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Study of the Reaction of a Chiral Oxazolone with Oxosulphonium Methylides as Cyclopropanating Agents

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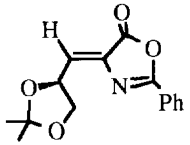
Abstract: *The behaviour of the chiral Z-oxazolone derived from 1,2-O-isopropylidene-D-glyceraldehyde towards oxosulphonium methylides as cyclopropanating agents has been studied. The solvent and temperature dependence of the ratio of the products is described.*

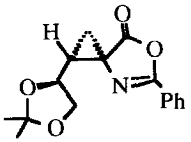
Since the first report[1] on the isolation and identification of 1-aminocyclopropanecarboxylic acid (ACC) as an intermediate in the biosynthesis of ethylene in higher plants,[2] the synthesis of this compound and its derivatives has attracted special interest.[3] Of particularly interest is the development of substrates that may induce an inhibition of ethylene production, thus allowing potential control of the ripening process. In this context, extensive efforts have been directed towards the asymmetric synthesis of ACC analogues monosubstituted in the cyclopropane ring in order to conserve the α-amino acid moiety.[4]

α,β-Didehydroamino acid derivatives are useful prochiral building blocks in synthetic organic chemistry. In particular, oxazolones unsaturated in C_4 have proved to be versatile intermediates in the synthesis of amino acids,[5] cycloaliphatic[6] and cyclopropylamino acids.[7] Moreover, these compounds are easily transformed into N-acyl-α,β-didehydroamino acid derivatives, which are powerful synthetic tools.[8] Our interest in the asymmetric synthesis of cyclopropylamino acids has prompted us to use a chiral oxazolone **1Z** as a synthetic precursor of these compounds.

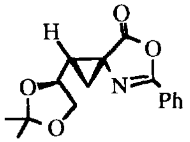


1Z

In this endeavour we reported[9] recently that Z-2-phenyl-4-[(*S*)-2,2-dimethyl-1,3-dioxolan-4-ylmethylene]-5(4H)-oxazolone **1Z** underwent *cis*-stereoselective and highly diastereofacial selective 1,3-dipolar cycloaddition with diazomethane to afford spirocompounds ***cis*-2a**, ***cis*-2b**, ***trans*-2a**, and ***trans*-2b**. The *cis/trans* selectivity and the diastereofacial selectivity as well as the presence or absence of a C-methylation by-product depended on temperature and solvent polarity.



***cis*-2a**



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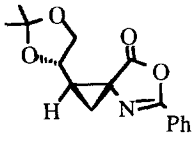
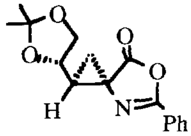


***trans*-2a**



***trans*-2b**

In the best conditions (hexane, -75 °C) we obtained the major compound *(1S,2R)*-2-[*(S)*-2,2-dimethyl-1,3-dioxolan-4-yl]-1-spiro{4'[2'-phenyl-5'(4'H)-oxazolone]}cyclopropane ***cis*-2a** with a *cis/trans* selectivity of 83/17 and a *cis* diastereofacial selectivity of 90/10.

This compound could be converted[10] to enantiomerically pure *(1S,2R)*-allocoronamic acid in a 37 % overall yield by standard transformations, proving its versatility as intermediate in the synthesis of 2-substituted cyclopropylamino acids.

Diazomethane is a very harmful and hazardous reagent that must be handled with caution and whose preparation in large amounts should be avoided. For this reason we have looked for an alternative procedure to obtain spirocompounds by using oxazolone **1Z** which is easily accessible on a multigram-scale, without using diazomethane as cyclopropanating agent. Attention was then directed to the search for a reagent that could cyclopropanate **1Z** in a high stereo and diastereofacial selective fashion.

