Study of a Model System for Asymmetric Induction in [2C + 2C] Photoannelation Reactions

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Photocycloaddition of cyclopent-2-enone and (*S*)-(+)-2-methyl-1-(2-methylbutoxy)-1-trimethylsilyloxyprop-1-ene leads both to oxetanes and cyclobutanes. The asymmetric induction, experimentally determined, in the head-to-tail [2C + 2C] cyclobutane adducts amounts to about 30%, but the intrinsic induction is nearly quantitative. The absolute configuration of the predominant enantiomer conforms to that expected from the sterically preferred reaction mode. The chiral handle can easily be recovered and recycled.

The induction of optical activity is a currently much investigated facet of synthetic organic chemistry. However, enantioselective [2π + 2π] photocycloadditions have only been marginally studied. One straightforward aspect involves transformation of an optically active substrate, usually derived from naturally occurring terpenes or steroids.[1] Another approach uses the reaction between an achiral substrate and a chiral reagent which, after work-up, can be removed. The few examples hitherto reported are for Paterno–Büchi-type photoadditions. Chiral alkyl glyoxylates were added to either olefins [up to 53% enantiomeric excess (e.e.)][2] or furans (maximum 7.3% optical purity), yielding oxetanes and cyclic acetals, respectively.[3] A low optical yield (<17%) was also obtained in the photoreaction between xanthione (xanthene-9-thione) and (*R*)-(−)-menthyl methacrylate.[4]

Here we report the first example of asymmetric induction in a [2C + 2C] photocycloaddition reaction.

