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ASYMMETRIC SYNTHESIS BY CHIRAL RUTHENIUM COMPLEXES

IV. REDUCTION OF CARBON—CARBON DOUBLE BONDS IN PROCHIRAL α,β-UNSATURATED CARBOXYLIC ACIDS BY HYDROGEN TRANSFER CATALYSED BY $H_4Ru_4(CO)_8[(-)\text{-DIOP}]_2$ *

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Summary

The enantioface-discriminating hydrogen transfer reduction of α,β-unsaturated acids takes place at 120°C in the presence of $H_4Ru_4(CO)_8[(-)\text{-DIOP}]_2$. Secondary alcohols are satisfactory hydrogen donors. Selectivity, optical yields, and rates are lower than those obtained when working in the presence of hydrogen under pressure.

Introduction

The chiral cluster ruthenium carbonyl hydride $H_4Ru_4(CO)_8[(-)\text{-DIOP}]_2$ has been successfully used as catalyst in the homogeneous asymmetric hydrogenation of prochiral organic substrates containing C=C [2—4], C=O [2,3,5,6], and C=N— [5] groups. In the hydrogenation of prochiral α,β-unsaturated carboxylic acids optical yields were shown to increase as the hydrogen pressure was lowered [4]. We have therefore investigated the possibility of using the above complex as catalyst in hydrogen transfer reactions in order to achieve reduction of carbon—carbon double bonds without the need for hydrogen under pressure.

While the reduction of carbon—carbon double bond by hydrogen transfer in the presence of ruthenium catalysts is well documented in the literature [7—20],

* Preliminary results were presented at the IXth International Conference of Organometallic Chemistry [1].

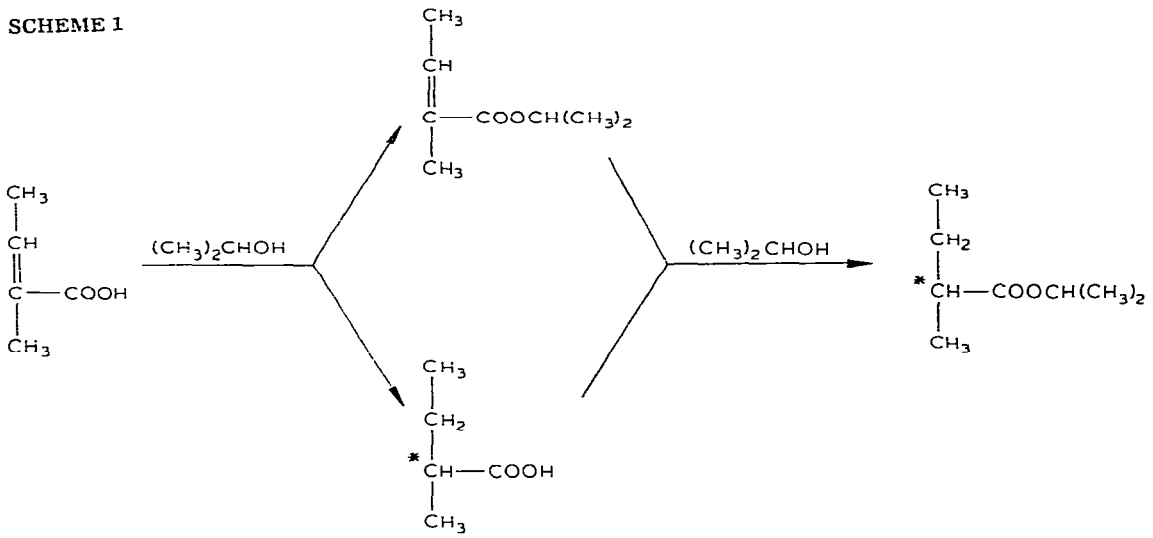
only a few examples are reported of asymmetric reductions performed with chiral hydrogen donors [11,13] and/or chiral catalysts [13,20].

Results and discussion

Secondary alcohols, indoline, and dioxane, frequently used as hydrogen donors, were tested in exploratory experiments (Table 1) using $H_4Ru_4(CO)_8$-[(—)-DIOP]$_2$ as catalyst and tiglic acid as substrate.

The reduction of the carbon—carbon double bond proceeds satisfactorily at 120°C when propan-2-ol or octan-2-ol is used as hydrogen supplier. Considerable amounts of esterification products are formed however (Scheme 1).