The first reagent investigated in this endeavour was the Corey ylide, dimethyloxosulphonium methylide.[11] Upon treatment of **1Z** with 1.2 molar equiv. of the NaH-derived ylide in dimethylformamide at room temperature, cyclopropanation products were obtained with *trans* selectivity, a *cis/trans* ratio 40/60, a *cis* diastereofacial selectivity of 61/39 and a *trans* diastereofacial selectivity of 78/22. As the reaction is supposed to take place through an open chain intermediate,[12] *cis/trans* selectivity as well as diastereofacial selectivities can be greatly influenced by the solvent polarity. The same reaction carried out in dimethylsulphoxide afforded cyclopropanation products with an even better *trans* selectivity, but with very low *cis* and *trans* diastereofacial selectivities. By using methylene chloride as the solvent, we observed a moderate *trans* selectivity and better *cis* and *trans* diastereofacial selectivities and, with the use of toluene as solvent, good *cis* and *trans* diastereofacial selectivities were obtained but the amount of *cis* and *trans* spirocompounds was almost equimolecular. (Table 1)

In general when the reaction was carried out at lower temperatures, the yield of *cis* spirocompounds was increased and a slight improvement in *cis* and *trans* diastereofacial selectivities was observed. Nevertheless, in no case was the Corey ylide better or even equal to diazomethane as the cyclopropanating agent.

These disappointing results prompted us to examine (diethylamino)phenyloxosulphonium methylide,[13] which has proved to be both more selective and diastereofacialselective,[12] as analternative cyclopropanating agent. Cyclopropanation of **1Z** with 1.2 molar equiv. of (diethylamino)phenyloxosulphonium methylide in DMF at room temperature provided cyclopropanation products in an almost equimolecular *cis/trans* ratio and with a very low diastereofacial selectivity. The same reaction carried out in dimethylsulphoxide also afforded cyclopropanation products without selectivity and with poor *cis* and *trans* diastereofacial selectivities. With other solvents, *cis* selectivity as well as *cis* and *trans* diasterofacial selectivities were improved in all cases except when methylene chloride was used as the solvent. In this case, *trans* spirocompounds were the major products with a moderate *trans* selectivity and a good diastereofacial *trans* selectivity. When the reaction temperature was reduced, the amount of *cis* spirocompounds did not change in some cases and in other cases was improved to a small extent, while diastereofacial selectivities were slightly influenced, except when dimethylformamide was used as the solvent. In this case, low temperatures considerably increased diastereofacial selectivities. From the results shown in table 1 we can conclude that (diethylamino)phenyloxosulphonium methylide in hexane at 0 °C can be an alternative to the use of diazomethane as cyclopropananting the agent to obtain spirocompound ***cis*-2a** on large-scale.

Table 1. Reaction of **1Z** with Oxosulphonium Ylides as Cyclopropanating Agents.

Reagent	Solvent[a]	temp (°C)	cis/trans[a]	cis d.r.[a]	trans d.r.[a]
$(CH_3)_2SOCH_2$	DMF	r. t.	40/60	61/39	78/22
	DMF	- 20	35/65	61/39	81/19
	DMF	0	28/32	63/37	85/15
	DMSO	r. t.	25/75	56/44	60/40
	CH_2Cl_2	r. t.	37/63	88/12	97/3
	CH_2Cl_2	0	47/53	91/9	98/2
	CH_2Cl_2	- 20	52/48	94/6	98/2
	toluene	r. t.	49/51	82/18	96/4
	toluene	0	54/46	81/19	97/3
	toluene	- 20	70/30	85/15	97/3
$PhNEt_2SOCH_2$	DMF	r. t.	56/44	57/43	63/37
	DMF	0	67/33	75/25	80/20
	DMF	- 20	73/27	80/20	86/14
	DMSO	r. t.	53/47	62/38	70/30
	CH_2Cl_2	r. t.	34/66	73/27	90/10
	CH_2Cl_2	0	38/62	74/26	90/10
	CH_2Cl_2	- 20	53/47	74/26	91/9
	toluene	r. t.	61/39	79/21	97/3
	toluene	0	63/37	85/15	98/2
	toluene	- 20	62/38	87/13	98/2
	ether	r. t.	57/43	82/18	97/3
	ether	0	55/45	81/19	97/3
	ether	- 20	55/45	83/17	98/2
	THF	r. t.	51/49	77/23	92/8
	THF	0	50/50	78/22	93/7
	THF	- 20	51/49	80/20	96/4
	hexane	r. t.	72/28	86/14	96/4
	hexane	0	82/18	87/13	96/4
	hexane	- 20	83/17	87/13	96/4

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[a] The product ratio was determined by HPLC. Column radial pack silica (8 mp 10 mm). Eluent hexane-ethyl acetate 80/20. Flow rate 3 ml/min. Detection 248 nm.

