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Abstract: The specific nonpurely thermal effects of microwaves were evidenced according to neutral or charged leaving groups during nucleophilic substitution of benzylic electrophiles with triphenylphosphine and tributylphosphine. Microwave (MW) irradiation considerably enhanced the reactions with charged alkylating agents, especially under solventfree conditions. Results are interpreted considering the magnitude of MW effects according to the position of the transition state along the reaction coordinates.

Key words: microwave irradiation, specific effects, phosphonium salts, leaving group effects.

Résumé : Des effets spécifiques non purement thermiques des micro-ondes ont été mis en évidence. Ils dépendent de la nature neutre ou chargée des groupes partants au cours de la substitution nucléophile par la triphénylphosphine ou la tributylphosphine sur des agents benzylants. L'irradiation micro-onde augmente considérablement les vitesses de réaction avec les agents alkylants chargés, particulièrement dans des conditions sans solvant. Les résultats sont interprétés en considérant les effets des micro-ondes en fonction de la position de l'état de transition sur les coordonnées réaction-nelles.

Mots clés : irradiation aux micro-ondes, effets spécifiques, sels de phosphonium, effets de groupes partants.

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Introduction

Application of microwave (MW) irradiation in organic synthesis is well documented (1-10). Most of the publications describe significant accelerations for a wide range of organic reactions especially when carried out under solventfree conditions. They can find their origins in either thermal effects and (or) specific nonpurely thermal effects. Therefore, a vivid discussion was going on the possible intervention of any specific microwave effect resulting from decrease in the free energy of activation or if the enhancement of the reactions is due to a local overheating of the reaction mixture (11-13) (a hot spot effect as advocated in sonochemistry) (14).

Microwaves consist of electromagnetic waves generated by an alternating electric field of high frequency. The energy associated with a MW photon (1 J mol⁻¹ by application of Planck's law E = hv with v = 2450 MHz) is by far too small to induce any excitation of molecules. It can, however, provoke thermal effects because of some internal friction

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among polar molecules during their changes in orientation with each alternation of the electric field. In addition, they can induce some electrostatic interactions with polar materials by dipole–dipole interactions, rather similar to the behaviour of a dipolar solvent. It was, for instance, shown that the regioselectivity of phenacylation of 1,2,4-triazole is the same under conventional heating in a dipolar aprotic solvent (DMF) and under MW irradiation in a non-polar medium (xylene), or even in the absence of any solvent (15). By analogy and extension of the interpretation of solvent effects, the carbon–halogen bond breaking in S_N2 reactions can be facilitated by an increase in the polarity of the system during the reaction progress from the ground state to its transition state and could depend on the leaving group ability.

A working hypothesis was therefore advanced very recently according to which it is possible to predict (according to the type of reaction) if a significant specific (non-purely thermal) MW effect can be observed (15, 16). It considers medium and mechanism influences on the MW-assisted reactions. MW stabilizations by electrostatic dipole–dipole interactions between materials and the electromagnetic field are foreseen to be increased if the polarity of the systems are increased when the reaction is progressing. From a reactivity point of view, a decrease in the energy of activation by extending stabilization from the ground state can be expected towards the transition state can be expected (15–17). It would be the case when polar mechanisms are concerned, i.e., when there is a development of charge during the course of the reaction. It would also be the case if the position of

Entry	Х	Solvent	t (min)	<i>Т</i> (°С)	Yield for 3 using MW (%) ^{<i>a,b</i>}	Yield for 3 using CH $(\%)^{a,c}$
1	Br (2a)	No	10	100	99 (3ba)	99
2		No	2	100	99	98
3	Cl (2b)	Xylene	30	140	33 (3bb)	11
4		No	10	150	94	91
5		No	10	100	78	24
6	$N^{+}Me_{3}Cl^{-}$ (2c)	No	10	150	70 (3bb)	0
7		No	10	250	95	70

Table 1. Reaction of triphenylphosphine 1b with benzylating agents 2a-2c.

^aYields in isolated products.

 ${}^{b}MW$ = microwave irradiation inside a monomode S 402 reactor.

^cCH = conventional heating inside a thermostatted oil bath under similar conditions.

the transition state lies later along the reaction coordinates (Hammond's postulate) (18).

