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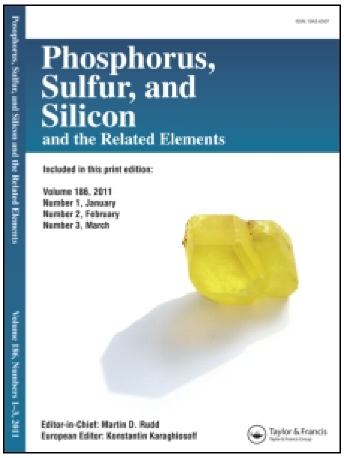

Phosphorus, Sulfur, and Silicon and the Related Elements

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New Phosphonated Methacrylate Monomers with C2/C3 Spacers

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Syntheses of new phosphonated methacrylates with 2 or 3 hydrocarbon methylene spacers were investigated in order to avoid the conventional methacrylation of hydroxyphosphonate compounds with methacryloyl chloride. The first possibility concerns the esterification of methacrylic anhydride in the presence of either 2-hydroxyethylphosphonate or 3-hydroxypropylphosphonate. This reaction was proved to be quantitative when a basic catalyst, i.e. n-methylimidazole, was used at 60°C. However, this reaction also generates a side product, i.e. methacrylic acid, which was difficult to remove due to it having similar solubility to both dimethyl(2-methacryloyloxyethyl)phosphonate and dimethyl(2-methacryloyloxypropyl)phosphonate. The second process was based on the alcoholysis of MMA in the presence of the above hydroxy compounds. This reaction also proceeded quantitatively with Zr(AcAc)$_4$ as acid catalyst. Unlike esterification of methacrylic anhydride, this second process did not require any solvent. The final phosphonated methacrylates were obtained with high purity, as the side product of the reaction (i.e., methanol) could be easily removed due to the azeotropic behavior of MMA / Methanol.

Keywords Alcoholysis; phosphonated methacrylate; transesterification

INTRODUCTION

Organophosphorus monomers are widely studied as they can be used for flame resistance improvement[1–4] or as adhesion promoters for paints

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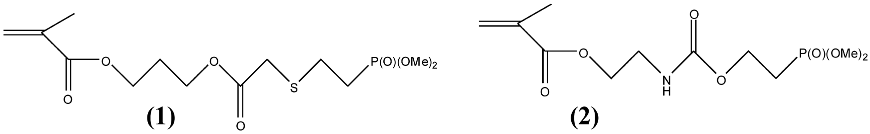
and adhesives.[5] More specifically, phosphonated monomers were used in emulsion polymerisation, conferring a very good stability to the corresponding lattices.[6–8] However the synthesis of such phosphonated monomers sometimes requires different organic reaction steps,[9–11] which can limit their applications. This paper will focus on providing a one-step synthesis of a new phosphonated methacrylate monomer $CH_2{=}C(CH_3)C(O)O(CH_2)_nP(O)(OR_1)(OR_2)$. Methacrylate has been chosen for its ability to polymerize through almost all controlled and conventional radical polymerizations, and due to its widespread application in paints for metals[12] and surfactant formulations.[13,14] This particular methacrylate monomer shows a hydrocarbon methylene spacer (with n being either 2 or 3) between the carbonyl and the phosphonate group, which is important as it brings stability towards hydrolysis. More recently some new phosphonated methacrylate monomers were attempted with CH_2 spacers, as illustrated in Figure 1, and bearing either an ester group (1)[15] or an urethane group (2)[16] in the spacer, both these functions could be however easily hydrolyzed. Finally, the above-mentioned structure shows R_1 and R_2 groups, which can be equivalent or not and can be an ester, acid or a salt function, bringing different functionalities to the further polymeric structure.

As depicted in Figure 2, the literature affords different pathways for reaching such phosphonate methacrylate structure, perfectly described in the paper of Senhaji et al.[17] These reaction proceed as follows: Arbuzov reaction (A)[18,19] using a trialkylphosphite, radical addition onto vinyl methacrylate (B),[20] Michael addition onto vinyl phosphonate (C)[21] and methacrylation using a hydroxyphosphonate precursor under the Schoten-Baumann conditions (D).[22] However, due to the experimental conditions (high temperatures) of reactions (A) and (C), radical thermal polymerization of methyl methacrylates is likely to occur. Reaction (B) may also lead to some extent of methyl methacrylate polymerizations by telomerization as hydrogenophosphonate is a well-known chain transfer agent. Pathway (D) is certainly the most extensively used because it usually leads to completion of methacryloyl chloride. Our group[23–25] applied this technique to reach a series of phosphonated



(1) **(2)**

FIGURE 1 Phosphonate methacrylate monomers with hydrocarbon methylene spacers.

