

Studies on Fluoroalkylation and Fluoroalkoxylation. Part 28. Palladium(0)-induced Addition of Fluoroalkyl Iodides to Alkenes: an Electron Transfer Process

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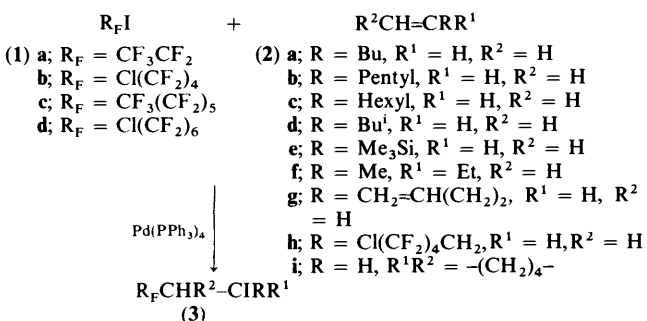
In the presence of catalytic amounts of tetrakis(triphenylphosphine)palladium, fluoroalkyl iodides react readily with alkenes under mild conditions to give the corresponding adducts in high yields. Dichlorobis(triphenylphosphine)palladium or fluoroalkylbis(triphenylphosphine)palladium iodide fails to induce the reaction under the same conditions. Di-iodobis(triphenylphosphine)palladium, but not the fluoroalkylated complex of palladium, $\text{Pd}(\text{PPh}_3)_2\text{R}_F$, is formed in the reaction confirmed by X-ray photoelectron spectroscopy. The reaction can be partially suppressed by radical inhibitors, such as 2-nitro-2-nitrosopropane or di-*t*-butyl nitroxide, but no effects are observed by the presence of oxygen in air or *p*-dinitrobenzene [molar ratio *p*-DNB: $\text{Pd}^0 = 1:1$] unless an excess of *p*-DNB (10:1) was added. In the presence of diallyl ether, fluoroalkylated tetrahydrofuran derivatives are formed. All these results indicate that a radical-chain process initiated by single electron transfer from palladium(0) to iodide might be involved. Also, the formation of fluoroalkylbis(triphenylphosphine)palladium iodide is proved to proceed through a radical intermediate by e.s.r. trapping techniques.

Metals, especially transition metals, and their complexes have found increasing use in organic chemistry, both as reagents and catalysts for a variety of synthetic reactions.^{1,2} Applications of transition metals and their complexes have also been found in fluorine chemistry.³ Recently, a series of metals, e.g. Cu,⁴ Raney-Ni,⁵ Pt⁰,⁶ Fe⁰,⁷ Zn,⁸ and Mg⁹ *etc.* have been reported to catalyze the addition reactions of fluoroalkyl iodides to alkenes and alkynes in our laboratory. In 1985, we gave preliminary results of the palladium(0)-initiated addition of fluoroalkyl iodides to alkenes.¹⁰ A year later, Ishikara reported similar results.¹¹ Here, we discuss the reaction and mechanism in more detail.

Results and Discussion

Palladium(0) can catalyze the reactions of aryl or alkenyl halides with alkenes to give the carbon-carbon coupled products (Heck reaction¹²). In the presence of catalytic amounts of tetrakis(triphenylphosphine)palladium (0.5–1 mol%), we found that the fluoroalkyl iodides also reacted with alkenes to give the corresponding adducts in high yields, under mild conditions (Scheme 1).

The reaction occurred at room temperature, and no solvent was needed. For example, the chloro dodecafluoro iodide



Scheme 1.

Table. Pd⁰-Catalyzed additions of fluoroalkyl iodides to alkenes^a

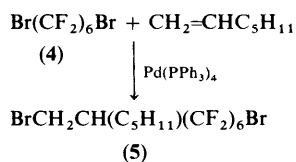
R _F I	Alkene	T(°C)	t(min)	Yield(%) ^b
(1b)	(2b)	15	60	91
(1b)	(2b)	40	30	96
(1b)	(2b)	100	30	87
(1b)	(2c)	20	30	78
(1b)	(2d)	20	30	94
(1c)	(2d)	20	60	79
(1b)	(2f)	20	20	90
(1a)	(2f)	15	30	85
(1b)	(2e)	70	480	93
(1c)	(2e)	100	480	80
(1b)	(2g)	15	20	62
(1a)	(2g)	15	30	50
(1b)	DAE ^g	20	20	78 ^c
(1a)	DAE ^g	20	30	61 ^c
(1a)	(2a)	20	20	97
(1b)	(2a)	80	240	88 ^d
(1b)	(2i)	80	60	34 ^e
(4)	(2b)	100	360	43 ^f
(1b)	(2h)	20	40	93

