Table II. Selected Ions from the Flash-Vaporization Mass Spectrum of Dilithiomethane

possible ions	m/e	typical rel intensity, %
$CHLi_2$	27	42.1
N_2, CH_2Li_2	28	95.0
CH_3Li_2	29	37.4
CH_4Li_2	30	5.7
$(CH_3Li)CH_3$	37	3.1
C_2Li_2	38	6.9
C_2HLi_2	39	47.9
Ar, C_2Li_2	40	4.0
$C_2H_3Li_2$	41	100
$C_2H_4Li_2$	42	40.5
$C_2H_5Li_2$	43	5.3
CO_2, $(CH_3Li)_2$	44	15.2
C_2Li_3, $C_2H_7Li_2$	45	12.1
$(CH_2Li_2)(CH_2Li)$	49	2.9
C_3Li_2, $(CH_2Li_2)(CH_3Li)$	50	22.8
C_3HLi_2	51	8.3
$C_3H_2Li_2$, C_2Li_4	52	7.0
$C_3H_3Li_2$, C_2HLi_4	53	15.0
$C_3H_4Li_2$, $C_2H_2Li_4$	54	10.0
$C_3H_5Li_2$, $C_2H_3Li_4$	55	91.1
$C_3H_6Li_2$, $(CH_2Li_2)_2$	56	79.6
$C_3H_7Li_2$, $C_2H_5Li_4$, C_3Li_3	57	39.2
$C_3H_6Li_3$	63	2.1
C_3HLi_4	65	4.6
$C_3H_2Li_4$, C_2Li_6	66	3.1
$C_3H_3Li_4$, C_2HLi_6	67	17.0
$C_3H_4Li_4$, $C_2H_2Li_6$	68	9.5
$C_3H_5Li_4$	69	27.6
$C_3H_6Li_4$	70	48.2
C_3Li_5	71	62.3
C_3HLi_5	72	6.4
$C_3H_2Li_5$	73	4.4
$C_3H_3Li_5$	74	7.2
$C_3H_4Li_5$	75	5.9
$C_3H_5Li_5$	76	30.6
$C_3H_6Li_5$	77	9.2
$C_3H_7Li_5$, C_3Li_6	78	11.4
$C_3H_8Li_5$, C_3HLi_6	79	6.0
$C_3H_2Li_6$	80	2.5
$C_3H_3Li_6$	81	7.8
$C_3H_4Li_6$	82	8.0
$C_3H_5Li_6$	83	18.0
$C_3H_6Li_6 = (CH_2Li_2)_3$	84	9.5
$C_3H_7Li_6$	85	5.3
$C_3H_8Li_7$	91	3.7
$C_4H_3Li_6$	93	2.8
$C_4H_4Li_6$	94	3.3
$C_4H_5Li_6$	95	11.5
$C_4H_6Li_6$	96	3.4
$C_4H_7Li_6$	97	7.6
$(CH_2Li_2)_3(CH_2)$	98	5.2
$(CH_2Li_2)_3(CHLi)$	104	15.6
$(CH_2Li_2)_3(CH_2Li)$	105	2.9
$(CH_2Li_2)_3(CLi_2)$	110	3.6
$(CH_2Li_2)_3(CHLi_2)$	111	2.4
$(CH_2Li_2)_4$	112	7.7
$(CH_2Li_2)_5$	140	<1.0
$(CH_2Li_2)_6$	168	<1.0

surprising that there are many fragment progressions in which subsequent hydrogens are lost.

These results suggest the possibility of condensing dilithiomethane into inert low-temperature matrices to seek evidence for unusual structural features (such as the proposed cis and trans isomers) by vibrational spectroscopy and other methods. It also opens the door to the possibility of using other types of gas-phase techniques for characterizing these interesting vapor species.

Acknowledgment. We are grateful for support of this work from the National Science Foundation and partial support from the Robert A. Welch Foundation.

Registry No. CH_2Li_2, 21473-62-1; C_2Li_2, 1070-75-3; C_3Li_4, 39323-44-9; $(CH_3Li)_4$, 35064-50-7.

