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Alkyl Nitrite Isomerism. PMR Investigation of Substituted Ethyl Nitrites

$XC\,[H(\beta)]_2C[H(\alpha)]_2ONO$

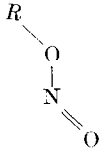
Børge Bak, P. O. Jensen, and Kjeld Schaumburg

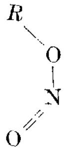
Chemical Laboratory V, University of Copenhagen, Copenhagen, Denmark

New microwave results confirm Brown and Hollis' *trans–cis* assignment for alkyl nitrites. In the present paper, the experimental material is widened by investigating compounds of the type XCH_2CH_2ONO where X = F, Cl, Br, I, CN. The barrier to *trans–cis* conversion is fixed to ca. 10 kcalmole^{-1} in all cases. Likewise, $E_{cis} - E_{trans}$ is close to 1 kcalmole^{-1}, and $S_{cis} - S_{trans} \sim 2$ gcalmole^{-1} deg^{-1}. Rotation about the C,C bond generates 3 isomers, 2 in which X is *gauche*, and 1 in which X is *trans* to the ONO group. By measuring proton chemical shifts and proton spin–spin couplings at room temperature where effective averaging over rotations about the C,O single bond and the ON single bond takes place, it is shown that the *gauche* forms are more abundant than statistics would indicate (⅔). Since the same *gauche*:*trans* ratio is observed in the case X = F for the pure trans (O,N) form at −70°C, we conclude that *gauche* preference also applies to the *cis* isomer. This rules out the idea of some intramolecular bond between non-neighbouring atoms, stabilizing the *cis* isomer. The new compounds X = F, Br, I, CN are characterized by their infrared spectra.

ALKYL NITRITE ISOMERISM

Alkyl nitrites have long been known to exist in two configurations:


trans(O,N)


cis(O,N)

separated by a barrier to interconversion of about 10 kcal, that is, not separable chemically. Many experiments and much discussion (*vide infra*) has been devoted to estimating the *trans–cis* ratios correctly.

In this respect, recent microwave results (*1*, *2*) seem important. The microwave spectrum of *methyl* nitrite primarly showed the existence of the *cis*-form with a dipole moment of 2.05 Debye (gas phase).

An earlier estimate had this moment at 1 D(*3*). However, Gray and Pearson (*3*) experimentally fixed the dipole moment of the methyl nitrite *trans–cis* mixture at $-70°\mathrm{C}$ to 2.20 D (liquid phase). In addition, PMR measurements (*4*) on methyl nitrite at $-70°\mathrm{C}$ showed the existence of 2 isomers in the ratio of 3:1, irrespective of their *trans–cis* affiliation.

Therefore, either

$$c(trans)/c(cis) = 3 \text{ and } \tfrac{1}{4}(2.05\cdot 1 + \mu(trans)\cdot 3) = 2.20 \qquad (1)$$

or

$$c(trans)/c(cis) = \tfrac{1}{3} \text{ and } \tfrac{1}{4}(2.05\cdot 3 + \mu(trans)\cdot 1) = 2.20. \qquad (2)$$

In case (1), $\mu(trans) = 2.25$ D. In case (2), $\mu(trans) = 2.65$ D. Since generally accepted bond-moment estimates of dipole moments agree in predicting $\mu(trans) > \mu(cis)$, alternative (2) must hold in the case of methyl nitrite.

In the PMR spectrum of methyl nitrite it is, therefore, the more intense signal from the CH_3 protons of the *cis* component which appears at the *higher* magnetic field. In the PMR spectra of higher alkyl nitrites, the role of the CH_3 protons in methyl nitrite is taken over by the α-CH_2 protons. In all cases, however, the CH_2-signal at the higher field is the weaker. Therefore, the quantity of *cis* is smaller than *trans*, in contrast to what was found for methyl nitrite. There are several ways of confirming this assignment. PMR spectra of *n*-propyl and *iso*-propyl nitrite, interpreted as suggested, show *trans*:*cis* ratios of 2:1 and 16:1, respectively. This is the expected trend (for sterical reasons). Vapor-phase dipole moment data for methyl-(2.20 D), ethyl- (2.40), *n*-propyl- (2.40), *iso*-propyl-(2.57), and *tert.*-butyl-nitrite(2.70) reveal the expected increase in concentration of the high-moment *trans* isomer. The *trans–cis* assignments of the present paper agree with the assignments made by Brown and Hollis (*5*) who, however, partially based their arguments for this *trans–cis* affiliation of nitrites upon the magnetic effects of the N, O double bond. Because of the inherent difficulty in transfering extinction coefficients from a *cis* to a *trans* modification we have omitted using the numerous infrared data (*6–8*) in the above arguments.