MW syntheses of several triphenylalkylphosphonium salts were recently described by Kiddle (19–21). Several representative organic halides were treated with triphenylphosphine to afford phosphonium salts in excellent yields. The reaction times were reduced to 4 min or less from conventional heating times ranging from 30 min to 14 days. However, owing to the lack of accurate control of the temperature and to strict comparisons with conventional heating under similar conditions, the real intervention of MW activation is questionable and needs more detailed experiments for better understanding (22). This prompted us to publish our results on the study and interpretation of the microwave effects on the S_N2 reactions of alkylating agents (neutral or charged) with neutral nucleophiles (phosphines) (eq. [1]). This kind of experiment was synthetically exploited for the preparation of imidazolium and ephedrinium salts as ionic liquids by the alkylation of imidazole (23–26) or *N*-methylephedrine (27). Some preliminary results were previously presented at an international microwave chemistry meeting (28).

	PR ₃ 1	+ PhCH ₂ X 2	$ PhCH_2^+PR_3X^-$ 3
[1]	1 (a) $R = n - C_4 H_9$ (b) $R = C_6 H_5$	2 (a) X = Br (b) X = Cl (c) X = N ⁺ Me ₃ Cl ⁻	3aa $R = n-C_4H_9$, $X = Br$ 3ab $R = n-C_4H_9$, $X = Cl$ 3ba $R = C_6H_5$, $X = Br$ 3bb $R = C_6H_5$, $X = Cl$

Results

Reactions of benzyl halides and benzyl trimethylammonium chloride with triphenyl-phosphine **1b** were carried out either in xylene (a non-polar solvent, i.e., transparent to MW) or under solvent-free conditions. To check the possible intervention of specific (non-purely thermal) MW effects, control experiments were performed using conventional heating (CH) in a thermostated oil bath at the same temperature for the same time. Identical profiles for increasing temperature were maintained for both types of activation mode, allowing for the elimination of the purely thermal contribution of MW radiation (Fig. 1).

Table 1 gives the main results for the reaction of 1b with the benzylating electrophiles 2a-2c.

Solvent-free conditions were by far the most convenient and efficient ones (entry 3). With benzyl bromide at 100 $^{\circ}$ C, no special microwave effects were observed (entries 1 and 2).

When using benzyl chloride, similar yields (>90%) of product **3** were obtained both under MW and CH within 10 min at 150 °C. Although the MW effect is not apprecia-

ble at 150 °C, it was however possible to put into evidence an important specific MW effect by lowering the temperature to 100 °C (entry 5).

When benzyl trimethylammonium chloride 2c was used as the electrophile, no reaction took place under thermal heating at 150 °C whereas 70% of the product was formed after 10 min at 150 °C under MW irradiation. A very noticeable specific MW is therefore clearly revealed in this case. The yield reached 95% at 250 °C under MW and remained limited to 70% by CH.

By comparing the magnitude of the specific MW effects according to electrophile, we have thus established the sequence: 2c >> 2b > 2a.

In Table 2, we give the main results obtained for the reaction of tributylphosphine with 2a-2c under solvent-free conditions.

In the case of the reaction with benzyl bromide, yields are quite similar whatever the mode of activation (entries 8 and 9).

Using benzyl chloride, a quite important specific MW effect was revealed by shortening the reaction time at 100 °C (entry 11). These observations are in agreement with some

		t	Т	Yield for 3 using	Yield for 3 using
Entry	Х	(min)	(°C)	MW $(\%)^{a,b}$	CH (%) ^{<i>a,c</i>}
8	Br (2a)	0.75	100	94 (3aa)	92
9		2	80	78	73
10	Cl (2b)	10	100	92 (3ab)	87
11		0.75	100	91	64
12	$N^+Me_3Cl^-$ (2c)	10	100	100 (3ab)	0

Table 2. Solvent-free reaction of tributylphosphine 1a with benzylating agents 2a-2c.

^aYields in isolated products.

 ${}^{b}MW$ = microwave irradiation inside a monomode S 402 reactor.

^cCH = conventional heating inside a thermostatted oil bath under similar conditions.