SCHEME 1



SCHEME 2

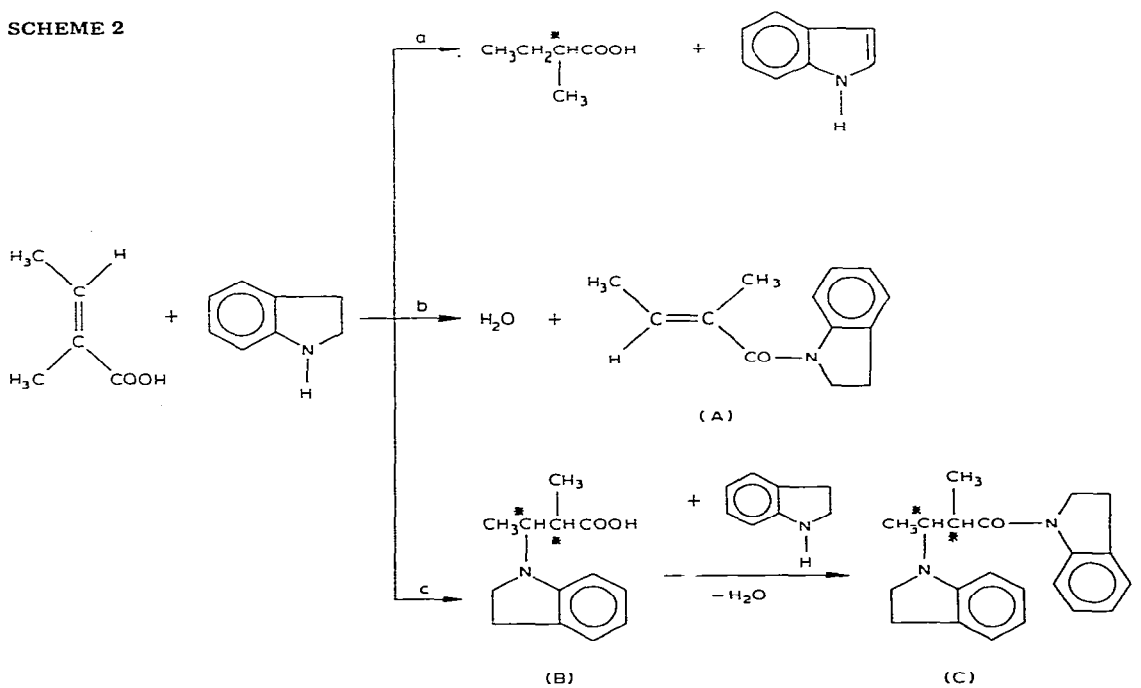


TABLE 1

HYDROGEN TRANSFER REDUCTION OF C=C IN TIGLIC ACID BY VARIOUS HYDROGEN DONORS IN THE PRESENCE OF $H_4Ru_4(CO)_8$[(—)-DIOP]$_2$
(Substrate 30 mmoles, hydrogen donor 389 mmoles, catalyst 0.100 g, T 120°C)

Hydrogen donor	Reaction time (h)	Reaction products	Yield (%)	Chirality of prevailing isomer [a]	O.P. [b] (%)
Dioxane	96	2-Methylbutanoic acid	<1	n.d. [c]	n.d. [c]
Indoline	186	2-Methylbutanoic acid	9.0	(*R*)	6.9
		1-[(*E*)-2-Methyl-2-butenoyl]-2,3-dihydro-1*H*-indole	40.0	—	—
		3-(2,3-Dihydro-1*H*-indol-1-yl)-2-methylbutanoic acid	5.2	n.d.	n.d.
		1-[2-Methyl-3-(2,3-dihydro-1*H*-indol-1-yl)butanoyl]-2,3-dihydro-1*H*-indole	35.0	n.d.	n.d.
Propan-2-ol	227	2-Methylbutanoic acid	42.4	(*R*)	5.4
		Isopropyl 2-methylbutanoate	22.9	n.d.	n.d.
		Isopropyl tigliate	9.1	—	—
Octan-2-ol [d]	135	2-Methylbutanoic acid	26.3	(*R*)	6.3
		2-Octyl 2-methylbutanoate	12.0	n.d.	n.d.
		2-Octyl tigliate	3.6	—	—

[a] See experimental; [b] O.P.: optical purity, see experimental; [c] n.d.: not determined; [d] The unreacted alcohol had $[\alpha]_D^{18}$ —0.010.

