Synthesis and Characterization of Second-Generation Dialkylphenacylsulfonium Salt Photoinitiators

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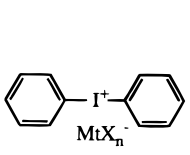
ABSTRACT: A new, simplified method for the synthesis of dialkylphenacylsulfonium salt cationic photoinitiators has been developed. This novel method was successfully used for the preparation of dialkylphenacylsulfonium salts bearing a wide variation in the length and structure of the alkyl chains as well as the light absorbing aryl ketone chromophores and the anions. Modification of the lengths of the alkyl chains permits the design of compatible photoinitiators for highly nonpolar monomers and oligomers such as epoxy functional silicones, epoxidized polybutadiene and vegetable oils. This article describes the synthesis and characterization of these photoinitiators.

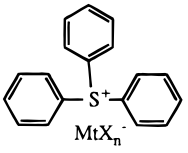
Introduction

In recent years, there has been considerable interest in this laboratory in the photoinduced cationic polymerization of many different types of monomers and oligomers.[1] Such photopolymerization systems are currently employed in a wide diversity of industrial applications including: adhesives, nonstick release coatings, abrasion resistant coatings for plastics, optical fiber coatings, reinforced composites, and optical waveguides. Considerable future potential for growth of cationically photopolymerizable systems exists because of the excellent properties of the resulting polymeric materials, their low energy consumption and the lack of environmental pollution which derives from the elimination of the use of solvents.

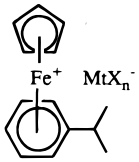
Key to the development of this technology was the discovery of highly photosensitive (i.e., high quantum yield) and efficient cationic photoinitiators which can be designed to be responsive to various UV wavelengths. Among the best photoinitiators which have been developed in recent years are diaryliodonium,[2] triarylsulfonium[3] and ferrocenium salts[4] with the structures **I**−**III** respectively:



I



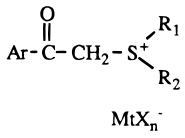
II



III

In the above photoinitiators, MtX_n^- is a nonnucleophilic anion such as $CF_3SO_3^-$, BF_4^-, ClO_4^-, FSO_3^-, PF_6^-, AsF_6^-, SbF_6^-, and $(C_6F_5)_4B^-$. On irradiation with UV light, these photoinitiators undergo irreversible fragmentation with the formation of Brønsted and Lewis acids which initiate cationic polymerization. Several of these photoinitiators are now available as commercial products.

An additional class of interesting photoinitiators is dialkylphenacylsulfonium salts (DPS) having the general structure **IV**:[5,6]



IV

Preliminary investigations in this laboratory have shown that DPS are excellent photoinitiators for the cationic polymerization of reactive monomers such as multifunctional epoxides and vinyl ethers. Mechanistic studies[7] revealed that unlike their triarylsulfonium salt analogues (**II**), DPS compounds mainly undergo reversible photolysis to generate an ylide and a strong protonic acid. This mechanism is depicted in Scheme 1.

Prolonged irradiation results in fragmentation of the photoinitiator by secondary processes to give a variety of free radical derived products.[8,9] A further useful property of these photoinitiators is their ability to undergo facile electron-transfer photosensitization with a variety of electron donor compounds.[10] Using photosensitization, the spectral sensitivity of these photoinitiators can be readily broadened to include the long wavelength UV and visible spectral regions.

Several methods for the preparation of DPS have been reported.[11,12] Previously, we have employed the two-step pathway shown in eqs 4 and 5 of Scheme 2.

First, the 2-bromoalkylaryl ketone was condensed with a dialkyl sulfide to generate the sulfonium bromide **V** (eq 4). Then, the bromide salt was isolated and subjected to a metathesis reaction with an alkali metal salt ($YMtX_n$) containing the desired nonnucleophilic anion, MtX_n^-, to give the active photoinitiator, **VI** (eq 5). Since eq 4 is a process in which the equilibrium lies mainly on the side of the starting materials, the overall success of the entire synthetic sequence shown above depends on the crystallization of the bromide salt **V** to shift the equilibrium to the right. Similarly, the metathesis reaction (eq 5) is also an equilibrium process which is driven to the right by the crystallization of either the active photoinitiator **VI** or YBr. Unfortunately, the DPS salts represented by structure **VI** which can be best prepared using this synthetic approach are those with very poor solubilities and this also limits their use as photoinitiators. For this reason, nonpolar

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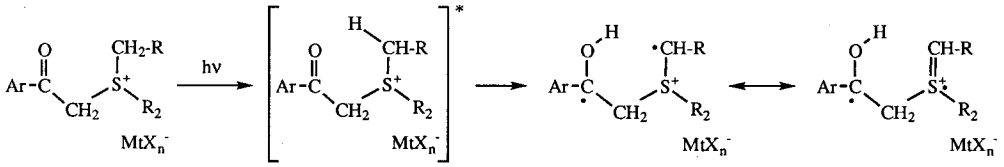
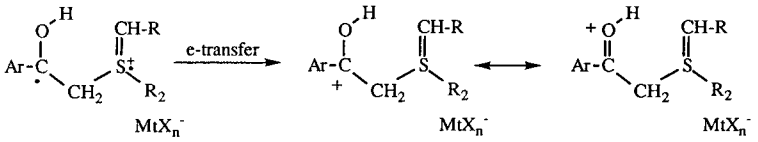
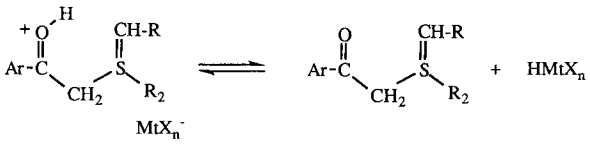
Scheme 1



(1)

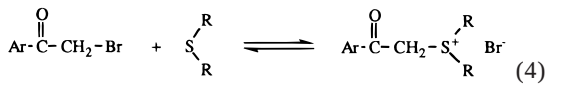


(2)



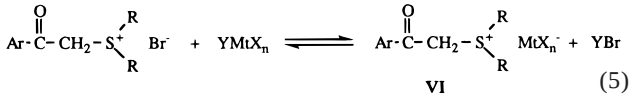
(3)

Scheme 2



(4)

V



(5)

VI

monomers such as epoxidized vegetable oils, vinyl, 1-propenyl, or 1-butenyl ethers and epoxy functionalized silicones cannot be polymerized using these photoinitiators without the use of polar solvents. Even in the case of polar monomers, the poor solubility of DPS photoinitiators results in partial and erratic polymerizations and, in some cases, the polymerizations fail altogether. Therefore, compared to diaryliodonium and triarylsulfonium salts, research in DPS has been rather inactive over the past 20 years.

