is a typical value for the peroxide ion bound to a transition-metal ion.[8] All the Cu–O distances are equivalent within experimental error. Hence, the coordination mode of the peroxide ion can be described as μ-η^2:η^2. To our knowledge, this is the first example of a μ-η^2:η^2 peroxo binuclear complex of a d-block element,[9,10] although such coordination modes are known for the U and La complexes.[11,12] It is notable that the Cu···Cu distance of 3.560 (3) Å is significantly shorter than that of the trans μ-1,2-peroxo binuclear Cu(II) complex (4.359 (1) Å)[2] and is consistent with the estimated values for oxy-Hc (3.58–3.66 Å)[13] and oxy-Tyr (3.63 Å)[14] by EXAFS analyses. Two of the Cu–N distances are normal, but the other Cu–N distance is considerably elongated. These indicate that the coordination geometry of the copper ion can be regarded as distorted square pyramidal with the N_3O_2 ligand donor set. The unusual coordination mode of the peroxide ion in **2** seems to reflect the strong preference of the copper(II) ion to pentacoordination (square pyramidal) rather than tetracoordination (tetrahedral) with the hindered tripod N_3 ligand such as in the present system.

A cis μ-1,2 coordination mode of the peroxide ion with an additional bridging ligand (such as OH^-) has been proposed for oxy-Hc (or oxy-Tyr) on the basis of (1) the strong magnetic interaction (diamagnetism) between the two copper ions and (2) the extensive spectroscopic studies on met-Hc.[1] However, to date no direct evidence for the existence of such a bridging ligand has been provided. If there is no additional ligand in these proteins, one could also postulate the possibility of μ-η^2:η^2 coordination of the peroxide ion, since Hc contains three hystidyl nitrogens as ligands for each copper ion.[15] The close resemblance of the physicochemical properties between **2** and oxy-Hc (and oxy-Tyr), including the diamagnetism, may suggest the hypothesis, although more adequate investigations are required to lead to the conclusion.

Acknowledgment. We thank Prof. T. Kitagawa, Dr. S. Hashimoto of the Institute for Molecular Science for resonance Raman measurements, and Prof. T. Ishimura and Drs. R. Makino and Y. Watanabe of Keio University for low-temperature measurements of electronic spectra. We are grateful for the kind suggestion on the choice of the space group in the X-ray analysis by a reviewer and by Prof. S. J. Lippard of Massachusetts Institute of Technology. This research was supported in part by the Ministry of Education, Science and Culture, Japan (62430018 and 1607003), for which we are grateful. N. Kitajima is also grateful to the Kawakami Memorial Foundation for financial support.

Supplementary Material Available: An ORTEP drawing of the molecular structure with atomic numbering, a perspective view of the crystal structure, and tables of the summary of X-ray analysis, bond distances, bond angles, atomic coordinates, anisotropic thermal parameters, and hydrogen atom coordinates for **2**·$6CH_2Cl_2$ (12 pages); observed and calculated structure factors for **2**·$6CH_2Cl_2$ (7 pages). Ordering information is given on any current masthead page.

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[7] **2**·$6CH_2Cl_2$ ($C_{60}H_{104}N_{12}O_2B_2Cl_{12}Cu_2$, MW 1599.71) crystallized in the monoclinic space group $C_{2/c}$ with $a = 22.36$ (2) Å, $b = 13.290$ (4) Å, $c = 29.29$ (2) Å, $\beta = 114.59$ (6)°, $V = 7915$ (9) Å^3, $Z = 4$. Intensity data were collected on a Rigaku AFC-5 diffractometer with graphite-monochromated Mo Kα radiation. The data collection was made at −75 ± 5 °C with a crystal sealed in a glass capillary, since the crystals were found to lose CH_2Cl_2 of crystallization very quickly at room temperature. The structure was solved by a heavy-atom method and refined by a block-diagonal least-squares technique with anisotropic thermal factors for non-hydrogen atoms. Hydrogen atoms on the boron, pyrazolyl rings, and tertiary positions of iPr groups were calculated and fixed in the refinement. The other hydrogen atoms were not included in the calculations. The weighting scheme is $w = [\sigma_c^2 + (0.05|F_o|)^2]^{-1}$. The current R and R_w values are 0.101 and 0.148 for 3003 reflections ($2\theta < 45°$, $F_o > 3\sigma(F_o)$). The slightly high residual values are probably due to the deterioration of the crystallinity during the mounting of the crystal, positional disorders of CH_2Cl_2 molecules and the isopropyl groups, and the fluctuation of the measurement temperature.