The stereochemical assignments of all compounds were made after conversion to their methyl esters, upon treatment with 1 % sodium methoxide in methanol. The *cis/trans* stereochemistries of the cyclopropyl esters were assigned on the basis of NOE difference ^{1}H NMR experiments.[9] In those cyclopropyl esters which were assigned as *cis* the amide hydrogen exhibited a significant NOE enhancement on presaturation of the corresponding proton H_a whereas in those cyclopropyl esters which were assigned as *trans* the amide hydrogen exhibited a significant NOE enhancement on presaturation of both corresponding protons H_b and H_x (Figure 1).

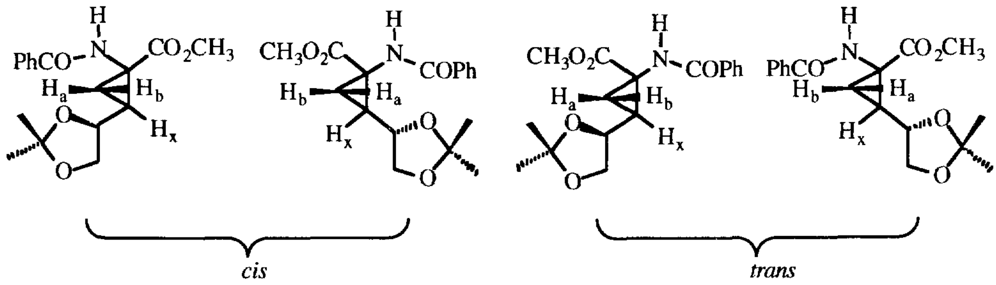


Figure 1

The absolute stereochemistry of the major *cis* compound ***cis*-2a** *(1S,2R)* was assigned by single crystal X-ray analysis, as reported previously,[9] and the absolute stereochemistry of the crystalline minor *trans* spirocompound ***trans*-2b** was unambiguously determined by single crystal X-ray analysis,[14] (Figure 2), which showed that the cyclopropyl moiety has a *1S,2S* configuration. So the absolute stereochemistry of the major *trans* spirocompound ***trans*-2a** is *1R,2R*.

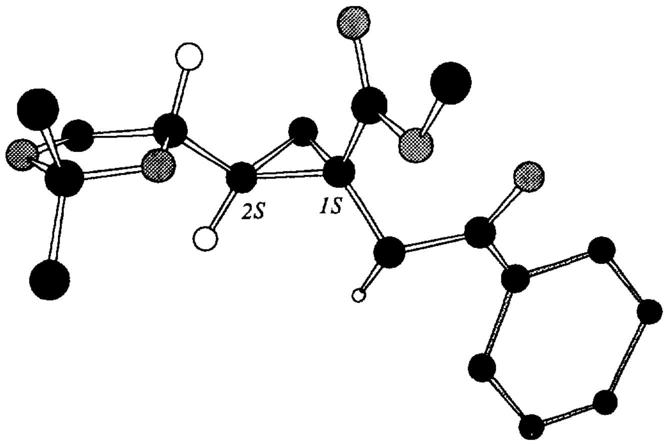
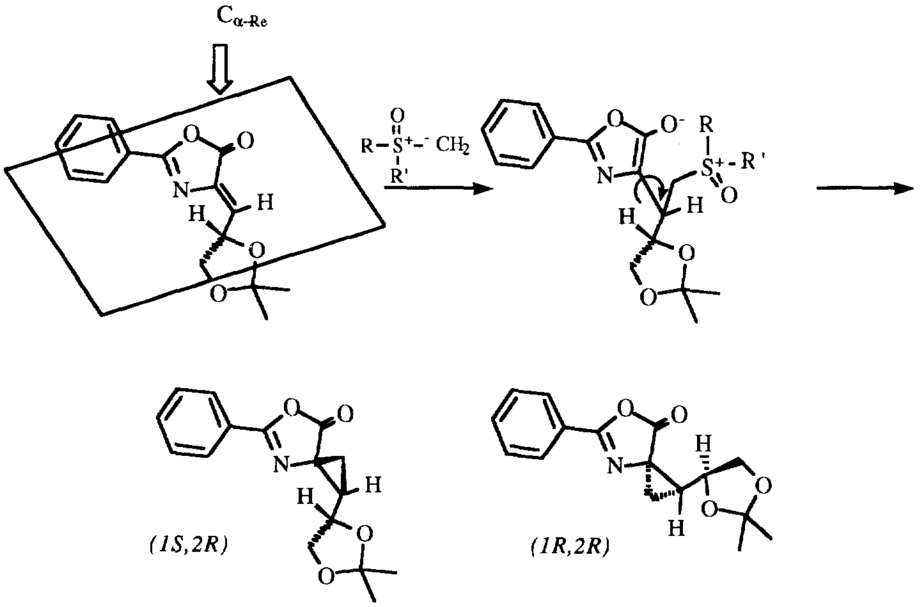


