(4) Singer, K. D.; Kuzyk, M. G.; Holland, W. R.; Sohn, J. E.; Lalama, S. J.; Commizzoli, R. B.; Katz, H. E.; Schilling, M. L. *Appl. Phys. Lett.* **1988**, *53*, 1800–1802.
(5) (a) Eich, M.; Sen, A.; Looser, H.; Yoon, D. Y.; Bjorklund, G. C.; Twieg, R.; Swalen, J. D. In reference 1b, pp 128–135. (b) Eich, M.; Sen, A.; Looser, H.; Bjorklund, G. C.; Swalen, J. D.; Twieg, R.; Yoon, D. Y. *J. Appl. Phys.* **1989**, *66*, 2559–2567.
(6) (a) $T_g \lesssim 125$ °C for all of these materials.[2-5] Such data of course provide only a partial index of motional characteristics, which are likely to be rather complex for randomly functionalized macromolecules.[6b,c] (b) Rudin, A. *The Elements of Polymer Science and Engineering*; Academic Press: New York, 1982; Chapter 11. (c) Rabek, J. F. *Experimental Methods in Polymer Chemistry*; Wiley: New York, 1980; Chapter 32.
(7) Aycock, D.; Abolins, V.; White, D. M. In *Encyclopedia of Polymer Science and Technology*; Wiley: New York, 1988; Vol. 13, pp 1–30, and references therein.
(8) White, D. M. *J. Org. Chem.* **1969**, *34*, 297–303.
(9) From intrinsic viscosity measurements in toluene and tabulated[7] constants. We thank Dr. J. C. Stevens of Dow Chemical Corp. for this measurement.
(10) Cabasso, I.; Jagur-Grodzinski, J.; Vofsi, D. *J. Appl. Polym. Sci.* **1974**, *18*, 196, 1986.
(11) For a typical sample purified by dissolution in $CHCl_3$ and precipitation with MeOH. Anal. Calcd for $[C_6H_2(CH_2Br)_{1.79}(CH_3)_{0.21}O]_n$: C, 36.76; H, 2.40; Br, 54.72. Found: C, 35.93; H, 2.35; Br, 54.67. ^1H NMR ($CDCl_3$, 400 MHz): δ 6.70–7.11 (m, arom), 4.33 (s, $-CH_2Br$), 2.11 (s, CH_3).
(12) (a) Zyss, J.; Nicour, J. F.; Coquillay, M. *J. Chem. Phys.* **1984**, *81*, 4160–4167. (b) Barzoukas, M.; Joose, D.; Fremaux, P.; Zyss, J.; Nicoud, J. F.; Morely, J. *J. Opt. Soc. Am. B: Opt. Phys.* **1987**, *4*, 977–986.
(13) For a typical sample. Anal. Calcd for $[C_6H_2(CH_2OC_{11}H_{13}N_2O_2)_{1.43}(CH_2Br)_{0.36}(CH_3)_{0.21}O]_n$: C, 63.24; H, 5.54; N, 8.89, Br, 3.55. Found: C, 61.89; H, 5.36; N, 8.10; Br, 3.25. ^1H NMR (DMSO-d_6, 90 °C, 400 MHz): δ 7.85 (s, br, arom), 6.94–6.20 (m, br, arom), 4.28 (s, br, arom–CH_2Br), 3.88 (s, br, arom–CH_2O–), 3.60–2.81 (m, br, aliph), 1.82 (s, br, CH_3).
(14) Comizzoli, R. B. *J. Electrochem. Soc.* **1987**, *134*, 424–429.
(15) (a) Singer, K. D.; Sohn, J. E.; Lalama, S. J. *Appl. Phys. Lett.* **1986**, *49*, 248–250. (b) Singer, K. D.; Kuzyk, M. G.; Sohn, J. E. *J. Opt. Soc. Am. B: Opt. Phys.* **1987**, *4*, 968–975.
(16) Jerphagon, J.; Kurtz, S. K. *J. Appl. Phys.* **1970**, *41*, 1667–1681.
(17) (a) Reported d_{33} (in units of 10^{-9} esu) = 18 for contact-poled 48% (PS)O-NPP,[3c,17b] 51 for corona-poled DCV/PMMA,[4,17c] and 73 for corona-poled PPNA.[5,17d] (b) (PS)O-NPP = NPP-functionalized poly(*p*-hydroxystyrene). (c) DCV-MM = copolymer of methyl methacrylate and a 4-(dicyanovinyl)-4′-(dialkylamino)azobenzene-substituted methacrylate. (d) PPNA = poly(*N*-allyl-*p*-nitroaniline).
(18) Singer, K. D.; Sohn, J. E.; King, L. A.; Gordon, H. M.; Katz, H. E.; Dirk, C. W. *J. Opt. Soc. Am. B: Opt. Phys.* **1989**, *6*, 1339–1351.
(19) (a) Hampsch, H. L.; Yang, J.; Wong, G. K.; Torkelson, J. M. *Macromolecules* **1988**, *21*, 526–528. (b) Hampsch, H. L.; Yang, J.; Wong, G. K.; Torkelson, J. M. *Polym. Commun.* **1989**, *30*, 40–43.
(20) (a) Yu, W.-C., Sung, C. S. P.; Robertson, R. E. *Macromolecules* **1988**, *21*, 355–364 and references therein. (b) Victor, J. G.; Torkelson, J. M. *Macromolecules* **1987**, *20*, 2241–2250. (c) Struik, L. C. E. *Physical Aging in Amorphous Polymers and Other Materials*; Elsevier: Amsterdam, The Netherlands, 1978.
(21) (a) Hubbard, M. A.; Marks, T. J.; Yang, J.; Wong, G. K. *Chem. Mater.* **1989**, *1*, 167–169. (b) Park, J.; Marks, T. J.; Yang, J.; Wong, G. K. *Chem. Mater.*, in press.
(22) The role of charge dissipation effects[14] on the kinetics is presently under investigation.
(23) Minami, N.; Ye, C.; Marks, T. J.; Yang, J.; Wong, G. K., to be submitted for publication.
(24) Karasz, F. E.; Bair, H. E.; O'Reilly, J. M. *J. Polym. Sci., Polym. Phys. Ed.* **1967**, *6*, 1141–1148.
(25) Tien, P. K. *Appl. Opt.* **1971**, *10*, 2395–2413.