Accordingly, we have long sought to circumvent these difficulties. This article reports a new, general and simplified approach to the synthesis of DPS which makes it possible to prepare a wide variety of structurally diverse and soluble DPS photoinitiators. In a companion paper,[13] we report the results of a kinetic study of the cationic photoinduced and thermally induced polymerizations of several different monomers using DPS.

Experimental Section

Materials and Characterization Techniques. All organic reagents and solvents employed in this investigation were reagent quality and were used as purchased from the Aldrich Chemical Co. (Milwaukee, WI) unless otherwise noted. Methyl octyl sulfide was purchased from TCI America (Portland, OR). $NaSbF_6$, $KAsF_6$, and KPF_6 were obtained from Advance Research Chemicals, Inc., Catoosa, OK. $KB(C_6F_5)_4$ was obtained from the Rhone-Poulenc Co., Saint-Fons, France.

^1H NMR spectra were obtained using Varian XL-300 and XL-500 spectrometers at room temperature in $CDCl_3$. All chemical shifts were reported relative to tetramethylsilane as an internal standard. Gas chromatographic (GC) analyses were performed on a Hewlett-Packard HP-5890A gas chromatograph equipped with a 15 m × 0.53 μm × 1.5 μm film thickness cross-linked methyl silicone gum column and a flame ionization detector.

Synthesis of Dialkylphenacylsulfonium Salts. The following examples for the synthesis of DPS are typical of those carried out for all the compounds shown in Table 1.

Synthesis of *S*-Methyl *S*-1-Octadecyl Phenacylsulfonium Hexafluoroantimonate. Into a 100 mL round-bottom flask equipped with a magnetic stirrer and a reflux condenser were placed 27.7 g (0.097 mol) of 1-octadecanethiol, 21.3 g (0.15 mol) of iodomethane, 11.2 g (0.2 mol) of potassium hydroxide, 3.0 g (0.01 mol) of tetra-*n*-butylammonium bromide, and 20 mL of toluene. The reaction mixture was heated at reflux for 1 h and then cooled to room temperature. After being diluted with dichloromethane, the reaction mixture was placed in a separatory funnel and washed several times with distilled water to remove excess potassium hydroxide and potassium bromide. Next, the organic layer was placed on a rotary evaporator, and the solvents and excess iodomethane were removed under reduced pressure. There remained methyl 1-octadecyl sulfide as a white crystalline solid, mp 53−56 °C.

Combined together in a 100 mL Erlenmeyer flask were 10 g (0.05 mol) of phenacyl bromide (2-bromoacetophenone), 12.93 g (0.05 mol) of sodium hexafluoroantimonate, 15 g (0.05 mol) of methyl 1-octadecyl sulfide, and 40 mL of 2-butanone (methyl ethyl ketone). The reaction mixture was heated to the boiling point of 2-butanone (80 °C) and maintained at that temperature for 30 min. During this time, sodium bromide was observed to precipitate. The reaction mixture was cooled and filtered to remove the inorganic salts, and the resulting solution was placed on a rotary evaporator to remove the solvent. The resulting product crystallized to give the desired *S*-methyl *S*-1-octadecyl phenacylsulfonium hexafluoroantimonate as a tan solid. Recrystallization from 2-propanol gave a 62% yield of a very light beige salt with a melting point of 80−82 °C.

Synthesis of *S*-Methyl *S*-1-Octyl Phenacylsulfonium Hexafluoroantimonate. Into a 100 mL round-bottom flask equipped with a magnetic stirrer and reflux condenser were placed 16.0 g (0.1 mol) of methyl 1-octyl sulfide 19.9 g (0.1 mol) of phenacyl bromide, 25.87 g (0.1 mol) of sodium hexafluoroantimonate, and 40 mL of acetone. The reaction mixture was brought to reflux and held at this temperature for 15 min. The mixture was filtered through a plug of glass wool to remove the sodium bromide which was formed during the reaction. Then, the solvent was removed on a rotary evaporator, leaving 43.1 g (83.6% yield) of the desired *S*-methyl *S*-1-octyl phenacylsulfonium hexafluoroantimonate as a tan solid.

Table 1. Structures and Characteristics of Dialkylphenacylsulfonium Salts $C_6H_5-CO-CH_2-S^+R_1(R_2)MtX_n^-$

