

Tris(4-bromophenyl)aminium Hexachloroantimonate
: A Versatile Radical Cation Catalyst for Olefin
Addition Reactions ?

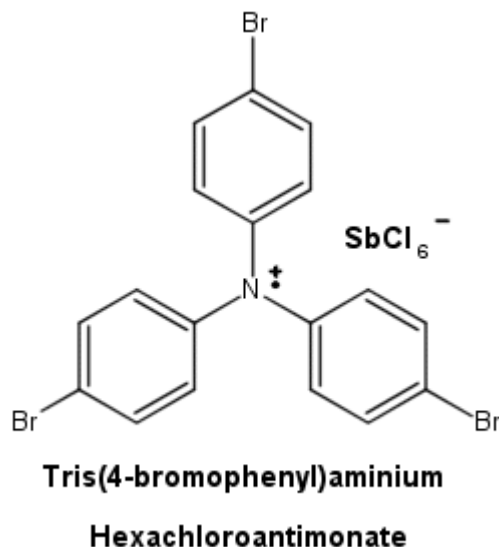
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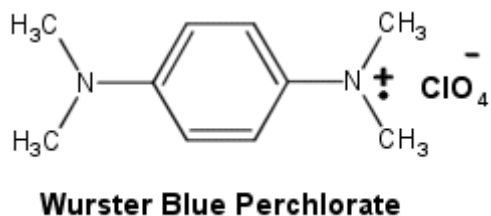
June 26 , 2004

Tris(4-bromophenyl)aminium Hexachloroantimonate :
A Versatile Radical Cation Catalyst for Olefin Addition Reactions ?

The title compound , which I'll refer to as "tris" throughout this report , is a type of Wurster Blue salt , with an organic radical cation and the accompanying hexachloroantimonate anion :



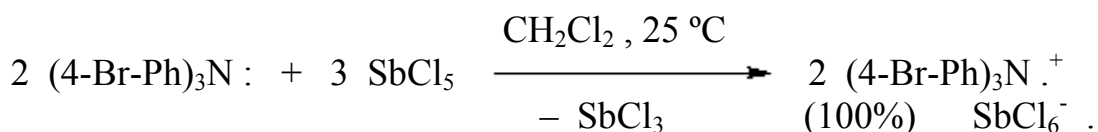
The original Wurster Blue compound was a para-phenylenediamine :



Although I haven't indicated it in the sketches above , the two aminium compounds are resonance-stabilized , and indeed are quite stable at room temperature . We note a sort of mixed-valency in the latter compound , with an electron resonance occurring between the two nitrogen atoms , one of which formally has the lone pair of electrons (N:) , while the other has been shown in the sketch with a missing electron (N.+) and a resulting cationic charge .

In the case of tris , it is conceivable that an electron resonance is occurring between the nitrogen atom and the three bromine atoms , via the pi electron cloud over the benzene rings : $(N^{\cdot+}) + (Br \cdot) \leftrightarrow (N \cdot) + (Br^{\cdot+})$. It should be noted that the hexachloroantimonate anion is an **oxidizer** ; the standard reduction potential of Sb(V) in a chloride environment is $E^0_{red} = 0.82 \text{ V}$, which is in the “moderate” range . Tris is known to chemically oxidize aromatic amines , ferrocene , phenoxide anions , and iodide anion (ref. 1 , page 7) .

Tris can be readily prepared by a one-electron oxidation of the parent tertiary amine , tris(4-bromophenyl)amine , by antimony pentachloride :



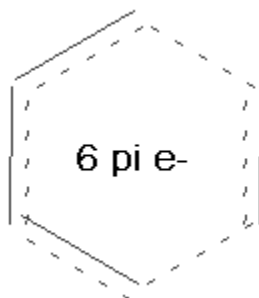
Upon addition of dry ether to the deep blue methylene chloride solution of tris , the radical cation salt is precipitated as “fine , blue , needle-shaped crystals” (ref. 2) . Tris is also commercially available , eg. from the Aldrich Chemical Company .

Tris has been found to catalyze the Diels-Alder reaction in cases where the dienophile is non-electrophilic (ref. 3) . Generally , a reasonably electrophilic dienophile , $\text{CH}_2=\text{CH-X}$, is required for reaction with the diene , to obtain a cyclohexene product . The pendant atom or group “X” is usually electron withdrawing in nature , such as $-\text{COOH}$, $-\text{COOR}$ (ester , amide , etc.) , $-\text{CN}$, $-\text{NO}_2$, and so on . If “X” is electron donating in nature , such as H or R (alkyl , aryl) , the Diels-Alder reaction may not succeed .