PMR SPECTRA OF HALOGEN SUBSTITUTED ETHYL NITRITES

Barrier Height

The present investigation was undertaken in order to study the effect of substituting the "neutral" alkyl R with more electronegative groups. We have preliminarily refrained from studying compounds of the type $RCHXONO$ because of difficulty of access. Instead, we prepared the compounds XCH_2CH_2ONO with X = F, Cl, Br, I, and CN, four of which are "new" (see experimental part). These compounds have two extra internal axes of rotation, the C,C and the C,O single bonds, in addition to the O,N bond (which has partial double-bond character). The barriers to internal rotation about the C,C and C,O single bonds are, however, so much lower than the O,N-barrier that the various *gauche* and *trans* forms involved are effectively averaged from the standpoint of a PMR experiment. Only *trans–cis* isomers, in the sense initially defined, give rise to separate spectra and only so in a limited temperature interval (between ca. −50°C and their freezing point). At room temperature, all spectra refer to the molecule, averaged over all 3 internal axes. The five spectra thus belong to the type studied by Piette and Anderson (*4*).

At the lowest accessible temperature (−70°C) they are well separated into spectra of isomers, although in all cases, except $X = F$, not sharp enough to permit spin–spin coupling measurements. Taking E_a as the barrier height we have used

$$\log(\Delta\nu - \Delta\nu_0) = \log\frac{2\pi V_0 \Delta\nu_0^{\,2}}{V} + \frac{E_a}{2.30RT} = K + \frac{E_a}{2.30RT}, \tag{3}$$

which is easily derived from Piette and Anderson's Eq. (24). Here, $\Delta\nu$ is the full linewidth at one-half maximum of one of the α-hydrogen resonances which changes its linewidth with temperature, $\Delta\nu_0$ is the corresponding value of a reference line (one of the β-hydrogen lines at 40°C), and K is a constant in this context.

Figure 1 depicts the results obtained for X = Cl, Br, I, and CN. $X = F$ had to be omitted because the fluorine spin caused superposition of the *trans* and *cis* spectra. Table I summarizes our results together with a few of the previous determinations (*6*) and an estimate of the FCH_2CH_2ONO barrier, based on the close similarity between the fluorine derivative spectrum and the remaining spectra.

As seen, the introduction of a halogen atom in the β-position has no dramatic effect on the barrier. Brown and Hollis (*5*) have discussed whether we are at all observing *trans–cis* isomerization *via* a barrier. Instead, they have suggested an ionic mechanism:

$$\underset{trans}{RONO} \rightleftharpoons RO^+ + NO^- \rightleftharpoons \underset{cis}{RONO}$$

based on the observation that, at room temperature, with alkyls:

$$R'ONO + R''OH \rightleftharpoons R''ONO + R'OH$$

takes place rather rapidly. We have mixed *anhydrous* $NCCH_2CH_2ONO$ and $NCCH_2CH_2OH$ at room temperature. Sharp, permanent component spectra were obtained. At 14 000 oersteds, the chemical shift difference between the two sets of β-CH_2 protons is only 20 cps. However, when 1% of water was added to the same mixture, a rapid exchange between the alcohol and the nitrite occurred, revealing itself through complete coincidence of the two β-CH_2 signals.

