Protonation-induced Isomerization of Gaseous Bromoxylenes: a Radiolytic and Mass Spectrometric Study

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The isomerization of bromoxylenes following protonation by X_3^+ (X = H or D), $C_nH_5^+$ (n = 1 or 2), iso-$C_3H_7^+$, and t-$C_4H_9^+$ ions in the dilute gas state has been investigated. Further evidence has been derived from chemical ionization mass spectrometry and related radiolytic experiments concerning methylation of bromotoluenes by gaseous $(CH_3)_2F^+$ ions. The results suggest that the observed intramolecular Br migration involves the intermediacy of a radical cation–bromine atom pair. The mechanistic relevance of the results to gas-phase aromatic substitution by free bromine cations is discussed.

Gas-phase ionic reactions, occurring in an environment free of solvation and ion-pairing effects, provide a simple and general model of the corresponding processes in condensed media.

Recently, the classic mass-spectrometric approach to ion–molecule reactions has been complemented by experimental techniques which allow isolation of the neutral end products, thus providing structural and stereochemical information fully comparable with that obtained from solution-chemistry studies.[1-4]

Aromatic substitution by a variety of charged electrophiles has been extensively investigated in the gas phase,[5-7] and detailed information on kinetic and mechanistic aspects is currently available. The present paper reports the results of a radiolytic and mass spectrometric study concerning the isomerization of bromoxylenes promoted by their protonation with gaseous Brønsted acids.

Protonation of bromoxylenes had been investigated previously in superacid solutions ($HF·SbF_5$);[8] several intriguing features of the isomerization process suggest that extension of this study to the dilute gas state could shed light on the mechanism of aromatic substitution by gaseous bromine cations, previously investigated by a nuclear-decay technique.[9,10]

Experimental

Materials.—The gases used (H_2, D_2, CH_4, C_3H_8, iso-C_4H_{10}) were reagent-grade products from Matheson Gas Products Co. The aromatic compounds used as substrates, or as reference standards in g.l.c., were obtained from Fluka AG or Aldrich Chemical Co., and were analysed by g.l.c. on the same columns as employed for the assay of the irradiation products.

The analysis revealed that 4-bromo-*m*-xylene contained as an impurity 2-bromo-*m*-xylene, and therefore required preliminary purification by g.l.c.

Among the columns employed, the best results were obtained with a 6 mm i.d. 3 m long stainless steel column packed with Bentone 34 (5%) on Chromosorb W, and operated at 135 °C.

Despite repeated purification steps, the final specimen still contained 0.1—0.2% 2-bromo-*m*-xylene, the proportion of which could not be reduced further; this material was used as such in the irradiation.

Procedure.—The samples to be irradiated were prepared by conventional techniques using a vacuum line equipped with greaseless stopcocks.

The aromatic substrate was weighed in fragile glass ampoules that were sealed off and introduced into 500 ml Pyrex vessels equipped with greaseless stopcocks (H_2, D_2, or CH_4 samples) or with fragile break-seal tips (C_3H_8, iso-C_4H_{10} samples). After introduction of the gaseous components, the vessels were closed, the fragile ampoules broken, and the contents allowed to mix at room temperature. The γ-irradiations were performed at 40 °C in a 220 Gammacell (Nuclear Canada Ltd.); the total dose ranged between 2 and 3 Mrad, at a dose rate of 1 Mrad h^{-1}.

Analysis.—The radiolysis products were analysed by g.l.c. and g.l.c.–mass spectrometry, using a Sigma 1 instrument (Perkin-Elmer) equipped with an f.i.d. unit or a Sigma 3 instrument equipped with a photoionization detector (HNU Systems, Inc.). The g.l.c.–mass spectrometric analyses were carried out with a Hewlett-Packard 5982 A quadrupole spectrometer, connected to a 5934 A data system, or with a ZAB-2F high-resolution spectrometer from Micromass Ltd.

The following columns were employed in the g.l.c. and g.l.c.–mass spectrometric analyses of the xylenes and bromoxylenes from the radiolysis experiments: (i) a 50 ft stainless steel capillary column, 0.05 in i.d., coated with MBMA stationary phase and operated at 115 °C; (ii) several $\frac{1}{8}$ in i.d. stainless steel columns of lengths 1.8—5 m, packed with Bentone 34 (1.75%) and SP-1200 (5%) on 100—120 mesh Supelcoport, operated between 125 and 140 °C.

