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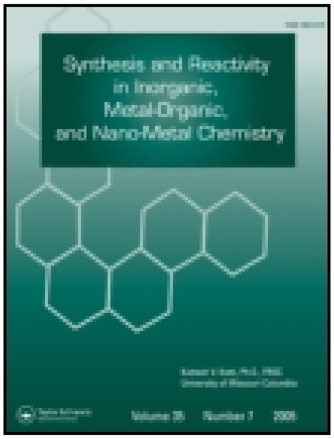

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Trichloroisocynuric Acid/DMF as Efficient Reagent for Chlorodehydration of Alcohols Under Conventional and Ultrasonic Conditions

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Trichloroisocynuric Acid/DMF as Efficient Reagent for Chlorodehydration of Alcohols Under Conventional and Ultrasonic Conditions

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A new and efficient method for the chlorodehydration of alcohols utilizing TCCA/DMF is described. Various alcohols can be converted smoothly into their corresponding alkyl chlorides in high yields under mild conditions with short reaction times.

Keywords: Alcohols, alkyl chlorides, chlorodehydration, N, N dimethyl formamide, sonication, trichloroisocyanuric acid

Introduction

Chlorination reactions are part of various processes in the chemical industry, to manufacture heavy chemicals, specialty chemicals, pesticides, and pharmaceuticals, in inorganic and organic chemistry. They are valuable tools in organic synthesis. Chlorodehydration[1–3] is one of the most important and commonly used transformations in organic synthesis and development of such a procedure is still desirable in industrial research. A number of reagents[4–16] have been employed to carry out this transformation Chlorination of alcohols using HCl[17] gas is a basic transformation, which often causes undesired side reactions. Ross Denton[18] et al. recently found that chlorination reaction of primary and secondary alcohols catalyzed by phosphine oxide under Appel conditions.[19] Halophosphonium[20] salts have emerged as versatile reagents for the conversion of aliphatic alcohols to alkyl halides. Recent reports of Yoshikazu Kimura[21] shows that new preparation method for Vilsmeier reagent using phthaloyl dichloride, which is a versatile synthetic reagent for the transformation of alcohols to chlorides. Direct Chlorination of alcohols catalyzed by lewis acids[22–25] under mild conditions afforded the corresponding alkyl chlorides. PPh_3/halogenated[26–28] reagents have been reported as viable ways for the chlorination of alcohols with high efficiency. Cynuric chloride/DMF[29] can be used as efficient transformation of alcohols to the corresponding chlorides at room temperature in DCM solvent.

Trichloroisocyanuric acid (TCCA) is an inexpensive, easily available reagent, low toxicity, and less corrosive, has been widely used in organic reactions13, but it has not been carefully studied as a catalyst in the synthesis of 2′-amino-benzo-thiazolo-arylmethyl-2-naphthols until now. In continuation of our efforts to explore newer reactions for the synthesis of heterocyclic compounds 14, we decided to explore the possibility of synthesizing TCCA is a stable, inexpensive, and versatile industrial chemical usually used as bleaching agent and bactericide. It is a disinfectant, algicide, and bactericide mainly for swimming pools and dyestuffs, and is also used as a bleaching agent in the textile industries. It is widely used in civil sanitation, pools, and spas, preventing and curing diseases in husbandry and fisheries, fruits and vegetables preservation, wastewater treatment, algicide for recycling water of industry and air conditioning, antishrink treatment for woolen, treating seeds, bleaching fabrics, and owing to their function as chlorinating agents and oxidants in organic synthesis.[30–32] Besides, it has found applications in organic chemistry as a chlorinating agent or oxidant, allowing conversion of various alcohols, aldehydes, and primary amines into the corresponding nitriles,[33,34] aryl-, heteroaryl-, alkenyl-, alkynyl-, and alkyltrifluoroborates into the corresponding chlorinated products.[35] Certain amonoacids were also cleanly and efficiently converted into nitriles by means of a decarboxylation reaction carried out with TCCA in water or methanol in the presence of pyridine.[36] 1, 3, 5-trisubstituted pyrazolines underwent oxidation to the corresponding pyrazoles by TCCA under both heterogeneous and solvent-free conditions.[37] Keeping in with these economically viable ongoing synthetic protocols, authors want to present certain results on chlorodehydrationusing