When tiglic acid is reacted with indoline condensation and addition products are mainly obtained and only minor amounts of 2-methylbutanoic acid (9.0%) (Scheme 2, path a). The main product is the unsaturated amide A (Scheme 2, path b), and this does not react further with indoline, as shown in a separate experiment. The saturated amide B, containing two indoline moieties, is therefore formed according to Scheme 2, path c. The optical rotation of the acid B ($\alpha_{D(l=1)}^{20}$ +0.010°; c 1.748, chloroform) shows that the Michael type addition of the N—H bond of indoline to the carbon—carbon double bond of tiglic acid also takes place stereoselectively. Dioxane does not supply hydrogen at temperatures below 150°C; at higher temperatures the catalyst decomposes.

Propan-2-ol, readily available and as good a hydrogen donor as any other secondary alcohol, was therefore used in all our subsequent reduction experiments with chiral mono- and bi-carboxylic acids such as α-methylcinnamic, citraconic, mesaconic, and itaconic (Table 2). α-Methylcinnamic acid and tiglic acid yield the corresponding saturated acids and their isopropyl esters. (—)(*R*)-2-Methyl-3-phenylpropanoic acid obtained had an optical purity of 1.5%.

Citraconic acid under the conditions used is mainly decarboxylated (86.3%) to give 2-methylpropanoic and methacrylic acids and their isopropyl esters; the only reduction product of the substrate (Scheme 3) is diisopropyl methylsuccinate (8.3%). Mesaconic acid on the other hand is mainly reduced (92.6%) to (—)(*S*)-methylsuccinic acid and its diisopropyl ester (optical purity 5.6%).

(+)(*R*)-Methylsuccinic acid having an optical purity of 3.5% was obtained from itaconic acid; extensive isomerization of the substrate to mesaconic acid and its ester was also observed (20.1%). The formation of mesaconic acid which on hydrogenation gives methylsuccinic acid having the predominant (*S*) configuration, opposite to that of the reaction product of itaconic acid, gives a false

TABLE 2

REDUCTION OF UNSATURATED MONO- AND BI-CARBOXYLIC ACIDS BY HYDROGEN TRANSFER FROM PROPAN-2-OL IN THE PRESENCE OF $H_4Ru_4(CO)_8[(-)\text{-DIOP}]_2$
(Catalyst 100 mg, substrate 30 mmoles, propan-2-ol 389 mmoles, T 120°C)

Acid substrate	Reaction time (h)	Conv. (%)	Reaction products	Comp. (%)	Chirality of prevailing isomer [a]	O.P. [b] (%)
Tiglic	227	74.4	2-Methylbutanoic acid	57.0	(*R*)	5.4
			Isopropyl 2-methylbutanoate	30.8	n.d. [c]	n.d. [c]
			Isopropyl tigliate	12.2	—	—
α-Methylcinnamic	135	83.9	2-Methyl-3-phenylpropanoic acid	48.9	(*R*) [d]	1.5 [d]
			Isopropyl 2-methyl-3-phenylpropanoate	38.5		
			Isopropyl α-methylcinnamate	12.6	—	—
Citraconic	146	100	Diisopropyl methylsuccinate	8.3	n.d.	n.d.
			2-Methylpropanoic acid	40.8	—	—
			Isopropyl 2-methylpropanoate	34.6	—	—
			Methacrylic acid	5.0	—	—
			Isopropyl methacrylate	6.9	—	—
			Diisopropyl citraconate	4.4	—	—
Mesaconic	85	93.3	Methylsuccinic acid	49.1	(*S*) [d]	5.6 [d]
			Diisopropyl methylsuccinate	43.5		
			Diisopropyl mesaconate	7.4	—	—
Itaconic	64	92.7	Methylsuccinic acid	11.2	(*R*) [d]	3.5 [d]
			Diisopropyl methylsuccinate	40.1		
			Mesaconic acid	8.8	—	—
			Diisopropyl mesaconate	11.3	—	—
			Diisopropyl itaconate	28.6	—	—