Figure 2

The sense of the diastereofacial selectivity for *cis* and *trans* spirocompounds can be rationalised considering that the sulfoximide attack on the oxazolone proceeds from the $C_{\alpha\text{-}Re}$ face of the double bond,which is sterically less hindered in the conformer with minimum energy, as we have shown by AM1 semi-empirical calculations.[15] This attack affords a Michael-type adduct which can rotate prior to cyclisation to the cyclopropane, which explains the poorer selectivity, affording the *cis* spirocompounds of *1S,2R* configuration and the *trans* spirocompound of *1R,2R* configuration as the major products.(Scheme 1)



Scheme 1

In conclusion, the methodology described here satisfactorily completes our initial approach to the asymmetric synthesis of cyclopropylamino acids using the chiral oxazolone derived from *D*-glyceraldehyde as the chiral starting material.

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EXPERIMENTAL

Apparatus: ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Varian Unity 300 MHz spectrometer in deuterochloroform using the solvent signal as internal standard, chemical shifts are expressed in ppm. IR spectra were recorded on a Perkin-Elmer 1600 FTIR infrared spectrophotometer. Optical rotations were measured on a Perkin-Elmer 241-C polarimeter at 25°C. Melting points were determined on a Büchi 510 capillary melting point apparatus and are uncorrected. HPLC analyses were carried out with a Waters 600-E chromatograph equiped with a photodiode array detector. Analyses were determined on a Perkin-Elmer 2400 C, H, N, S analyzer.

Chemicals: All reactions were carried out under Ar with magnetic stirring. Solvents were dried prior to use. Trimethyloxosulphonium iodide was purchased from Aldrich Chemical Co. Oxazolone **1Z**[15,16] and (diethylamino)methylphenyloxosulphonium tetrafluoroborate[13] were prepared following the methods described in the literature. TLC was performed on Merck precoated silicagel plates, which were visualised using UV light. Medium Pressure chromatography was performed using 230-400 mesh (Merck) silicagel.

General procedure for oxosulphonium methylide additions

A typical experiment was carried out as follows: A mixture of the corresponding oxosulphonium salt (1.2 mmol) and 95 % sodium hydride (30.3 mg, 1.2 mmol) in the appropriate dry solvent (3 mL) was stirred at room temperature for several minutes. When the evolution of gas had ceased, the freshly prepared ylide was added *via* cannula to a solution of compound **1Z** (273 mg, 1 mmol) in the same solvent as above (5 mL) at the appropiate temperature. The solution was stirred until the reaction was complete. To the mixture was added brine (3 mL) followed by extraction with ethyl acetate (3 x 10 mL). The organic fractions were combined, washed with water (3 x 10 mL), dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. Medium pressure chromatography on silicagel eluting with hexane/ethyl acetate 8:2 enabled us to isolate of the four spirocompounds ***cis*-2a**, ***cis*-2b**, ***trans*-2a** and ***trans*-2b** in diastereomerically pure form.

