

Electrophilic nitration of triphenylamines as a route to high oxidation potential electrocatalysts. Polynitration, nitrodebromination, and bromine dance

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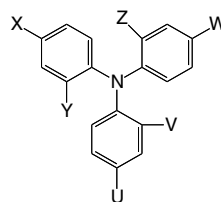
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Abstract—The nitration of triphenylamine derivatives is facile, readily leading to an introduction of up to three nitro groups at room temperature. The nitration of 4,4',4''-tribromotriphenylamine results in nitrodebromination on one or more rings and bromination at other sites.

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Our discovery that β -aryl- α -silyl esters can be anodically oxidized to afford unstable α -carbonyl carbocations¹ has aroused our interest in the possible synthetic applications of such cations. However, the fact that that oxidation of these silyl esters requires quite positive potentials¹ means that relatively few nucleophiles can be used in such applications. The electrocatalytic oxidation of these and related silanes, if feasible, would by definition occur at a lower potential. α -Silyl esters, however, will require electrocatalysts exhibiting more positive oxidation potentials than that of 4,4',4''-tribromotriphenylamine (**1b**), the best known catalyst of this type. Schmidt and Steckhan and co-workers synthesized a series of polybromotriphenylamines and found that the oxidation potentials of these substances increase with the increasing degree of bromine substitution.² These substances are attractive as potential electrocatalysts for organosilanes: they are readily soluble in a variety of organic solvents and afford stable cation radicals when all *para*-positions are substituted to sterically block dimerization of the cation radical.³ Indeed, we recently reported the use of an electrode-bound dibromotriarylamine for the electrocatalytic oxidation of a benzyl silane.⁴ The catalytic oxidation of α -silyl esters will require more positive oxidation potentials than are accessible with these substances. Since the electron-withdrawing effect of the nitro group is considerably greater than that of bromine, our interest turned to the synthesis

of nitrotriphenylamines, particularly those containing bromine substituents to improve solubility and further increase their redox potentials. Here we report the nitration of several triarylamines and the phenomena which take place upon nitration of **1b** under even very mild conditions.⁵



- 1a**, U = W = X = H = V = Y = Z = H
1b, U = W = X = Br; V = Y = Z = H
1c, U = NO₂; W = X = V = Y = Z = H
1d, U = W = NO₂; X = V = Y = Z = H
1e, U = W = X = NO₂; V = Y = Z = H
1f, W = X = U = CH₃; Y = V = Z = H
1g, Z = NO₂; V = Y = H; U = W = X = CH₃
1h, V = Y = NO₂; Z = H; U = W = X = CH₃
1i, V = Y = Z = NO₂; U = W = X = CH₃
1j, U = W = CH₃; X = Y = V = Z = H
1k, X = V = Z = NO₂; U = W = CH₃; Y = H
1l, X = Y = W = Br; Z = U = NO₂; V = H
1m, X = W = Br; Z = U = NO₂; Y = V = H
1n, X = Y = Br; U = W = NO₂; V = Z = H
1o, X = Br; U = W = NO₂; V = Y = Z = H
1p, X = Y = W = Br; U = V = Z = H
1q, X = W = Br; U = NO₂; U = Y = Z = H

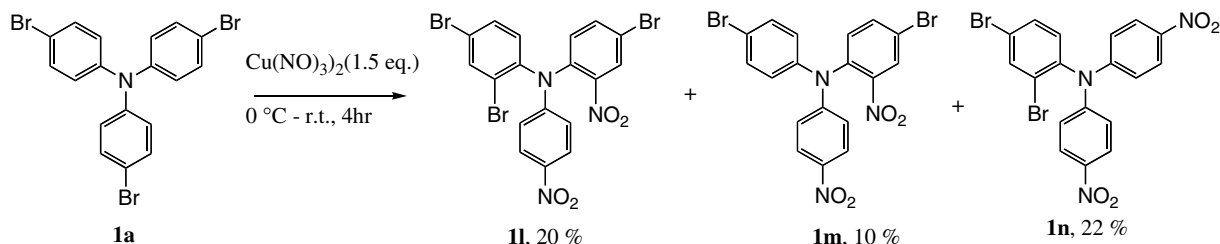
The nitration of triphenylamine (**1**) can be effected using Cu(NO₃)₂ in Ac₂O for 1–2 h at room temperature. The activating effect of the central nitrogen is quite striking, since even with a relatively small excess of nitrating agent (Cu(NO₃)₂/**1a** = 2:1) a mixture of mono-, di-, and trinitro 4-substituted triphenylamines (**1c–e**) is obtained, which can be separated by chromatography.⁶ Of these three, the only one likely to prove to be a stable electrocatalyst is **1e** because the other two have

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unblocked *para* positions. Unfortunately, this compound is rather insoluble in most solvents. It was of interest, therefore, to nitrate triphenylamines substituted at one or more *para* positions by other groups. The nitration of 4,4',4''-trimethyltriphenylamine (**1f**) for a few minutes at room temperature afforded a mixture of 2,2'-dinitro- and 2,2',2''-trinitro derivatives (**1h** and **1i**), separable by flash chromatography (90:10 hexane/EtOAc). By varying the conditions, it is possible to obtain reaction mixtures in which either the mono-, di-, or trinitro derivative (**1g–i**) constitutes the principal product (94–95% purity), though each is always accompanied by small amounts of the other congeners (see [Supplementary data](#)). In a like fashion, the reaction of 4,4'-dimethyltriphenylamine (**1j**) with excess nitrating agent readily affords 2,2',4''-trinitro-4,4'-dimethyltriphenylamine (**1k**). These substances are much more soluble in common solvents than **1d**.

