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STEREOCHEMISTRY OF CYCLIC COMPOUNDS—I

SYNTHESIS AND CONFIGURATIONAL ASSIGNMENT OF DIASTEREOMERIC 2,4-DIOXASPIRO[5.5]UNDEC-8-ENES

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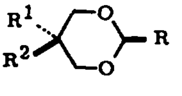
Abstract—Several 2,4 - dioxaspiro[5.5]undec - 8 - enes have been prepared from the Diels–Alder adducts of butadiene and 2,3-dimethylbutadiene with acrolein. Contrary to literature reports on some 3-substituted derivatives, which were assumed to be pure compounds, it is shown that these spiro compounds are generally obtained as 1:1 mixtures of two diastereomers. The isomers have been separated in the case of the 3-methyl and 3-ethyl derivatives by fractional distillation. On the basis of ^{1}H NMR spectroscopy, the nature of the isomerism is shown to be of *cis, trans* type and an unambiguous configurational assignment of the isomers has been achieved. Although the diastereomers are of similar topography, they have distinctly different olfactory properties.

Recently[1,2] there has been great interest in the *cis, trans* isomerism of 2,5-disubstituted and 2,5,5 - trisubstituted 1,3 - dioxanes 1. By equilibration of the isomers with BF_3 in ether, the A values of various groups in these two positions have been determined and it was shown that the equatorial preference of alkyl groups, for instance, is larger in the 2-position than in the 5-position.



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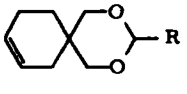

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The same type of *cis, trans* isomerism is to be expected for the spirodioxanes 2, the diastereomers of which may be characterized as r - 3 - R - 2,4 - dioxaspiro[5.5]undec - c - 8 - ene and r - 3 - R - 2,4 - dioxaspiro[5.5]undec - t - 8 - ene.[3,4] However, although several derivatives of 2(R=CH(CH_3)$_2$,[5] CH=CH_2,[6] and CH=CH-CH_3[6]) have been described, an isomerism of this type was not observed. While these compounds were not studied by NMR spectroscopy, their saturated analogs, which are configurationally uniform, have been intensively investigated by NMR to derive the effect of the spiro linkage on the ring inversion barrier.[7]

In this paper we wish to show that compounds of type 2 are generally obtained as 1:1 mixtures of the two diastereomers and not as pure compounds as was previously assumed. Our interest in the stereochemistry of these spiro compounds was prompted by their usefulness[8] as components in perfumes. We therefore attempted to obtain the pure diastereomers, to assign their configuration, and to compare their olfactory properties.

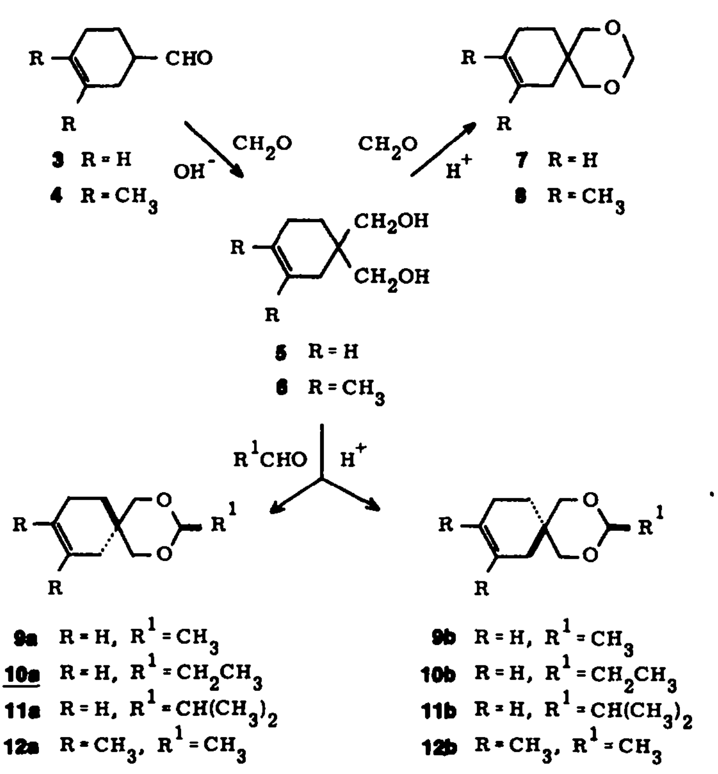
SYNTHESIS

The spirodioxanes 7–12 were prepared from the easily available Diels–Alder adducts 3[9] and 4.[10] On treatment with an aqueous alkaline solution of formaldehyde, these cyclohexenals undergo an aldol condensation followed by a cross Cannizzaro reaction to give 1,1 - dimethanol - 3 - cyclohexene 5[11] and the 3,4 - dimethyl derivative 6, respectively. The acid-catalyzed acetalization of the diols 5 and 6 with formaldehyde yielded the 2,4 - dioxaspiro[5.5]undec - 8 - enes 7 and 8. The corresponding acetalization with acetaldehyde, propionaldehyde, and isobutyraldehyde, respectively, let to isomeric mixtures of the 3 - alkyl - 2,4 - dioxaspiro[5.5]undec - 8 - enes 9–12.