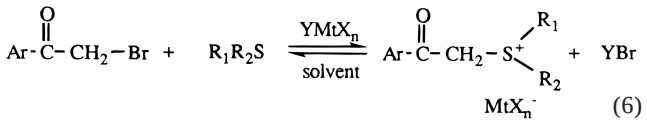
							elemental analysis		
notation	R_1	R_2	MtX_n^-	MW	mp (°C)	yield (%)		% C	% H
1	C_4H_9	C_4H_9	SbF_6^-	501.17	88−89	60	calcd	38.35	5.03
							found	38.53	5.10
2	C_6H_{13}	C_6H_{13}	SbF_6^-	557.28	oil	85	calcd	43.11	5.97
							found	43.52	5.88
3	C_8H_{17}	C_8H_{17}	SbF_6^-	613.39	oil	67	calcd	47.00	6.74
							found	46.85	6.83
4	$C_{10}H_{21}$	$C_{10}H_{21}$	SbF_6^-	669.50	oil	53	calcd	50.23	7.38
							found	50.49	7.22
5	$C_{12}H_{25}$	$C_{12}H_{25}$	SbF_6^-	725.60	46−47	17	calcd	52.97	7.92
							found	53.05	7.90
6	$C_{14}H_{29}$	$C_{14}H_{29}$	SbF_6^-	783.13	60−61	26	calcd	55.17	8.62
							found	55.07	8.44
7	CH_3	C_8H_{17}[a]	SbF_6^-	515.20	51−52	63	calcd	39.63	5.28
							found	39.73	5.23
8	CH_3	C_8H_{17}	SbF_6^-	515.20	75−76	84	calcd	39.63	5.28
							found	39.72	5.28
9	CH_3	$C_{10}H_{21}$	SbF_6^-	542.10	oil	53	calcd	42.01	5.75
							found	42.02	5.90
10	CH_3	$C_{12}H_{25}$	$B(C_6F_5)_4$	1014.61	oil	66	calcd	53.27	3.48
							found	53.12	3.39
11	CH_3	$C_{12}H_{25}$	PF_6^-	480.53	49−51	82	calcd	52.49	7.34
							found	52.20	7.34
12	CH_3	$C_{12}H_{25}$	AsF_6^-	524.48	48−50	87	calcd	48.09	6.73
							found	48.32	6.65
13	CH_3	$C_{12}H_{25}$	SbF_6^-	571.31	58.5−60	50	calcd	44.15	6.17
							found	44.31	6.22
14	CH_3	$C_{14}H_{29}$	SbF_6^-	599.36	65−66.5	60	calcd	46.09	6.56
							found	46.33	6.63
15	CH_3	$C_{16}H_{33}$	SbF_6^-	627.42	74−75.5	63	calcd	47.86	6.91
							found	48.00	7.00
16	CH_3	$C_{18}H_{37}$	SbF_6^-	655.50	80−82	62	calcd	49.48	7.23
							found	49.86	7.26
17	C_2H_5	$C_{12}H_{25}$	SbF_6^-	585.34	oil	90	calcd	45.14	6.37
							found	45.42	6.49
18	C_2H_5	$C_{14}H_{29}$	SbF_6^-	613.39	50−52	77	calcd	46.92	6.89
							found	46.97	6.57
19	C_2H_5	$C_{16}H_{33}$	SbF_6^-	641.44	60−62	67	calcd	48.68	7.07
							found	48.37	7.11
20	C_2H_5	$C_{18}H_{37}$	SbF_6^-	669.50	70−71	70	calcd	50.16	7.52
							found	49.88	7.43
21	C_3H_7	$C_{18}H_{37}$	SbF_6^-	683.53	72−74	67	calcd	50.96	7.52
							found	51.01	7.40
22	C_4H_9	$C_{18}H_{37}$	SbF_6^-	697.55	50−51	72	calcd	51.66	7.66
							found	52.01	7.69

[a] $(C_8H_{17}) = -CH_2-CH(C_2H_5)C_4H_9$.

The product was further purified by recrystallization: first, from a 1:3 mixture of water and ethanol; then, 2-propanol. The pure, colorless, crystalline photoinitiator had a melting point of 75−76 °C. The photoinitiator was soluble in a wide variety of common solvents such as acetone, 2-butanone, chloroform, and dichloromethane.

Results and Discussion

Synthesis and Characterization of Dialkylphenacylsulfonium Salts. A new simplified synthetic procedure has been developed in this laboratory for the preparation of DPS. As shown in eq 6, the synthesis



(6)

involves a one-pot reaction of phenacyl bromides (2-bromoacetophenones) or their aryl (naphthyl, anthracenyl, or pyrenyl) counterparts with the appropriate dialkyl sulfides in the presence of an alkali metal salt of the desired nonnucleophilic anion. Typically, this reaction is carried out in the presence of a ketonic solvent such as acetone, 2-butanone, or 4-methyl-2-pentanone. Although the overall synthesis involves two simultaneous equilibrium processes, the reaction is strongly driven to the right by precipitation of the insoluble alkali metal halide, YBr. The above one-pot reaction may be carried out at room temperature or at temperatures up to the boiling point of the solvent which is employed. When the reaction is complete, the reaction mixture is simply filtered to remove the alkali metal halide and the desired photoinitiators isolated by evaporation of the solvent. Thereafter, the photoinitiators can be rigorously purified by conventional crystallization techniques. Alternatively, those photoinitiators which are liquids may be readily purified by solvent extraction and precipitation methods. The photoinitiators were characterized by means of their melting points, ^{1}H NMR and UV spectra, and elemental analyses.

Given in Table 1 are the structures, yields, and physical characteristics of the various DPS prepared during the course of this work. As may be noted, this synthetic method may be applied to the preparation in good yields of a wide variety of DPS including those bearing different aryl groups, alkyl groups of differing chain lengths, and structures and with different anions.

