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S'_H TYPE REACTIONS OF SUBSTITUTED ALLYLIC COMPOUNDS

T. Migita, M. Kosugi, K. Takayama and Y. Nakagawa
Department of Chemistry, Gunma University, Kiryu, Gunma, Japan

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Abstract—S'_H reactions of allyl sulfides and halides with phenyl radicals are reported. Thermal decomposition of phenylazotriphenylmethane with allyl sulfides and bromide has been shown to give allylbenzene. This apparent substitution reaction involves attack of a phenyl radical on the terminal unsaturated carbon atom of the allyl sulfide; the reaction in α,α-dimethylallyl ethyl sulfide produced 2-methyl-4-phenylbutene-2. To estimate the relative reactivities of allylic substrates towards phenyl radicals, competitive reactions of phenyl radicals with allylic compounds and carbon tetrachloride were investigated. The data indicate that the radical formed by addition of a phenyl radical to the allylic sulfide looses thiyl radicals almost quantitatively.

The reversibility of the addition of thiyl radicals or halogen atoms to an olefinic double bond has been well established,[1] and suggests that allyl sulfides or halides react with a radical according to the S'_H scheme, since terminal attack of a radical on an allylic compound gives a β-halo- or β-thiyl-alkyl radical which is expected to loose a halogen atom or a thiyl radical.

$$R\cdot + CH_2{=}CHCH_2X \longrightarrow RCH_2CH{=}CH_2 + X\cdot \qquad (1)$$

X : SR′, Halogen

Such cases have been reported in the reaction of allyl halides with radicals. Kharasch and Sage[2] observed the formation of 4,4,4-trichlorobutene-1 as a byproduct in the radical addition of bromotrichloromethane to allyl bromide. Similar reactions of allyl halides with thiyl radicals have also been reported by Hall.[3] Cain and Noyes[4] have shown iodine-exchange accompanied allylic rearrangement between iodine and allyl iodide. Kampmeier *et al.*[5] have shown that when phenyl radicals react with t-butyl sulfide, the yields of benzene and isobutylene are quantitative. This indicates that the β-thiylalkyl radical, formed by hydrogen abstraction from the sulfide, easily decomposes to give the olefin and thiyl radical. To our knowledge, however, there have been few reports of S'_H type reactions of allyl sulfides.

In this paper the capabilities for S'_H reactions of allyl sulfides and halides with phenyl radicals are considered. Phenyl radicals are conveniently and efficiently generated by the thermal decomposition of phenylazotriphenylmethane (PAT) at moderate temperatures.[6,7] N-Nitrosoacetanilide (N-NA) was also used as a precursor of phenyl radicals at rather lower temperatures.[8] The expected product of the S'_H reaction is an allylbenzene as shown in the following equation;

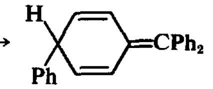
$$Ph\cdot + CH_2{=}CHCH_2X \longrightarrow PhCH_2CH{=}CH_2 + X\cdot \qquad (2)$$

RESULTS AND DISCUSSION

The reactions of phenyl radicals with allylic compounds were accomplished by the thermal decomposition of PAT and N-NA in dilute solutions (~ 0·1 mole/l.) of the allylic compounds at 60° and at 35°, respectively. The yields of allylbenzene and benzene were determined by VPC. The average results of several runs are in Table 1.

The 65–80% of phenyl radicals produced by the decomposition of PAT in allyl sulfides are accounted for by the formation of benzene and allylbenzene. The formation of benzene may be the result of hydrogen abstraction from the sulfides by phenyl radicals. The remainder of the phenyl radicals may have been consumed by the formation of addition products to the allylic double bond (Eq. 4) or by the reaction of phenyl radicals with triphenylmethyl radicals[5] generated from PAT, (Eq. 3). Attempts to determine the yields of these products were frustrated by the complexity of the products.

$$Ph\cdot + \cdot CPh_3 \longrightarrow Ph_4C$$

$\longrightarrow$  (3)

$$Ph\cdot + CH_2{=}CHCH_2SR \longrightarrow PhCH_2{-}\dot{C}H{-}CH_2SR \longrightarrow \text{products} \qquad (4)$$

