

Electrolysis in Non-nucleophilic Media

Part I. Anodic Oxidation of Durene, Mesitylene and *p*-Xylene in Methylene Chloride

KLAS NYBERG

*Division of Organic Chemistry, University of Lund, Chemical Center,
P.O.Box 740, S-220 07 Lund 7, Sweden*

Anodic oxidation of durene in methylene chloride with tetrabutylammonium tetrafluoroborate as supporting electrolyte produced as major product a heptamethyldiphenylmethane formed in an electrophilic reaction between 2,4,5-trimethylbenzyl cation and durene. Oxidation of *p*-xylene gave mainly polymers but a trimethyldiphenylmethane was formed in a similar way as the product from durene. Anodic oxidation of mesitylene resulted in a one-electron transfer to give mesitylene cation radicals that react either by coupling or by attack on mesitylene to give bimesityl as the major product. Besides the hydrocarbons, chlorinated hydrocarbons were also formed but these were a result of molecular chlorination of the substrates.

Anodic oxidation of aromatic compounds has been shown to produce cationic species that in the presence of nucleophiles react to form stable products.¹ Anodic acetoxylation of methylbenzenes in acetic acid containing sodium acetate gives nuclear as well as side-chain substituted acetates²⁻⁷ and the mechanism of this reaction is now well understood. The phenyl acetates are formed by reaction between oxidized aromatics (cation radicals or dications) and acetate ions, while the benzyl acetates arise by transformation of the initially formed cations to benzyl cations (or to benzyl radicals that are rapidly oxidized to cations) and subsequent reaction with the electrolysis medium. The presence of acetate ions is not necessary for formation of benzyl acetates.⁷ A similar reaction mechanism has been proposed for other anodic substitution reactions.¹ For a more detailed description of anodic substitution mechanisms it is of interest to know whether the products are formed by oxidation of the substrate to a dication followed by chemical reaction (EEC mechanism) or oxidation to a cation radical followed by chemical reaction and a second electron transfer (ECE mechanism).^{8,9} Several groups have been interested in distinguishing between these two reaction paths. From studies on anodic oxidation of 9,10-diphenylanthracene it has been suggested

that the ECE mechanism should be operating in most anodic substitution reactions.¹⁰⁻¹³ These investigations have included cyclic voltammetric studies as well as observation of the cation radical by ESR.

Although nuclear substitution of aromatic compounds clearly involves initial oxidation of the aromatic compounds in most cases, and the same mechanism has been suggested for side-chain substitution,^{6,7,14,15} some authors have suggested a different course in the latter case.^{16,17} They propose that the supporting electrolyte or the solvent would be oxidized to radicals that abstract hydrogen atoms from the benzylic position of the aromatic side-chain and benzyl radicals would be formed. These could either couple with another radical or be oxidized to benzyl cations that react with the nucleophiles in the electrolysis medium. This mechanism has, however, little support from experimental data and in most cases it has been shown that the supporting electrolyte or the solvent are not oxidized at the anode potential employed for oxidation of the aromatic substrates.

The preparative study of anodic reactions of aromatic hydrocarbons has so far been restricted to media that contain nucleophiles strong enough to form stable products with the oxidized aromatics. In some cases products have been detected that are formed by attack of the oxidized aromatic compound on the substrate or by coupling of two radicals. These include diphenylmethanes,^{15,18} bibenzyls^{15,16,18} and biphenyls.¹⁸ The yields of these products are generally low.

