_2=CH, out of plane bending), 756 and 699 (CH, aromatic, out of plane bending); NMR ($CDCl_3$) δ 1.02 (t, 3 H), 2.67 (d, 2 H), 4.01 (quartet, 2 H) overlapping with a multiplet (1 H), 4.90 (m, 1 H), 5.12 (m, 1 H), 5.98 (m, 1 H), and 7.21 (s, broad, 5 H).

Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.31; H, 7.77.

Ethyl 2-Methyl-3-phenyl-4-pentenoate. Ethyl 3-phenyl-4-pentenoate (5.72 g, 28 mmol) was added, dropwise and with stirring, to a solution of lithium diisopropylamide (33.6 mmol) in THF (7.7 mL) at −78 °C and under argon. The reaction mixture was stirred for 40 min, and a solution of methyl iodide (5.56 g, 39.2 mmol) in THF (2 mL) was added dropwise at −78 °C. The light-yellow mixture was allowed to warm to 25 °C and then stirred for 2–3 h. Cold HCl (50 mL, 1 M) was then added, the layers were separated, and the aqueous layer was extracted with ether (3 × 30 mL). The combined organic layers were washed with saturated sodium bicarbonate solution (50 mL) and water (50 mL) and then dried ($MgSO_4$). Evaporation of the solvents on a rotary evaporator gave a yellow oil (5.2 g). Distillation gave the pure ester (4.31 g, 70.5%): bp 65.5 °C (0.05 mm). A very complex NMR spectrum showed clearly the two expected diastereoisomers in unequal quantities: NMR ($CDCl_3$) δ 0.896 (t) and 1.187 (t, 3 H), 1.21 (d, 1 H), 2.74 (quartet), 2.91 (quartet, 1 H), 3.465 (d, broad, 1 H), 3.89 (quartet), 4.16 (quartet, 2 H), 5.12 (m, broad, 2 H), 5.97 (octet), ~6.44 (octet, 1 H), and 7.31 (s, broad, 5 H).

Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 76.82; H, 8.30.

The same procedure using lithium diisopropylamide in THF (7.7 mL) and HMPA (4 mL) gave 5.32 g (87.1%) of the desired ester.

Ethyl 2,2-Dimethyl-3-phenyl-4-pentenoate (8a). Ethyl 2-methyl-3-phenyl-4-pentenoate (3.27 g, 15 mmol) was added, dropwise and with stirring, to a solution of lithium diisopropylamide (18 mmol) in THF (4.1 mL) at −78 °C and under argon. The reaction mixture was stirred for 40 min, and a solution of methyl iodide (2.98 g, 21 mmol) in THF (1 mL) was added dropwise at −78 °C. The light-yellow mixture was allowed to warm to 25 °C and then stirred for 6 h. Cold HCl (30 mL, 1 M) was then added, the layers were separated, and the aqueous layer was extracted with ether (3 × 20 mL). The combined organic layers were washed with saturated sodium bicarbonate solution (30 mL) and water (30 mL) and then dried ($MgSO_4$). Evaporation of the solvents on a rotary evaporator gave a yellow oil (3.2 g) whose NMR spectrum indicated the presence of **8a** and some starting material (5–10%). The crude product was purified on a column of alumina (hexane as a solvent) to give the pure colorless ester (2.79 g, 80%): bp 67 °C (0.05 mm); NMR ($CDCl_3$) δ 1.07 (t, 3 H), 1.14 (d, 6 H), 3.62 (d, 1 H), 3.99 (quartet, 2 H), 4.94 (m, 1 H), 5.18 (m, 1 H), 6.27 (m, 1 H) and 7.19 (s, broad, 5 H). The product was rechromatographed on a column of alumina (hexane as a solvent) before analysis.

Anal. Calcd for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68. Found: C, 77.37; H, 8.75.

The same procedure, using lithium diisopropylamide in THF (4.1 mL) and HMPA (2 mL), gave a yellow oil (3.21 g) whose NMR spectrum did not indicate the presence of any starting material. Distillation gave 3.14 g (90%) of **8a**.

Ethyl 5-Phenyl-4-pentenoate (7b). A solution of 1-phenyl-2-propenol[10] (5.37 g, 40 mmol), triethyl orthoacetate (51.91 g, 320 mmol), and propionic acid (0.2 g, 2.7 mmol) was stirred for 2 h at 138 °C with a continuous distillative removal of ethanol. Another portion of propionic acid (0.2 g, 2.7 mmol) was then added, and the reaction continued for 4 h. The reaction mixture was cooled and the solvent evaporated under reduced pressure (vacuum pump, 1 mm) to give a light-yellow liquid product (7.36 g, 90%) whose NMR spectrum was indistinguishable from the pure product. Distillation gave the pure colorless ester (6.15 g, 75.3%): bp 115–116 °C (1 mm) or 107 °C (0.75 mm) [lit.[17] 115–116 °C (1 mm)]; IR (neat film) (cm^{-1}) 1735 (C=O), 1596 (C=C), 1489, 1444, and 1372 (C=C, aromatic), 1252, 1189, and 1161 (C—O), 965 (trans CH=CH), 742 and 691 (CH, aromatic, out of plane bending); NMR ($CDCl_3$) δ 1.16 (t, 3 H), 2.40 (m, 2 H), 2.44 (m, 2 H), 4.1 (quartet, 2 H), 6.25 (m, 2 H) and 7.27 (s, broad, 5 H).