Electron Transfer from Nitrogen in Microsomal Oxidation of Amine and Amide. Simulation of Microsomal Oxidation by Anodic Oxidation[1]

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In enzymatic reactions catalyzed by the cytochrome *P*-450 monooxygenase system, secondary and tertiary amines and amides are oxidized to give N-dealkylated amines and amides.[2] In a number of studies on the mechanism of reaction of the *P*-450, an intermediate containing an iron–oxygen species has been proposed to be involved in some step following the initial formation of a complex of *P*-450–substrate–O_2.[3] However, the mechanism of the cytochrome *P*-450 catalyzed N-dealkylation reaction, especially that of the oxidation step of amines and amides, still remains vague. The initial formation of aminium cation radicals from amines by one-electron transfer from nitrogen to oxidizing agents has been described as one of the possibilities.[4,5]

We have reported previously that anodic oxidation is an effective method to simulate the microsomal oxidation of amines and to prepare N-dealkylated metabolites from unstable drugs under mild conditions.[6]

Since the reaction mechanism of anodic oxidation of amines and amides has been rather clearly established,[7] we compared the selectivity of liver microsomal N-dealkylation of *N,N*-dialkyl amines and amides with that of anodic oxidation to get an insight into the cytochrome *P*-450 catalyzed N-dealkylation. The substrates used in the present study were N-substituted and deuterated derivatives of imipramine, an antidepressant drug, and of hydrocinnamide.[8] The microsomal oxidation was carried out with

(1) Electroorganic Chemistry. 57.

(2) (a) McMahon, R. E. *J. Pharm. Sci.* **1966**, *55*, 457. (b) Fish, M. S.; Johson, N. M.; Horning, E. C. *J. Am. Chem. Soc.* **1956**, *78*, 3668. (c) McMahon, R. E.; Culp, H. W.; Occolowitz, J. C. *Ibid.* **1969**, *91*, 3389.

(3) (a) Hrycay, E. G.; Gustafsson, J. A.; Sundberg, M. I.; Ernster, L. *Biochem. Biophys. Res. Commun.* **1975**, *66*, 209. (b) Lichtenberger, F.; Nastajnczyk, W.; Ullrich, V. *Ibid.* **1976**, *70*, 939. (c) Nordblom, G. D.; White, R. E.; Coon, M. J. *Arch. Biochem. Biophys.* **1976**, *175*, 524. (d) Groves, J. T.; Nemo, T. E.; Myers, R. S. *J. Am. Chem. Soc.* **1979**, *101*, 1032. (e) Chang, C. K.; Kuo, M. S. *Ibid.* **1979**, *101*, 3413.

(4) In the oxidation of amines catalyzed by mitochondrial monoamine oxidase, two one-electron transfers from the substrate to the flavin have been proposed.[5c]

(5) (a) Griffin, B. W.; Ting, P. L. *Biochemistry* **1978**, *17*, 2206. (b) Shannon, P.; Bruice, T. C. *J. Am. Chem. Soc.* **1981**, *103*, 4580. (c) Silverman, R. B.; Hoffman, S. J.; Williams, B. C. *Ibid.* **1980**, *102*, 7126.

(6) Shono, T.; Toda, T.; Oshino, N. *Drug Metab. Dispos.* **1981**, *9*, 481.

(7) In the anodic oxidation of amines and amides in methanol, the first products are the methoxylated compounds at the position α to nitrogen. The α-methoxylated products are, however, easily hydrolyzed to the N-dealkylated compounds in the solution or in the working up with acid. Thus, the selectivity of N-dealkylation in anodic oxidation is just the same as that of anodic α-methoxylation.

(8) Imipramine, demethylimipramine, and dedimethylimipramine were supplied from Schering AG (Berlin, GFR). The substrates **1**, **2**, and **3** were prepared from corresponding alkyl halides according to the general method.[9] Compound **7** was prepared by $LiAlD_4$ reduction of carbamate of demethylimipramine, obtained from the treatment of the amine with ethyl chloroformate.[10,11] NMR ($CDCl_3$) δ 7.30–6.70 (m, 8, aromatic), 3.75 (t, 2, iminodibenzyl N–CH_2), 3.15 (br s, 4, iminodibenzyl $(CH_2)_2$), 2.50–1.95 (m, 2, α-CH_2), 2.15 (s, 3, N–CH_3), 2.05–1.40 (m, 2, β-CH_2). The substrates **4–6** and **8** were prepared from the reaction of acyl chloride with corresponding amines.[12] NMR of **8** ($CDCl_3$) δ 7.40–7.05 (m, 5, phenyl), 3.15–2.85 (m, 2, benzyl CH_2), 2.95 (s, 2, N–CH_3), 2.75–2.45 (m, 2, α-CH_2).