Table 3. Solvent-free alky	ation of PR ₃ by	hexyl halides	$n-C_6H_{13}X$
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Entry	R	Х	t (min)	<i>Т</i> (°С)	Yield for 5 using MW (%) ^{<i>a,b</i>}	Yield for 5 using CH $(\%)^{a,c}$
13	$n-C_4H_9$ (1a)	Br	5	100	95 (5aa)	78
14			1	60	30	2
15		Cl	90	150	81 ^d (5ab)	40
16	$C_{6}H_{5}$ (1b)	Br	10	120	65 (5ba)	11
17			10	150	72	70
18		Cl	120	150	72^d (5bb)	11

^aYields in isolated products.

 ${}^{b}MW$ = microwave irradiation inside a monomode S 402 reactor.

^cCH = conventional heating inside a thermostatted oil bath under similar conditions.

^dUsing a CEM Discover microwave device in closed vessels and under magnetical stirring.

Fig. 1. Profiles for the rise in temperature for the MW and CH methods.



previous ones. To find any evidence of specific MW effects, a reduction in the temperature and (or) reaction time under CH is needed to start from a rather poor yield to have the possibility of observing any specific MW effects. These cases have been revealed in some studies where MW effects appeared at lower temperatures. They can be masked at higher temperatures when yields of CH reactions are high (29–32).

With the charged electrophile 2c, a very decisive specific effect is evidenced within 10 min at 100 °C; the reaction only occurred under MW and not at all by CH (entry 12).

The order of relative magnitude of specific MW effects leads to the same sequence as with 1b: 2c >> 2b > 2a. By comparing the two phosphines, it can be established that the specific MW effects are: 1b > 1a (compare entries 5 and 11 with 2b).

We finally examined the reaction of the two phosphines with n-hexyl halides (eq. [2]). The main results are given in Table 3.

$$\begin{array}{cccc} PR_3 & + & n - C_6 H_{13} & \longrightarrow & n - C_6 H_{13}^+ PR_3 X^- \\ 1 & 4 & 5 \end{array}$$

[2]
$$1 (a) R = n - C_4 H_9$$
 $4 (a) X = Br$
(b) $R = C_6 H_5$ (b) $X = Cl$ $5aa R = n - C_4 H_9, X = Br$
 $5ab R = n - C_4 H_9, X = Cl$
 $5ba R = n - C_6 H_5, X = Br$
 $5bb R = n - C_6 H_5, X = Cl$

Scheme 1.



Scheme 2.



(Tight ion pair)

In the case of 1a, within 5 min at 100 °C, the reaction essentially occurred with hexyl bromide and with only slight MW effects (entry 13). With hexyl chloride at 150 °C within 90 min in closed vessels, a yield of 81% was obtained under MW and only 40% via CH. The magnitude of specific MW effects is clearly 4b > 4a.

With **1b**, satisfactory yields were obtained as well with bromide and chloride. Important MW specific effects were revealed (entries 16 and 18). The magnitude of these specific MW effects are clearly 1b > 1a.

Discussion

If the problem of thermal homogeneity can be taken into account, essentially when the reaction gave a solid during the reactions of triphenylphosphine **1b** (Table 1, most of the products are solids), this is not the case for the reactions of tributylphosphine **1a** (Table 2, most of the products are liquids). These problems are, however, largely minimized due to efficient mechanical stirring and accurate measurement of the temperature with an optical fiber inside the mixture.

In recent reviews (15, 16, 33), a lot of specific MW effects were explained and foreseen by considering the enhancement in polarity during the progress of the reaction. It is stated, from numerous experiments from our laboratory and the literature that they can be observed in a reaction if the transition state (TS) is more polar than its ground state (GS). It thus results in an increase in its stabilization by dipole–dipole electrostatic interactions and, consequently, a decrease in the activation energy.

Another important rule for the observation of MW effects is connected to the position of the TS along the reaction coordinates. In a polar mechanism, the later the TS (more product-like) the most important the MW effects; they will be weak if the TS is more reactant-like.

Benzyl halides

It was shown in both cases that benzyl chloride is more prone to lead to MW effects. The mechanism of the reaction (Loose ion pair)

concerns two neutral reagents leading to a dipolar TS (Scheme 1).