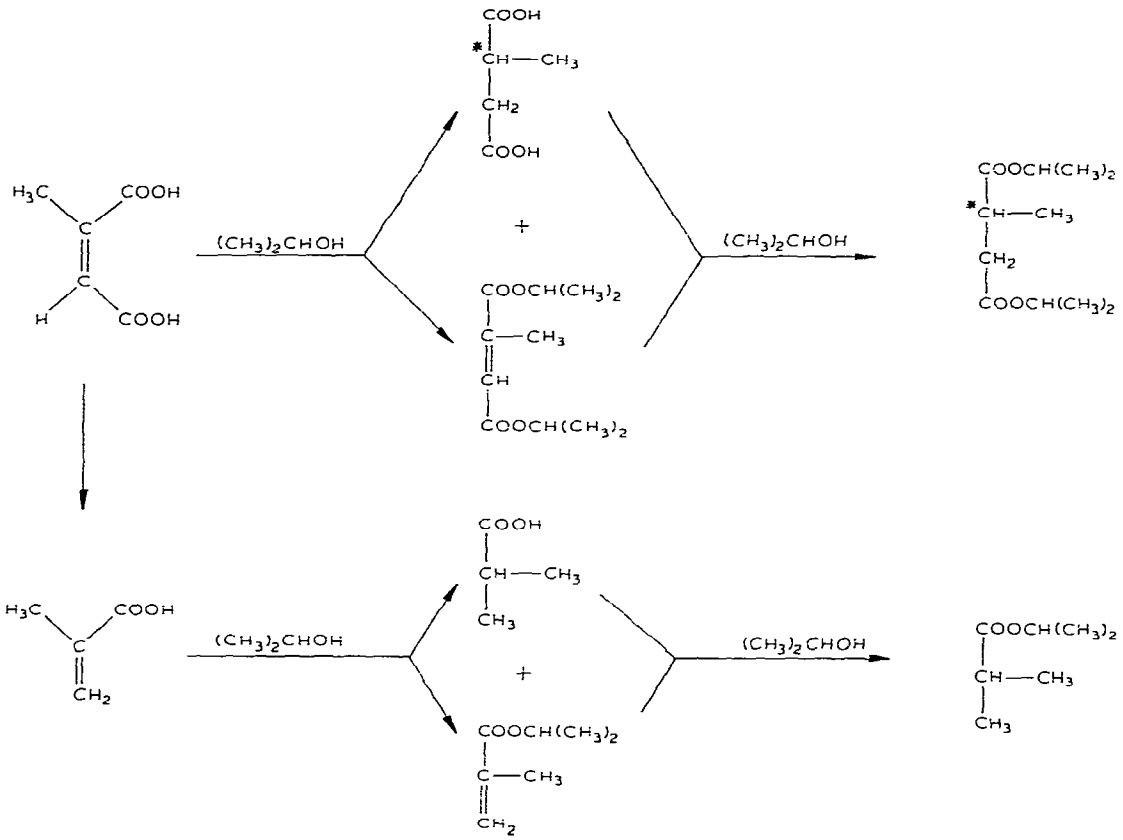
[a] See experimental; [b] O.P.: optical purity, see experimental; [c] n.d.: not determined; [d] measured on methylsuccinic acid recovered after saponification of the crude (see experimental).

indication of the stereoselectivity of the direct reduction of itaconic acid. In fact hydrogenation experiments interrupted at low conversions and thus also involving only a little isomerization (9.4%), gave (+)(*R*)-methylsuccinic acid with a much higher optical yield (7.1%).

The structure of the substrates apparently plays a fundamental role in determining both the type (decarboxylation, isomerization, or hydrogenation) and the stereochemistry of the reactions. The decarboxylation reaction was found to be both a stereospecific and a regiospecific process: citraconic acid having the carboxylic group in a *cis* position undergoes decarboxylation only at the less substituted carbon atom.

In all the experiments reported the optical purities of the reaction products were lower (except for itaconic acid) than those obtained when using molecular hydrogen under pressure. In the case of monocarboxylic acids the opposite configuration was obtained. This could be ascribed either to the different catalytic activities of the species active in the presence of gaseous hydrogen or to the interference to the reduction by the unsaturated esters which are always formed in the hydrogen transfer experiments with propan-2-ol. The reduction of unsaturated esters occurs with a very low stereoselectivity: thus diisopropyl mesaconate gives (*R*)-diisopropyl methylsuccinate having 0.3% optical purity. This result is

SCHEME 3



in keeping with those obtained in the presence of $Ru_2Cl_4[(-)\text{-DIOP}]_3$: α,β-unsaturated esters give reduction products having lower optical purity than the corresponding acids although at a higher rate [20].

In conclusion, the hydrogen transfer reduction of α,β-unsaturated acids in the presence of $H_4Ru_4(CO)_8[(-)\text{-DIOP}]_2$ offers no advantages over the hydrogenation in the presence of molecular hydrogen; and in fact, the selectivity, optical yield and reaction rate are all lower. The effect of hydrogen under pressure probably reflects the action of a hydrogen-containing catalytic species capable of existence in sufficient concentration only under pressure of the gas.

Experimental section

GLC analyses were performed on a Perkin Elmer F 30 instrument; NMR spectra were recorded on a Perkin Elmer R 32 spectrometer; mass spectra were recorded with a Perkin Elmer 270B spectrometer; the rotatory powers were measured with a Perkin Elmer 241 polarimeter; IR spectra were recorded with a Perkin Elmer 580 spectrophotometer.

