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The concerted addition of HBr to aryl alkynes; orthogonal pi bond selectivity †

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In a weakly acidic solution, the addition of HBr to 1-phenylprop-1-yne produces predominantly the anti-Markovnikov product. In this paper, we consider five possible explanations for this behavior and conclude that the concerted addition is occurring on the acetylenic π bond orthogonal to the extended aromatic π system. The electronic effect of the distal methyl group and the steric hindrance of the coplanar phenyl ring combine to promote bromide attack at the β carbon. Attack on this π bond is insensitive to the electronic effect of *meta* and *para* substituents on the ring but is very (sterically) sensitive toward all *ortho* substituents.

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Introduction

In the preceding paper,[1] we reported that the reaction of 1-phenylprop-1-yne with 20% trifluoroacetic acid and bromide ion in methylene chloride leads to the addition of HBr by two different mechanisms. At low bromide ion concentration in a highly acidic solution, the Markovnikov product, 1-bromo-1-phenylprop-1-ene is formed exclusively through the intermediacy of a resonance stabilized cation. In less acidic solutions, the cationic mechanism becomes unavailable and the bromide ion attack on an acid–alkyne complex becomes increasingly competitive. This "concerted" Ad3 mechanism produces significant amounts of the anti-Markovnikov product, 2-bromo-1-phenylprop-1-ene (Scheme 1). This has been explained[1,2] by the assumption that the transition state of the concerted mechanism develops less positive charge in the π system than in the cationic mechanism and, therefore, the preference for resonance stabilization by the phenyl substituent is diminished. At the highest concentrations of bromide ion, however, the anti-Markovnikov product becomes dominant and the reasons for this are less obvious. Furthermore, this result calls into question the otherwise reasonable explanation of why the anti-Markovnikov product has been increasing at the lower acidities and higher concentrations of bromide ion. We have considered five possible explanations for this behavior.

1) Free radical addition

Hydrogen bromide is renowned[3] for its ability to add to alkynes by a free radical mechanism leading to an anti-Markovnikov product. However, our earlier work[4] with terminal unconjugated alkynes in the same reaction media showed no evidence of such behavior. Although oxygen was not excluded from these reactions, there were no anti-Markovnikov products and no discoloration of the acid–bromide solutions over long periods of time. This was not surprising since trifluoroacetic acid is weaker than hydrogen bromide and incapable of generating enough HBr to maintain a free radical mechanism. Furthermore, our reaction produced only the (*Z*)-isomer of 2-bromo-1-phenylprop-1-ene, a result inconsistent with a radical mechanism. However, as a further test of this possibility, we ran the reaction in a solution containing di-*t*-butylmethylphenol and found results identical to those that we had found in the absence of this radical inhibitor.

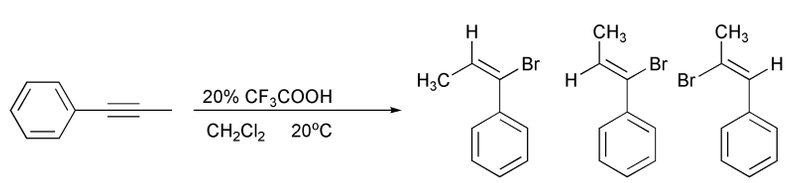
2) Protonation in the phenyl ring

If the acid complexes with the phenyl ring, bromide attack at the β position of the triple bond could produce an allene intermediate that would subsequently rearrange to the anti-Markovnikov product (Scheme 2). Computer simulation of this mechanism was reasonable. However, the isomerization of the allene intermediate would presumably generate both stereoisomers of the 2-bromo-1-phenylprop-1-ene and we were never able to detect the (*E*)-isomer in these reactions. We synthesized a mixture of all four isomers of the bromopropenes to insure that all isomers were separable with our chromatographic method. In addition, we further tested this mechanism by performing the reaction using deuterated trifluoroacetic acid. Negligible amounts of the doubly deuterated product were found.