Concerning the leaving group ability, it is clear that chloride is a poorer electrofugal group when compared to the bromide equivalent, if we consider, for instance, the bond energies (C-Br, 66 kcal mol⁻¹ and C-Cl 79 kcal mol⁻¹) (34). Therefore, the TS involving C—Cl bond breaking will occur later on the reaction coordinates than the one involving C-Br. It, therefore, can justify the increase in the magnitude of MW effects according to the sequence 2b > 2a.

Charged electrophiles

When benzyl trimethylammonium chloride 2c was used as the reagent no reaction took place under thermal heating at 150 °C, whereas 70% of the product was formed after 10 min at 150 °C under MW irradiation. The magnitude of the specific MW effect is strongly amplified. It can be readily attributed to the very loose structure of the ion pairs in the TS (additionally involving the phenyl groups of the phosphine) and which are therefore far more polar than the initial tight ion pairs in the GS (positive charge is localized on the nitrogen atom) (Scheme 2).

This behavior can also be foreseen if one considers the poor leaving ability of the ammonium moiety and which induces a late TS along the reaction coordinates, and consequently, important MW effects.

Phosphine substituent effects

Effects are more important with triphenylphosphine **1b**. If one considers the reaction between two neutral reagents (Scheme 1), the polarity of the TS may be deeply affected by the substituent on the phosphorous atom. Triphenylphosphine is less nucleophilic than tributylphosphine and the phenyl ring being able to delocalize the δ^+ charge, the structure of the transition state is shifted to the product (late transition state), which results in the increase of the polarity of the TS when compared to an alkyl group. The consequence is that the MW effects are increased according to **1b** > **1a**, Fig. 2. Profiles for the rise in temperature for the MW absorption of 1a (–) and 1b (–) in toluene.



essentially due to the extended polarity of the TS when an aromatic ring is concerned.

This interpretation is corroborated by the fact the two phosphines in their initial states have similar polarities if one considers their rises in temperature during MW irradiation (Fig. 2). A careful comparison between the two phosphines needs the addition of toluene for solubility (**1a** being liquid and **1b** solid).

Conclusions

We have observed specific MW effects depending essentially on the leaving group. Whereas they are rather weak with benzyl bromide, they are increased with chloride and even more with benzyl trialkylammonium salts. This behavior is compatible with the consideration of the position of the TS along the reaction coordinates, which induces an increase in the MW effects. The effects are more pronounced with triphenylphosphine **1b** due to the partial positive charge delocalization in the phenyl ring in the TS. The result is an enhancement in the polarity of the TS and consequently an improvement in the MW effects' magnitude. They could be perhaps better quantitatively understood in the future by consideration of some theoretical approaches including quantification of the polarity of the transition state when compared to the ground state (17, 35, 36).

Experimental

Microwave equipment

We have used a monomode reactor Synthewave[®] 402 from Prolabo (France) (37). The temperature was measured all along the reaction by IR detection, which indicates the surface temperature after previous calibration of emissivity in each case using an optical fibre inside the reaction mixture. The representative given temperatures are therefore accurate measurements of bulk homogeneous temperatures. The reactions were conducted using a cylinder tube in Pyrex under mechanical stirring to allow homogeneity inthe temperature. The power was monitored during irradiation to maintain a constant temperature. Occasionally, when reactions under closed vessels were necessary (entries 15 and 18), a CEM Discover microwave device was used.

Typical MW reactions

A mixture of 10 mmol of benzylating or alkylating electrophiles with 10 mmol of phosphine (1a (2.49 mL), 1b (2.62 g)) was homogenized by stirring and shaking. It was irradiated in the Synthewave[®] monomode MW reactor for the times and the temperatures indicated in the tables. After cooling down to room temperature, the solid materials were filtered off, washed with toluene, and dried. They were analyzed by ¹H and ¹³C NMR and the spectra were in agreement with authentic samples and the literature (38). They were also characterized by their melting points.

In the case where products are ionic liquids, they were washed with organic solvents to remove starting materials: cold diethyl ether for **5aa** and **5ab**, cold diethyl ether then hot toluene for **5ba** and **5bb**.

Experiments with xylene as the solvent (20 mL) were performed with 20 mmol of both starting materials. The product (phosphonium salts) were insoluble in xylene and were isolated by filtration followed by washing of the solid materials with fresh portions of xylene and diethyl ether.