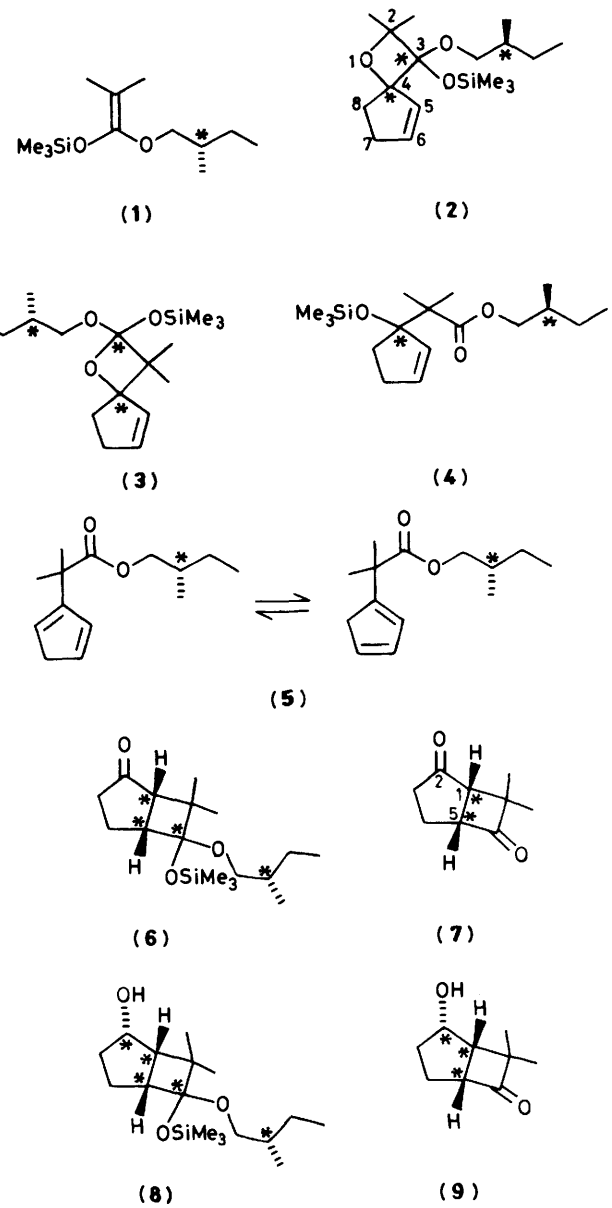
Results and Discussion

It is clear from our own[5] and others'[6] work that ketene acetals are excellent reagents in [2C + 2C] photocycloadditions to (n→π*) excited cyclic α,β-enones. Application of this reaction to the problem of asymmetric induction led in a first approach to the selection of optically active ketene acetals as ideal reagents. Trans-acetalization of 2-bromoacetaldehyde dimethyl acetal[6a] using appropriate chiral alcohols, such as (*S*)-(−)-2-methylbutan-1-ol, occurred readily, but the subsequent, base-promoted, elimination reaction gave rise to mixtures containing acetates due to hydrolysis, and unidentified material of a polymeric nature.

We then turned our attention to the use of ketene alkyl trimethylsilyl acetals,[7,8] although it was realized that the different substitution pattern could be a disadvantage for the degree of enantioselectivity. Thus, lithium di-isopropylamide treatment of (*S*)-(+)-2-methylbutyl isobutyrate (from the optically active alcohol, 80% enantiomeric purity) and trapping of the anion with trimethylsilyl chloride produced (90%) the corresponding (*S*)-(+)-2-methyl-1-(2-methylbutoxy)-1-trimethylsilyloxyprop-1-ene (**1**). The amount of *C*-silylated product was <1%, as observed for α-disubstituted carboxylates.[8]

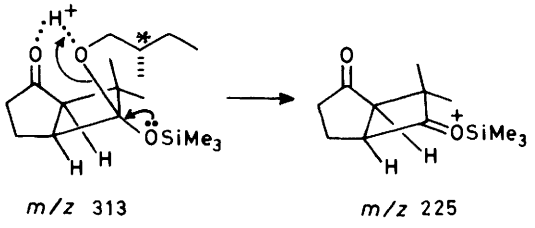
Photoaddition of ketene acetal (**1**) to cyclopent-2-enone in hexane, irradiated at the (n→π*) absorption band at 350 nm, proceeded readily. The reaction products were separated by column chromatography. Oxetanes, resulting from a Paterno–Büchi reaction with the carbonyl function, and cyclobutanes arising from addition to the enone double bond, were isolated in the ratio 6.5:3.5 with a total yield of 60%.

Within the oxetane series, two compounds (**2**) and (**4**) were isolated. Identification of the oxetane acetal (**2**) was straightforward (4 singlets between δ 1.3—1.4 in the relative



Asterisks denote chiral carbon atoms

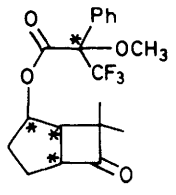
proportions 3:1:1:3 and an AB-spin system around δ 5.85—5.97 in the ^{1}H n.m.r. spectrum). The complexity of the spectrum results from the presence of four diastereoisomers due to the formation of two extra chiral centres at C-3 and C-4. The regioisomers actually found are those expected from electronic effects governing the characteristics of the excited enone and the ground-state alkene.[5a] The minor component (**4**) was apparently formed by a trimethylsilyl shift to the oxetane oxygen atom in (**3**). The orthoester group, incorporated into a four-membered ring, rearranged to the more stable trimethylsilyloxy ester (**4**). Analogous transformations of a cyclobutane trimethylsilyloxy function have been reported.[9] Structure (**4**), deduced from spectroscopic data (see Experimental section), was confirmed upon treatment of compound (**4**) with toluene-*p*-sulphonic acid in benzene which gave both isomeric cyclopentadienes (**5**). The *cis* [2C + 2C] addition of alkene (**1**) to cyclopent-2-enone was completely regioselective and led to the four diastereoisomeric head-to-tail cycloadducts (**6a**—**d**) (**a**—**d** refer to the elution sequence in capillary g.c.) in the proportions 6:29:33:32, respectively. The mixture (**6**) gave, upon acid hydrolysis, 7,7-dimethylbicyclo[3.2.0]heptane-2,6-dione (**7**) as the only product. Cycloadducts (**6**) and dione (**7**) were characterized by spectroscopy (see Experimental section). The isobutane chemical ionization mass spectra, obtained *via* coupling with g.c., revealed that the diastereoisomers (**6**) belong to two series with peaks at *m/z* 225 and *m/z* 223, respectively, as the main fragment ion peaks. Loss of 2-methylbutan-1-ol from the molecular ion afforded the ion of *m/z* 225 (**6a** and **b**), while loss of trimethylsilanol gave rise to the ion of *m/z* 223 (**6c** and **d**). It is very likely that the elimination process starts with insertion of a proton from the reactant gas between the carbonyl function and the *endo* oxygen atom,[10] followed by carbon–oxygen bond cleavage, which is facilitated by the adjacent electron-donating oxygen atom. The sequence is illustrated for the loss of 2-methylbutan-1-ol in Scheme 1. From this analysis it was deduced that the cycloadduct with the *endo*-orientated trimethylsilyloxy group represents *ca.* 66% of the mixture.



