Formation of 1,2,4-Triazoles by Cation Radical Induced Oxidative Addition of Arylhydrazones of Benzaldehyde and Butyraldehyde to Nitriles

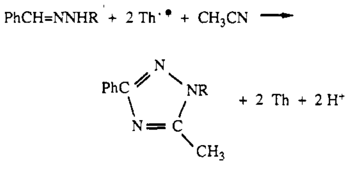
Henry J. Shine* and A. K. M. Mansurul Hoque

Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, Texas 79409

Received March 25, 1988

1,3,5-Trisubstituted 1,2,4-triazoles have been made in excellent yields by oxidative cycloaddition of arylhydrazones of benzaldehyde and butyraldehyde to aceto-, propio-, and acrylonitrile. Oxidation was achieved with the cation radicals thianthrenyl perchlorate ($Th^{\bullet+}ClO_4^-$) and tris(2,4-dibromophenyl)aminium hexachloroantimonate ($Ar_3N^{\bullet+}SbCl_6^-$). The triazoles thus had a phenyl, *p*-nitrophenyl, or 2,4-dinitrophenyl group in the 1-position, either a phenyl or propyl group in the 3-position, and a methyl, ethyl, or vinyl group in the 5-position. The formation of 5-vinyltriazoles was confirmed by their hydrogenation to 5-ethyltriazoles, which were obtained also by cycloadditions to propionitrile. New triazoles (eight) were also synthesized by a known alternative route, but in lower yields. The fact that 5-vinyltriazoles were formed instead of 5-cyano-2-pyrazolines shows that cation radical induced cycloadditions do not go through the nitrilimines. Cycloadditions with *N*-phenylbenzohydrazonoyl chloride and acrylonitrile in the presence of aluminum chloride and of triethylamine were carried out for comparison with the corresponding cation radical reaction.

Cation radical catalyzed Diels–Alder reactions[1] have stimulated interest in the possibility that other pericyclic cation radical reactions can be found. In 1985 we reported the formation of 1,2,4-triazoles (2) by the oxidative cycloaddition of benzaldehyde phenyl- and benzylhydrazones to acetonitrile, caused by reaction of the hydrazones with thianthrene cation radical ($Th^{\bullet+}$) perchlorate in the nitrile as solvent (eq 1).[2,3] The cycloaddition was represented as a concerted reaction between the cation radical of the hyrazone and the nitrile (Scheme I). At the same time, the possibility was noted that a two-electron oxidation of the hydrazone might also occur first, resulting in the formation of a nitrilimine which, then, would add to the nitrile in the well-known pericyclic way (Scheme II).[4]

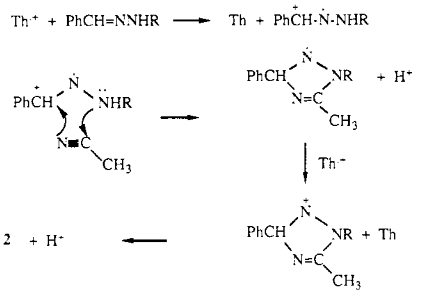


(1)

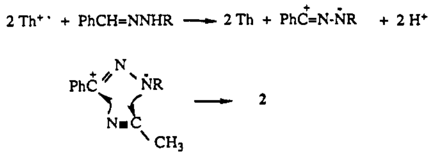
R = PhCH$_2$, Ph

We have now studied the cation radical reaction in more detail. We report the reactions of a series of phenyl-, (4-nitrophenyl)-, and (2,4-dinitrophenyl)hydrazones of benzaldehyde and of butyraldehyde with aceto-, propio-, and acrylonitrile. The cation radical oxidants which were used were $Th^{\bullet+}ClO_4^-$ and tris(2,4-dibromophenyl)amine cation radical ($Ar_3N^{\bullet+}$) hexachloroantimonate. The results from the use of acrylonitrile tell us quite clearly that the pericyclic route shown in Scheme II is not correct. It is probable, furthermore, that the cycloaddition shown as being concerted in Scheme I is also not correct.

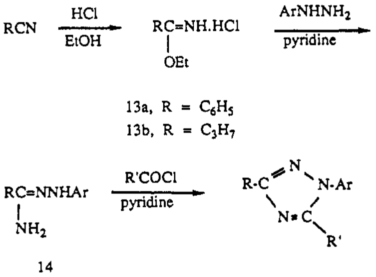
Scheme I



Scheme II

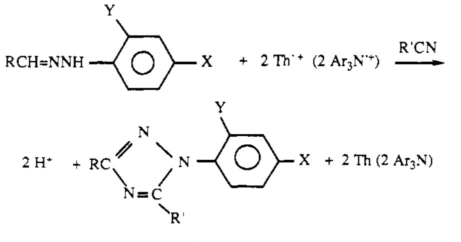


Scheme III



Results and Discussion

We list in Table I the results of 12 examples of cycloaddition, each of which was carried out in duplicate. In each case a 1,2,4-triazole was formed in which the 5-position is occupied by the group R′ (eq 2) from the nitrile, R′CN. The table shows that $Th^{\bullet+}$ was able to oxidize phenyl- and (4-nitrophenyl)hydrazones, while $Ar_3N^{\bullet+}$ was needed for the oxidation of (2,4-dinitrophenyl)hydrazones.