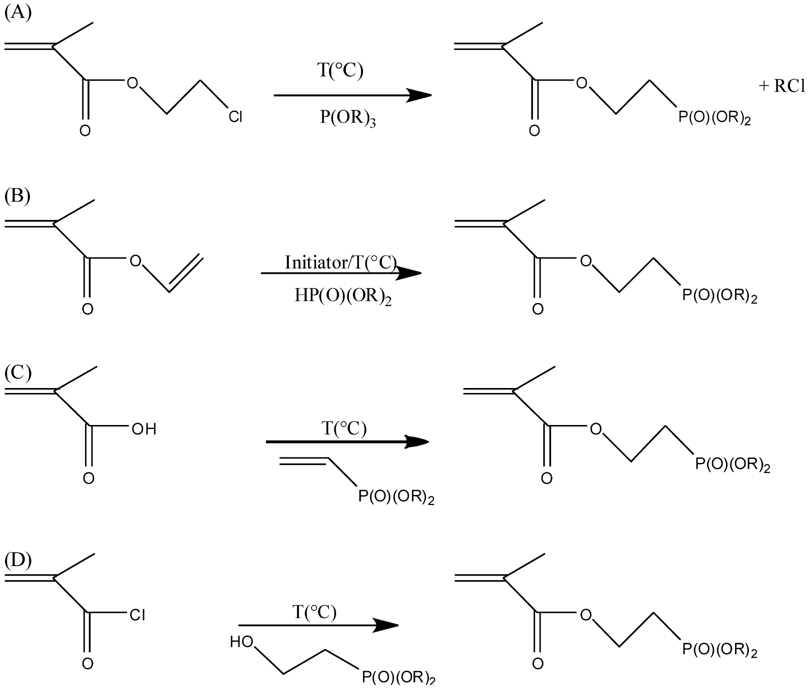


FIGURE 2 Synthetic pathways for reaching the $CH_2{=}C(CH_3)C(O)O(CH_2)_n P(O)(OR_1)(OR_2)$ structure.

metacrylate (and their acid derivatives), recently patented by Riondel et al.,[12] and also synthesized more recently a phosphonated methacrylate with a C11 spacer using this methacrylation technique.[17] However, as shown in pathway (D) of Figure 2, this synthesis requires the use of methacryloyl chloride, this product being highly toxic and also expensive, which limits its industrial application. This paper aims at supplying alternatives to the use of methacryloyl chloride for the synthesis of new phosphonated methacrylate with a C2/C3 spacer.

RESULTS AND DISCUSSION

This paper describes the methacrylation of both 2-hydroxyethylphosphonate and 3-hydroxypropylphosphonate, previously synthesized by our group,[26] by using either methacrylic anhydride through an esterification reaction or methyl methacrylate, proceeding by an alcoholysis reaction, as shown in Figure 3.

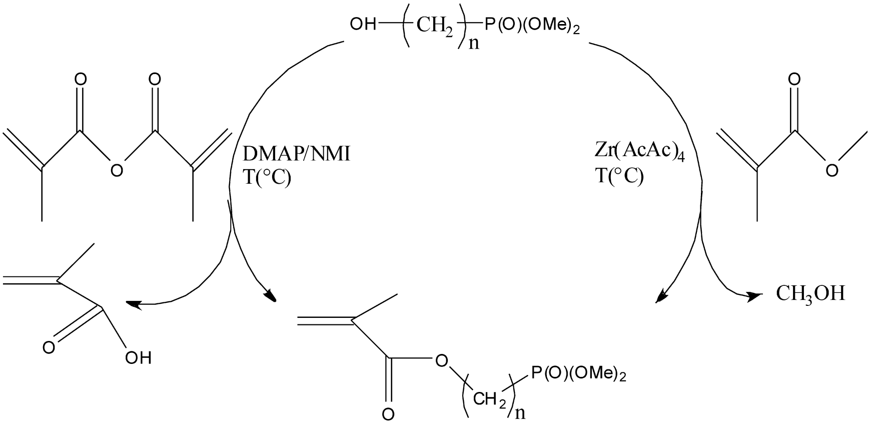


FIGURE 3 Syntheses of $CH_2{=}C(CH_3)C(O)O(CH_2)_nP(O)(OMe)_2$ with n = 2 or 3.

