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# METALATION REACTIONS—VI

## REARRANGEMENT OF A PROPARGYLIC ANION

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**Abstract**—Dimetalation of 1-phenylpropyne is faster than the monometalation and yields a dianion different from the dianion derived from 3-phenylpropyne or phenylallene. Deuteration of the first dianion yields 3-phenylpropyne-d$_2$ in which the hydrogen is transferred from the terminal to the benzylic position. A similar migration occurs on treatment of the dianion with trimethylsilyl chloride.

PROPARGYLIC anions are generally assumed to be intermediates in the isomerization[1,2] of acetylenes to allenes, dienes and positional isomers of acetylenes. The existence of these anions is usually inferred from the fact that these reactions are base catalysed, but very little work has been done on the formation and properties of propargylic anions. It was observed recently, that acetylenes can be metalated with the usual reagents such as butyllithium even polymetalated derivatives being produced.[3–8] These metalated compounds were either isolated,[3,4] or identified by NMR,[5] or by their reactions with deuterium oxide,[6] trimethylsilyl chloride[3,7] and carbon dioxide.[4,8]

Although the metalation of 1-phenylpropyne (I) was shown by deuteration to proceed to the trilithio-compound,[6] we undertook to examine this reaction more closely. Our aim was to study by NMR the relative ease of the consecutive abstraction of protons and to compare the anions formed from I to those that might be obtained from its isomers 3-phenylpropyne (II) and phenylallene (III). These last two compounds posed the additional problem of determining the relative kinetic acidities of the different kinds of protons. The positions of protonations and reaction with trimethylsilyl chloride were also investigated.

$C_6H_5C{\equiv}CCH_3$ I

$C_6H_5CH_2C{\equiv}CH$ II

$C_6H_5CH{=}C{=}CH_2$ III

$C_6H_5{-}C{\equiv}C{-}CH_2^{\ominus}$ IV

$C_6H_5C{\equiv}C{-}CH^{2\ominus}$ V

$C_6H_5{-}\overset{\ominus}{C}H{-}C{\equiv}C^{\ominus}$ VI

### *Metalation*

Addition of approximately equimolecular amounts of I to a solution of butyllithium in ether produced in the NMR spectrum of the solution a new signal at τ 7·98 and a decrease in the intensity of the methyl signal of I (τ 8·01). However, after a short time the signal at τ 7·98 disappeared and a new singlet appeared at τ 7·04 (Fig 1). The first signal was attributed to the $\equiv C{-}CH_2^{\ominus}$ of the monoanion (IV) of I and that at τ

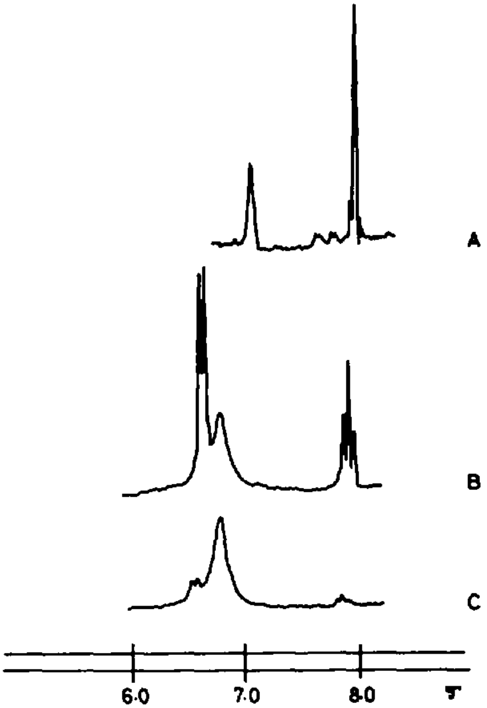


FIG 1. A 8·7 mmoles of I were injected at −70° into a solution of 8·7 mmoles of n-butyllithium in ether-$d_{10}$ (1·6F) in a NMR tube; the spectrum was recorded at 38° after 5 min. B 8·7 mmoles of II were injected at −70° into a solution of 17·4 mmoles of n-butyllithium in ether-$d_{10}$ (1·6F) in a NMR tube and the spectrum was recorded at 38° after 5 min. C as B but after 15 minutes.