The polynitro derivatives described thus far, or at any rate those fully substituted at the *para* positions, ought to be good electrocatalysts for processes requiring rather positive redox potentials. The triarylamines bearing more than three electron-withdrawing groups would be even more desirable, especially since the alkyl groups reduce the oxidation potentials of **1i** and **1k** to a degree. We have not observed **1d**, **1i**, and **1k** to exhibit heat or shock sensitivity. However, we have been reluctant to attempt to nitrate these substances any further, particularly since much more vigorous conditions would be required to do so. It appeared, though, that the nitration of 4,4',4''-tribromotriphenylamine (**1b**) could afford substances potentially bearing as many as six electron-withdrawing groups (three nitro and three bromo). The nitration of **1b**, however, took a very different course ([Fig. 1](#)). It was reacted at room temperature for 4 h with sufficient $\text{Cu}(\text{NO}_3)_2$ to introduce three nitro groups. The complex mixture that resulted could be separated only by a tedious procedure involving both flash column and preparative thin layer chromatographies. The products isolated, apart from several other substances formed in 1–5% yields, which could not be separated in pure form, consisted of 2,4,4'-tribromo-2',4''-dinitrotriphenylamine (**1l**) (20%), 4,4'-dibromo-2,4''-dinitrotriphenylamine (**1m**) (10%), and 2,4-dibromo-4',4''-dinitrotriphenylamine (**1n**) (22%) ([Fig. 1](#)). The bromination of 4,4'-dinitrotriphenylamine (**1d**) with 10 equiv of Br_2 at 0 °C also afforded **1n** (45%), together with the known⁴ monobromide (**1o**) (15%).

Triphenylamine (**1a**) and the di- and tri-*p*-tolyl derivatives **1f** and **1j** undergo the expected nitration at the



positions *para* or *ortho* to the central nitrogen atom. Bromination of **1d** also proceeds normally. Tribromide **1a**, however, reacts very differently under the same nitrating conditions. It is notable that in each of the three major products **1l–n** each of the rings exhibits a different substitution pattern. Products **1l–n** correspond to the replacement of one or more bromine atoms by the nitro groups; **1l** and **1n** correspond as well to intermolecular transfer of bromine. The first of these processes, nitrodebromination (Eq. 1) has been observed with a number of reactive aromatic systems, for example, bromine-containing furans, thiophenes, and pyrroles,⁷ phenols,^{8a} halophenylethers,^{8b} and porphyrins.^{9,10} Compound **1m** exhibits perhaps the simplest pattern: one of its nitro groups arises by the replacement of a bromine atom and the other by nitration *ortho* to the central nitrogen atom, suggesting that the attack at the *ipso* and *ortho* positions of **1a** has about the same activation energy. In compounds **1l** and **1n**, one of the rings contains two bromine atoms; the source of the second bromine atom is presumably the 'Br⁺' species released in the second stage of the nitrodebromination. In this sense, the bromine transfer is related to certain acid-promoted 'halogen dance' reactions.^{2,11–13} Not surprisingly, the second bromine is introduced only onto the rings carrying only a weakly deactivating bromine substituent, and not those bearing the strongly deactivating nitro group. To test for the liberation of Br⁺, a 4:1 mixture of tribromoamine (**1b**) and parent amine **1a** was subjected to the usual nitration conditions. The products consisted of a 60:40 mixture of 2,4,4'-tribromo-4''-nitrotriphenylamine (**1p**) and 4,4'-dibromo-4''-nitrotriphenylamine (**1q**). These products (and the absence of **1a** and **1b**) can only be explained by the release of free Br⁺ into the medium. In principle, nitrodebromination could also take place by acid-catalyzed debromination (Eq. 2) followed by the nitration of the debrominated material. This was ruled out by stirring **1b** overnight in acetic acid; no change was observed. Finally, the high reactivity of these triphenylamines is notable. The intrinsic reactivity of this system may be so high that nitration is encounter-controlled, even after the introduction of one or more nitro groups. It is likely that the reaction proceeds via an initial single electron transfer (SET) mechanism.¹⁴

Figure 1. Nitration of 4,4',4''-tribromotriphenylamine.

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Supplementary data

The NMR and mass spectrometric data for the new compounds and the experimental directions for their synthesis. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.tetlet.2006.08.139](https://doi.org/10.1016/j.tetlet.2006.08.139).

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5. The structures of all new compounds were established by 1-D and COSY ¹H NMR spectroscopy and both low and high resolution mass spectrometries; see [Supplementary data](#).
6. Nitration takes place at the 4-position of each ring, though 4-nitro compound **1c** is accompanied by a trace (<1%) of the 2-isomer.
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