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Desilylation and Michael Addition Reactions of (Trimethylsilyl)ethynyl Ketones: A Novel One-Pot Synthesis of Enamine Ketones, Bis(enamine ketones), and Poly(enamine ketones)

The conventional synthesis of enamine ketones involves the Michael-type addition of amines to hydrogen-terminated ethynyl ketones at room temperature and requires a long reaction period.[1-3] Hydrogen-terminated ethynyl ketones are traditionally prepared by desilylation of (trimethylsilyl)ethynyl ketones using aqueous borax or basic buffer solutions.[4,5] The classical synthesis of (trimethylsilyl)ethynyl ketones involves the Friedel–Crafts reaction of acyl chloride/$AlCl_3$ complexes with bis(trimethylsilyl)acetylene.[4,6] Aliphatic bis(enamine ketones) and aliphatic poly(enamine ketones) have been prepared similarly from aliphatic bis(hydrogen-terminated ethynyl ketones).[7,8] Aromatic bis(hydrogen-terminated ethynyl ketones) have been used to prepare aromatic bis(enamine ketones) and aromatic poly(enamine ketones).[9,10]

Other previously reported methods for the preparation of poly(enamine ketones) include the reaction of diamines with 1,6-diethoxy-1,5-hexadiene-3,4-dione[11] and 2,2′-disubstituted bis(4-ethoxymethylene-5-oxazolone)[12] and the trifluoroacetic acid catalyzed reaction of diamines with aromatic bis(1,3-diketones).[13] Our goal was to develop a more direct synthesis of enamine ketones and poly(enamine ketones) using readily available starting materials.

Herein we report the first example of a one-pot synthesis of enamine ketones and bis(enamine ketones) by the direct reaction of primary (1°) and secondary (2°) amines with (trimethylsilyl)ethynyl ketones and bis[(trimethylsilyl)ethynyl ketones], respectively, in the presence of methanol or ethanol and solvents such as benzene, dimethylformamide, *N*,*N*-dimethylacetamide, and *m*-cresol at temperatures of 90–110 °C. Under these conditions, enamine ketones and bis(enamine ketones) are formed rapidly (2–4 h) in high yield. Also, the one-pot synthesis of poly(enamine ketones) by the reaction of diamines with bis[(trimethylsilyl)ethynyl ketones] under similar conditions is reported for the first time.