3) Principal bonding by the bromide ion

As the reaction medium becomes less acidic, the acid participation in the transition state decreases and the bromide participation increases. Eventually, the bromide participation

† Dedicated to Frank H. Westheimer on the occasion of his 90th birthday.



PPy

	E1B	Z1B	Z2B
0.1 M Br	80%	20%	0%
1.0 M Br	7%	67%	26%
2.0 M Br	0%	15%	85%

Scheme 1

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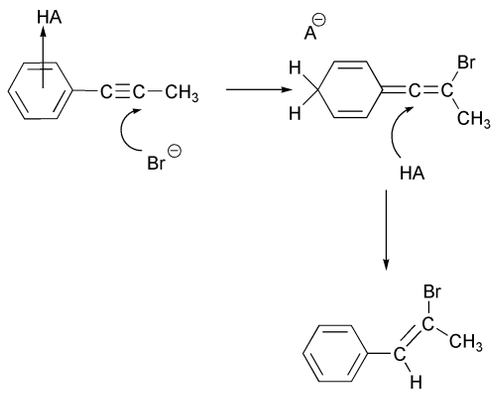
Table 1 Pseudo-first order rate constants and product distributions for the addition of HBr to phenylacetylenes in 0.1 M and 1.2 M bromide solutions

Phenylacetylene substituent	0.1 M Br k (min^{-1})	1.2 M Br			
		$k \times 10^5$ (min^{-1})	% Anti-Markovnikov product	$k(\alpha) \times 10^5$ (min^{-1})	$k(\beta) \times 10^5$ (min^{-1})
p-CF_3	0.00265	—	20	—	—
m-CF_3	0.00506	0.36	25	0.27	0.089
p-Br	0.597	4.2	3.0	4.1	0.125
p-Cl	1.33	3.9	3.6	3.8	0.14
H	1.40	3.3	1.6	3.3	0.054
p-F	4.25	10.5	0.68	10.3	0.071
p-CH_3	39.9	35.5	0.00	35.5	0.00
p-$C(CH_3)_3$	72.0	60.5	0.00	60.5	0.00



Scheme 2

becomes dominant and a *negative* charge is developed in the π system. This negative charge is best accommodated at the α carbon where it can be delocalized into the aromatic ring. This predominantly *nucleophilic* attack thus favors formation of the anti-Markovnikov product.

AM3 calculations supported this possibility and we proceeded to test it further. A Hammett series of ring-substituted phenylpropynes were submitted to these reaction conditions to ascertain whether a predominantly negative charge was developing at the α position. The outcome is discussed in the results section.

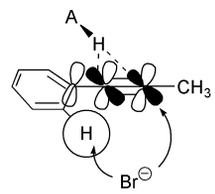
4) Steric interaction with the aromatic π cloud

Protonation of the β carbon of the triple bond should occur in the π system which includes the aromatic electrons, thereby allowing the greatest stabilization of the developing positive charge. The decreasingly acidic media demands increasing bromide participation in the transition state drawing the bromide ion closer to the π electrons of the aromatic ring thereby increasing steric repulsion and leaving bromide to attack at the alkyne carbon β to the aromatic ring.

In trying to model this behavior with AM3 calculations, we found that bringing the bromide ion closer to the α carbon in the transition state causes the carbon to rehybridize toward sp^2 and leads to *less* steric interaction with the aromatic π electrons.

5) Bromide attack at the α carbon occurs in the plane of the aromatic ring leading to steric interference by an *ortho* hydrogen.

If the proton and the bromide ion were to add synchronously, there would be no need to involve the aromatic ring to stabilize charge. Indeed, the alkyne π electrons which are orthogonal to the conjugated system might be more available for attack so as to leave the conjugated system intact leading to a lower energy transition state. In this situation, bromide attack on the α carbon would occur in the plane of the ring and might be hindered by the nearby *ortho* hydrogen (Scheme 3). Larger groups in the *ortho* position could be more effective in blocking the acid and/or the bromide ion. *Ortho*-substituted phenylpropynes were synthesized to test this possibility (*vide infra*).