Ethyl 2,2-Dimethyl-5-phenyl-4-pentenoate (8b). This ester was obtained by a two-step methylation of **7b** (5.72 g, 28 mmol) using the procedure described for the synthesis of **8a**. The crude product was purified by chromatography on alumina and hexane as solvent to give 4.29 g (65.9%) of **8b**: bp 107 °C (0.75 mm); NMR ($CDCl_3$) δ 1.13 (t, 3 H), 1.19 (s, 6 H), 2.39 (d, 2 H), 4.07 (quartet, 2 H), 6.27 (m, 2 H), and 7.24 (m, 5 H).

The structure assigned to **8b** was confirmed by an independent synthesis in which ethyl isobutyrate (2.32 g, 20 mmol) was alkylated with cinnamyl bromide (4.73 g, 24 mmol) to yield an

(16) T. W. Campbell and W. D. Young, *J. Am. Chem. Soc.*, **71**, 296 (1949).

(17) J. J. Ritter and T. J. Kaniecki, *J. Org. Chem.*, **27**, 622 (1962).

identical product (3.91 g, 84.2%).

2,2-Dimethyl-3-phenylpropanoic Acid (10a). A solution of benzyl isobutyrate (1.78 g, 10 mmol) in THF (5 mL) was added, dropwise and with stirring, to a solution of lithium diisopropylamide (12 mmol) in THF (2.8 mL) at −78 °C and under argon. The reaction mixture was stirred for 40 min at −78 °C. A solution of trimethylsilyl chloride (1.195 g, 11 mmol) in THF (2 mL) and HMPA (1 mL) was added at −78 °C, and the mixture allowed to warm to 70 °C over a period of 45 min. Stirring was continued for 5 h, the reaction mixture was cooled to 25 °C, HCl (50 mL, 2 M) was added, and the layers were separated. The aqueous layer was extracted with ether (2 × 30 mL), and the combined organic layers were washed with sodium hydroxide solution (2 × 25 mL). The combined aqueous layers were cooled to 0 °C and acidified with HCl (2 M). The acidic layer was extracted with ether, the organic layer dried ($MgSO_4$), and the solvent evaporated on a rotary evaporator to give the light-yellow oil (0.623 g). The crude product was chromatographed on a column of silica gel to give the colorless acid,[18] which failed to crystallize (0.534 g, 30%): NMR ($CDCl_3$) δ 1.143 (s, 6 H), 2.841 (s, 2 H), 7.17 (m, 5 H), and 12.514 (s, 1 H).

A solution of acid **10a** (0.5 g, 2.8 mmol) in ether (10 mL) was treated with an ethereal solution of diazomethane. Evaporation of the solvent gave a light-yellow liquid product (0.53 g, 98.5%) whose NMR spectrum was identical with pure methyl 2,2-dimethyl-3-phenylpropanoate.

Methyl 2,2-Dimethyl-3-phenylpropanoate. Methyl isobutyrate (2.04 g, 20 mmol) was added, dropwise and with stirring, to a solution of lithium diisopropylamide (24 mmol) in THF (5.5 mL) at −78 °C and under argon. The reaction mixture was stirred for 20 min, and a solution of benzyl chloride (2.53 g, 20 mmol) in THF (10 mL) was added dropwise at −78 °C. The mixture was allowed to warm to room temperature and then stirred for 4 h at 20 °C. Cold HCl (40 mL, 1 M) was added, the layers were separated, and the water layer was extracted with ether (3 × 30 mL). The combined organic layers were washed with saturated sodium bicarbonate solution (40 mL) and water (40 mL) and then dried ($MgSO_4$). Evaporation of the solvent on a rotary evaporator gave a yellow liquid product (2.85 g, 74%) whose NMR was indistinguishable from the pure ester. Distillation gave the pure ester[19] (2.35 g, 61%): bp 115 °C (13 mm); NMR ($CDCl_3$) δ 1.14 (s, 6 H), 2.82 (s, 2 H), 3.52 (s, 3 H), and 7.15 (m, 5 H).

Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.40. Found: C, 74.83; H, 8.51.