Studies of the reaction of a model (trimethylsilyl)ethynyl ketone, 3-(trimethylsilyl)-1-phenyl-2-propyn-1-one[4] (**1**), with aniline in the presence and absence of methanol (Scheme I) show that desilylation occurs only in the presence of both aniline and methanol. The product, *cis*-1-benzoyl-2-(*N*-phenylamino)ethene (**6**), was formed in

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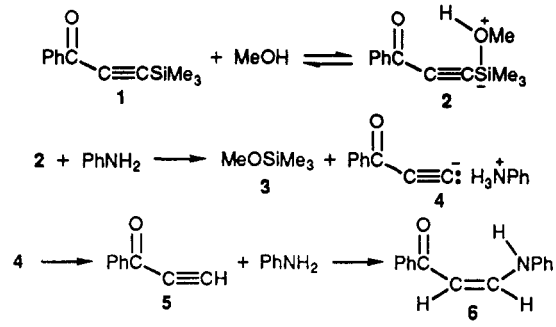
Scheme I



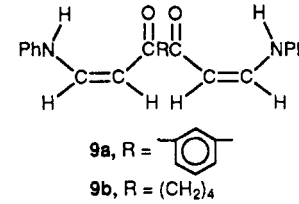
nearly quantitative yield from reactions run in methanol at 100 °C for 4 h.[14] Methoxytrimethylsilane (**3**) was isolated by distillation of the reaction mixture, and its structure was confirmed by its ^{1}H NMR spectrum.[15] Under similar conditions, the reaction of *N*-methylaniline with 1 gave a 38% yield of *trans*-1-benzoyl-2-(*N*-methyl-*N*-phenylamino)ethene (**7**).[16] In the absence of 1° and 2° amines but in the presence of equimolar amounts of methanol, triethylamine, and 1, desilylation occurs to give 3. However, enamine ketone formation is precluded, and the triethylamine catalyzes the polymerization of the intermediate ethynyl phenyl ketone (**5**).[17] Previous work has shown that ethynyl phenyl ketone reacts with trace amounts of triethylamine to give dark polymeric products.[18] Under similar conditions but with ethanol and benzene as solvent, ethoxytrimethylsilane and polymer are formed.[19] The reaction of equimolar amounts of 1 and triethylamine with excess methanol gave methoxytrimethylsilane and benzoylacetaldehyde dimethylacetal, which was formed by nucleophilic addition of the excess methanol with the intermediate ethynyl phenyl ketone.[20]

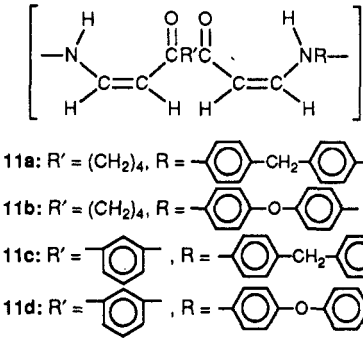
The reaction of 1 with a 10-fold excess of refluxing methanol for 2 h in the absence of amines, followed by removal of methanol by distillation, resulted in a nearly quantitative recovery of 1 as determined by ^{1}H NMR spectroscopy. The reaction of equimolar quantities of 1 and aniline in benzene solution without methanol for 4 h at 95–105 °C, followed by fractional distillation, afforded a 70% recovery of pure 1. The distillation forerun consisted of a 3/1 mixture of aniline and 1 as determined by ^{1}H NMR spectroscopy.