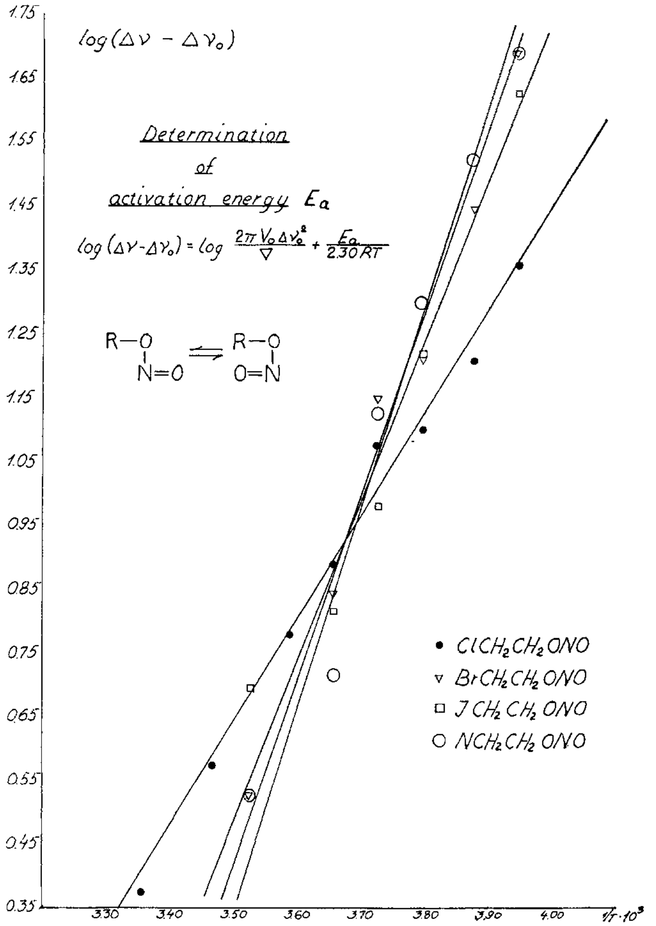


FIG. 1. Log ($\nu - \nu_0$) as a function of $10^3/T$ for evaluation of E_a

Since all our experiments were carried out using *dry* samples, isomerization through ionization is slow enough in our experiment to be of no importance to our measured line shapes.

TRANS–CIS RATIOS AND ISOMER ENERGY DIFFERENCES

The *trans–cis* ratios at −70°C were found by integration of the component spectra. At +40°C, where only "average" spectra can be observed, the less accurate estimate of the *trans–cis* ratio is based on the assumption that the chemical shifts of the components is unaffected by the temperature rise. For non-isomerizing chemical compounds, where this can be controlled, the assumption holds to a high degree of accuracy. The results are summarized in Table II.

In estimating ΔH of the *trans* to *cis* conversion we shall not go into detail

TABLE I

Energy Barrier, E_a kcal mole^{-1}, to *Trans–Cis* Isomerization in XCH$_2$CH$_2$ONO

X	E_a
F	~10
Cl	6.8 ± 2
Br	12.5 ± 2
I	10.7 ± 2
CN	13.0 ± 2
CH$_3$	9.0 ± 2
H	9.0 ± 2

TABLE II

Trans–Cis Ratios in XCH$_2$CH$_2$ONO at Low and High Temperature. ΔG in cal mole^{-1} for *Trans* to *Cis* Conversion

X	t°C	*trans/cis*	ΔG	t°C	*trans/cis*	ΔG
F	−70	4.0 ± 1	558	40	2.4	341
Cl	−70	4.0 ± 0.2	558	40	3.2	455
Br	−70	4.63 ± 0.1	618	40	2.8_6	406
I	−70	4.70 ± 0.1	667	40	2.6_4	375
CN	−70	4.5 ± 0.3	605	40	2.4	341
CH$_3$[a]	−75	2				
H[a]	−75	2				
CH$_3$[b]	−100	2		20	1.8	

[a] Reference *4*.

[b] Reference *9*.

because of the small scatter in the ΔG values. Let us consider

$$X\mathrm{CH_2CH_2ONO}(\mathit{trans}) \rightleftharpoons X\mathrm{CH_2CH_2ONO}(\mathit{cis})$$

with $\Delta G = 600$ gcalmole^{-1} at -70°C and $\Delta G = 380$ gcalmole^{-1} at $+40$°C. Using the relation $\Delta G = \Delta H - T\Delta S$, and considering ΔH and ΔS as practically temperature independent, one obtains

$$\Delta H \sim 1 \text{ kcalmole}^{-1} \sim \Delta E \quad \text{and} \quad \Delta S = 2 \text{ gcalmole}^{-1} \text{ deg}^{-1},$$

which are quite reasonable values for geometrical isomers. Because of experimental errors, the ΔH value is rather inaccurate, but we feel justified in concluding that $E_{trans} < E_{cis}$ with an energy difference of the order of ½–1 kcalmole^{-1}.