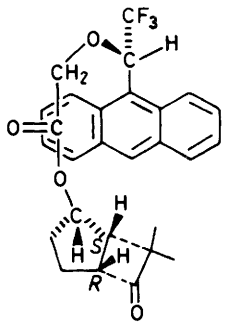
Scheme 1.

The preferential formation of oxetanes with respect to cyclobutanes must be due to the steric hindrance exerted by the highly substituted alkene (**1**). This effect will be more pronounced during the formation of the bicyclo[3.2.0]heptan-2-one (**6**) than during the Paterno–Büchi reaction. Indeed, simpler ketene acetals, such as 1,1-dimethoxyethene, react exclusively at the carbon–carbon double bond,[11] while, for example, tetramethylethene yields up to 30% of oxetanes in the photoreaction with cyclohex-2-ene-1,4-dione.[12,13] Thus, it seems that steric effects can outweigh electronic factors.[14]

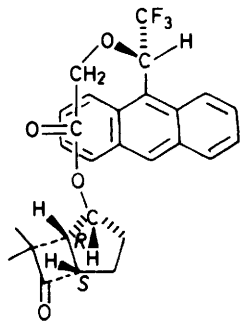
The extent of asymmetric induction should preferably be determined on compound (**7**). However, the use of the chiral shift reagent tris-[3-(heptafluoropropylhydroxymethylene)-(+)-camphorato]europium(III) complex[15] did not cause specific changes in the ^{1}H n.m.r. spectrum. Therefore, the isomeric cycloadducts (**6**) were reduced with sodium borohydride in a totally stereospecific fashion to give compound (**8**).[5a] Acid hydrolysis led to *endo*-2-hydroxy-7,7-dimethylbicyclo[3.2.0]heptan-6-one (**9**). Again, the chiral shift reagent did not allow determination of the enantiomeric purity. As a consequence of this it was necessary to prepare diastereoisomers. From esterification of (**9**) with (*S*)-(−)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride[16] the e.e. can be deduced based on the respective areas of the methoxy and the methyl ^{1}H n.m.r. signals of the two diastereoisomers (**10**). Enantiomeric purities up to 30% were found. The same result was obtained from the integration for the respective fluorine absorptions in the ^{19}F n.m.r. spectra. Taking into account the enantiomeric purity of the starting alcohol, the asymmetric induction amounts to some 36%.