These results are not in accord with an addition–elimination mechanism. The reaction most likely proceeds as illustrated in Scheme I and is similar to the tetrabutylammonium fluoride catalyzed desilylation of (trimethylsilyl)acetylenes.[21]

The presence of both a 1°, 2°, or 3° amine and methanol or ethanol is required for desilylation. In the presence of a 1° amine like aniline, desilylation occurs, giving the volatile methoxytrimethylsilane (bp 57 °C) and 4. The ionic intermediate (4) changes to ethynyl phenyl ketone (**5**) and aniline, which immediately undergoes a Michael-type addition to give the *cis*-enamine ketone (**6**). The reaction of 1° amines with **5** gives predominately the cis isomer and with 2° amines the trans isomer is formed.[3]

The formation of bis(enamine ketones) and poly(enamine ketones) proceeds similarly. The reaction of 1,1′-(1,3-phenylene)bis[3-(trimethylsilyl)-2-propyn-1-one][23] (**8**) (5.0 mmol) with aniline (11.0 mmol) in a solution of *N*,*N*-dimethylacetamide (9 mL) and methanol (9 mL) for 4 h at 110 °C in a N_2 atmosphere gave bis(enamine ketone) **9a** (89%), mp 195–196 °C (benzene).[24] Compound **9b** was prepared similarly by reaction of 1,10-bis(trimethylsilyl)-1,9-decadiyne-3,8-dione (**10**)[7,8] with aniline. Recrystallization from 1-hexanol gave **9b** (74%), mp 172–173.5 °C.[25]





The poly(enamine ketones) (**11a,b**) were prepared by reaction of **10** (2.5 mmol) with the appropriate diamine (2.53 mmol in a mixture of *N*,*N*-dimethylacetamide (5 mL) and methanol (5 mL) at 100–110 °C for 4 h in a N_2 atmosphere. Both **11a** and **11b** were obtained in 92% yield and had η_{inh} values of 0.49 and 0.62 dL/g, respectively.[26] The IR (KBr) spectrum of **11a** was identical with the poly(enamine ketone) prepared by reaction of (4,4′-diaminodiphenyl)methane with 1,9-decadiyne-3,8-dione (**12**).[7] The preparation of **11a,b** from **12** and the appropriate diamine has also been reported by Harris and co-workers,[8] but spectral data are not given. In a similar manner, the reaction of 8 with the appropriate diamine gave **11c** and **11d** (98%), with η_{inh} values of 0.12 and 0.36 dL/g, respectively.[26] Bass and co-workers[10] have reported the preparation of **11c,d** by reaction of the appropriate diamine with the aromatic bis(hydrogen-terminated ethynyl ketone) 1,1′-(1,3-phenylene)bis(2-propyn-1-one). Their reported IR spectra compare favorably with ours.[27] The poly(enamine ketones) **11a–d** precipitated during the polymerization. They were isolated by suction filtration, washed well with ether, and dried overnight at 63 °C (0.1 mm). These low molecular weight poly(enamine ketones) were soluble only in *m*-cresol.

We continue to explore the scope of this novel desilylation and nucleophilic addition reaction. A detailed account of this investigation will be published.

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References and Notes

(1) Bowden, K.; Braude, E. A.; Jones, E. R. H.; Weedon, B. C. L. *J. Chem. Soc.* **1946**, 45.
(2) Bowden, K.; Braude, E. A.; Jones, E. R. H.; Weedon, B. C. L. *J. Chem. Soc.* **1946**, 945.
(3) McMullen, C. H.; Sterling, J. M. *J. Chem. Soc. B* **1966**, 1217.
(4) Walton, D. R. M.; Waugh, F. J. *J. Organomet. Chem.* **1972**, *37*, 45.