[8] Gubelmann, M. H.; Williams, A. F. *Struct. Bonding (Berlin)* **1983**, *55*, 1.

[9] The possibility of μ-η^2:η^2 structure was suggested for several complexes: (a) Sakurai, F.; Suzuki, H.; Moro-oka, Y.; Ikawa, T. *J. Am. Chem. Soc.* **1980**, *102*, 1749. (b) Kim, K.; Collman, J. P.; Ibers, J. A. *Ibid.* **1988**, *110*, 4242. The novel coordination mode of bridged peroxide ion, μ_4-η^2:η^2, has been found recently in a tetranuclear iron complex. Micklitz, W.; Bott, S. G.; Bentsen, J. G.; Lippard, S. J. *J. Am. Chem. Soc.* **1989**, *111*, 372.

[10] Karlin et al. have proposed μ-η^2:η^2 coordination (nonplanar) as a possible structure for their peroxo binuclear copper complexes based on the EXAFS analyses. The complexes, as well as **1** and **2**, contain also N_3 ligands, and the copper ions are bridged solely by a peroxide ion. Blackburn, N. J.; Strange, R. W.; Farooq, A.; Haka, M. S.; Karlin, K. D. *J. Am. Chem. Soc.* **1988**, *110*, 4263.

[11] $[(UO_2Cl_3)_2(O_2)]^{4-}$: Haegele, R.; Boeyens, J. C. A. *J. Chem. Soc., Dalton Trans.* **1977**, 648.

[12] $[La(N(SiMe_3)_2)_2(PPh_3O)]_2(O_2)$: Bradley, D. C.; Ghota, J. S.; Hart, F. A.; Hursthouse, M. B.; Raithby, P. R. *Ibid.* **1977**, 1166.

[13] Woolery, G. L.; Powers, L.; Winkler, M.; Solomon, E. I.; Spiro, T. G. *J. Am. Chem. Soc.* **1984**, *106*, 86.

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[15] Gaykema, W. P. J.; Volbeda, A.; Hol, W. G. J. *J. Mol. Biol.* **1985**, *187*, 255.

Unexpected Regioselectivity in the Reductive Cleavage of Epoxides: A Theoretical Rationalization

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The reductive cleavage of epoxides to alcohols is a reaction of general use in synthetic organic chemistry.[1] It has been observed recently that the reduction of epoxides of general formula **1** with lithium naphthalenide proceeds with regiochemistry that is intuitively unexpected,[2,3] but precedented by reductions of epoxides by means of metals dissolved in liquid ammonia or amines.[4] Unsymmetrical alkyl-substituted epoxides give mainly the more substituted carbinol, which requires cleavage of the C–O bond to the *less* substituted carbon atom (Table I, entries 1–6). Only a strongly radical stabilizing substituent causes ring opening to occur at the atom bearing that substituent (entries 7–10).[2,3]

Although the mechanism of the Birch reduction of epoxides[4] has been discussed in terms of a nucleophilic ring opening by a solvated electron,[4b] it is more likely that the mechanism is analogous to that of radical-anion reductions of organic halides,[5] aryl ethers,[1b] and phenyl thioethers.[1b,6] It thus involves electron transfer to the epoxide, followed by ring cleavage of the radical anion **2** to give a species containing an oxyanion and a radical. However, an apparent weakness of this mechanism is that, contrary to intuitive expectations, the less substituted radical must be formed in this step. One possible explanation, proposed by Bartmann,[3] is that the electron is localized in the antibonding

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[†] University of California.