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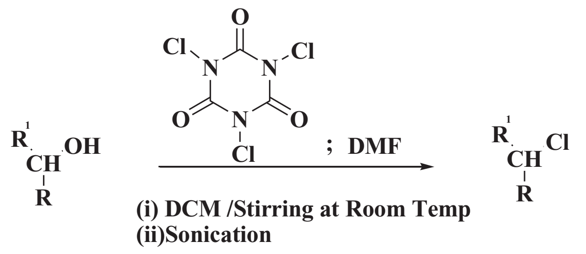
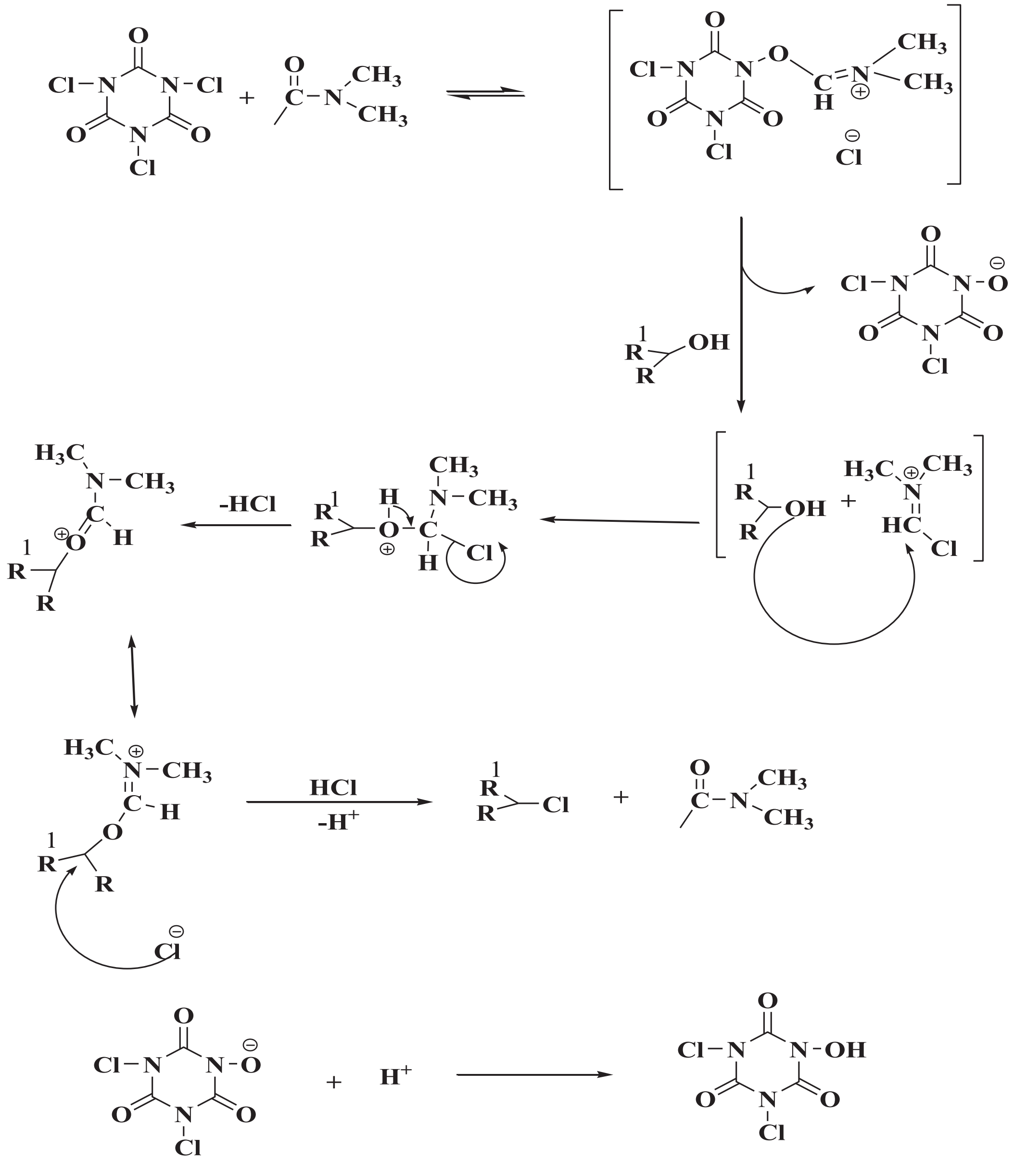


Sch. 1. TCCA/DMF mediated conversion of alcohols to alkyl chlorides.