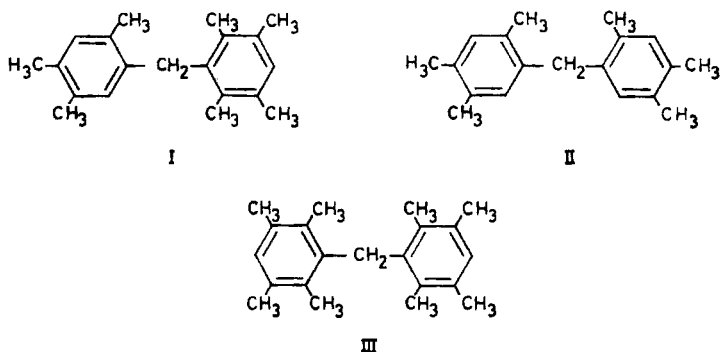
With no nucleophiles of appreciable strength in the electrolysis medium the substrate itself will act as a nucleophile towards the cations formed by anodic oxidation of aromatic hydrocarbons. Therefore one would expect the principal products to be hydrocarbons. Whether they are diphenylmethanes, biphenyls or bibenzyls is of interest in connection with the discussion of the mechanism of anodic substitution reactions. There have been some reports on anodic oxidation of aromatic compounds in media of low nucleophilicity, *e.g.* in methylene chloride¹¹ and nitrobenzene,¹² but these have been limited to electroanalytical studies. In the present work methylene chloride was chosen as solvent and tetrabutylammonium tetrafluoroborate (Bu_4NBF_4) as supporting electrolyte. The anodic limit for methylene chloride is reported to be 1.8 V (*vs.* SCE)¹⁹ and for Bu_4NBF_4 2.9 V (*vs.* Ag/Ag^+).²⁰ Durene, mesitylene, and *p*-xylene were chosen as substrates. Their anodic half-wave potentials in acetonitrile/sodium perchlorate have been determined and the reported figures are 1.29 V, 1.55 V, and 1.56 V, respectively, (*vs.* Ag/Ag^+).²¹

RESULTS

Anodic oxidation of the methylbenzenes was carried out in 0.1 M $\text{Bu}_4\text{NBF}_4/\text{CH}_2\text{Cl}_2$ between two platinum electrodes using the saturated calomel electrode as reference electrode.

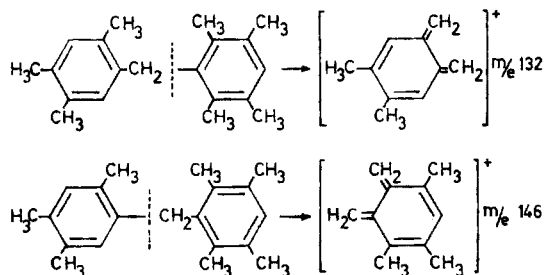
Anodic oxidation of durene (1.0 M) was carried out at an anode potential of 1.35 V until 1 *F* of charge per mole durene had been passed. GLC analysis revealed five peaks in the gas chromatogram. The major product was isolated by column chromatography on alumina and was identified as I. The mass spectrum showed the major peaks at *m/e* 266 (63 %), 251 (25 %), 146 (100 %),

and 132 (34 %). It is known that diphenylmethanes show characteristic mass spectra²² and they can be cleaved in two different ways as illustrated for I in Scheme 1. As a comparison bibenzyls give low abundance for the parent ion and high for the $m/2$ ion. The NMR spectrum of I (in CDCl_3) gave signals for the protons of the seven methyl groups (δ -values) at 2.03 ppm (9 H), 2.15 ppm (3 H), 2.23 ppm (6 H), and 2.33 ppm (3 H). The signal at highest field is assigned to the protons of the three methyl groups situated *ortho* to the methylene group, since they will be subjected to a diamagnetic shielding effect due to restriction in rotation by the phenyl rings. The methylene protons gave rise to a signal at 3.83 ppm and the aromatic protons to two signals at 6.25 ppm and 6.90 ppm (integrated area ratio 1:2). The signal at 6.25 ppm has a large upfield shift for a ring proton. It can be seen from a model that I is held with the rings perpendicular to each other because of steric hindrance due to the three methyl groups in the *ortho* positions. The *ortho* ring proton will therefore be situated under the opposite ring and this will cause a shield-



ing effect. The isolated yield of I (based on unrecovered durene) was found to vary from one run to another but was never lower than 25 %.

The other products from anodic oxidation of durene were identified as 3-chlorodurene, II, III, and chlorinated I on the basis of their mass spectra.



From the mass spectrum of chlorinated I it was shown that the chlorine atom was incorporated in the ring carrying four methyl groups since the two fragments corresponding to cleavage according to Scheme 1 were found at m/e 180 and 132, respectively.

In order to investigate the product distribution at an early stage of the electrolysis, anodic oxidation of durene was carried out until 0.1 F of charge per mole durene had passed. The major products were I and 3-chlorodurene with a small amount of chlorinated I as by-product, neither II nor III being formed. Using 0.2 M durene 14 % I and 14 % 3-chlorodurene were formed (current yields), with 1.0 M durene the corresponding figures were 29 % and 12 %, and with 2.0 M durene 32 % and 11 %, respectively. By varying the current density no appreciable difference in the yield of I was noted, but the yield of chlorodurene decreased somewhat with decreasing current density.