Very likely tris is forming a cationic complex with the electron-rich olefins , and it is this electrophilic complex that is reacting with the diene . The authors in ref. 3 have suggested that tris cleanly oxidizes the dienophile to the corresponding radical cation , which , thus activated , cyclizes with the diene to the cyclohexene product .

As an aside , I wonder if this is actually the case . I was under the impression

that the driving force for the Diels-Alder cyclization was the formation of a transient aromatic resonance in the transition state , which would require **six** electrons in the pi MO :



Would only **five** pi electrons in the ring be enough for aromatic stabilization of the transition state ?

Free radicals are known to catalyze the addition of various reagents to olefins . The following species will add to the olefin bond in the presence of free radicals :

R**S**H , C**Cl**₄ , C**Br**₄ , CH**Br**₃ , CCl₃**Br** , **Br**CH₂COOEt , R**CH**O , Ph₃Si**H** , and CO**Cl**₂ , where the abstracted atom is colored red (ref. 4) .

The table on the following page lists a variety of additions of specific reagents to specific olefins , with a brief mention of experimental conditions and the free radical inducing agent involved in each reaction (ref. 5) . Those reactions in which new carbon-carbon bonds are created will of course be of the greatest interest to the synthesis chemist .

My suggestion here is : could tris replace the free radical inducing agents used in these addition reactions ? Most of the free radical generating agents are peroxides of one sort or other : benzoyl peroxide is a common one , since it is reasonably stable under ambient conditions , and it decomposes smoothly to phenyl free radicals at about 80 °C (reactions with it are often conducted in refluxing benzene , at that temperature) . Persulfate salts , such as potassium persulfate , K₂S₂O₈ , are common free radical initiators in

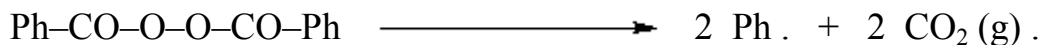
water-based addition reactions of olefins (for example , in the large-scale industrial production of latex emulsions) .

Free Radical Induced Additions of Reagents to Olefins

<u>Reagent</u>	<u>Olefin</u>	<u>Free Radical Initiator</u>	<u>Conditions</u>
isopropanol	ethylene	di-t-butyl peroxide	125-130 C , 20 h
$\text{CH}_2(\text{COOCH}_3)_2$	$\text{CH}_2=\text{CH-OAc}$	di-t-butyl peroxide	150-152 C , 4.5 h
CCl_3Br	styrene	acetyl peroxide	60-70 C , 4 h
CCl_4	1-octene	benzoyl peroxide	90-105 C , 4 h
CF_3I	$\text{F}_2\text{C}=\text{CF}_2$	ultraviolet light	ambient , 6h
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$	diethyl maleate	benzoyl peroxide	reflux , 18 h
HBr	1-chloro-1-cyclohexene	UV light	ambient , 2 h
HBr	n-butylacetylene	"peroxide"	cooling , 1 h
CF_3SH	$\text{F}_2\text{C}=\text{CH}_2$	X-rays	ambient , 3h
CH_3COSH	2-methyl-2-pentene	tungsten lamp	ambient , 1 h
CH_3COSH	propargyl acetate	azo-bis(isobutyronitrile)	ambient , 24 h
H_2S	$\text{Ph-O-CH}=\text{CH}_2$	ABIN	60 C , 53 h
NaHSO_3	$\text{CF}_2=\text{CF}-\text{CF}_3$	benzoyl peroxide	110-120 C , 9 h
p-Cl-Ph-SO ₂ Cl	ethylene	ABIN	70 C , 24h
Cl_3SiH	1-octene	diacetyl peroxide	50-63 C , 11 h
$\text{CH}_3\text{SiCl}_2\text{H}$	propylene	thermal	300 C , "overnight"
$(\text{EtO})_2\text{P}=\text{O}(\text{H})$	isopropenyl acetate	benzoyl peroxide	85-95 C , 4 h

Because it is an oxidizing agent , tris couldn't be used with those reagents listed that are sensitive to chemical oxidizers , such as H_2S , RSH , RCOSH , probably HBr , NaHSO_3 (which is water-based) , and possibly the silanes and the diethyl phosphite . That still leaves the most interesting ones , in my opinion : the ones in which C–C bonds are formed .