(**10**)



(**11**)



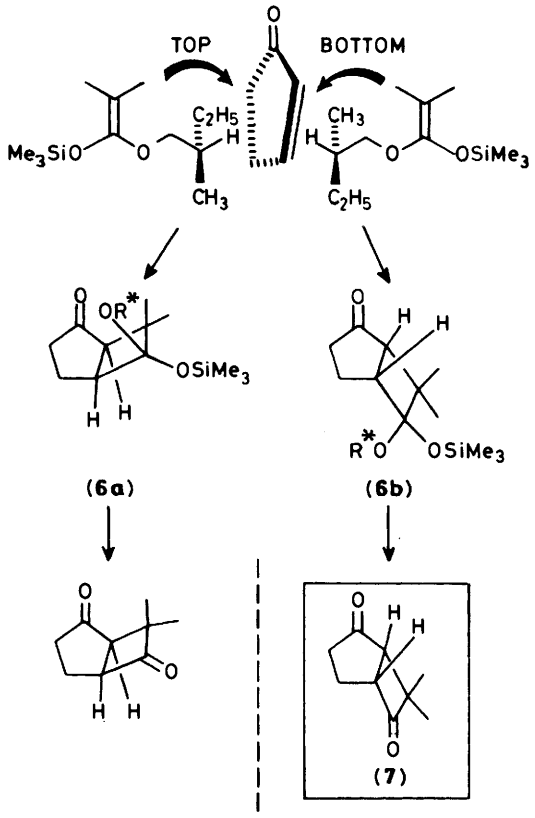
(**12**)

The absolute configuration of the predominant enantiomer of (**9**) was determined, both by Horeau's method[17] and Pirkle's technique.[18] In the latter case, the preferred conformation of the ester formed from (**9**) and (*R*)-(−)-[1-(9-anthryl)-2,2,2-trifluoroethoxy]acetic acid and is represented by structure (**11**). Protons directed towards the anthryl group are shielded much more than those pointing away from the aromatic moiety. As a consequence, the chemical shift non-equivalence between the *gem* dimethyl groups of the predominant diastereoisomer (**11**) relative to the minor diastereoisomer (**12**) is very pronounced: 0.33 p.p.m. and 0.30 p.p.m., respectively. The highest known value of the chemical shift differences for any ester of this type is only 0.14 p.p.m.[18] In the present case, owing to the fixed structural array, the *gem* dimethyl groups are literally buried in the anthryl electron cloud, leading to an unprecedented shielding effect. In the minor diastereoisomer the methyl proton resonances resemble very much those of the original bicyclic hydroxy ketone (**9**). Other shift differences were also noted, but these are either not pronounced or not unequivocally interpretable.

Both methods indicate the *S*-configuration for C-2 in (**9**). Since the relative configuration of the two chiral bridgehead centres in (**9**) with respect to the secondary alcohol function at C-2 was known, it follows that C-1 has the *S*-configuration and C-5 the *R*-configuration.

The asymmetric induction in (**6**), and consequently also in (**7**), was brought about by the interaction of the chiral centre in the alkene with the cyclopent-2-enone skeleton. Approach of the chiral alkene to cyclopent-2-enone can occur from either the top

or the bottom face (Scheme 2). Since the steric predisposition is different for both modes, one diastereoisomer will preferentially be formed. The predominant enantiomer, namely (1*S*,5*R*)-7,7-dimethylbicyclo[3.2.0]heptane-2,6-dione (**7**), is the one expected from the sterically least hindered reaction mode.



Scheme 2.

The intrinsic e.e. was easily deduced from the g.c. pattern of the cycloadduct mixture (**6**). Compounds (**6a** and **b**) are diastereoisomers with the alkoxy group in the *endo* position. The ratio (**6b**):(**6a**) then reflects the e.e., being around 80%. It should be pointed out, however, that formation of (**6a**) is due to the presence of the minor enantiomer in the chiral alcohol used (see above). On the other hand, when the chiral alkene approaches the substrate with the achiral trimethylsilyloxy group in the *endo* fashion, the chiral discrimination is negligible, as indicated by the ratio (**6c**):(**6d**), which is nearly unity.