7·04 to the $\equiv$C—CH$^{\ominus}$ of the dianion (V) of I. At the end of the metalation reaction (after a few min) only I and V in approximately equimolecular amounts were detected in the solution by NMR (and by subsequent reactions).

A similar metalation of II (Fig I) with two molar equivalents of butyllithium in ether did not change the position or the characteristic triplet and doublet pattern of the ethynyl and benzyl protons respectively. However, a new signal began to appear at τ 6·70 near the methylene protons of II. It increased until both the ethynyl and benzyl proton signals disappeared totally. This signal was attributed to the proton in the chain of the isomeric dianion (VI). This assignment was supported by deuteration and the reaction of the dianion with trimethylsilyl chloride. The NMR measurements in solution do not permit the establishment of the sequence in which the protons were abstracted from II. A faster abstraction of the ethynyl hydrogen should convert the benzylic doublet to a singlet. On the other hand the abstraction of a benzylic proton should convert the terminal proton to a doublet. These monometalations should also shift the signals of these protons relative to those of II. The possibility that the signal of the hydrogens of the monoanion is very near to that of VI cannot be ignored. In this case the pattern observed corresponds to that of the monoanion (VII), since its isomer (VIII) should exhibit two doublets for the hydrogens of the chain. The question of the sequence of proton abstraction was settled indirectly.

| | | | |
|---|---|---|---|
| $C_6H_5{-}CH_2C{\equiv}C^{\ominus}$ | $C_6H_5{-}\overset{\ominus}{C}H{-}C{\equiv}CH$ | $C_6H_5{-}CH_2{-}C{\equiv}CD$ | $C_6H_5\overset{\frown}{C{-}C{-}C}^{3\ominus}$ |
| VII | VIII | IX | X |

Addition of II to a solution of one equivalent of butyllithium in ether produced a precipitate that gave IX on reaction with $D_2O$, as evidenced by the absence of an ethynyl proton signal and the presence of a singlet indicating, by integration, two benzylic protons (Fig 2). The precipitate of the monolithium derivative of II dissolved in excess butyllithium to give VI.

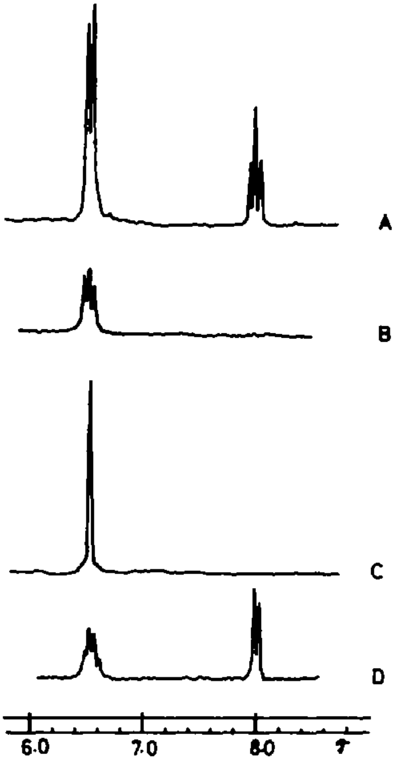


FIG 2. The NMR spectra in $CCl_4$ solution in the 6–8 τ region (the chain protons) of A $C_6H_5{-}CH_2{\equiv}CH$ (II); B $C_6H_5{-}CHDC{\equiv}CD$ (XVII); C $C_6H_5{-}CH_2C{\equiv}CD$ (IX); D $C_6H_5CHD{-}C{\equiv}CH$ (XVIII)

In the metalation of phenylallene (III) the monoanion could not be observed by NMR, but the dianion formed was VI, the same as that obtained from II. An addition of butyllithium to the allenic system also occurred during this metalation. Treatment of I or II with three or more equivalents of butyllithium in ether produced the trianion (X) showing only a broad band of the phenyl protons at τ 2·6–4·2.