The analysis of the spirodioxanes 9–12 by gas chromatography and ^{1}H NMR spectroscopy (see next section) revealed that independently of the nature of the alkyl group R 1:1 mixtures of two isomers were obtained. In the case of the methyl and ethyl derivatives 9 and 10, separation of the diastereomers was achieved by fractional distillation using a high resolution column; the boiling points of the isomers 9a and 9b and of 10a and 10b differ by 1.5° and 1.1°, respectively. The isopropyl derivative 11 has been previously synthesized by Rondestvedt[5] and was assumed to be a pure compound; it was characterized by boiling point, refractive index, and elemental analysis. Since Rondestvedt used a similar acetalization procedure, we believe that he obtained the same equimolar mixture of the two diastereomers 11a and 11b. The trimethyl compound 12 gave rise to only one peak in the gas chromatogram, but the analysis of the ^{1}H NMR spectrum clearly demonstrated the presence of the expected 1:1 mixture of the two isomers in this case too.

CONFIGURATIONAL ASSIGNMENT

As mentioned in the introduction, the isomerism of 3-substituted 2,4 - diosaspiro[5.5]undec - 8 - enes, which



9a $R = H, R^1 = CH_3$
10a $R = H, R^1 = CH_2CH_3$
11a $R = H, R^1 = CH(CH_3)_2$
12a $R = CH_3, R^1 = CH_3$

9b $R = H, R^1 = CH_3$
10b $R = H, R^1 = CH_2CH_3$
11b $R = H, R^1 = CH(CH_3)_2$
12b $R = CH_3, R^1 = CH_3$

has been overlooked by previous workers, is of *cis, trans* type. Since we have been able to separate the isomers in two cases, we tried to determine the configuration of these isomers by analysis of their ^1H NMR spectra. In the following we will prove that the compounds 9a and 10a belong to the *trans* series, while the corresponding isomers 9b and 10b, which have the higher boiling points and longer gas chromatographical retention times, belong to the *cis* series.

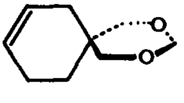
The time-average structure of the parent compound 7 can be depicted by two perpendicular planar rings, since the inversion of both the dioxane ring (chair form[1]) and the cyclohexene ring (half-chair[13]) is fast on the NMR time-scale at ambient temperature. In the case of the 3-methyl derivative, the shown sterical structures for both isomers, 9a and 9b, have the same time-average C_s symmetry as the parent compound, but the dioxane moiety now is anancomeric;[12] it is well known[1] that alkyl groups have a strong equatorial preference in the 2-position of 1,3 - dioxanes ($\Delta G°$ for CH_3: 4.0 kcal/mole).

As a consequence of this time-average C_s symmetry, the ^1H NMR spectra of the 2,4 - dioxaspiro[5.5]undec - 8 - enes are simplified and the analysis of the cyclohexene resonances only requires the identification of the methylene groups rather than of single protons. In Fig. 1 the spectra of the two diastereomers of the 3-methyl compound 9 are shown.

While the assignment of the low field resonances to the olefinic and the dioxane protons is straightforward, the assignment of the methylene protons of the cyclohexene ring requires some elaboration. Two major effects contribute to the chemical shifts of the methylene protons in positions 7, 10 and 11.

The first contribution originates from the double bond, which generally causes a downfield shift of the protons in allyl position. On the basis of this effect, the methylene protons H_{11} should resonate at higher field than the allyl protons H_7 and H_{10}. While obviously the observed methylene resonance patterns of the two isomers cannot be explained solely by a double bond effect, the verification of this contribution is obtained by analysis of the ^1H NMR spectrum of the conformationally mobile spirodioxane 7, which is shown in Fig. 2. The methylene protons H_{11} appear at highest field (δ 1.56 ppm; triplet, $J = 6.2$ Hz), while the resonances of protons H_7(δ 1.96 ppm; broad singulet) and H_{10}(δ 2.02 ppm; broad triplet) are shifted downfield as expected.