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[1] (a) House, H. O. *Modern Synthetic Reactions*, 2nd ed.; Benjamin: Menlo Park, CA, 1972; p 103–105. (b) Maercker, A. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 972.

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[5] Holy, N. L. *Chem. Rev.* **1974**, *74*, 243. Garst, J. F. *Acc. Chem. Res.* **1971**, *4*, 400. Garst, J. F. In *Free Radicals*; Kochi, J. F., Ed.; Wiley-Interscience: New York, 1973; pp 503–546. See also: Andrieux, C. P.; Gallardo, I.; Savéant, J. M.; Su, K. B. *J. Am. Chem. Soc.* **1986**, *108*, 638.

[6] Cohen, T.; Bupathy, M. *Acc. Chem. Res.* **1989**, *22*, 152 and citations therein.

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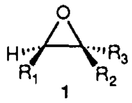
Table I. Epoxides **1** That Are Reduced Regiospecifically via Electron Transfer[a]

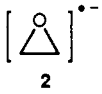
entry	R_1	R_2	R_3	ref.
1	H	H	Me	3
2	H	H	Et	3
3	H	H	$(CH_2)_9CH_3$	2
4	H	Me	Me	3
5	H	$-(CH_2)_5-$		2
6	H	$[(CH_2)_2CH(R)(CH_2)_2]$		2
7	SPh	$-(CH_2)_5-$		2
8	Ph	H	H	3
9	CO_2Et	H	H	3
10	CO_2Et	Me	H	3

[a] In all cases, the product arises from cleavage of the $(R_1)C-O$ bond.

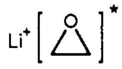
orbital associated with the less substituted CO bond of the epoxide and that this determines which bond is cleaved. While this concept is certainly reasonable,[7] we should like to present theoretical calculations and thermochemical data that indicate, rather surprisingly, that even if the assumption is made that the direction of opening is determined solely by the stabilities of the proximate products, there is a simple explanation for the observed regioselectivity.



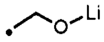
1



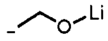
2



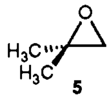
3a: (*) = •–
3b: (*) = 2–



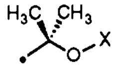
4a



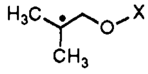
4b



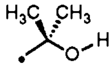
5



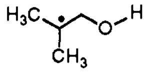
6a: X = Li
6b: X = –



7a: X = Li
7b: X = –



8



9

Ab initio molecular orbital calculations[8] were performed on structures **2–9**. Geometry optimizations were carried out with the 3-21G[9] basis set.[10] In the case of anions, single point energies were also calculated with diffuse functions on oxygen. Such species are not expected to be stable toward ejection of an electron, but small basis sets do not permit electron loss. Optimization of **2** gives the ring-opened radical anion, since **2** is not an energy minimum. Calculations with both C_{2v} and C_s symmetry constraints were carried out on the species **3a** and **3b**,[11,12] to better mimic species likely to be present in solution. The lithiated species **3a**, which is neutral overall, is a minimum on the energy surface and is more stable than ethylene oxide plus a lithium atom[13] by 24.1 kcal/mol. This species can either accept an electron to give **3b**, which would then cleave to give **4b**, or it can open directly to give **4a**. Compound **3b** is calculated to be 37 kcal/mol higher in energy than **3a**.[10] Solvation should stabilize **3b**, but capture of a second electron by **3a** before ring opening seems unlikely, because the ring opening to form **4a** is quite exothermic (24 kcal/mol by 6-31G*).[10] The heat of ring opening of the oxirane radical anion can be estimated from the heat of C–O homolysis of oxirane (68 kcal/mol)[14] and the electron affinities of the $^\bullet CH_2CH_2O^\bullet$ diradical and of oxirane. The electron affinity of the diradical should be similar to that of an alkoxy radical (37 kcal/mol for methoxy[15]). A very rough estimate of the electron affinity of oxirane (–51 kcal/mol) is derived from calculated values.[16–18] Using these quantities, we estimate that the ring opening of **2** is exothermic by 20 kcal/mol. These results would seem to rule out alternative mechanisms involving either reversible opening of the epoxide radical ion and faster reduction of the less stable acyclic radical anion or formation of a dianion before ring opening.