(9) Deno, N. C.; Fruit, R. E. *J. Am. Chem. Soc.* **1968**, *90*, 3506.

(10) Lindeke, B.; Anderson, E.; Jenden, D. J. *Biomed. Mass. Spectrom.* **1976**, *3*, 257.

(11) Marshall, F. J.; McMahon, R. E. *J. Labelled Compd. Radiopharm.* **1970**, 261.

(12) Marvel, C. S.; Lazier, W. A. *Org. Synth. Collect.* **1941**, *1*, 99.

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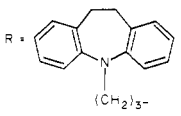
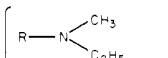
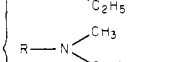
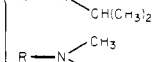
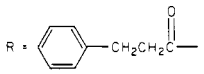
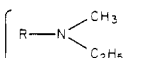
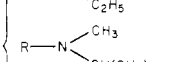
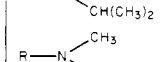
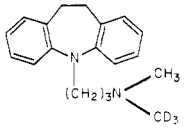
Table I. Selectivity of Microsomal and Anodic N-Dealkylation of Amines and Amides

substrates		metabolites[a]	N-demethylation/N-dealkylation[b] microsomal method	N-demethylation/N-dealkylation[b] anodic method[c]
R = 	 1	R–NHC_2H_5 R–$NHCH_3$	2.02 ± 0.07	2.34 ± 0.06
	 2	R–$NHCH(CH_3)_2$ R–$NHCH_3$	3.40 ± 0.12	4.09 ± 0.08
	 3	R–$NH(CH_2)_3CH_3$ R–$NHCH_3$	2.05 ± 0.09	2.51 ± 0.07[d]
R = 	 4	R–NHC_2H_5 R–$NHCH_3$	1.70 ± 0.10	1.72 ± 0.07
	 5	R–$NHCH(CH_3)_2$ R–$NHCH_3$	3.27 ± 0.14	3.39 ± 0.08
	 6	R–$NH(CH_2)_3CH_3$ R–$NHCH_3$	1.86 ± 0.09	1.78 ± 0.07

[a] No other N-dealkylated metabolites such as primary amines and amides were detected. [b] Anodic oxidation and the incubation of substrates with liver microsomes of a rat were carried out five times for each substrates. The product ratios (N-demethylation/N-dealkylation) were given as means ±SD. [c] 1, 2, and 3 were oxidized anodically at 1.5 V and 4, 5, and 6 at 2.0 V vs. SCE. [d] A negligible extent of the cleavage of the R-N bond was observed in the anodic oxidation of the substrate 3, the ratio (cleavage of R-N bond/N-dealkylation) being less than 0.05.

Table II. Intramolecular Isotope Effects[a]

substrates	microsomal method	anodic method[b]
 7	1.64 ± 0.05	1.88 ± 0.06
$C_6H_5CH_2CH_2CON(CH_3)(CD_3)$ 8	1.75 ± 0.06	1.80 ± 0.05

[a] The values K_H/K_D, determined by the NMR method, were given as means ±SD ($n = 5$; see footnote *b* of Table I). [b] Anodic oxidations of 7 and 8 were carried out at 1.5 and 2.0 V vs. SCE, respectively.

incubation for 10 min at 37 °C.[13] The incubation mixture contained 0.5 mM substrate, 4 mM G6P, 0.5 mM NADPH, 5 mM $MgCl_2$, 0.5 IU/mL of G6P dehydrogenase, 0.1 M Tris hydrochloride buffer (PH 7.4), and microsomal suspension containing 3.0 mg of protein/mL.[14] The anodic oxidation was carried out at room temperature under conditions of controlled potential at 1.5 or 2.0 V vs. SCE with a platinum electrode. Through the solution of 0.5 mM substrate and 10 mM $NaClO_4$ in methanol was passed 2 F/mol of electricity. The N-dealkylated products obtained by microsomal and anodic methods were determined by HPLC.[17] Results are shown in Tables I and II.