The large deviations of the shift patterns of the isomers 9a and 9b (Fig. 1) from that of the parent compound 7 (Fig. 2) are caused by the anancomerism of



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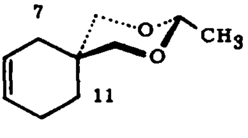
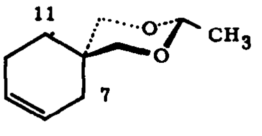


9a

(trans)



9b

(cis)

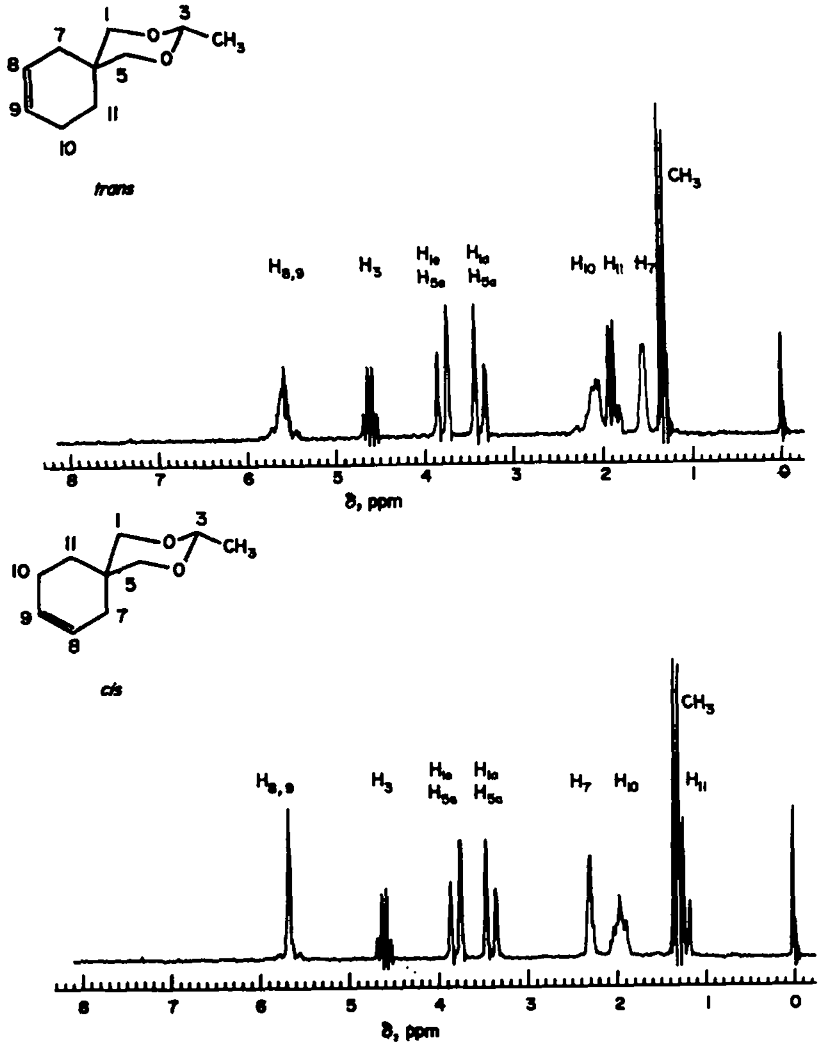


Fig. 1. ^{1}H NMR spectra of r-3-methyl-2,4-dioxaspiro[5.5]undec-t-8-ene 9a and r-3-methyl-2,4-dioxaspiro[5.5]undec-c-8-ene 9b.

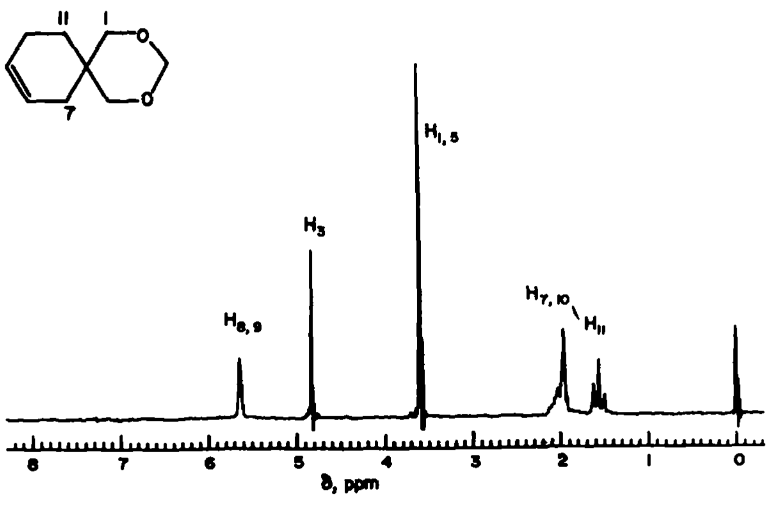


Fig. 2. ^{1}H NMR spectrum of 2,4-dioxaspiro[5.5]undec-8-ene 7.