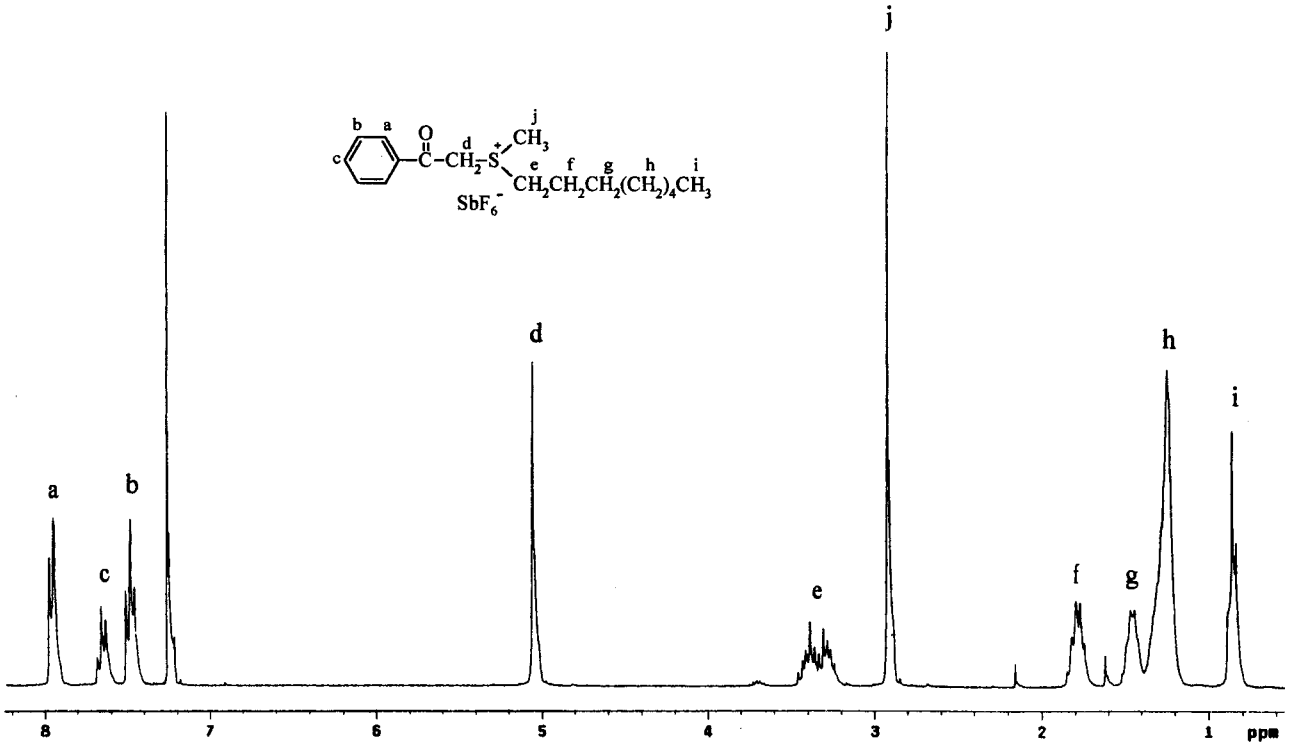


Figure 1. 300 MHz ^{1}H NMR spectrum of C_1C_8−DPS(SbF_6) in $CDCl_3$.

For the most part, the yields reported in Table 1 are preliminary and have not been optimized. DPS salts prepared by this method are stable, colorless, light-sensitive compounds. Crystalline DPS salts do not appear to undergo thermal decomposition at temperatures up to their melting points. In Figure 1 is shown the ^{1}H NMR spectrum of photoinitiator **1** in $CDCl_3$, which is typical of this series of compounds. A summary of the ^{1}H NMR chemical shifts for these photoinitiators is given in parts A and B of Table 2. Interestingly, the −COCH_2− resonance in these spectra shifts to increasingly lower fields as the anion is varied from $(C_6F_5)_4B^-$ to PF_6^- to AsF_6^- to SbF_6^-.

Ideally, a photoinitiator should be stable in the desired monomer in the absence of light for as long as possible, yet on irradiation it should efficiently initiate cationic polymerization. For this reason, the photoinitiator should be as pure as possible since even slight trace impurities may induce polymerization over a long period of time. The most effective method of purification of DPS and other onium salt photoinitiators is by recrystallization. Normally, photoinitiators that can be readily crystallized have meting point substantially above room temperature. However, high melting point DPS photoinitiators are generally insoluble in nonpolar monomers. Hence, manipulation of the structure of the photoinitiator is generally required to simultaneously optimize these two properties. Alternatively, several different photoinitiators may be required, each for use with a different monomer system. With these caveats in mind, the extensive series of photoinitiators shown in Table 1 was prepared.

Shown in Figure 2 are the relationships of the melting points of two related series of methyl and ethyl alkyl phenacylsulfonium hexafluoroantimonate photoinitiators (abbreviated C_1C_x−DPS(SbF_6) and C_2C_x−DPS-(SbF_6), respectively) to the alkyl chain length. We have prepared only those DPS containing alkyl groups (R_2) with an even number of carbons. For short alkyl chain

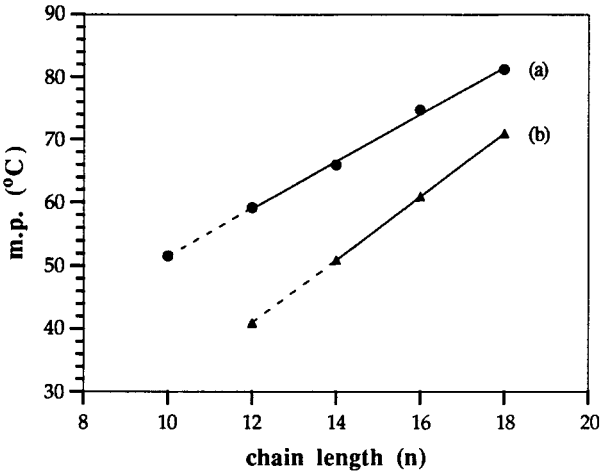


Figure 2. Melting point vs alkyl chain length plots for (a) alkyl methyl phenacylsulfonium hexafluoroantimonates and (b) alkyl ethyl phenacylsulfonium hexafluoroantimonates.