It appears that the protons of the methylene group in III are more acidic than that proton near the phenyl group. The formation of VI from III indicates that the terminal proton in the intermediate anion VIII is also more acidic than that near the phenyl group (however, see below). The higher kinetic acidity of the ethynyl proton in II is also of interest, since it is predicted to have an acidity similar to that of the benzyl proton.[9]

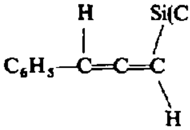
The chemical shifts of the hydrogens in the anions are unexpected. Abstraction of a proton from an allylic position generally shifts [10,11,12] the resonance of the protons remaining in this position by 1–1·3 ppm to lower field, due to a combination of two effects, a shielding due to the charge and deshielding which is a consequence of a change of hybridization and the inclusion of this position in the olefinic system. Abstraction of a proton from the 3-position of a 1,4-enyne[5] shifts the remaining proton by 0·2–0·5 ppm downfield. In the case of I a very slight (0·03 ppm) downfield shift was observed on abstraction of the first proton, but a much larger one (0·94 ppm) after the abstraction of the second proton. An attempt to explain these shifts in terms of the extent of charge withdrawal from the propargylic carbon could be misleading, since the electric field effects in the system containing the propargylic carbon and the triple bond with one or two charges are unknown. However, this naïve rationalization is in agreement with electron localization and electronegativity of the whole segment containing two charges (sesquiacetylene[5]) which are larger than in the similar group with one charge only. This was inferred previously from downfield shifts of protons in a similar system where anisotropy effects should be small due to the insensitivity of the chemical shifts of the protons to their configuration and distance from the propargylic group. It is probable that this effect, which is apparently connected with the higher degree of bonding and greater stability of the dianion relative to the monoanion, is also the reason for the larger kinetic acidity of the protons in IV than those in I.

*Reactions with Trimethylsilyl Chloride*

Metalation of I with one mole equivalent of butyllithium in ether and subsequent treatment of the solution with excess trimethylsilyl chloride produced a mixture that contained 43% of I, 16% of a mixture of monosilyl derivatives and 40% of a disilyl derivative. The products were separated by GLC and characterized by analysis and their spectra. One of the monosilyl derivatives was acetylenic (XI) as shown by its bands in the IR at 2200 and 2250 cm$^{-1}$, its UV absorption maxima at 282 mμ and 250 mμ and its NMR spectrum which showed five phenyl protons at τ 2·81, a singlet [$(CH_3)_3Si$] at τ 9·85 and a singlet (two propargylic protons) at τ 8·35. Its isomer (XII), (which was not isolated pure from XI), was characterized by its NMR signals—

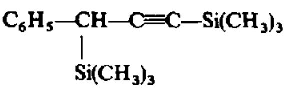
$C_6H_5C{\equiv}CCH_2Si(CH_3)_3$

XI



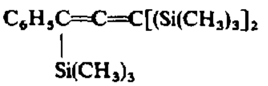
$C_6H_5\text{—}\overset{H}{C}{=}C{=}C\begin{smallmatrix}Si(CH_3)_3\\ H\end{smallmatrix}$

XII



$C_6H_5\text{—}\underset{Si(CH_3)_3}{CH}\text{—}C{\equiv}C\text{—}Si(CH_3)_3$

XIII



$C_6H_5\underset{Si(CH_3)_3}{C}{=}C{=}C[(Si(CH_3)_3]_2$

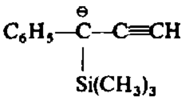
XIV

two doublets at τ 4·12 and 4·65 with a coupling constant of 3·5 Hz. The bis-trimethylsilyl derivative proved to be XIII, since it exhibited a band at 2175 cm$^{-1}$, a pattern of four absorption maxima between 247 and 274 mμ with an extinction coefficient of between 300 and 1000 and a strong absorption maximum at 224 mμ. The NMR spectrum confirmed this structure by the presence of a signal corresponding to the benzylic proton τ 6·89 (definitely not an allenic proton) in addition to the five phenyl protons at τ 2·88 and two singlets due to two $Si(CH_3)_3$ groups at τ 9·82 and 9·96.

Metalation of I with two mole equivalents of butyllithium and subsequent treatment with trimethylsilyl chloride yielded 10% of I and 90% of XII. The same product was obtained on metalation of II in similar conditions.

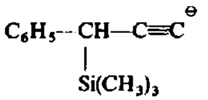
Treatment of either I or II with three or more molar equivalents of butyllithium followed by an excess of trimethylsilyl chloride produced the tris-(trimethylsilyl) derivative (XIV). This showed an allenic band at 1880 $cm^{-1}$, a maximum absorption at 265 mμ with a high extinction, a $C_6H_5$ signal at τ 2·90, one $(CH_3)_3Si$ signal at τ 9·85 and the other 18 protons of $(CH_3)_3Si$ at τ 9·90.