The formation of allylbenzene suggests production of the thiyl radical. By analogy with the results obtained by Kampmeier *et al.*[5] in the reaction with PAT the thiyl radical would be expected to be trapped by the triphenylmethyl radical, affording alkyl triphenylmethyl sulfide. However, its formation was not observed in the reaction of PAT with allyl ethyl sulfide even by careful TLC analysis. On the other hand, from the reaction with N-NA, diethyl disulfide was obtained in reasonable yield

Table 1. Products of the reactions of phenyl radicals with allylic compounds

Substrates $CH_2{=}CHCH_2X$ X—	Initiator of Phenyl Radical	Products (%) $PhCH_2CH{=}CH_2$	PhH		
MeS—	PAT	40	—		
EtS—	PAT	39	35		
	N-NA	45	38	$(EtS)_2$	13
Me_3CS—	PAT	42	22		
PhS—	PAT	53	26		
	N-NA	54	24		
p-$MeOC_6H_4S$—	PAT	50	25		
p-ClC_6H_4S—	PAT	52	23		
p-$NO_2C_6H_4S$—	PAT	50	20		
EtO—	PAT	0	—		
	N-NA	0	—		
PhO—	PAT	0	—		
	N-NA	0	—		
Cl—	PAT	7·8	—	PhCl	trace
	N-NA	1	—	PhCl	trace
Br—	PAT	63	—	PhBr	16
	N-NA	49	—	PhBr	20
I—	PAT	trace	—	PhI	83
	N-NA	trace	—	PhI	69
Me_3Si—*	PAT	1	—		

*MeCN as solvent.

(Table 1). This apparent substitution reaction of an allyl sulfide with phenyl radicals (Eq. 2) was found to involve attack of a phenyl radical on the terminal unsaturated carbon atom of allyl sulfide, based on the fact that reaction in α,α-dimethylallyl ethyl sulfide produced 2-methyl-4-phenylbutene-2.

$$Ph\cdot + CH_2{=}CHCMe_2SEt \longrightarrow PhCH_2CH{=}CMe_2 + SEt \quad (5)$$

Two possible path-ways for the formation of allylbenzene can be considered. One is stepwise and involves addition of a phenyl radical to the terminal methylene, followed by elimination of radical X.

SCHEME 1

$$Ph\cdot + CH_2{=}CHCH_2X \longrightarrow PhCH_2{-}\dot{C}H{-}CH_2X \longrightarrow PhCH_2CH{=}CH_2 + X\cdot \quad (6)$$

The other is concerted and may be called an S_H2' reaction.

$$Ph\cdot + CH_2{=}CHCH_2X \longrightarrow (Ph\cdots CH_2{\cdots}CH{\cdots}CH_2 \quad X) \longrightarrow PhCH_2CH{=}CH_2 + X\cdot \quad (7)$$

Whichever mechanism applies it is likely that allyl compounds bearing better leaving groups (X) will give allylbenzene in better yield, and the smaller the C–X bond dissociation energy the better the leaving group. This tendency is clearly shown by reactions with various types of allylic compounds (Table 1 and 2). No allylbenzene was formed in the reaction of allyl ethers and allyl esters, and only small amounts of allylbenzene were detected in allylsilanes. The result with the allyl ester suggests that addition of the acyloxy radical to an olefinic double bond is not reversible, although a number of pieces of evidence indicate that addition of an acyloxy radical to an aromatic ring is reversible.[9] Of the allyl halides, allyl bromide gave allylbenzene in highest yield, while allyl iodide which is considered to possess the best leaving group afforded only a trace amount of allylbenzene, but gave iodobenzene as major product. As would be expected from the C–X bond energies, the extent of halogen abstraction by a radical will decrease in the order; iodide > bromide > chloride. The present result shows that the facile iodine abstraction[10] by phenyl radicals is much faster than attack on terminal methylene.

To estimate the relative reactivities of allylic substrates towards phenyl radicals, competitive reactions of phenyl radicals derived from PAT with allylic compounds and carbon tetrachloride were carried out.

$$Ph\cdot + CCl_4 \xrightarrow{k_{Cl}} PhCl \quad (8)$$

$$Ph\cdot + CH_2{=}CHCH_2X \longrightarrow PhH$$
$$\xrightarrow{k_{add}} PhCH_2CH{=}CH_2 \text{ or addition product} \quad (9)$$

It can be assumed that phenyl radicals which were converted into neither benzene (by hydrogen abstraction from allylic substrates and hydrogen transfer with triphenylmethyl radicals) nor chlorobenzene (by chlorine abstraction from carbon tetrachloride) would have been mainly consumed

