



Journal of the Mexican Chemical Society

ISSN: 1870-249X

editor.jmcs@gmail.com

Sociedad Química de México

México

Gómez, Elizabeth; Contreras, Guadalupe; Toscano, Rubén A.
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Journal of the Mexican Chemical Society, vol. 51, núm. 1, january-march, 2007, pp. 3-7
Sociedad Química de México
Distrito Federal, México

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Synthesis of Monomeric and Dimeric Siloxanes Derived of β -Aminoalcohols

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Recibido el 27 de abril del 2006; aceptado el 11 de agosto del 2006

Abstract. The preparation and structural characterization of dimeric and monomeric siloxanes are described. The silicon complexes were obtained from β -amino alcohols and dichlorodimethylsilane, bisdimethylaminodimethylsilane and diphenyldichlorosilane. The complexes were characterized by ^1H , ^{13}C and ^{29}Si NMR spectroscopy and mass spectrometry. The X-ray crystallography study for one compound confirmed the formation of a sixteen-membered heterocycle.

Key words: Siloxanes, ^{29}Si NMR, X-ray crystallography, aminoalcohols.

Resumen. En este trabajo se describe la preparación y la caracterización de siloxanos diméricos y monoméricos. Los complejos de silicio se obtuvieron por reacción de β -amino alcoholes con diclorodimetilsilano, bisdimetilaminodimetilsilano y diclorodifenilsilano. Los complejos se caracterizaron por RMN de ^1H , ^{13}C y ^{29}Si , y espectrometría de masas. La estructura molecular de un anillo de 16 miembros para uno de los compuestos se confirmó por difracción de rayos-X.

Palabras clave: Siloxanos, RMN de ^{29}Si , Difracción de rayos-X, aminoalcoholes.

Introduction

Hypervalent silicon compounds have attracted much interest in view of their diverse structure, reactivity, interesting physical and chemical properties and a wide range of potential applications [1,2] such as their use in cross-coupling reactions with aryl triflates and halides derivatives [3]. However, few examples of silicon-bridged macrocycles have been described despite their potential applications as host-guest complexes [4-10]. Silicon compounds present advantages for the design of new macrocycles, due in part to the fact that the silicon atom is mainly tetra-coordinated, which are ideal to be used as Lewis acids. Likewise, their solubility in non polar organic solvents make these compounds interesting for the transport of metal ions [11,12]. In the course of our research concerning the preparation and structural characterization of pentacoordinated organosilanes from tridentate ligands we reported a study in which we described the effect of the substituents in the formation of pentacoordinated and macrocyclic silicon compounds. [13-16]. Despite of the fact that silicon compounds containing triethanol amines have been investigated [17-21], few reports regarding the study of silicon compounds containing cyclic derivatives of diethanolamine have been reported so far [22-25].

The aim of this work is to study the effect of the substituents at the silicon atom on the formation of dimeric or monomeric silicon complexes.

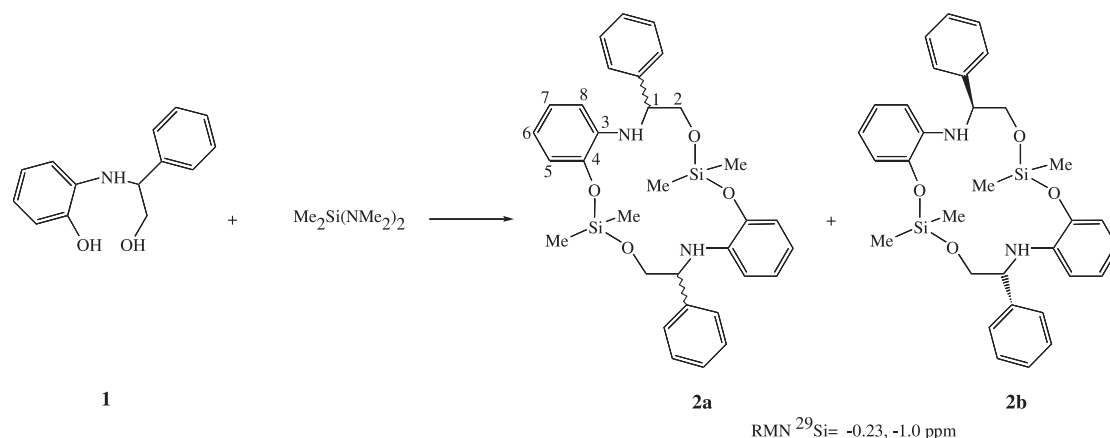
Results and discussion

The tridentate ligands **1**, **4** and **6** were synthesized following a new synthetic method under solvent-free conditions, which consisted in mixing 2-aminophenol or ethanolamine with the appropriate epoxide in a sealed ampoule at 90 °C to give the corresponding β -amino alcohol in yield ranging from 90 to 99% [26].