Scheme 3

Results and discussion

A reasonable number of *meta* and *para* substituted phenylacetylenes were commercially available and these were reacted with the 20% trifluoroacetic acid in methylene chloride containing 0.1 M or 1.2 M bromide ions. As with the reaction of 1-phenylprop-1-yne in the 0.1 M bromide solution, all of the substituted phenylacetylenes produced only the Markovnikov addition products and were assumed to react through a cationic intermediate. The pseudo-first order rate constants for these reactions are listed in Table 1 and their logarithms are graphed against the σ^+ values in Fig. 1. The ρ value of −4.9 supports the idea that a significant positive charge was developing at the benzyl-type position in the transition state of the slow step.

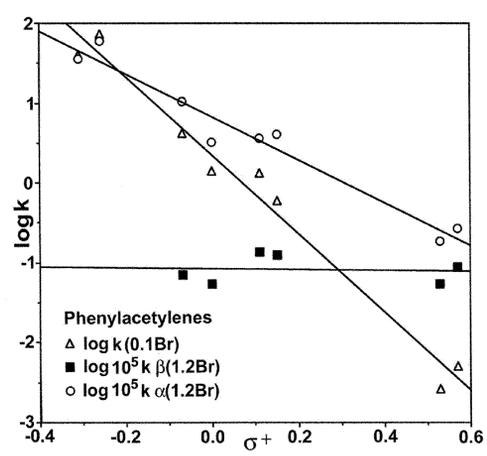


Fig. 1 Logarithm of rate constants of phenylacetylenes from Table 1 *versus* Hammett σ^+ values.

The reaction of the substituted phenylacetylenes with 1.2 M bromide ion was more interesting. Although 1-phenylprop-1-yne had been found to produce almost 50% of the anti-Markovnikov adduct at this bromide ion concentration, (consistent with the expectations of a concerted mechanism) phenylacetylene was found to produce little anti-Markovnikov adduct under these conditions. This was perhaps due to the difficulty of developing any positive charge on the terminal carbon of the phenylacetylene. Phenylacetylenes bearing electron withdrawing substituents formed larger proportions of the anti-Markovnikov product and this supported the idea that predominant bonding to the bromide ion was generating a negative charge at the α carbon. From the relative yields of the

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Table 2 Pseudo-first order rate constants and product distributions from phenylpropynes in 0.1 M, 1.2 M and 2.0 M bromide solutions

	0.1 M Br		1.2 M Br		2.0 M Br	
1-Phenylprop-1-yne substituent	*via* Ad_E2 k/ min^{-1}	*E* : *Z* ratio	*via* Ad3 $k \times 10^5$/ min^{-1}	% Anti-Markovnikov Product	$k(\beta) \times 10^5$/ min^{-1}	% Anti-Markovnikov product
m-CF_3	0.00027	1.8	0.94	93	0.87	100
p-Cl	0.068	3.45	4.3	80	3.4	98
H	0.516	3.6	6.2	46	2.9	86
p-F	0.254	4.0	14	55	7.7	92
p-CH_3	21.6	3.25	21	12[a]	2.5	60
o-Cl	—	6.6	0.32	24	0.08	—
o-CH_3	1.36	8.0	6.5	<1	<0.06	—

[a] % anti-Markovnikov product from Ad3 mechanism based upon a 24% yield of the **E1B** product arising from the cationic Ad_E2 mechanism being accompanied by 8% of the **Z1B** product from this Ad_E2 mechanism. The remaining **Z1B** yield was ascribed to the concerted Ad3 route.

