

Metal Cation-Exchanged Montmorillonite-Catalyzed Addition of Organic Disulfides to Alkenes

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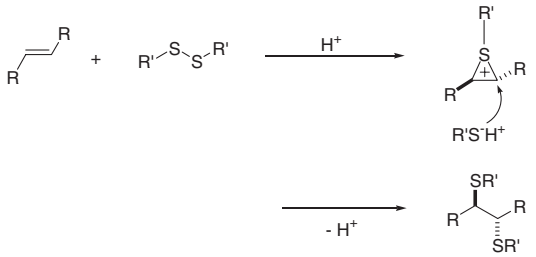
The addition of organic disulfides to alkenes, giving *vic*-bis(alkylthio)alkanes and *vic*-bis(arylthio)alkanes, proceeds in chlorobenzene in the presence of a catalytic amount of a variety of metal cation-exchanged montmorillonites (abbreviated as M^{n+}-monts), Al^{3+}, Fe^{3+}, Zr^{4+}, and In^{3+} being effective as M^{n+}. The most effective Fe^{3+}-mont can be reused for the addition of diphenyl disulfide to cyclohexene at least 8 times without an appreciable loss of catalytic activity.

Organic syntheses using the solid catalysts such as silicas, aluminas, clays, zeolites, and polymers under mild conditions have been well-developed.[1] Among a variety of solid catalysts, metal cation-exchanged montmorillonites are known to be among the useful and environmentally friendly clay catalysts that have many advantages over others, such as an ease of handling, noncorrosiveness, low cost, and reusability.

The addition of organic disulfides to alkenes is one of the useful reactions to synthesize various sulfur-containing compounds. Several reports on this type of reaction have appeared so far (Eq. 1) using either a stoichiometric or a catalytic amount of a variety of acids, such as $GaCl_3$,[2] $Me_2O \cdot BF_3$,[3] and PhIO–TfOH[4] or a catalytic amount of a transition metal complex such as [Cp*RuCl(cod)].[5]



(1)

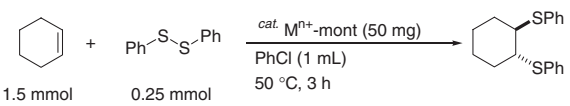
On the other hand, Clark and co-workers reported the reaction of dimethyl disulfide with cyclohexene in the presence of a stoichiometric amount of K-10 montmorillonite and excess $ZnCl_2$, but due to the formation of dithioalkane-ligated Zn-complexes, it was difficult to reuse these reagents.[6]

As one of our series of studies in the use of clay catalysts for useful organic transformations,[7] we have now investigated the addition of organic disulfides to alkenes in the presence of a catalytic amount of M^{n+}-mont and found that some M^{n+}-monts show a high reactivity for this reaction under mild conditions.

Results and Discussion

First, the catalytic activity of a variety of M^{n+}-monts for the addition of diphenyl disulfide to cyclohexene at 50 °C for 3 h was investigated in chlorobenzene as solvent (Table 1). Many M^{n+}-monts (especially Fe^{3+}-mont, Zr^{4+}-mont, and In^{3+}-mont) as well as K-10 worked as efficient catalysts to give *trans*-1,2-bis(phenylthio)cyclohexane in high yields (entries 1–5) stereoselectively, while some M^{n+}-monts such as Na^+-mont and Zn^{2+}-mont were not effective (entries 6 and 7). From these results together with economical and environmental concerns, we chose Fe^{3+}-mont as a catalyst for further examination.

Table 1. Effect of M^{n+}-mont



Entry	Catalyst	Acid sites/mmol[a)]	GLC yield/%[b)]
1	K10	0.016	89
2	Al^{3+}-mont	0.027	78
3[c)]	Fe^{3+}-mont	0.017	96
4	Zr^{4+}-mont	0.037	98
5[c)]	In^{3+}-mont	0.0098	85
6	Na^+-mont	0	0
7	Zn^{2+}-mont	0.019	9
8[d)]	K10	0.016	21
9[d)]	Fe^{3+}-mont	0.017	96

a) The amount of acid sites of M^{n+}-mont was estimated by NH_3-TPD analysis. b) Biphenyl was used as an internal standard. c) We also examined the addition of diphenyl disulfide to cyclohexene catalyzed by transiton metal chlorides under similar reaction conditions. The addition catalyzed by $FeCl_3$ (0.017 mmol equal to 50 mg Fe^{3+}-mont) and $InCl_3$ (0.0098 mmol equal to 50 mg In^{3+}-mont) afforded *trans*-1,2-bis(phenylthio)cyclohexane only in 21% yield and in 28% yield, respectively. d) At 20 °C for 24 h.

