

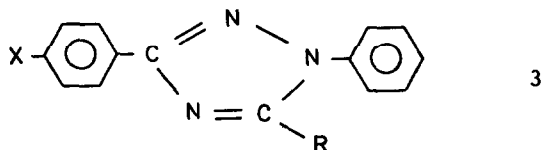
1,3-DIPOLAR CYCLOADDITIONS INDUCED BY CATION RADICALS. FORMATION OF
1,2,4-TRIAZOLES FROM OXIDATIVE ADDITION OF 1,4-DIPHENYLAZOMETHANE AND ARYL
ALDEHYDE PHENYLHYDRAZONES TO NITRILES

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Summary: Reaction of thianthrene cation radical perchlorate ($\text{Th}^+\text{ClO}_4^-$) with 1,4-diphenylazomethane (DPAM) in MeCN and EtCN led to the formation of 1,2,4-triazoles. Triazole formation is attributed to oxidative cycloaddition of benzaldehyde benzylhydrazone, the tautomer of DPAM, to the solvent nitriles. In confirmation, analogous cycloadditions were achieved by reaction of $\text{Th}^+\text{ClO}_4^-$ with some benzaldehyde phenylhydrazones in the same solvents.

We have found that 1,4-diphenylazomethane (DPAM) and a number of aryl aldehyde phenylhydrazones react with cation radicals and undergo facile oxidative cycloaddition with the nitrile solvent to form 1,2,4-triazoles. These reactions represent a novel cation-radical-induced cycloaddition. DPAM reacted rapidly with thianthrene cation radical perchlorate ($\text{Th}^+\text{ClO}_4^-$) in acetonitrile and propionitrile solvents. The major products are listed in Table I. It is seen that they account for 94.3% of the Th^+ and 98.4% of the DPAM in acetonitrile, and for 100.8% of the Th^+ and 95.9% of the DPAM in propionitrile. The surprising products from these reactions are the triazoles. We propose that these were formed from the oxidative cycloaddition of benzaldehyde benzylhydrazone, a tautomer of DPAM, to the solvent nitrile (Scheme 1). In order to test the validity of Scheme 1 we carried out reactions of the phenylhydrazones of some aryl aldehydes with $\text{Th}^+\text{ClO}_4^-$ in nitrile solvents. Oxidative cycloaddition occurred and the triazoles **3a-e** were obtained in high yield. Results are given in Table II.



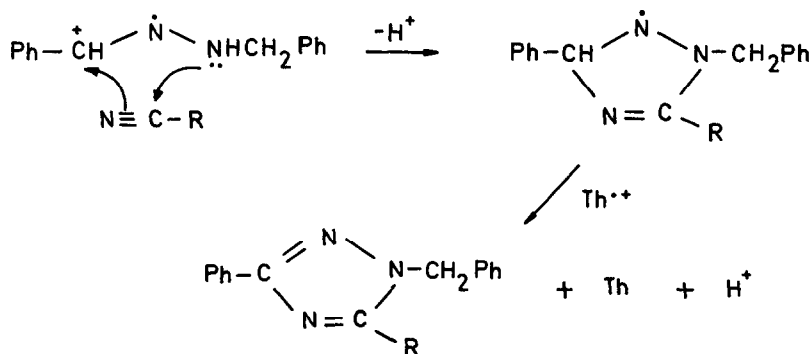
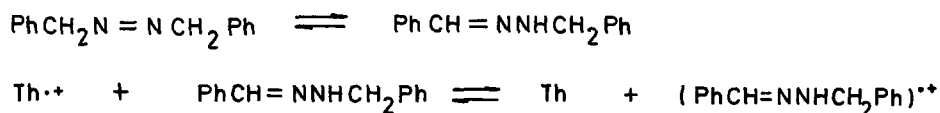
3a, X = H, R = Me ; **3b**, X = H, R = Et
3c, X = Me, R = Me ; **3d**, X = MeO, R = Me ; **3e**, X = MeO, R = Et

Triazole 1 was also obtained in 25% yield when DPAM reacted with $(p\text{-BrC}_6\text{H}_4)_3\text{N}^+\text{SbF}_6^-$ (4) in acetonitrile. Bibenzyl (28%) was again formed. Further separation of products proved not to be quantitative and their complete assay was not pursued.

