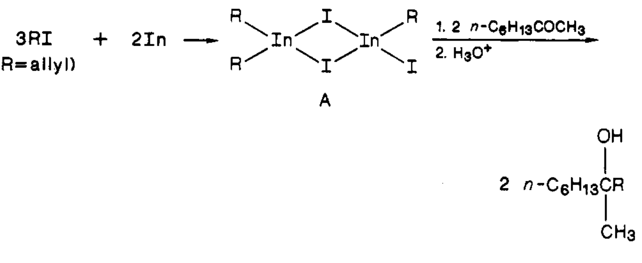
Table II. Yields of 4-Methyl-1-decen-4-ol with Various Ratios of Indium:Allyl Iodide:2-Octanone

molar ratio, indium:allyl iodide:2-octanone	yield,[a,b] %
3:3:2	89 (100)
2:3:2	84 (100)
2:2:2	64 (67)
2:3:3	58 (67)
1:3:2	48 (50)

[a] Based on 2-octanone. [b] Figures in parentheses refer to the theoretical yields expected from Scheme I.

Scheme I



mixture was stirred at room temperature for 1 h, and then the reaction was quenched by the addition of diluted hydrochloric acid. The product was extracted with ether and purified by column chromatography on silica gel to afford 2-phenyl-4-penten-2-ol (196 mg, 91% yield). Results for other carbonyl compounds are listed in Table I. Allylic bromides are equally reactive, however, the reactivity of allyl chloride is markedly depressed. Allylic phosphates themselves are much less reactive, but with an equimolar amount of lithium iodide, moderate yields of products were attained. Various types of ketones and aldehydes are allylated in high yields, but ester and cyano groups were not susceptible to allylation by the present method. It is worthy of note that even the substrates having active hydrogen such as ethyl acetoacetate and salicylaldehyde could be readily allylated in good yields. The present allylation is highly regiospecific; allylic halides react only at the γ-position, and α,β-unsaturated carbonyl compounds give regiospecific 1,2-addition products. On the other hand, propargyl bromide gave a mixture of the acetylenic and allenic products. 4-*tert*-Butylcyclohexanone gave the axial alcohol predominantly (axial:equatorial, 8:2), and the reaction of benzaldehyde with crotyl bromide afforded a mixture of the erythro and threo alcohols in the ratio of 66:34.

In order to clarify the intermediate indium species of this reaction, we carried out the indium-mediated coupling of allyl iodide and 2-octanone with various molar ratios of indium:allyl iodide:2-octanone, and the yields of the product were examined. The results (Table II) show that the stoichiometric ratio of this reaction is 2:3:2, suggesting the intermediacy of the sesquiiodide[11,12] A and two-thirds of the allyl group being transferred to the carbonyl compound (Scheme I).

Indium-mediated synthetic reactions have been scarcely studied.[14] The present allylation of carbonyl compounds is superior to the existing ones using other metals in regard to its generality, high yields, and mildness of reaction conditions. Further mechanistic studies and extension of this interesting reaction are now under way.

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[5] Butsugan, Y.; Ito, H.; Araki, S. *Tetrahedron Lett.* **1987**, *28*, 3707.

[6] Imamoto, T.; Kusumoto, T.; Tawarayama, Y.; Sugiura, Y.; Mita, T.; Hatanaka, Y.; Yokoyama, M. *J. Org. Chem.* **1984**, *49*, 3904.

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[8] Wada, M.; Akiba, K.-y. *Tetrahedron Lett.* **1985**, *26*, 4211. Wada, M.; Okhi, H.; Akiba, K.-y. *Tetrahedron Lett.* **1986**, *27*, 4771.

[9] For examples of the allylation of carbonyl compounds using low-valent metal, see: Hiyama, T.; Okude, Y.; Kimura, K.; Nozaki, H. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 561. Girard, P.; Namy, J. L.; Kagan, H. B. *J. Am. Chem. Soc.* **1980**, *102*, 2693. Souppe, J.; Namy, J. L.; Kagan, H. B. *Tetrahedron Lett.* **1982**, *23*, 3497 and references cited therein.

[10] Indium powder, stabilized by 0.5% of MgO, was obtained from Nakarai Chemicals Co. Ltd. and used as received.

[11] The reactions of indium metal and alkyl halides (RX) were reported,[13] in most cases of which were isolated sesquihalides $R_3In_2X_3$.