TCCA/DMF. Keeping in with these economically viable ongoing synthetic protocols, authors want to present certain results on chlorodehydration of alcohols (Scheme 1) using TCCA under conventional (stirring at room temp) and non-conventional methods such as Sonication.[38]

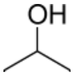
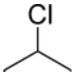
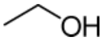
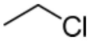
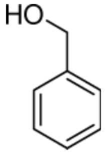
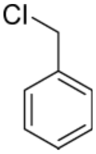
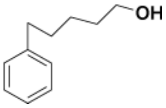
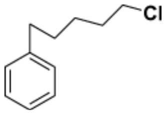
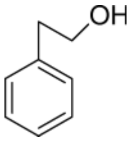
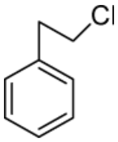
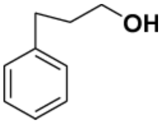
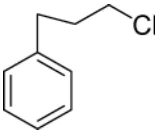
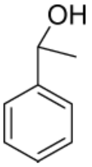
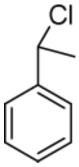
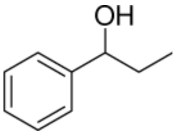
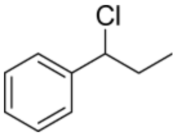
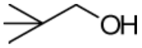
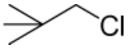
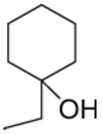
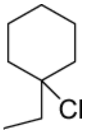
Results and Discussion

In the present study a variety of secondary alcohols underwent chloro dehydration under stirred conditions at room temperature and afforded alkyl chlorides in very good yields, when TCCA/DMF is used as a reagent in dichloromethane (Table 1). Mechanism of the reaction could be explained by the interaction of TCCA with DMF to afforded Vilsmeier-Haack (VH) type complex in the pre-equilibrium step. When alcohol is added, the hydroxyl group of the alcohol interacts with cholorome-thyleniminium species (cationic species). A subsequent nucleophilic attack of halide ion probably produces the corresponding chloride as depicted in Scheme 2. The observed stereo chemical results may further indicate the occurrence of a SN_2 reaction mechanism, shown in this reaction path.



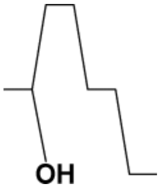
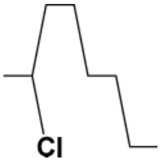
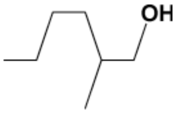
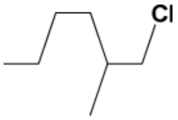
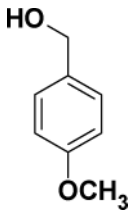
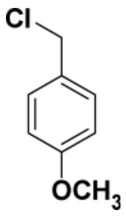
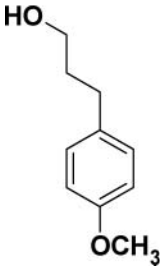
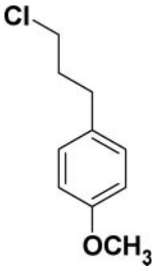
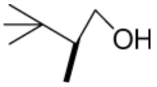
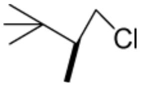
Sch. 2. Mechanism of Chlorodehydrationusing TCCA/DMF.

Table 1. Chlorination of Alcohols using TCCA/DMF.