(2)

For R, R′, X, Y see Table I

---

[1] (a) Lorenz, K.; Bauld, N. L. *J. Catal.* **1985**, *95*, 613. (b) Ghosh, S.; Bauld, N. L. *J. Catal.* **1985**, *95*, 300. (c) Pabon, R. A.; Bauld, N. L. *J. Am. Chem. Soc.* **1984**, *106*, 1145 and references therein.

[2] Hoque, A. K. M. M.; Kovelesky, A. C.; Lee, W.-K.; Shine, H. J. *Tetrahedron Lett.* **1985**, *26*, 5655.

[3] Shine, H. J.; Bae, D. H.; Hoque, A. K. M. M.; Kajstura, A.; Lee, W.-K.; Shaw, R. W.; Soroka, M.; Engel, P. S.; Keys, D. E. *Phosphorus Sulfur* **1985**, *23*, 111.

[4] Huisgen, R.; Grashey, R.; Seidel, M.; Wallbillich, G.; Knupfer, H.; Schmidt, R. *Justus Liebigs Ann. Chem.* **1962**, *653*, 105.

0022-3263/88/1953-4349$01.50/0

Table I. Yields of Products of Reaction of Hydrazones with Solvent Nitriles (R′CN) Induced by Cation Radicals According to Eq 2

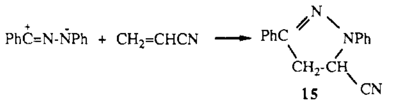
hydrazone				nitrile,		products,[b,c] %					
no.	R	X	Y	R′	cation radical[a]	Th	ThO	ThO_2	Ar_3N	triazole	
1	Ph	H	H	Me	A	92.1	5.0	0.65		**2a**[d]	80.2
1	Ph	H	H	Et	A	87.3	6.0	1.1		**2b**[e]	94.2
1	Ph	H	H	$CH{=}CH_2$	A	91.6	5.7	1.5		**2c**	74.4
1[f]	Ph	H	H	$CH{=}CH_2$	A	92.4	3.1	1.2		**2c**	81.5[g]
1[h]	Ph	H	H	$CH{=}CH_2$	A	95.8				**2c**	48.9[g]
3	Ph	NO_2	H	Me	A	93.8	3.6	1.6		**4a**[i]	87.8
3	Ph	NO_2	H	Et	A	95.8	2.8	1.6		**4b**	95.9
3	Ph	NO_2	H	$CH{=}CH_2$	A	94.1	3.7	2.2		**4c**	94.9
5	Ph	NO_2	NO_2	Me	B				90.7	**6a**	91.1
5	Ph	NO_2	NO_2	Et	B				94.1	**6b**	95.1
5	Ph	NO_2	NO_2	$CH{=}CH_2$	B				92.8	**6c**	93.7
7	Pr	H	H	Me	A	97.2	1.5			**8**	93.4
9	Pr	NO_2	H	Me	A	97.0	3.3			**10**	85.4
11	Pr	NO_2	NO_2	Me	B				90.9	**12**	91.9

[a] A, $Th^{\bullet+}ClO_4^-$; B, $(Br_2C_6H_3)_3N^{\bullet+}SbCl_6^-$. [b] Th, thianthrene; ThO, thianthrene 5-oxide; ThO_2, thianthrene *cis*-5,10-dioxide; Ar_3N, $(Br_2C_6H_3)_3N$. [c] Each yield is the average from two runs, except for entries 4 and 5, in which only one run was carried out. Yields of Th, ThO, and ThO_2 were determined by GC. The yield of triazole was determined by isolation. The yield of Ar_3N was determined by a combination of isolation and GC. [d] Mp 95–96 °C (lit.[4,8] mp 95–96 °C). [e] Mp 76–77 °C (lit.[8] mp 77 °C). [f] 2,6-Di-*tert*-butyl-4-methylpyridine (1.5 mmol) was present in this run. [g] 5-Cyano-1,3-diphenyl-2-pyrazoline was not found in the mixture of products. [h] Triethylamine (2 mmol) was present in this run. A substantial amount of 1 was recovered but not measured. Small amounts of ThO and benzaldehyde were formed but not measured. $Th^{\bullet+}$ reacts rapidly with triethylamine. [i] Mp 145–146 °C (lit.[20] mp 147 °C).

The oxidation potential of thianthrene (Th) is 1.3 V[5a] and of tris(2,4-dibromophenyl)amine (Ar_3N) is 1.5 V vs SCE.[5b] Each oxidative cycloaddition was a "clean" reaction. The only other products obtained from use of $Ar_3N^{\bullet+}SbCl_6^-$ were Ar_3N and (after hydrolysis) antimony oxide(s). Use of $Th^{\bullet+}ClO_4^-$ gave Th as the major redox-partner product, small amounts of thianthrene 5-oxide (ThO), and thianthrene *cis*-5,10-dioxide (ThO_2). Further comment is made about the last two products later.