Table 2. Bond energy C—X[11] (kcal. per gram-bond) and extent of allylbenzene formation

C—X	C—C	C—O	C—Si	C—S	C—Cl	C—Br	C—I
Bond Energy	80	81	68	65	77	64	56
Allylbenzene Formation	—	no	small	large	small	large	trace

by reaction with the allylic substrates, producing allylbenzene or other addition products, and by the recombination with triphenylmethyl radicals, giving tetraphenylmethane etc. Then, the reactivity of each substrate relative to that of carbon tetrachloride toward phenyl radicals, k_{add}/k_{Cl} will be determined by the following equation;

$$\frac{k_{add}}{k_{Cl}}=\frac{(PAT)_i-(PhH)_f-(PhCl)_f-(\text{coupling products})_f}{(PhCl)_f}\times\frac{(CCl_4)_i}{(\text{substrates})_i}$$

where $(PAT)_i$, $(CCl_4)_i$ and $(\text{substrates})_i$ represent initial concentration of PAT, carbon tetrachloride and allylic substrates, $(PhH)_f$, $(PhCl)_f$ and (coupling products)$_f$ are concentrations of benzene, chlorobenzene and coupling products, respectively, in the reaction. Although total coupling product amounts considered to be formed by the cage reaction were not determined precisely, it was estimated to be about 0·15 mole/mole of PAT, on the basis that regardless of the initial concentration of PAT, only 82–88% of phenyl radicals derived from PAT have been accounted for by the formation of benzene and chlorobenzene when PAT was decomposed in carbon tetrachloride solutions.[6] On the other hand, apparent relative rates of the formation of allylbenzene referred to the formation of chlorobenzene, k_{al}/k_{Cl} were also determined as follows;

$$\frac{k_{al}}{k_{Cl}}=\frac{(PhCH_2CH{=}CH_2)_f}{(PhCl)_f}\cdot\frac{(CCl_4)_i}{(\text{substrates})_i}$$

Both k_{add}/k_{Cl} and k_{al}/k_{Cl} were independent of solvent composition within experimental error, over a range of 0·2–0·8 molar fraction of allyl sulfide in the reaction solvent. (experimental) The average values of k_{add}/k_{Cl} and k_{al}/k_{Cl} are in Table 3.

If the mechanism of the formation of allylbenzene were concerted (Scheme 2), the reactivities of allyl sulfides toward addition of phenyl radicals would be enhanced by the C-S bond breaking. Table 3 shows that the values, k_{add}/k_{Cl} of allyl sulfides and bromide which give allylbenzene are only slightly larger than those of other allylic substrates or l-hexene which do not afford allylbenzene. This slight enhancement might be due to some electronic effects caused by participation of groups SR and halogen. Effects of such participation on the rate of the hydrogen abstraction reaction have been discussed.[12] Thus, the rate data cannot be said to offer strong evidence in support of concerted mechanism. On the other hand, considerable amounts of the coupling products of β-thiylalkyl radicals have been detected, besides other products, when di-t-butylperoxide was allowed to decompose in various dialykl sulfides.[13]

$$EtSEt \xrightarrow{t\text{-}BuO\cdot} \underset{2\cdot9\%}{EtSCHMeSEt} + \underset{2\cdot2\%}{EtSCH_2CH_2SEt} + \underset{32\%}{EtSCHMeCHMeSEt} + \underset{3\cdot6\%}{EtSCH_2CH_2CHMeSEt} \quad (10)$$

This indicates that under these conditions, at least some of the β-thiylalkyl radicals recombine without decomposing into olefin and thiyl radical. With this in mind, we feel that the stepwise (Scheme 1) is more plausible than the concerted mechanism.

Table 3 also shows that for each allylic sulfide the values of k_{al}/k_{Cl} coincide reasonably with the

Table 3. Competitive reactions of phenyl radical generated from PAT with allylic compounds and carbon tetrachloride