Cation-radical Diels-Alder cycloadditions, catalyzed by 4, have recently attracted much attention.^{2,3} The cycloadditions we report here are not catalytic since a net two-electron oxidation is needed in the formation of the triazole.

1,2,4-Triazoles have been prepared earlier by the 1,3-dipolar cycloaddition of nitrilimines (e.g., $\text{ArC}^+=\text{N}^-\text{Ar}$) and nitriliminium ions, (e.g., $\text{ArC}^+=\text{NNHAr}$) to nitriles. These species are generated *in situ* from hydrazinoyl chlorides (e.g., $\text{ArC}(\text{Cl})=\text{NNHAr}$) by the action of triethylamine⁴ or aluminum chloride.⁵ The hydrazinoyl chlorides are prepared first from reaction of the hydrazides with PCl_5 .⁶ The method of cycloaddition reported here, insofar as these examples are concerned, provides a more direct preparation of 1,2,4-triazoles, and raises the interesting consideration of the possibility of 1,3-dipolar cation-radical cycloadditions.

Scheme 1



1, R = Me; 2, R = Et

We rationalize the formation of the other products listed in Table I as follows. Formation of the aldehyde can be attributed to hydrolysis of the hydrazone. The ThO resulted, we believe, from hydrolysis of some of the $\text{Th}^{*\cdot}$ by incompletely dried solvent during reaction, and/or of unused $\text{Th}^{*\cdot}$ during work up.⁷ Bibenzyl and the *N*-benzylamide resulted from the oxidative decomposition of DPAM by $\text{Th}^{*\cdot}$.⁸ The stoichiometry of the oxidations can be expressed by the equations 1-6. These equations tell us that benzyl radicals and benzyl cations are formed from an initial one-electron oxidation of DPAM. Some benzyl radicals are oxidized again

Table I. Products (%) of Reaction of Thianthrene Cation Radical with 1,4-Diphenylazomethane (DPAM) in Nitrile Solvents at Room Temperature.^a

RCN	Th ^d	ThO ^d	PhCH ₂ NHCOR ^d	(PhCH ₂) ₂ ^d	Triazole ^e , mp, °C
MeCN ^b	88.3	6.0	54.1	18.8	1, 25.5 70-71
EtCN ^c	98.0	2.8	25.2	10.5	2, 60.2 81-82

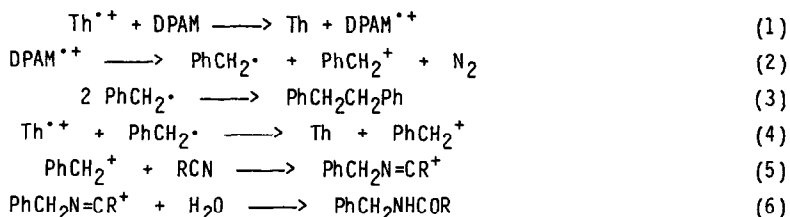
^a, A solution of DPAM was added by syringe to a stirred, septum-capped solution of Th^{•+}ClO₄⁻ under argon until the color of Th^{•+} was discharged. Stirring was continued for 24 h. Water was then added, the solution was neutralized with NaHCO₃ and extracted repeatedly with CH₂Cl₂. ^b, 21 mL containing 1.0 mmol of Th^{•+}ClO₄⁻ and 0.56 mmol of DPAM. ^c, 26 mL containing 2.0 mmol of Th^{•+}ClO₄⁻ and 1.1 mmol of DPAM. ^d, Identity confirmed by ¹H NMR, gc/ms, and comparison with authentic sample. ^e, Identity by ¹H NMR, gc/ms, and elemental analysis; crystallized from petroleum ether, 40-60°C/CH₂Cl₂.

