$10^4-10^5\,M^{-1}$. Increasing the polarity of the solvent to 25% CD_2Cl_2 in CD_3CN (v/v) allowed association constants to be determined. In all cases the stoichiometry of the solution state complexes was determined to be 1:1.

The host was found to exhibit enhanced binding of acetate and nitrate over cyanide, chloride, dihydrogen phosphate and bromide, while the binding of hydrogen sulfate was negligible. This enhanced binding is most likely due to encapsulation of these geometrically equivalent guests and the formation of several hydrogen bonds from both above and below the plane defined by the anions.

Several pieces of data lead to the conclusion that the host/guest complex with nitrate involves the encapsulation of this anion in the cavity with six hydrogen bonds. First is the comparison of the geometry of acetate and nitrate, and the fact that acetate is encapsulated. Moreover, acetate binds only a factor of 2.6 times better than nitrate, although it is 10^6 times more basic. Further, dihydrogen phosphate is also significantly more basic than nitrate, yet it is precluded from the cavity due to size and therefore has a much lower affinity.

The results presented here demonstrate that amide NH proton donors are effective for hydrogen bonding to planar anions. Although acetate had the largest association constant of all the anions studied, hydrogen bonding between the geometrically matched host and nitrate led to enhanced binding, overcoming the weak coordinative ability of this anion.

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Tetraethylammonium Trichloride: A Versatile Reagent for Chlorinations and Oxidations**

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Functional-group manipulation is fundamental to synthetic organic chemistry, and the development of new reagents remains of great interest. Organic polyhalide salts have established themselves as useful reagents for halogenations.[1] Solid organic tribromides are a practical source of electrophilic bromine. However, the development of new reagents for chlorination is still unexplored, and only a few organic salts have been studied.[2] Here we demonstrate the efficiency of tetraethylammonium trichloride, a new organic salt that is a practical source of chlorine. This reagent was easily prepared by bubbling

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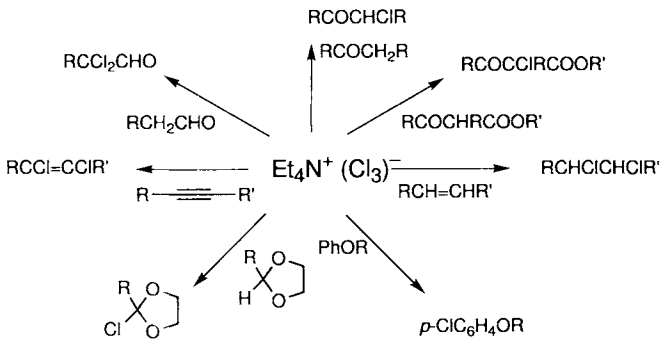
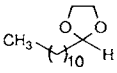
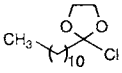
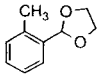
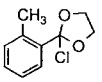
chlorine through a solution of tetraethylammonium chloride in dichloromethane. The content of active chloride was 3.2 mmol g^{-1}, and no decrease in activity was observed upon storage for several months at room temperature.

Several substrates including alkynes, alkenes, aldehydes, ketones, esters, acetals, and arenes were easily chlorinated under mild conditions (Scheme 1, Table 1). Alkenes and alkynes were converted into vicinal dichloroalkanes and dichloroalkenes, respectively, in good yields (entries 1–13). All reactions of the alkynes afforded the (*E*) stereoisomer exclusively, as determined from ^{1}H NMR spectra of the crude mixtures and confirmed by comparison with authentic samples. The reagent is equally compatible with alkynols (entry 4) or silylated alcohols (entry 5). THP-protected alkynols gave the desired product in low yields (entry 6, THP = tetrahydro-2*H*-pyran-2-yl), since side products probably arose from chlorination of the acetal group (entries 21 and 22).



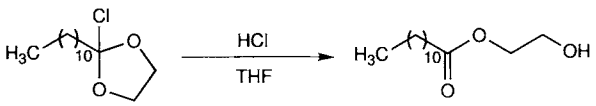
Scheme 1. Reactions with tetraethylammonium trichloride.