Materials

Tiglic acid (Fluka), citraconic acid (Fluka), mesaconic acid (Ega), α-methyl-

cinnamic acid (Ega), itaconic acid (Fluka), methylsuccinic acid (Fluka), and methacrylic acid (Fluka) were analytical grade products. Dioxane (Carlo Erba) was purified according to Hess and Frahm [21]; indoline (Merck-Schuchardt) and propan-2-ol (Carlo Erba) were distilled before use.

Isopropyl 2-methylpropanoate was prepared from the alcohol and the acid by a published procedure [22].

Diisopropyl mesaconate: mesaconic acid (6.5 g), propan-2-ol (30 g), benzene (50 ml), H_2SO_4 (few drops) were refluxed and the water produced was separated by a Dean Stark apparatus. The product was fractionated to give diisopropyl mesaconate (3.8 g), b.p. 234°C, n_D^{20} 1.4438, and consistent NMR and mass spectra. NMR spectrum at δ(ppm) (TMS, C_6D_6): 0.98 (dd, 12 H, $(CH_3)_2CHOOCCH=C(CH_3)COOCH(CH_3)_2$), 2.37 (d, 3 H, $—CH=C(CH_3)CO-$), 4.98 (m, 2 H, $OCH(CH_3)_2$), 6.95 (m, 1 H, $—OCCH=C(CH_3)—$). The mass spectrum shows peaks at *m/e*: 214 $[M]^+$, 172 $[M - CH_3CH=CH_2]^+$, 155 $[M - OCH(CH_3)_2]^+$, 130 $[HOOCCH=C(CH_3)COOH]^+$, 113 $[OCCH=C(CH_3)COOH]^+$, 59 $[OCH(CH_3)_2]^+$, 43 $[CH(CH_3)_2]^+$.

Isopropyl methacrylate, prepared as described for diisopropyl mesaconate, had b.p. 126°C and n_D^{25} 1.4108 [23].

$H_4Ru_4(CO)_8[(—)\text{-DIOP}]_2$ was prepared as described [4] elsewhere.

Transfer hydrogenation procedure

Experiments using propan-2-ol as hydrogen donor were carried out in a 125 ml stainless steel rocking autoclave. The air was evacuated from the autoclave containing the solid substrate and the catalyst, and propan-2-ol was introduced by suction. Nitrogen was then introduced to atmospheric pressure. The autoclave was rocked and heated at 120°C for the appropriate time (Table 2). For diisopropyl mesaconate the time was 324 h, and for 1-[(*E*)-2-methyl-2-butenoyl]-2,3-dihydro-1*H*-indole 48 h.

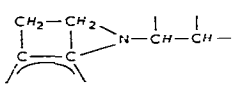
Analysis and identification of products

Reaction of tiglic acid and propan-2-ol. GLC analysis of the crude product mixture (2 m column packed with FFAP 5% on Chromosorb G(AW-DMCS at 150°C) indicated the presence of isopropyl 2-methylbutanoate (22.9%), isopropyl tigliate (9.1%), 2-methylbutanoic acid (42.4%) and tiglic acid (25.6%).

The mass spectrum of the isopropyl 2-methylbutanoate showed significant peaks at *m/e*: 144 $[M]^+$, 129 $[M - CH_3]^+$, 103 $[CH_3CH_2CH(CH_3)C(OH)=OH]^+$, 102 $[CH_3CH_2CH(CH_3)COOH]^+$, 85 $[M - OCH(CH_3)_2]^+$, 57 $[M - COOCH(CH_3)_2]^+$, 43 $[CH(CH_3)_2]^+$. The mass spectrum of the isopropyl tigliate showed significant peaks at *m/e*: 142 $[M]^+$, 100 $[CH_3CH=C(CH_3)COOH]^+$, 83 $[M - OCH(CH_3)_2]^+$, 59 $[OCH(CH_3)_2]^+$, 55 $[M - COOCH(CH_3)_2]^+$, 43 $[CH(CH_3)_2]^+$.

The crude mixture was treated with a 5% $NaHCO_3$ solution with vigorous stirring at room temperature. A mixture of tiglic acid and (—)(*R*)-2-methylbutanoic acids was recovered from the aqueous layer by the usual procedure. After distillation the fraction containing the (—)(*R*)-2-methylbutanoic acid (69.0% by GLC) showed D_4^{25} 0.9395, $\alpha_{D(l=1)}^{25}$ —0.697°, $[\alpha]_D^{25}$ —0.742. The (—)-(*R*)-2-methylbutanoic acid, α_D^{25} —0.742, present in the mixture was therefore present in 5.4% optical purity [24].

