Registry No.—**1**, 55820-93-4; **2**, 55820-92-3; **5**, 57766-46-8; **6**, 57766-47-9; **7a**, 57811-82-2; **7b**, 57808-62-5; **8a**, 61664-37-7; **8b**, 58165-65-4; **9**, 61587-64-2; **10**, 61664-38-8; **11**, 57781-98-3.

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(8) All melting points are uncorrected. Infrared and visible spectra were recorded on a Perkin-Elmer 457 and a Cary 118 spectrophotometer, respectively. Proton magnetic resonance (^1H NMR) and ^{13}C NMR spectra were recorded on a Perkin-Elmer Model R-12 and a Varian Model XLS-100, respectively. The chemical shift values are expressed in δ values (ppm) relative to tetramethylsilane internal standard and the coupling constants in hertz (s = singlet, d = doublet, t = triplet, q = quadruplet, m = multiplet). Mass spectra (70 eV) were recorded on a LKB 9000 mass spectrometer equipped with a direct inlet system. Combustion analysis were performed by the Service Central de Microanalyses du C.N.R.S., Division de Strasbourg. Separation and purification of the products were obtained using Merck silica gel 60 (70–230 mesh) or Merck standardized alumina (II–III).

Photolysis of Allyl Iodide in Aromatic Solvents

Carlo Maurizio Camaggi,* Rino Leardini, and Paolo Zanirato

Istituto di Chimica Organica dell'Università, Viale Risorgimento, 4, 40136 Bologna, Italy

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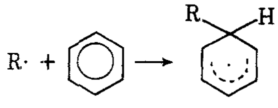
Photolysis of allyl iodide in aromatic solvents gives rise to allylated products. Isomer distribution and both total and partial rate factors determined for this reaction show a slightly electrophilic character of the substitution reaction. Total rate factors correlate well with the first ionization potentials of the aromatic substrates (slope −0.56, correlation coefficient 0.9966).

The first step in homolytic aromatic substitution in most of the cases investigated is a nonreversible exothermic addition of the attacking radical to the π system of the substrate, leading to a σ complex (**1**).



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This reaction path is typical for highly reactive radicals like phenyl.[1] Positional selectivity and polar effects are normally low, if particular choice of highly polar solvents and substrates does not affect the original nonpolar character of the transition state.[2] The reaction may become reversible if the attacking species gives a relatively weak bond with the aromatic in the σ complex or if the stability of the attacking radical is increased; for instance, the homolytic aromatic thioarylation is very likely a reversible reaction, in which the aromatization step is of great importance in determining the products.[3,4] We wish now to report experiments in which a possible precursor of the stable π-delocalized allyl radical was decomposed in aromatic solvents.

Results

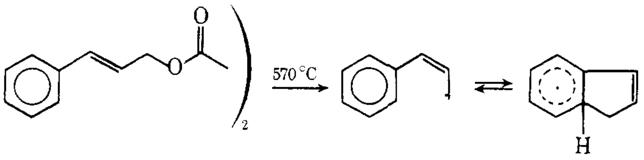
Photolysis of allyl iodide in aromatic substrates gives in almost every case investigated a good yield of isomeric allyl arenes (Scheme I); the presence of propene as a by-product was proved by mass spectrometry and no hydrogen iodide was observed in the reaction mixture. Low yields of high molecular weight iodinated by-products were detected in the reaction at very high reaction times; this does not seem, however, to affect isomer distribution of substitution products and relative reactivities between different substrates; reaction products are stable in the condition employed. In order to avoid any possible source of errors, in the quantitative experiments test analyses were carried out at different reaction times, but no variation of results was observed.

Scheme I

$$CH_2{=}CHCH_2I \xrightarrow[ArH]{h\nu} CH_2{=}CHCH_2Ar$$
$$+ I_2 + CH_2{=}CHCH_3 + (CH_2{=}CHCH_2)_2 \text{ (traces)}$$

No isotope effect on the products was found in the allylation of equimolecular benzene/benzene-d_6 mixtures. This result may be considered as indicative of the unimportance of the reverse reaction in the addition step at room temperature. Actually, a *reversible* intramolecular allylation reaction has been proposed by Trahanowsky and Ong[5] to explain an isotope effect k_H/k_D of 2.92 determined by analysis of the indene fraction obtained from pyrolysis of di-*trans*-*o*-deuteriocinnamyl oxalate at 570 °C (Scheme II).