Table 1. Chlorinations with tetraethylammonium trichloride.

Entry	Starting material	Product	Yield [%]
1	$CH_3(CH_2)_3$—≡—$(CH_2)_3CH_3$	(*E*)-$CH_3(CH_2)_3CCl{=}CCl(CH_2)_3CH_3$	88
2	$CH_3(CH_2)_8$—≡	(*E*)-$CH_3(CH_2)_8CCl{=}CHCl$	100
3	$CH_3(CH_2)_5$—≡—$CH(OEt)_2$	(*E*)-$CH_3(CH_2)_5CCl{=}CClCH(OEt)_2$	82
4	$CH_3(CH_2)_6$—≡—CH_2OH	(*E*)-$CH_3(CH_2)_6CCl{=}CClCH_2OH$	100
5	$CH_3(CH_2)_6$—≡—$CH_2OSi\,tBuMe_2$	(*E*)-$CH_3(CH_2)_6CCl{=}CClCH_2OSi\,tBuMe_2$	56
6	$THPOCH_2$—≡—$(CH_2)_2OTHP$	(*E*)(*E*)-$THPOCH_2CCl{=}CCl(CH_2)_2OTHP$	29
7	3-hexyne	(*E*)-3,4-dichlorohexene	100
8	≡—COOEt	(*E*)- CHCl=CClCOOEt	76
9	$CH_3(CH_2)_5CH{=}CH_2$	$CH_3(CH_2)_5CHClCH_2Cl$	100
10	(*E*)-$EtOOCCH_2CH{=}CHCH_2COOEt$	$EtOOCCH_2CHClCHClCH_2COOEt$	100
11	$CH_3(CH_2)_2CH{=}CH\text{-}CH_2OH$	$CH_3(CH_2)_2CHClCHClCH_2OH$	100
12	cyclooctene	*trans*-1,2-dichlorocyclooctane	100
13	$PhCH_2CH{=}CH_2$	$PhCH_2CHCl\text{-}CH_2Cl$	100
14	$CH_3(CH_2)_9CH_2CHO$	$CH_3(CH_2)_9CCl_2CHO$	83
15	$PhCOCH_3$	$PhCOCH_2Cl$	100
16	(*E*)-PhCOCH=CHPh	(*Z*)-PhCOCCl=CHPh	100
17	cyclohexenone	2-chlorocyclohexenone	100
18	$CH_3COCHEtCOOEt$	$CH_3COCClEtCOOEt$	100
19	$PhOCH_3$	*p*-$ClC_6H_4OCH_3$	80
20	$PhOCH_2$—≡	*p*-$ClC_6H_4OCH_2$—≡	100
21			100
22			100

Direct dichlorination of saturated aldehydes at the α-position was achieved under mild conditions with two equivalents of tetraethylammonium trichloride (entry 14). Even with one equivalent of reagent, the reaction proceeded beyond the monochlorinated product. Ketones were selectively monochlorinated at the α-position (entry 15), but, unlike in the case of aldehydes, the reactions did not proceed to di- or trichloro derivatives. α,β-Unsaturated ketones (entries 16 and 17) were converted into the corresponding α,β-unsaturated α-chloroketones, probably via vicinal α,β-dichloroketones which underwent spontaneous dehydrohalogenation. Esters, with the exception of activated β-keto esters, failed to react (entry 18). Aromatic compounds activated with an electron-donating group were easily chlorinated at the *para* position (entry 19), and a bifunctional compound with both an activated aromatic ring and an alkyne functionality was preferentially chlorinated at the *para* ring position (entry 20).