(1S,2R)-2[*(S)*-2,2-Dimethyl-1,3-dioxolan-4-yl]-1-spiro-{4'[2'-phenyl-5'(4'H)-oxazolone]}cyclopropane ***cis*-2a.** M.p. 132 °C; $[\alpha]_D$ = - 15.8 (c = 1 in $CHCl_3$); IR 1816, 1636 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.38 (s, 3H), 1.45 (s, 3H), 1.98 (dd, 1H, J = 9.5 Hz, J = - 4.1 Hz), 2.01 (dd, 1H, J = 8.7 Hz, J = - 4.1 Hz), 2.19 (m, 1H, J = 9.5 Hz, J = 9.4 Hz, J = 8.7 Hz), 3.61 (dd, 1H, J = - 8.2 Hz, J = 6.4 Hz), 4.04 (dd, 1H, J = - 8.2 Hz, J = 6.1 Hz), 4.17 (m, 1H, J = 9.4 Hz, J = 6.4 Hz, J = 6.1 Hz), 7.42-7.48 (m, 2H), 7.52-7.58 (m, 1H), 7.92-7.98 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 24.4, 25.7, 26.8, 34.3, 50.8, 69.0, 76.3, 109.6, 126.0, 127.4, 128.8, 132.6, 162.4, 177.5. Anal. Calcd. for $C_{16}H_{17}NO_4$: C, 66.89; H, 5.96; N, 4.87. Found C, 66.98; H, 5.82; N, 4.96.

(1R,2S)-2[*(S)*-2,2-Dimethyl-1,3-dioxolan-4-yl]-1-spiro-{4'[2'-phenyl-5'(4'H)-oxazolone]}cyclopropane ***cis*-2b.** Mp 89 °C; $[\alpha]_D$ = + 19.0 (c = 1 in $CHCl_3$); IR 1815, 1638 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.33 (s, 3H), 1.41 (s, 3H), 1.70 (dd, 1H, J = 8.4 Hz, J = - 5.1 Hz), 1.87 (dd, 1H, J = 9.6 Hz, J = - 5.1 Hz), 2.22 (m, 1H, J = 9.6 Hz, J = 8.5 Hz, J = 8.4 Hz), 3.84-3.92 (m, 1H), 4.12-4.26 (m, 2H), 7.42-7.48 (m, 2H), 7.50-7.56 (m, 1H), 7.94-8.00 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.3, 25.6, 26.8, 34.6, 51.4, 68.6, 75.0, 109.9, 126.3, 127.5, 128.7, 132.4, 162.2, 177.7. Anal. Calcd. for $C_{16}H_{17}NO_4$: C, 66.89; H, 5.96; N, 4.87. Found C, 66.77; H, 5.92; N, 4.73.

(1R,2R)-2[*(S)*-2,2-Dimethyl-1,3-dioxolan-4-yl]-1-spiro-{4'[2'-phenyl-5'(4'H)-oxazolone]}cyclopropane ***trans*-2a.**

Mp 80 - 82°C; $[\alpha]_D$ = + 7.9 (c = 1 in $CHCl_3$); IR 1812, 1638 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.36 (s, 3H), 1.47 (s, 3H), 1.93 (dd, 1H, J = 8.3 Hz, J = - 5.1 Hz), 2.17 (dd, 1H, J = 9 Hz, J = - 5.1 Hz), 2.38 (m, 1H, J = 9.7 Hz, J = 9 Hz, J = 8.3 Hz), 3.67 (dd, 1H, J = - 8.3 Hz, J = 6.2 Hz), 4.04 (dd, 1H, J = - 8.3 Hz, J = 6.1 Hz), 4.37 (m, 1H, J = 9.7 Hz, J = 6.2 Hz, J = 6.1 Hz), 7.42-7.50 (m, 2H), 7.52-7.58 (m, 1H), 7.90-7.96 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 25.4, 25.5, 26.9, 34.8, 50.8, 68.8, 73.8, 109.6, 125.8, 127.3, 128.8, 132.5, 161.8, 176.8. Anal. Calcd. for $C_{16}H_{17}NO_4$: C, 66.89; H, 5.96; N, 4.87. Found C, 66.93; H, 6.05; N, 4.91.