the dioxane ring, which mainly influences the resonance positions of the protons H_7 and H_{11} adjacent to the spiro linkage. The protons of the two isomers at the distant position 10 are affected only to a minor degree and resonate at 2.08 and 1.96 ppm, respectively, i.e. close to the chemical shift (2.02 ppm) of H_{10} of the parent compound 7. The chemical shifts of the H_7 and H_{11} protons, however, strongly depend on whether the methylene groups are in the equatorial or the axial position of the anancomeric dioxane ring. These resonances also can be assigned by reference to the conformationally mobile parent compound 7, since the chemical shifts of the allylic protons H_7 and of the nonallylic protons H_{11} in 7 should be the average of the corresponding proton shifts of the two isomers, i.e. of the equatorial methylene protons of one isomer and the axial methylene protons of the other isomer. The methyl group in position 3 is too far to affect the chemical shifts of these protons. By this method it is very easy to assign the remaining high field multiplets to the allylic H_7 and the nonallylic H_{11} protons: the H_7 resonances of **9a** and **9b** appear at 1.54 and 2.30 ppm, respectively (average: 1.92 ppm; 7: 1.96 ppm) and the H_{11} protons resonate at 1.88 and 1.24 ppm, respectively (average: 1.56 ppm; 7: 1.56 ppm). The shape of the multiplets provides a further confirmation of the assignment. Thus, while the allylic protons H_7 give rise to narrow multiplets (half width *ca.* 7 Hz), the nonallylic H_{11} resonances are triplets due to the coupling to the H_{10} protons (J *ca.* 6.5 Hz).

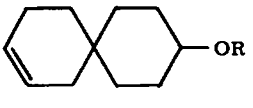
The large differences of the chemical shifts of the H_7 protons as well as of the H_{11} protons in the equatorial and axial positions allow an unambiguous assignment of the configuration of the two isomers **9a** and **9b**. It is well established[2] that in anancomeric 5,5-dialkyl-1, 3-dioxanes the protons of an axial 5-methyl group absorb 0.5–0.6 ppm downfield to the protons of an equatorial CH_3 group. The differences observed here between the H_7 chemical shifts and between the H_{11} chemical shifts of the two isomeric spiro compounds **9a** and **9b** amount to 0.76 ppm and 0.64 ppm, respectively. Since in the lower boiling isomer **9a** the allylic H_7 protons reasonate at a higher field than the nonallylic H_{11} protons, its configuration must be *trans*, while the reverse situation in isomer **9b** clearly proves its *cis* configuration.

In the same way the configuration of the separated isomers of the 3-ethyl derivative, **10a** and **10b**, were established to be *trans* and *cis*, respectively. These assignments also allowed the analysis of the ^1H NMR spectra of the isomeric mixtures **11a**/**11b** and **12a**/**12b**.

The chemical shifts and coupling constants of the *trans* and *cis* isomers **9a**–**12b** as well as of the parent compounds 7 and 8 are listed in Table 1. It must be emphasized that the parameters were obtained by first-order analysis.

DISCUSSION

The results described above revealed for the first time the occurrence of a *cis, trans* isomerism in 3-substituted 2,4 - dioxaspiro[5.5]undec - 8 - enes. While previously synthesized derivatives[5,6] were assumed to be pure compounds, Farges and Dreiding [3] discussed the possibility of *cis, trans* isomerism in the carbocylic analogues 13. However, the ^1H NMR spectra of the compounds 13 were too complex to provide any configurational information. In view of the similar topography of the expected *cis, trans* isomers, the sharp melting point of the alcohol 13 (R=H) was not taken as evidence against the presence of an isomeric mixture.



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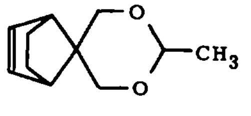

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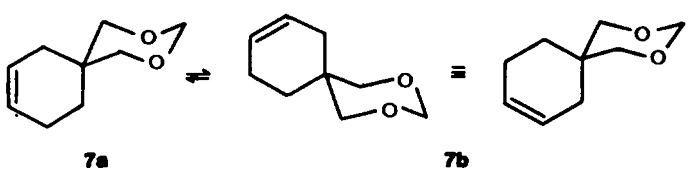
The compounds described in this study proved to be more advantageous in establishing the *cis, trans* isomerism, since the proton resonances of the anancomeric dioxane ring appear downfield to those of the cyclohexene moiety. Furthermore, as shown in the previous section, the axial/equatorial shift effect and the double bond effect lead to separated multiplets for the methylene protons of the cyclohexene moiety in both isomers, thus facilitating the assignment of their configuration. Another use of the large axial/equatorial shift effect caused by the anancomeric dioxane ring has been reported by Anteunis *et al.*;[14] the analysis of the ^1H NMR spectrum of the spiro compound 14 allowed the determination of the long-range coupling constants in the norbornene moiety.