Anodic oxidation of mesitylene (1.0 M) was carried out at an anode potential of 1.80 V until 1 F of charge per mole mesitylene had passed. GLC analysis revealed five peaks in the gas chromatogram. The first peak was found to correspond to 2-chloromesitylene (isolated in a later experiment), the second to bimesityl IV by isolation and comparison with an authentic sample, the third to a chlorinated bimesityl identified on the basis of its mass spectrum; the fourth peak was identified as VI on the basis of its mass spectrum. The compound corresponding to the fifth GLC peak was isolated by column chromatography on alumina and structure V is proposed on the basis of mass and NMR spectra. The terphenyl would be expected to give a mass spectrum similar to biphenyls and this was confirmed by the fragmentation pattern that showed peaks at m/e 356 (100 %), 341 (30 %), and 326 (9 %). The NMR spectrum (in $CDCl_3$) is also in good agreement with the proposed structure. The signals appeared at 1.35 ppm (3 H), 1.78 ppm (18 H), 2.18 ppm (6 H), 6.83 ppm (4 H) and 6.97 ppm (1 H). The signal at 1.35 ppm is assigned to the protons in the methyl group situated in the middle ring *ortho* to the outer rings. The protons in this methyl group will be subjected to diamagnetic shielding effects by the two outer rings and therefore a large upfield shift is observed. The signal at 1.78 ppm is assigned to the protons in the six methyl groups situated in the remaining *ortho* positions. The protons in the two *para* methyl groups in the outer rings give rise to the signal at 2.18 ppm. The low field signals correspond to the four aromatic protons in the outer rings (6.83 ppm) and the proton in the middle ring (6.97 ppm).

Anodic oxidation of mesitylene carried out until 0.1 F of charge per mole mesitylene had passed gave with 0.2 M mesitylene 3 % (current yield) of 2-chloromesitylene and 1 % of IV. Using 1.0 M mesitylene the yields were 5 % of 2-chloromesitylene, 30 % of IV and 16 % of V. Finally, with 2.0 M mesitylene, the yields were 8 % of 2-chloromesitylene, 53 % of IV and 10 % of V. Electrolysis at different current densities had no effect on the yields.

The anodic oxidations of mesitylene (and also of *p*-xylene) produced polymeric material at the anode. This material was formed from the beginning of the electrolyses. This is not an unusual result in anodic oxidations and often causes a decrease in the current. In this work the opposite effect was observed and in order to keep the current within the range of the potentiostat the anode

potential was lowered. Therefore the anode potentials given for anodic oxidation of mesitylene and *p*-xylene are the starting anode potentials.

Anodic oxidation of *p*-xylene (1.0 M) was carried out at an anode potential of 2.10 V until 1 *F* of charge per mole *p*-xylene had passed. GLC analysis revealed several peaks in the gas chromatogram. The major peaks were identified as 2-chloro-*p*-xylene (identified by isolation) and the diphenylmethane VII. By comparison with authentic samples small amounts of 2,2',5,5'-tetramethylbiphenyl and 4,4'-dimethylbibenzyl were detected. From the mass spectra of other GLC peaks it was possible to identify a dichlorinated *p*-xylene, two chlorinated derivatives of VII, and trimeric compounds.

Anodic oxidation of *p*-xylene carried out until 0.1 *F* of charge per mole *p*-xylene had passed gave with 0.2 M or 1.0 M *p*-xylene 5 % of 2-chloro-*p*-xylene and 5 % of VII. Using 2.0 M *p*-xylene increased the yield of VII to 10 % while the yield of 2-chloro-*p*-xylene remained unchanged. In this experiment 2,2',5,5'-tetramethylbiphenyl was detected in less than 1 % yield.