[12] The reaction of indium metal and allyl iodide in DMF in the absence of carbonyl compounds gave an organoindium species as a viscous oil after removal of the solvent. The compound showed absorptions of 472, 387, 168, and 148 cm^{-1} in the far infrared region. The ^{1}H NMR spectrum (DMF-d_7, −30 °C) revealed two sets of allyl signals with a 2:1 intensity ratio: δ 1.75 (d, J = 8 Hz, 4 H, CH_2), 2.02 (d, J = 8 Hz, 2 H, CH_2), 4.40–4.79 (m, 6 H, $=CH_2$), and 5.94 (m, 3 H, $=CH$). These data are consistent with the formulation of $R_3In_2I_3$ (R = allyl). The organoindium compound thus obtained reacted with 2-octanone to give an 86% yield of the coupling product. Further structural elucidation on this compound is now in progress.

[13] Gynane, M. J. S.; Worrall, I. J. *J. Organomet. Chem.* **1974**, *81*, 329.

[14] See, for example: Chao, L.-C.; Rieke, R. D. *J. Org. Chem.* **1975**, *40*, 2253.

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Received November 11, 1987

Triphenylsulfonium Salt Photochemistry. New Evidence for Triplet Excited State Reactions

Summary: Direct and sensitized photolysis of triphenylsulfonium salts can generate the triplet state which yields diphenyl sulfide as the major photoproduct. Triplet sensitization is observed in the presence of ketones with E_T > 74 kcal/mol, and the efficiency of sensitization correlates qualitatively with increasing E_T of the sensitizer. In contrast, the singlet excited state yields mainly (phenylthio)biphenyls in addition to diphenyl sulfide.

Sir: Triphenylsulfonium salts are increasingly used as photoinitiators for acid-catalyzed processes in resist applications.[1,2] The proposed mechanisms for photodecomposition involve homolysis to generate the diphenylsulfinyl radical cation and phenyl radical, or heterolysis to phenyl cation and diphenyl sulfide.[3,4] Each pathway ultimately yields diphenyl sulfide and generates acid. Recently we reported a new decomposition pathway from direct photolysis of triphenylsulfonium salts in solution which yields (phenylthio)biphenyls (**3**–**5**) as the major products by rearrangement, in addition to the escape product diphenyl sulfide (**2**) (Scheme I).[5] These rearrangement products

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[2] Jones, R. G. *J. Chem. Soc., Chem. Commun.* **1985**, 842.

[3] Knapzyck, J. W.; McEwen, W. E. *J. Org. Chem.* **1970**, *35*, 2539.

[4] For reviews on studies of triarylsulfonium salts in polymer films, see: Crivello, J. V. *Adv. Polym. Sci.* **1984**, *62*, 1. Pappas, S. P. *J. Imaging Technol.* **1985**, *11*, 146. Pappas, S. P. *Prog. Org. Coat.* **1985**, *13*, 35.

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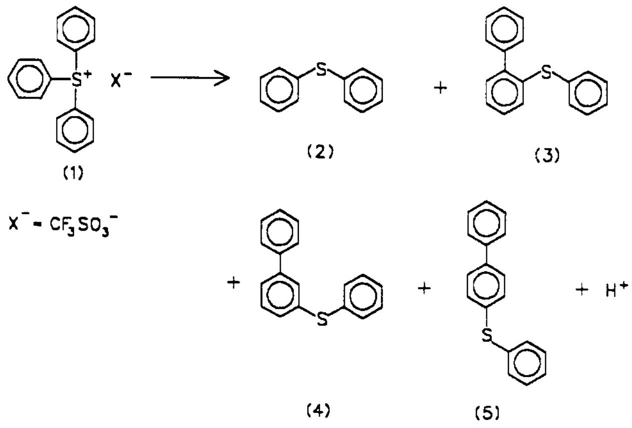
are consistent with in-cage recombination from both homolytic and heterolytic fragmentation reactions (Scheme II). The in-cage recombination products also result in the generation of acid and rationalize the observation by others that acid production greatly exceeds diphenyl sulfide production.[6] In view of this new photochemical pathway for direct irradiation, sensitized photolysis of triphenylsulfonium triflate was studied to determine how the triplet excited state affects product formation.