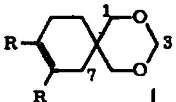
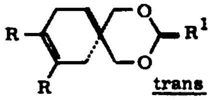
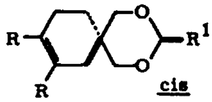
In the previous section it was shown that the chemical shifts of the methylene protons of the cyclohexene ring in the parent compound 7 are the average of the shifts of the corresponding protons in the *cis* and *trans* isomers **9a**–**11b** (see Table 1). This fact indirectly implies that the thermodynamic stability of the diastereomers is very similar, since the two conformers **7a** and **7b** of the parent compound are present in about equal proportions. The two conformers are seen to differ in the position of the double bond in the same way as the *cis, trans* isomers. The similar thermodynamic stability of the conformers and of the diastereomers is easily understood since sterically there should be no difference between the axial allylic methylene group (position 7 in the b or *cis* series) and the axial nonallylic methylene group (position 11 in the a or *trans* series).

Due to this similarity it is not surprising that in the acetalization reaction of the dimethanolcyclohexenes 5 and 6 there is no discrimination between the two orientations of the cyclohexene moiety relative to the newly formed dioxane ring, thus leading to 1:1 mixtures of the *cis, trans* isomers independently of the nature of the aldehyde. No conclusions can be drawn however on whether the 3-alkyl group immediately enters into the more favorable equatorial position, or some amount of



7a **7b**

Table 1. ^1H chemical shifts δ in ppm and coupling constants[a] in Hz of 2,4-dioxaspiro[5,5]undec-8-enes 7–12

Compound		H_{1a} H_{5a}	H_{1e} H_{5e}	H_{3a}	$R^1{}_{3e}$ α	β	H_7	$R_{8,9}$	H_{10}	H_{11}
										
R=H	7	3.58 s		4.81 s			1.96 bs	5.64 m	2.02 m	1.56 t J=6.2
R=CH_3	8	3.55 s		4.80 s			1.88 bs	1.61 bs	1.9 m	1.52 t J=6.0
 trans										
R=H $R^1=CH_3$	9a	3.38 bd J=11.5	3.80 bd	4.62 q J=5.0	1.32 d		1.54 bs	5.59 m	2.08 m	1.88 "t"
R=H $R^1=\overset{\alpha}{CH_2}\overset{\beta}{CH_3}$	10a	3.38 bd J=11.4	3.80 bd	4.40 t J=4.9	1.64 "dq"	0.94 t J=7.5	1.53 bs	5.59 m	2.08 m	1.88 "t"
R=H $R^1=\overset{\alpha}{CH}(\overset{\beta}{CH_3})_2$	11a	3.34 bd J=11	3.82 bd	4.19 d J=5	1.8 m	0.94 d J=7	1.54 bs	5.59 m	2.07 m	1.86 "t"
R=CH_3 $R^1=CH_3$	12a	3.36 bd J=11	3.75 bd	4.60 q J=5	1.32 d		1.46 bs	1.59 bs	1.95 m	1.83 "t"
 cis										
R=H $R^1=CH_3$	9b	3.41 bd J=11.2	3.80 bd	4.61 q J=5.1	1.32 d		2.30 bs	5.67 m	1.96 m	1.24 t J=6.6
R=H $R^1=\overset{\alpha}{CH_2}\overset{\beta}{CH_3}$	10b	3.42 bd J=11.2	3.81 bd	4.39 t J=5.0	1.64 "dq"	0.94 t J=7.5	2.30 bs	5.68 m	1.97 m	1.24 t J=6.6
R=H $R^1=\overset{\alpha}{CH}(\overset{\beta}{CH_3})_2$	11b	3.37 bd J=11	3.82 bd	4.19 d J=5	1.8 m	0.94 d J=7	2.28 bs	5.67 m	1.97 m	1.24 t J=6.5
R=CH_3 $R^1=CH_3$	12b	3.39 bd J=11	3.75 bd	4.60 q J=5	1.32 d		2.21 bs	1.59 bs	[b]	1.20 t J=6.5

[a] Coupling constants not determined for signals characterized as broad (b) or multiplet (m).