1-Naphthylmethyl Isobutyrate. A solution 1-(chloromethyl)naphthalene (35.33 g, 200 mmol) in THF (20 mL) was added dropwise over a period of 1 h to a stirred solution of isobutyric acid (17.62 g, 200 mmol), triethylamine (20.24 g, 200 mmol), and THF (20 mL) at 20 °C. The reaction mixture was warmed to 70 °C and stirred for 2 h, at which time a heavy, white precipitate formed. The mixture was then allowed to cool to 25 °C and poured onto ice, and the layers were separated. The aqueous layer was extracted with ether (2 × 40 mL); the combined organic layers were washed with HCl (60 mL, 2 M), saturated sodium bicarbonate solution (60 mL), and water (60 mL) and then dried ($MgSO_4$). Evaporation of the solvent on a rotary evaporator gave the light-yellow liquid product (39.6 g, 86.7%) whose NMR spectrum was indistinguishable from that of the pure ester. Distillation gave the pure, colorless ester (38.5 g, 84.3%): bp 127–128 °C (1 mm); NMR ($CDCl_3$) δ 1.05 (d, 6 H), 2.45 (septet, 1 H), 5.47 (s, 2 H), and 7.11–8.09 (m, 7 H).

Anal. Calcd for $C_{15}H_{16}O_2$: C, 78.92; H, 7.065. Found: C, 79.06; H, 7.22.

2,2-Dimethyl-3-(1′-naphthyl)propanoic Acid (10b). A solution of 1-naphthylmethyl isobutyrate (2.28 g, 10 mmol) in THF (5 mL) was added dropwise to a stirred solution of lithium diisopropylamide (12 mmol) in THF (2.8 mL) at −78 °C and under argon. The mixture was stirred for 30 min, and a solution of trimethylsilyl chloride (1.195 g, 11 mmol) in THF (2 mL) and HMPA (1 mL) was added at −78 °C. The mixture was allowed to warm to 70 °C over a period of 45 min and stirred for 5 h. It was allowed to cool to 25 °C, HCl (50 mL, 2 M) was added, and the layers were separated. The aqueous layer was extracted with ether (2 × 30 mL), and the combined organic layers were washed with sodium hydroxide solution (2 × 25 mL). The combined aqueous layers were cooled to 0 °C and acidified with HCl (2 M). The acidic layer was extracted with ether, the organic layer dried ($MgSO_4$), and the solvent evaporated on a rotary evaporator to give the yellow oil which crystallized on standing (1.36 g). Recrystallization from ligroin gave the white crystalline acid (1.18 g, 51.8%): mp 96–97 °C; NMR ($CDCl_3$) δ 1.23 (s, 6 H), 3.43 (s, 2 H), 7.32–8.30 (m, 7 H), and 11.76 (s, 1 H).

Anal. Calcd for $C_{15}H_{16}O_2$: C, 78.92; H, 7.065. Found: C, 78.73; H, 7.18.

Methyl 2,2-Dimethyl-3-(1′-naphthyl)propanoate. Methyl isobutyrate (1.02 g, 10 mmol) was added, dropwise and with stirring, to a solution of lithium diisopropylamide (12 mmol) in THF (3 mL) at −78 °C and under argon. The reaction mixture was stirred for 30 min, and a solution of 1-(chloromethyl)-naphthalene (1.77 g, 10 mmol) in THF (5 mL) was added dropwise at −78 °C. The mixture was allowed to warm to 20 °C, and stirring was continued for 4 h. Cold HCl (20 mL, 1 M) was then added, the layers were separated, and the water layer was extracted with ether (3 × 30 mL). The combined organic layers were washed with saturated sodium bicarbonate solution (20 mL) and water (20 mL) and then dried. Evaporation of the solvent on a rotary evaporator gave a yellow oil (2.24 g, 92.6%) whose NMR spectrum showed no impurities: NMR ($CDCl_3$) δ 1.168 (s, 6 H), 3.295 (s, 2 H), 3.43 (s, 3 H), 7.19–8.19 (m, 7 H).

Saponification of this ester with sodium hydroxide, followed by acidification, gave the pure acid **10b**.

Registry No. 3a, 60533-01-9; **3b**, 72524-18-6; **6a**, 104-54-1; **6b**, 4393-06-0; **7a**, 60066-61-7; **7b**, 5629-57-2; **8a**, 72524-19-7; **8b**, 72524-20-0; **9a**, 103-28-6; **9b**, 72524-21-1; **10a**, 5669-14-7; **10b**, 29206-08-4; cinnamyl isobutyrate, 103-59-3; 1-phenyl-2-propenyl isobutyrate, 72524-22-2; triethyl orthoacetate, 78-39-7; ethyl 2-methyl-3-phenyl-4-pentenoate, isomer 1, 72524-23-3; ethyl 2-methyl-3-phenyl-4-pentenoate, isomer 2, 72524-24-4; methyl iodide, 74-88-4; ethyl isobutyrate, 97-62-1; cinnamyl bromide, 4392-24-9; methyl 2,2-dimethyl-3-phenylpropanoate, 14248-22-7; benzyl chloride, 100-44-7; 1-naphthylmethyl isobutyrate, 72524-21-1; 1-(chloromethyl)-naphthalene, 86-52-2; isobutyric acid, 79-31-2; methyl 2,2-dimethyl-3-(1-naphthyl)propanoate, 72524-25-5; methyl isobutyrate, 547-63-7.

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