Table II. Major Products (%) of Reaction of Thianthrene Cation Radical with Phenylhydrazones (*p*-XC₆H₄CH=NNHC₆H₅) in Nitrile Solvents at Room Temperature.^a

X	Solvent	ArCHO	Th	ThO	Triazole (3)	mp, 3, °C
H	MeCN	3.3	91.0	3.0	a, 80.8 ^b	95-96 ^c
H	EtCN	3.7	84.6	5.8	b, 95.8	76-77 ^d
Me ^e	MeCN	10.4	95.2	6.3	c, 71.8	103-104
Me ^e	MeCN	11.2	91.0	6.0	c, 68.6	103-104
MeO	MeCN	7.6	92.3	5.9	d, 93.4	88-89
MeO	EtCN	20.4	94.1	4.2	e, 61.7	104-105

^a, For brief exptl. details, see ref. 10. ^b, Yld using 2:1 stoichiometric amounts of reactants in CH₂Cl₂ soln. was 52%. ^c, Lit. mp 95-96°C.^{4,5} ^d, Lit. mp 77°C.⁵ ^e, Duplicate runs.

into benzyl cations which react with solvent in a Ritter-type way, leading to an N-benzylamide. Some benzyl radicals escape oxidation and dimerize to form bibenzyl. We emphasize that the eqs. 1-6 are not intended to be mechanistically explicit, and that oxidations may instead involve first the formation of a complex between Th^{•+} and DPAM.⁹



We have formulated the cycloaddition in Scheme 1 as between the hydrazone cation radical and nitrile. It is possible, though, that two-electron oxidation of the hydrazone occurs first, and that cycloaddition involves, instead, the nitriliminium ion (e.g. $\text{PhC}^+\text{H}=\text{N}=\text{NCH}_2\text{Ph}$). Clarification between these alternatives needs yet to be made. A third possible pathway to the triazole is that acid formed from hydrolysis of Th^{++} caused cycloaddition of hydrazone to acetonitrile, forming a dihydrotriazole, and that it was the oxidation of this by Th^{++} which led to the triazole. However, we were unable to detect the presence (by gc and gc/ms) of a dihydrotriazole when a solution of benzaldehyde phenylhydrazone in acetonitrile was acidified for several hours with a small amount of non-oxidizing $\text{CF}_3\text{SO}_3\text{H}$. Much of the hydrazone remained, along with benzaldehyde and a trimer of acetonitrile.

References and Notes

- Supported by the Robert A. Welch Foundation, Grant No. D-028, the National Science Foundation, Grant No. CHE 8314947, and the Center for Energy Research, Texas Tech University.
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- See Hammerich, D.; Parker, V. D. Adv. Phys. Org. Chem. **1984**, 20, 55-189 for discussions of complexation.
- A solution of the hydrazone (approx 0.7 mmol) in 10 mL of solvent was added by syringe dropwise to a stirred, septum-capped solution of $\text{Th}^+\text{ClO}_4^-$ (approx 1.4 mmol) in 25 mL of solvent under argon. The mmolar ratio of Th^+ /hydrazone was always 2.00:1.00. Stirring was continued for 4 h (5 h in case **3e**), after which the solution was diluted with water, neutralized with either Na_2CO_3 or NaHCO_3 , and extracted repeatedly with CH_2Cl_2 . Products were assayed in the CH_2Cl_2 solution by capillary (25 ft SE-30) and packed column (5% OV-101 on GHP 100/120) gc, and were identified by capillary gc/ms. Triazoles **3a** and **3b** were separated from the mixture of products by preparative TLC on Merck 2-mm plates. Triazoles **3c-e** were separated from the mixture of products by column chromatography on silica gel (Woelm). In these cases the other products were eluted first with petroleum ether (40-60°C) and mixtures of CH_2Cl_2 /petroleum ether, while the triazoles were eluted last with CH_2Cl_2 alone. Separation of triazoles from ThO was difficult. In preparing samples for elemental analysis the complete absence of ThO was first checked by capillary gc. Samples were then crystallized from CH_2Cl_2 /petroleum ether and sublimed. All triazoles had satisfactory ^1H NMR. All new triazoles had satisfactory elemental analyses (Micanal Lab, Tucson, Ariz.).

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