The compounds **2a** and **2b** were obtained by reaction of ligand **1** with bisdimethylaminodimethylsilane (Scheme1). The ^1H NMR spectra showed four distinct resonances at δ 0.26, 0.31, 0.37 and 0.39, which were assigned to the protons of the two nonequivalent methyl groups bonded to silicon. This fact might be attributed to the presence of two possible stereoisomers, which was evidenced by the ^{13}C NMR that revealed the presence of the isomers **2a** and **2b**; this mixture resulted to be inseparable. Although the spectra showed distinct signals for both isomers, the full assignment of the individual spectral resonances was not possible. However, the integration of the methyl group signals allowed us to find out an isomeric ratio of 60:40. Additional evidence of the stereoisomers formation was provided by the ^{29}Si NMR spectroscopy, that showed two different signals at δ -1.03 and -0.23 ppm, which suggest that both isomers correspond to tetracoordinated species, these chemical shifts are in agreement with complexes containing methyl groups bonded to silicon [5, 14].

The mass spectrometry spectrum revealed the molecular ion m/z 570 which is consistent with the formation of a dimeric compound, the fragment ions at m/z 555 and m/z 480 agreed with the loss of the methyl groups and SiO_2Me_2 moiety from the molecular ion. Additionally, the fragment ion displayed at m/z 285 corresponding to the monomeric fragment was also detected. Since the NMR data do not allow to discriminate directly between a dimer and a monomer and in order to assess that the monomer detected in the mass spectrometry is not a by-product of the reaction, we carried out a linked-scan mass spectrometry experiment. Indeed, the results revealed that the ion m/z 555 generates the ion m/z 285 as well as the base peak m/z 254, which indicates that the former, attributed to the dimeric species, is responsible for the formation of the monomeric ion during the fragmentation process.

The disiloxane **3** was prepared from the reaction of ligand **1** with diphenyldichlorosilane, after several weeks at 10 °C this



Scheme 1

compound was precipitated from diethyl ether (Scheme 2). The mass spectrometry showed the molecular ion m/z 409 corresponding to the molecular weight of the siloxane **3**. The loss of phenyl group m/z 332 from the molecular ion was also detected. The ^{29}Si NMR for this compound showed a signal at $\delta -35.9 \text{ ppm}$, which is shifted $\Delta\delta$ 8.8 to higher frequencies with respect to diethanolamine derivative (-44.7 ppm) which presents transannular $\text{N} \rightarrow \text{Si}$ bond [23].

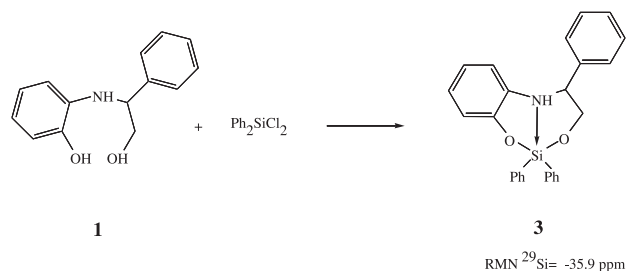
Although this shift is similar to those found for complexes where does not Si-N interaction has been detected, a weaker N-Si interaction for complex **3** might be suggested which could be associated with a more rigid conformation of the eight-membered ring.

The ^1H NMR signals corresponding to methylene protons are shifted to low frequencies ($\sim\Delta\delta$ 1) with respect to the ligand. As regards the formation of complexes **2a**, **2b** and **3** they exhibit different geometries around the silicon atom which can be associated with the type of substituents bonded to the silicon atom, indeed the phenyl groups increase the Lewis acidity at the silicon atom which favors the formation of the $\text{N} \rightarrow \text{Si}$ bond as observed in complex **3**.