[b] Multiplet overlapped by the H_{11} resonance of the trans isomer.

the axial conformer is also formed, since the latter can convert into the stable equatorial conformer of the other isomer. In cases where both the axial and equatorial isomers are anancomeric, it has been shown that the acid-catalyzed acetalization to 1,3-dioxanes is largely thermodynamically controlled.[1]

The *cis*, *trans* isomers are not only of similar thermodynamic stability, but, as has been pointed out by Farges and Dreiding[3] in the case of the carbocyclic analogues, they also have a very similar topography. It is therefore of interest to compare the physical, olfactory, and spectroscopic properties of the separated diastereomers **9a**, **9b** and **10a**, **10b**.

Table 2 reveals small but regular differences of the isomers in boiling point and gas chromatographical retention time: the *cis* isomers **9b** and **10b** have higher boiling points and longer retention times than their *trans* counterparts **9a** and **10a**. On the other hand, the refractive indices (Table 2) do not show a regular pattern.

Distinct differences are noticed in the olfactory properties of the *cis*, *trans* isomers (Table 2). Since acetals of various structures are widely used as fragrances[15] and the isomeric spiro acetals described in this study are topographically similar but differ in the position of the double bond, it is of interest to make a comparison with the known stereochemical relationships of the odor sensation.[16] Differences in odor quality and intensity have been observed in numerous cases for constitutional isomers, diastereomers, as well as for enantiomers.[17] Two examples of isomeric compounds containing a double bond may be given for comparison with the present spiro dioxanes.

In the case of *cis* and *trans* p - menth - 8 - ene, the different topography leads to a drastic change in odor quality.[17] While the *cis* isomer has the typical odor of saturated hydrocarbons, the *trans* isomer smells pleasantly sweet with an orange note. As example of topographically similar compounds, the well studied con-

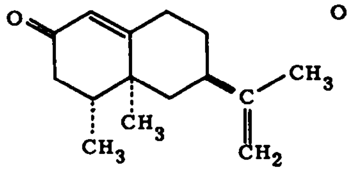
Table 2. Properties and analytical data of 2,4-dioxaspiro[5.5]undec-8-enes 7–12

Compd no.	GLC[a] Rt$_a$ cm/%	Rt$_b$ cm/%	Bp °C/mm	n_D^{20}	El. Anal.	C,%	H,%	Odor
7	17.25/>98		70/3	1.4869	calc. found	70.10 69.80	9.15 9.19	unpleasant
9a/9b	15.9/50.3	16.3/49.7	76/6	1.4777	calc. found	71.39 70.50	9.59 9.44	sweet, camphorous, neroli note, potato note
9a	15.75/94.0	16.15/6.0	97.2/14-15	1.4773	found	70.50	9.77	green, mouldy; stronger than cis isomer 9b
9b	15.70/2.3	16.10/97.7	98.7/14-15	1.4769	found	71.10	10.30	fruity, jasmin note, banana note
10a/10b	17.3/42.7	17.8/48.8	86/6	1.4773	calc.	72.49	9.95	rose note, cachou note
10a	17.3/94.7	17.8/5.3	110.0/14-15	1.4793	found	72.50	9.93	rosaceous, flowery, geranium note; stronger than cis isomer 10b
10b	17.3/1.4	17.8/98.2	111.1/14-15	1.4841	found	72.50	9.70	green, finer than trans isomer 10a
11a/11b	17.4/51.2	18.0/48.1	81/1.8[b]	1.4748[b]	calc. found[b]	73.43 72.20	10.27 10.70	herbaceous, spicy
8	20.3/98		70/0.1	1.4903	calc. found	72.49 72.50	9.95 9.91	benzyl salicylate note, quinoline note, neroli note
12a/12b	18.85/>98		58/0.05	1.4822	calc. found	73.43 72.40	10.27 10.10	herbaceous, petitgrain note, styrolylacetate note

[a] Glas capillary (WG-11, 50 m); carrier gas: 10 psi N_2; temperature program: 120-230°, 6°/min; Rt = retention time; purity or proportion of diastereomers in per cent.

[b] Rondestvedt[5] reports bp 98.5-100/6 mm, n_D^{25} 1.4730, 73.46% C, 10.27% H.

stitutional isomers nootkatone 15 and α-vetivone (isonootkatone) 16 are of special interest. The change in position of the double bond alters the olfactory quality but not the intensity:[17,18] the odor of nootkatone is grapefruity, whereas the α-vetivone odor has been characterized as floral, waxy, and woody.