lengths (R_2 < $C_{10}H_{23}$ in plot a and R_2 < $C_{12}H_{25}$ in plot b), the melting point characteristics are dominated by the phenacyl group. Increasing the alkyl chain length disrupts the packing of the molecules in the crystal, and consequently, the melting points of the corresponding sulfonium salts decrease. In contrast, when the chain lengths of the alkyl groups reach 10 or more carbons, these groups dominate the melting point characteristics of the DPS. The melting points of each series increases linearly as the lengths of the alkyl groups are increased. Similar observations were made for alkoxy substituted diaryliodonium salts.[14] If C_1C_{10}−DPS(SbF_6) and C_2C_{12}−DPS(SbF_6) followed the same trend, they would be expected to have melting points of approximately 51−52 and 41−42 °C, respectively, as indicated by the extrapolated lines. Instead, these salts were isolated as viscous oils. Recrystallization of C_2C_{12}−DPS(SbF_6) can be achieved at low temperatures; however, this

Table 2

A. ^{1}H NMR Characterization of Ph−CO−CH_2−$S^+R_1(R_2)$ MtX_n^- (300 MHz, in $CDCl_3$)[a]

structure R_1 =	−*Ar* δ, ppm (m; *J*, Hz)	−CO-*CH_2*− δ ppm (m; J_{AB}, Hz)	−*R_1* δ ppm (m; *J*, Hz)
$-CH_3$	SbF_6^- salts: -*Ph* 7.46−8.01 (m)	∼5.15 (d, 17.7), H_B ∼5.08 (d, 17.7), H_A	-*CH_3* ∼2.95
	AsF_6^- salt: −*Ph* 7.42−7.96 (m)	5.07 (s)	-*CH_3* 2.91 (s)
	PF_6^- salt: −*Ph* 7.41−7.95 (m)	5.06 (s)	-*CH_3* 2.88 (s)
	$B(C_6F_5)_4^-$ salt: −*Ph* 7.51−7.84 (m)	4.89 (d, 16.8), H_B 4.80 (d, 16.8), H_A	-*CH_3* 2.91 (s)
$-CH_2CH_3$	-*Ph* 7.52−8.06 (m)	∼5.14 (d, 17.7), H_B ∼5.07 (d, 17.7), H_A	-*CH_2*CH_3; 3.33−3.54 (m) -CH_2*CH_3* 1.57 (t, 7.5)
$-CH_2CH_2CH_3$	-*Ph* 7.51−8.05 (m)	5.11 (s)	-*CH_2*CH_2CH_3: 3.31−3.49 (m) -CH_2*CH_2*CH_3: 1.81−1.95 (m) -CH_2CH_2*CH_3*: 1.18 (t, 7.2)
$-CH_2CH_2CH_2CH_3$	-*Ph* 7.49−8.05 (m)	5.10 (s)	-*CH_2*$CH_2CH_2CH_3$: 3.36−3.42 (m) -CH_2*CH_2*CH_2CH_3: 1.77−1.87 (m) -CH_2CH_2*CH_2*CH_3: 1.42−1.62 (m) -$CH_2CH_2CH_2$*CH_3*: 1.00 (t, 7.3)
$-R_2$	-*Ph*: 7.53−8.06 (m)	∼5.13 (s)	refer to part B for R_2

B. General Chemical Shift Range for R_2

$$R_2 = -\overset{1}{CH_2}\overset{2}{CH_2}\overset{3}{CH_2}\overset{4}{(CH_2)_{n-4}}\overset{5}{CH_3}$$

	δ ppm (m; *J*, Hz)				
	1	2	3	4	5[b]
SbF_6^- salts	3.27−3.54 (m)	∼1.75−1.93 (m)	∼1.45−1.55 (m)	∼1.20−1.42 (m)	∼0.88 (t, 6.6−6.9)
AsF_6^- salt	3.24−3.43 (m)	1.69−1.81 (m)	1.35−1.50 (m)	1.16−1.44 (m)	0.88 (t, 6.4)
PF_6^- salt	3.25−3.43 (m)	1.67−1.78 (m)	1.35−1.50 (m)	1.16−1.41 (m)	0.87 (t, 6.8)
$B(C_6F_5)_4^-$ salt	3.12−3.43 (m)	1.79−1.89 (m)	1.43−1.51 (m)	1.19−1.40 (m)	0.88 (t, 6.9)

[a] All the salts have SbF_6^- anion unless specified. [b] For (C_4C_4−DPS)SbF_6: δ 1.00 (t, 7.2).

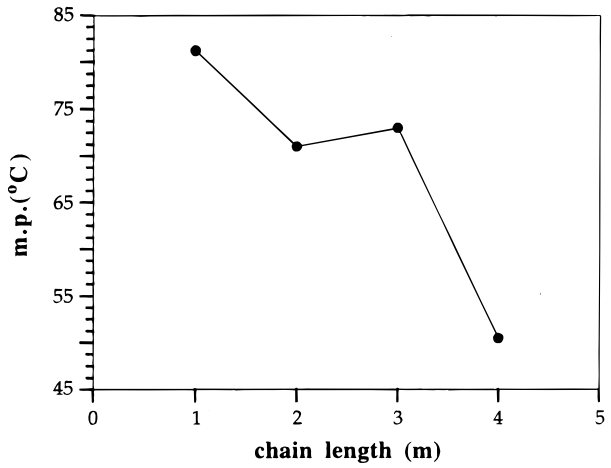


Figure 3. Melting point vs alkyl chain length plot for C_nC_{18}−DPS(SbF_6) salts.

compound appears to have a melting point slightly below room temperature. Thus, in the border region, the crystallinity of DPS salts is counterbalanced by both phenacyl and alkyl structural factors, making it difficult to predict the melting point characteristics. An analogous pattern was observed for C_xC_x−DPS(SbF_6) salts that were prepared from symmetrical sulfides (Table 1).