(5) Bhattacharya, A. N.; Josiah, B. M.; Walton, D. R. M. *Organomet. Chem. Synth.* **1970/1971**, *1*, 145.
(6) Birkofer, L.; Ritter, A.; Uhlenbrauck, H. *Chem. Ber.* **1963**, *96*, 3280.
(7) Wilbur, J. M., Jr.; Bonner, B. A. Presented in part at the Missouri Academy of Science, 22nd Annual Meeting, Northeast Missouri State University, Kirksville, MO, April 1988; *Trans. Mo. Acad. Sci.* **1988**, in press.
(8) Harris, F. W.; Gupta, R. K.; Beltz, M. W. *Polym. Prepr.* **1988**, *29* (2), 306.
(9) Harris, F. W.; Beltz, M. W. *Polym. Prepr.* **1986**, *27* (1), 114.
(10) Bass, R. G.; Sinsky, M. S.; Connell, J. W.; Waldbauer, R. W.; Hergenrother, P. M. *J. Polym. Sci., Polym. Chem. Ed.* **1989**, *27*, 171.
(11) Ueda, M.; Otaira, K.; Imai, Y. *J. Polym Sci., Polym. Chem. Ed.* **1978**, *16*, 2809.
(12) Ueda, M.; Kino, K.; Hirono, T.; Imai, Y. *J. Polym. Sci., Polym. Chem. Ed.* **1976**, *14*, 931.
(13) Pavlisko, J. A.; Huang, S. J.; Benicewicz, B. C. *J. Polym. Sci., Polym. Chem. Ed.* **1982**, *20*, 3079.
(14) A solution of **1** (5.0 mmol) and aniline (5.1 mmol) in 4 mL of methanol was heated under a N_2 atmosphere in an oil bath at 100 °C for 4 h. After cooling to 0 °C, the yellow solid was collected and recrystallized from methanol to give 1.05 g (94%) of 6 mp 138–139 °C (lit.[3] mp 140–141 °C). ^{1}H NMR (200 MHz, $CDCl_3$): δ 12.18 (1 H, d, J = 12 Hz, NH) 6.1 (d, J = 7.9 Hz, 1 H), 7.9 (d, J = 7.9 Hz, 1 H, *cis*-vinyl protons), 7.1–7.6 (m, 10 H, aromatic).
(15) A solution of **1** (5.0 mmol), aniline (5.1 mmol), and methanol (5.0 mmol) in 10 mL of benzene was stirred at 20 °C for 10 min and then heated at reflux in an oil bath at 90 °C for 2 h without a N_2 atmosphere. About 5 mL of the reaction mixture was collected by distillation. Analysis by ^{1}H NMR showed the distillate contained only methoxytrimethylsilane and benzene. ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.1 (s, 9 H), 3.4 (s, 3 H, $MeOSiMe_3$), 7.3 (s, 6 H, C_6H_6).
(16) A solution of **1** (5.0 mmol) and *N*-methylaniline (5.3 mmol) in 5 mL of methanol was heated under a N_2 atmosphere in an oil bath at 100 °C for 5.5 h. Removal of solvent under reduced pressure left 0.8 g of residual solid. Recrystallization from petroleum ether (30–60 °C)/CH_2Cl_2 gave 0.45 g (38%) of **7**, pale yellow plates, mp 88.5–89.5 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.12–7.95 (m, 10 H, aromatic protons), 6.08 (d, J = 12.7 Hz, 1 H), 8.21 (d, J = 12.7 Hz, 1 H, *trans*-vinyl protons), 3.38 (s, 3 H, CH_3). Anal. Calcd for $C_{16}H_{15}NO$: C, 80.98; H, 6.37; N, 5.90. Found: C, 80.78; H, 6.40; N, 6.18.
(17) Triethylamine (10.0 mmol) was added via syringe to a mixture of **1** (10.0 mmol) and methanol (10.0 mmol) in a flask equipped with a rubber septum and a reflux condenser. The addition of triethylamine resulted in a vigorous exothermic reaction and the formation of a dark solid. After heating 15 min in an oil bath at 85–95 °C, distillation of the reaction mixture gave 0.93 g of liquid, bp 49–60 °C. ^{1}H NMR analysis of the distillate showed it consisted of methoxytrimethylsilane and triethylamine.
(18) Wilbur, J. M., Jr. Presented at the 23rd Annual Meeting of the Missouri Academy of Science, Missouri Southern State University, Joplin, MO, April 1989. The abstract is in press.