Most of the triazoles reported in Table I are, to our knowledge, new. Therefore, they were prepared by an authentic route shown in Scheme III. This route involved the preparation of the imino ester hydrochlorides (**13a**,**b**), from which the amidrazones (**14**) were prepared and converted in situ into the corresponding triazoles by reaction with R′COCl. In every case the yield of triazole obtained by the cation radical route was larger than that obtained by the conventional route. Comparative data are given in Table II.

1,3-Dipolar cycloaddition of nitrilimines to the nitrile group of nitriles, giving 1,2,4-triazoles as products, has been known for some years. The nitrilimines were made in situ by reaction of hydrazonoyl chlorides (chloro hydrazones, RC(Cl)=NNHAr) with triethylamine.[4] However, when acrylonitrile was used, cycloaddition of diphenylnitrilimine occurred at the vinyl rather than at the nitrile group. That is, instead of forming a 5-vinyl-1,2,4-triazole, this reaction gave 5-cyano-1,3-diphenyl-2-pyrazoline (**15**, eq 3).[6] The



15

(3)

reason for this, as Huisgen and co-workers pointed out, is that the nitrile group lies below the vinyl group in dienophile activity.[4] We repeated Huisgen's reaction of *N*-phenylbenzohydrazonoyl chloride with triethylamine and acrylonitrile and confirmed that **15** is formed in excellent yield.

Table II. Yields and Properties of New Triazoles Prepared by Direct Synthesis (Scheme III) and Cycloaddition

	method of preparation		
triazole	A:[a] yield,[b] %	B:[c] yield,[d] %	mp,[e] °C
4b	74	96	138–139
4c	59	95	144–145
6a	67	91	124–125
6b	71	95	120–121
6c	62	94	146–147
8	70	93	oil
10	69	85	oil
12	65	92	130–131

[a] Synthesis. [b] Based on **13a** or **13b** (Scheme III). [c] Cycloaddition. [d] Based on hydrazone. [e] Satisfactory combustion analysis in C, H, N was obtained for each new triazole, except for **8** and **10**, which were not analyzed.

In contrast, the cation radical induced reaction of benzaldehyde phenylhydrazone and its analogues with acrylonitrile gave 5-vinyl-1,2,4-triazoles in good yield. To be certain of the position of the vinyl group, we reduced each of the 5-vinyltriazoles (**2c**, **4c**, **6c**, Table I) to a 5-ethyl-1,2,4-triazole and found complete correspondence with the 5-ethyltriazoles (**2b**, **4b**, **6b**) which had been obtained from cation radical reactions in propionitrile.

These results make it clear, therefore, that the cation radical reactions do not go through the nitrilimines (Scheme II). This distinction is made even more marked by considering the results of Gladstone and co-workers.[7] These workers oxidized **1**, **3**, and propanal (*p*-nitrophenyl)hydrazone with lead tetraacetate in acrylonitrile solution. The corresponding 5-cyano-2-pyrazoles were obtained in 64%, 60%, and 26% yield, respectively. Formation of each pyrazole was attributed to the initial formation and continued oxidation of a 5-cyanopyrazoline. The source of the pyrazoline was the cycloaddition of the nitrilimine to solvent acrylonitrile. Thus, in this oxidation each arylhydrazone was indeed converted into a nitrilimine.

Formation of 1,2,4-triazoles has also been achieved by Condê and co-workers in the reaction of *N*-phenyl-

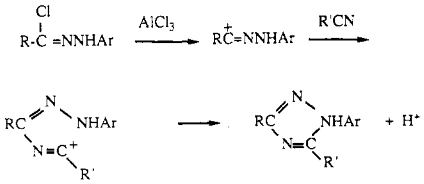
---

(5) (a) Shine, H. J. In *The Chemistry of the Sulfonium Groups*; Stirling, C. J. M., Patai, S., Eds.; Wiley: New York, 1981; pp 523–570; see p 549. (b) Hammerich, O.; Parker, V. D. *Adv. Phys. Org. Chem.* **1984**, *20*, 55–189; see p 96.

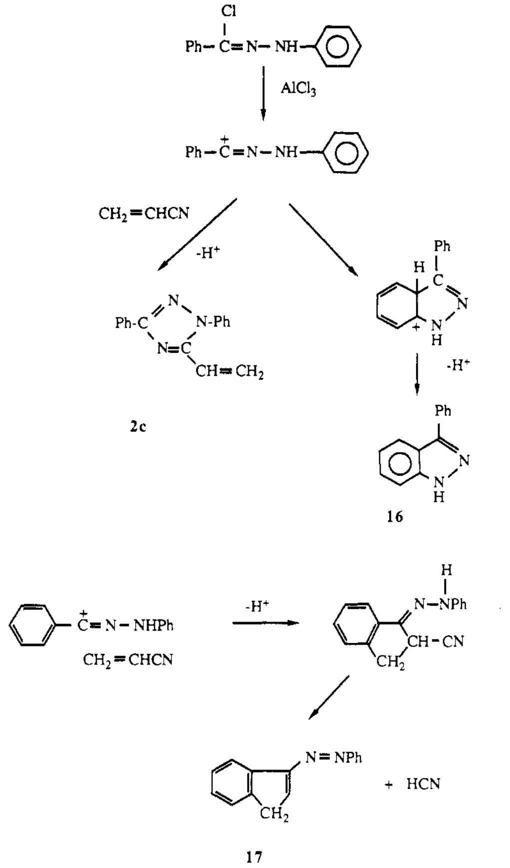
(6) Huisgen, R.; Seidel, M.; Wallbilich, G.; Knupfer, H. *Tetrahedron* **1962**, *17*, 3.