Irradiation of a N_2-purged 0.01 M acetone solution of triphenylsulfonium triflate (**1**) in a quartz tube to low conversion (<10%) in a Rayonet reactor (λ = 254 nm) yields diphenyl sulfide (**2**) as the major product along with 2-(phenylthio)biphenyl (**3**), 3-(phenylthio)biphenyl (**4**), and 4-(phenylthio)biphenyl (**5**).[7] This contrasts with direct photolysis in N_2-purged acetonitrile (Table I), where the cage product (**3**) becomes a major product. Furthermore, irradiation of acetonitrile solutions of triphenylsulfonium triflate saturated with oxygen, a triplet quencher, decreases some of the diphenyl sulfide formation.[8] Irradiation of acetone solutions of **1** in Pyrex tubes at λ = 300 nm, where acetone absorbs >90% of the incident light (acetone absorbs 40–45% at λ = 254 nm), yields diphenyl sulfide as the sole sulfur-containing product. Also, irradiation of acetonitrile solutions of **1** at λ = 300 nm in the presence of acetophenone, 1-indanone, or xanthone also yields diphenyl sulfide as the major photoproduct, whereas only small amounts of photoproduct [(phenylthio)biphenyls and diphenyl sulfide] could be observed upon irradiation in the absence of these species under identical conditions.

Scheme I. Photoproducts from Irradiation of Triphenylsulfonium Triflate



Scheme II. Homolytic and Heterolytic Pathways for Product Formation

Homolytic Cleavage

$$Ph_3S^+ X^- \xrightarrow{h\nu} [Ph_3S^+ X^-]^*$$
$$[Ph_3S^+ X^-]^* \longrightarrow \overline{Ph_2S^{+\cdot} + Ph^\cdot + X^-}$$
$$\overline{Ph_2S^{+\cdot} + Ph^\cdot + X^-} \xrightarrow{\text{cage recombination}} (1) + (3) + (4) + (5)$$
$$Ph_2S^{+\cdot} + RH \xrightarrow{\text{escape}} Ph_2S^+{-}H + R^\cdot$$
$$Ph_2S^+{-}H \longrightarrow Ph_2S + H^+$$
$$Ph^\cdot + RH \longrightarrow Ph\text{-}H + R^\cdot$$
$$Ph^\cdot + R^\cdot \longrightarrow Ph\text{-}R$$
$$Ph^\cdot + Ph^\cdot \longrightarrow Ph\text{-}Ph$$
$$R^\cdot + R^\cdot \longrightarrow R\text{-}R$$

Heterolytic Cleavage

$$[Ph_3S^+ X^-]^* \longrightarrow \overline{Ph_2S + Ph^+ + X^-}$$
$$\overline{Ph_2S + Ph^+ + X^-} \xrightarrow{\text{cage recombination}} (1) + (3) + (4) + (5)$$
$$Ph_2S + Ph^+ + X^- \xrightarrow{\text{escape}} (2)$$
$$Ph^+ + RH \longrightarrow Ph\text{-}R + H^+$$

It has been reported that triplet sensitizers are ineffective for triphenylsulfonium salt photodecomposition and that electron transfer is the only process by which photodecomposition can occur.[6,10] However, electron transfer between triphenylsulfonium salts and acetone, indanone, or acetophenone is unfavorable.[11] Pappas and Jilek have determined a triplet energy of 75 kcal/mol for **1** from emission spectroscopy at 77 K and claim that although acetophenone phosphorescence is quenched by **1**, no photochemistry is observed with acetophenone.[12] In contrast, our results (Table I) indicate that acetophenone sensitizes decomposition of **1**. Even an oxygenated acetonitrile solution of **1** irradiated in the presence of acetophenone gives diphenyl sulfide, although the yield is lower than that resulting from irradiation in N_2-purged solutions due to triplet quenching by oxygen. The relative quantum yield of diphenyl sulfide increases with increasing triplet energy of the sensitizer, a good indication of efficiency for energy transfer.[13] A control experiment in acetonitrile with benzophenone, which has an E_T too low for efficient sensitization, gave only traces of photoproduct. The observation that added oxygen reduces the amount of diphenyl sulfide formed upon direct irradiation of **1** suggests that there is intersystem crossing from the singlet to the triplet excited state and that some of the triplet is quenched by oxygen. We reported that acetanilide was formed upon direct irradiation of triphenylsulfonium salts in acetonitrile solution, by reaction of phenyl cation with

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(5) (a) Dektar, J. L.; Hacker, N. P. *J. Chem. Soc., Chem. Commun.* **1987**, 1591. (b) We are grateful to a reviewer for the following reference: Pappas, S. P.; Gatechair, L. R. *Proc. Water-Borne Higher-Solids Coat. Symp., 8th* **1981**, 85. These authors speculated that a radical recombination process to give 4-(phenylthio)biphenyl may be possible, but no experimental data to support or refute this hypothesis was reported.

