enantiomer of **6**, since two chiral centers are present. However, the NMR spectra of both enantiomers, **1a** and **1b**, and **6a** gave no indication whatsoever of the presence of diastereomeric material.

Resolution was accomplished by treatment of the racemic bromide salt (**9**)[7] with silver (+)-10-camphorsulfonate and recrystallization of the diastereomeric salts utilizing a triangular scheme of recrystallization.[8] The head fraction was recrystallized to give **7a** of constant rotation and melting point (cf. Scheme I). **7a** was metathesized with sodium iodide in boiling acetone to provide **1a**, which was also recrystallized to constant rotation and melting point (cf. Scheme I). The tail fractions, enriched in **7b**, were combined and similarly converted to the optically impure iodide (**1b**), which was recrystallized from acetone to a constant rotation of $[\alpha]^{22}D$ $-2.14 \pm 0.11°$ (*c* 16.22, $CDCl_3$) and melting point of 184–185°. Because of the greater solubility of the racemic mixture in acetone, it was likewise possible to obtain optically pure **1a** as the less soluble fraction from mixtures of **1a** and **1b**, enriched in **1a**, by simple recrystallization from acetone.

Preparation of only one other simple five-membered ring phosphine oxide in optically active form has been reported previously. **10** was partially resolved with (+)-9-camphorsulfonic acid to afford the levorotatory isomer.[9]

Reduction of (+)-**6a** with phenylsilane yielded optically pure dextrorotatory phosphine **8a**. The optical purity of the phosphine is attested to by its conversion to the (+) oxides **6a′** and **6a″**, both of which showed, within experimental error, the same rotation as the dextrorotatory parent phosphine oxide **6a**. This is the first report of the preparation of an optically active saturated heterocyclic phosphine. It should be noted that two optically unstable isomers of the phosphorus heterocycle **11**[10] have been prepared by lithium aluminum hydride reduction of the corresponding optically active oxides, but that the activity of **11** may be due to molecular dissymmetry.[11] Optically active analogs of the oxides of **11** fail to undergo lithium aluminum hydride reduction to produce optically active phosphines[12] but fragment instead.

We have recently shown that alkoxyphospholanium salts (**12**) experience nucleophilic displacement at phosphorus to yield a mixture of oxides of inverted and retained configuration at phosphorus.[13] This observation leads us to believe that the preparation of optically pure phospholane oxides such as **6** by Mislow's method,[14] so useful for the synthesis of optically active acyclic phosphine oxides, would probably not be successful. Our resolution thus provides ready access to both optically isomeric phospholane oxides and phospholanes useful for stereochemical studies. The optically active phosphines may have additional value in the preparation of chiral phosphine–metal complexes.[15]

Experimental Section

(+)-1-Benzyl-3-methyl-1-phenylphospholanium Camphorsulfonate (7a). To 80.52 g of **9**[6] dissolved in 500 ml of ethanol was added 78.24 g of silver (+)-10-camphorsulfonate. Silver bromide was removed by filtration and the filtrate was further clarified by filtration through diatomaceous earth. The filtrate was evaporated to dryness and the residue was redissolved in a minimum amount of hot ethanol to which ethyl acetate was added dropwise to the cloud point. Triangular recrystallization,[8] carried out in this manner, gave a head fraction of constant melting point and rotation (cf. Scheme I).

Anal. Calcd for $C_{28}H_{37}O_4PS$: C, 67.18; H, 7.45. Found: C, 66.91; H, 7.40.

(+)-1-Benzyl-3-methyl-1-phenylphospholanium Iodide (1a). To 61 ml of 0.05 *M* sodium iodide in acetone was added 1.542 g of optically pure **7** and the mixture was stirred under gentle reflux for 45 min. Precipitated sodium camphorsulfonate was recovered in quantitative yield by filtration of the cooled reaction mixture. Crude **1a**, obtained after evaporation of the filtrate, was recrystallized from acetone to constant rotation and melting point (cf. Scheme I).

Anal. Calcd for $C_{18}H_{22}IP$: C, 54.56; H, 5.60. Found: C, 54.61; H, 5.55; S, 0.00.