(7) Gladstone, W. A. F.; Aylward, J. B.; Norman, R. O. C. *J. Chem. Soc. C* **1969**, 2587. Curiously, an isomer, 4-cyano-1,3-diphenylpyrazole, was also obtained, in 2% yield.

Scheme IV



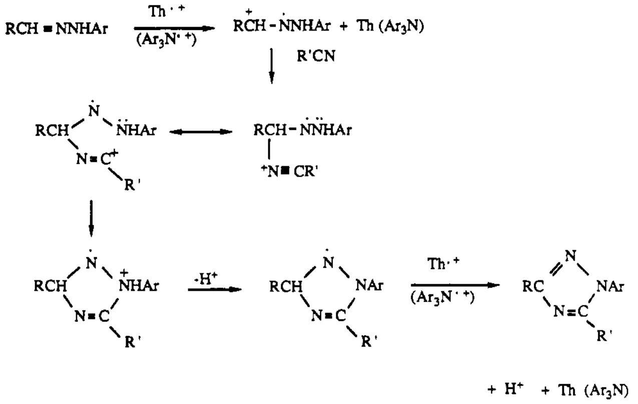
Scheme V



hydrazonoyl chloride with some alkyl- and arylnitriles in the presence of aluminum chloride.[8] Here, a nitriliminium ion is believed to be the reactive intermediate, and the cycloaddition takes place in a two-step sequence, the first of which is a Ritter reaction in which the lone pair of electrons on the nitrile group's nitrogen atom takes part (Scheme IV).

Condê and co-workers did not report the reaction of *N*-phenylbenzohydrazonoyl chloride with aluminum chloride and acrylonitrile. Therefore, we carried out that reaction. At least five products were formed, among which was 1,3-diphenyl-5-vinyl-1,2,4-triazole (**2c**) in about 37% yield. A second major product was 3-phenylbenzpyrazole (**16**), in 50% yield, and a third, minor product (8%) is believed to be 3-(phenylazo)indene (**17**). Formation of these products is shown in Scheme V. The presence, also, of 1,3,5-triphenyl-1,2,4-triazole among the mixture of products was indicated by GC–MS. Further work was not carried out on the products of this reaction. 5-Cyano-1,3-diphenyl-2-pyrazoline (**15**) could not be found among the products by GC or GC–MS. It is evident that cycloaddition to acrylonitrile was far superior by the cation radical than the aluminum chloride route. The difference in results no doubt lies in involvements of the strong Lewis acid in the aluminum chloride reaction.

Scheme VI



The difference between the cation radical and lead tetraacetate oxidations appeared to us, therefore, to be between nitriliminium ion and nitrilimine cycloadditions. In the lead tetraacetate reactions it seemed probable that the presence of a strong base (acetate ion) prevented the protonation of a nitrilimine, whereas a strong base was absent from the cation radical reactions. Our reactions, therefore, appeared to follow a route analogous to that of Condê and co-workers, the nitriliminium ion being generated as shown in eq 4. However, when the cation radical

$$\mathrm{RCH{=}NNHAr} + 2\mathrm{Th}^{\bullet+} \rightarrow \mathrm{RC^{+}{=}NNHAr} + 2\mathrm{Th} + \mathrm{H}^{+} \quad (4)$$

oxidation of **1** in acrylonitrile was carried out in the presence of 2,6-di-*tert*-butyl-4-methylpyridine, the vinyltriazole **2c** was again formed, in 81.5% yield. Reaction was carried out, therefore, in the presence of triethylamine, and, again, **2c** was formed, albeit in lower (48.9%) yield. $\mathrm{Th}^{\bullet+}$ reacts only slowly with 2,6-di-*tert*-butyl-4-methylpyridine (TBMP), but quickly with triethylamine,[9] for which reason the lower yield of **2c** in the presence of triethylamine is understandable. The cyanopyrazoline **15** was not found in either case. Surprisingly, therefore, the cycloaddition induced by cation radical oxidation appears to be unlike either of the two cycloadditions documented in the literature. It seems probable that an arylhydrazone cation radical is the intermediate, adding not in a concerted (Scheme I) but in a two-step way (Scheme VI). We are unable to say specifically why the rate of reaction, as evidenced by the rapid disappearance of $\mathrm{Th}^{\bullet+}$, is increased by added TBMP. It may be that the function of the base is to increase the rate of loss of the first proton (Scheme VI), without which the second oxidation step by $\mathrm{Th}^{\bullet+}$ would be slow. Regardless of mechanistic uncertainty, it is clear that the cation radical oxidation route is a useful one for making 1,2,4-triazoles in good yields.