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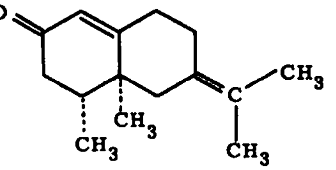

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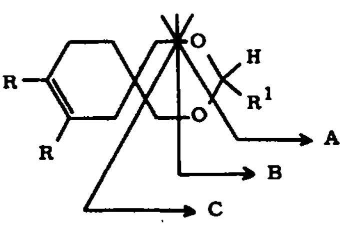
Although the topography of the diastereomers described in this work is even more similar, it is remarkable that their olfactory properties differ in odor quality as well as in intensity (Table 2). Both *trans* isomers 9a and 10a, in which the osmophoric groups,[17] i.e. the double bond and the acetal group, are further apart than in the *cis* isomers, give rise to a stronger odor.

Finally we wish to mention that in addition to the large differences in the ^1H NMR spectra of the isomers, small differences also occur in the IR and mass spectra. The IR spectra (Table 3) of the diastereomeric compounds 9a, 9b and 10a, 10b, respectively, are almost identical. Only in the region 1465–1434 cm^{-1} of the CH_2 and asymmetrical CH_3 bending vibrations[19] there are distinct differences in intensity presumably originating from the bending vibrations of the methylene groups of the cyclohexene moiety. The absorptions near 1435 cm^{-1} may be assigned to vibrations of the methylene groups adjacent to the double bond.[19]

As shown in Table 4, the mass spectra of all studied spiro compounds 7–12 may be rationalized by a common fragmentation pattern. It is proposed that the fragmentation of the parent ion is initiated by cleavage of the dioxane ring, which occurs in three different ways as indicated in Scheme 1. The formation of fragments A, B and C formally corresponds to an elimination of R^1CHO, $R^1CO_2H_2$ and $R^1CO_2CH_3$, respectively. As seen from the relative intensities given in Table 4, these fragmentations strongly compete with the loss of hydrogen or alkyl at



Scheme 1.

Table 3. IR spectral data[a] of 2,4-dioxaspiro[5.5]undec-8-enes 7–12

Compd.	νH-C=	νOCH$_2$O	νC=C	δCH$_2$, δ_{as}CH$_3$	δ_sCH$_3$	νC-O	δHC=CH
7	3021	2763	1650	1438	-	1173, 1159, 1119, 1070, 1030	660
9a	3012	-	1651	1465(0.14), 1448(0.52), 1434(0.29)	1402	1152, 1131, 1120, 1099, 1038, 1032	658
9b	3015	-	1653	1464(0.20), 1440(0.43), 1434(0.23)	1405	1154, 1130, 1124, 1100, 1041, 1028	662
10a	3020	-	1652	1464(0.16), 1450(0.30), 1434(0.15)	1400[b]	1160, 1132, 1120, 1084, 1055, 1034	655
10b	3020	-	1650	1464(0.22), 1450(0.17), 1438(0.25)	1400[b]	1158, 1130, 1120, 1084, 1055, 1029	660
11a/11b	3013	-	1650	1473, 1450, 1438	1395, 1380	1160, 1143, 1120, 1087, 1030	660
8	-	2760	-	1438	c	1165, 1131, 1108, 1060, 1032	-
12a/12b	-	-		1438	1405	1154, 1135, 1115, 1100, 1075, 1035	-

[a] Absorption positions in cm^{-1}; the numbers in parentheses are relative abundances.
[b] Weak absorption.
[c] Not assigned.

position 3. It is interesting to note the different intensities of the fragments M^+-R^1 and A(M^+-R^1CHO) for the isomeric methyl derivatives **9a** and **9b** and the isomeric ethyl derivatives **10a** and **10b**. The reason for this stereochemical dependence is not clear. Apparently it cannot be explained by the known stereochemical relationships.[20] On the basis of these differences, the configuration of the two unseparated isomers of the isopropyl compound 11 may also be tentatively assigned. It appears that, as in the cases **9a/9b** and **10a/10b**, the isomer with the longer gas chromatographical retention time (Table 2) is of *cis* configuration, i.e. **11b**.

EXPERIMENTAL

^{1}H NMR measurements were performed in CW mode at 100 MHz on a Varian XL-100 spectrometer using CDCl$_3$ as solvent and TMS as internal standard. IR spectra of neat compounds were recorded on a Perkin–Elmer 157-G spectrometer. Mass spectra were obtained by a Varian CH-7-A instrument coupled with a Varian 1400 gas chromatograph (25 m glass capillary WG-11). Gas chromatographical measurements were performed on a Packard 417 insturment (FID, 50 m glass capillary WG-11) equipped with a Spectra-Physics electronical integrator. M.ps (Kofler heating block) and boiling points are uncorrected.