Substrates $CH_2{=}CHCH_2X$ X—	$\frac{(CCl_4)_i}{(\text{Allylic Sub.})_i}$	PhH	Products PhCl	$PhCH_2CH{=}CH_2$	$\frac{k_{add}}{k_{Cl}}$	$\frac{k_{al}}{k_{Cl}}$
p-$MeOC_6H_4S$-	2·51	22·1	25·5	36·7	3·7	3·6
PhS—	see Table 6				4·1	3·7
p-ClC_6H_4S—	1·27	23·8	15·1	39·0	3·9	3·3
p-$NO_2C_6H_4S$—	2·36	19·9	22·3	32·2	4·5	3·4
MeS—	2·05	—	19·3	35·8	—	3·8
EtO—	1·07	57·1	11·3	0	1·6	—
PhO—	1·25	28·5	19·1	0	2·4	—
$CH_3CH_2CH_2$—	1·06	28·0	16·3	—	2·6	—

corresponding k_{add}/k_{Cl} values. This fact indicates that the radicals which are formed by addition of phenyl radicals to allylic sulfides loose thiyl radicals almost quantitatively, in contrast to the β-thiylalkyl radicals derived by hydrogen abstraction from alkyl sulfide (*vide supra*). Perhaps, this is due to the fact that the allylic substrate serves as an acceptor of thiyl radicals.

$$\mathrm{PhCH_2\dot{C}HCH_2SR} + \mathrm{CH_2{=}CHCH_2SR} \longrightarrow \mathrm{PhCH_2CH{=}CH_2} + \mathrm{RSCH_2\dot{C}HCH_2SR} \qquad (11)$$

Such a radical acceptor effect of an unsaturated molecule has been also observed in the reaction of a thiyl radical with allylic halides.[3] Situations were quite similar in the case of decomposition of p-chlorophenylazotriphenylmethane. Table 4 shows the reaction products when carried out in pure allyl sulfides, and the values k_{add}/k_{Cl} and k_{al}/k_{Cl} are listed in Table 5. Again, a reasonable coincidence in the value between k_{add}/k_{Cl} and k_{al}/k_{Cl} are observed. Comparing these values with those obtained for PAT, it is notable that addition reactivity of the p-chlorophenyl radical is apparently larger than that of the phenyl radical.

EXPERIMENTAL

Phenylazotriphenylmethane, prepared by oxidation of the corresponding hydrazo compound obtained from triphenylmethyl chloride and phenylhydrazine with bromine solution,[14] was recrystallized by dissolving in a minimum amount of benzene and adding EtOH. The material crystallized as yellow needles: m.p. 110–112°, lit.,[15] 110–112°. p-Chlorophenylazotriphenylmethane, similarly prepared, had m.p. 108°, lit.,[16] 108°. N-Nitrosoacetanilide was prepared from acetanilide and nitrous acid.[17] m.p. 53° decomp., lit.,[17] 53°. Allyl methyl sulfide, b.p. 93°, allyl ethyl sulfide, b.p. 48–50°/74·5 mm, allyl t-butyl sulfide, b.p. 57–58°/43 mm, allyl phenyl sulfide, b.p. 105·5°/25 mm, allyl p-methoxyphenyl sulfide, b.p. 95–98°/2 mm, allyl p-chlorophenyl sulfide, b.p. 100–103°/4 mm and allyl p-nitrophenyl sulfide, m.p. 37–38° were prepared from allyl chloride and the corresponding thioalkoxides[18,19,20] (structures were confirmed by their NMR spectra).

α,α-Dimethylallyl ethyl sulfide; γ,γ-Dimethylallyl mercaptan was prepared from isoprene and thiourea in 48% HBr aq.[21] Treatment of this mercaptan with diethyl disulfide (below) and alkaline catalyst, gave γ,γ-dimethylallyl ethyl disulfide.[22,23] This disulfide and triphenylphosphine (below) were sealed *in vacuo*, heated at 90° for 140 h. α,α-Dimethylallyl ethyl sulfide distilled at 52–57°/30–40 mm from the reaction.[22,23] Diethyl disulfide, b.p. 60–64°/30 mm, lit.,[24] 152°/736 mm, triphenylphosphine, m.p. 78·5–79·5°, lit.,[25] 79·5° were prepared by the ordinary method.[24,25] Triphenylmethyl ethyl sulfide was prepared from chlorotriphenylmethane and ethyl mercaptan in pyridine.[5] m.p.