Reaction of tiglic acid and 2,3-dihydro-1 H-indole (indoline). The crude mixture was treated with aqueous HCl solution (10%) up to pH 1 and extracted with diethyl ether and then with $CHCl_3$. The $CHCl_3$ fraction was subjected to TLC (SiO_2 as solid phase and CH_2Cl_2 as eluent) to give 3-(2,3-dihydro-1*H*-indol-1-yl)-2-methylbutanoic acid (B) (0.28 g), which, after treatment with a CH_3OH/HCl solution and then with an NaOH solution (10%), gave the corresponding methyl ester having a mass spectrum with peaks at *m/e*: 233 $[M]^+$, 201 $[M - CH_3OH]^+$, 146 $[C_8H_8N{-}CH(CH_3)]^+$, 131 $[146 - CH_3]^+$, 119 $[C_8H_9N]^+$, 117 $[C_8H_7N]^+$, 91 $[C_7H_7]^+$, 83 $[CH_3CHC(CH_3){=}CO]^+$, 57 $[CH_3CH_2CHCH_3]^+$, 55 $[CH_2{=}CHCHCH_3]^+$, NMR spectrum δ(ppm) (TMS, $CDCl_3$): 1.07 (d, 3 H, $NCH(CH_3)CH$), 1.16 (d, 3 H, $NCH(CH_3)CH(CH_3)$-), 2.53—4.02 (m, 6 H,

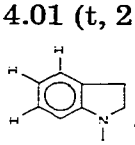


), 3.53 (s, 3 H, —$COOCH_3$), 6.36—6.68 (m, 2 H, aromatics), 6.80—7.20 (m, 2 H, aromatics), IR spectrum with ν(CO) band at 1740 cm^{-1} (CCl_4) and $\alpha^{20}_{D(l=1)}$ +0.010° (c 1.748, $CHCl_3$).

The ether portion was treated with NaOH solution (10%); from the resulting aqueous layer, by the usual procedure, a mixture of tiglic acid (0.27 g) and 2-methylbutanoic acid (0.23 g) was recovered. After the addition of pentanoic acid (0.80 g) the mixture had $\alpha^{25}_{D(l=1)}$ —0.220°, D^{25}_4 0.9493, $[\alpha]^{25}_D$ —0.232. The optical purity of (—)(*R*)-2-methylbutanoic acid present in the mixture was therefore 6.9% [24].

From the residual ethereal solution 1-[(*E*)-2-methyl-2-butenoyl]-2,3-dihydro-1*H*-indole (2.00 g) (A), 1-[2-methyl-3-(2,3-dihydro-1*H*-indol-1-yl)butanoyl]-2,3-dihydro-1*H*-indole (2.80 g) (C), and indole (trace) were separated by TLC (SiO_2 as solid phase and CH_2Cl_2/CH_3OH (90/10) as eluent).

A showed a mass spectrum with peaks at *m/e*: 201 $[M]^+$, 186 $[M - CH_3]^+$, 146 $[C_8H_8N{-}CO]^+$, 119 $[C_8H_9N]^+$, 117 $[C_8H_7N]^+$, 91 $[C_7H_7]^+$, 83 $[CH_3CH{=}C(CH_3)CO]^+$, 55 $[CH_2{=}CHCHCH_3]^+$, an NMR spectrum δ(ppm) (TMS, $CDCl_3$): 1.74 (d, 3 H, CH_3CH=), 1.89 (s, 3 H, CH_3C=), 3.03 (t, 2 H, NCH_2CH_2—), 4.01 (t, 2 H, NCH_2CH_2—), 5.87 (q, 1 H, CH_3CH=), 6.85—7.26 (m, 3 H,

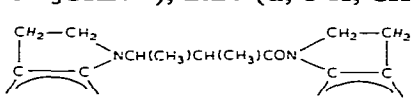


), 7.76 (d, 1 H,

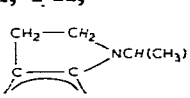
), an IR spectrum with ν(CO) band at 1640 cm^{-1} (CCl_4). Analysis: Found C, 77.20; H, 7.43; N, 7.20; $C_{13}H_{15}NO$ calcd. C, 77.58; H, 7.51; N, 6.9%.

After saponification (NaOH 20%), tiglic acid and indoline were recovered.