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two products, the pseudo-first order rate constants could be split into rate constants for the formation of each product and plotted separately against σ^+. These data are shown in Table 1 and graphed in Fig. 1. A ρ value of -2.9 was found for the formation of the α products. A ρ value of -0.05 was found for the formation of the β-bromostyrenes suggesting that little if any positive (or negative) charge was developing at the benzyl-type position in the transition state leading to the anti-Markovnikov products.

A number of these substituted phenylacetylenes were converted into phenylpropynes and reacted with the 0.1 M, 1.2 M and 2.0 M bromide ion solutions. In the most acidic 0.1 M bromide solutions, all of the substrates still formed the Markovnikov products consistent with a cationic mechanism. Furthermore, the constant *E* : *Z* ratio of the Markovnikov products with the majority of *para*-substituted phenylpropynes supports our idea that the free cation was involved in all but the most deactivated of these cases. These substituents were neither inducing an alternate mechanism *nor modifying the degree of bromide association in their transition states*. The ρ value for the phenylpropynes in 0.1 M bromide was -5.5 also supporting the idea of a cationic intermediate. The rate and product data are listed in Table 2 and graphed in Fig. 2.

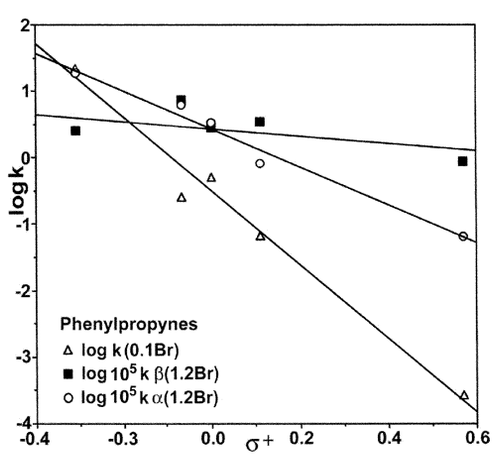

Fig. 2 Logarithm of rate constants of phenylpropynes from Table 2 *versus* Hammett σ^+ values.

In the less acidic solutions containing 1.2 M bromide, the anti-Markovnikov product was found in every case. For the phenylpropyne with the most electron withdrawing substituent reacting with the 1.2 M bromide, the anti-Markovnikov product comprised 93% of the adducts. The reason for this result may be seen in a comparison of the curves of Figs. 1 and 2. While the slopes of these lines are quite similar for the acetylenes and the propynes, the rates of formation of the β-bromopropenes are more than ten times the values for the corresponding β-bromoethylenes.

The data graphed in Figs. 1 and 2 make it clear that the anti-Markovnikov products are not arising from electron withdrawing groups promoting nucleophilic attack at the β position but, rather, from the electron withdrawing groups discouraging protonation at the β position, thus causing production of the anti-Markovnikov adducts by default. Indeed, the *meta* and *para* substituents had very little effect on the rate of formation of the anti-Markovnikov products ($\rho = -0.5$). This suggests that in the transition state of this reaction, there was little charge built up in the conjugated π system and that the proton and bromide were adding quite simultaneously. However, if there was minimal charge development, there was little reason for the attack to occur in the conjugated system. Attack on the isolated, orthogonal π bond became preferred since this allowed the conjugated system to remain intact. Furthermore, this orthogonal π bond was little affected by the aryl substituents and a low ρ value should be expected. HBr addition in the plane of the aromatic ring should be subject to significant steric effects leading to a preference for the anti-Markovnikov product. In addition, the small positive charge expected in this transition state should be better stabilized by the methyl group than by the coplanar aromatic ring. Therefore, electronic effects in the isolated π bond would also favor anti-Markovnikov addition. Indeed, the anti-Markovnikov addition to the phenylpropyne occurs by a Markovnikov addition to the isolated π bond.