^a At room temperature; (1):(2):Pd⁰ = 1:1:0.5–1%. ^b Isolated yield. ^c (10), *cis:trans* = 2:1. ^d Catalyzed by PdCl₂(PPh₃)₂-Et₃N. ^e E:Z = 1:2; ^f (5). ^g DAE = diallyl ether.

(1d) when mixed with hept-1-ene in the presence of 0.5 mol% of Pd⁰ reagent at 20 °C, and stirred for 20 min, gave an adduct in 97% yield. Increasing the temperature from room temperature to 100 °C had little effect on the reaction. When dichlorobis(triphenylphosphine)palladium was used instead of Pd(PPh₃)₄, the reaction did not occur unless a base, e.g. potassium carbonate or triethylamine, was present. The representative results are summarised in the Table.

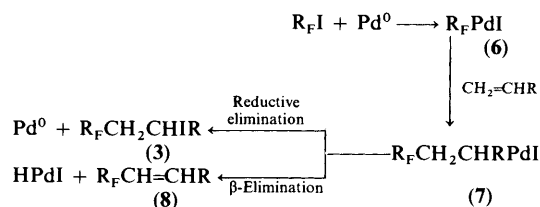
The reaction was highly specific. Under the same conditions, alkenes with electron-withdrawing groups, such as pentafluoroethyl, were unreactive, whereas those bearing electron-donating groups reacted rapidly. Moreover, non-terminal alkenes, e.g. cyclohexane, underwent lower conversion (*ca.* 30%). Interestingly, perfluoroalkyl or ω-chloroalkyl bromides did not react with alkenes although α,ω-dibromoalkanes did give adducts (*ca.* 30%) (Scheme 2).

† Formerly spelt as Ching-Yun Chen.



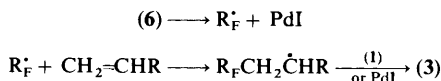
Scheme 2.

It is well-known that palladium(0)-catalyzed reactions of aryl or alkenyl halides with alkenes proceed through an oxidative addition process involving palladium complexes.¹² Also, fluoroalkyl iodides have been found to react readily with a series of transition metals to give the corresponding complexes.¹³ These results prompted us to investigate the possibility of forming the palladium complex intermediates (6) which should then add to the alkene (Scheme 3).



Scheme 3.

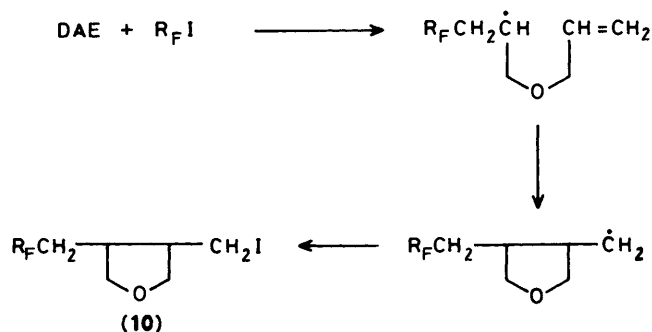
The intermediate (7) could react by two possible reaction pathways, namely reductive elimination to give the adduct (3) or β -hydrogen elimination to afford carbon-carbon coupling products (8). The latter is similar to the Heck reaction and has been proved to proceed very fast.¹⁴ However, no coupling product (8) was found in our studies even if the reaction was carried out in the presence of triethylamine. This fact seems to exclude the possibility of forming (7) in the reaction. An alternative route for (6) to yield the adducts is *via* the decomposition of the complex (6) to give the fluoroalkyl radical intermediates which in turn can add to the alkene (Scheme 4).



Scheme 4.