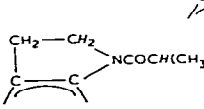
C showed a mass spectrum with peaks at *m/e*: 320 $[M]^+$, 202 $[C_8H_8N{-}CH(CH_3)CH(CH_3)CO]^+$, 187 $[202{-}CH_3]^+$, 174 $[C_8H_8N{-}CH(CH_3)CH(CH_3)]^+$, 159 $[174 - CH_3]^+$, 146 $[C_8H_8N{-}CHCH_3]^+$, 131 $[146 - CH_3]^+$, 119 $[C_8H_9N]^+$, 117 $[C_8H_7N]^+$, 91 $[C_7H_7]^+$, an NMR spectrum δ(ppm) (TMS, $CDCl_3$): 1.10 (d, 3 H, CH_3CHN), 1.17 (d, 3 H, CH_3CHCO), 2.60—3.13 (m, 4 H,



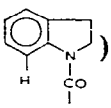
), 3.13—3.45 (m, 3 H,



), 3.78—4.16 (m, 3 H,



), 6.38—6.65 (m, 2 H, aromatics), 6.76—7.19 (m, 5 H,

aromatics), 8.10—8.40 (m, 1 H, ), an IR spectrum with a ν(CO) band at 1660 cm^{-1} (CCl_4). Analysis: Found C, 78.98; H, 7.62; N, 8.40; $C_{21}H_{24}N_2O$ calcd. C, 78.71; H, 7.55; N, 8.74%.

Reaction of tiglic acid with octan-2-ol. GLC analysis on the crude (2 m column packed with FFAP 5% on Chromosorb G AW-DMCS at 150°C) showed the presence of 2-methylbutanoic acid (26.3%), 2-octyl tigliate and 2-octyl 2-methylbutanoate (total 15.6%), and tiglic acid (58.1%). Treatment of the mixture with $NaHCO_3$ solution (5%) and the usual work up of the resulting aqueous layer gave a mixture of (—)(*R*)-2-methylbutanoic acid (0.51 g) and tiglic acid (1.00 g) which mixed with pentanoic acid (1.40 g) showed $\alpha^{25}_{D(l=1)}$ —0.209°, D^{25}_4 0.9614, $[\alpha]^{25}_D$ —0.217. The optical purity of (—)(*R*)-2-methylbutanoic acid present in the recovered mixture was therefore 6.3% [24].

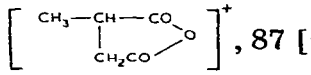
The residual organic layer was subjected to preparative GLC (3 m column packed with Carbowax 20 M 20% on Chromosorb A at 120°C) to give a mixture of 2-octyl 2-methylbutanoate and 2-octyl tigliate, and this after treatment with NaOH solution (50%) and the usual work up gave octan-2-ol and a mixture of 2-methylbutanoic acid (77.0%) and tiglic acid (23.0%). The unreacted octan-2-ol had $\alpha^{18}_{D(l=1)}$ —0.008°, $[\alpha]^{18}_D$ —0.010. The optical purity of (—)(*R*)-octan-2-ol [25] was therefore 0.1% [26].

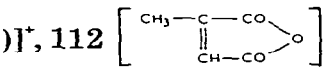
Reaction of α-methylcinnamic acid with propan-2-ol. GLC on a sample of the product mixture after treatment with CH_2N_2 (2 m column packed with DEGS 20% on Chromosorb W HMDS at 180°C) showed the presence of isopropyl 2-methyl-3-phenylpropanoate (32.3%), methyl 2-methyl-3-phenylpropanoate (41.0%), isopropyl α-methylcinnamate (10.6%) and methyl α-methylcinnamate (16.1%).

The mass spectrum of isopropyl 2-methyl-3-phenylpropanoate showed significant peaks at *m/e*: 206 $[M]^+$, 164 $[C_6H_5CH_2CH(CH_3)COOH]^+$, 147 $[M - OCH(CH_3)_2]^+$, 119 $[M - COOCH(CH_3)_2]^+$, 91 $[C_7H_7]^+$, 43 $[CH(CH_3)_2]^+$. The mass spectrum of isopropyl α-methylcinnamate showed significant peaks at *m/e*: 204 $[M]^+$, 162 $[C_6H_5CH{=}C(CH_3)COOH]^+$, 145 $[M - OCH(CH_3)_2]^+$, 117 $[M - COOCH(CH_3)_2]^+$, 91 $[C_7H_7]^+$ 43 $[CH(CH_3)_2]^+$.