Table 4. The reaction of p-chlorophenyl radical with allylic compounds

Substrates $\mathrm{CH_2{=}CHCH_2X}$	CAT (mole/l.)	Products (mole/mole of CAT) PhCl	p-$\mathrm{ClC_6H_4CH_2CH{=}CH_2}$	p-$\mathrm{ClC_6H_4X}$
—$\mathrm{SCH_3}$	0·103	25·6	54·6	—
—SPh	0·096	18·5	61·9	—
—Br	0·104	—	73	13·5
	0·097	8·9	76·5	15·1

Table 5. The values of k_{add}/k_{Cl} and k_{al}/k_{Cl} towards phenyl and p-chlorophenyl radical

substrates	Phenyl radical		p-Chlorophenyl radical	
$\mathrm{CH_2{=}CHCH_2X}$	k_{al}/k_{Cl}	k_{add}/k_{Cl}	k_{al}/k_{Cl}	k_{add}/k_{Cl}
—SMe			7·0	8·9
—SPh	3·7	4·1	14·3	15·3
—Br	6·2		16·8	

Table 6. Variation of solvent composition and relative reactivities

$\dfrac{(\mathrm{CCl_4})_i}{(\mathrm{CH_2{=}CHCH_2SPh})_i}$	Product (mole/mole of PAT) PhH	PhCl	$\mathrm{PhCH_2CH{=}CH_2}$	$\dfrac{k_{add}}{k_{Cl}}$	$\dfrac{k_{al}}{k_{Cl}}$
0·884	26·0	10·3	40·8	4·16	3·5
0·884	25·2	10·5	39·6	4·15	3·3
2·23	24·0	20·8	34·6	4·32	3·7
2·23	24·2	22·2	34·0	3·86	3·4
2·72	23·0	23·7	32·5	4·40	3·7
6·15	18·0	39·6	24·6	4·24	3·8
7·40	16·7	41·3	20·4	4·80	3·7
10·89	15·5	48·0	16·6	4·78	3·8

126°. The NMR spectra shows a triplet at τ 9·03 (3H), quarter at 8·90 (2H) and multiplet at 2·7 (15H).

Allyl ethyl ether, b.p. 63–65°, lit.,[26] 66°/745 mm, allyl phenyl ether, b.p. 89·5°/26 mm, lit.,[27] 89°/26 mm, allyltrimethylsilane, b.p. 83–85°, lit.,[28] 85°, allylbenzoate, b.p. 110–115°/17 mm, lit.,[26,29] 242°/760 mm, allyl bromide, b.p. 68–70°, lit.,[30] 69–70°, allyl iodide, b.p. 90–92°, n_D^{17}: 1·5565, lit.,[31] 101–102°, n_D^{22}: 1·5542, were prepared as described. Allylbenzene, b.p. 75°/46 mm, lit.,[32] 153–154°/725 mm and *p*-chloroallylbenzene, b.p. 101–102·5°/36 mm, lit.,[33] 199–201°/760 mm were also prepared as described. Benzene, chlorobenzene, *p*-dichlorobenzene, bromobenzene, *p*-chlorobromobenzene, iodobenzene and allyl chloride were available commercially.

Decomposition of PAT (N-NA) in the allylic compounds. A solution of known concentration of PAT (N-NA) in the allylic compound was prepared and transferred to glass tubes. These were degassed by three or four successive freezing-thawing processes, sealed under vacuum and immersed in a thermostat at 60° (35°) for 4 h. The tubes were cooled in Dry Ice-acetone opened, and an internal standard for VPC analysis added. Analysis were performed on an Ohkura, Model-701 gas chromatograph with flame-ionization detectors, using a calibration graph giving relation of peak area *vs.* molarity. The results of several runs are in Table 1. PAT (N-NA) concentration were usually about 0·1 mole/l.

2-Methyl-4-phenylbutene-2 was isolated from the reaction of α,α-dimethylallyl ethyl sulfide and PAT by VPC and the structure confirmed from its NMR spectra: τ 8·32 (6H, s, 6·73 (2H, d), 4·73 (1H, t) and multiplet at 2·90 (5H).

Absence of triphenylmethyl ethyl sulfide in the reaction of allyl ethyl sulfide and PAT was confirmed by TLC. The nature of a spot with low R_f was not investigated.

Diethyl disulfide was isolated from the mixtures of allyl ethyl sulfide and N-NA by VPC and the structure confirmed by IR spectra comparison with that of an authentic sample.

In *competitive reactions* with carbon tetrachloride and allylic compound, similar procedures were employed and benzene, chlorobenzene and allylbenzene were determined by VPC. The results are listed in Table 3 and 5. The relative reactivities (both k_{add}/k_{Cl} and k_{al}/k_{Cl}) were almost independent of solvent composition within experimental error (Table 6).

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