Conclusions

The chirality induced in 7,7-dimethylbicyclo[3.2.0]heptane-2,6-dione *via* a [2C + 2C] photoannelation by the aid of a chiral alkene is partially obscured by the presence of the non-chiral trimethylsilyloxy group in the alkene substrate. It follows that the experimentally measured e.e. of 30% reflects the chiral induction in only one third of the cycloadduct mixture (**6a** and **b**). As a consequence, the intrinsic chiral induction, *i.e.* when the chiral entity reacts in the *endo* mode, should be nearly quantitative. Such a situation would occur if an optically pure ketene acetal containing two chiral alkoxy groups could be used as a chiral handle.

Experimental

Spectroscopy and Chromatography.—I.r. spectra were taken on a Beckman IR-4230 spectrophotometer. 360 MHz ^{1}H and ^{19}F n.m.r. spectra were obtained (except where otherwise stated) on a Bruker WH 360 machine (tetramethylsilane as internal standard in $CDCl_3$; trifluoroacetic acid as external standard in ^{19}F n.m.r.). C.i. (isobutane) and e.i. (He) mass spectra were recorded with a Finnigan 1200 mass spectrometer connected to a Data General Nova C INCOS System. G.c. analyses were carried out on a Varian 1200 gas chromatograph equipped with a glass capillary column coated with OV-1 (3 mg ml^{-1}; 0.25 μm film thickness; length 20 m; i.d. 0.5 mm); t.l.c. was performed on precoated plates (Merck silica gel 60F 254); for h.p.l.c. (high-performance liquid chromatography) separations a Waters Associates Prep LC/System 500 was used.

Synthesis of (S)-(+)-2-*Methyl*-1-(2-*methylbutoxy*)-1-*trimethylsilyloxyprop*-1-*ene* (**1**).—To a solution of di-isopropylamine (110 ml, 0.78 mol) in THF (500 ml) was added, at 0 °C under N_2, a hexane solution (480 ml) of n-butyl-lithium (1.6M; 0.76 mol) during 10 min. After 30 min the mixture was cooled to −78 °C and (S)-(+)-(2-*methylbutyl*)*isobutyrate* (120 g, 0.76 mol) was added (10 min). The stirred solution was maintained at −78 °C for 30 min. Then trimethylsilyl chloride (240 ml, 1.9 mol) was added (10 min). After being warmed to 20 °C and having been stirred (30 min), the mixture was filtered and concentrated. The residue was washed with dry ether and filtered. After removal of ether under reduced pressure, the remaining oil was distilled (20 mmHg, 88 °C) to yield compound (**1**) (157 g, 90%), $\nu_{max.}$ 1 705s, 1 250s, 1 190s, 1 150s, 965w, 870s, 840s, and 750w cm^{-1}; δ_H (Varian EM-390 90 MHz) 0.18 (9 H, s), 0.92—1.0 (6 H, d + t), 1.53 (3 H, s), 1.6 (3 H, s), 1.4—1.8 (3 H, m), and 3.4—3.8 (2 H, m); *m/z* (e.i.) 230 (5%), 161 (3), 144 (22), 129 (25), 43 (50), and 41 (100).

Photocycloaddition between Cyclopent-2-*enone and* (**1**).—Cyclopent-2-enone (11 g, 0.134 mol) and (*S*)-(+)-2-methyl-1-(2-methylbutoxy)-1-trimethylsilyloxyprop-1-ene (**1**) (60 g, 26 mmol) were irradiated in a photoreactor (Rayonet; New England Ultraviolet Company, Hamden, Connecticut, U.S.A.) at 350 nm (n→π* excitation in hexane 220 ml). The photoaddition was monitored by t.l.c. (ethyl acetate-hexane (4:96); R_F values: 0.21, 0.25, and 0.44 for (**6**), (**2**), and (**4**) respectively]; after disappearance of cyclopent-2-enone (150 h) the reaction mixture was separated by h.p.l.c. [silica gel; ethyl acetate–hexane (2:98)] or by column chromatography [Florisil; ethyl acetate–hexane (0.5:99.5).