Hydrolysis of cation radicals generates hydronium ion. For example, hydrolysis of $\mathrm{Th}^{\bullet+}\mathrm{ClO_4}^-$ leads to perchloric acid along with equal amounts of Th and ThO (eq 5).[10]

$$2\mathrm{Th}^{\bullet+} + \mathrm{H_2O} \rightarrow \mathrm{Th} + \mathrm{ThO} + 2\mathrm{H}^{+} \quad (5)$$

Therefore, the possibility that acid formed from hydrolysis of $\mathrm{Th}^{\bullet+}$ by water remaining in the solvent could initiate acid-catalyzed cycloaddition[11] needed to be checked. Acid-catalyzed cycloaddition would have to give a triazo-

---

[8] Condê, S.; Corral, C.; Madroñero, R. *Synthesis* **1974**, 28.

[9] Unpublished study.

[10] Murata, Y.; Shine, H. J. *J. Org. Chem.* **1969**, 34, 3368. **CAUTION**: *$\mathrm{Th}^{\bullet+}\mathrm{ClO_4}^-$ is explosive.* It should be prepared in small quantities only and used soon after preparation. Sintered glass should *not* be used for filtration.

[11] Grigg, R. *Chem. Soc. Rev.* **1987**, *16*, 89–121.

lidine, after which oxidation to the triazole would follow. Acid-catalyzed cycloaddition seemed to be ruled out by an earlier observation that the acid-catalyzed addition of acetaldehyde phenylhydrazone to acrylonitrile gives a mixture of isomeric cyanopyrazolidines.[12] Nevertheless, we examined the action of trifluoromethanesulfonic acid on benzaldehyde phenylhydrazone (**1**) in acetonitrile. Under the conditions of our cycloaddition reactions, **1** in acetonitrile containing this acid remained largely unaffected. A small amount of hydrolysis to benzaldehyde occurred, while the trimer of acetonitrile was detected by mass spectrometry.

When $Th^{\bullet+}ClO_4^-$ was used for cycloadditions, small amounts of ThO and ThO_2 were formed (Table I). Formation of ThO in reactions of $Th^{\bullet+}$ is not unusual because hydrolysis of $Th^{\bullet+}$ occurs (eq 5) by water either remaining in the solvent or added during workup to react with unused $Th^{\bullet+}$. It is, however, quite unusual to find ThO_2 as a product. Kim[13] has reported that small amounts of ThO_2 were formed when a solution of $Th^{\bullet+}ClO_4^-$ in acetonitrile was boiled under reflux in air. Sugiyama and Shine obtained small amounts of ThO_2, also, in reactions of $Th^{\bullet+}$ with diethylmercury under oxygen, reactions in which ethyl radical is thought to be involved.[14] Thus, there may be in our cycloaddition reactions a free-radical, oxygen-transfer component, occurring because small amounts of air were present when reactions were carried out in argon-flushed vessels. This possibility is being studied.

Experimental Section

WARNING: One of us was found to be *extremely* sensitive to acrylonitrile. A severe rash developed on the hands in spite of wearing heavy protective gloves. Eyes, protected by goggles, were not affected, but exposed areas of the neck and ears were affected even though all work was carried out in the hood. No other laboratory workers were sensitive to acrylonitrile.

Preparative-scale thin-layer chromatography (TLC) was carried out with 2-mm silica gel plates (Merck 5766). Silica gel for column chromatography was Woelm 402809, 30–70 mesh, 0.2–0.5 mm. Gas chromatography (GC) was carried out on a Varian Model 3740 gas chromatograph with a 50-cm, $^1/_8$-in. stainless steel column packed with 5% OV-101 on Chrom GHP 100/120. ^{1}H NMR spectra were recorded with Brucker 200- and 300-MHz spectrometers. Mass spectra (GC–MS) were recorded on a Hewlett-Packard spectrometer, Model 5995. Solvent acetonitrile (Eastman Kodak 1063072) was dried by distillation over phosphorus pentoxide and was collected and transferred to reaction vessels under argon without further contact with the atmosphere. Propionitrile and acrylonitrile were distilled under reduced pressure. Vessels for cation radical reactions were flushed with argon before use. Thianthrene (Th) (Fluka) was purifed by column chromatography and crystallization from acetone. Thianthrene cation radical ($Th^{\bullet+}$) perchlorate was prepared as described earlier.[10] Tris(2,4-dibromophenyl)amine (Ar_3N) was prepared by two-stage bromination of triphenylamine, and $Ar_3N^{\bullet+}SbCl_6^-$ was prepared as described by Schmidt and Steckhan.[15] Neither $Th^{\bullet+}ClO_4^-$ nor $Ar_3N^{\bullet+}SbCl_6^-$ was further purified. Iodometric assay of $Th^{\bullet+}ClO_4^-$ showed 95+% $Th^{\bullet+}$ content. Iodometric assay of $Ar_3N^{\bullet+}SbCl_6^-$ was complicated by (presumably) reduction of Sb(V) by I^-.[16] The arylhydrazones of benzaldehyde and butyraldehyde were prepared in standard ways and, after crystallization from ethanol, had melting points agreeing with those in the literature.