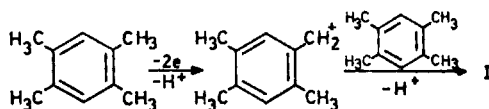
Some electrolyses were carried out in order to establish the mode of formation of the chloro compounds. When each of the substrates (1.0 M) were electrolyzed in 0.1 M $\text{Bu}_4\text{NBF}_4/\text{CH}_2\text{Cl}_2$ containing 0.2 M tetraethylammonium chloride until 0.1 *F* of charge per mole of methylbenzene had passed, the only products produced were the same chloro compounds that were formed when the substrates were oxidized in the absence of Et_4NCl . It was also found that when 0.1 M $\text{Bu}_4\text{NBF}_4/\text{CH}_2\text{Cl}_2$ was electrolyzed without addition of methylbenzene, chloride ions were formed at the cathode and chloride ions were oxidized to chlorine at the anode. If the electrolysis was interrupted and any of the three substrates were added to the electrolysis mixture chloro compounds were formed and they were identical to those formed in the electrolysis of the substrates in 0.1 M $\text{Bu}_4\text{NBF}_4/\text{CH}_2\text{Cl}_2$.

DISCUSSION

From the experimental data it is clear that the chlorinated products are not formed by oxidation of the aromatic substrates. Methylene chloride is reduced at the cathode and the resulting chloride ions are then oxidized to chlorine at the anode and molecular chlorination of the substrates gives the chloro compounds. In the presence of Et_4NCl oxidation of the aromatic compounds is inhibited. In the electrolysis without added Et_4NCl there is probably a slow formation of chloride ions and therefore oxidation of the substrates will not be inhibited. It is known that molecular chlorination of mesitylene and durene gives 2-chloromesitylene and 3-chlorodurene,²³ respectively.

Since there are results available from anodic oxidation of durene in different media it is of interest to make a comparison between these and the result from anodic oxidation in methylene chloride. Anodic oxidation of durene in sodium acetate/acetic acid gives 2,4,5-trimethylbenzyl acetate as major product and 2,3,5,6-tetramethylphenyl acetate as minor product while I is not formed.⁶ In $\text{Bu}_4\text{NBF}_4/\text{acetic acid}$ the major product is the trimethylbenzyl acetate and I is formed in about 5 % yield.²⁴ In sodium perchlorate/acetonitrile the major product is 2,4,5-trimethylbenzyl acetamide and I is formed in 25 % yield.¹⁵ Finally in $\text{Bu}_4\text{NBF}_4/\text{CH}_2\text{Cl}_2$ I is the major product. Thus

decreasing the nucleophilicity of the medium gives rise to an increase in the formation of I. This points to an electrophilic reaction where durene is oxidized to a benzyl cation that attacks durene to give I. The reaction path in Scheme 2 is suggested for the formation of I. From the data it is not possible to distinguish between an EEC or ECE mechanism.

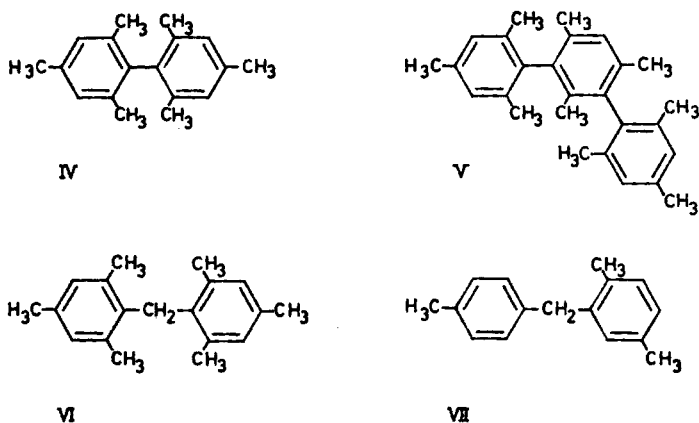


Scheme 2.

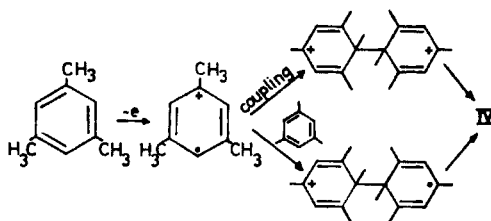
Two minor products were also detected in the oxidation of durene. The formation of II probably occurs by attack of the 2,4,5-trimethylbenzyl cation on durene and loss of a methyl cation. In III a methylene group has been incorporated between two durene units but there is no good explanation for its formation.

From the anodic oxidation of durene, the major product, I, could be isolated by column chromatography on alumina and the yield based on unrecovered durene could be calculated. It was found that the preparative yield mostly was higher than the current yield and sometimes as high as 85 %.