The following are indicated in Tables I and II: (1) With respect to all the compounds examined, good accordance of the selectivity between microsomal and anodic dealkylations is observed, suggesting that the anodic method is one of the best tools to simulate the microsomal N-dealkylation. (2) Demethylation is always faster than elimination of higher alkyl groups. (3) Intramolecular isotope effects[18] are also almost the same in both microsomal and anodic oxidations. The isotope effect is small when it is compared with the intramolecular isotope effect ($K_H/K_D = 7.2 \pm 0.8$) observed in the microsomal hydroxylation of the γ position of *N*-benzoylpiperidine.[19]

The first step of the microsomal oxidation of amines may be either electron transfer from nitrogen or hydrogen abstraction from α carbon. The isotope effect observed for direct hydrogen atom abstraction from benzyl-*tert*-butylamine by chlorine dioxide is 4.97,[20] which is a reasonable value for the hydrogen abstraction by a relatively reactive radical species. The intramolecular isotope effect in hydrogen abstraction from the α carbon of tetrahydrofuran and tetrahydropyrane by *tert*-butyl radical is about 3.2.[21] Compared with these isotope effects, the intramolecular isotope effects (1.64, 1.75) shown in Table II[22] are small. Thus it can be said that in microsomal dealkylation, both hydrogen abstraction from the α-carbon and the reaction[24] similar to the microsomal γ hydroxylation of the amide ($K_H/K_D = 7.2 \pm 0.8$) are not involved in the selectivity determining step.

On the other hand, the mechanism of anodic oxidation of amines and amides has rather clearly been established. The first step of the oxidation is an electron transfer from nitrogen to generate an aminium cation radical.[21,26] The intramolecular isotope effects

(13) The mixtures were incubated for 0, 5, 10, 15, 20, and 30 min to determine the relation among the amounts of the substrate, metabolites, and reaction time. The reaction was terminated by the addition of methanol. The formation of the metabolites showed a linear correlation with the incubation time for at least 15 min.

(14) Liver microsomal fractions were prepared from the liver homogenates of male Sprague–Dawley rats by using conventional differential ultracentrifugation technique.[15] Microsomal protein was determined by the method of Lowry.[16]

(15) Mazel, P. "Fundamentals of Drug Metabolism and Drug Disposition"; La Du, B. N., Mandel, H. G., Way, E. L., Ed.; Williams & Wilkins: Baltimore, 1971; p 527.

(16) Lowry, O. H.; Rosebrough, N. J.; Farr, A. H.; Randall, R. J. *J. Biol. Chem.* **1951**, *193*, 265.

(17) HPLC was monitored at 220 nm with a solvent system of methanol–water by using a Zorbax NH_2 and ODS column. No other N-dealkylated products were detected under the reaction conditions. The fact that the cleavage of a bond between R and N in the substrates 1–3 is negligible may draw attention. The detailed explanation of this selectivity is not possible, but that R is very much bulkier than methyl, ethyl, isopropyl, and butyl groups may play an important role to bring about this selectivity.

(18) In the microsomal and anodic oxidations, the intermolecular isotope effect is not related directly with the selectivity of the reaction, because both reactions are multistep heterogeneous reaction.

(19) A reaction similar to hydrogen abstraction has been proposed: Shono, T.; Ohmizu, Y.; Toda, T.; Oshino, N. *Drug Metab. Dispos.* **1981**, *9*, 476.

(20) Hull, L. A.; Davis, G. T.; Rosenblatt, D. H.; Williams, H. K. R.; Weglein, R. C. *J. Am. Chem. Soc.* **1967**, *89*, 1163.

(21) Shono, T.; Hamaguchi, H.; Matsumura, Y. *J. Am. Chem. Soc.* **1975**, *97*, 4264.

(22) The values obtained in this study are similar to those obtained by N-demethylation with isolated cytochrome *P*-450.[23]

(23) Miwa, G. T.; Garland, W. A.; Hodshon, B. J.; Lu, A. Y. H.; Northrop, D. B. *J. Biol. Chem.* **1980**, *255*, 6049.