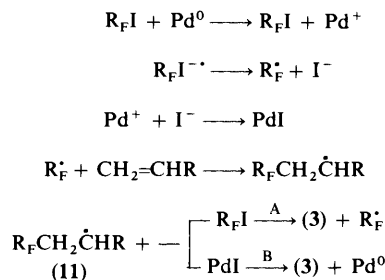
However, this possibility has also been ruled out by the following. (a) Stone *et al.* have proved that the fluoroalkylated palladium complex, $\text{R}_F\text{PdI}(\text{PPh}_3)_2$, was thermally stable and melted between 250 and 300 °C without decomposition.¹³ Certainly, it was impossible for (6) to decompose at room temperature; (b) according to Stone *et al.*,¹³ we have prepared the complex, $\text{C}_2\text{F}_5\text{PdI}(\text{PPh}_3)_2$, but no reaction was observed when the complex was mixed with alkenes at room temperature; (c) X-ray photoelectron spectroscopy (XPS) showed only Pd^{II} and iodide, with no indication of the presence of fluorine atoms, in the solid obtained from the system, which means that only $\text{PdI}_2(\text{PPh}_3)_2$, rather than $\text{R}_F\text{PdI}(\text{PPh}_3)_2$, was formed in the reaction. Obviously, the fluoroalkylated complex (6) as a reaction intermediate could be excluded. This prompted us to search for other reasonable reaction pathways.

Fluoroalkyl iodides are known to be excellent radical precursors, and many examples have been reported.¹⁵ On the other hand, some transition metals and their low-valent complexes have been proved to catalyze or induce the radical reactions of fluoroalkyl iodides efficiently.⁴⁻⁸ A palladium(0) single-electron transfer (SET)-initiated radical reaction was then suggested. The formation of fluoroalkylated tetrahydrofuran derivatives provided strong evidence for a radical mechanism, in the case of the reaction of diallyl ether (DAE) with fluoroalkyl iodide in the presence of palladium(0).



Scheme 5.

In order to further confirm this possibility, scavenging experiments with radical inhibitors were carried out. Addition of 2-nitro-2-nitrosopropane or di-*t*-butyl nitroxide suppressed the reaction successfully and the conversion decreased to 45 and 5%, respectively as compared with that of the control (100%). However, atmospheric oxygen failed to suppress the reaction. Also, the electron transfer inhibitor, *p*-dinitrobenzene [*p*-DNB: Pd⁰ = 1:1], did not suppress the reaction unless excess amounts of *p*-DNB [*p*-DNB: Pd⁰ = 10:1] were used, which may indicate that the reaction is occurring too fast for inhibition by *p*-DNB or oxygen at room temperature. All these results seemed to support the suggested radical mechanism initiated by single-electron transfer from palladium(0) to the iodide (Scheme 6).



Scheme 6.

As mentioned above, Stone *et al.* have reported that fluoroalkyl iodides react with tetrakis(triphenylphosphine)palladium in benzene to give the oxidative addition complex, $\text{PdI}(\text{PPh}_3)_2\text{R}_F$. This was confirmed in our experiment. However, when we ran the reaction in the presence of hept-1-ene, *i.e.* the alkene was mixed with palladium(0) in benzene before adding the fluoroalkyl iodide, high yields of adducts were obtained, instead of the fluoroalkylated complex, (6). In fact, (6) was formed only if hept-1-ene was added to the homogenous solution of fluoroalkyl iodide and $\text{Pd}(\text{PPh}_3)_4$ in benzene. Whether the formation of the complex (6) also involves a radical intermediate might be an interesting problem. Therefore an e.s.r. spectroscopic study on the reaction was carried out.

Because the high reactivity and low concentration of the possible radical species produced in the reactions, a flow technique was adapted for e.s.r. experiments, but no direct e.s.r. signal due to any radical species was obtained. However, using the phenyl *t*-butyl nitron (PBN) as the spin trapping agent, a well resolved e.s.r. spectrum of the spin adduct of the trapped $\text{Cl}(\text{CF}_2)_4$ radical, $\text{Cl}(\text{CF}_2)_4\text{CHPhN}(\text{O})\text{Bu}^\cdot$ [(11); $a = 14.0$ G] was observed when the 4-chlorododecafluorobutyl iodide (1b) was vigorously shaken in an e.s.r. tube with the mixture of $\text{Pd}(\text{PPh}_3)_4$ and PBN in F113 at low temperature and then detected by e.s.r. spectroscopy at 20 °C (Figure 1).