Anodic oxidation of mesitylene in $\text{Bu}_4\text{NBF}_4/\text{CH}_2\text{Cl}_2$ afforded as major products IV and V and neither a diphenylmethane resulting from attack of 3,5-dimethylbenzyl cation on mesitylene nor a bibenzyl resulting from coupling between two 3,5-dimethylbenzyl radicals were detected. Thus the major reaction path is a one-electron oxidation of mesitylene to give a cation radical. From the results using different concentrations of mesitylene it is seen that the yield of IV and V is dependent on the mesitylene concentration. One should also note that V is formed even when only 0.1 F of charge per mole mesitylene has passed. The mesitylene cation radical can couple with another



cation radical to give a bimesityl dication that by loss of protons gives IV. It can attack mesitylene to give a bimesityl cation radical that can undergo a further one-electron oxidation to the dication and then form IV by loss of protons. A third possible reaction involves loss of a proton from the mesitylene cation radical and formation of a mesityl radical, which then can undergo several reactions. The intermediacy of cation radicals or radicals is supported by the dependence of IV and V on the mesitylene concentration. In a recent study it was suggested that anodic oxidation of benzene (in acetonitrile) gives cation radicals that form phenyl radicals by loss of protons.²⁵ The phenyl radicals would then initiate polymerisation. A similar reaction could also be operating in oxidation of mesitylene, but with regard to the low nucleophilicity of the electrolysis medium and to the fact that IV is formed in such a large yield it is suggested that either a coupling between two cation radicals or attack of a cation radical on mesitylene is responsible for formation of IV (Scheme 3). The formation of IV by anodic oxidation of mesitylene is also supported by a recent investigation, where anodic oxidation of mesitylene dissolved in a complex between mesitylene, AlCl_3 and HCl produces IV.²⁶



Scheme 3.

The formation of V could occur either by oxidation of IV (the oxidation potential of IV was found to be about the same as for mesitylene) and subsequent attack of bimesityl cation radical on mesitylene or by attack of mesitylene cation radical on IV. The latter route is more probable at the early part of the electrolysis, since there will then be a much higher concentration of mesitylene cation radicals than bimesityl cation radicals at the anode.

The formation of VI from anodic oxidation of mesitylene is probably analogous to the formation of III from durene. It should also be noted that while oxidation of durene also gave II, where loss of a methyl cation has occurred, the same type of product was not detected in the mesitylene oxidation. This suggests that the incorporated CH_3 group originates from the solvent.

The yield of volatile products from anodic oxidation of *p*-xylene was low and it seems as if the major reaction path is polymerisation. It is seen that both one-electron and two-electron transfer take place although the product resulting from one-electron transfer is formed in low yield.

The suggestion that anodic substitution reactions involve initial one-electron transfers to give cation radicals is supported by the results from the anodic oxidation of mesitylene and in part from *p*-xylene in methylene chloride. The result from anodic oxidation of durene, however, only shows that I is

formed in an over-all transfer of two electrons. The reason for diphenylmethane formation in oxidation of durene but not in oxidation of mesitylene is probably due to better stabilization of the 2,4,5-trimethylbenzyl cation than of the 3,5-dimethylbenzyl cation. If durene is oxidized to a cation radical, this will probably be rapidly converted to a benzyl cation by further oxidation and loss of a proton.

Other interesting aspects of anodic oxidation of aromatic compounds in solvents of low nucleophilicity will be reported later.

EXPERIMENTAL

The electrolyses were carried out in a water-jacketed cell (volume 60 ml) equipped with a cylindrical platinum anode (surface area 50 cm²) and a platinum foil electrode and with stirring using a magnetic stirrer. The saturated calomel electrode was used as reference electrode. The anode potential was controlled by means of the Model 557 potentiostat from Amel, Milan, Italy. The amount of charge passed through the electrolyte was measured by an Amel Model 558 Integrator. The cell temperature was maintained at about 25°. Gas chromatographic analysis was carried out with a Perkin-Elmer Model 880 gas chromatograph, equipped with a Perkin-Elmer Model D 24 integrator on a 2 m × 0.3 cm 5 % NPGS on Chromosorb W column and a 2 m × 0.3 cm 5 % SE-30 on Chromosorb W column. Mass spectrometric analysis was carried out with an LKB 9000 mass spectrometer in combination with GLC at 70 eV. NMR spectra were recorded with a Varian A 60 A NMR spectrometer.