Esterification of Methacrylic Anhydride

Figure 3 shows that this reaction can be either basic or acid catalyzed but usually the basic catalysis proceeds more efficiently. The reactions were optimized by using different solvents at 40 and 60°C and by using two well-known basic catalysts, dimethylaminopyridine (DMAP) and N-methylimidazole (NMI). The results are gathered in Table I.

The reaction is completed when DMAP acts as a basic catalyst at 40°C but the reaction time remains high (16 h). With NMI at 60°C in ketone, the reaction time decreases to 5 h and the monomer is quantitatively obtained. Using these well-established reaction conditions, the conversions of both dimethyl 2-hydroxyethyl-phosphonate

TABLE I Methacrylation of Dimethyl 2-Hydroxyethylphosphonate and Dimethyl 3-Hydroxypropylphosphonate with Methacrylic Anhydride (1/1:% mol) Using a Basic Catalyst (5% mol.)

Hydroxyphosphonate	Basic catalyst	Solvent	T (°C)	Time (h)	[a]Monomer conversion (%)
$HO{-}(CH_2)_2P(O)(OMe)_2$	DMAP	CH_2Cl_2	40	5	68
$HO{-}(CH_2)_2P(O)(OMe)_2$	DMAP	CH_2Cl_2	40	16	100
$HO{-}(CH_2)_2P(O)(OMe)_2$	NMI	CH_2Cl_2	40	5	80
$HO{-}(CH_2)_2P(O)(OMe)_2$	NMI	CH_2Cl_2	40	16	100
$HO{-}(CH_2)_2P(O)(OMe)_2$	NMI	Butanone	60	5	100
$HO{-}(CH_2)_3P(O)(OMe)_2$	NMI	Propanone	60	9	100

[a] Determined by gas chromatography.

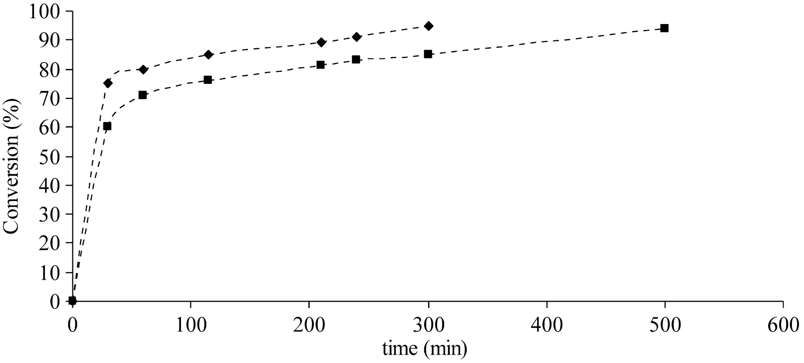


FIGURE 4 Kinetic evolution for the reaction of dimethyl 2-hydroxyethylphosphonate (◆) and dimethyl 3-hydroxypropylphosphonate (■) with methacrylic anhydride (1/1:% mol) at 60°C using NMI (5%) in butanone.

and dimethyl 3-hydroxypropylphosphonate into dimethyl(2-methacryloyloxyethyl)phosphonate and dimethyl(2-methacryloyloxypropyl)phosphonate, respectively, were plotted vs. time and reported in Figure 4. The esterification reaction of these two alcohols proceeds similarly, i.e., the reaction starts quickly, as more than 60% of alcohols reacted with methacrylic anhydride, then the rate of esterification dramatically decreases until complete conversion. This behavior can be explained by the formation of methacrylic acid, which then acts as efficient inhibitor for the basic catalyst. If this reaction is quantitative and operates in soft reaction conditions, it however requires the elimination of a side product, i.e., methacrylic acid, which may be hard to remove due to the very close solubilities than that of the resulting phosphonated methacrylates. An alternative to this procedure has to be found, in order to facilitate the purification.