The formation of XIII from I requires an isomerization step. This necessary hydrogen transfer does not occur in the dianion, since the two dianions V and VI are stable and are not interconvertible even on standing. It does not seem probable that an initially produced allenic disilyl derivative is isomerized to XIII (viz protonation section). We have therefore to conclude that hydrogen transfer occurs after the reaction of V with one mole of trimethylsilyl chloride and the formation of a monoanion. The most probable position for the initial attack is the benzylic position giving (XV), since in this case it is easy to rationalize the driving force for this rearrangement in terms of the formation of a more stable anion (XVI). This then gives XIII.



$C_6H_5{-}\underset{Si(CH_3)_3}{\overset{\ominus}{C}}{-}C{\equiv}CH$

XV



$C_6H_5{-}\underset{Si(CH_3)_3}{CH}{-}C{\equiv}\overset{\ominus}{C}$

XVI

$C_6H_5{-}CHD{-}C{\equiv}CD$

XVII

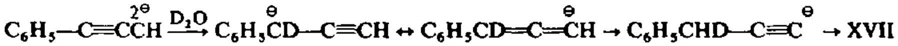
$C_6H_5CHD{-}C{\equiv}CH$

XVIII

The formation of XII may be a result of an isomerization of XI, for its yields were erratic (3–12%) when the total yield in the monosilyl derivatives was approximately constant. It could also be formed from the dianion of II, or from the rearranged anion VIII.

### *Protonation and deuteration*

The rearrangement observed during the silylation of the dianion V raised the question, whether a similar hydrogen transfer would be observed during the protonation of V. Protonation of V with water yielded II. The reaction of V with deuterium oxide yielded a product whose IR spectrum exhibited ≡CD stretching at 2605 $cm^{-1}$, a C≡C band at 1965, 1995 $cm^{-1}$, and ultraviolet absorption similar to that of II. Its NMR spectrum showed a phenyl signal and a triplet corresponding to one benzylic proton at τ 6·52 with an HD coupling constant of 2·5 Hz, (Fig 2). The same product was obtained from II by way of VI. This compound, to which the structure XVII was attributed was hydrogenated on $Rh/CaCO_3$ and yielded 1,3-$d_2$-1-phenylpropane, showing in the NMR one benzylic proton at τ 7·50 as a triplet ($J_{HH}$ 6·4 Hz) with a secondary splitting to an additional triplet ($J_{HD}$ 2Hz) due to the geminal deuterium. The terminal $CH_2D$ group appeared also as a triplet of triplets at τ 9·17. All these data sustained the formula XVII for the deuteration product, and its formation was a result of a hydrogen transfer in some stage of the reaction. Again, this transfer could not occur in the dianion stage due to the observed stability of V, nor in the final product, since neither I nor III, nor their deuterated derivatives were found in the products of the reaction. We have found previously[13] that II is isomerized rapidly in basic conditions to III and then to I without H—D exchange with the solvent. The rearrangement has to take place in the monoanion. This cannot be the anion IV, since an intramolecular isomerization of this anion (for a discussion of the possibility of an intermolecular hydrogen transfer see below) would have occurred during metalation even better than during the much faster protonation. Such a hydrogen transfer in IV during metalation would give VIII which is the first intermediate formed during the metalation of III and thus would have given VI and not V on further reaction. The species undergoing isomerization is therefore VIII and the first protonation of the dianion V occurs at the benzylic position. The monoanion VIII rearranges into VII, the driving force being the larger stability of the latter. The formation of XVII proceeds therefore by scheme 1.

1 

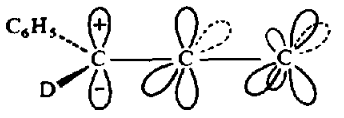
$$C_6H_5{-}C{\equiv}\overset{2\ominus}{C}CH \xrightarrow{D_2O} C_6H_5\overset{\ominus}{C}D{-}C{\equiv}CH \leftrightarrow C_6H_5CD{=}C{=}\overset{\ominus}{C}H \rightarrow C_6H_5CHD{-}C{\equiv}C^{\ominus} \rightarrow \text{XVII}$$

Phenylallene III will therefore give VIII in the first stage of metalation. This anion is isomerized to VII and yields VI on further reaction.