Mechanistically , all of the free radical producing agents listed in the above table are known to generate **neutral** free radicals when they decompose . For example , benzoyl peroxide is a good source of phenyl free radicals :



Tris , on the other hand , is a **radical cation** ; the third type of free radical is the radical anion , not discussed any further here . How would tris , as a radical cation , interact with the systems listed above in the table , and with others , in which neutral free radicals traditionally have been used to activate the olefin additions ? In particular , can tris activate methylene olefins (for example , ethylene , $\text{CH}_2=\text{CH}_2$; propylene , $\text{CH}_2=\text{CH}-\text{CH}_3$; isobutylene , $\text{CH}_2=\text{C}(\text{CH}_3)_2$; vinyl chloride , $\text{CH}_2=\text{CH}-\text{Cl}$; vinylidene chloride , $\text{CH}_2=\text{C}(\text{Cl})_2$; vinyl acetate , $\text{CH}_2=\text{CH}-\text{OAc}$; etc.) without **polymerizing** them ? These are of course monomers , the precursors of all the familiar modern polymers , our beloved plastics .

Tris might thus offer its catalytic services to synthesis chemists , greatly extending the range of olefin addition reactions , including cyclizations such as the Diels-Alder reaction , which seems to have received only a cursory evaluation so far . Such olefin additions might be carried out , with the activation by tris , under mild ambient conditions , short reaction times , simple experimental methods , and with good yields of clean products . While tris as a chemical reagent is moderately expensive , it is used only in catalytic quantities , and might be recovered from a workup of the spent reaction solvent . It is readily available , either commercially , or prepared fresh by the researcher from the tertiary amine and SbCl_5 . Finally , a novel synthesis method for creating new carbon-carbon and carbon-heteroatom bonds is well worth investigating .

(The references follow on the next page) .

References

1. G.W. Cowell , A. Ledwith , A.C. White , and H.J. Woods ,
“Electron-transfer Oxidation of Organic Compounds with
Hexachloroantimonate [SbCl₆]- Ion” , J. Chem. Soc. B (2) ,
pp. 227-231 (1970) .
2. F.A. Bell , A. Ledwith , and D.C. Sherrington , “Cation-radicals :
Tris-(p-bromophenyl)amminium Perchlorate and
Hexachloroantimonate” , J. Chem. Soc. C (19) ,
pp. 2719-2720 (1969) .
The authors conclude , “For routine oxidations , therefore , the
hexachloroantimonate salt is to be preferred [to the perchlorate]”
(p. 2720) . The latter compound was found to be thermally and
photolytically more stable than the perchlorate . I might add that
perchlorate salts of organic compounds , when heated , are prone
to **sudden detonation** , an unfortunate consequence of compacting
together oxygen atoms (in ClO₄⁻) with carbon and hydrogen atoms ,
in the organic cation . As pointed out earlier , the Sb(V) atom in the
SbCl₆⁻ anion is a moderately strong one-electron oxidizer ;
nevertheless , I wouldn't expect SbCl₆⁻ salts with organic cations to
be explosive in nature , unlike the violent C-H-O oxidizing oxidizers
like perchlorate and nitrate anions .
3. D.J. Bellville , D.D. Wirth , and N.L. Bauld , “The Cation-Radical
Catalyzed Diels-Alder Reaction” , J. Amer. Chem. Soc. 103 (3) ,
pp. 718-720 (1981) .
4. D.J. Cram and G.S. Hammond , Organic Chemistry , 2nd ed. ,
McGraw-Hill , New York , 1964 ; p. 529 .
5. C. Walling and E.S. Huyser , “Free Radical Additions to Olefins
to Form Carbon-Carbon Bonds” , Ch. 3 , pp. 91-149 in
Organic Reactions , vol. 13 , A.C. Cope (ed.) , John Wiley ,
New York , 1963 ; and ,

F.W. Stacy and J.F. Harris Jr. , “Formation of Carbon-Hetero Atom Bonds by Free Radical Chain Additions to Carbon-Carbon Multiple Bonds” , Ch. 4 , pp. 150-376 in Organic Reactions , vol. 13 , A.C. Cope (ed.) , John Wiley , New York , 1963 .