The substituted epoxide **5** can ring open via the lithiated species to give two isomers, **6a** and **7a**. The primary radical **6a** is calculated to be 2.3 kcal/mol more stable than the tertiary radical **7a**. The preferred conformations of both **6a** and **7a** have the CO bond approximately in the plane of the alkyl radical. These surprising results might be the consequence of the greater gas-phase stability of tertiary alkoxide anions as compared to primary. However, the lithium has little influence, since the primary radical anion **6b** was also found to be 2.5 kcal/mol more stable than the tertiary radical anion **7b**, when the 3-21G basis set plus diffuse functions on the oxygen atom were used. Solvation effects might be expected to reverse the order and to favor the primary alkoxide, given the lower basicity of primary alkoxides in solution.[19] While a calculation on the solvated species is beyond the scope of this investigation, a calculation on the corresponding alcohols, **8** and **9**, was performed since these represent extreme models for solvated anions. Even the uncharged β-hydroxy primary radical, **8**, is calculated to be more stable than the tertiary radical, **9**, but by a smaller amount (1.1 kcal/mol).[10] Thus, there is an intrinsic preference for the formation of a branched-chain compound, irrespective of its nature and charge. The difference between the stabilities of tertiary and primary alcohols is larger than between tertiary and primary radicals!

These conclusions are confirmed by the thermochemical stabilities of *tert*-butyl alcohol and isobutyl alcohol. The experimental heats of formation of *tert*-butyl alcohol and isobutyl alcohol are –74.7 and –67.8 kcal/mol, respectively.[20] Thus, the former is enthalpically more stable by 6.9 kcal/mol, or 4.8 kcal/mol from RHF/3-21G geometry optimizations.[21] On the other hand, the heat of formation of the *tert*-butyl radical is only 5.3 kcal/mol lower than that of the isobutyl radical from thermochemistry,[14] or 3.8 kcal/mol from UHF/3-21G optimizations.[21,22] Thus, the energetic preference for **8** over **9** should be approximately equal to the difference between two terms, one favoring a tertiary carbinol, the other favoring a tertiary radical. The experimental and computational data indicate that **8** should be favored by 1.6

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[7] For an example in which the position of the odd electron apparently determines the regiochemistry of cleavage in a radical anion, see: Maslak, P. M.; Guthrie, R. D. *J. Am. Chem. Soc.* **1986**, *108*, 2628.

[8] Binkley, J. S.; Frisch, M. J.; DeFrees, D. J.; Raghavachari, K.; Whiteside, R. A.; Schlegel, H. B.; Fluder, E. M.; Pople, J. A. *GAUSSIAN 82*; Department of Chemistry, Carnegie-Mellon University; Pittsburgh, PA.

[9] 3-21G: Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939. 6-31G*: Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.

[10] HF/3-21G energies (au) are as follows: **3a** (–159.42061), **3b** (–159.36315), **4** (159.45914), **6a** (–237.11005), **7a** (–237.10647), **6b** (–229.62964), **7b** (–229.62587), **8** (–230.24225), **9** (–230.24044).

[11] C_{2v}-**3a** was found to have the same energy as a C_s-**3a** structure having the lithium atom inclined ~9° above the ring plane. **3b** was found to favor a C_s geometry, which has the lithium atom inclined ~39° above the plane, at both HF/3-21G (by 0.7 kcal/mol) and MP2[12]/6-31G*//HF/3-21G (by 2.2 kcal/mol) levels.

[12] Moller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618. Pople, J. A.; Binkley, J. S.; Seeger, R. *Int. J. Quantum. Chem.* **1976**, *S10*, 1.