Next, the addition of diphenyl disulfide to cyclohexene was carried out in various kinds of solvents (Table 2). Among the solvents examined were chlorobenzene, fluorobenzene, toluene, 1,2-dichloroethane, ethyl acetate, chloroform, DMF (*N*,*N*-dimethylformamide), and DME (1,2-dimethoxyethane)

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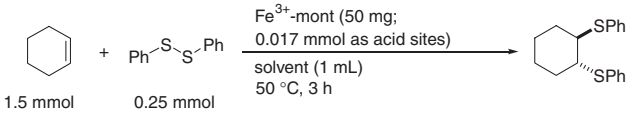
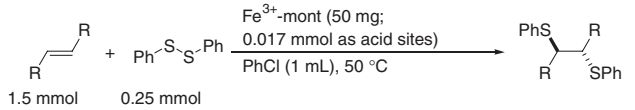
Table 2. Effect of Solvent

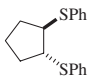
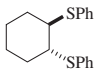
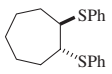
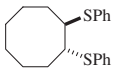
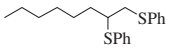
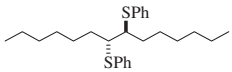


Entry	Solvent	Conv./%[a)]	GLC yield/%[b)]
1	PhCl	97	96
2	PhF	63	63
3	Toluene	74	65
4	1,2-Dichloroethane	54	53
5	AcOEt	0	0
6	$CHCl_3$	0	0
7	DMF	0	0
8	DME	0	0

a) Conversion of diphenyl disulfide. b) Biphenyl was used as an internal standard.

Table 3. Addition of Diphenyl Disulfide to a Variety of Alkenes



Entry	Product	Time/h	Isolated yield/%
1		5	95
2		5	98
3		12	96
4[a)]		24	34
5[a)]		27	89
6[a)]		96	58

a) Fe^{3+}-mont (200 mg; 0.068 mmol as acid sites).

(entries 1–8); chlorobenzene was revealed to be the solvent of choice (entry 1).

The results of diphenyl disulfide addition to a variety of alkenes are shown in Table 3.[8] Cyclopentene, cyclohexene, and cycloheptene reacted smoothly to give the corresponding sulfur-containing products in high yields (entries 1–3). Cyclooctene was also converted to the corresponding product by using a larger amount of catalyst, but in a low yield (entry 4). The reactions of linear alkenes, such as 1-octene and 7-tetradecene, also gave the corresponding 1,2-dithioalkanes in moderate yield (entries 5 and 6). The treatment of alkenes, such as styrene, 4-methoxystyrene, *trans*-stilbene, indene, norbornene, 3,4-dihydropyran, propyl vinyl ether, and allyl alcohol, unfortunately, did not afford the corresponding products at all. Further, no reaction occurred between diphenyl disulfide and 1-octyne.

The addition of various organic disulfides to cyclohexene was also investigated; typical results are listed in Table 4.[8] A variety of diaryl disulfides can be available, but not di(2-pyridyl) disulfide (entries 1–6). Dialkyl disulfides, such as dibenzyl disulfide, dipropyl disulfide, dicyclohexyl disulfide, and bis[2-(ethoxycarbonyl)ethyl] disulfide reacted to give the corresponding 1,2-dithioalkanes in moderate to good yields (entries 7–10). The use of bis(4-methoxyphenyl) disulfide, bis(4-nitrophenyl) disulfide, bis(6-hydroxy-2-naphthyl) disulfide, or *N*,*N*′-dithiobisphthalimide, however, failed to give the corresponding sulfur-containing product. Further, the reaction of diphenyl diselenide with cyclohexene did not afford the corresponding selenium-containing product at all.

Considering the trans stereochemistry of the products as well as Lewis acid nature of M^{n+}-mont, we conclude that all of the reactions proceed via an episulfonium ion shown in Eq. 1 and give *trans*-bis(alkylthio)alkanes and *trans*-bis(arylthio)alkanes. However, we do not have any more experimental evidence to discuss the reaction pathway in detail at the present.

Finally, the reusability of Fe^{3+}-mont was investigated in the reaction of diphenyl disulfide with cyclohexene in chlorobenzene at 50 °C. After 5 h, the reaction mixture was cooled to room temperature. Then, the catalyst was removed by the centrifuge, washed with acetone three times, and dried in vacuo at room temperature, and then at 120 °C for 5 h under an atmospheric pressure. The use of this recovered catalyst gave the same product in a high yield for the next run. It was revealed that by this procedure Fe^{3+}-mont could be used for this addition at least 8 times, as shown in Table 5.