70 °C/4 mmHg (Found: C, 26.9; H, 2.8. C₁₀H₁₂ClF₈I requires C, 26.89; H, 2.71%; v_{max}. 2950, 2920, 2860, 1995, 1355, 1080, 970, and 855 cm⁻¹; δ_F -10.0 (2 F), 34.2 (1 F), 35.6 (1 F, m), 42.0 (2 F), and 45.2 p.p.m. (2 F); δ_H 4.20 (m, 1 H), 2.5–3.2 (m, 2 H), 1.2–2.1 (m, 3 H), and 0.95 (d, 3 H, J 6 Hz); m/z 319 (M⁺ - I, 68.98%), 321 (22.04), 85 (ClCF₂⁺, 6.20), 69 (C₅H₉⁺, 26.16), 55 (C₄H₇⁺, 12.84), 43 (C₃H₇⁺, 100), and 41 (27.75).

[3; R_F = CF₃(CF₂)₅, R = Bu¹, R¹ = H, R² = H]: b.p. 72–74 °C/5 mmHg (Found: C, 27.2; H, 2.4; F, 46.3. C₁₂H₁₂F₁₃I requires C, 27.18; H, 2.28; F, 46.58%; v_{max}. 2940, 2910, 1230, 1200, and 1145 cm⁻¹; δ_F 3.7 (3 F), 34.5 (1 F), 35.8 (1 F), 45.3 (2 F), 46.0 (4 F), and 49.0 p.p.m. (2 F); δ_H 4.0 (m, 1 H), 2.2–3.0 (m, 2 H), 1.0–1.8 (m, 3 H), 0.75 (d, 3 H, J 6 Hz), and 0.55 (d, 2 H, J 6 Hz).

(3; R_F = CF₃CF₂, R = Me, R¹ = Et, R² = H): b.p. 58 °C/30 mmHg (Found: C, 26.7; H, 3.05; F, 31.5. C₇H₁₀F₅I requires C, 26.60; H, 3.17; F, 30.06%; v_{max}. 2960, 2910, 2850, 1315, 1160–1200, 1135, 1060, and 990 cm⁻¹; δ_F 7.30 (3 F) and 35.8 p.p.m. (2 F); δ_H 2.85 (t, 2 H, J 20 Hz), 2.11 (s, 3 H), 1.65 (q, 2 H, J 6 Hz), 1.02 (t, 3 H, J 6 Hz); m/z 189 (M⁺ - I, 100%), 127 (I⁺, 11.20), and 119 (C₂F₅⁺, 1.82).

[3; R_F = CF₃CF₂, R = CH₂=CH(CH₂)₂, R¹ = H, R² = H] (Found: C, 29.5; H, 3.05; F, 29.6. C₈H₁₀F₅I requires C, 29.86; H, 3.05; F, 28.96%; v_{max}. 3060, 2950, 1640, 1190, 1135, and 920 cm⁻¹; δ_F 8.0 (3 F) and 39.5 (m, 2 F) p.p.m.; δ_H 5.4–6.0 (m, 1 H), 4.85–5.15 (m, 2 H), 4.27 (m, 1 H), and 1.60–3.15 (m, 6 H); m/z 328 (M⁺, 0.61%), 201 (M⁺ - I, 19.35), 127 (2.48), 57 (46.47), 55 (22.90), and 43 (100).

[3; R_F = Cl(CF₂)₄, R = CH₂=CH(CH₂)₂, R¹ = H, R² = H]: b.p. 86–88 °C/5 mmHg (Found: C, 27.25; H, 2.27; F, 33.9. C₁₀H₁₀ClF₈I requires C, 27.02; H, 2.27; F, 34.19%; v_{max}. 3050, 2950, 2900, 1640, 1310, 1195, 1120, 995, and 920 cm⁻¹; δ_F -10.0 (2 F), 35.2 (2 F), 42.2 (2 F), and 45.4 (2 F) p.p.m.; δ_H 5.4–5.9 (m, 1 H), 4.88–5.18 (m, 2 H), 4.25 (m, 1 H), and 3.18–1.75 (m, 6 H); m/z 444 (M⁺, 0.72%), 403 (0.87), 317 (M⁺ - I, 80.00), 319 (33.04), 85 (11.16), 67 (27.85), and 41 (C₃H₅⁺, 100).