Chemical Ionization Mass Spectra.—Weighed amounts of the aromatic substrate were introduced into Pyrex vessels together with a large excess (>1 000 : 1) of the bulk gas (D_2, H_2, CH_4, C_3H_8, or iso-C_4H_{10}).

The spectra were taken in the ion source of the quadrupole mass spectrometer, operated in the chemical ionization mode at 169 °C. The pre-mixed gaseous mixtures were allowed to bleed into the source *via* heated needle valves and transfer lines. The pressure was measured with a Bourdon gauge inserted directly into the source; the readings, however internally consistent, were regarded as approximate, owing to the many sources of systematic error. The spectra were recorded at *nominal* pressures in the range 0.05—0.3 Torr, and the dependence of ionic abundance on the source pressure was investigated within this interval.

Ion Cyclotron Resonance Measurement of the Proton Affinity of Bromoxylenes.—The proton affinities of 2-bromo-*m*-xylene and 4-bromo-*m*-xylene were determined at 100 °C in a Nicolet FT MS 1000 i.c.r. mass spectrometer by equilibrium measurements, based on the following scale of absolute proton affinity values: benzene 767,[11] toluene 797,[12] *m*-xylene 823 kJ mol^{-1}.[13]

Table 1. Yields of products from the protonation of gaseous bromoxylenes

System composition (Torr)						Yields of products $[G_{(+M)}]$			
X_2 [a]	CH_4	O_2	NH_3	Substrate [b]	Reagent	*m*-Xylene	4-Br-*m*-xylene	5-Br-*m*-xylene	2-Br-*m*-xylene
720		10		2-Br-*m*-xylene	X_3^+	1.91 ± 0.19	0.63 ± 0.11	0.17 ± 0.06	
720		10	18	2-Br-*m*-xylene	X_3^+	0.05	0.05	0.05	
720		10		4-Br-*m*-xylene	X_3^+	1.87 ± 0.04		0.20 ± 0.05	0.35 [c]
	720	10		4-Br-*m*-xylene	$C_nH_5^+$	1.55 ± 0.12		0.1 [c]	0.50 [c]

[a] H_2 or D_2. [b] Substrate pressure 0.5—0.7 Torr. [c] See text.

Table 2. Methylation of bromotoluenes by gaseous $(CH_3)_2F^+$ ions

System composition (Torr)			Composition of products (%)		
CH_3F	O_2	Substrate			
700	10	2-Br-toluene [a]	2-Br-*m*-xylene 2-Br-*p*-xylene } 53.4 [b]	4-Br-*m*-xylene 13.7	3-Br-*o*-xylene 32.8
700	10	4-Br-toluene	4-Br-*m*-xylene 72.0	4-Br-*o*-xylene 28.0	

[a] Substrate pressure 0.5 Torr. [b] Combined yield; the products defied satisfactory resolution by g.l.c.

Results

Radiolytic Experiments.—The yields of the isomerization products from the reaction of radiolytically formed X_3^+ (X = H or D) or $C_nH_5^+$ (n = 1 or 2) ions with 2-bromo-*m*-xylene and 4-bromo-*m*-xylene, in H_2 or CH_4 gas at atmospheric pressure, are given in Table 1, together with those of the debromination product, *m*-xylene. In view of the presence of traces of the 2-bromo-isomer in the 4-bromo-*m*-xylene, even after preparative g.l.c., only the *lower limit* of the 2-bromo-*m*-xylene yields from the irradiation of the 4-bromo-isomer are listed in the Table.

When the reaction involves D_3^+ ions from D_2, the isomerized products contain one D atom per molecule, as shown by g.l.c.–mass spectrometry, whilst *m*-xylene is only partially (*ca.* $\frac{1}{3}$) deuteriated, even though a small fraction of the *m*-xylene molecules contains more than one D atom.

In order to ascertain the influence of the exothermicity of the protonation process on the rate of the isomerization reaction, bromoxylenes were allowed to react with milder Brønsted acids, including iso-$C_3H_7^+$ from the radiolysis of propane and t-$C_4H_9^+$ from the radiolysis of isobutane carried out at atmospheric pressure in the presence of small amounts (10 Torr) of O_2. No debromination or isomerization was observed in these systems, the only products identified being a mixture of isopropylated or t-butylated bromoxylenes respectively.

