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LETTERS

Tetrakis(pentafluorophenyl)gallates (I)

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Abstract

The synthesis of certain iodonium tetrakis(perfluorophenyl)gallate salts is reported. The rates of acid formation when these compounds are irradiated with a broad spectrum mercury arc in EtOH are compared. © 2000 Published by Elsevier Science Ltd.

Keywords: iodonium tetrakis(pentafluorophenyl)gallates; photoacid production.

The formation of photopolymers from acid susceptible monomers has been a matter of intense interest.[1] Though cationic photopolymerization traces its origins to diazonium salt reactivity, the most successful systems have been iodonium and sulfonium salts paired with poorly nucleophilic anions. The reactivity of a specific iodonium cation, anion pair increases in an order that parallels a decrease in anion nucleophilicity[1]; $BF_4^-<PF_6^-<AsF_6^-<SbF_6^-$. The reagents of choice for cationic polymerization of epoxides have been diaryliodonium, Ar_2I^+, SbF_6^- or triarylsulfonium hexafluoroantimonates, Ar_3S^+, SbF_6. The general mechanism by which they initiate polymerization when irradiated is[2]

$$Ar_2ISbF_6 \xrightarrow{h\nu} ArI^{\bullet}SbF_6 + {}^{\bullet}Ar$$

$$ArI^{\bullet}SbF_6 + RH \rightarrow ArI + R^{\bullet} + HSbF_6.$$

Though there have been extensive reports on modifications of the cation in such initiators, few systems with modified anions had been reported until Fouassier synthesized iodonium salts with tetrakis(perfluorophenyl)borate gegen ions.[3] These compounds represented an important breakthrough in the technology, in that they are particularly soluble, and hence effective, in nonpolar monomers.[4] Though borate salts had been important in photoinitiator design since the original report of the cyanine borates[5] virtually all such compounds were selected with borate anions

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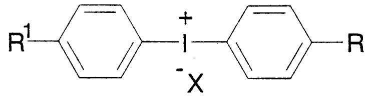
that were active electron transfer donors. The Fouassier papers were the first in which the anion was chosen specifically because it was not a reducing agent. The anion $^{-}B(\phi F_5)_4$ appears to proffer higher reactivity in cationic photopolymerization, better solubility, lower toxicity and, when paired with iodonium salts, is less hydroscopic, than are antimony counterparts. This parallels similar advantages of $B(C_6F_5)_3$ in comparison to $B(C_6H_5)_3$[6] which is difficult to handle in the absence of neutralizing hydroxide.

Boron is grouped with aluminum, gallium and indium in the periodic table. Accordingly we suspected that tetrakis(perfluorophenyl) anions of one or more of these other elements, would provide important onium salts to be used as photoinitiators. As near as we know, the only other report of a gallate being used in a photochemical process was that of triphenylbutyl gallate used as an electron donor in an intramolecular system.[7]

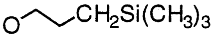
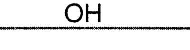
Our targets were iodonium salts based on perfluorophenyl gallate. We were seeking better solubility and activity through replacing the smaller boron with the bigger gallium atom. The first report of tetrakis(perfluorophenyl) gallate was as an ammonium salt.[8] The anion was synthesized from gallium trichloride. A crystal structure[9] on $Ph_3P{=}N{=}PPh_3,Ga(C_6F_5)_4$ showed the gallate to have almost tetrahedral geometry.

Results: Lithium tetrakis(pentafluorophenyl)gallate was prepared by a modified procedure.[8] The hydroscopic product was obtained in 95% yield and stored under argon. ^{19}F NMR δ ($CDCl_3$): −124.2 (sm, 2F), −158.2 (sm, 1F), −164.0 (sm, 2F). UV (EtOH) λ_{max} (ε): 260 (1533).

Table 1
Diaryliodonium tetrakis(perfluorophenyl)gallates



I : X= $Ga(C_6F_5)_4$

No.	R^1	R	Characteristics/Yield (%)	% C: % H: Calc/Found
I_a*	H	H	White powder 68	C, 42.43; H, 0.99. C, 42.51; H, 1.00.
I_b*	Me	Me	Slightly yellow Powder 54	C, 43.59; H, 1.35. C, 43.64; H, 1.20.
I_c*	Me	i-Pr	Slightly yellow Liquid 75	C, 44.69; H, 1.69. C, 44.62; H, 1.82.
I_d*	$C_{12}H_{25}$	$C_{12}H_{25}$	Slightly yellow Liquid 59	C, 53.16; H, 4.31. C, 53.47; H, 4.34.
I_e*	H	OC_8H_{17}	Slightly yellow Liquid 62	C, 46.06; H, 2.28. C, 46.15; H, 2.32.
I_f*	H		Yellow sticky liquid 73	C, 43.89; H, 2.10. C, 44.17; H, 2.24.
I_g*	H		Transparent sticky liquid 80	C, 48.14; H, 3.07 C, 48.23; H, 3.19.