Scheme II



Tables I and II report the reactivity data obtained from competitive experiments in which allyl iodide was photolyzed in a large excess of equimolecular solution of benzene and a substituted benzene or thiophene; total and partial rate factors were calculated in the usual way, assuming a reaction scheme in which products were formed by nonreversible parallel reactions of the same order, and the yield of conversion Ia → allyl arene not dependent on the particular isomer formed. This aromatization step is probably similar to that proposed by other workers[6] in the photolysis of CH_3HgI in aromatic solvents; iodine atoms are the oxidizing species, possibly through an addition–elimination process, and the so-formed hydrogen iodide then reduces the unreacted allyl iodide to propene. Product analysis is consistent with this mechanism.

Table I. Isomer Distribution of Allylation Products in the Photochemical Reaction between Arenes and Allyl Iodide

$$\mathrm{ArH} + \mathrm{CH_2{=}CHCH_2I} \xrightarrow{h\nu}$$

$$\underset{\mathbf{Ia}}{\mathrm{CH_2{=}CHCH_2ArH]\cdot}} + \mathrm{I}\cdot \rightarrow \mathrm{CH_2{=}CHCH_2Ar}$$

Arene	% ortho (or α)	% meta (or β)	% para
−OMe anisole	47.6 (69.4)	16.0 (18.1)	36.4 (12.5)
$-CH_3$ toluene	45.8 (66.5)	32.4 (19.3)	21.8 (14.2)
−Cl chlorobenzene	51.9 (50.1)	27.9 (31.6)	20.2 (18.3)
Methyl benzoate	(57.0)	52.4 (17.5)	47.6 (25.5)
Benzonitrile	46.0 (60.0)	25.9 (10.0)	28.1 (30.0)
Thiophene	63.8 (93.1)	36.2 (6.9)	

In parentheses are reported the corresponding data for the homolytic phenylation reaction.[7]

Analysis of the data reported in the tables reveals a generalized low reactivity of ortho positions in the aromatic substrates with respect to the data observed in homolytic substitution reactions, particularly pronounced when the substituent is bulky, and "electrophilic character" of the attacking species.

In addition, isomer distribution and partial rate factors indicate that electronic stabilizing factors on σ complexes (Ia) have a low effect in determining reactivity.

On the other hand, it is of particular interest to note that the logarithms of *total* rate factors (K_{tot}) correlate well with the first ionization potentials (I_1) of the aromatic reagent,[9] giving a straight line (correlation coefficient 0.9966; slope −0.56) (Figure 1). The only point that does not fall on the straight line is that for anisole. This correlation includes substituted benzenes, thiophene, and naphthalene. The same kind of correlation does not hold for the homolytic phenylation of the same substrates. In addition, no good σ–ρ relationship is obtainable from *partial* rate factors of the allylation reaction, although there exists a fairly good correlation between Hammett σ constants and *total* rate factors for this reaction (slope −0.55; correlation coefficient 0.988).

The linear relationship observed between first ionization potentials of the substrates and relative reactivities may be an indication of a mechanism in which the rate-determining step has a small but defined charge-transfer character.

A quantum yield study on the products of this photochemically initiated substitution may clarify details of the reaction mechanism.

Experimental Section

GLC analyses were carried out with Varian 1520 and 712 gas chromatographs, equipped with flame-ionization detectors, and with the gas chromatograph–mass spectrometer system JEOL JMS D100.

Reference Compounds. *o*-,[10] *m*-,[11] and *p*-[12] allylanisole, *o*-,[13] *m*-,[11] and *p*-[13] allyltoluene, *o*-,[14] *m*-,[11] and *p*-[11] allylchlorobenzene, *p*-allylmethyl benzoate,[15] 2-allylthiophene,[15] and α- and β-allylnaphthalene[16] were synthesized as reported in the literature.