Figure 3 shows the melting point characteristics of a series of four alkyl octadecylphenacylsulfonium hexafluoroantimonate salts in which the short chain alkyl group (R_1) is systematically varied. Generally, increasing the length of the short chain alkyl group tends to lower the melting point as indicated by Figure 2. The higher melting point of C_3C_{18}−DPS(SbF_6) was unexpected. However, a similar pattern has been observed in some diaryliodonium salt photoinitiators with an odd number of carbon atoms in the alkoxy side chain.[14]

It is interesting to note in Table 1 that symmetrical DPS with identical alkyl groups have lower melting points than the corresponding asymmetrical DPS having the same total number of carbon atoms in the two alkyl groups. In addition, branching may also lower the melting point as shown in the case of isomeric DPS salts in entries 7 and 8. The latter, branched C_1C_8−DPS(SbF_6) salt has a much lower melting point.

Four C_1C_{12}−DPS photoinitiators with identical DPS (S-1-dodecyl S-methyl phenacylsulfonium) cations but differing in the structure of their anions ($B(C_6F_5)_4^-$, SbF_6^-, AsF_6^-, PF_6^-) were also prepared (entries 10−13). Both the AsF_6^- and the PF_6^- salts are solids with melting points of approximately 50 °C which is unexpectedly lower than the corresponding SbF_6^- salt. The underlying reason for this effect is not clear to us. Usually, for onium salts, the melting point typically tends to decrease as the size of the anion increases (i.e., $PF_6^- > AsF_6^- > SbF_6^- > B(C_6F_5)_4^-$).[15] The $B(C_6F_5)_4^-$ photoinitiator was isolated as a highly viscous oil. This compound was difficult to free from the last traces of solvent even when subjected to long-term drying at 50 °C at 0.01 mmHg.

Manipulation of the respective lengths of the two alkyl groups also allows considerable latitude in the modification of the solubility characteristics of DPS. Table 3 gives the solubility profile of several of these compounds in common organic solvents and provides a comparison with a DPS derived from the cyclic sulfide, tetrahydrothiophene (THT).[5] The best solubility is provided by liquid DPS such as C_8C_8−DPS(SbF_6) or crystalline DPS bearing at least 30 carbon atoms; for example, $C_{14}C_{14}$−DPS(SbF_6) and C_4C_{18}−DPS(SbF_6). These latter photoinitiators have low melting points, can be easily purified by recrystallization, and are soluble in most common solvents with the exception of normal alkanes. The

Table 3. Solubility of C_mC_n−DPS(SbF_6) in Common Organic Solvents at Room Temperature[a]

solvent	THTP	C_4C_4	C_8C_8	$C_{14}C_{14}$	C_1C_{12}	C_1C_{18}	C_4C_{18}
hexane	−	−	−	−	−	−	−
toluene	−	−	+	+	+	/	+
ether	−	−	+	+	−	−	+
THF	+	+	+	+	+	+	+
chloroform	−	/	+	+	+	+	+
dichloromethane	−	+	+	+	+	+	+
methanol	+	+	+	/	+	/	/
ethanol	/	/	+	/	+	/	/
2-propanol	−	/	+	/	/	−	/
acetone	+	+	+	+	+	+	+
MIBK	/	+	+	+	+	+	+
ethyl acetate	/	+	+	+	+	+	+
acetonitrile	+	+	+	+	+	/	+
DMSO	+	+	+	+	+	+	+

[a] Key: (+) readily soluble, >15 mg/mL; (/) borderline solubility, 3−15 mg/mL; (−) insoluble, <3 mg/mL.

solubility characteristics are also greatly influenced by the character of the anion present. As the size of the anion increases, so also does the solubility of the photoinitiator. For example, for entries 10−13 of Table 1, the order of increasing solubility is as follows: $PF_6^- < AsF_6^- < SbF_6^- < B(C_6F_5)_4^-$.

DPS salts which differ only in the length and type of alkyl groups bonded to the positively charged sulfur atom share identical UV absorption characteristics. This is indicative of the fact that the phenyl ketone group in these DPS is the light absorbing chromophore. The major absorption maxima (CH_3CN) of these compounds are: 206, 251, and 281 nm with molar extinction coefficients of 11 000, 12 000, and 1600 M^{-1} cm^{-1}, respectively. In addition, the UV spectra of these photoinitiators characteristically exhibit a low intensity tail absorption which extends out to approximately 320 nm. Attempts to prepare DPS salts with longer wavelength absorptions will be reported in a forthcoming article from this laboratory.

Mechanism and Optimization of Dialkylphenacylsulfonium Salt Formation. To probe the reaction mechanism of eq 6 and further optimize the synthesis conditions, a series of reactions were carried out and

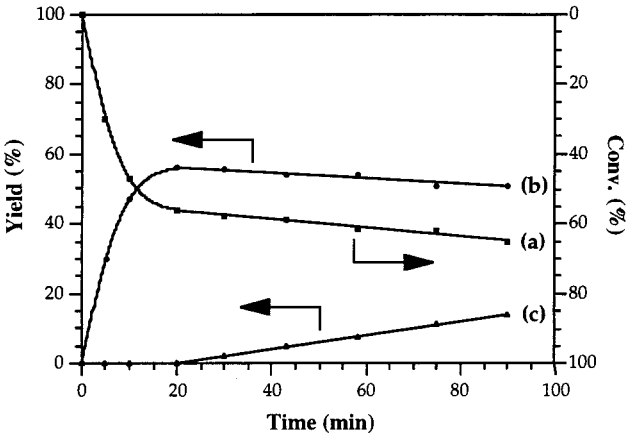
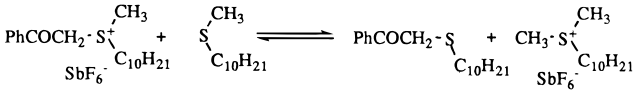


Figure 4. Conversion /yield vs time plots of run 1 in Table 4: (a) phenacyl bromide; (b) phenacyl sulfonium salt; (c) decyl phenacyl sulfide.

are summarized in Table 4. In the first study (run 1), the reaction of an equimolar mixture of phenacyl bromide, 1-decyl methyl sulfide (**DMS**) and sodium hexafluoroantimonate at 80 °C was monitored by ^1H NMR. It was observed, as shown in Figure 4, that after the initial rapid consumption of phenacyl bromide (first 20 min, curve a), a maximum yield of the desired sulfonium salt (curve b) was obtained. Prolonged heating at 80 °C resulted in the formation of a byproduct (curve c), which increased linearly with reaction time. The byproduct was subsequently identified as 1-decyl phenacyl sulfide (DcPS).