Cycloaddition Reactions. A general procedure was used for each cation radical. An example of each procedure is given.

Formation of Triazole 2a by Reaction of Benzaldehyde Phenylhydrazone (1) with $Th^{\bullet+}ClO_4^-$ in Acetonitrile. A solution of 196 mg (1.0 mmol) of **1** in 15 mL of acetonitrile was added dropwise by syringe to a stirred solution of 630 mg (2.0 mmol) of $Th^{\bullet+}ClO_4^-$ in 15 mL of acetonitrile under argon. Stirring was continued overnight, by which time all of the purple color of $Th^{\bullet+}$ had disappeared. Water (10 mL) was added followed by sodium bicarbonate solution to neutralize perchloric acid formed during reaction and by hydrolysis of $Th^{\bullet+}ClO_4^-$. The mixture was extracted with 5 × 30 mL of methylene chloride. The methylene chloride solution was dried over magnesium sulfate and evaporated to give 549 mg of solid residue. This residue was dissolved in 10.0 mL of methylene chloride. Portions of this solution were used for identification of products by GC–MS, for quantitative analysis by GC, and for quantitative separation of products by TLC. Thianthrene (Th), thianthrene 5-oxide (ThO), and thianthrene *cis*-5,10-dioxide (ThO_2) were assayed by GC with the use of an internal standard and predetermined concentration factors (CF). The triazole **2a** was isolated quantitatively by TLC and column chromatography. The stock methylene chloride solution was streaked on TLC plates and developed with methylene chloride. The band containing **2a** and ThO was removed with methanol, and the two components were separated by column chromatography with methylene chloride/acetone, 1:1. Separation gave 190 mg (0.808 mmol, 80.8%) of **2a**. Crystallization from ethanol gave mp 95–96 °C (lit.[4,8] mp 95–96 °C).

All other reactions of hydrazones with $Th^{\bullet+}ClO_4^-$ in nitrile solvents were carried out in the same way, and each reaction was carried out twice. Results are given in Table I.

Formation of Triazole 6a by Reaction of Benzaldehyde (2,4-Dinitrophenyl)hydrazone (5) with $(Br_2C_6H_3)_3N^{\bullet+}SbCl_6^-$ ($Ar_3N^{\bullet+}SbCl_6^-$). Acetonitrile (25 mL) was added by syringe to a septum-capped flask containing 2.11 g (2.0 mmol) of solid $Ar_3N^{\bullet+}SbCl_6^-$ and 286 mg of solid **5** under argon. The mixture was stirred for 8 h, until the color of $Ar_3N^{\bullet+}$ had disappeared, at which time some solid Ar_3N had precipitated. Water (5 mL) was added by syringe, and the precipitate of Ar_3N was collected, washed with a little acetonitrile, and dried, giving 1.18 g. The filtrate was then neutralized with sodium bicarbonate solution. This caused the formation and precipitation of (presumed) antimony oxides, which were removed by filtration. The filtrate was extracted with 5 × 20 mL of methylene chloride. The methylene chloride solution was dried and evaporated, and the solid residue (445 mg) was treated as described in the $Th^{\bullet+}ClO_4^-$ reaction. Residual Ar_3N was assayed by GC, and the result was combined with the earlier amount of solid Ar_3N, while 294 mg (90.4%) of **6a** was obtained by quantitative TLC. Crystallization from ethanol gave mp 124–125 °C.

All other reactions with $Ar_3N^{\bullet+}SbCl_6^-$ were carried out in the same way, and all were in duplicate. Results are given in Table I.

Hydrogenation of 5-Vinyltriazoles. Each of the 5-vinyltriazoles was hydrogenated to give a 5-ethyltriazole. In each case the 5-ethyltriazole corresponded with that which was formed from the appropriate cation radical reaction in propionitrile solution. An example follows.

Hydrogen gas from a balloon was bubbled overnight into a stirred suspension of 8 mg of Pd/C catalyst in a solution of 73 mg (0.25 mmol) of **4c** in 40 mL of ether. Workup of the ether solution gave 65 mg (0.22 mmol, 88%) of **4b**, mp 139–140 °C after crystallization from ethanol. The ^{1}H NMR spectrum was identical with that of authentic 5-ethyl-1-(4-nitrophenyl)-3-phenyl-1,2,4-triazole (**4b**).

Reaction of 1 with $Th^{\bullet+}ClO_4^-$ in Acrylonitrile Containing an Amine Base. A. With 2,6-Di-*tert*-butyl-4-methylpyridine. A solution of 98 mg (0.5 mmol) of **1** in 10 mL of acrylonitrile was added to a stirred solution of 315 mg (1.0 mmol) of $Th^{\bullet+}ClO_4^-$ and 308 mg (1.5 mmol) of the base in 10 mL of acrylonitrile under argon. The color of $Th^{\bullet+}$ was completely gone after 30 min. Stirring was continued overnight, after which 10 mL of dilute sodium bicarbonate solution was added. The organic products were extracted with methylene chloride. Workup gave 626 mg of solid. GC–MS and quantitative GC showed the presence of eight products, six of which were benzaldehyde (3.2%), Th

---

[12] Le Fevre, G.; Sinbandhit, S.; Hamelin, J. *Tetrahedron* **1979**, *35*, 1821.