Metathesis yielded the iodonium salt (Table 1). The crude product was chromatographed through a short plug of silica gel (3–5 cm in length) by elution with CH_2Cl_2 to give the desired iodonium tetrakis(pentafluorophenyl)gallate as a solid or a light yellow sticky liquid. The product was vacuum dried overnight, away from light.

The most important characteristic of these compounds is that they produce acid under UV irradiation. In order to examine their ability to do this, we designed a simple test using an acid sensitive indicator dye that changed color at moderate pH. The respective onium salts [7.0×10^{-3} M] were dissolved in a dilute ethanol solution containing quinaldine red which is pink in basic and neutral media and colorless in aqueous solution at pH>1.5. The disappearance of the peak at 530 nm was monitored as acid was produced during irradiation. A 1 cm quartz cuvette filled with the onium salt solution and sealed. The cuvette was irradiated with Fusion H-bulb high-pressure mercury lamp (all lines) by passing it on the conveyor belt under the lamp at the certain line speed. All the synthesized tetrakis(perfluorophenyl)gallates can be considered photoacid generators. It is apparent from Fig. 1 that gallates with longer alkyl chains (with or without oxygen) produce more acid when compared to diphenyl- or ditolyl tetrakis-(perfluorophenyl)gallates, I_a–I_g. The tetrakis(perfluorophenyl)borate and tetrakis(perfluorophenyl)gallate (Rhodorsil 2074 and I_c, respectively) produce the same level of acid production when paired with similar cations.

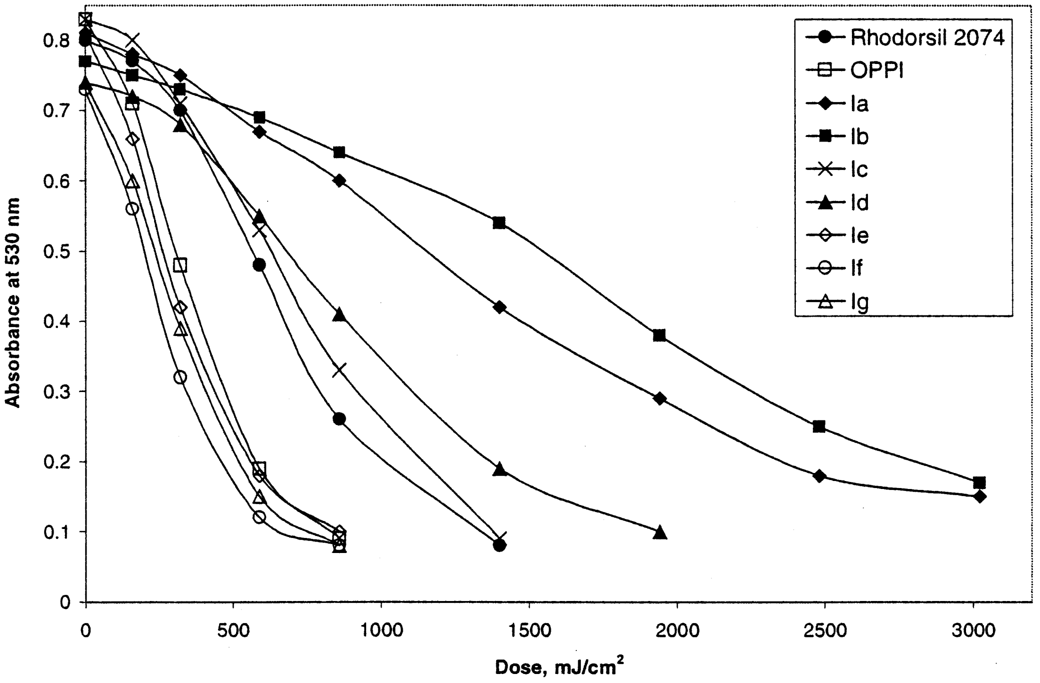


Figure 1. The formation of acid from several anions. Disappearance of 530 nm absorption: Rhodorsil 2074, OPPI [(octyloxyphenyl)phenyl iodonium hexafluoroantimonate], compounds I_a–I_g

Preliminary evaluation showed the new gallates are useful UV photoinitiators for the polymerization of epoxy silicone monomers and other acid susceptible compounds (diglycidyl ethers of bisphenol A, cycloaliphatic epoxides and vinyl ethers). This is being continued in our labs.

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