TRANS–GAUCHE ABUNDANCE

In the discussion on the PMR spectra of XCH$_2$CH$_2$ONO so far, mainly linewidths and intensity relations have been used. We shall now proceed to using the measured chemical shifts and spin–spin couplings of the protons. Primarily, these quantities are expected to yield information on the abundance of *trans–gauche* conformations generated by rotation about the C,C single bond (Fig. 2).

One may ask about the role of the hindered rotation about the C,O bond. From the microwave investigation of methyl nitrite it follows that the barrier to this rotation is probably lower ($\sim$2 kcalmole^{-1}) than the barrier to the rotation about the C,C bond ($\sim$3 kcalmole^{-1}). Therefore, the C,O bond rotational degree of freedom is also averaged. In what follows we have to assume that this averaging does not differ significantly from *trans*(O,N) to *cis*(O,N), or from one halogenated derivative to another. In the analysis of our PMR spectra we have treated these molecules as yielding spectra of the type $AA'BB'$. These can be analyzed in terms of 4 proton–proton spin coupling constants, $J_{AA'}$, $J_{BB'}$, J_1, and J_2. Only J_1 and J_2 can be found from the present data. With reference to Fig. 2 we shall use the relations (4) and (5):

$$J_1 = x_g J_g + x_g J_g + x_t J_t \ [= \mathrm{H}(\alpha 1), \mathrm{H}(\beta 1) \text{ coupling}] \tag{4}$$

$$J_2 = x_g J_g + x_t J_g + x_g J_t \ [= \mathrm{H}(\alpha 1), \mathrm{H}(\beta 2) \text{ coupling}] \tag{5}$$

combining the observable quantities J_1 and J_2 with J_g and J_t, the proton–proton *gauche*, respectively, *trans*, spin coupling constants.

The assignment of observed couplings to J_1 and J_2 represents a problem. However, forming

$$J_1 - J_2 = x_g(J_g - J_t) + x_t(J_t - J_g) = (J_t - J_g)(x_t - x_g), \tag{6}$$

we know beforehand that $J_t > J_g$. Now, in the case of FCH_2CH_2ONO, we have observed an unusually large F, H(α) coupling constant, *viz.*, 29 cps. This must mean that $x_g \gg x_t$, from which $J_2 > J_1$ follows. For the remaining halogen

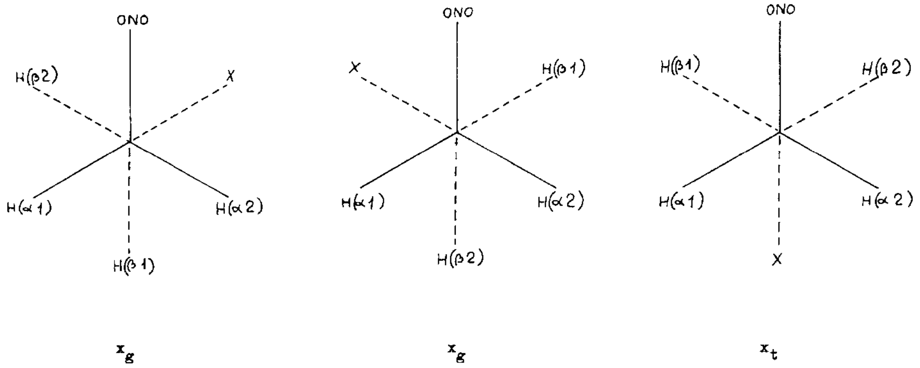


FIG. 2. *Trans*(C,C) and *gauche*(C,C) isomers of $XC[H(\beta)]_2C[H(\alpha)]_2ONO$ where ONO stands for *cis* or *trans* ONO conformation, each averaged with respect to C,O rotation. $2x_g$ and x_t are mole ratios of *gauche*(C,C) and *trans*(C,C) conformations.

derivatives, J_2 will be taken to be the *larger* of the two observable coupling constants. The results are summarized in Table III, in which the calculated values of x_g and x_t are based on the arbitrary assumption $J_t - J_g = 10$.