(24) Large intramolecular isotope effects ($K_H/K_D > 10$) were also observed in cytochrome *P*-450 dependent carbon oxidation reactions,[25] in which hydrogen abstraction by a radical species was suggested.

(25) (a) Foster, A. B.; Jarman, M.; Stevens, J. D.; Thomas, P.; Westwood, J. H. *Chem.-Biol. Interact.* **1974**, *9*, 327. (b) Hjelmeland, L. M.; Aronow, L.; Trudell, J. R. *Biochem. Biophys. Res. Commun.* **1977**, *76*, 541. (c) Groves, J. T.; McClusky, G. A.; White, R. E.; Coon, M. J. *Ibid.* **1978**, *81*, 154.

observed in the anodic α methoxylation of *N*-carbomethoxypiperidine and -pyrrolidine are 1.81 ± 0.05 and 1.84 ± 0.05, respectively.[21] The electron-transfer process is also involved in the oxidation of benzyl-*tert*-butylamine by chlorine dioxide, the isotope effect being 1.8.[20] In comparison of these isotope effects with those shown in Table II, the good agreement suggests that the electron-transfer process is involved in the selectivity determining step of the microsomal dealkylation of amines and amides. This suggestion may also be supported by the agreement of the selectivity of dealkylation between microsomal and anodic dealkylations shown in Table I.

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Registry No. 1, 19009-26-8; **2**, 81256-33-9; **3**, 81256-34-0; **4**, 81256-35-1; **5**, 81256-36-2; **6**, 81256-37-3; **7**, 65100-48-3; **8**, 81256-38-4; 10,11-dihydro-*N*-ethyl-5*H*-dibenz[*b*,*f*]azepine-5-propanamine, 2095-96-7; 10,11-dihydro-*N*-methyl-5*H*-dibenz[*b*,*f*]azepine-5-propanamine, 50-47-5; 10,11-dihydro-*N*-isopropyl-5*H*-dibenz[*b*,*f*]azepine-5-propanamine, 2292-76-4; *N*-butyl-10,11-dihydro-5*H*-dibenz[*b*,*f*]azepine-5-propanamine, 2064-08-6; *N*-ethylbenzenepropanamide, 81256-39-5; *N*-methylbenzenepropanamide, 940-43-2; *N*-isopropylbenzenepropanamide, 56146-87-3; *N*-butylbenzenepropanamide, 10264-11-6; demethylimipramine carbamate, 27097-69-4.

(26) (a) Smith, P. J.; Mann, C. K. *J. Org. Chem.* **1969**, *34*, 1821. (b) Portis, L. C.; Bhat, V. V.; Mann, C. K. *Ibid.* **1970**, *35*, 2175. (c) Masui, M.; Sayo, H. *J. Chem. Soc. B* **1971**, 1593. (d) Lindsay smith, J. R.; Masheder, D. J. *J. Chem. Soc., Perkin Trans. 2* **1976**, 47.

Electrogenerated Chemiluminescence. 40. A Chemiluminescent Polymer Based on the Tris(4-vinyl-4′-methyl-2,2′-bipyridyl)ruthenium(II) System

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We report the electron-transfer chemiluminescence resulting from reaction between oxidized and reduced centers in a polymer produced by electroinitiated polymerization of tris(4-vinyl-4′-methyl-2,2′-bipyridyl)ruthenium(II) ($Ru(v\text{-}bpy)_3^{2+}$) (bpy = 2,2′-bipyridine) onto a platinum electrode surface. The generation of luminescent excited states via electron-transfer reactions of electrogenerated intermediates (called electrogenerated chemiluminescence, ECL) has been extensively investigated for systems based on organic molecules (e.g., the radical ions of 9,10-diphenylanthracene) as well as for transition-metal complexes (e.g., the +1 and +3 species generated from $Ru(bpy)_3^{2+}$).[1-3] The emission of light arises from the solution in the vicinity of the electrode surface where the reactants are produced. ECL studies are usually carried out in aprotic solvents in which the highly reactive oxidized and reduced forms are stable. We have become interested in polymer electrodes[3-5] and in the possibility of studying electron-transfer reactions and charge transfer in polymers by carrying out ECL experiments with these. Thus we recently reported chemiluminescence of $Ru(bpy)_3^{2+}$ incorporated into a Nafion polymer film on an electrode surface.[3] However, this was not a regenerative ECL system and involved the irreversible oxidation of oxalate ion in the reaction.