[3; R_F = Cl(CF₂)₆, R = Bu, R¹ = H, R² = H]: b.p. 114 °C/4 mmHg (Found: C, 26.1; H, 2.3; F, 41.65. C₁₂H₁₂ClF₁₂I requires C, 26.37; H, 2.21; F, 41.71%; v_{max}. 2960, 2920, 2850, 1210, 1150, 1120, and 1080 cm⁻¹; δ_F -10.0 (2 F), 35.5 (2 F), 42.5 (2 F), 43.5 (4 F), and 45.8 (2 F) p.p.m.; δ_H 4.30 (m, 1 H), 2.5–3.2 (m, 2 H), and 0.9–2.75 (m, 9 H); m/z 546 (M⁺, 0.22%), 421 (M⁺ - I, 34.43), 419 (100), 69 (C₂H₉⁺, 13.16), and 55 (17.87).

[3; R_F = Cl(CF₂)₄, R = Bu, R¹ = H, R² = H]: b.p. 96–98 °C/7 mmHg (Found: C, 26.1; H, 2.3; F, 41.65. C₁₀H₁₂ClF₈I requires C, 26.89; H, 2.21; F, 41.71%; v_{max}. 2960, 2920, 2850, 1210, 1150, and 1120 cm⁻¹; δ_F -10.0 (2 F), 35.5 (2 F), 42.5 (2 F), and 45.2 (2 F) p.p.m.; δ_H 4.00 (m, 1 H), 2.15–3.80 (m, 2 H), and 0.70–1.60 (m, 9 H); m/z 321 (M⁺ - I, 42.95%), 319 (100), 85 (7.15), 69 (14.55), and 55 (21.23).

(10; R_F = CF₃CF₂): b.p. 84 °C/4 mmHg (Found: 27.95; H, 3.05; F, 27.3. C₈H₁₀F₅I requires C, 27.92; H, 2.93; F, 27.60%; v_{max}. 2920, 2850, 1320, 1190, 1050, and 1015 cm⁻¹; δ_F 8.0 (3 F) and 39.5 (m, 2 F) p.p.m.; δ_H 1.8–4.0 (m); m/z 345 (M⁺ + 1, 100%), 343 (19.14), 217 (M⁺ - I, 86.94), 127 (14.25), and 73 (23.39).

(5): b.p. 120 °C/4 mmHg (Found: C, 28.4; H, 2.6; F, 40.4. C₁₃H₁₄Br₂F₁₂ requires C, 27.98; H, 2.53; F, 40.85%; v_{max}. 2950, 2900, 2800, 1470, 1380, 1190, 1135, 1080, 975, 840, and 800 cm⁻¹; δ_F 15.0 (2 F), 35.7 (2 F), 39.2 (2 F), 43.3 (4 F), and 45.7 p.p.m. (2 F).

The analyses of [3; R_F = Cl(CF₂)₄, R = pentyl, R¹ = H, R² = H], [3; R_F = Cl(CF₂)₄, R = hexyl, R¹ = H, R² = H], [3; R_F = Cl(CF₂)₄, R = Me, R¹ = Et, R² = H], [3; R_F = Cl(CF₂)₄, R = Me₃Si, R¹ = H, R² = H], [3; R_F = CF₃(CF₂)₅, R = Me₃Si, R¹ = H, R² = H], [3; R_F = Cl(CF₂)₄, R = H, R¹R² = -(CH₂)₄-], and [10; R_F = Cl(CF₂)₄] were in accord with literature values.^{4a,b,6,8}

Inhibition Experiments: Palladium(0)-induced Reaction of (1b) with Hept-1-ene in the Presence of Radical Inhibitors.—To a mixture of Pd(PPh₃)₄ (50 mg, 0.043 mmol) and hept-1-ene (0.5 g, 5 mmol) was added di-*t*-butyl nitroxide (10 mg, 0.078 mmol) and (1b) (0.9 g, 2.5 mmol) under an atmosphere of nitrogen. The mixture was stirred for 60 min at room temperature after which time ¹⁹F n.m.r. spectroscopic analysis showed that no reaction had occurred.

Similarly, the conversion was found to be only 45% when 2-nitro-2-nitrosopropane was used in the reaction instead of Bu¹NO.