(19) The reaction and workup were similar to that described in ref 17, but absolute ethanol (10.0 mmol) and 15 mL of benzene were used. After 20 min at 20 °C and 30 min at 90–95 °C, distillation of the reaction mixture gave 12.1 g of liquid, bp 70–80 °C. The ^{1}H NMR analysis of the distillate indicated it was a mixture of ethoxytrimethylamine, benzene, and a trace amount of triethylamine. ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.1 (s, 9 H), 1.2 (t, 3 H), 3.6 (q, 2 H, $CH_3CH_2OSi(CH_3)_3$), 7.3 (s, 6 H, C_6H_6), 1.9 (t, 3 H), 2.4 (q, 2 H, Et_3N).
(20) Triethylamine (5.0 mmol) was added via syringe to a mixture of **1** (5.0 mmol) and 5 mL of MeOH in a flask equipped with a rubber septum and reflux condenser. As soon as the exothermic reaction subsided, the reaction mixture was heated for 2.0 h in an oil bath at 110–115 °C. The ^{1}H NMR analysis of the distillate, bp 55–68 °C, showed the presence of methoxytrimethylsilane, methanol, and triethylamine. Continued fractional distillation gave 0.8 g (82%) of benzoylacetaldehyde dimethylacetal, bp 88–90 °C (0.2 mm) (lit.[22] bp 99–100 °C (0.6 mm)). ^{1}H NMR (60 MHz, $CDCl_3$): δ 3.3 (d, 2 H, CH_2), 3.4 (s, 6 H, CH_3), 5.0 (t, 1 H, CH), 7.5–8.0 (m, 5 H, aromatic).
(21) Nakamura, E.; Kuwajima, I. *Angew. Chem. Int. Ed. Engl.* **1976**, *15*, 498.
(22) van Dam, M. J. D. *Recl. Trav. Chim. Pays-Bas* **1962**, *81* (5), 435.
(23) Compound **8** was prepared by a Friedel–Crafts reaction of isophthaloyl chloride and bis(trimethylsilyl)acetylene in a manner similar to that described by Walton and Waugh.[4] Recrystallization from petroleum ether (30–60 °C) using Nuchar gave light tan crystals (62% yield), mp 98–99 °C. Anal. Calcd for $C_{18}H_{22}Si_2O_2$: C, 66.21; H, 6.79. Found: C, 65.98; H, 6.84. IR (KBr, cm^{-1}) 3074 (=CH); 2963, 2905 (CH_3); 2153 (C≡C); 1651 (C=O); 1591 (C=C); 1252 (CH_3Si). ^{1}H NMR (60 MHz, CCl_4): δ 0.1 (s, 18 H, trimethylsilyl), 7.4–8.6 (m, 4 H, aromatic).
(24) Two recrystallizations from benzene gave **9a** (67%), yellow plates, mp 197–198 °C. Anal. Calcd for $C_{24}H_{20}N_2O_2$: C, 78.24; H, 5.47; N, 7.61. Found: C, 78.18; H, 5.47; N, 7.78. IR (KBr, cm^{-1}): 3468 (NH); 3069, 3043 (=CH), 1642 (C=O), 1601 (C=C, aromatic), 1582, 1545, 1479, 1473 (C=C) 687 (*cis*-vinyl protons), 887, 750, 671, 677 (aromatic CH). ^{1}H NMR (200 MHz, $CDCl_3$): δ 12.18 (2 H, d, J = 12.1 Hz, NH), 8.47–7.05 (m, 14 H, aromatic; 2 H, vinyl), 6.1 (2 H, d, J = 7.8 Hz, *cis*-vinyl proton adjacent to C=O). ^{13}C NMR (200 MHz, $CDCl_3$): δ 190.94 (C=O), 145.87, 140.67, 139.82, 130.79, 130.30, 129.25, 126.69, 124.38 (8 C, aromatic), 116.92, 94.09 (2 C, vinyl).
(25) Two recrystallizations from 1-hexanol gave an analytical sample of **9b**, mp 176–178 °C. Anal. Calcd for $C_{22}H_{24}N_2O_2$: C, 75.83; H, 6.94; N, 8.04. Found: C, 75.76; H, 7.08; N, 7.90. IR (KBr, cm^{-1}) 3249 (NH), 3154, 3110, 3061, 3036 (=CH), 2944, 2932, 2901, 2890, 2867 (CH_2), 1674 (C=O), 1647, 1601, 1566, 1493 (C=C), 1462 (CH_2).
(26) The inherent viscosity (dL/g) was determined in *m*-cresol with a concentration of 0.5 g/dL at 25 °C.
(27) Compound **11c**. IR (KBr, cm^{-1}): 1630 (C=O), 1599, 1581, 1551, 1487 (C=C). Compound **11d**. IR (KBr, cm^{-1}): 1629 (C=O), 1601, 1584, 1552, 1487 (C=C).

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