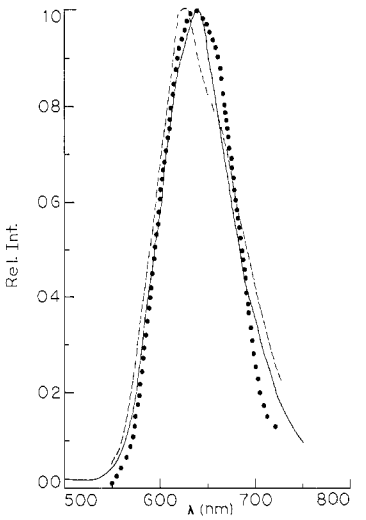

Figure 1. Normalized emission for: (A) luminescence spectrum for $Ru(v\text{-}bpy)_3^{2+}$ in CH_3CN solution (—); (B) electrogenerated chemiluminescence (ECL) for 1.0 mM $Ru(v\text{-}bpy)_3^{2+}$ solution in CH_3CN, 0.1 M TBAP (···); (C) surface ECL for a Pt electrode coated with a film of $Ru(v\text{-}bpy)_3^{2+}$ polymer in CH_3CN, 0.1 M TBAP (---). For B and C, pulses between +1.5 and −1.45 V vs. SSCE with a width of 1 s were used (response (uncorrected) of Hamamatsu Model R928 photomultiplier tube).

The polymer employed in the work reported here was prepared by electroreduction of $Ru(v\text{-}bpy)_3^{2+}$ in an acetonitrile solution onto a platinum electrode surface following the procedure of Murray and co-workers.[5] This method produces a layer of polymer (from ~40 Å to ~1 μm thick) containing Ru(II) centers distributed along hydrocarbon chains originating from the vinyl groups. The work reported here involves a 3 mm by 3 mm Pt flag electrode covered with a film containing $2\text{–}6 \times 10^{-8}$ mol/cm^2 electroactive species. When such a modified electrode is placed in CH_3CN, 0.1 M tetra-*n*-butylammonium perchlorate (TBAP) and the potential of the electrode is pulsed at a frequency of 0.5 Hz between +1.5 and −1.5 V vs. SSCE, an orange emission is observed from the electrode surface (Figure 1C). Since there is no complex in solution, the emission must arise from the immobilized complex, presumably via an electron-transfer (annihilation) reaction between electrogenerated +1 and +3 centers, by analogy to the previous $Ru(bpy)_3^{2+}$ results.[2,3] Further evidence that the ECL reaction involves polymer species comes from studies of ECL of the dissolved monomer itself (Figure 1B). The surface ECL (Figure 1C) is blue-shifted by ~15–20 nm relative both to the luminescence spectrum of $Ru(v\text{-}bpy)_3^{2+}$ obtained in CH_3CN solution (Figure 1A) and to the ECL spectrum observed in solution (Figure 1B).[6]

The surface ECL is rather short-lived (~20 min of continuous pulsing at ±1.5 V vs. SSCE with 1-s pulse durations). As with the $Ru(bpy)_3^{2+}$ system in solution, this instability is probably associated with the +1 Ru form. Previous studies have shown instability of polymers containing immobilized $Ru(bpy)_3^{2+}$ centers.[7] The ECL lifetime is remarkably long, however, considering the thin layer of the film and the very small amount of electroactive

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(6) A 12-nm blue shift in the luminescence of $Ru(bpy)_3^{2+}$ incorporated in Nafion 120 compared to the emission in aqueous solution was reported by Lee (Lee, P. C.; Meisel, D. *J. Am. Chem. Soc.* **1980**, *102*, 5477).

(7) Abruña, H. D.; Meyer, T. J.; Murray, R. W. *Inorg. Chem.* **1979**, *18*, 3233. Some instability of the reduced forms of $Ru(bpy)_3^{2+}$ have been previously noticed in solution studies.[2]

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