Control experiments under conventional heating (Fig. 1)

In a thermostated oil bath at the same temperature as for MW irradiation, inside identical vessels and mechanical stirring, the two reactants were independently heated and mixed together. Temperature was evaluated inside the reaction mixture using the same optical fibre as for the MW evaluation (FISO, Universal Fiber Optic Sensor, FT1-10). Then the reaction was pursued for the same reaction time. The treatment and analysis remained identical.

Benzyltriphenylphosphonium bromide (3ba) (21, 38)

White crystals, mp 296 to 297 °C. ¹H NMR (CDCl₃, 300 MHz) & 5.44 (d, 2H, ² $J_{\text{Hgem}} = 14.56$ Hz, -CH₂), 7.11–7.13 (m, 4H, -Ph), 7.60–7.66 (m, 6H, -Ph), 7.72–7.79 (m, 10H, -Ph). ¹H NMR (DMSO- d_6 , 200 MHz) & 5.25 (d, 2H, ² $J_{\text{Hgem}} = 15.6$ Hz, -CH₂), 7.0 (d, 2H, ³J = 6.8 Hz, -Ph), 7.24 (m, 2H, -Ph), 7.6–7.8 (m, 14H, -Ph), 7.8–8.0 (m, 2H, -Ph). ¹³C NMR (DMSO- d_6 , 200 MHz) & 28.0 (d, ¹ $J_{\text{CP}} = 46.7$ Hz), 117.8 (d, ¹ $J_{\text{CP}} = 85.1$ Hz), 127.8 (d, ² $J_{\text{CP}} = 8.5$ Hz), 128.2, 128.7, 130.0 (d, ³ $J_{\text{CP}} = 12.2$ Hz), 130.7, 133.9 (d, ² $J_{\text{CP}} = 8.9$ Hz), 135.0.

Benzyltriphenylphosphonium chloride (3bb) (38)

White crystals, mp 333–337 °C. ¹H NMR (CDCl₃, 300 MHz) δ : 5.59 (d, 2H, ²J_{Hgem} = 14.40 Hz, -CH₂), 7.10–7.12 (m, 4H, -Ph), 7.59–7.65 (m, 6H, -Ph), 7.71–7.78 (m, 10H, -Ph).

Benzyltributylphosphonium bromide (3aa) (39):

White crystals, mp 149 °C. ¹H NMR (CDCl₃, 300 MHz) δ : 0.93 (t, 9H, ³J_{HH} = 6.96 Hz, 3 × -CH₃), 1.42–1.50 (m, 12 H, 3 × -CH₂CH₂), 2.38–2.47 (m, 6H, 3 × -CH₂P), 4.28 (d, 2H, ²J_{Hgem} = 15.02 Hz, -CH₂P), 7.33–7.39 (m, 3H, -Ph), 7.45–7.49 (m, 2H, -Ph). ¹H NMR (DMSO-*d*₆, 200 MHz) δ : 0.90 (t, 9H, ³J_{HH} = 6.6 Hz, 3 × -CH₃), 1.30–1.50 (m, 12H, 3 × -CH₂CH₂), 2.10–2.30 (m, 6H, 3 × -CH₂P), 3.95 (d, 2H, ²*J*_{Hgem} = 15.6 Hz, -CH₂P), 7.30–7.50 (m, 5H, -Ph). ¹³C NMR (DMSO-*d*₆, 200 MHz) δ: 13.1, 16.9 (d, ¹*J*_{CP} = 46.7 Hz), 22.5 (d, ²*J*_{CP} = 4.2 Hz), 23.3 (d, ³*J*_{CP} = 15.5 Hz), 25.4 (d, ¹*J*_{CP} = 44.2 Hz), 127.8, 129.0, 129.3, 129.9.