Table III shows that at 40°C, *gauche* configurations are favored, but decreasingly so through the series. In itself, this continuity affirms the validity of assigning the larger, measured coupling constant to J_2. Further confirmation of existing *gauche* abundance is obtained by considering the measured chemical shifts.

As seen, the chemical shifts of the α-protons are very little influenced by the inductive and magnetic effects of the X-substituent and the N—O group. If the role of the X-substituent is eliminated by forming the *trans–cis* chemical shift difference (column 3 of Table IV), an almost constant series of numbers results.

This indicates a nearly constant influence (inductive and magnetic) of the N=O group on the α-protons. We may infer from this that the heterogeneous magnetic field from the N=O group in the space occupied by the β-protons

TABLE III

Observed Coupling Constants in cps in XCH_2CH_2ONO at +40°C (Pure Liquids). Calculated *Trans* and *Gauche* Mole Ratios, Arbitrarily Assuming $J_{trans} - J_{gauche} = 10$ cps

X	J_2	J_1	$J_2 - J_1$	x_g	x_t
F	5.8	2.4	3.4	0.45	0.10
Cl	6.7_5	4.8_5	1.9	0.40	0.20
Br	6.7	4.7	2.0	0.40	0.20
I	7.5	6.2	1.3	0.38	0.24
CN	5.9_5	5.9_5	0	0.33	0.33

TABLE IV

Chemical Shifts in cps of α and β Protons in XCH_2CH_2ONO (Pure Liquids) at 14 000 Oersted, Relative to Internal TMS Standard

X	α Protons			β Protons			$x_g + x_t$
	trans	*cis*	*trans–cis*	*trans*	*cis*	*trans–cis*	
F	319.5	256.5	63.0	294.0	289.0	5.0	0.55
Cl	318.0	254.0	64.0	230.3	222.0	8.3	0.60
Br	327.1	262.9	64.2	224.8	215.1	9.7	0.60
I	324.5	260.1	64.4	211.9	199.3	12.6	0.62
CN	319	253	66.0	179.4	Unobservable		
CH_3[a]			64.5				
H[a]			64.5			10.8	0.66

[a] Reference 4.

varies only insignificantly throughout the series XCH_2CH_2ONO. So far, we would, therefore, expect a constant difference when forming the *trans–cis* chemical shift differences for the β-protons. The sixth column of Table IV shows that monotonously increasing values are obtained instead. If the analysis above is accepted, the numbers of Table IV, column 6, may be interpreted by noting that in the case of ethyl nitrite, with its 3 equivalent β-protons, a particular hydrogen atom [for example, H(β1) of Fig. 2] is under strongest magnetic influence from the N═O group when in an appropriate *gauche* position (the middle one of Fig. 2) or in the *trans* position in the sense, in which *gauche* and *trans* have been defined in Fig. 2. For ethyl nitrite, $x_g = x_t = 0.33$, and the corresponding chemical shift difference between *trans* and *cis* is 10.8. [cps.] We can take $x_g + x_t$ as a rough measure of the probability of finding a β-proton in a region of significant magnetic influence from the N═O group. For convenience, $x_g + x_t$ forms the seventh column of Table IV. It is seen that the chemical shift difference for the β-protons increases with increasing $x_g + x_t$. We take this as indicating *gauche* preponderance for $X = F$, the preponderance decreasing throughout the series. This conclusion agrees with what was found by considering the observable coupling constants J_1 and J_2.

That the *gauche* preponderance may be even larger than suggested in Table IV follows from our experimental determinations of J_2, J_1, and $J_{F,H(\alpha)}$ coupling constants for pure *trans*(O,N)FCH_2CH_2ONO at −70°C. The results were $J_2 = 5.8$, $J_1 = 2.4$, and $J_{F,H(\alpha)} = 29$ cps the same as for the equilibrium *trans* (O,N), *cis*(O,N) mixture at 40°C.

This coincidence will be hard to understand unless the *gauche*(C,C) and the *trans*(C,C) forms of the *trans*(O,N) isomer possess an energy difference, $\Delta E(g \rightarrow t)$, large enough to prevent any noteworthy increase in x_t during the rise of temperature from −70°C to 40°C.

If $\Delta E(g \rightarrow t)$ is of the order of 1 kcalmole^{-1}, this will suffice (ignoring entropy differences). This energy difference is compatible with a barrier to *gauche–trans* interconversion of 2–3 kcalmole^{-1}.