			Reaction time (min)		
S. no	Alcohol	Product	Conventional	Sonication	Yield (%)
1			10	2	98
2			5	2	92
3			15	5	96
4			15	5	92
5			10	2	98
6			15	8	96
7			30	10	82
8			90	10	96
9			90	15	98
10			300	25	95
11			15	4	96

(*continued on next page*)

Table 1. Chlorination of Alcohols using TCCA/DMF. *(Continued)*

			Reaction time (min)		
S. no	Alcohol	Product	Conventional	Sonication	Yield (%)
12			25	8	93
13			10	2	97
14			15	6	98
15			15	6	98
16			20	4	96
17			20	6	95

Formation of [TCCA-DMF] adduct has been confirmed from infrared spectroscopic studies of DMF, TCCA, and prepared adduct (Figures 1–3). Infrared spectrum of DMF (Figure 1) depicted two broad bands in the range of 3336–3485 cm^{-1} (L, Broad) corresponding to N—H stretching (amide) and another broad band at 1675 cm^{-1} corresponding to C=O stretching frequency, which is lower than an unsubstituted C=O bond. This observation could be probably because of the contribution of the two possible resonance structures of amide which also caused a reduction in the bond order of the carbonyl C=O bond followed by an increase in the carbon-nitrogen bond order. The infrared spectrum of TCCA, in Figure 2, indicated three bands in the range 3240–3472 cm^{-1}(L), which can be attributed to N—Cl stretching frequency and another broad band at 1737 cm^{-1}, attributed to C=O stretching frequency. In the infrared spectrum of TCCA-DMF adduct (Figure 3), all the above bands underwent significant shifts, which can be seen at 3456 (L, Broad), 1671 (H, broad), and 1747.15(M to H) attributed to the interaction of TCCA with DMF.

The chlorodehydration reactions under present experimental conditions are generally fast which can be seen from the data presented Table 1. The reaction times for most of the studied reactions are in the range of 10–15 min. However, for 1-phenylpropan-1-ol, 2, 2-dimethylpropan-1-ol and 1-ethylcyclohexanol (entries 8–10) the reaction times were too high

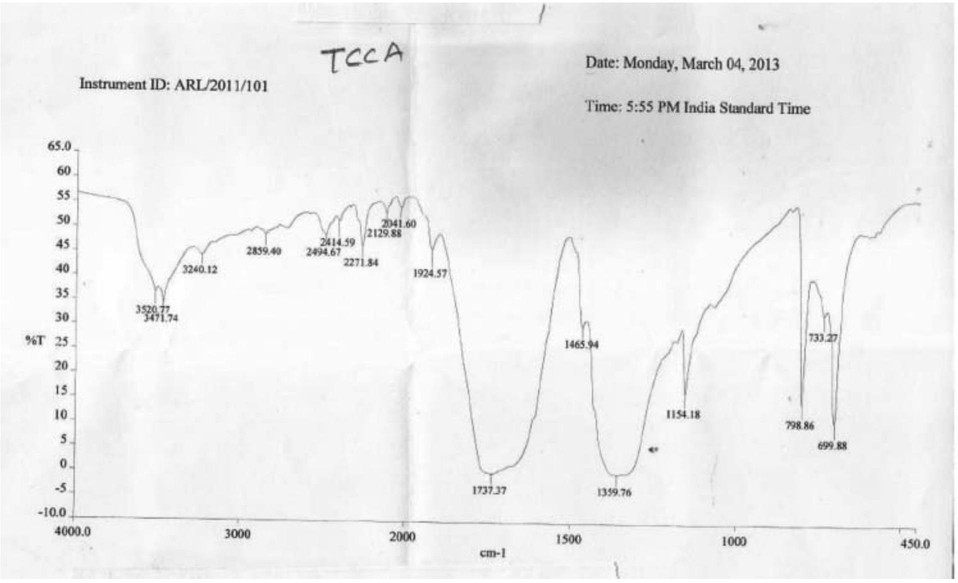


Fig. 1. Infrared Spectrum of TCCA.