Tetrahydrobenzaldehydes (3,4). 3,4 - Dimethyl - 3 - cyclohexen - 1 - al 4 was synthesized by heating a mixture of 1.0 mol of 2,3 - dimethyl - butadiene and 1.0 mol of acrolein in an autoclave under 5 bar nitrogen at 100° for 3 hr. After removal of the volatile components under reduced pressure, distillation of the residue afforded the pure cycloadduct 4 in 90% yield: b.p. 75° (9 mm) [lit.[10] b.p. 79° (10 mm)]. 3 - Cyclohexen - 1 - al 3[9] was obtained from Bayer AG.

3 - *Cyclohexene* - 1,1 - *dimethanols* (5,6). To a mixture of 1.0 mol of 37% aqueous formaldehyde and 0.6 mol of 25% aqueous sodium hydroxide was added 0.4 mol of tetrahydrobenzaldehyde 3 or 4 with cooling in a water bath. After stirring at 55° for 1 hr, the reaction mixture was extracted with 70 ml of methylisobutylketone. The organic phase was washed with 50 ml of water and the aqueous phase was extracted with 50 ml of methylisobutylketone. The combined organic extracts were washed with water until neutral and dried over Na$_2$SO$_4$. After evaporation of the solvent, the corresponding diols were isolated. 3 - Cyclohexene - 1,1 - dimethanol 5 was obtained in 92% yield: m.p. 93–94° (ethanol) [lit.[11] m.p. 92.5°; lit.[21] m.p. 94.5–95.0°]. 3,4 - Dimethyl - 3 - cyclohexene - 1,1 - dimethanol 6 was recrystallized from petroleum ether/toluene: 67% yield: m.p. 99.5–100.5°. *Anal.* of 6. Calc. for $C_{10}H_{18}O_2$: C, 70.55; H, 10.66. Found: C, 71.30; H, 10.60%.

Table 4. Mass spectral data[a] of 2,4-dioxaspiro[5.5]undec-8-enes 7–12

Compd.	M^+	M^+-H	M^+-R^1	A	B	C	C - 15
7	154(1.3)	-	-	124(9)	-	94(25)	79(100)
9a	168(0.8)	167(2.6)	153(21)	124(19)	107(18)	94(38)	79(100)
9b	168(0.2)	167(1.2)	153(3)	124(33)	107(17)	94(25)	79(100)
10a	182(<1)	181(2)	153(51)	124(1.2)	107(48)	94(25)	79(100)
10b	182(<1)	181(2)	153(19)	124(26)	107(43)	94(19)	79(100)
11a	196(0.4)	195(2.7)	153(57)	-	107(81)	94(24)	79(100)
11b	196(0.3)	195(2.3)	153(44)	124(28)	107(81)	94(23)	79(100)
8	182(31)	-	-	152(17)	-	121(95)	107(100)
12a/12b	196(10)	-	-	152(77)	135(14)	121(68)	107(100)

[a] The numbers in parentheses are relative intensities in per cent.

Table 5. Data for distillative separation of diastereomers **9a**/**9b** and **10a**/**10b**

	9a/9b	10a/10b
pressure, mm	14-15	14-15
dist. flask temperature, °C	101-120	114.5-159
oil bath temperature, °C	119-145	140-180
jacket temperature, °C	35.5-37.7	34.7-47.3
reflux ratio	1:50	1:50
number of theoretical plates	90	90
charge of column	100 ml/h	100 ml/h
starting mixture for		
trans isomer, % (GLC)	80.2/19.8	77.4/19.7
cis isomer, % (GLC)	50.3/49.7	42.5/49.0
purity of separated isomers		
trans isomer, % (GLC)	94.0	94.7
cis isomer, % (GLC)	97.7	98.2

2,4 - *Dioxaspiro*[5.5]*undec* - 8 - *enes* (**7**–**12**). To a mixture of 0.1 mol of the appropriate aldehyde, 0.1 mol of triethyl orthoformate, and 0.1 mol of diol **5** or **6** was added catalytic amounts of p - toluene - sulfonic acid, causing a slightly exothermic acetalization reaction. After stirring at room temperature overnight, ethanol and ethyl formate were removed by distillation. The residue was diluted with ether, extracted with 2N sodium carbonate solution, washed with water until neutral, and dried over Na_2SO_4. After evaporation of the solvent, fractional distillation afforded the respective spirodioxane in 80–90% yield. Analytical data of the products are listed in Table 2.

Separation of Isomers (**9a**/**9b**; **10a**/**10b**). The isomers were separated by fractional distillation using the Fischer Labortechnik HMS-500 high resolution column (length 50 cm) with automatic regulation of column head and oil bath and an electronical vacuum stabilizer VKH. The distillations were performed as indicated in Table 5.

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