Suppressing Reactions with p-DNB.—To a mixture of Pd(PPh₃)₄ (50 mg, 0.043 mmol), *p*-DNB (80 mg, 0.46 mmol), and hept-1-ene (1.2 g, 10 mmol) was added (1b) (1.8 g, 5 mmol). The mixture was stirred at room temperature for 10 min, after which time the conversion of (1b) was 45% as shown by ¹⁹F n.m.r. spectroscopy. However, the conversion went to completion if only *p*-DNB (8 mg, 0.046 mmol) was used under the same conditions.

Similarly, the conversion of (1b) went to completion in the presence of hydroquinone (30 mg, 0.27 mmol) or oxygen.

The Reaction of (1b) with Hept-1-ene in the Presence of Pentafluoroethylbis(triphenylphosphine)palladium Iodide.—A Pyrex tube was charged with CF₃CF₂PdI(PPh₃)₂ (30 mg, 0.034 mmol), hept-1-ene (0.2 g, 2 mmol) and (1b) (0.36 g, 1 mmol) was added under nitrogen at room temperature. The reaction was stirred for 1 h after which time ¹⁹F n.m.r. spectroscopic analysis showed that no reaction had occurred.

PdCl₂(PPh₃)₂-Et₃N-induced Reaction of (1b) with Hept-1-ene.—To a mixture of (1b) (1.8 g, 5 mmol), triethylamine (excess), and hept-1-ene (0.6 g, 6 mmol) was added Pd(PPh₃)₄ (150 mg, 0.21 mmol) at room temperature under nitrogen. The reaction was stirred for 20 min, when ¹⁹F n.m.r. spectroscopic analysis showed that the reaction was complete (100%).

In the absence of triethylamine, no product was observed in the reaction.

Palladium(0)-induced Reaction of the 1,6-Dibromopolyfluoroalkane (6) with Hept-1-ene.—To a mixture of hept-1-ene (0.4 g, 5 mmol) and Pd(PPh₃)₄ (200 mg, 0.17 mmol) was added the 1,6-dibromopolyfluorohexane (6) (2.4 g, 5 mmol) under nitrogen. The mixture was stirred at 100 °C for 6 h when ¹⁹F n.m.r. spectroscopic analysis showed that 50% of (6) had been converted. Distillation of the crude product gave the adduct (7) (1.3 g, 85%).

XPS Experiment for Determining the Valency of Palladium during the Reaction of (1b), Hept-1-ene, and Pd(PPh₃)₄.—Hept-1-ene (1.0 g, 10.2 mmol) and Pd(PPh₃)₄ (90 mg, 0.078 mmol) Pd(PPh₃)₄ were mixed with (1b) (1.8 g, 5 mmol) under nitrogen in a solid-CO₂ trap. The mixture was allowed to stand at room temperature for 30 s after which time it was placed back into solid-CO₂ bath and some solid was taken out under nitrogen for XPS analysis which revealed Pd⁰, E_b 343 (3d 3/2) and 336 eV (3d 5/2); Pd^{II}, E_b 345 (3d 3/2) and 337.7 eV (3d 5/2); I, E_b 630.9 (2p) and 619.5 eV (2p); P, E_b 131 eV (2p). After the mixture had been allowed to react at room temperature for 30 min, the XPS analysis of the solid sample showed Pd^{II}, E_b 345.1 (3d 3/2) and 337.4 eV (3d 5/2); I, E_b 619.6 eV; P, E_b 131.4 eV.

*E.S.R. Study of the Reaction of (1b) with Pd(PPh₃)₄ in the Presence of Phenyl *t*-Butyl Nitron in F113.*—A solution of Pd⁰ and phenyl *t*-butyl nitron in F113 (0.5 ml) were syringed into an e.s.r. tube and a corresponding aliquot of (1b) in F113 was syringed into the side bulb of the e.s.r. tube. After having been

degassed, the reagents were mixed as quickly as possible by shaking the sample tube at room temperature and the e.s.r. signal was monitored at appropriate time intervals. The e.s.r. spectrum of the radical intermediate was recorded as shown in Figure 1.

Also, the e.s.r. spectrum of the nitroxide (**12**) generated from (**1b**), (**2b**), and NNP in the presence of Pd⁰ was recorded at 10 °C using a similar procedure (Figure 2).

Acknowledgements

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