In conclusion, metal cation-exchanged montmorillonites (M^{n+}-monts) were revealed to be efficient catalysts for the addition of a variety of organic disulfides to various alkenes, where Fe^{3+}-mont was most effective. Fe^{3+}-mont could be reused at least 8 times in the addition of diphenyl disulfide to cyclohexene.

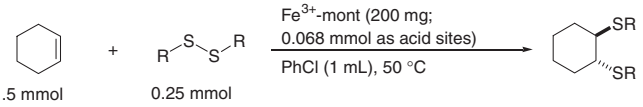
Experimental

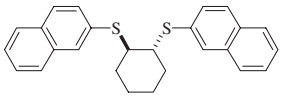
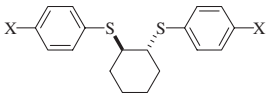
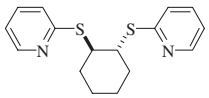
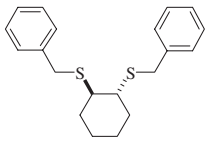
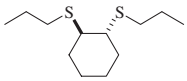
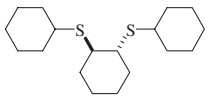
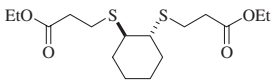
General Method. ^1H NMR spectra were obtained in $CDCl_3$ at 270, 300, or 400 MHz with Me_4Si as an internal standard. ^{13}C NMR spectra were obtained at 67.8, 75.5, or 100 MHz. Elemental analyses were performed at the Microanalytical Center of Kyoto University.

Materials. All commercially available organic and inorganic compounds were used without further purification. Kunipia G, namely Na^+-mont, was obtained from Kunimine Industries Co., Ltd. Montmorillonite K-10 was commercially available from Aldrich Chemical Co., Inc. M^{n+}-monts ($M^{n+} = Fe^{3+}$, Zr^{4+}, In^{3+}, Al^{3+}, and Zn^{2+}) were prepared by treatment of Na^+-mont with the corresponding metal chloride oxide or nitrate in aqueous acetone, as described previously.[7,9]

Typical Procedure for Addition Reaction of Organic Disulfides to Alkenes Catalyzed by Metal Cation-Exchanged Montmorillonite. To a mixture of diphenyl disulfide (54.6 mg, 0.25 mmol), Fe^{3+}-mont (50 mg, 0.017 mmol as active acid sites), and chlorobenzene (1 mL) in a 5-mL test tube was added cyclohexene (0.15 mL, 1.50 mmol) and the mixture was then stirred at 50 °C for 5 h. The reaction mixture was cooled to room temperature and then the catalyst was separated by filtration through a glass filter. For the isolation of the product, the solvent was evapo-

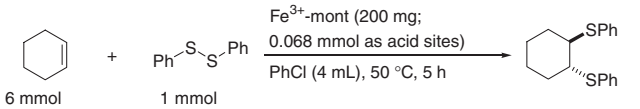
Table 4. Addition of a Variety of Organic Disulfides to Cyclohexene



Entry	Product		Time/h	Isolated yield/%
1			24	91
2[a]		X = H	5	98
3		Me	14	85
4		Cl	24	50
5		Br	24	66
6			40	13
7			72	68
8			24	73
9			24	51
10[b]			24	42[c]

a) Fe^{3+}-mont (50 mg; 0.017 mmol as acid sites). b) Five-fold scale reaction. c) Isolated by HPLC.

Table 5. Reusability of Fe^{3+}-mont



Run	Conv./%	GLC yield/%[a]	Run	Conv./%	GLC yield/%[a]
1st	95	94	5th	91	91
2nd	98	98	6th	91	86
3rd	98	98	7th	97	97
4th	98	98	8th	72	72

a) Biphenyl was used as an internal standard.

rated and the residue was purified by column chromatography (Merck silica gel 60; hexane/ethyl acetate as an eluent).

***trans*-1,2-Bis(phenylthio)cyclopentane.**[4] Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.67–1.77 (m, 2H), 1.82–1.91 (m, 2H), 2.30–2.41 (m, 2H), 3.55–3.58 (m, 2H), 7.19–7.25 (m, 10H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 23.1, 30.9, 52.7, 126.7, 128.9, 131.2, 135.4.

***trans*-1,2-Bis(phenylthio)cyclohexane.**[4] Colorless oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.40–1.69 (m, 6H), 2.21–2.30 (m, 2H), 3.24–3.31 (m, 2H), 7.21–7.33 (m, 10H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 23.5, 29.8, 49.6, 126.9, 128.8, 132.2, 134.6.