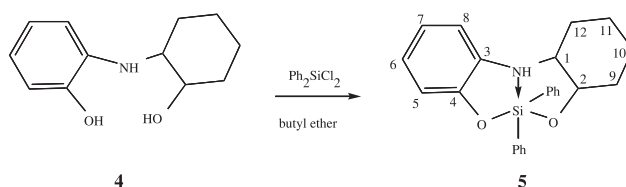
When the ligand **4** was reacted with diphenyldichlorosilane the compound **5** was obtained (Scheme 3). The mass spectrometry of **5** showed the molecular ion m/z 387 corresponding to the monomeric compound, the spectrum also exhibited the fragment ion m/z 310 which according with the loss of the phenyl (Ph-Si) from the molecular ion. The ^1H NMR spectrum of **5** showed slight differences in chemical shifts with respect to the ligand, in the ^{13}C NMR spectrum the C-1 and C-2 are shifted to low frequencies ($\Delta\delta = 4$). However, no signal for ^{29}Si -NMR were detected at ambient temperature, therefore a ^{29}Si -NMR experiment was recorded at -45°C which showed a singlet at -47.3 ppm , this chemical shift is similar to that found for a diethanolamine derivative (-44.7 ppm) which presents transannular $\text{N} \rightarrow \text{Si}$ bond [23].

The selective formation of compound **7** was accomplished by reacting ligand **6** with dichlorodimethylsilane, the mass spectrometry fragmentation pattern showed the molecular ion

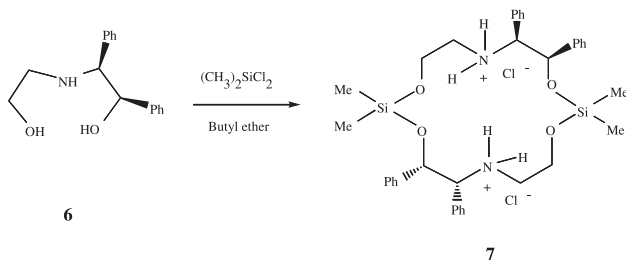
m/z 626 which corresponds to the dimeric compound (Scheme 4). The ^1H NMR spectra showed two singlets at $\delta -0.39$ and 0.39 ppm attributed to the protons of the nonequivalent methyl groups attached to the silicon atom. The ^{13}C NMR spectrum of **7** showed two different signals at $\delta -3.30$ and -1.50 for the methyl groups. Signals of carbons C-3, C-4, C-1 and C-2 are slightly shifted to high frequencies compared to ligand **6**. The ^{29}Si NMR spectrum showed only one signal at $\delta -1.87 \text{ ppm}$ typical of tetracoordinated silicon atom [5,14]. The tetracoordination of the silicon atom was confirmed by an X-ray crystallography, selected bond lengths and angles are summarized in table 1. The molecular structure of a sixteen-membered ring complex is depicted in fig. 1. The bond angles around the silicon are in the range of 111.38 (16) to 109.52 (14), which confirms the tetracoordinated geometry around the silicon atom, this fact is a consequence of the formation of the amine



Scheme 2



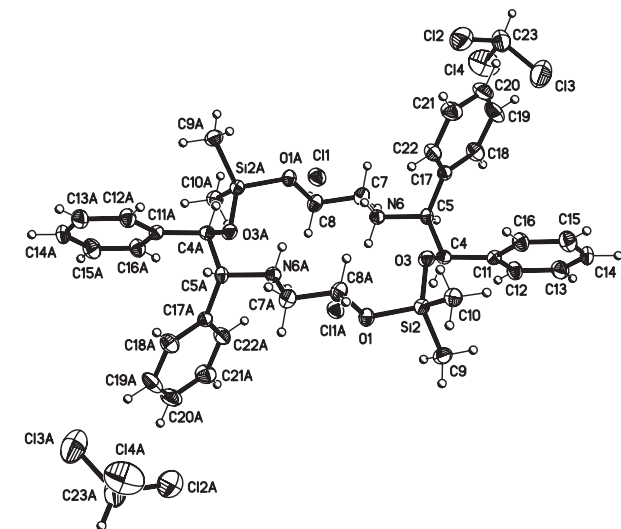
Scheme 3

Table 1. Synthesis of Monomeric and Dimeric Siloxanes Derived of β -Aminoalcohols**Scheme 4**

hydrochloride. The distances Si-C and Si-O are within the values expected. The isolation of the amine hydrochloride complex might be associated with the basicity of the aminoalcohol used.