It then follows that the *cis*(O,N) isomer which is in equilibrium with the *trans*(O,N) isomer at 40°C, is also present in the same, high x_g:x_t ratio.

If, on the other hand, it is assumed that $\Delta E(g \rightarrow t)$ is appreciably smaller than 1 kcalmole^{-1}, then $(x_g{:}x_t)$(*trans* O,N at −70°C) $\gg$ $(x_g{:}x_t)$(*trans* O,N at 40°C). This represents a "loss" in F, H(α) coupling together with corresponding changes in J_2 and J_1. Now, in order to reproduce J_2, J_1, and $J_{F,H(\alpha)}$ for the equilibrium mixture at 40°C, the *cis*(O,N) component would have to make up for the "losses." But this could only happen by a fortuitous compensation for which the chances *a priori* are very small since we know that the *cis*(O,N) isomer constitutes only about one-third of the equilibrium mixture.

The idea of pronounced *gauche* preference for both the *trans*(O,N) and the *cis*(O,N) isomer is, therefore, far the more probable. Assuming $J_{trans} - J_{cis} =$

9 csec^{-1} instead of 10, one obtained $x_t = 0.050$, $x_g = 0.475$ and $E(g \to t) = 900$ gcalmole^{-1} for the *trans*(O,N) isomer at −70°C. At 40°C, $x_t = 0.10$ and $x_g = 0.450$. For the *cis*(O,N) isomer, the x_t and x_g values are about the same.

Since the *trans*(O,N) and the *cis*(O,N) isomers show such great similarities there is no special reason to assume the existence of an intramolecular bond, stabilizing the *cis* isomer relative to the *trans*.

EXPERIMENTAL PART

The five nitrites were prepared from their corresponding alcohols by the orthodox $NaNO_2$ + HCl process (*10*). Extra care was taken to prepare the alcohols in a pure state because the resulting nitrites are all unstable at elevated temperatures (>60°C) and reactive to humidity and air, so that elaborate separation procedures are not feasible. The final purification consisted in careful drying after removal of excess alcohol by water, and removal of aldehyde by $NaHSO_3$. A final distillation on a vacuum line was performed under temperature and pressure conditions as summarized below:

X	p mm Hg	T°C
F	38	0
Cl	20	12
Br	12	17
CN	2	20

All PMR spectra were taken on sealed-off samples in 5-mm i.d. glass tubes. Since these compounds, except the chloride, are "new" we have recorded the infrared absorption spectra of ca. 20v/v/% CCl_4 solutions in the 700–4000 cm^{-1} interval except for X = CN for which a 10 v/v% chloroformic solution was investigated, the compound being insoluble in CCl_4. KBr cuvette thickness 0.025 mm. Instrument: Perkin–Elmer 125. Table V summarizes frequencies and a few assignments of a number of lines, sufficient for future identification of the compounds (Table V).

While $NCCH_2CH_2ONO$ apparently is infinitely stable in a sealed-off glass

TABLE V

Characteristic Strong Infrared Absorption Bands of XCH_2CH_2ONO

F	Cl	Br	CN	Type
—	—	—	2248	C≡N stretch
1669*	1675	1674	1683	N=O stretch
1620	1622	1622	1631	N=O stretch
1362	1302	1285	1413	—
1348	1056	1060	1330	—
1142	1010	995	—	—

* All in cm^{-1}.

tube, it decomposed slowly by contact with the infrared cuvette material by the unavoidable contact with air. Its identity should, however, be sufficiently established by the frequencies of Table V and by the PMR data (Tables III and IV).

The PMR spectrometer was a Varian A-60 instrument with temperature control to within 2°. The temperature was calibrated by recording the spectrum of CH_3OH at the lower temperatures and the spectrum of $HOCH_2CH_2OH$ at the higher. After testing the sweep linearity, spectra were recorded on "precalibrated" cards. The measured chemical shifts are good to 1 cps, all our data representing average values of three recordings.

An ALGOL program NMR9 was used for calculating our $AA'BB'$-type spectra. By trial and error, the program parameters were changed until satisfactory agreement was obtained, *viz.*, until a change of one parameter by 0.1 cps did not improve the fit. Of course, for $X = F$, two fluorine sub-spectra were calculated and afterwards superimposed.

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