***trans*-1,2-Bis(phenylthio)cycloheptane.**[4] Colorless oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.54–1.90 (m, 8H), 2.14–2.24 (m, 2H), 3.44–3.51 (m, 2H), 7.18–7.28 (m, 10H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 23.9, 28.5, 30.4, 53.2, 126.7, 128.8, 131.8, 135.2.

***trans*-1,2-Bis(phenylthio)cyclooctane.** Colorless oil; IR (neat) 2924, 2850, 1479, 1438, 737, 691 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.43–1.62 (m, 6H), 1.77–1.93 (m, 4H), 2.17–2.25 (m, 2H), 3.42–3.47 (m, 2H), 7.19–7.38 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.2, 26.3, 29.0, 52.9, 126.7, 128.8, 131.9, 135.5. Anal. Calcd for $C_{20}H_{24}S_2$: C, 73.12; H, 7.36; S, 19.52%. Found: C, 73.22; H, 7.47; S, 19.78%.

1,2-Bis(phenylthio)octane.[5] Yellow oil; IR (neat) 2928, 2855, 1480, 1438, 738, 691 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, J = 6.6 Hz, 3H), 1.24–1.62 (m, 9H), 1.93–2.01 (m, 1H), 2.89 (dd, J = 13.5, 9.8 Hz, 1H), 3.09–3.16 (m, 1H), 3.25 (dd, J = 13.5, 4.2 Hz, 1H), 7.17–7.33 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ

14.2, 22.7, 26.8, 29.1, 31.7, 32.6, 39.4, 48.4, 126.2, 127.1, 128.8, 128.9, 129.7, 132.4, 134.3, 135.8. Anal. Calcd for $C_{20}H_{26}S_2$: C, 72.67; H, 7.93; S, 19.40%. Found: C, 72.94; H, 7.95; S, 19.51%.

***trans*-7,8-Bis(phenylthio)tetradecane.** Colorless oil; IR (neat) 2954, 2927, 2855, 1584, 1479, 1466, 1438, 744, 691 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.86 (t, $J = 6.8$ Hz, 6H), 1.17–1.43 (m, 14H), 1.49–1.55 (m, 2H), 1.61–1.70 (m, 2H), 1.74–1.83 (m, 2H), 3.30 (dt, $J = 11.2$, 4.3 Hz, 2H), 7.16–7.26 (m, 6H), 7.33–7.36 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 22.6, 27.5, 29.0, 31.7, 32.6, 55.1, 126.5, 128.7, 131.6, 136.4. Anal. Calcd for $C_{26}H_{38}S_2$: C, 75.30; H, 9.24; S, 15.46%. Found: C, 75.40; H, 9.36; S, 15.25%.

***trans*-1,2-Bis(*p*-tolylthio)cyclohexane.** Colorless oil; IR (neat) 2931, 2854, 1491, 1445, 810 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.32–1.42 (m, 2H), 1.54–1.68 (m, 4H), 2.15–2.22 (m, 2H), 2.33 (s, 6H), 3.12–3.20 (m, 2H), 7.06 (dd, $J = 7.9$, 0.5 Hz, 4H), 7.24 (d, $J = 8.2$ Hz, 4H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 21.2, 23.7, 30.2, 50.0, 129.5, 130.8, 132.9, 137.1. Anal. Calcd for $C_{20}H_{24}S_2$: C, 73.12; H, 7.36; S, 19.52%. Found: C, 73.34; H, 7.47; S, 19.35%.

***trans*-1,2-Bis(2-naphthylthio)cyclohexane.** White solid, mp = 102.2–102.7 °C; IR (KBr) 2930, 2913, 822, 740, 480, 469 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.36–1.65 (m, 6H), 2.23–2.31 (m, 2H), 3.36 (br s, 2H), 7.27–7.71 (m, 14H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 23.4, 29.9, 49.7, 126.1, 126.4, 127.3, 127.6, 128.4, 129.8, 130.9, 132.1, 132.3, 133.6. Anal. Calcd for $C_{26}H_{24}S_2$: C, 77.95; H, 6.04; S, 16.01%. Found: C, 77.70; H, 6.11; S, 16.01%.

***trans*-1,2-Bis(4-chlorophenylthio)cyclohexane.** Colorless oil; IR (neat) 2933, 2855, 1475, 1094, 1012, 819 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.36–1.43 (m, 2H), 1.61–1.67 (m, 4H), 2.16–2.23 (m, 2H), 3.10–3.17 (m, 2H), 7.21–7.29 (m, 8H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 23.7, 30.4, 50.3, 129.0, 132.9, 133.3, 133.9. Anal. Calcd for $C_{18}H_{18}Cl_2S_2$: C, 58.53; H, 4.91; S, 17.36%. Found: C, 58.65; H, 5.05; S, 17.60%.