Alcoholysis of Methyl Methacrylate

Figure 3 shows that the phosphonated methacrylate monomer can be obtained by transesterification reaction between methyl methacrylate and the corresponding hydroxyphosphonate, requiring the use of either an acid or basic catalyst. A series of basic (NMI, DMAP, tBuOK, $Mg(OEt)_2$) and acid ($Zr(AcAc)_4$, $Ti(OBu)_4$, APTS) catalysts have been employed for the methacrylation of dimethyl 2-hydroxyethylphosphonate without using any organic solvent at 90–100°C. Despite the relative acidity of dimethyl 2-hydroxyethylphosphonate, the preliminary results show that the basic catalysts are unexpectedly not efficient, as no conversion was observed,

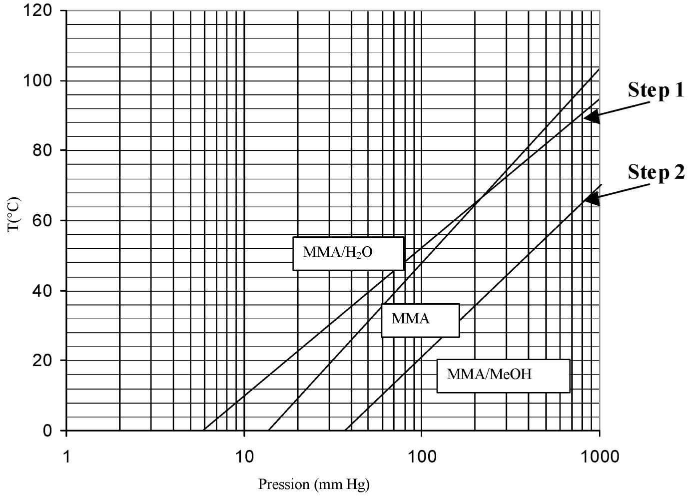


FIGURE 5 Temperature vs. pressure for MMA, MMA/MeOH and MMA/H_2O azeotropes.

which could be due to the steric effect of the reactive hydroxy group. Concerning the acid catalysts, only the Lewis acids are efficient, and more specifically $Zr(AcAc)_4$ catalyst. Wolf et al. demonstrated that these catalysts act through a ligand exchange which results in an activation of both ester electrophilicity and alcohol nucleophilicity[27] If tetraalcoxytintanates form clusters that decreases their catalytic efficiency, this behavior is not observed for $Zr(AcAc)_4$, which can explain their efficiency for the alcoholysis of MMA. Furthermore, $Zr(AcAc)_4$ catalyst shows a low toxicity and can be usually destroyed using phosphoric acid.[28] These preliminary tests led us to choose $Zr(AcAc)_4$ as catalyst for the alcoholysis of MMA with the corresponding phosphonated alcohol, using the following procedure. MMA is first used as a solvent in which phosphonated alcohol can be introduced and then both the pressure and temperature are adjusted in order to eliminate the MMA/H_2O azeotrope, boiling at a lower temperature than that of MMA itself (Step 1 of Figure 5).

As the system becomes anhydrous, which avoids any catalyst hydrolysis, $Zr(AcAc)_4$ can be added, allowing the reaction to start. The temperature then drops until reaching the corresponding temperature of the MMA/Methanol azeotrope (Step 2 of Figure 5) and the equilibrium can be displaced by methanol extraction until complete hydrolysis of MMA. This process, patented by Atofina,[12] affords the quantitative synthesis of phosphonated methacrylate monomers with C2 and C3 spacers, which were characterized by ^1H NMR (Figures 6 and 7), showing a