[13] Whiteside, R. A.; Frisch, M. J.; Pople, J. A. *The Carnegie-Mellon Quantum Chemistry Archive*; Department of Chemistry, Carnegie-Mellon University, Pittsburgh, PA; 1983.

[14] Benson, S. W. *Thermochemical Kinetics*; John Wiley & Sons: New York, 1976.

[15] Janousek, B. K.; Brauman, J. I. In *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 2, p 53.

[16] In practice, we estimate the electron affinity to differ from the negative of the calculated LUMO energy (153 kcal/mol) by 102 kcal/mol. This correction factor was derived from that calculated by Burrow and Jordan[17] (79 kcal/mol) for alkyl halides. The difference between the correction factors for an alkyl halide and oxirane was extimated from a comparison of the calculated SOMO energies of hydroxyl radical and chlorine atom with the experimental electron affinities of the two species. See also ref 18 for a discussion of Koopmans' theorem.

[17] Burrow, P. D.; Modelli, A.; Chiu, N. S.; Jordan, K. D. *J. Chem. Phys.* **1982**, *77*, 2699.

[18] Szabo, A.; Ostlund, N. S. In *Modern Quantum Chemistry*; Macmillan Publishing Co.: New York, 1982; pp 127 ff.

[19] March, J. *Advanced Organic Chemistry*, 3rd ed.; John Wiley & Sons: New York, 1987; Chapter 8.

[20] Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic Press: London, 1970.

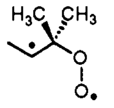
[21] Isobutyl radical: Dorigo, A. E.; Houk, K. N., unpublished (–155.80307 au).

[22] *tert*-Butyl radical: Paddon-Row, M. N.; Houk, K. N. *J. Am. Chem. Soc.* **1981**, 103, 5046.

or 1.0 kcal/mol, respectively, in good agreement with the 1.1 kcal/mol difference between carbinol and radical stabilities.

In conclusion, the regioselectivity observed in the oxirane reductive ring opening is consistent with a mechanism involving cleavage of a radical anion to give the more substituted *carbinol* or *carbinolate*, rather than the more substituted radical. Such control necessarily leads to intermediacy of the less substituted radical. We are assuming that the rate of ring opening is related to the stability of the acyclic product.

These results are reminiscent of calculations by Goddard and co-workers on the anti-Markovnikov addition of singlet oxygen to unsymmetric olefins,[23] which predict that diradicals of type **10** are more stable than their regioisomers **11** by about 0.6 kcal/mol.



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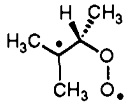

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The larger stability of branched over linear species is quite general; for example, 2,2-dimethylpropane is more stable than 2-methylbutane by 3.4 kcal/mol.[20] Here the preference for the branched molecule is not as large as in the case of the alcohols, and the derived radicals, neopentyl and 1,1-dimethylpropyl, are in the traditional relative stability order, although the tertiary radical is only 1.9 kcal/mol more stable than the primary. In general, the magnitude of this preference depends on how the C–X bond strength varies with substitution at carbon. Thus, while the tertiary C–H bond in isobutane is about 6 kcal/mol weaker than the primary C–H bond,[14] the heats of homolysis of *tert*-butyl and isobutyl halides differ by only 0.5–1.5 kcal/mol,[24] and the heat of dissociation of *tert*-butyl alcohol is actually higher than that of isobutyl alcohol by about 1 kcal/mol.

Acknowledgment. We are grateful to the National Science Foundation for financial support of this research at Pittsburgh and Los Angeles.

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(23) Harding, L. B.; Goddard, W. A., III *J. Am. Chem. Soc.* **1977**, *99*, 4520. Harding, L. B.; Goddard, W. A., III *Ibid.* **1980**, *102*, 439.

(24) Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*; Harper & Row: New York, 1981; Chapter 9.