Interestingly, the diethylene acetal of *n*-dodecanal was successfully chlorinated; the chlorine atom is on the dioxy carbon atom (entries 21 and 22). Treating this compound with 10% aqueous HCl afforded the corresponding ester in quantitative yield (Scheme 2). This is an unusual transformation, because the product usually isolated from the reaction of acetals with halogens is an α-halogenated acetal.[3] However, it was reported that acetals derived from non-enolizable aldehydes can be oxidized to the corresponding ester with *N*-bromosuccinimide under photolytic conditions[4] or in the presence of a radical initiator such as azobis(isobutyronitrile) (AIBN) or *t*-butyl peroxide.[5] However, in contrast to our chlorinated acetal derivatives, the intermediate brominated acetal could not be isolated.



Scheme 2. Hydrolysis of the chlorinated acetal.

In the presence of pyridine/1,4-diazabicyclo[2.2.2]octane (DABCO) in acetonitrile, tetraethylammonium trichloride oxidizes secondary and benzylic alcohols to the corresponding ketones or aldehydes (Table 2). The oxidation failed when dichloromethane was used instead of acetonitrile, or triethylamine in place of pyridine. Secondary alcohols were selectively

Table 2. Oxidations with tetraethylammonium trichloride.

Entry	Starting material	Product	Yield [%]
1	$PhCH_2OH$	PhCHO	100
2	$PhCHOHCH_2CH_3$	$PhCOCH_2CH_3$	71
3	menthol	menthone	100
4	$CH_3(CH_2)_2CH{=}CHCH_2OH$	$CH_3(CH_2)_2CHClCHClCH_2OH$	100
5	cyclohexanol	cyclohexanone	56
6	cyclooctanol	cyclooctanone	70
7	$CH_3(CH_2)_5CHOHCH_2OH$	$CH_3(CH_2)_5COCH_2OH$	100

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oxidized over primary alcohols (entry 7). Allyl alcohols were not oxidized, but chlorinated at the double bond (entry 4).

Compared to other reagents,[2] tetraethylammonium trichloride has several advantages as a chlorinating or oxidizing agent. This stable, crystalline solid is more convenient to handle, and—unlike in the case of iodoperchloride salts—the reaction times are greatly reduced, and no iodine is produced that can give rise to by-products. In general, chlorination of alkenes or alkynes proceeded stereoselectively in excellent yields. Interesting results were obtained with acetals, which afforded stable chloroacetals in which the chlorine atom is located on the dioxy carbon atom.

Experimental Section

Synthesis of $Et_4N^+(Cl_3)^-$: A solution of Et_4NCl in CH_2Cl_2 was saturated with Cl_2. The solvent was then removed in vacuo to afford a yellow solid which can be stored for months under an argon atmosphere.

Chlorination: $Et_4N^+(Cl_3)^-$ (1.5–3 equiv) was added in one portion under an argon atmosphere at −78 or 0 °C to a solution of the substrate (1 equiv) in CH_2Cl_2 (0.3 M). After addition of water, the organic phases were dried over $MgSO_4$ and filtered on celite. The solvent was removed in vacuo, and the crude compound purified by column chromatography.

Oxidation: $Et_4N^+(Cl_3)^-$ (1–3 equiv) was added to a solution of the alcohol in CH_3CN (0.3 M) and pyridine (4 equiv) at room temperature. After disappearance of the yellow color, DABCO (1 equiv) was added. After completion of the reaction, the crude mixture was concentrated in vacuo, and the residue was purified by column chromatography.