(1S,2S)-2[*(S)*-2,2-Dimethyl-1,3-dioxolan-4-yl]-1-spiro-{4'[2'-phenyl-5'(4'H)-oxazolone]}cyclopropane ***trans*-2b.**

Mp 113 °C; $[\alpha]_D$ = - 22.0 (c = 0.5 in $CHCl_3$); IR 1795, 1638 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.30 (s, 3H), 1.39 (s, 3H), 1.66 (dd, 1H, J = 8.6 Hz, J = - 5.3 Hz), 2.02 (dd, 1H, J = 9.5 Hz, J = - 5.3 Hz), 2.37 (m, 1H, J = 9.6 Hz, J = 9.5 Hz, J = 8.6 Hz), 3.81 (dd, 1H, J = - 8.3 Hz, J = 6.1 Hz), 4.14 (dd, 1H, J = - 8.3 Hz, J = 6.2 Hz), 4.35 (m, 1H, J = 9.6 Hz, J = 6.2 Hz, J = 6.1 Hz), 7.40-7.48 (m, 2H), 7.50-7.56 (m, 1H), 7.92-7.96 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 22.5, 25.4, 26.9, 35.1, 50.7, 68.5, 72.6, 109.7, 126.0, 127.3, 128.7, 132.3, 161.8, 176.4. Anal. Calcd. for $C_{16}H_{17}NO_4$: C, 66.89; H, 5.96; N, 4.87. Found C, 66.81; H, 5.85; N, 5.01.

General procedure for spirooxazolone methanolysis

A suspension of the corresponding spirooxazolone (2.9 g, 10 mmol) in a solution of sodium methoxide (0.02 g) in absolute methanol (80 ml) was stirred at room temperature for 30 min. After the reaction was complete, the solution was concentrated *in vacuo* and the residue was dissolved in chloroform, washed with water, dried with anhydrous magnesium sulphate and concentrated *in vacuo* to afford the corresponding methyl ester in nearly quantitative yield.

Methyl *(1S,2R)*-1-benzamido-2-[*(S)*-2,2-dimethyl-1,3-dioxolan-4-yl]cyclopropanecarboxylate ***cis*-3a**

M.p. 153 °C; $[\alpha]_D$ = - 80.3 (c = 1 in $CHCl_3$); IR 3340, 1732, 1643 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.28 (s, 3H), 1.31 (dd, 1H, J = 7.7 Hz, J = - 5.3 Hz), 1.43 (s, 3H), 1.73 (dd, 1H, J = 9.6 Hz, J = - 5.3 Hz), 2.18 (m, 1H, J = 9.6 Hz, J = 7.7 Hz, J = 7.4 Hz), 3.70 (s, 3H), 3.86 (m, 1H, J = 7.4 Hz, J = 6.2 Hz, J = 6.1 Hz), 3.94 (dd, 1H, J = - 8.5 Hz, J = 6.1 Hz), 4.08 (dd, 1H, J = - 8.5 Hz, J = 6.2 Hz), 6.56 (brs, 1H), 7.40-7.46 (m, 2H), 7.48-7.56 (m, 1H), 7.74-7.78 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 19.9, 25.5, 26.8, 30.0, 37.9, 52.8, 69.8, 75.2, 109.0, 127.1, 128.7, 132.0, 133.7, 168.6, 171.8. Anal. Calcd. for $C_{17}H_{21}NO_5$: C, 63.94; H, 6.63; N, 4.38. Found C, 64.02; H, 6.71; N, 4.29.