***trans*-1,2-Bis(4-bromophenylthio)cyclohexane.** Colorless oil; IR (neat) 2932, 1472, 1091, 1009, 817 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.37–1.44 (m, 2H), 1.54–1.74 (m, 4H), 2.16–2.25 (m, 2H), 3.10–3.17 (m, 2H), 7.18 (td, $J = 8.6$, 2.3 Hz, 4H), 7.38 (dt, $J = 8.6$, 2.3 Hz, 4H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 23.7, 30.4, 50.2, 121.3, 131.9, 133.5, 134.0. Anal. Calcd for $C_{18}H_{18}Br_2S_2$: C, 47.18; H, 3.96; S, 13.99%. Found: C, 47.39; H, 4.00; S, 14.02%.

***trans*-1,2-Bis(2-pyridyl)cyclohexane.** Colorless oil; IR (neat) 2928, 1578, 1384, 1122, 756 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.55–1.59 (m, 2H), 1.70–1.81 (m, 4H), 2.34–2.40 (m, 2H), 4.20–4.26 (m, 2H), 6.95 (dd, $J = 7.6$, 5.0 Hz, 2H), 7.22 (d, $J = 7.6$ Hz, 2H), 7.45 (td, $J = 7.6$, 1.4 Hz, 2H), 8.38 (dd, $J = 5.0$, 1.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.2, 31.5, 46.7, 119.3, 122.9, 135.8, 149.2, 158.8. Anal. Calcd for $C_{16}H_{18}N_2S_2$: C, 63.54; H, 6.00; S, 21.20%. Found: C, 63.73; H, 6.18; S, 20.99%.

***trans*-1,2-Bis(benzylthio)cyclohexane.** Colorless oil; IR (neat) 2929, 1494, 1453, 1445, 1070, 699 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.26–1.64 (m, 6H), 2.06–2.14 (m, 2H), 2.69–2.76 (m, 2H), 3.69 (s, 4H), 7.18–7.32 (m, 10H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 23.7, 30.8, 36.0, 47.4, 126.8, 128.3, 128.8, 138.3. Anal. Calcd for $C_{20}H_{24}S_2$: C, 73.12; H, 7.36; S, 19.52%. Found: C, 73.10; H, 7.35; S, 19.46%.

***trans*-1,2-Bis(propylthio)cyclohexane.** Colorless oil; IR (neat) 2959, 2931, 2870, 2855, 1456, 1445 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 0.93 (t, $J = 7.3$ Hz, 6H), 1.19–1.65 (m, 10H), 2.07–2.15 (m, 2H), 2.49 (t, $J = 7.2$ Hz, 4H), 2.67–2.74 (m, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 13.6, 23.1, 24.0, 31.4, 33.6, 48.3. Anal. Calcd for $C_{12}H_{24}S_2$: C, 62.00; H, 10.41; S, 27.59%. Found: C, 61.92; H, 10.61; S, 27.35%.

***trans*-1,2-Bis(cyclohexylthio)cyclohexane.** Colorless oil; IR (neat) 2928, 2851, 1446, 1263, 1198, 1000 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.24–2.19 (m, 28H), 2.68–2.76 (m, 2H), 2.88–2.94 (m, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 23.4, 25.9, 26.2, 31.2, 34.0, 43.6, 46.7. Anal. Calcd for $C_{18}H_{32}S_2$: C, 69.16; H, 10.32; S, 20.52%. Found: C, 68.86; H, 10.18; S, 20.34%.

***trans*-1,2-Bis[2-(ethoxycarbonyl)ethylthio]cyclohexane.** Colorless oil; IR (neat) 2980, 2931, 1735, 1371, 1243, 1178 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.27 (t, $J = 7.1$ Hz, 6H), 1.31–1.40 (m, 2H), 1.48–1.55 (m, 2H), 1.67–1.71 (m, 2H), 2.15–2.20 (m, 2H), 2.60 (t, $J = 7.4$ Hz, 4H), 2.74–2.80 (m, 2H), 2.85 (t, $J = 7.4$ Hz, 4H), 4.16 (q, $J = 7.1$ Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3, 24.2, 26.6, 31.9, 35.0, 48.9, 60.7, 171.8. Anal. Calcd for $C_{16}H_{28}O_4S_2$: C, 55.14; H, 8.10; S, 18.40%. Found: C, 55.09; H, 8.20; S, 18.67%.

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