(90–300 min). This can be explained due the enhanced steric effect compared to simple alcohols. The constrained alcohols required more time to reach the transition state because of the bulky groups attached to the functional carbon. In recent past, ultrasonic-assisted reactions have received the attention of Chemists with a view to save energy and improve greenery of the reaction protocols.[38] The pioneering work of Mason and Suslick on ultrasonics has emerged as boon to chemists to use ultrasonics as green reaction tool to achieve organic synthesis[39,40] with enormous reduction of reaction time associated with regioselectivity. The reactions were also studied under ultrasonic sonication with a view to reduce the reaction times of sluggish reactions. The efforts were found to fruitful. Reaction times of sluggish reactions (entries 8–10) reduced amazingly (from the 90–300 min range under conventional methods to 10–25 min) in ultrasonically assisted method. The dramatic sonocatalysis could be attributed to cavitation phenomenon as explained in earlier literature reports.[38–40]

In conclusion, we have developed a new and efficient method for the chlorodehydration of alcohols utilizing (trichloroisocyannuric acid) TCCA/DMF. Varieties of alcohols have been converted smoothly into their corresponding alkyl chlorides in high yields under mild conditions with short reaction times. It is an efficient, mild, and greenery method for the synthesis of alkyl chlorides. The developed method is environmentally safe, economically cheap, and most of the

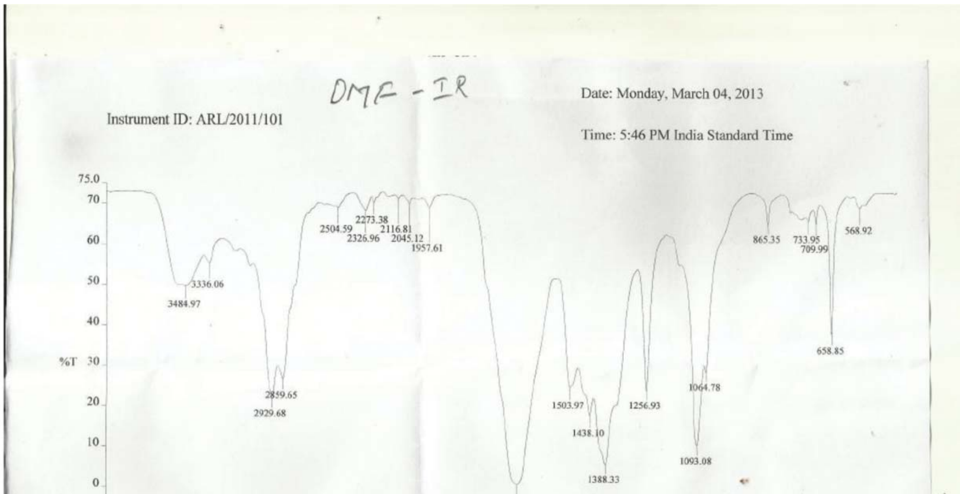


Fig. 2. Infrared spectrum of DMF.