It was discovered that head fractions of optically impure camphorsulfonate (**7a**) could be similarly converted to the optically impure iodide (**1a**) and the iodide conveniently recrystallized from acetone to the optically pure dextrorotatory form. Likewise, tail fractions concentrated in the more soluble diastereomeric camphorsulfonate, when treated as described above, produced the optically pure levorotatory isomer of mp 184.0–185.0°, $[\alpha]^{22}D$ $-2.14 \pm 0.11°$ (*c* 16.220, $CDCl_3$).

Anal. Calcd for $C_{18}H_{22}IP$: C, 54.56; H, 5.60. Found: C, 54.44; H, 5.76.

Hydroxide Cleavage of 1a and Recovery of Product. The procedure followed was essentially as described elsewhere for the racemic bromide salt.[6]

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Registry No.—(±)-**1**, 54964-37-3; **1a**, 54964-38-4; **1b**, 54932-22-8; **6a**, 54932-23-9; **7a**, 54932-25-1; **7b**, 54932-27-3; **8a**, 54932-28-4; **9**, 54932-29-5; silver (+)-10-camphorsulfonate, 20520-61-0.

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Hydrogenation of Unsaturated Carboxylic Acids with Alkanes by Aluminum Chloride Catalysis

Angelo G. Giumanini,* Annamaria Drusiani, and Laura Plessi

Istituto Chimico G. Giamician and Centro di Gascromatografia-Spettrometria di Massa, Università di Bologna, 40126 Bologna, Italy

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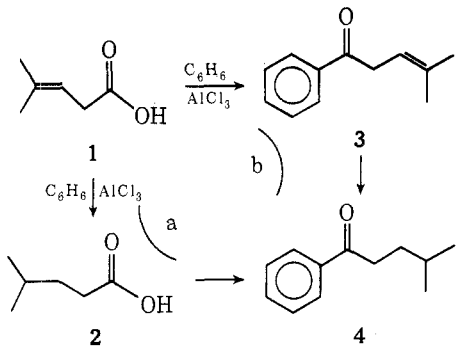
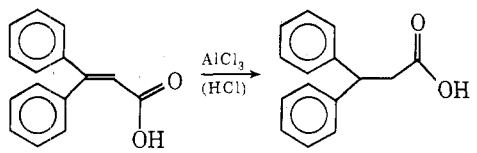
In the course of a previous study[1] of the Friedel–Crafts reactions of some unsaturated carboxylic acids on benzene, we observed the presence of an unexpected saturated ketone **4**, which could possibly arise from the reaction of the saturated counterpart **2** of the starting material **1** (Scheme I, pathway a). An alternative route (Scheme I, pathway b) was of course possible.[2] The finding that even a poor hydride donor like 4,4-dimethyltetralone, one of the reaction products, was able to perform the hydrogenation of **1** in the presence of aluminum chloride led us to investigate better hydrogen donors for the reduction, also in view of the great practical importance of the hydrogenation of fatty acids.

Alkanes were the obvious first choice. It should be mentioned that hydrogen transfer to unsaturated carboxylic acids was reported previously only in the particular case of

Scheme I



a highly hindered double bond during attempted Friedel–Crafts alkylation of benzene with aluminum chloride.[3]



Our preliminary experiments show that hydrogen can be transferred from alkanes to unsaturated fatty acids by means of aluminum chloride. 4-Methyl-3-pentenoic acid (1), 4-methyl-2-pentenoic acid (5), 3-methyl-2-butenoic acid (6), and cinnamic acid (7) underwent reduction to different extents to the corresponding saturated compounds 2, 2, 9 and 10 with *n*-hexane or ligroin (Table I).

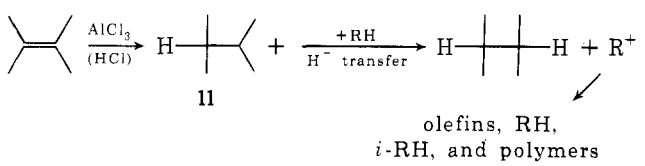
Table I
Reactions of Some Unsaturated Carboxylic Acids with Alkanes and $AlCl_3$[a]

Unsaturated acid	Alkane	Acid product(s)	Yield, %
4-Methyl-3-pentenoic (1)	*n*-Hexane	4-Methylpentanoic (2)	89
4-Methyl-2-pentenoic (5)	Ligroin	4-Methylpentanoic (2)	22
3-Methyl-2-butenoic (6)	*n*-Hexane	3-Methylbutanoic (9)	72
2-Butenoic (14)	*n*-Hexane or ligroin	Butanoic (8)	Trace
Cinnamic	Ligroin	Hydrocinnamic (10)	19
		p-Phenylenedipropanoic (12)	11

[a] Experimental details are recorded in the Experimental Section.