Metalation of 3-phenylpropyne-1-3,3-$d_3$ with two equivalents of butyllithium and subsequent treatment of the metalation product with water yielded 3-phenyl—propyne-3-$d_1$ (XVIII), whose NMR spectrum exhibited a $\equiv$CH signal at $\tau$ 7·96 in the form of doublet with a coupling constant of 2·4 Hz, and one benzylic proton at $\tau$ 6·52 as a quartet formed by superposition of doublet and triplet (couplings of $J_{HH}$ 2·4 Hz and $J_{HD}$ 2·5 Hz) (Fig 2). The HD coupling B similar to that observed by Tiers.[14]

Suprafacial 1,3-sigmatropic hydrogen migrations in allylic systems are thermally forbidden.[15] It would therefore be expected, that the observed isomerization is an intermolecular specific process, occurring by transfer of proton from one molecule of the anion to another and without the intervention of protons from water. Protonation of carbanions by water has a rate close to the diffusion controlled process.[16] Despite the presence of a two phase system during the studied protonation it is difficult to conceive that deuteration by deuterium oxide will be slower than a series of hydrogen transfers from one molecule of the monoanion to another, a reaction that may in principle account for the isomerization. Such transfers would have to be very fast to be able to compete with protonation by water and at the same time very specific not to give up the hydrogen to molecules of the dianion still present in the solution at the beginning of the reaction. Such an intermolecular proton transfer mechanism would require the deuteron transfer from deuterium oxide to be much faster to the dianion V than to the monoanion, but proton transfer from the hydrocarbons to be much faster to the mono- than to the dianion. A metalation reaction of I using slightly less than two molecular equivalents of butyllithium and subsequent treatment with deuterium oxide yielded XVII and I in a 2:1 ratio. I did not contain deuterium in amounts detectable by NMR, proving that I was not the protonating agent. A proton abstraction from VIII by deuterium oxide and its transfer to the 3-position does not seem probable, since a rotation of the formed oxonium ion $D_2HO^{\oplus}$ or of HDO should also give deuteration. Furthermore, hydrogen migration was observed in the trimethylsilyl reaction, where no water was present.

It seems to us that an unassisted intramolecular concerted hydrogen shift during the reaction from VIII to VII is a more likely possibility. This does not contradict the Woodward–Hoffmann rules,[15] since the symmetry properties of an allylic system do not apply to a propargylic anion, where an additional $\pi$ bond is present. Instead of one AO of the HOMO on an extreme carbon of an allylic system, there are three such AO in our system that can undergo a transformation during the hydrogen shift. This MO can be depicted in the transition state by (XIX), where the terminal carbon is $sp^2$-p hybridized. The AO on the terminal carbon participating in this transformation probably has a component with a proper phase for a migration. It is possible that the AO perpendicular to that on the benzylic carbon participates particularly in this process. It seems also that the structure of the anion VIII should be rather allenic than acetylenic for this hydrogen migration to occur so easily.



XIX

The fingerprint part of the IR spectrum of II, its deuterated derivatives, IX, XVII, XVIII and II-$d_3$, all containing either $\equiv$CH or $\equiv$CD groups, permits the differentiation of the compounds by intense bands at 650 $cm^{-1}$ for compounds containing the $\equiv$CH group and at 505 $cm^{-1}$ for those containing the CD group. The ratio of the frequencies of these bending modes is 1·27–1·29, similar to the ratio of the $\equiv$CH and $\equiv$CD stretching modes in our compounds and in other acetylenes.[17,18]

## EXPERIMENTAL

The NMR spectra were recorded in ether on Varian 56/60 or T60 instruments. The chemical shifts of the organometallics were measured relative to the low field component of the ether quartet. The IR spectra were taken on a Perkin–Elmer 337 instrument, and UV spectra were recorded in ethanol solutions on a Unicam SP.800. GLC analyses were performed on a Aerograph Autoprep A90–P3 or F & M 720.