Conclusions

The formation of monomeric or dimeric species is influenced by the nature of substituents attached to the silicon atom; the formation of dimeric compounds **2a**, **2b** and **7** is attributed to the methyl groups bonded to the silicon atom. However, in the case of diphenyl substituted silicon derivatives the formation of pentacoordinated monomeric compounds was observed, in this case the pentacoordination around the silicon atom was evidenced by ^{29}Si NMR. The reaction of ligand **6** with dichlorodimethylsilane led selectively to the formation of macrocyclic compound **7** where the silicon atom is tetracoordinated, this fact is attributed to the presence of amine hydrochloride which prevents the formation of the N-Si coordinative bond. The study of aminoalcohols **1** and **4** as well as

**Fig. 1.** Molecular structure of compound **7**.

another aminoalcohols with dichlorodimethylsilane is in progress.

Experimental

2-Aminophenol, dichlorodiphenylsilane, bisdimethylaminodimethylsilane, methylphenyldichlorosilane, butyl ether were purchased from Aldrich. All reactions were carried out under nitrogen atmosphere, and the solvents were carefully dried and distilled from the appropriate drying agents prior to use. ^1H , ^{13}C , and ^{29}Si -NMR spectra were recorded on a JEOL Eclipse

Table 1. Selected bond lengths (Å) and angles (°) of compound **7**.

Bond lengths			
O(1)-C(8)	1.403(4)	C(5)-N(6)	1.512(5)
C(4)-C(11)	1.507(5)	Si(2)-C(9)	1.843(4)
O(3)-C(4)	1.420(4)	N(6)-C(7)	1.497(5)
C(4)-C(5)	1.529(5)	Si(2)-C(10)	1.856(4)
O(1)-Si(2)	1.638(3)	C(7)-C(8)	1.501(5)
C(5)-C(17)	1.496(5)	C(8)-O(1)	1.403(4)
O(3)-Si(2)	1.650(3)		
Bond angles			
C(8)-O(1)-Si(2)	122.7(2)	C(9)-Si(2)-C(10)	114.2(2)
O(1)-Si(2)-O(3)	109.5 (1)	C(4)-O(3)-Si(2)	124.3(2)
O(1)-Si(2)-C(9)	105.6 (2)	O(3)-C(4)-C(11)	112.7(3)
O(3)-Si(2)-C(9)	111.4(2)	O(3)-C(4)-C(5)	110.3(3)
O(1)-Si(2)-C(10)	109.1(2)	C(11)-C(4)-C(5)	109.5(3)
O(3)-Si(2)-C(10)	107.0 (2)	C(17)-C(5)-N(6)	112.2(3)
N(6)-C(5)-C(4)	110.1(3)	C(7)-N(6)-C(5)	111.5(3)

+300, chemical shifts (ppm) are relative to the TMS. The ^{29}Si -NMR was obtained using the INEPT sequence pulse. The mass spectra were obtained on a JEOL JMS-AX505 HA. Melting points were measured on a Melt Temp II and are uncorrected. The Elemental analyses were performed by Galbraith Laboratories Inc. The X-Ray Crystallography studies were done on a Bruker Smart Apex CCD diffractometer $\lambda(\text{Mo-K}\alpha)=0.71073\text{\AA}$, graphite monochromator, $T = 293\text{K}$, $\omega - 2\theta$ scan range $1.7 < \theta < 25$. Corrections were done for Lorentz and polarization effects. The structures were solved by direct methods, all non hydrogen atoms were refined anisotropically by full least squares and the structure was refined by full-matrix least square on F^2 using all data with assigned anisotropic displacement parameters for all non-hydrogen atoms and hydrogen atoms bound to carbon atoms inserted at calculates position with isotropic temperature factor 1.2 times the U_{iso} of the parent carbon atom. The program used in the final refinements was SHELXL 97 [27]. Crystallographic data for the structural analysis has been deposited with Cambridge Data center CCDC 604918 Crystal data: Compound **7** ($\text{C}_{38}\text{H}_{50}\text{Cl}_8\text{N}_2\text{O}_4\text{Si}_2$). $\text{MW}=938.58$, $a = 7.326(1)\text{\AA}$, $b = 21.739(2)\text{\AA}$, $c = 14.415(1)\text{\AA}$, $\beta = 99.594(2)^\circ$, $V = 2263.6(4)\text{\AA}^3$, space group $P2_1/n$, $Z=2$, $\rho_{\text{calc}} = 1.377\text{ g/cm}^3$, 18336 reflection collected, 4001 independent reflections, No. of variables 254, final $R = 0.0627$, $R_w = 0.1081$, crystal size $0.470 \times 0.110 \times 0.064\text{ mm}$ colorless.