Methyl *(1R,2S)*-1-benzamido-2-[*(S)*-2,2-dimethyl-1,3-dioxolan-4-yl]cyclopropanecarboxylate ***cis*-3b**

Mp 69 - 70 °C; $[\alpha]_D$ = + 78.8 (c = 1 in $CHCl_3$); IR 3304, 1724, 1646 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.32 (dd, 1H, J = 6.9 Hz, J = - 5.4 Hz), 1.38 (s, 3H), 1.45 (s, 3H), 1.88 (m, 1H, J = 9 Hz, J = 6.9 Hz, J = 9.3 Hz), 2.04 (dd, 1H, J = 9.0 Hz, J = - 5.4 Hz), 3.70 (s, 3H), 3.75-3.83 (m, 1H), 3.81-3.88 (m, 1H), 4.16 (dd, 1H, J = 7.8 Hz, J = 5.7 Hz), 7.07 (brs, 1H), 7.40-7.48 (m, 2H), 7.48-7.54 (m, 1H), 7.74-7.82 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 22.4, 25.9, 26.9, 30.1, 37.0, 52.7, 68.8, 77.3, 109.6, 127.0, 128.6, 131.9, 133.8, 168.2, 172.2. Anal. Calcd. for $C_{17}H_{21}NO_5$: C, 63.94; H, 6.63; N, 4.38. Found C, 64.05; H, 6.56; N, 4.43.

Methyl *(1R,2R)*-1-benzamido-2-[*(S)*-2,2-dimethyl-1,3-dioxolan-4-yl]cyclopropanecarboxylate ***trans*-3a**

Oil; $[\alpha]_D$ = + 9.9 (c = 1 in $CHCl_3$); IR 3317, 1730, 1649 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.35 (s, 3H), 1.43 (s, 3H), 1.50-1.59 (m, 1H), 1.70-1.82 (m, 2H), 3.67 (s, 3H), 4.02-4.14 (m, 2H), 4.24-4.34 (m, 1H), 6.77 (brs, 1H), 7.36-7.46 (m, 2H), 7.46-7.52 (m, 1H), 7.70-7.78 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 22.7, 25.6, 26.8, 33.9, 37.1, 52.8, 68.9, 75.0, 109.1, 127.0, 128.6, 132.0, 133.5, 168.3, 171.3. Anal. Calcd. for $C_{17}H_{21}NO_5$: C, 63.94; H, 6.63; N, 4.38. Found C, 63.82; H, 6.57; N, 4.23.

Methyl *(1S,2S)*-1-benzamido-2-[*(S)*-2,2-dimethyl-1,3-dioxolan-4-yl]cyclopropanecarboxylate ***trans*-3b**

Mp 125 °C; $[\alpha]_D$ = + 62.2 (c = 1 in $CHCl_3$); IR 3317, 1733, 1650 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.26 (s, 3H), 1.40 (s, 3H), 1.45 (dd, 1H, J = 9.3 Hz, J = - 5.4 Hz), 1.65-1.75 (m, 1H), 1.78 (dd, 1H, J = 7.8 Hz, J = - 5.4 Hz), 3.68 (s, 3H), 3.65-3.74 (m, 1H), 4.03-4.12 (m, 2H), 7.06 (brs, 1H), 7.34-7.42 (m, 2H), 7.42-7.50 (m, 1H), 7.70-7.78 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 20.1, 25.4, 26.9, 32.2, 37.8, 52.7, 68.8, 73.8, 109.3, 127.1, 128.5, 131.8, 133.6, 168.1, 170.6. Anal. Calcd. for $C_{17}H_{21}NO_5$: C, 63.94; H, 6.63; N, 4.38. Found C, 63.92; H, 6.57; N, 4.40.

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14. Crystal data: $C_{17}H_{21}NO_5$, orthorhombic, space group $P2_12_12_1$, a = 9.352(2), b = 17.525(3), c = 22.201(4) Å, V = 3638.6 Å^3, Z = 8. Mo-K_α radiation, λ = 0.71069 Å, graphite monochromator. A total of 5677 reflections were measured at 298 °K, and merged to 4677 unique reflections (R_{int} = 0.0671). From these, 1729 with $F \geq 4.0\ \sigma(F)$ were considered observed. The structure was solved by direct methods and refined with t=the SHELXL-93 program considering all the reflections. Least-squares (full matrix) refinement yielded R 0.0812 and 0.2411 for the observed data and all data respectively. The final goodness-of-fit was 1.021. Complete data have been deposited at the Cambridge Crystallographic Data Centre.
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