In order to prepare bromoxylenium ions *via* an alternative route, *o*- and *p*-bromotoluene were methylated with $(CH_3)_2F^+$ ions from the radiolysis of gaseous CH_3F at 720 Torr. The results, summarized in Table 2, show that both bromotoluenes undergo methylation, but there is no indication of the occurrence of any Br shift with respect to the methyl group of the original molecules; the bromoxylenes formed contain at least one methyl group *in the same position* with respect to Br as in the starting bromotoluenes.

Chemical Ionization Spectra.—The relevance of the chemical ionization data to the interpretation of protonation-induced isomerization is of course indirect and highly qualitative, owing in the first place to the inability to discriminate amongst isomeric ionic species, typical of mass spectrometry, and to the widely different reaction environment, *i.e.* 40 °C and 720 Torr in the radiolysis experiments *versus* 169 °C and <0.3 Torr in the chemical ionization source. Nevertheless, consideration of chemical ionization spectra is useful, in that they may provide a clue to the ionic intermediate in the isomerization process in the systems at atmospheric pressure.

The chemical ionization spectra of 2- and 4-bromo-*m*-xylene are similar, and analogous to those reported by Leung and Harrison [14] for the bromotoluenes. In the H_2 spectra, the protonated substrate, $(M + H)^+$, is only a minor peak, even at the highest pressure, while the two major ionic products are the $(M + H - Br)^+$ and the $(M - Br)^+$ ions, the ratio of which increases at higher pressures in a way that parallels the behaviour of the corresponding species in the spectra of the bromotoluenes.

The interpretation of the D_2 chemical ionization spectra of the bromoxylenes is complicated by overlapping of peaks. Nevertheless, the $(M + H - Br)^+$ species detected in the H_2 spectra is shifted upward by one mass unit, indicating the formation of the $(M + D - Br)^+$ ion. In the CH_4 spectra of the bromoxylenes the abundance of the protonated substrate, $(M + H)^+$, is high and increases rapidly with pressure, becoming the major ionic product at pressures of *ca.* 0.1 Torr, whilst the abundances of the $(M + H - Br)^+$ and $(M - Br)^+$ ions is relatively low (<10%). In the C_3H_8 and iso-C_4H_{10} chemical ionization spectra, protonated bromoxylenes are the only significant ions, apart from alkylation products in low abundance.

Discussion

Reagents.—X_3^+ ions (X = H or D) are formed in the radiolysis of X_2 gas according to well established processes; [15] $C_nH_5^+$ ions (n = 1 or 2) are the major charged species from the radiolysis of methane.[16,17] Both X_3^+ and $C_nH_5^+$ ions undergo many unreactive collisions with their parent molecules before a reactive encounter occurs with the highly diluted aromatic substrate. Gaseous iso-$C_3H_7^+$ and t-$C_4H_9^+$ are formed in high yields from the radiolysis of propane [17,18] and isobutane,[17,19] and behave both as protonating agents and as Lewis acids.

$(CH_3)_2F^+$ is the major charged species from the radiolysis of gaseous CH_3F,[20] and reacts exclusively as a methylating agent toward *n*-type and π-type nucleophiles.

Table 3. Energetics of relevant ionic reactions

Reaction	ΔH° / kJ mol^{-1}	Ref.
H_3^+ + 2-Br-*m*-xylene $\longrightarrow$ H_2 + $C_8H_{10}Br^+$ [a]	−405	21
CH_5^+ + 2-Br-*m*-xylene $\longrightarrow$ CH_4 + $C_8H_{10}Br^+$	−299	21
$(CH_3)_2F^+$ + 2-Br-*m*-toluene $\longrightarrow$ CH_3F + $C_8H_{10}Br^+$	−245	22, 23
$C_2H_5^+$ + 2-Br-*m*-xylene $\longrightarrow$ C_2H_4 + $C_8H_{10}Br^+$	−160	21
iso-$C_3H_7^+$ + 2-Br-*m*-xylene $\longrightarrow$ C_3H_6 + $C_8H_{10}Br^+$	−78	21
t-$C_4H_9^+$ + 2-Br-*m*-xylene $\longrightarrow$ iso-C_4H_8 + $C_8H_{10}Br^+$	−28	21
$C_8H_{10}Br^+$ $\longrightarrow$ *m*-$C_6H_4(CH_3)_2{}^{\rceil\cdot+}$ + $Br^\cdot$	+230	24
$C_8H_{10}Br^+$ $\longrightarrow$ *m*-xylene + Br^+	+540	24
$C_8H_{10}Br^+$ $\longrightarrow$ $C_8H_9^+$ + HBr	+94	25

[a] Taken as the most stable isomer of protonated 2-Br-*m*-xylene; see text.