3,3,15,15-Tetramethyl-6,18-diphenyl-2,4,14,16-tetraoxa-7,19-diaza-3,15-disila-tricyclo [18.4.0.0^{8,13}]tetracosal(24),8,10,12, 20,22-hexaene (2a and 2b)

To a solution of **1** g (4.36 mmol) of 2-(2-Hydroxy-1-phenylethylamino)phenol (**1**) in 30 mL of toluene at room temperature 0.65g (4.36 mmol) of bis (dimethylamino) dimethylsilane was added dropwise. After 24 h of refluxing the solvent was removed, the crude product was treated with diethyl ether, leading to the precipitation of 0.98 g (39 %) of a white solid; mp 200-204; ^1H NMR (300 MHz, CDCl_3) δ : 0.26 (s, 3H, Si-Me) 0.31 (s, 3H, Si-Me), 0.38 (s, 3H, Si-Me), 0.40 (s, 3H, Si-Me), 3.7-3.9 (2H, m, CH_2), 4.08 (1H, dd, $J = 3.6$, CH), 5.43, (1H, s, NH), 6.1 (1H, dd, $J = 1.3, 7.5$, H-6), 6.4 (2H, m, H-5, H 4), 6.7 (1H, dd, $J = 1.5, 7.4$, H-3), 7.3-7.4 (4H, m, arom); ^{13}C NMR (75.5 MHz, CDCl_3) δ : -2.3 (CH_3 -Si), 2.0 (CH_3 -Si), 60.0 (C-1), 60.4(C-1), 67.9 (C-2), 68.3 (C-2), 112.7 (C-8), 113.3 (C-5), 116.9 (C-6), 117.0 (C-6), 118.1 (C-7), 118.3 (C-7), 122.8 (C-m), 122.9 (C-m), 126.9 (C-p), 127.0 (C-p), 127.5 (C-o) 128.7 (C-o), 139.7 (C-3), 140.7 (C-3), 140.5 (C-4), 140.7 (C-4), 141.5 (C-i), 141.8 (C-i). ^{29}Si NMR (59 MHz, CDCl_3) δ : -1.02, 0.23. MS (EI^+ , m/z (%): 570 [M^+ (15)], 360 (12), 303 (20), 285 (75), 254 (100).

6,6,8,8,11-Pentaphenyl,11,12-dihydro-10H-5,7,9-trioxa-12-aza-6,8-disila-benzocyclodecene (3). To a solution of **1** g (4.36 mmol) of **1** in 30 mL of butylether, 1.1 g (4.46 mmol) of diphenyldichlorosilane was added dropwise. After 72 h of refluxing the solvent was evaporated giving a yellow oil

which was precipitated from ethyl ether to give 0.529 g (20 %) of a white solid; mp 170 $^\circ\text{C}$. ^1H -NMR (300 MHz, CDCl_3) δ : 4.43 (1H, dd, $J = 4.95, 12.6$, CH_2), 4.67 (1H, d, $J = 12.4$, CH_2), 4.78 (1H, s, CH), 6.79 (3H, m, H-Ar), 7.00-7.90 (25H, m, H-Ar); ^{13}C -NMR (75.5 MHz, CDCl_3) δ : 62.7 (C-1), 67.7 (C-2), 117.5, 120.0, 121.4, 125.0, 127.9, 128.1, 129.0, 129.3, 129.7, 130.0, 130.3, 131.1, 134.5, 134.7; ^{29}Si NMR (CDCl_3 , 59.71 MHz) δ : -35.9 ppm MS (EI^+ , m/z (%): 409 (8), 376 (3) 332 (25), 198 (100), 120 (13), 91 (12), 77 (10).