1-*Phenylpropyne* (*I*) is a commercial product and was also prepared by a known procedure.[19]

3-*Phenylpropyne* (*II*) was prepared by the methods of Gaudemar[20] and also of Mulvaney.[6]

*Phenylallene* (*III*) was prepared by a known procedure[20] and also in the following way: 0·1 ml of a 2F soln of methylsulfinyl carbanion[21] in DMSO was added at 10° to a soln of 2 g of II in 10 ml of DMSO. The reaction was followed by NMR. When the $CH_2$ signal disappeared, the soln was poured onto cold water (20 ml) and the product extracted with ether (50 ml). The ether layer was washed with 5 × 50 ml portions of water and then dried and distilled giving 1·7 g III b.p. 70–72°/(12 mm).

Solutions of n-butyllithium in ether were prepared by evaporating the solvent *in vacuo* at room temp from a hexane soln of butyllithium (Foote) and then by dissolving the residue in ether. The concentrations of butyllithium in ether solns was found by titration with secondary butyl alcohol using benzylamine as indicator.[22]

Metalations were carried out by addition of the hydrocarbon to a 2F soln of butyllithium in ether kept at −50°. NMR spectra of the anions were recorded at room temperature.

Protonations and deuterations were performed by injection at 5° of water or deuterium oxide to the soln containing the metalation product.

3-*Phenylpropyne*-1-$d_1$ (*IX*) was prepared by the addition at −70° of 4·35 mmoles of II to an equimolar amount of 3·6F butyllithium in ether (1·3 ml). The precipitate formed was decomposed at 0° by the addition of $D_2O$. $\bar{\nu}_{max}$: 3080, 3055, 3030, 2595, 1990, 1945, 1600, 1500, 1450, 1080, 1035, 738, 700, 607, 503 $cm^{-1}$.

*Products of the reactions with trimethylsilyl chloride* (*XI–XIV*). The metalations were carried out as above at low temperature. 8·7 mmoles of I were treated with the appropriate amount of butyllithium in ether (1·2F): (a) 8·7 mmoles in order to obtain a mixture of the starting material, the dianion and a small quantity of the monoanion, (b) 17·4 mmoles to obtain the dianion and (c) 50 mmoles to obtain the trilithio derivative. The solns were allowed to reach room temp and were left for 5 h, then cooled to 0° and excess trimethylsilyl chloride was added. After 30 min water and ether were added, the layers were separated, the ether fraction was dried and the solvent removed by distillation. (a) gave a mixture of I, XI, XII and

XIII, (b) gave a mixture of XIII with a small quantity of I, b.p. 95–120°/(25 mm) and (c) gave XIV, b.p. 130–140°/(25 mm). The products were separated by GLC on 1·5 m × ¼" column of 20% SE-30 89/100 mesh on Chromosorb W. Analyses of XI—$C_{12}H_{16}Si$—(Calc: C, 76·6; H, 8·52. Found: C, 76·64; H, 8·52%), XIII—$C_{15}H_{24}Si_2$—(Calc: C, 69·25; H, 9·24. Found: C, 69·36; H, 9·32%) and XIV—$C_{18}H_{32}Si_3$—(Calc: C, 65·00; H, 9·65. Found: C, 65·18; H, 9·51%).

3-*Phenylpropyne*-1,3-$d_2$ (XVII) was obtained by treating the dianion soln prepared as above (procedure b) with an excess of $D_2O$. $\bar{\nu}_{max}$: 3095, 3070, 3040, 2605, 1995, 1965, 1620, 1500, 1460, 1285, 1085, 1040, 1030, 740, 725, 705, 605, 510 cm$^{-1}$.

3-*Phenylpropyne*-3-$d_1$ (XVIII). The dianion was prepared as above (procedure b) from 3-phenylpropyne-1,3,3-$d_3$[6] and the mixture decomposed on $H_2O$. $\bar{\nu}_{max}$: 3295, 3085, 3055, 3025, 2955, 2925, 2125, 1605, 1500, 1450, 1280, 1255, 1080, 1035, 1015, 925, 740, 720, 700, 645, 600 cm$^{-1}$. The IR spectrum of 3-phenylpropyne-1,3,3-$d_3$ has $\bar{\nu}_{max}$: 3075, 3050, 3010, 2580, 1980, 1945, 1600, 1490, 1445, 1090, 1070, 1040, 1024, 715, 595, 503 cm$^{-1}$.

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