The energetics of ion–molecule reactions relevant to the present discussion are listed in Table 3.

The Isomerization Process.—2-Bromo- and 4-bromo-*m*-xylene undergo isomerization with relatively high yields following protonation by X_3^+ and $C_nH_5^+$ ions. Thus, 2-bromo-*m*-xylene gives 4-bromo-*m*-xylene and 5-bromo-*m*-xylene in the ratio *ca.* 4 : 1. Under the same conditions, 4-bromo-*m*-xylene gives predominantly 2-bromo-*m*-xylene. Neither iso-$C_3H_7^+$ nor t-$C_4H_9^+$ ions promote isomerization, and no change in the position of Br with respect to the original methyl group is detectable in the products from the methylation of bromotoluenes by gaseous $(CH_3)_2F^+$ ions.

The isomerization process is of ionic character. It is not inhibited by an excess of O_2, an effective radical scavenger, but is totally suppressed by a gaseous base (NH_3) known as an efficient interceptor of charged reagents.

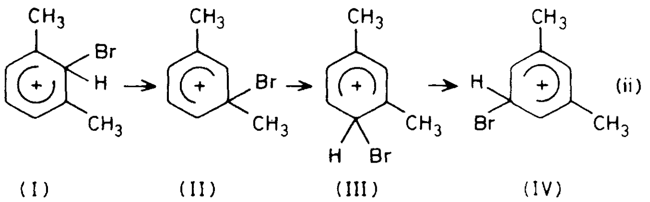
Even the most energetic Brønsted acid, the X_3^+ ion, does not promote appreciable migration of the methyl groups; these retain their *meta*-position both in the isomerized and in the dehalogenated products. Thus, introduction of the Br substituent into the arene molecule appears to depress the migratory aptitude of the methyl groups, which are known to undergo 1,2-shifts following protonation of unsubstituted xylenes by X_3^+ ions in X_2 gas at pressures up to 500 Torr.[26]

Mechanistic Aspects of Bromine Migration.—Any discussion of the process must take into account its ionic and intramolecular character, and the fact that it requires preliminary protonation of the substrate. The latter observation, of particular mechanistic value, follows directly from the incorporation of one D atom into the isomerized products from the reaction of D_3^+ with bromoxylenes. In addition, the Br migration must be characterized by an appreciable activation energy, since it occurs only when the protonation process (i) is sufficiently exothermic. The upper limit of the

$$C_6H_3Me_2Br + AH^+ \longrightarrow [C_6H_4Me_2Br]_{exc}^+ + A \quad (i)$$

excitation energy of the protonated adduct can be evaluated from the data of Table 3, on the assumption that the energy released in (i) is entirely stored in the internal degrees of freedom of the charged product. The upper limit of the activation energy required for Br migration can be estimated as between 80 and 160 kJ mol^{-1} (Figure).

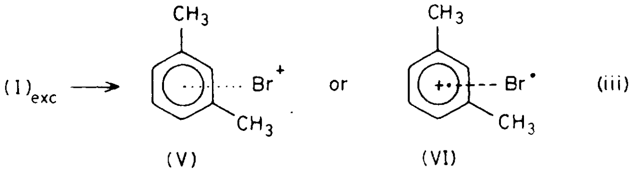
Among the conceivable migration mechanisms, one can consider a sequence of consecutive 1,2-Br-shifts within the excited arenium ion from (i), *e.g.* (ii). Similar mechanisms have been successfully adopted to explain intramolecular isomerization of excited arenium ions from other reactions.[1] However, serious reasons militate against sequence (ii) in the present case, including energetic considerations concerning the *ipso*-brominated ion (II),[27] the competition undergone by the Br atom in each 1,2-shift by H or CH_3, and especially the fact that, in order to account for the relatively high yields of 5-bromo-*m*-xylene from 2-bromo-*m*-xylene one must invoke three consecutive intramolecular shifts in a gaseous system at atmospheric pressure, where collisional deactivation of the excited arenium ions is expected to be very effective. In this connection, the ratio of the yields of 5-bromo-*m*-xylene is unreasonably high for a mechanism like (ii) where any additional shift necessarily causes a sharp decrease of the rate of formation of the corresponding isomer.[28]