[13] Kim, K.-T. *Chayon Kwahak Taehak Nomunjip* (*Soul Taehakkyo*) **1977**, *2*, 53.

[14] Sugiyama, K.; Shine, H. J. *J. Org. Chem.* **1983**, *48*, 143.

[15] Schmidt, W.; Steckhan, E. *Chem. Ber.* **1980**, *113*, 577.

[16] Results from Donald T. Robertson in this laboratory. For reaction of $SbCl_6^-$ with I^-, see: Cowell, G. W.; Ledwith, A.; Woods, H. J. *J. Chem. Soc. B* **1970**, 227.

(94.2%), ThO (3.1%), ThO_2 (1.2%), recovered base (93.8%), and triazole **2c**. Two minor products could not be identified. The 5-cyanopyrazoline **15** was not detected. Identity of **2c** was established first by GC "spiking" and next by isolation. Preparative TLC gave 101 mg (0.407 mmol, 81.5%) of **2c**, with a satisfactory ^1H NMR spectrum.

B. With Triethylamine. Triethylamine reduces $Th^{\bullet+}$ quickly. Even so, reaction with **1** was carried out as follows. A solution of 202 mg (2 mmol) of triethylamine in 20 mL of acrylonitrile was added to a mixture of solid $Th^{\bullet+}ClO_4^-$ (316 mg, 1.0 mmol) and **1** (98 mg, 0.5 mmol) under argon. The color of $Th^{\bullet+}$ disappeared immediately. Stirring was continued overnight. Workup gave 402 mg of solid. GC and GC–MS showed the presence of eight products again, among them being benzaldehyde, Th, ThO, unused **1**, and **2c**. Only Th (95.8%) and **2c** (48.9%) were assayed. The 5-cyanopyrazole **15** was not detected.

Synthesis of Triazoles According to Scheme III. The general procedure was to prepare and isolate the imino ester hydrochloride **13** and to carry out its reaction with the arylhydrazine $ArNHNH_2$ to form the amidrazone **14**, in pyridine solution at room temperature. Isolation of an amidrazone from pyridine solution proved to be difficult. Therefore, reaction with the acid chloride R′COCl was carried out, without isolation, in the same pyridine solution. We used the procedure of McElvain and Nelson[17] for preparing an imino ester hydrochloride (**13a,b**). After it had precipitated from solution, the hydrochloride was collected by filtration and was washed repeatedly with a total of 300 mL of anhydrous ether which had been cooled in a dry-ice acetone bath. The hydrochloide was then dried by pumping at high vacuum, giving **13a** ($R = C_6H_5$, 90%, mp 122–123 °C) and **13b** ($R = C_3H_7$, 61%, mp 66–67 °C). The ^1H NMR spectrum of each imino este hydrochloride was in accord with its structure.

The formation of some amidrazones in pyridine solution and their isolation have been described by Atkinson and Polya.[18] These authors have also described the conversion of an amidrazone into a 1,2,4-triazole by heating with an acyl chloride. We followed this method of making triazoles in principle, as described below for **4a**.

To a stirred solution of 5.6 g (30 mmol) of **13a** in 50 mL of dry pyridine was added 4.6 g (30 mmol) of (4-nitrophenyl)hydrazine. A thick, brown solution, containing the amidrazone **14** ($R = C_6H_5$, $Ar = 4\text{-}NO_2C_6H_4$), was obtained after stirring for 24 h. Acetyl chloride (20 mmol) was added slowly by syringe to a stirred portion of this solution containing an estimated 8 mmol of amidrazone. The mixture was heated under reflux for 6 h, cooled, and diluted with aqueous sodium bicarbonate solution. The triazole was extracted with 4 × 50 mL of methylene chloride and purified by chromatography on a column of silica gel with methylene chloride elution. Crystallization gave 1.55 g (5.52 mmol, 69%) of **4a**, mp 145–146 °C. The ^1H NMR spectrum and GC–MS fragmentation pattern of **4a** prepared in this way were the same as those of **4a** that was obtained from the cation radical cycloaddition reaction (Table I). A mixture of **4a** from both routes gave a single GC peak.

In this way the following amidrazones (**14**) were also prepared in pyridine solution: $R = C_6H_5$, $Ar = 2,4\text{-}(NO_2)_2C_6H_3$; $R = C_3H_7$, $Ar = C_6H_5$, $4\text{-}NO_2C_6H_4$, $2,4\text{-}(NO_2)_2C_6H_3$. Reaction with the appropriate acyl chloride gave the eight new triazoles which had also been obtained by the cation radical route. These triazoles, and comparative data, are listed in Table II.

^1H NMR data for the new triazoles are listed in Table III (see paragraph on supplementary material).

