Reference Data

Sesquiterpenes. ¹³C and ¹H NMR Chemical Shifts of New Thujopsane and Nootkatane Derivatives

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The ¹³C and ¹H NMR spectra of thujopsanone oxime, 7-halo-7-nitrosothujopsanes, nootkat-1-one oxime and 1-chloro-1nitrosonootkatane are reported.

KEY WORDS ¹³C NMR ¹H NMR Thujopsanes Nootkatanes

INTRODUCTION

gem-Chloronitroso and gem-bromonitroso derivatives of thujopsane and nootkatane were prepared with the intent of investigating the CD effects of gem-halonitrososes- quiterpene oximes. These compounds are new, and their ¹³C NMR and pertinent ¹H NMR chemical shifts are reported.

EXPERIMENTAL

All reactions were carried out in the usual manner. The compounds were purified by column chromatography, using silica gel and light petroleum-ethyl acetate mixtures as eluent. Compound 13 was prepared by tosylation of 2^{1} , and reduction with LiAlH₄ then gave 1. Oximes 4, 5, 9 and 10 were prepared by reaction of the known ketones 3¹ and 8,¹ respectively, with hydroxylamine. Compounds 6, 11 and 12 were synthesized by chlorination of the corresponding oximes with chlorine and 7 and 22 by bromination of the corresponding oximes with Nbromosuccinimide and bromine, respectively. Oxime 14 was prepared from 20^2 as described above and 15 by chlorination of 14 with chlorine. Compound 19 resulted from the total hydration of valencene. The structures were identified by mass, IR and NMR spectroscopy or by comparison with authentic materials.

All ¹H, ¹³C and two-dimensional NMR measurements were carried out in 5 mm tubes in CDCl₃ (25 mg ml⁻¹) on a Bruker AM 400 spectrometer, operating at 100.6 MHz for ¹³C and 400.1 MHz for ¹H. Other experimental data for ¹³C were pulse width 4.0 μ s, acquisiton time 0.66 s, flip angle 90°

and spectral width 25 kHz. Corresponding data for ¹H were pulse width 12.6 μ s, acquisition time 4.1 s, flip angle 10° and spectral width 4000 Hz.

RESULTS AND DISCUSSION

The structures of the compounds are defined in Fig. 1 and Table 1.

The ¹³C chemical shifts are given in Table 2; Tables 3 and 4 only show pertinent hydro-

Table 1. Compounds studied

No.	R,	R ₂	No.	R,	R ₂				
1	н	н	11	CI	NO				
2	н	ОН	12	NO	CI				
3		0	13	н от					
4	=NOH	(anti) ^b	14	=NOH	(anti) ^c				
5	=NOH	(syn) ^b	15	CI	NO				
6	CI	NO	19	н	н				
7	Br	NO	20	-	0				
8	-	0	22	Br	NO				
9	=NOH	(anti) ^ь							
10	=NOH	(<i>syn</i>) ^b							
°OSO ₂ C ₆ H ₄ CH ₃ .									
^ь Re	lative to	C-13.							
° Re	lative to	C-8a.							



Figure 1. Structures and numbering scheme.

Table 2. ¹³C NMR shifts (ppm)

								Carbon No.							
Compound	1	2	3	4	4a	5	6	7	8	· 8a	9	10	11	12	13
1	38.3	19.3	40.7	31.5	39.0	27.4	38.0	26.5	45.3	41.4	4.6	28.5	26.2	24.1	13.1
2	37.6	18.9	40.7	32.9	33.4	25.1	40.2	71.2	47.1	34.7	13.5	29.5	27.1	29.3	21.1
3	38.5	19 .0	40.3	33.0	33.4	24.4	41.6	213.3	53.0	38.4	10.6	29.5	26.7	28.4	18.2
4	37.9	19.1	40.4	32.7	33.5	25.5	34.3	161.1	36.4	36.2	11.3	29.5	26.9	28.6	20.0
5	38.0	19.3	39.9	31.4	33.4	24.5	29.4	161.5	42.5	34.3	8.2	29.4	27.0	28.9	20.6
6	39.9	19.2	40.4	33.9	34.1	26.7	46.1	123.9	55.9	35.7	17.3	29.3	27.5	29.5	15.6
9	37.6	1 9 .2	40.2	32.6	33.7	23.9	31.0	161.8	35.1	36.1	6.5	29.3	26.9	28.4	19.6
10	37.0	18.9	40.3	33.5	33.6	23.3	25.8	161.9	41.7	35.5	6.5	29.4	26.9	28.2	16.3
11	38.0	19.5	39.7	31.3	34.1	24.1	41.5	118.9	44.8	36.3	8.1	29.0	27.5	29 .0	14.3
12	38.8	19.1	39.2	31.4	33.8	23.6	28.3	119.0	48.1	35.4	8.2	29.1	27.7	28.8	17.4
13	37.1	18.6	40.5	32.7	33.3	24.5	37.0	84.0	43.3	35.2	13.4	29.3	26.9	28.9	20.4
14	160.9	24.3	28.9	43.2	29.9	41.8	38.3	29.9	22.3	51.1	32.9	19.5	20.0	14.8	11.7
15	120.6	29.6	39.4	43.4	40.0	44.1	38.3	29.8	21.0	58.5	32.8	19.5	20.0	15.3	15.1
19	29.2	29.1	31.0	43.6	36.8	42.5	38.9	30.0	26.8	46.8	33.2	19.6	20.1	15.2	11.4
20	213.1	41.3	31.4	42.8	41.8	42.3	38.1	28.2	20.7	58.0	32.8	19.5	19.9	14.5	12.0