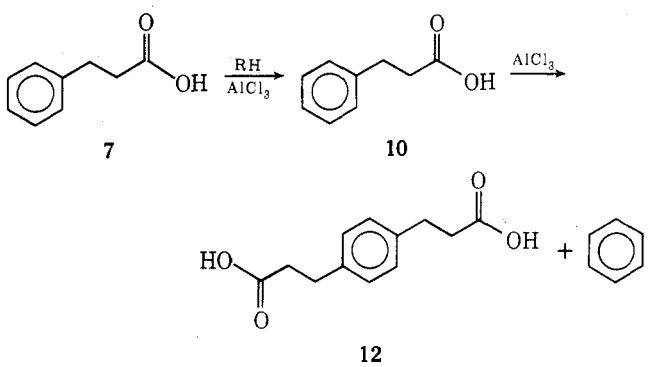
The results show some correlation of the yields with the structural possibilities of producing, directly or by hydride shift, a relatively stable intermediate carbonium ion, say 11. This observation leads us to offer the mechanistic hypothesis shown in Scheme II.

Scheme II



An analogy to this behavior is presented by the reduction of some alkyl halides by hydrocarbon in the presence of Friedel–Crafts reagents,[4] where the initial carbonium ion interacts with the hydrocarbon, which may eventually transfer a hydride ion.

Cinnamic acid (7) underwent hydrogenation to 19% hydrocinnamic acid (10) and 11% *p*-phenylenedipropanoic acid (12); a third less separated peak in the GLC profile of



the methyl esters of the acidic fraction from the reaction mixture was not identified. Disproportionation in Friedel–Crafts reactions of alkyl-substituted aromatics is very common. It seems quite reasonable that 10 underwent such a reaction to 12 and benzene (13).

Experimental Section

Materials. 4-Methyl-3-pentenoic acid (1), 4-methyl-2-pentenoic acid (5), and their saturated counterpart 2 were prepared as previously described.[1] 2-Butenoic acid (14), cinnamic acid (7), and their saturated analogs were obtained from Erba (Milan, Italy) and 3-methyl-2-butenoic acid (6) from Schuchardt; they were used as such after preliminary purity checks by GLC on the corresponding methyl esters prepared by treatment with ethereal diazomethane of the free acids. *n*-Hexane and ligroin (bp 100–110°) were dried with sodium before use.

Analyses. The reaction mixtures from the interaction of the unsaturated acids with hydrocarbons in the presence of aluminum chloride were poured into crushed ice–hydrochloric acid. The ether extracts were treated with aqueous sodium hydroxide (10%); the acids were recovered by acidification with concentrated hydrochloric acid and ether from the aqueous solution. The ether solution of the acidic material was directly chromatographed (GLC), when suitable, or pretreated with diazomethane and chromatographed (GLC). A suitable column for the free acids was a 2 m × 0.25 mm column packed with 1% FFAP–10% phosphoric acid on Chromosorb W (80–100 mesh). A 2 m × 0.25 mm column packed with GAL (10%) on Chromosorb W washed with acid (60–80 mesh) was used for the quantitative determination of the methyl esters. Yields were evaluated with the internal standard method with preliminary weight–area response calibration. Glc analyses were performed with a Perkin-Elmer 900 gas chromatograph equipped with a flame ionization detector. Identification of the GLC peaks was secured by the enhancement technique, mass spectrometry (gas chromatograph–mass spectrometer, Perkin-Elmer 270), and ir and NMR techniques on separated samples, when deemed necessary.[5]

4-Methyl-3-pentenoic Acid (1), *n*-Hexane, and $AlCl_3$. The acid 1 (20 mmol), *n*-hexane (25 ml), and aluminum chloride (40 mmol) were stirred at room temperature during 8 hr and left standing during 46 days. The obtained acid material did not react with bromine in carbon tetrachloride and showed no olefinic bond absorption in the ir: bp 61° (1 Torr); GLC homogeneous; yield 86%. Its properties (ir, GLC retention time, mass spectrum) were identical with those of an authentic sample of 4-methylpentanoic acid (2). A similar yield of 2 (89%) was obtained in a shorter time (4 hr) by refluxing 1 (20 mmol) with *n*-hexane (25 ml) and aluminum chloride.