We synthesized 1-(2-methylphenyl)-prop-1-yne and subjected it to our reaction conditions. The results were striking. In the 0.1 M bromide mixture, the Markovnikov products were evidence of a cationic intermediate much as had been seen with the 1-(4-methylphenyl)-prop-1-yne. No evidence of a steric effect was seen. However, in the less acidic 1.2 M bromide solution, the *ortho* methyl group appeared to block all reaction of the in-plane π bond and less than 1% of the anti-Markovnikov product was found. The 1-(4-methylphenyl)-prop-1-yne had produced approximately 12% of the anti-Markovnikov product.

We also synthesized and reacted 1-(2-chlorophenyl)-prop-1-yne. In the 1.2 M bromide, the corresponding *para* isomer had produced 80% of the anti-Markovnikov HBr adduct with an overall rate constant of 4.3×10^{-5} $min.^{-1}$. In contrast, the *ortho* isomer produced only 24% of the anti-Markovnikov product with a rate constant of 3.2×10^{-6} $min.^{-1}$. Clearly, the *ortho* chlorine hinders reaction at the π bond coplanar with the ring.

Conclusion

Electrophilic attack on the unconjugated π bonds of phenylacetylenes and phenylpropynes has been suggested previously but has not been universally accepted. Coplanar iodonium ions have been postulated in an addition of IN_3 to phenylpropyne[5] but the idea was criticized[6] for the experimental absence of stereochemically pure *anti* addition. An episulfonium ion was also suggested[7] to result from the attack

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of dinitrobenzenesulfenyl chloride on the π bond in the plane of the ring of phenylacetylene. The activation parameters and secondary kinetic isotope effects for this reaction were more similar to the addition to unconjugated alkynes than to styrene. The ρ value was also less negative than those for other electrophilic additions to phenylacetylenes. The exclusive Markovnikov addition was explained by the significant positive charge on the carbons of the episulfonium ion being better stabilized next to the aromatic ring.

We feel that the HBr additions at high bromide concentrations present a clearer case for this behavior. The absence of *syn* addition products at bromide ion concentrations above one molar is strong evidence for the Ad3 mechanism at these concentrations. As Okuyama *et al.*[7] pointed out, the greater reactivity of the propynes over the ethynes is further evidence for reaction *via* the π complex. Such a complex at the *conjugated* π bond of the alkyne would be heavily polarized toward positive charge developing adjacent to the aromatic ring and the resulting transition state would be strongly affected by substituents in the ring. Nucleophilic attack would occur at the position α to the ring. Furthermore, this transition state would suffer attack and rehybridization in the plane orthogonal to the plane of the ring and show minimal steric interaction with the phenyl ring. We believe that this transition state predominates at intermediate bromide concentrations and that it leads to exclusive formation of the **Z1B** Markovnikov products. The ρ for **Z1B** formation at 1.2 M bromide is −2.9, consistent with this model. If any anti-Markovnikov products were coming from addition to the conjugated π system, we would expect to see it reflected in the ρ value for the formation of those products.

As the concentration of bromide ion increases, the acidity of the solution drops and the polarized transition state with its strong bonding to the acid, becomes less feasible. Because the weaker acid requires more bonding from the nucleophilic bromide, the Ad3 transition state becomes less polarized and little charge builds up on the acetylenic carbon atoms. A π complex between an acid and an unconjugated alkyne has been shown[8] to distort the alkyne structure very little and presumably to develop little charge on these carbons. With little charge to stabilize, reaction at the isolated π bond becomes favored as it leaves the conjugated π system intact. This π bond, orthogonal to the conjugated π system, is well insulated from the electronic effects of the phenyl substituents. Neither the rate of reaction nor the regiochemistry at this π bond should be strongly influenced by *meta* or *para* substituents in the ring. The rates of formation of the anti-Markovnikov products were very similar for all members of the phenylpropyne series and for the phenylacetylene series at 1.2 M bromide concentration leading to ρ values close to zero. The greater rates for the phenylpropyne series derived from the added methyl group stabilizing the π complex and/or stabilizing the positive charge building at the β carbon in the transition state.