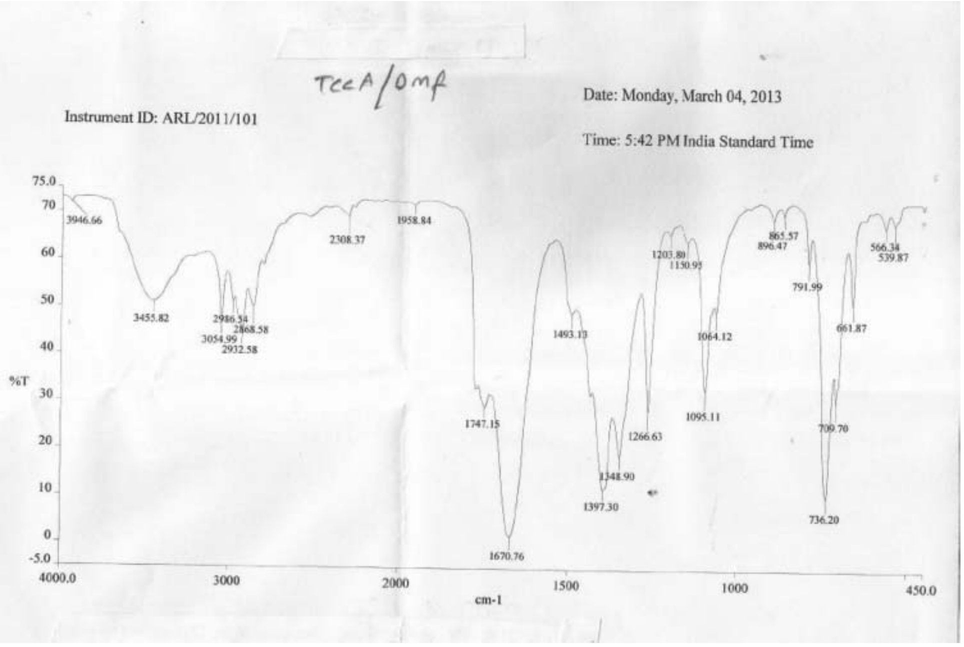


Fig. 3. Infrared spectrum of TCCA/DMF reagent.

chemicals used are available on the laboratory desktop. In view of these reasons, it is noteworthy to say that the developed methodology would make a good contribution in the field of green organic synthesis.

Experimental Section

Materials

All the chemicals were purchased from Aldrich or Arcos Organics and used without further purification. Analytical TLC was carried out using Merck aluminum-backed 0.2 mm silica gel 60 F-254 plates. Column chromatography was conducted using Merck silica gel 60 (230–400 mesh).

Synthetic Procedure

a) Preparation of TCCA-DMF reagent: TCCA-DMF reagent was always prepared fresh prior to the dehydrohalogenation reaction. One mole of each reactant viz., TCCA and DMF were added to CH_2Cl_2 solvent in a round bottomed flask and stirred for about 3 h at room temperature (25°C).
b) Dehydrohalogenation reaction using TCCA-DMF reagent: To the prepared TCCA-DMF reagent, one mole of alcohol was added under stirred conditions. Progress of the reaction was checked by TLC till the completion of the reaction. Then water was added to the reaction mixture and stirred for few more minutes to extract inorganic component into water. Organic layer was separated and washed with saturated solutions of K_2CO_3 and NaCl, dried over Na_2SO_4, and concentrated to obtain crude product. The crude product thus obtained was further purified with column chromatography (silica gel, ethyl acetate/*n*-hexane).
c) Dehydrohalogenation reaction using TCCA-DMF reagent under sonication: Methodology for the ultrasonically assisted dehydrohalogenation of alcohols by TCCA-DMF under sonication is by and large similar to the classical method. One mole of the prepared TCCA-DMF reagent and one mole of alcohol were placed in a reaction flask and clamped in a Sonicator. Progress of the reaction was checked by TLC till the completion of the reaction. After completion of the reaction as ascertained by TLC, similar work up procedure mentioned in the above section (classical method) is adopted to the alkyl chloride product. Products obtained were characterized by spectroscopic methods.

Representative Spectral data of certain compounds:

3. Benzyl chloride: ^{1}H NMR ($CDCl_3$): δ7.42–7.68 (m, Ar—H), 4.26 (s, 2H); m/z = 126

4. 5-Chloro pentyl benzene: ^{1}H NMR ($CDCl_3$) δ 7.34 (m, 2H), 7.24 (m, 3H), 3.38 (t, J = 6.9 Hz, 2H), 2.65 (m, 2H), 1.96 (m, 2H), 1.72 (m, 2H), 1.56 (m, 2H); m/z = 182

5. 2-Phenethyl chloride: ^{1}H NMR ($CDCl_3$): δ7.22 (m, 5H), 3.63 (t, J = 7.5 Hz, 2H), 2.95 (t, J = 7.5 Hz, 2H); m/z = 140

11. 1-Octyl chloride: ^{1}H NMR ($CDCl_3$): δ 3.55 (t, J = 6.5 Hz, 2H), 1.75 (m, 2H), 1.32 (m, 10H), 0.89 (t, J = 6.5 Hz, 3H); m/z = 148

12. S-(+)-2-octyl chloride: ^{1}H NMR ($CDCl_3$): δ 4.12 (J = 6.5 Hz, 1H), 1.72 (m, 2H), 1.42 (m, 11H), 0.95 (t, J = 6.5 Hz, 3H); m/z = 148

13. **2-chlorobutane:** ^{1}H NMR ($CDCl_3$): δ 3.84 (m, 1H), 1.65 (m, 2H), 1.42 (m, 3H), 0.95 (m, 3H); m/z = 92

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