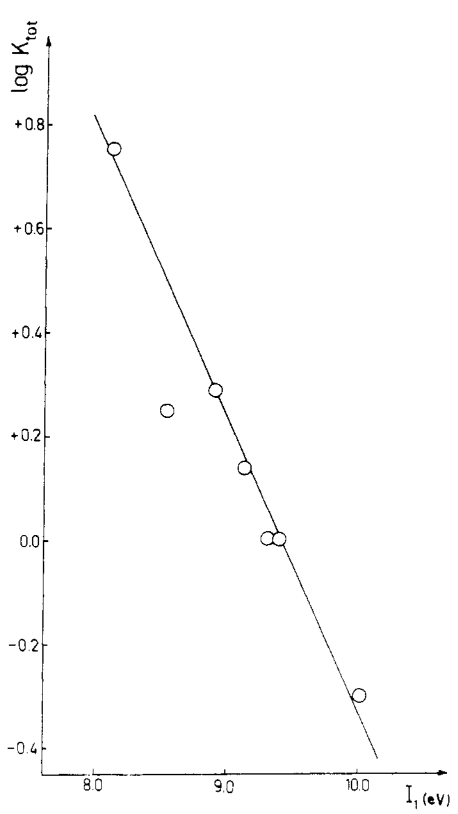


Figure 1. Plot of logarithms of total rate factors for the homolytic allylation reaction against the first ionization potentials of the aromatic reagents.

***o*-Allylbromobenzene.** To the solution of Grignard reagent obtained from *o*-iodobromobenzene (21.2 g) and magnesium turnings (2.1 g) in dry ether was slowly added under stirring 10.3 g of allyl bromide and the solution was refluxed for 1 h. Workup of the hydrolyzed reaction mixture gave the title product as an oil (11.5 g), bp 96–98 °C (18 mm).

Anal. Calcd for C_9H_9Br: C, 54.85; H, 4.60; Br, 40.55. Found: C, 54.70; H, 4.51; Br, 40.48.

***o*-Allylmethyl Benzoate.** To a solution of *n*-butyllithium [prepared from *n*-butyl bromide (11 mL) and lithium wires (1.4 g) in dry ether] was slowly added at 0 °C *o*-allylbromobenzene (18.0 g), and the solution was stirred for 3 h. The solution was then added to a mixture of solid CO_2 and dry ether and left overnight. The carboxylic acid obtained after workup was directly treated with diazomethane; 11 g of *o*-allylmethyl benzoate was obtained as an oil, bp 133–134 °C (18 mm).

Anal. Calcd for $C_{11}H_{12}O_2$: C, 75.01; H, 6.86. Found: C, 75.02; H, 6.96.

***m*-Allylmethyl Benzoate:** bp 136–137 °C (18 mm).

Anal. Calcd for $C_{11}H_{12}O_2$: C, 75.01; H, 6.86. Found: C, 74.86; H, 6.96.

***o*-Allylbenzonitrile** was prepared from *o*-allylbromobenzene (1.9 g) and cuprous cyanide (1.9 g) in boiling dimethylformamide, yield 1.1 g, bp 122–124 °C (18 mm).

Anal. Calcd for $C_{10}H_9N$: C, 83.87; H, 6.34; N, 9.78. Found: C, 83.92; H, 6.44; N, 9.85.

Table II. Total and Partial Rate Factors for the Photochemical Allylation of Some Aromatic Substrates

Substrate	K_{tot}	$f_{ortho\ (or\ \alpha)}$	$f_{meta\ (or\ \beta)}$	f_{para}
C_6H_6	1	1	1	1
$C_6H_5OCH_3$	1.77 (1.71)	2.52 (3.56)	0.85 (0.93)	3.86 (1.29)
$C_6H_5CH_3$	1.37 (1.23)	1.88 (2.50)	1.33 (0.71)	1.79 (1.00)
C_6H_5Cl	1.01 (1.06)	1.55 (1.60)	0.83 (1.00)	1.20 (1.20)
C_6H_5COOMe	0.69 (1.77)	(3.00)	1.08 (0.93)	1.99 (2.70)
C_6H_5CN	0.50 (3.70)	0.70 (6.50)	0.39 (1.1)	0.85 (6.50)
Thiophene	1.94 (2.6)[8]	3.75 (7.25)	2.12 (0.5)	
Naphthalene	5.71	Not determined		

Table III

Substrate	No. of expts	Standard deviation on				Yield, %
		% ortho (f_o)	% meta (f_m)	% para (f_p)	K_{tot}	
$PhOCH_3$	3	0.70 (0.07)	1.01 (0.05)	0.52 (0.07)	0.03	46
$PhCH_3$	3	0.62 (0.05)	0.50 (0.05)	0.44 (0.04)	0.03	34
PhCl	3	0.85 (0.15)	0.46 (0.07)	1.13 (0.18)	0.1	
PhCOOMe	5		1.20 (0.09)	1.20 (0.11)	0.04	
PhCN	3	0.17 (0.03)	0.46 (0.01)	0.35 (0.04)	0.02	15
Thiophene	4	[α] 0.61 (0.08)	[β] 0.61 (0.07)		0.04	