Material. Durene, mesitylene, *p*-xylene, and methylene chloride were of reagent grade quality. Tetrabutylammonium tetrafluoroborate, m.p. 164–165°, was prepared by mixing equivalent amounts of tetrabutylammonium hydrogen sulphate²⁷ and sodium tetrafluoroborate in water. The precipitate was dissolved in methylene chloride and dried over molecular sieves. Finally the solvent was removed and the residue washed with ether and dried in an oven at 70°. 2,4,5-Trimethylbenzyl chloride and 3,5-dimethylbenzyl chloride were prepared from the corresponding alcohols,²⁸ bimesityl was kindly supplied by Dr. Rolf Håkansson, 4,4'-dimethylbibenzyl, 2,2',5,5'-tetramethylbiphenyl and VIII were kindly supplied by Fil.kand. Luis Gomez at this department.

Electrolyses. After each electrolysis, methylene chloride was removed by evaporation *in vacuo*, ether was added to the residue and the insoluble Bu₄NBF₄ was filtered off. The ether solution was then analyzed by GLC and mass spectrometry. The results that have not been presented earlier are given below.

The electrolysis residue from anodic oxidation of durene (when 1 *F* of charge per mole durene had passed) was dissolved in pentane and subjected to column chromatography on alumina. Successive elution gave unreacted durene and a white solid, m.p. 160–162°, identified as I. (Found: C 89.8; H 9.75. Calc. for C₂₀H₂₆: C 90.2; H 9.80). From mass spectra of the GLC peaks II, III, and chlorinated I were identified. II gave *m/e* 252 (87 %), 237 (46 %), 152 (100 %), III gave *m/e* 280 (59 %), 265 (19 %), 146 (100 %), and Cl-I gave *m/e* 302 (28 %), 300 (81 %), 285 (21 %), 265 (19 %), 182 (36 %), 180 (100 %), 132 (43 %). The GLC peak that was assigned as 3-chlorodurene was not altered after the electrolysis residue had been treated with boiling sodium acetate/acetic acid. Comparison with 2,4,5-trimethylbenzyl chloride showed different retention times. The mass spectrum of 3-chlorodurene gave peaks at *m/e* 170 (30 %), 168 (92 %), 153 (16 %), 133 (100 %).

The electrolysis residue from anodic oxidation of mesitylene (when 1 *F* of charge per mole mesitylene had passed) was dissolved in pentane and subjected to column chromatography on alumina. Successive elution gave mesitylene, bimesityl IV, identified by comparison with an authentic sample, and crude V that could be obtained pure enough for NMR identification. 2-Chloromesitylene was obtained by electrolysis of mesitylene, Et₄NCl, Bu₄NBF₄ in CH₂Cl₂ at an anode potential of 1.20 V. After work-up 2-chloromesitylene was isolated by distillation; mass spectrum gave *m/e* 156 (21 %), 154 (65 %), 119 (100 %), NMR spectrum (in CCl₄) gave signals at δ = 2.13 ppm (3 H), 2.23 ppm (6 H), 6.70 ppm (2 H). Chlorinated IV and VI were identified on the basis of their

mass spectra, CI–IV gave m/e 274 (27 %), 272 (100 %), 259 (12 %), 257 (37 %), 237 (22 %), 222 (54 %), 207 (15 %), and VI gave m/e 252 (16 %), 237 (9 %), 132 (100 %).

The ether solution from anodic oxidation of *p*-xylene was analyzed by GLC and mass spectrometry and 2,2',5,5'-tetramethylbiphenyl, 4,4'-dimethylbibenzyl, and VII were identified by comparison with authentic samples (retention times, mass spectra). 2-Chloro-*p*-xylene, prepared in the same way as 2-chloromesitylene, was identified on the basis of its mass spectrum that gave peaks at m/e 142 (22 %), 140 (67 %), 105 (100 %) and NMR spectrum (in CCl_4) that showed signals at $\delta=2.20$ ppm (3 H), 2.27 ppm (3 H), 6.87 ppm (1 H), 6.93 ppm (1 H), 7.07 ppm (1 H).

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