The above considerations dictate that Br migration must proceed along reaction pathways requiring no multiple consecutive shifts, probably *via* charged, gaseous adducts, *e.g.* (iii). Energetic considerations tend to exclude adduct (V) (see Figure) in favour of the radical cation–bromine atom pair (VI). Strong, if indirect, experimental evidence for the intervention of (VI) is provided by the $H_2(D_2)$ CI spectra, showing that protodebromination of bromoxylenes (iv) is a major reaction channel, while no bromine cation can be detected. It is natural to assume that process (iv) involves the

$$X_3^+ + C_6H_3Me_2Br \longrightarrow X_2 + Br^\cdot + C_6H_4Me_2{}^{\rceil\cdot+} \quad (iv)$$

unimolecular dissociation of (VI), excited by the exothermicity of the protonation process, and the collisional deactivation of which is relatively inefficient at the low pressures (<0.3 Torr) prevailing in the ion source. At the much higher pressure (720 Torr) that characterizes the radiolysis systems, it is reasonable to assume that an appreciable fraction of (VI) can survive fragmentation, and subsequently collapse to



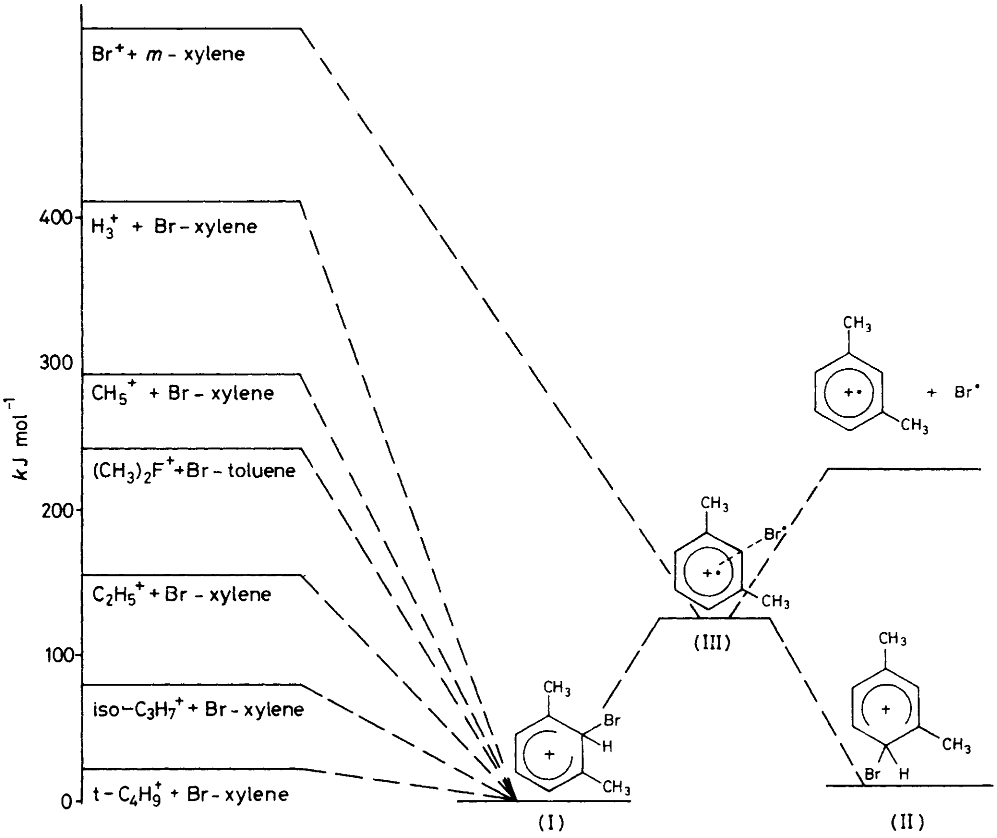


Figure. Energetics of the isomerization processes

isomeric arenium ions, along reaction pathways characterized by different activation energies (v). The relative abundances