The produced mixture was treated with NaOH solution (50%) (12 h at reflux), acidified with H_2SO_4, and extracted with diethyl ether. The ethereal solution was fractionated. The fraction b.p. 160—165°C/14 mmHg contained 2-methyl-3-phenylpropanoic acid (71.0%) and α-methylcinnamic acid (29.0%) having $\alpha^{25}_{D(l=1)}$ —0.220°, D^{25}_4 1.0749. The (—)(*R*)-2-methyl-3-phenylpropanoic acid [27] present in the mixture having $[\alpha]^{25}_D$ —0.288 has an optical purity of 1.5% [28].

Reaction of citraconic acid with propan-2-ol. A sample of the produced mixture was treated with CH_2N_2 then subjected to GLC (2 m column packed with PPG 15% on Chromosorb W at 60°C for 12 minutes and after up to 120°C at 30°C/min), which showed the presence of isopropyl 2-methylpropanoate (34.6%), isopropyl methacrylate (6.9%), methyl 2-methylpropanoate (40.8%), methyl methacrylate (5.0%), diisopropyl methylsuccinate (8.3%), and diisopropyl citraconate (4.4%). Diisopropyl methylsuccinate was identified by its mass spectrum showing peaks at *m/e*: 216 $[M]^+$, 174 $[M - CH_3CH{=}CH_2]^+$, 157 $[M - OCH(CH_3)_2]^+$, 115 $[M - (CH_3CH{=}CH_2) - (OCH(CH_3)_2)]^+$, 114

 , 87 $[COOCH(CH_3)_2]^+$, 59 $[OCH(CH_3)_2]^+$, 43 $[CH(CH_3)_2]^+$.

Diisopropyl citraconate was identified by its mass spectrum showing peaks at *m/e*: 214 $[M]^+$, 172 $[M - CH_3CH{=}CH_2]^+$, 155 $[M - OCH(CH_3)_2]^+$, 113 $[M - (CH_3CH{=}CH_2) - (OCH(CH_3)_2)]^+$, 112  , 87 $[COOCH(CH_3)_2]^+$, 59 $[OCH(CH_3)_2]^+$, 43 $[CH(CH_3)_2]^+$.

Reaction of mesaconic acid with propan-2-ol. After appropriate treatment of the mixture GLC and mass spectrometry led to the identification of dimethyl methylsuccinate (45.8%), diisopropyl methylsuccinate (40.6%), dimethyl mesaconate (6.7%) and diisopropyl mesaconate (6.9%).

Treatment of the crude, as described for α-methylcinnamic acid gave (—)(*S*)-methylsuccinic acid (2.1 g) having $\alpha^{20}_{D(l=1)}$ —0.068° (c 7.075, C_2H_5OH), $[\alpha]^{20}_D$ —0.961, 5.6% optical purity [29].

Reaction of itaconic acid with propan-2-ol. After appropriate treatment of the mixture GLC and mass spectrometry led to the identification of dimethyl methylsuccinate (10.4%), diisopropyl methylsuccinate (37.2%), dimethyl mesaconate (8.2%), diisopropyl mesaconate (10.5%), diisopropyl itaconate (26.4%), and dimethyl itaconate (7.3%). Diisopropyl itaconate was identified by its mass spectrum, which showed peaks at *m/e*: 214 $[M]^+$, 172 $[M - CH_3CH{=}CH_2]^+$, 155 $[M - OCH(CH_3)_2]^+$, 130 $[CH_2{=}C(COOH)CH_2COOH]^+$, 113 $[M - (CH_3CH{=}CH_2) - (OCH(CH_3)_2)]^+$, 112 $[M - (2\ CH_3CH{=}CH_2) - (H_2O)]^+$, 87 $[COOCH(CH_3)_2]^+$, 59 $[OCH(CH_3)_2]^+$, 43 $[CH(CH_3)_2]^+$.

Treatment of the mixture as described for α-methylcinnamic acid, gave (+)-(*R*)-methylsuccinic acid (1.1 g) having $\alpha^{20}_{D(l=1)}$ +0.032° (c 5.4, C_2H_5OH), $[\alpha]^{20}_D$ +0.592, 3.5% optical purity [29].

Reaction of diisopropyl mesaconate with propan-2-ol. Diisopropyl methylsuccinate was the only compound present in the products. Treatment of the product as described for α-methylcinnamic acid gave (+)(*R*)-methylsuccinic acid (2.6 g) having $\alpha^{20}_{D(l=1)}$ +0.003° (c 5.27, C_2H_5OH), $[\alpha]^{20}_D$ +0.057, 0.3% optical purity [29].

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