Compound (**4**) (20 mg, 64 μmol) was dissolved in benzene (5 ml) containing a trace of toluene-*p*-sulphonic acid for 3 h. After addition of sodium hydrogencarbonate, filtration, and evaporation, the residue was purified by column chromatography [Florisil; ethyl acetate–hexane (2:98)] to yield compound (**5**) (12.3 mg, 88%)].

Data for compound (**2**): $\nu_{max.}$ 1 610w, 1 245s, 1 195s, 1 155s, 1 090s, 835s, and 745s cm^{-1}; δ_H 0.13 and 0.20 (9 H, 2 s), 0.85—1.0 (6 H, m), 1.0—1.5 (2 H, m), 1.3—1.4 (6 H, 4 s, proportions 3:1:1:3), 1.58—1.73 (1 H, m), 1.75—1.9 (1 H, m), 2.16—2.34 (1 H, m), 2.38—2.55 (2 H, m), 3.07—3.46 (2 H, m), and 5.85—6.0 (2 H, m); *m/z* (c.i.) 313 (2%), 255 (100), 225 (8), 223 (7), 155 (3), 83 (1), 75 (2), and 73 (9).

Data for compound (**4**): $\nu_{max.}$ 1 725s, 1 615w, 1 245s, 1 075s, 835s, and 750s cm^{-1}; δ_H 0.02 (9 H, s), 0.88—0.98 (6 H, m), 1.12 and 1.19 (6 H, 2 s), 1.12—1.55 (2 H, m), 1.62—1.80 (2 H, m), 2.18—2.31 (1 H, m), 2.38—2.56 (2 H, m), 3.78—4.20 (2 H, m), and 5.89—5.97 (2 H, m); *m/z* (c.i.) 313 (1%), 255 (1), 225 (2), 223 (100), 153 (39), and 83 (2).

Data for compound (**5**): $\nu_{max.}$ 1 730s, 1 600w, 1 250s, 1 110s, and 990w cm^{-1}; δ_H 0.75—1.00 (6 H, m), 0.90—1.95 (3 H, m), 1.40 (6 H, s), 2.94 (2 H, m), 3.83—4.16 (2 H, m), and 6.05—6.60 (3 H, m); *m/z* (c.i.) 222 (5%), 152 (3), 107 (100), and 91 (45).

Data for compound (**6**): $\nu_{max.}$ 1 735s, 1 255s, 1 180s, 1 135s,

1 070s, 895w, 840s, and 755w cm^{-1}; δ_H 0.17—0.20 (9 H, 2 s), 0.86—1.00 (9 H, m), 1.09—1.73 (3 H, m), 1.15—1.20 (3 H, 4 s), 1.79—1.93 (1 H, m), 2.05—2.37 (3 H, m), 2.42—2.65 (1 H, m), and 3.05—3.53 (3 H, m); *m/z* (c.i.) (**6a**): 313 (5%), 298 (6), and 225 (100); (**6b**) 313: (3%) and 225 (100); (**6c**): 313 (3%) and 223 (100); (**6d**): 313 (1.5%) and 223 (100).

Hydrolysis of Compound (**6**).—A solution of compound (**6**) (319.4 mg, 1.02 mmol) and toluene-*p*-sulphonic acid (5 mg) in benzene (10 ml) was stirred for 8 h and was then neutralized with sodium hydrogencarbonate. Column chromatography [ethyl acetate–hexane (2:98)] afforded the pure dione (**7**) (82.4 mg, 54%), $\nu_{max.}$ 1 780vs and 1 735vs cm^{-1}; δ_H 1.05 (3 H, s), 1.28 (3 H, s), 1.98—2.15 (1 H, m), 2.25—2.48 (3 H, m), 2.71 (1 H, dd, *J* 7.8 and 1.0 Hz), and 3.95 (1 H, 2 t, *J* 7.8 and 1.0 Hz); *m/z* (c.i.) 152 (1%), 124 (8), 82 (28), 70 (100), 55 (20), and 42 (36).