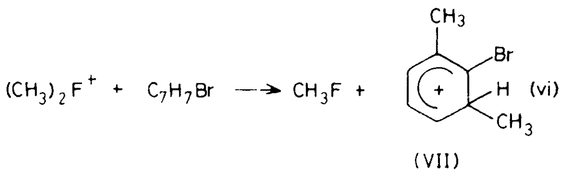
$$\text{(VI)} \longrightarrow \text{(I)} + \text{(III)} + \text{(IV)} \qquad \text{(v)}$$

of the arenium ions, and consequently of the neutral products from their deprotonation, is thus determined by the relative reactivity of the ring positions of the radical cation toward Br•. Unfortunately, a complete picture of the population of arenium ions from (v) cannot be obtained in the analysis of the corresponding neutral products, since one of the intermediates gives a product identical with the starting material.

Nevertheless, the isomeric composition of products is typical of a rather unselective electrophilic substitution. Thus, protonation of 2-bromo-*m*-xylene causes prevalent migration of Br to position 4, activated by two methyl groups, rather than to position 5. Protonation of 4-bromo-*m*-xylene is characterized by prevalent Br migration to position 2, again activated by two methyl groups, rather than to position 5. As expected, the positional selectivity increases when $C_nH_5^+$ ions are used instead of X_3^+ as the protonating reagent, owing to the lower internal energy available to the intermediate adduct (VI).

Methylation of Bromotoluenes.—Alkylation of *o*- and *p*-bromotoluenes by gaseous dimethylfluoronium ions yields, either directly or conceivably *via* the intermediacy of bromonium ions, excited arenium ions (VII), isomeric with those from the protonation of bromoxylenes.

Despite the large overall exothermicity of the reaction (vi), no Br migration can be detected in its products. Consistent with previous considerations, this finding can be rationalized by noting that (VII) is protonated at the ring position bearing the methyl group, and one or more proton shifts are required to obtain the isomeric ion (I), protonated at the ring position bearing the Br atom.



Alkylation of bromotoluenes provides, in addition, interesting information on the relative directive properties of the CH_3 and Br substituents in a gas-phase aromatic substitution by a free cation. The results, especially those concerning *p*-bromotoluene, the products from which could be completely resolved, demonstrate preferential methylation *ortho* to the Br atom, consistent with the general trend prevailing in aromatic substitution in the dilute gas state by charged reagents. In fact, high proportions of *ortho*-substituted isomers are invariably obtained from halogenobenzenes and other substrates containing *n*-type nucleophilic centres, the participation of which has been invoked to explain their directive effect.[29]

Conclusion

The evidence from radiolysis and chemical ionization experiments, as well as energetic considerations, suggests that Br migration within gaseous protonated bromoxylenes involves the intermediacy of a radical cation–bromine atom pair. No evidence concerning the specific structure of the adduct is at present available, although a model based on electrostatic interaction of the highly polarizable Br atom with the organic cation seems as good as any.

The results of the present study are relevant to the gas-phase aromatic substitution by free bromine cations,[9,10,30,31] since the reaction is likely to involve, as the first step, the exothermic charge exchange (vii), leading, *via* a different route, to the same radical cation–bromine atom pair postulated in this study.

$$\mathrm{Br}^+ + \mathrm{ArH} \longrightarrow \mathrm{ArH}^{]\cdot+} + \mathrm{Br}^{\cdot} \qquad \text{(vii)}$$

Extension of the model to condensed media is also conceivable. In particular, the study of aromatic substitution by free Br cations generated in liquid aromatic solvents by a nuclear-decay technique indicates the intervention of *neutral* Br atoms that form an 'excited reaction complex' with the substrate.[32] The pair (VI), formed again *via* the exothermic charge exchange process (vii), could represent a likely candidate for the reaction complex required to account for the kinetic features of the reaction, in particular its peculiar selectivity.

Finally, in a wider context, formation of a radical cation–electrophile pair has been postulated as a kinetically significant step in aromatic nitration in solution,[33] and there is evidence for its intervention in the dilute gas phase as well.[34]

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