4-Methyl-2-pentenoic Acid (5), Alkanes, and $AlCl_3$. A. The acid 5 (20 mmol), *n*-hexane (25 ml), and aluminum chloride (40 mmol) were kept at reflux during 4 hr. Usual work-up gave an acid residue (2.12 g); GLC analyses showed the presence of 4-methylpentanoic acid (2) and unreacted 5 in a 1:2 ratio.

B. When hexane was substituted by ligroin (bp 100–110°), 24% hydrogenated acid 2 was present with no more starting acid 5 left.

3-Methyl-2-butenoic Acid (6), *n*-Hexane, and $AlCl_3$. The acid 6 (20 mmol), *n*-hexane (25 ml), and aluminum chloride (40 mmol) were refluxed during 4 hr to give 3-methylbutanoic acid (9), yield 72%. No starting material was present in the final acidic part of the reaction mixture.

2-Butenoic Acid (14), Alkanes, and $AlCl_3$. The acid 14 (20 mmol), *n*-hexane or ligroin (25 ml), and aluminum chloride (40 mmol) were refluxed during 4 hr to yield only a small transformation into butanoic acid (8). Most of the starting material did not react.

Cinnamic Acid (7), Ligroin, and $AlCl_3$. The acid 7 (20 mmol), ligroin (25 ml), and aluminum chloride (40 mmol) were refluxed during 4 hr to yield 1.99 g of acid material from which crystals of *p*-phenylenedipropanoic acid (12) separated on cooling. The recrystallized (water) solid showed mp 230° (lit. mp 230°,[6] 224° [7]); ir (KBr) 3030 m, 2924 m, 2858 m, 2728 w, 2649 w, 1703 s, 1520 w, 1434 s, 1405 m, 1362 w, 1312 m, 1275 m, 1222 s, 1189 m, 1133 w, 945 w, and 830 cm^{-1} m. Its methyl ester **15**, mp 120° (methanol) (lit.[7] mp 117–118°), was obtained by treatment with diazomethane in ether: ir (KBr) 3024 w, 2929 m, 2894 w, 2838 w, 1728 s, 1520 m, 1434 s, 1368 s, 1303 s, 1272 m, 1193 s, 1180 s, 1141 s, 1105 w, 1050 m, 1000 w, 976 m, 900 w, 838 s, and 793 cm^{-1} w; mass spectrum (80 eV) *m/e* (rel abundance) 117 (100), 91 (28), 130 (28), 190 (28), 131 (19), 115 (19), 77 (13), 176 (12), 118 (12), 59 (11), 250 (M^+, 11), and 39 (9); metastable ions *m/e* 144.5, 113.5, and 89; doubly charged ions (at half integer masses) *m/e* 95.5[8] and 88.5; ^1H NMR (60 MHz, $CDCl_3$, TMS) δ 2.74 (AA'BB' multiplet, 8 H), 3.67 (singlet, 6 H), and 7.13 ppm (singlet, 4 H). GLC quantitative analysis showed **12** to be present in 11% yield and **10** in 19% yield together with other unidentified materials. None of the starting acid **7** survived the treatment.

Registry No.—**1**, 504-85-8; **5**, 10321-71-8; **6**, 541-47-9; **7**, 621-82-9; **12**, 4251-21-2; **14**, 3724-65-0; **15**, 5312-03-8; $AlCl_3$, 7446-70-0; hexane, 110-54-3.