We suspected that a transmethylation reaction as depicted in eq 7 may have occurred during the above reaction, leading to the formation of *S*,*S*-dimethyl 1-decylsulfonium hexafluoroantimonate and DcPS.



(7)

Table 4. Synthesis of Dialkylphenacylsulfonium Salts under Various Reaction Conditions

	reactants (equiv)						yield (%)[a]	
run	$PhCOCH_2Br$	R_1SR_2	$NaSbF_6$	solvent; vol (mL)	temp (°C)	time (min)	DPS[b]	APS[c]
1	1.0	DMS,[d] 1.0	1.0	MEK,[h] 6.3	80	20	56	trace
						90	51	14
2	1.0	DMS, 4.0	1.0	MEK, 5.0	80	180	trace	>98
3	1.0	DMS, 1.0	1.0	MEK, 1.0	80	20	83	6
4	1.0	DMS, 1.0	1.5	MEK, 1.0	80	20	80	6
5	1.5	DMS, 1.0	1.0	MEK, 1.0	80	20	87	9
6	1.0	EHS[e],1.0	1.0	MEK, 1.0	80	20	83	0
7	1.0	DMS, 1.0	1.0	acetone, 1.0	25	90	80	0
						150	88	0
8	1.0	DMS, 1.0	1.0	MEK, 1.0	25	90	75	0
						150	85	0
						4 da	96	trace
9	1.0	DMS, 1.0	1.0	MIBK,[i]1.0	25	90	67	0
						150	85	0
10	1.0	DOS[f], 1.0	1.0	MEK, 1.0	25	150	58	0
						360	88	0
11	1.0[g]	DMS, 1.0	1.0	MEK, 1.0	25	150	0	0
12	1.0[g]	DMS, 1.0	1.0	MEK, 1.0	reflux	30	33	13
	1.0[g]							
14	(3 mol % NaI)	DMS, 1.0	1.0	MEK, 1.0	reflux	30	56	8
						60	63	13

[a] By ^1H NMR. [b] DPS: $PhCOCH_2S^+R_1(R_2)SbF_6^-$. [c] APS: $PhCOCH_2SR$. [d] DMS: $CH_3SC_{10}H_{21}$. [e] EHS: $CH_3CH_2SC_{16}H_{33}$. [f] DOS: $C_8H_{17}SC_8H_{17}$. [g] $PhCOCH_2Cl$. [h] Methylethyl ketone(2-butanone). [i] Methylisobutyl ketone(3-methyl-2-pentanone).

Thus, in run 2, 1-decyl methyl sulfide was used in large excess to favor this process. Refluxing the reactants in 2-butanone for 3 h and again monitoring the reaction by ^{1}H NMR resulted in the quantitative consumption of the initially formed *S*-methyl *S*-1-decyl phenacylsulfonium salt. After the reaction mixture was filtered and the solution was poured into *n*-hexane, a two-phase mixture was obtained. The top layer contained a single product as determined by GC analysis. The product was identified as 1-decyl phenacyl sulfide, DcPS, by comparison of the GC chromatogram and the ^{1}H NMR spectrum with those of an authentic sample of this compound prepared by reaction of phenacyl bromide with 1-decanethiol in the presence of a base. This compound was also identical to the byproduct observed in run 1. It is interesting to note that the other possible product of the transalkylation reaction, methyl phenacyl sulfide was not observed. Thus, the less bulky methyl group is preferentially transferred during the transalkylation reaction. Additional evidence of the transalkylation reaction was found in the ^{1}H NMR spectrum of the lower layer obtained from the reaction mixture which suggested the formation of the *S*,*S*-dimethyl 1-decylsulfonium salt.

As expected, the concentration of the reactants used in the synthesis plays an important role in determining the rate of reaction. Comparing run 3 in which the amount of methyl ethyl ketone is substantially lowered as compared to that of run 1, one can see a considerable increase in the yield of the desired DPS and also an increase in the amount of byproducts. Identical reaction times were used in both cases. Within experimental error, increasing the amount of the $NaSbF_6$ used in the reaction did not have an appreciable effect on the yield (run 4 vs run 1). This is probably due to the fact that $NaSbF_6$ is only partially soluble in the reaction mixture at the start of the reaction. The use of additional $NaSbF_6$ (run 4) does not substantially increase the overall effective concentration of this reagent in the reaction mixture. In contrast, an increase in the concentration of phenacyl bromide (run 5 vs run 3) resulted in a faster reaction rate and a slightly increased yield of the desired DPS salt. Formation of the byproduct, DcPS**,** could not be eliminated in the presence of excess phenacyl bromide.