6,6-Diphenyl-2,3,4,4a,12,12a-hexahydro-1H-5,7-dioxa-12-aza-6-sila-dibenzo[a,d] cyclooctene (5). Compound **5** was synthesized following the procedure described for **2** from **1** g (4.83 mmol) of 2-(2-hydroxycyclohexylamino-phenol) and 1.22 g (0.98 mL) (4.83 mmol) of diphenyldichlorosilane giving 0.8 g (42%) of a beige solid mp 175-177 $^\circ\text{C}$. ^1H NMR (300 MHz, CDCl_3) δ : 1.15-1.74 (6H, m, H-cyclohex), 2.1-2.27 (2H, m, H-cyclohex), 2.48-2.50 (1H, m, H-1, 3.68 (1H, ddd, $J = 4.03, 9.2, 12$, H-2), 6.60-6.65 (2H, m, arom), 7.12-7.34 (2H, m, arom), 7.73-7.76 (10H, m, arom); ^{13}C -NMR (75.5 MHz, CDCl_3) δ : 24.3 (C-10), 25.4 (C-11), 32.4 (C9), 34.1 (C-12), 66.8 (C-1), 76.9 (C2), 119.3 C, 121.2, 125.8, 126.4, 127.6, 127.9, 129.0, 129.2 132.5, 134.5, 135.6, 137.6, 138.7, 151.5; ^{29}Si NMR (CDCl_3 , 59.71 MHz) δ : -47.3; MS (EI^+ , m/z (%): 387 [M^+ , (30)], 310 [M^+-77 (100)], 230 (12), 212 (40), 197 (5), 181 (5); HR-MS (FAB $^+$) m/z : 387.1655 (Calcd for $\text{C}_{24}\text{H}_{25}\text{NO}_2\text{Si}$). Observed: 387.1651.

2,2,10,10-Tetramethyl-4,5,12,13-tetraphenyl-1,3,9,11-tetraoxo-6,14-diaza-2,10-disila-cyclohexadecane dihydrochloride (7). To a solution of 0.3 g (1.16 mmol) of 2-(2-hydroxyethylamino)-1,2-diphenylethanol (**6**) in 30 mL of ether, 0.2 mL (1.16 mmol) of dimethyldichlorosilane was added dropwise. The mixture was stirred for 72 h at room temperature, then the solvent was evaporated resulting a white solid, after being crystallized from CHCl_3 0.65g (90%) of colorless crystals were obtained; mp 227-229 $^\circ\text{C}$; ^1H NMR (300 MHz, CDCl_3) δ : -0.39 (3H, s, Si- CH_3), 0.38 (3H, s, Si- CH_3), 2.81-2.87 (2H, m, H-3) 3.70 (2H, d, $J = 9.21$, CH), 4.14 (1H, d, $J = 9.21$, H-2), 5.97 (1H, t, $J = 10.57$, H-4), 6.84-7.09 (10H, m, H-Ar). ^{13}C -NMR (75.5 MHz, CDCl_3) δ : -3.3 (Si-Me), -1.5 (Si-Me), 50.5 (C-3) 58.9 (C-4), 70.9 (C-1), 73.2(C-2), 126.6 (C-p), 127.8 (C-m), 129.0 (C-o), 129.3 (C- o'), 139.6 (C-i); ^{29}Si NMR (59.71 MHz, CDCl_3) δ : -1.87; MS (EI^+ , m/z (%): 626 [M^+ , (32)], 611 [M^+-15 (3)], 520 (5), 477 (30), 314 (7), 298 (7), 206 (100), 180 (50) 163 (12), 118 (11). Anal. Calcd. for $\text{C}_{36}\text{H}_{48}\text{N}_2\text{O}_4\text{Si}_2\text{Cl}_2$: C, 61.58, H, 7.12, N, 4.46 %. Found: C, 61.22; H, 6.87; N, 4.40.

Acknowledgements

The authors thank Francisco Javier Pérez and Luis Velasco for their valuable collaboration in recording mass spectra. DGAPA UNAM for the financial support (IN207103).

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