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A Novel Cyclization Catalyzed By Magnesium Methyl Carbonate

S. Danishefsky,* [1] T. A. Bryson, and J. Puthenpurayil

Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260

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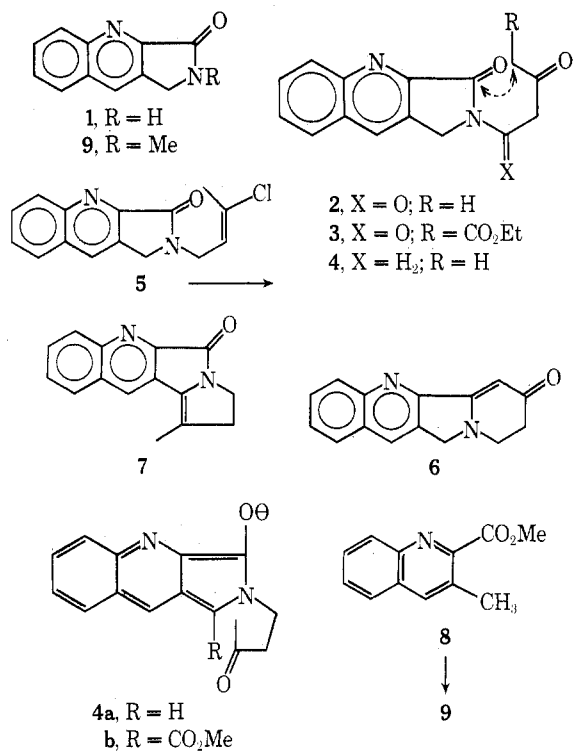
The synthesis of the tricyclic lactam **1** in 75% yield from 2-oxobutyric acid and *o*-aminobenzaldehyde has been described.[2,3] Its ready availability made it an attractive substrate for studying lactam annelation reactions with a view toward the syntheses of camptothecin and analog structures.[4,5] The strategy was based on acylation of the lactam nitrogen, followed by cyclization of a nucleophilic center in the side chain with the lactam carbonyl group.

Our original efforts were addressed to the acetoacetyl derivative **2** (X = O; R = H). This compound, mp 242–245°, was prepared (55%) by the reaction of **1** with *n*-butyllithium followed by diketene. In our hands, compound **2** could not be induced to undergo cyclodehydration in the sense indicated, under a variety of catalytic situations. Under mild conditions (e.g., boron trifluoride etherate or sodium acetate–acetic anhydride), **2** was recovered in high yield. Under more severe conditions (sodium ethoxide or potassium *tert*-butoxide) deacylation, leading to a high recovery of **1**, resulted. Parallel results have been reported by Sugasawa.[6] The eventual solution, which was discovered by the Japanese workers,[6] involved the use of the 3-ketoglutaryl system, **3** (X = O; R = CO_2Et). The added acidity conferred by the β-keto ester linkage allowed for smooth dehydration.



In the light of the serious competing reaction of deacylation in the case of **2**, we investigated the preparation and reactions of the β-acetoethyl derivative **4** (X = H_2; R = H). Lactam **1** was alkylated with 1,3-dichloro-2-butene to give **5**, mp 202–203°, in 57% yield. The chloroolefin linkage was smoothly cleaved (86%) with concentrated H_2SO_4 to give **4**, mp 184–185°.

Treatment of **4** with triethylamine resulted in high recovery of starting material. However, reaction of **4** with pyrrolidine gave (71%) lactam **1**. Presumably this transformation occurs by reversible formation of the trisubstituted enamine which suffers retro-Michael type elimination of **1**. Substantial β-elimination was also observed in the reaction of **4** with potassium *tert*-butoxide.

Treatment of **4** with sodium methoxide–methanol gave, in 2% yield, a yellow, crystalline product, mp 283–284°, whose mass spectrum and combustion analysis define it to be a dehydration product. The NMR spectrum of this compound establishes it to be pyrrolizidinone derivative **7** rather than the desired (and expected) dehydration product, **6**. Clearly, **7** arises by deprotonation of a benzylic carbon followed by internal aldolization. It will be seen that this deprotonation produces an extensively delocalized anion, one resonance form of which is drawn as **4a**.

In an effort to influence the course of cyclodehydration in the direction of compound **6**, lactam **4** was treated with magnesium methyl carbonate (MMC) in methanol.[7-9] The high tendency of MMC to effect specific carboxylation of the methyl group of methyl alkyl ketones is well known.[10] The hope was that such a carboxylation would increase the likelihood of Knoevenagel-type attack toward the carbonyl group of the lactam function.

We were thus surprised to find that reaction of **4** with MMC in methanol turned out to be the best way we have yet devised (65–75%) to effect its transformation to **7**. Initially it was assumed that carboxylation would occur at the