Benzyltributylphosphonium chloride (3ab) (40, 41)

White crystals, mp 163 to 164 °C. ¹H NMR (CDCl₃, 300 MHz) δ : 0.92 (t, 9H, ³*J*_{HH} = 6.59 Hz, 3 × -CH₃), 1.43–1.48 (m, 12H, 3 × -CH₂CH₂), 2.38–2.48 (m, 6H, 3 × -CH₂P), 4.31 (d, 2H, ²*J*_{Hgem} = 15.38 Hz, -CH₂P), 7.33–7.39 (m, 3H, -Ph), 7.45–7.49 (m, 2H, -Ph). ¹H NMR (DMSO-*d*₆, 200 MHz) δ : 0.90 (t, 9H, ³*J*_{HH} = 6.75 Hz, 3 × -CH₃), 1.30–1.50 (m, 12H, 3 × -CH₂CH₂), 2.10–2.30 (m, 6H, 3 × -CH₂P), 3.90 (d, 2H, ²*J*_{Hgem} = 15.6 Hz, -CH₂P), 7.30–7.50 (m, 5H, -Ph). ¹³C NMR (DMSO-*d*₆, 200 MHz) δ : 13.0, 17.5 (d, ¹*J*_{CP} = 46.8 Hz), 22.5 (d, ²*J*_{CP} = 5 Hz), 23.5 (d, ¹*J*_{CP} = 15.7 Hz), 25.5 (d, ¹*J*_{CP} = 80 Hz), 128.0, 129.0, 129.5, 130.0

Hexyltriphenylphosphonium bromide (5ba) (42, 43)

mp 195–198 °C. ¹H NMR (CDCl₃, 300 MHz) δ : 082 (t, 3H, ³J = 6.78 Hz, -CH₃), 1.19–1.28 (m, 4H, 2 × -CH₂), 1.57–1.69 (m, 4H, 2 × -CH₂), 3.80 (m, 2H, -CH₂P), 7.68–7.89 (m, 15H, 3 × -Ph). Insoluble in diethyl ether or toluene at their respective boiling points; soluble in acetone.

Hexyltriphenylphosphonium chloride (5bb)

mp 209 to 210 °C. ¹H NMR (CDCl₃, 300 MHz) & 0.82 (t, 3H, ³J = 6.87 Hz, -CH₃), 1.18–1.28 (m, 4H, 2 × -CH₂), 1.57–1.68 (m, 4H, 2 × -CH₂), 3.92 (m, 2H, -CH₂P), 7.67– 7.92 (m, 15H, 3 × -Ph). ¹³C NMR (CDCl₃, 200 MHz) & 13.0, 21.2, 21.5 (d, ²J_{CP} = 3.7 Hz), 21.5 (d, ¹J_{CP} = 49.6 Hz), 29.1 (d, ³J_{CP} = 15.3 Hz), 30.2, 117.3 (d, ¹J_{CP} = 82.5 Hz), 129.6 (d, ³J_{CP} = 12.3 Hz), 132.6 (d, ²J_{CP} = 9.8 Hz), 134.2. Insoluble in diethyl ether or toluene at their respective boiling points; soluble in acetone.

Hexyltributylphosphonium bromide (5aa)

¹H NMR (CDCl₃, 300 MHz) δ : 0.87–1.01 (m, 12H, 4 × –CH₃), 1.29–1.35 (m, 4H, 2 × –CH₂), 1.47–1.60 (m, 16H, 8 × –CH₂), 2.40–2.53 (m, 8H, 4 ×-CH₂P). The product behaves like an ionic liquid and becomes solid upon freezing (–18 °C); insoluble in diethyl ether at room temperature.

Hexyltributylphosphonium chloride (5ab)

¹H NMR (CDCl₃, 250 MHz) & 0.90 (t, 3H, ³*J* = 6.96 Hz, -CH₃), 1.00 (t, 9H, ³*J* = 6.79 Hz, 3 × -CH₃), 1.20–1.40 (m, 4H, 2 × -CH₂), 1.40–1.70 (m, 16H, 8 × -CH₂), 2.30–2.60 (m, 8H, -CH₂P). ¹³C NMR (CDCl₃, 250 MHz) & 13.2, 13.7, 18.7 (d, ¹*J*_{CP} = 47.4 Hz), 18.9 (d, ¹*J*_{CP} = 47.0 Hz), 21.5 (d, ²*J*_{CP} = 5 Hz), 22.1, 23.6, 23.7 (d, ³*J*_{CP} = 15.2 Hz), 30.2 (d, ³*J*_{CP} = 14.7 Hz), 30.8. The product behaves like an ionic liquid and becomes solid upon freezing (-18 °C); insoluble in diethyl ether at room temperature.

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