					Hydrogen position				
ompound	6	7	8 eq	8 ax	9	10	11	12	13
1	2.00 m	1.20	1.10	0.65 q	0.18 d	0.54 s	0.98 s	0.99 s	0.86 c
2		3.28 m			0.12 t/0.45 q	0.49 s	0.96 s	1.07 s	1.14 c
3	2.40 q		2.17 d	1.65 d	0.61 m	0.56 s	1.04 s	1.13 s	1.18 c
4	2.53 q		2.65 d	1.53 d	0.33 t/0.51 m	0.54 s	1.01 s	1.16 s	1.26 c
5	3.19 q		2.00 d	1.84 d	0.35 m	0.60 s	1.05 s	1.10 s	1.44 c
6	2.48 q		2.13 d	1.38 d	0.60 t/1.03 m	0.69 s	1.08 s	1.21 s	0.75 c
7	2.69 q		2.34 d	1.62 d		0.68 s	1.08 s	1.22 s	0.82 (
9	2.85 i		2.45 d	1.65 d	0.28 t/0.33 m	0.55 s	1.03 s	1.15 s	1.09 (
10	3.42 i		1.95 d	1.49 d	0.31 m/0.38 t	0.53 s	1.02 s	1.10 s	1.07 c
11	3.06 m		2.25 d	1.12 d		0.73 s	1.13 s	1.17 s	0.70 (
12	3.21 m		2.20 d	1.75 d		0.66 s	1.03 s	1.15 s	0.87 (
13		4.23 m			0.09 t/0.45 m	0.44 s	0.91 s	0.99 s	0.91 c
22	2.60 i		2.10 d	1.68 d		0.60 s	1.07 s	1.13 s	1.12 (

Table 4. ¹H NMR shifts* (ppm)

	Hydrogen position													
Compound	2	3	5	7	8	8a	10	11	12	13				
14	1.67/3.30	0.90/1.75	0.75/1.67	1.48/1.61	1.43/1.70	1.83 dd	0.81 d	0.82 d	0.83 d	0.63 s				
15	1.75/2.25	2.10/2.25	0.90/1.83	0.91/1.75	0.88/1.78	1.97 dd	0.82 d	0.84 d	1.01 d	0.79 s				
19	1.25	1.35	0.60 t/1.67 m	0.95 m/1.67 m	1.67 m	0.95 m	0.83 d	0.84 d	0.77 d	0.68 s				
^a See footn	ote to Table 3	3.												

gen chemical shifts. The unstable gembromonitroso compounds 7 and 22 allow only the monitoring of the ¹H NMR spectra and slight impurities do not influence the correct determination of the shift values. The absolute configurations of 2 and 3 are known,4 and the proposed conformations1 for 4-13 are confirmed by the ¹H shielding of methyl group 10 and H-8ax influenced by the anisotropy of the cyclopropane ring. The configuration at C-7 of the gem-halonitroso compounds 6, 7, 11, 12 and 15 (in position 1) correlates very well with those in similar compounds.5,6 Only one isomer was isolated for 6, 7 and 15. The configuration is based on the stereochemical properties of the reactions and CD measurements, which showed positive Cotton effects⁷ for 6, 7 and 15, pointing to an axial position of NO in these compounds.⁵ The H-6 shift of 12 was at δ 3.21 and that of 11 at δ 3.06 ppm. This known deshielding of protons which are near a CNO plane allowed these isomers to be distinguished.

The ¹³C NMR spectra of oximes showed significant differences in the β -carbon chemical shifts. The negative β -effect, -8.6 (C-6, 5), -8.9 (C-8, 4) and -4.8 (C-2, 14), correlates with the syn position of the oxime-OH and corresponds to those of other oximes,⁸ and also to the ¹³C chemical shifts of the β -carbons in oximes 9 and 10.

References

1. S. P. Acharya and H. C. Brown, J. Org. Chem. 35, 3874 (1970).

- G. W. Shaffer, E. H. Eschinasi, K. L. Purzycki and A. B. Doerr, *J. Org. Chem.* 40, 2181 (1975).
- S. D. Sastry, M. L. Mahes-Wari, K. K. Chakravarti and S. C. Bhattacharyya, *Tetrahedron* 23, 2491 (1967).
- 4. W. G. Dauben and P. Oberhäusli, J. Org. Chem. 30, 3947 (1965).
- T. Bosch, G. Kresze and J. Winkler, Justus Liebigs Ann. Chem. 1009 (1975).
- G. Kresze, N. M. Mayer and J. Winkler, Justus Liebigs Ann. Chem. 747, 172 (1971).
- 7. To be published.
- M. J. Ponet, Org. Magn. Res. 19, 229 (1982).

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