(6) Pappas, S. P.; Pappas, B. C.; Gatechair, L. R.; Jilek, J. H.; Schnabel, W. *Polym. Photochem.* **1984**, *5*, 1.

(7) Triphenylsulfonium triflate[8] solutions (0.01 M) were purged with solvent-saturated nitrogen at room temperature for 20 min, sealed, and irradiated on a merry-go-round in a Rayonet reactor (Southern New England Ultraviolet Co.) using RPR-2537 bulbs for λ = 254 nm or RPR-3000A bulbs for λ = 300 nm. Quartz sample tubes were used for photolysis at λ = 254 nm, and Pyrex sample tubes were used for photolysis at λ = 300 nm. Conversions were typically <15%, and all photoproducts were identified by GC retention times and compared with authentic samples (see ref 5). Compensation for response ratios was made by calibration with authentic samples of photoproducts.

(8) Endo, Y.; Shudo, K.; Okamoto, T. *Chem. Pharm. Bull.* **1981**, *12*, 3753.

(9) The decrease in diphenyl sulfide formation is about 7% in oxygenated solutions; the variance for eight experiments run side by side was less than 2%.

(10) Pappas, S. P.; Gatechair, L. R.; Jilek, J. H. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 77.

(11) ΔG values for electron transfer reaction: acetone, 5.6 kcal/mol; acetophenone, 12.8 kcal/mol; and xanthone, −4.8 kcal/mol. See ref 6. The value for 1-indanone cannot be calculated because its oxidation or ionization potentials have not been measured.

(12) Pappas, S. P.; Jilek, J. H. *Photogr. Sci. Eng.* **1979**, *23*, 140.

(13) Turro, N. J. *Modern Molecular Photochemistry*; Benjamin/Cummings: Menlo Park, 1978; p 334.

(14) Relative quantum yields for diphenyl sulfide production (Rel ϕ) from 0.01 M triphenylsulfonium triflate in acetonitrile at λ = 300 nm were scaled to xanthone = 1.0. Sensitizer concentrations were adjusted to absorb 97% of the incident light at 300 nm. The acetone sensitized reaction was measured in 100% acetone.

(15) E_T values in kilocalories/mole from the following: Murov, S. L. *Handbook of Photochemistry*; Dekker: New York, 1973.

Table I. Photoproduct Distribution from Irradiation of Triphenylsulfonium Triflate

			concn, $\times 10^{-4}$ M			
solvent	sensitizer	λ, nm	**2**	**3**	**4**	**5**
CH_3CN	none	254	3.1	3.0	0.3	0.6
acetone	acetone	254	3.9	1.7	0.3	0.4
CH_3CN	none[a]	254	2.9	3.0	0.3	0.6
acetone	acetone	300	13.2	0	0	0
CH_3CN	none	300	0.2	0.2	trace	trace

sensitizer	rel ϕ[b]	E_T[c]	sensitizer	rel ϕ[b]	E_T[c]
acetone	81	79–82	xanthone	1.0	74.0
1-indanone	10.1	75.8	benzophenone	0.2	69.2
acetophenone	7.5 (0.80)[a]	74.1	none	0.95	

[a] O_2 saturated. [b] Reference 14. [c] Reference 15.

Scheme III. Photochemical Pathway for Product Formation

Direct Photolysis

$$\begin{aligned}
&Ph_3S^+X^- \xrightarrow{h\nu} [Ph_3S^+X^-]^1\\
&[Ph_3S^+X^-]^1 \longrightarrow [Ph_2S^{+\cdot} + Ph^\cdot + X^-]^1\\
&[Ph_2S^{+\cdot} + Ph^\cdot + X^-]^1 \xrightarrow{RH} (1) + (2) + (3) + (4) + (5) + Ph\text{-}H + H^+\\
&[Ph_3S^+X^-]^1 \longrightarrow [Ph_2S + Ph^+ + X^-]^1\\
&[Ph_2S + Ph^+ + X^-]^1 \xrightarrow{RH} (1) + (2) + (3) + (4) + (5) + Ph\text{-}R + H^+\\
&[Ph_3S^+X^-]^1 \longrightarrow [Ph_3S^+X^-]^3\\
&[Ph_3S^+X^-]^3 \longrightarrow [Ph_2S^{+\cdot} + Ph^\cdot + X^-]^3\\
&[Ph_2S^{+\cdot} + Ph^\cdot + X^-]^3 \xrightarrow{RH} (2) + H^+ + Ph\text{-}H
\end{aligned}$$