Matrix Isolation Studies of Chemical Vapor Deposition: Isolation and Characterization of the Trimethylgallium–Arsine Adduct

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Chemical vapor deposition (CVD) is a widely used technique for the production of thin semiconductor films such as gallium arsenide (GaAs) and related III–V compounds.[1,2] These films have applications in such diverse areas as solar energy conversion and microelectronics. In CVD, gaseous precursors are passed over a heated substrate, initiating a complex series of homogeneous (gas phase) and heterogenous chemical reactions. Despite the commercial importance of these semiconductors, relatively little is known about the mechanism of thin-film formation. The most common precursors[3] for GaAs CVD are trimethylgallium and arsine, with an overall reaction $(CH_3)_3Ga(g) + AsH_3(g) \rightarrow GaAs(s) + 3CH_4(g)$. On the basis of the Lewis acid/base tenets,[4] initial formation of an adduct is reasonable, yet this adduct has never been conclusively identified or characterized, and its existence and role in CVD have been debated. One group reported[5] formation of this adduct, but the primary evidence was a slight decrease in intensity of the parent absorptions upon mixing; no spectral features attributable to the adduct were reported. Likewise, one patent[6] invokes formation of GaAs(s) from the adduct; here, too, scientific data that conclusively identified the adduct were not presented. GaAs CVD has also been initiated[7] photochemically through excimer laser irradiation at 193 nm; again, little is known about the initial photochemical steps.

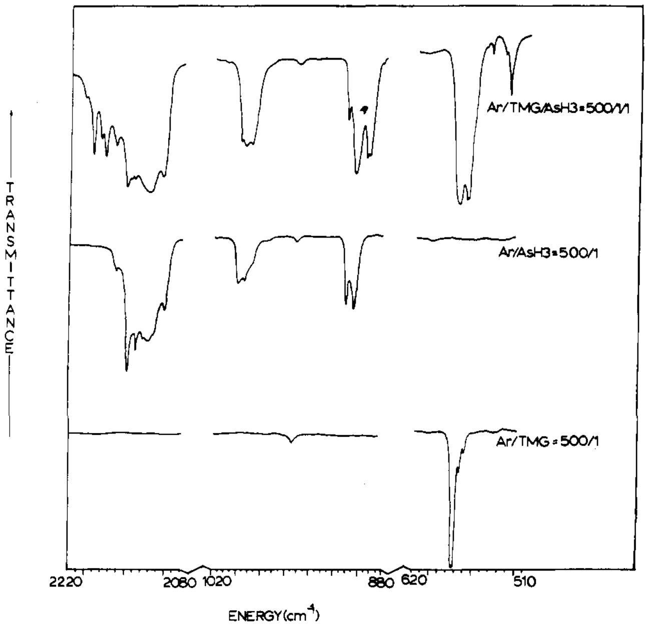

Figure 1. Infrared spectrum, over selected spectral regions, of a sample of $Ar/(CH_3)_3Ga/AsH_3 = 500/1/1$ (top trace) compared to blank spectra of each reagent alone in argon (middle and bottom spectra).

In this communication, the first definitive identification and infrared spectroscopic characterization of the 1:1 molecular complex of $(CH_3)_3Ga$ with AsH_3 is reported. Matrix isolation[8,9] is well suited to the study of transient intermediates, particularly weakly bound or reactive molecular complexes.[10] Preliminary photochemical studies of the dissociation/rearrangement of this complex by an excimer laser operating at 193 nm are also reported.

The experiments in this study were carried out on a conventional matrix isolation apparatus.[11,12] $(CH_3)_3Ga$ (Alfa Products) and AsH_3 (Alphagaz) were introduced into the vacuum system and purified by freeze–thaw cycles at 77 K. Samples of $(CH_3)_3Ga$ contained residual amounts of CH_4. Argon was used as the matrix gas in all experiments. Samples were deposited in both the twin-jet and the single-jet mode; in the former, separate samples were prepared of each reagent and codeposited simultaneously onto the cold window. In the latter, the reagents were premized in a single vacuum manifold with argon, and the mixture was deposited. Spectra were recorded after 20–24 h of deposition at 2 mmol/h

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