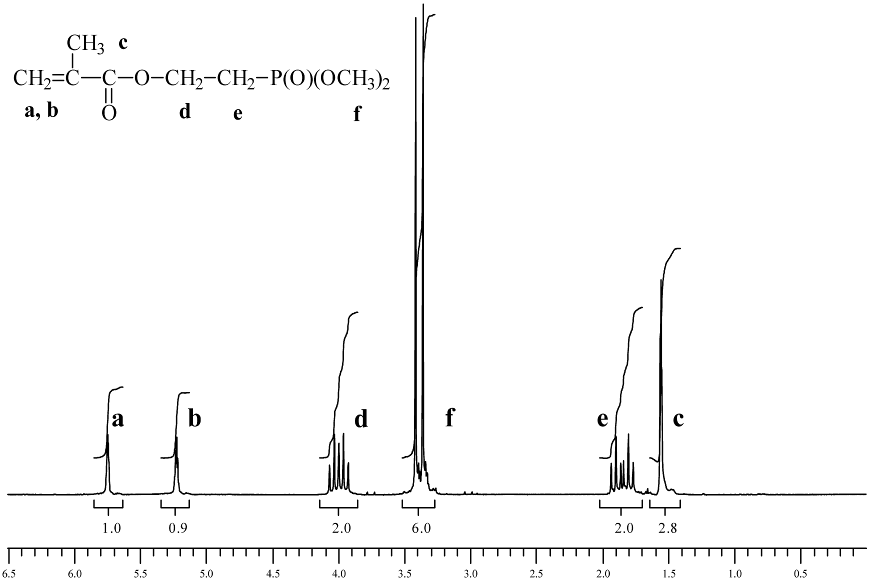


FIGURE 6 ^{1}H NMR ($CDCl_3$) of dimethyl 2-methacryloxyethylphosphonate.

very high purity (>95% purity). Both spectra especially show a doublet, centered at about 3.5 ppm, characterizing the methyl ester of the phosphonate group.

CONCLUSION

This paper supplied two new routes for the synthesis of phosphonated methacrylates in order to replace highly toxic methacryloyl chloride as starting product. These pathways are either the esterification of methacrylic anhydride or the alcoholysis of methyl methacrylate and are based on the use of hydroxyphosphonate compounds with 2 or 3 hydrocarbon methylene spacers. Despite the high conversion into phosphonated methacrylate, the esterification of methacrylic anhydride is limited by the purification of the resulting monomer. In the other way, the alcoholysis of MMA was shown to be highly efficient when $Zr(AcAc)_4$ catalyzed the reaction. No solvent was also required as MMA was both reactant and solvent of the reaction. High purity phosphonated methacrylates have been easily reached in a quantitative yield by simply adjusting both temperature and pressure, using the azeotrope behavior of MMA/H_2O and MMA/Methanol.

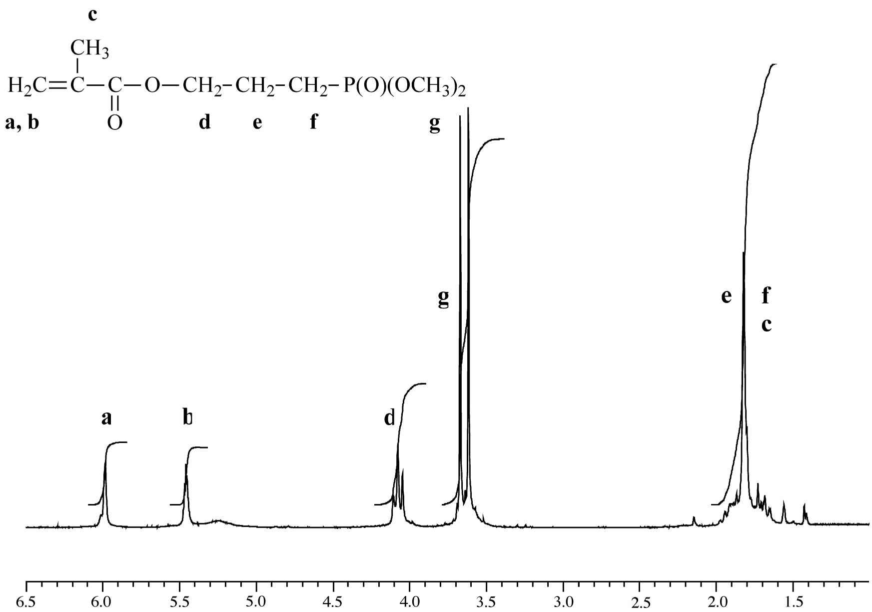


FIGURE 7 ^1H NMR ($CDCl_3$) of dimethyl 3-methacryloxypropylphosphonate.