Sensitized Photolysis

$$\begin{aligned}
&Sens \xrightarrow{h\nu} [Sens]^1 \longrightarrow [Sens]^3\\
&[Sens]^3 + Ph_3S^+X^- \longrightarrow Sens + [Ph_3S^+X^-]^3\\
&[Ph_3S^+X^-]^3 \longrightarrow [Ph_2S^{+\cdot} + Ph^\cdot + X^-]^3\\
&[Ph_2S^{+\cdot} + Ph^\cdot + X^-]^3 \xrightarrow{RH} (2) + H^+ + Ph\text{-}H
\end{aligned}$$

solvent.[5a] Acetanilide is not observed in any of the triplet sensitized reactions in acetonitrile, which indicates that phenyl cation is not formed from the triplet excited state. The only other photoproduct is benzene, which is probably formed by reaction of phenyl radical with solvent. Furthermore, in our experiments no significant amount of biphenyl is formed at low conversion.[16]

The proposed photochemical pathway for decomposition of **1** is shown in Scheme III. The triplet excited state of **1** can be formed by intersystem crossing from the singlet excited state upon direct irradiation or by energy transfer from the excited triplet state (E_T > 74 kcal/mol) of the sensitizer. The triplet excited state yields only diphenyl sulfide, presumably from the triplet diphenylsulfinyl radical cation–phenyl radical pair. The triplet radical pair would require spin inversion prior to recombination to yield the (phenylthio)biphenyl species (**3**–**5**) and starting material (**1**); instead, escape from the solvent cage to yield diphenyl sulfide is favored. The singlet excited state does not require spin inversion for recombination, and the cage reaction to yield **1** and **3**–**5** becomes the predominant process, accompanied by some escape to give **2**.

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[16] At higher conversions, biphenyl concentration markedly increases upon direct photolysis. This suggests that much of the biphenyl observed is a secondary photoproduct, probably formed from the (phenylthio)biphenyls **3**–**5**.

Modulation of π-Facial Selectivity in Diels-Alder Cycloaddition to Isodicyclopentafulvenes by Remote Para Substitution of an Exocyclic Phenyl Group

Summary: Isodicyclopentafulvenes that carry an exocyclic para-substituted phenyl group as in **3** enter into Diels–Alder cycloaddition with highly reactive dienophiles exclusively from below-plane. The situation with the more sterically hindered and less reactive reagent (*Z*)-1,2-bis(phenylsulfonyl)ethylene is one where addition occurs from both faces.

Sir: No assessment has heretofore been made of the potential for modulating the π-facial selectivity of a [4 + 2] cycloaddition by means of remote electronic perturbation. Studies of the effects of substituents on rate, stereochemistry, and orientation abound,[2] and correlations based upon the Hammett equation are extant.[3] In the case of a system such as isodicyclopentadiene (**1**), dienophiles can in principle bond to either face. However, there exists a strong preference for below-plane capture,[4] except where steric factors become dominant in either reaction partner.[5] This single fact has been the source of considerable mechanistic

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(1) Lubrizol Fellow, 1987.

(2) (a) Wasserman, A. *Diels–Alder Reactions*; Elsevier: New York, 1965. (b) Seltzer, S. In *Advances in Alicyclic Chemistry*; Hart, H., Karabatsos, G. J., Eds.; Academic: New York, 1968, Vol. 2, Chapter 1. (c) Houk, K. N. In *Pericyclic Reactions*; Marchand, A. P., Lehr, R. E., Eds.; Academic: New York, 1977; Vol. II, Chapter 4.

(3) (a) Charton, M. *J. Org. Chem.* **1966**, *31*, 3745; **1965**, *30*, 552, 557, 969, 974. (b) Charton, M. *J. Chem. Soc.* **1964**, 1205. (c) Charton, M.; Meislich, H. *J. Am. Chem. Soc.* **1958**, *80*, 5940. (d) Inukai, T.; Kojima, T. *Chem. Commun.* **1969**, 1334.

(4) Paquette, L. A. In *Stereochemistry and Reactivity of Pi Systems*; Watson, W. H., Ed.; Verlag Chemie International: Deerfield Beach, FL, 1983; pp 41–73.

(5) See, for example: (a) Bartlett, P. D.; Wu, C. *J. Org. Chem.* **1984**, *49*, 1880. (b) Paquette, L. A.; Künzer, H.; Green, K. E.; DeLucchi, O.; Licini, G.; Pasquato, L.; Valle, G. *J. Am. Chem. Soc.* **1986**, *108*, 3453.

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