Synthesis of Compound (**9**).—A solution of cycloadduct (**6**) (12.5 mg, 40 μmol) and sodium borohydride (3.5 mg, 145 μmol) in EtOH (4 ml) was stirred during 15 h. The mixture was neutralized (saturated aqueous NH_4Cl) and extracted with ether. After being dried ($MgSO_4$), the solvent was removed and the residue was hydrolysed in a two-phase system (3M HCl–CH_2Cl_2, 2 ml each). Work-up and column chromatography [silica gel; EtOAc–hexane (1:1)] afforded the pure hydroxyketone (**9**) (2.8 mg, 51%), $\nu_{max.}$ 3 440br, 1 765vs, 1 465s, 1 115s, 1 080s, and 1 055s cm^{-1}; δ_H 1.23 and 1.30 (6 H, 2 s), 1.55—2.10 (5 H, m), 2.57 (1 H, t, *J* 7.5 Hz), 3.57 (1 H, t, *J* 7.5 Hz), and 4.48 (1 H, ddd, *J* 7.5, 6.25, and 11.25 Hz).

Resolution of Diastereoisomers of Compound (**9**).—(*a*) Following Horeau's method, a solution of compound (**9**) (5.17 mg, 34 μmol) and racemic 2-phenylbutyric anhydride (22 mg, 0.71 mmol) in pyridine (0.5 ml) was stirred for 10 h at room temperature. After addition of a few drops of water, the mixture was stirred for a further 30 min on a hot-water bath. Then the reaction mixture was poured into a solution of water–benzene (2 ml:3 ml) and titrated with 0.1M NaOH (phenolphthalein) until pH 9.0. After extraction with benzene (10 ml portions) the aqueous layer was acidified (2M; pH 1) and again extracted with benzene (10 ml portions). The extract was concentrated and the optical rotation measured (negative plain o.r.d. curve).

(*b*) A solution of compound (**9**) (15.4 mg, 0.1 mmol) in dry THF (1 ml) and pyridine (0.3 mmol) was refluxed for 2 h with the appropriate acid chloride {(−)-α-methoxy-α-trifluoromethylphenylacetyl chloride[16] or (−)-[1-(9-anthryl)-2,2,2-trifluoroethoxy]acetyl chloride[18]}. Work-up afforded the respective diastereoisomeric esters of (**9**) in quantitative yield after purification by column chromatography [silica gel; EtOAc–hexane (3:17)]. It was ascertained that the relative composition of the diastereoisomeric mixture remained unchanged during this operation.

Data for compounds (**10**): δ_H 0.75 (0.35 × 3 H, s), 0.9 (0.65 × 3 H, s), 1.1 (0.35 × 3 H, s), 1.2 (0.65 × 3 H, s), 1.3—2.3 (5 H, m), 2.68—2.79 (1 H, m), 3.47 (0.65 × 3 H, s), 3.52 (0.35 × 3 H, s), 5.4—5.52 (1 H, m), and 7.4—7.6 (5 H, m); δ_F 4.47 (0.35 H, s) and 4.34 (0.65 H, s).

Data for diastereoisomer (**11**): δ_H 0.75 (0.65 × 3 H, s), 0.92 (0.65 × 3 H, s), 1.08 (0.35 × 3 H, s), 1.22 (0.35 × 3 H, s), 1.4—2.2 (5 H, m), 2.70 (0.35 × 3 H, t), 2.77 (0.65 × 3 H, t), 3.8—4.2 (2 H, m), 3.86 and 4.14 (0.35 × 2 H, AB pattern, *J* |17| Hz), 3.97 and 4.17 (0.65 × 2 H, AB pattern, *J* |17| Hz), 5.1—5.2 (1 H, m), 6.65 (0.65 × 1 H, q, *J* 7.5 Hz), 6.76 (0.35 × 1 H, q, *J* 7.5 Hz), and 7.5—9.0 (9 H, m).

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