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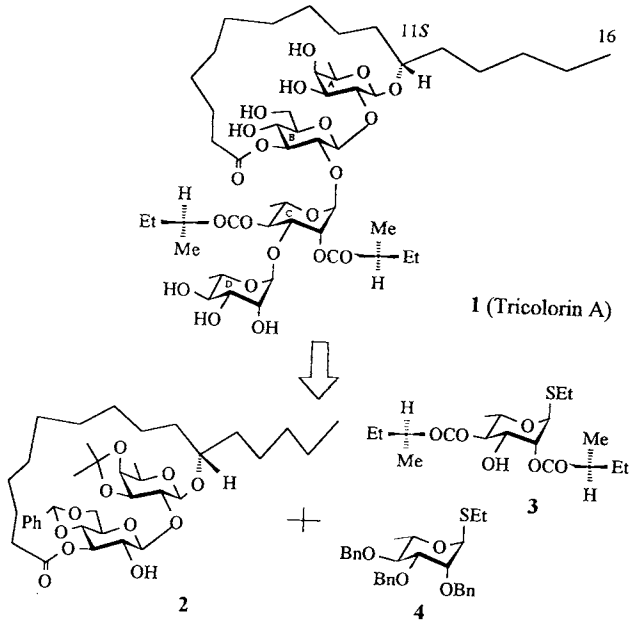
The First Total Synthesis of Tricolorin A

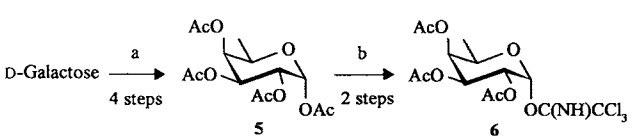
Shou-Fu Lu, QinQin O'yang, Zhong-Wu Guo, Biao Yu,* and Yong-Zheng Hui*

Tricolorin A, a member of the resin glycoside family, was first isolated by Pereda-Miranda et al. in 1993 from *Ipomoea tricolor cav.* (convolvulaceae), a plant used in traditional Mexican agriculture as a weed controller.[1] Bioassays showed that tricolorin A was not only largely responsible for weed-growth inhibition by the plant, but it also possessed significant cytotoxic activity against cultured P-388 and human breast cancer cells ($ED_{50} = 2.2\ \mu g\,mL^{-1}$).[1a] What attracted us most was the beauty of the structure of tricolorin A, which, bearing a disaccharide containing a 19-membered macrolactone, represents a perfect balance between hydrophobicity and hydrophilicity. We therefore directed our efforts towards the total synthesis of this interesting molecule, during the course of which Schmidt et al. accomplished a first total synthesis of another molecule of the resin glycoside family (calonyctin A).[2] Heathcock recently reported the synthesis of a macrolactone disaccharide subunit (**2**) of tricolorin A.[3] Coincidentally, we employed a similar strategy for assembling **2** in our total synthesis. Here we describe this total synthesis of tricolorin A. Of particular interest is the regioselective macrolactonization of a 1-hydroxycarbonyl-pentadec-10(s)-yl disaccharide to form the macrolactone disaccharide **2**, and a one-pot assembly of two monosaccharide donors (**3** and **4**, Scheme 1).[4]



Scheme 1. Retrosynthesis of tricolorin A.

First, four monosaccharide building blocks (**6**,[5] **8**,[6] **3**,[7] and **4**[4c]) were prepared as shown in Schemes 2–4. All are glycosyl donors either with a neighboring participating group (**6**, **8**, **3**) or with a strong anomeric effect (**3**, **4**) that is sufficient to cause highly selective β-glycosidation (for **6**, **8**) or α-glycosidation (for **3**, **4**). Methyl 11(s)-jalapinolate [methyl 11(s)-hydroxyhexadecanoate (**14**)][8] was prepared by employing a chiral-pool approach starting from D-(+)-mannitol (Scheme 5).[9]



Scheme 2. Preparation of monosaccharide synthon **6**: a) 1. anhydrous Cu_2SO_4, acetone, H_2SO_4 (concd, cat.), RT, 29 h, 62%; 2. *p*-TsCl (Ts = $H_3CC_6H_4SO_2$), pyridine (Py), 55 °C, 4 h, 94%; 3) $NaBH_4$, Me_2SO (DMSO), 120 °C, 5 h, 75%; 4. Ac_2O/HOAc (2/1), H_2SO_4 (concd, cat.), −15 °C, 4 h, 20%; b) 1. NH_3 in MeOH/THF (3:7), 0 °C, 3 h, 50%; 2. $CNCCl_3$, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), CH_2Cl_2, RT, 14 h, 79%.

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