When ethyl 1-hexadecyl sulfide (EHS) was used to replace DMS (run 6), no byproduct alkyl phenacyl sulfide (APS) were observed. Presumably, the replacement of the methyl group with the considerably more bulky ethyl group substantially slows the transalkylation reaction (eq 7). Runs 7−9 were all carried out at room temperature. Although longer reaction times are required to reach high conversions, the formation of the byproduct APS was not observed. Change of the solvent from 2-butanone to acetone or 4-methyl-2-pentanone (MIBK) did not appear to have a significant effect on the yield of products obtained. After 4 days at room temperature (run 8), the yield of the DPS was maximized (96%) with only a trace of APS formed. When the symmetrical di(1-octyl) sulfide was used (run 10), a slower rate of reaction was observed. However, a high yield of the desired sulfonium salt product could be obtained using an extended reaction time (6 h). Repetition of the same conditions but replacing phenacyl bromide with phenacyl chloride (run 11) gave essentially no reaction. Raising the temperature to 80 °C (refluxing

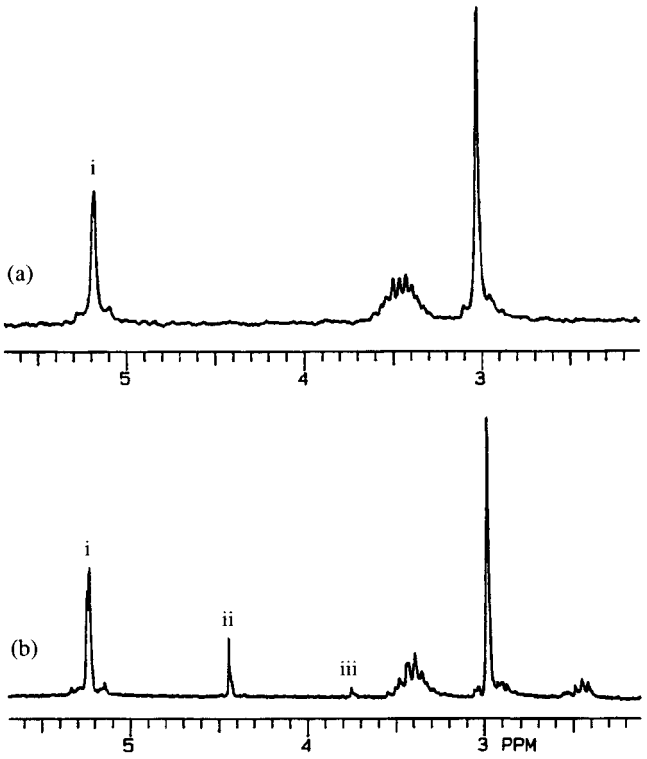


Figure 5. ^{1}H NMR spectra in $CDCl_3$: (a) C_1C_{12}−DPS(SbF_6) before reaction and (b) after refluxing for 1.5 h with a molar equivalent of NaBr in 2-butanone. Assignments: (i) $PhCOCH_2$-$S^+CH_3(C_{12}H_{25})$; (ii) $PhCOCH_2Br$; (iii) $PhCOCH_2SC_{12}H_{25}$.

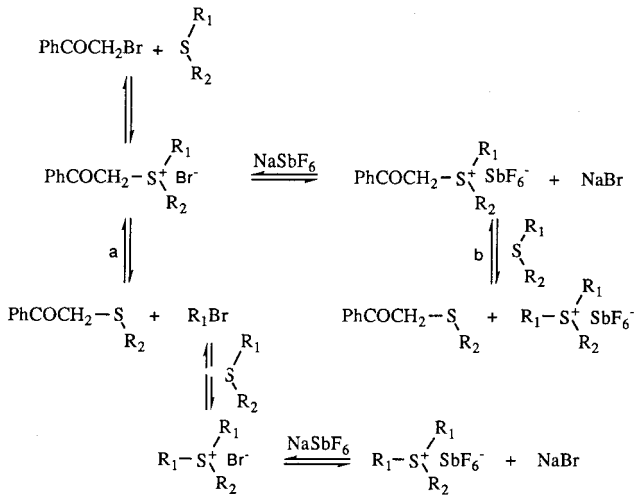
2-butanone) gave a 33% yield of the desired DPS after $^1/_2$ h (run 12); however, there was also an appreciable amount of byproduct APS formed. Thus, when phenacyl chloride is used to replace phenacyl bromide, a higher reaction temperature and longer reaction time are required to achieve a satisfactory conversion to product. In run 14, the reaction using phenacyl chloride was catalyzed by the addition of NaI and the yield was substantially increased.

As a final demonstration of the equilibrium character of the synthesis, 0.25 mmol of *S*-1-dodecyl *S*-methyl phenacylsulfonium hexafluoroantimonate was refluxed in 1.3 mL of 2-butanone with a molar equivalent amount of sodium bromide for 1.5 h. Shown in Figure 5 are the ^{1}H NMR spectra before (a) and after (b) the reaction. Resonances which can be attributed respectively to phenacyl bromide (Figure 5b, peak ii) and the transalkylation product, dodecyl phenacyl sulfide (Figure 5b, peak iii), can be clearly seen.

Our preliminary attempts to prepare DPS by condensing alkyl allyl sulfides or alkyl benzyl sulfides and phenacyl bromide were not successful. It was found that, under the usual reaction conditions, extensive side reactions took place resulting in the formation of a complex mixture of sulfonium salts among which were the desired phenacylsulfonium salts. For example, when alkyl benzyl sulfides were allowed to react with phenacyl bromide in the presence of sodium hexafluoroantimonate at room temperature for 24 h, the main products were an alkyl phenacyl sulfide and benzyl bromide. The presence of these products in the reaction mixture can be attributed to a transalkylation process as depicted in Scheme 3.

All the DPS described in this article were found to be efficient photoinitiators of cationic polymerization. The results of kinetic studies of the photoinitiated cationic

Scheme 3



R_1 = -CH_3, -$CH_2CH{=}CH_2$, -CH_2Ph
R_2 = -C_nH_{2n+1}

a. crossover reaction
b. transalkylation reaction

polymerizations of several monomer systems are presented in a companion paper.

Conclusions

A novel synthesis of dialkylphenacylsulfonium salts has been developed which makes it possible to prepare a wide and diverse series of these cationic photoinitiators and to tailor them for specific applications by rational design and synthesis. We have found that UV absorption characteristics of these photoinitiators may be manipulated by modifications in the aryl ketone portion of the molecule. Similarly, the melting points and solubilities are readily manipulated by control of the lengths of the alkyl chains and by modification of the anions. The use of several of these novel DPS photoinitiators to carry out a variety of photoinitiated cationic polymerizations is described in a companion paper.

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