***m*-Allylbenzonitrile,** bp 124–126 °C (18 mm) (Found: C, 83.72; H, 6.41; N, 10.03), and *p*-allylbenzonitrile, bp 128–129 °C (18 mm) (Found: C, 83.75; H, 6.42; N, 9.69), were prepared as described above for the ortho isomer from the corresponding bromo derivatives.[17]

3-Allylthiophene. To a solution of *n*-butyllithium prepared from *n*-butyl bromide (22.6 mL) and lithium wires (2.73 g) in dry ether was added 3-bromothiophene (32.6 g) at −70 °C, and the reaction mixture was stirred for 1 h. Allyl bromide was then added and the solution after 1 h at −70 °C was allowed to reach room temperature. After workup 12.0 g of the title product was obtained as an oil, bp 66–68 °C (18 mm).

Anal. Calcd for C_7H_8S: C, 67.70; H, 6.49; S, 25.82. Found: C, 67.58; H, 6.53; S, 26.04.

Photolysis of Allyl Iodide in Benzene. A solution of allyl iodide (0.1 mL) in benzene (4 mL) in a quartz vessel was carefully degassed in a vacuum line, then photolyzed for 12 h in a water bath at 25 °C using a Hanovia 100-W medium-pressure mercury lamp, about 5 cm away.

The vessel cooled at −20 °C was then directly connected to the gas inlet of a JEOL JMS D100 mass spectrometer. The presence of propene was detected by recording the spectrum.

The solution was then analyzed by GLC; unreacted allyl iodide was recovered (60% of the starting material) and the yield of allylbenzene was 26% (based on the reacted iodide). Small quantities of biallyl were also detected.

Isotope Effect in the Allylation of Benzene. The reaction was carried out as above on a solution of benzene (5 mL) and benzene-d_6 (Merck Uvasol 99.5% D, 5 mL). The molar ratio benzene:benzene-d_6 was determined by mass spectrometry, at a nominal ionizing voltage of 15 eV (relative intensities of $M^{\cdot +}$ and $M^{\cdot +} + 6$). No substantial quantities of less deuterated benzenes were present in the solution.

After irradiation, the allylbenzene + allylbenzene-d_5 fraction was separated by preparative GLC [Varian 712 instrument; Bentone 34–didecyl phthalate (1:1), 15% on Chromosorb W AW-DMCS 45–60] and analyzed by mass spectrometry (15 eV). The ratio allylbenzene: allylbenzene-d_5 determined both by the relative intensities of $(M^{\cdot +}):(M^{\cdot +} + 5)$ and $(M^{\cdot +} - 1):(M^{\cdot +} + 4)$ was identical with the initial ratio benzene:benzene-d_6.

Competitive Experiments. In a typical experiment, to an equimolecular mixture of benzene (1.7504 g) and toluene (2.0271 g) was added freshly distilled allyl iodide (0.816 mL) and the solution was irradiated in a sealed quartz vessel at 25 °C with a Hanovia 100-W medium-pressure mercury lamp. The reaction was directly analyzed first with a GC/MS system [5% Bentone 34:didecyl phthalate (1:1) on Varaport 30; 80–100 mesh; 3-m chromatographic column] in order to identify the reaction products, then isomer ratios and partial and total rate factors were determined by normal gas chromatography (flame ionization detector).

The results, reported in Tables I and II, are mean values of at least three determinations; Table III reports the number of independent experiments, standard deviations, and, when determined, total yield of allylated products.

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Registry No.—*o*-Allylbromobenzene, 42918-20-7; *o*-iodobromobenzene, 583-55-1; allyl bromide, 106-95-6; *o*-allylmethyl benzoate, 61463-59-0; CO_2, 124-38-9; diazomethane, 334-88-3; *m*-allylmethyl benzoate, 61463-60-3; *o*-allylbenzonitrile, 61463-61-4; cuprous cyanide, 544-92-3; *m*-allylbenzonitrile, 61463-62-5; *p*-allylbenzonitrile, 51980-05-3; *m*-allylbromobenzene, 18257-89-1; *p*-allylbromobenzene, 2294-73-1; 3-allylthiophene, 33934-92-8; 3-bromothiophene, 872-31-1; allyl iodide, 556-56-9; benzene, 71-43-2; anisole, 100-66-3; toluene, 108-88-3; chlorobenzene, 108-90-7; methyl benzoate, 93-58-3; benzonitrile, 100-47-0; thiophene, 110-02-1.

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