EXPERIMENTAL

Reagents

Methyl methacrylate was purchased from Atofina and used as received. The syntheses were performed with commercial chemicals avalaible from Aldrich. The syntheses of 2-hydroxyethylphosphonate and 3-hydroxypropylphosphonate were described elsewhere.[26]

Characterizations

The chemical structure of the products was determined by ^1H NMR (Bruker AC 400 MHz) at room temperature in $CDCl_3$ solution. The INVGATE procedure with delay D1 of 10s was used to quantify the final yield. Gas Chromatography were recorded with a Hewlett Packard 5890 series II, using a DB210 capillary column (1μm, 30m) in a temperature range of 60 to 200°C at 20°C/min.

Synthesis of $CH_2{=}C(CH_3)C(O)O(CH_2)_nP(O)(OMe)_2$ with $n = 2$ or 3 by Esterification of Methacrylic Anhydride

In a 100 ml two-necked flask, equipped with a stirrer, a rubber septum and a condenser connected to a high purity nitrogen source, 15.4 g (0.1 mol) of 2-hydroxyethylphosphonate, 0.04 g (0.5% mol) of N-methylimidazole and 20 ml of butanone were introduced. The temperature was brought to 60°C and 15.4 g (0.1 mol) of methacrylic anhydride in 15 ml of butanone were added in a dropwise manner. The mixture was then stirred for 6 h. Solvent and residual products were evaporated under vacuum to yield a colorless dimethyl(2-methacryloyloxyethyl)phosphonate liquid (yield 100%).

The same procedure was repeated with 3-hydroxypropylphosphonate to yield dimethyl(2-methacryloyloxypropyl)phosphonate as a colorless liquid (yield 100%).

Synthesis of $CH_2{=}C(CH_3)C(O)O(CH_2)_nP(O)(OMe)_2$ with $n = 2$ or 3 by Alcoholysis of Methyl Methacrylate

In an 1l autoclave, equipped with a stirrer, a rubber septum and a condenser, 154.1 g (1 mol) of 2-hydroxyethylphosphonate**,** 300 g (3 mol) of MMA, 133.3 mg de MEHQ (600 ppm qsp) and 2.4361 g (0.5% mol) of $Zr(AcAc)_4$ were introduced. Vacuum is then adjusted to reach a temperature range of 95–110°C, which allows the elimination of MMA/MeOH azeotrope. After 2 h, the same amount of $Zr(AcAc)_4$ is added to complete the reaction. After 4 h residual MMA is eliminated and 200 g (yield $>$ 90%) of high purity ($>$95% by ^{1}H NMR) dimethyl(2-methacryloyloxyethyl)phosphonate are obtained by filtration.

The same procedure was repeated with 3-hydroxypropylphosphonate to yield dimethyl(2-methacryloyloxypropyl)phosphonate (yield $>$ 90%).

Dimethyl(2-methacryloyloxyethyl)phosphonate

^{1}H NMR($CDCl_3$) δ: 1.7 (s, 3H, $CH_2{=}C(C\underline{H}_3)$); 2.00 (td, 2H, $C\underline{H}_2$-PO, $^2J_{HP} = 16$Hz, $^3J_{HH} = 7.3$Hz); 3.7 (d, 6H, $POC\underline{H}_3$, $^3J_{HP} = 11.2$Hz); 4.2 (td, 2H, –O–$C\underline{H}_2$,$^3J_{HP} = 13.2$Hz, $^3J_{HH} = 7.3$Hz); 5.5–6.0 (d, 2H, $C\underline{H}_2 = C(CH_3)$).

^{31}P NMR ($CDCl_3$) δ: 29.88 (s).

Dimethyl(2-methacryloyloxypropyl)phosphonate

^{1}H NMR ($CDCl_3$) δ: 1.7 (s, 3H, $CH_2{=}C(\underline{CH_3})$); 1.7 (m, 2H+2H, $\underline{CH_2}\underline{CH_2}$-PO); 3.7 (d, 6H, $PO\underline{CH_3}$); 4.1 (t, 2H, –O–$\underline{CH_2}$); 5.4–6 (d, 2H, $\underline{CH_2}{=}C(CH_3)$).

^{31}P NMR ($CDCl_3$) δ: 35.18 (s).

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