Preparation of 5-Cyano-1,3-diphenyl-2-pyrazoline. Reaction of *N*-phenylbenzohydrazonoyl chloride (1.15 g, 5.0 mmol) with acrylonitrile (4.0 mL) in the presence of triethylamine (3.0 mL) was carried out as described by Huisgen and co-workers.[6] Triethylammonium chloride (703 mg, mp 252–253 °C) precipitated and was recovered. Evaporation of the filtrate gave 998 mg (4.05 mmol, 81%) of 5-cyano-1,3-diphenylpyrazoline (**15**), mp 134–136 °C. Crystallization from methanol gave mp 138–139 °C (lit.[6] mp 138–140 °C). The 200-MHz ^1H NMR spectrum was fully in accord with the pyrazoline structure. No trace of the 5-vinyltriazole **2c** was seen by GC and GC–MS.

Reaction of Acrylonitrile with *N*-Phenylbenzohydrazonoyl Chloride and $AlCl_3$. *N*-Phenylbenzohydrazonoyl chloride (1.15 g, 5.0 mmol) was added to a suspension of 668 mg (5.0 mmol) of anhydrous $AlCl_3$ in 20 mL of acrylonitrile. The mixture was heated at 120–130 °C for 30 min, cooled, and made alkaline with 2% sodium hydroxide solution. The organic products were extracted with methylene chloride (instead of ethyl acetate[8]). Evaporation of the dried solvent (instead of steam distillation[8]) gave 1.32 g of a viscous oil. Of this, 652 mg was separated into six components on successions of TLC plates. The major compounds were the vinyltriazole **2c**, 231 mg (0.935 mmol, 37.4%), and 3-phenylindazole (**16**), 242 mg (1.25 mmol, 50%), mp 106–107 °C after crystallization from ethanol (lit.[19] mp 107–108 °C). The identity of **2c** was confirmed by GC–MS and ^1H NMR. The identity of **15** was deduced from the possible pathways of reaction and from ^1H NMR and GC–MS data: m/e (relative intensity) 195 (15.2), 194 (M^+, 100), 193 (21.6). Of the smaller components, three were obtained as oils and could not be identified. The fourth (44 mg), obtained as a sticky solid, appeared to be 3-(phenylazo)indene (**17**), from GC–MS data: m/e (relative intensity) 221 (17.5), 220 (M^+, 100), 219 (68.6). GC–MS on the mixture of products before separation showed also the presence of 1,3,5-triphenyl-1,2,4-triazole (m/e 297), but this could not be found among the separated products. Neither GC nor GC–MS showed the presence of 5-cyano-1,3-phenyl-2-pyrazoline (**15**, eq 3).

Reaction of 1 with Acetonitrile in the Presence of Trifluoromethanesulfonic Acid. A solution of 150 mg (1.00 mmol) of trifluoromethanesulonic acid in 10 mL of acetonitrile was added to a stirred solution of 1.96 g (10.0 mmol) of **1** in 20 mL of acetonitrile in a septum-capped vessel. Stirring was continued for 20 h at room temperature. Water was added, and the solution was then neutralized with aqueous sodium bicarbonate solution. Organic products were extracted with methylene chloride, and the methylene chloride solution was dried over magnesium sulfate. The dried solution was concentrated for GC analysis and gave recovered **1**, 1.5 g (7.65 mmol, 76.5%), and benzaldehyde, 155 mg (1.46 mmol, 14.6%). The GC trace showed also the presence of 2,4,6-trimethyltriazine, a trimer of acetonitrile, but the amount was not assayed. The identity of **1** and benzaldehyde was confirmed by GC–MS. The trimer was identified by GC–MS: m/e (relative intensity) 123 (M^+, 31), 82 ($dimer^+$, 54.6), 42 ($monomer - H^+$, 100), 41 (monomer, 33), and 40 (23.5).

Acknowledgment. This work was supported by grants from the Robert A. Welch Foundation (No. D-028) and the National Science Foundation (No. CHE 86-12031). The 200-MHz and 300-MHz NMR spectrometers were purchased by Texas Tech University with the aid of a Chemical Instrumentation Grant (CHE 8514104) from the National Science Foundation. This paper was written in part while H.J.S. was an awardee of the Alexander von Humboldt Foundation. He thanks the Foundation for its award and the Institut für Organische Chemie, Universität Hamburg, for hospitality.

Supplementary Material Available: Table III, containing ^1H NMR data for triazoles **2c**, **4a–c**, **6a–c**, **8**, **10**, and **12** (1 page). Ordering information is given on any current masthead page.

---

(17) McElvain, S. M.; Nelson, J. W. *J. Am. Chem. Soc.* **1942**, *64*, 1825.
(18) Atkinson, M. R.; Rolya, J. B. *J. Chem. Soc.* **1954**, 3319.
(19) von Auwers, K.; Hütenes, K. *Chem. Ber.* **1922**, *55*, 3665.
(20) Baccar, B. G.; Barrans, J. *C. R. Hebd. Seances Acad. Sci.* **1964**, *259*, 1340.