On the other hand, the aromatic ring should have a strong steric effect on this π bond, hindering bromide attack at the α position and promoting the production of anti-Markovnikov adducts. At the highest concentration of bromide ion, the anti-Markovnikov adduct was the principal product from all of the phenylpropynes tested. We therefore believe that the attack at the isolated π bond leads to exclusive formation of the anti-Markovnikov product. *Ortho* substituents on the phenyl ring further hinder attack in this plane, leading to a rate retardation and increased Markovnikov products coming from the slow attack on the conjugated system.

As we reported in our preceding paper,[1] a competition experiment using equimolar bromide and iodide ions produced 90% iodide adducts indicating the involvement of the halide ions in the rate and product-determining step. More significantly, the ratio of anti-Markovnikov to Markovnikov products was little affected by this increased nucleophilicity of iodide showing that both regioisomers were similarly promoted by the higher nucleophilicity of the iodide ion. Therefore, both products were generated by nucleophilic attack on an acid–alkyne complexes.

At the lowest concentration of bromide ion, attack on the conjugated π bond produces a free cation leading to the Markovnikov product primarily by a *syn* addition. As the bromide ion increases, the less acidic solutions require bromide participation in the transition state causing a polarized concerted addition in the conjugated π system and more Markovnikov *anti* addition. Higher concentrations of bromide ion caused decreased acidity and a less polarized transition state. This leads to the concerted reaction occurring preferentially in the isolated π bond of the alkyne and exclusive formation of the anti-Markovnikov *anti* addition product.

Experimental

The HBr additions were performed as described in the preceding paper.[1] Product identification was based upon their relative retention times in the chromatographic analysis and the relative abundance of the molecular ion to the (M^+–Br) peak in the mass spectra. In questionable cases, isomeric mixtures were synthesized and analyzed by NMR and GC/MS. The results of these analyses identified the chromatographic peaks and supported our assumption of similar detector responses for isomeric products. NMR spectra were recorded on a Varian Mercury 300 MHz spectrometer utilizing a deuterium lock and TMS as internal reference. Mass spectra and chromatographic analyses were performed on a Hewlett Packard 5890 Chromatograph with a 12 m HP-1 capillary column and a 5971A mass selective detector.

General synthesis of substituted phenylpropynes[9]

To a flame dried flask under N_2 atmosphere was added 60 mL of a THF solution containing 8.6 mmol of the phenylacetylene. The solution was cooled to −20 °C. Methyl lithium 13.0 mL of a 1.4 M solution in ether (2.1 eq.) was added dropwise to the cooled solution over a 10 minute period. After allowing the reaction to stir at −20 °C for 30 minutes, methyl iodide (1.15 mL, 2.1 eq.) was added. The reaction was allowed to proceed for 30 minutes at −20 °C, slowly allowed to warm to room temperature over the next 30 minutes and then quenched with water. The product was extracted with hexanes, washed with water and brine and dried over anhydrous sodium sulfate. Flash chromatography on silica gel with hexanes yielded a 66–95% yield of a colorless liquid. Any unreacted starting material was removed by treatment with 1% silver nitrate solution in ethanol.

1-(4-Chlorophenyl)-prop-1-yne

R_f = 0.43, silica, hexanes; δ_H(300 MHz; $CDCl_3$; Me_4Si) 2.02 (3 H, s), 7.20–7.29 (4 H); *m*/*z* 150 (M+, 54%), 115 (100).

1-(4-Fluorophenyl)-prop-1-yne

R_f = 0.41, silica, hexanes; δ_H(300 MHz; $CDCl_3$; Me_4Si) 2.01 (3 H, s), 6.94 (2 H), 7.33 (2 H); *m*/*z* 133 (M+, 100%), 134 (67), 107(10).

1-(4-Methylphenyl)-prop-1-yne

R_f = 0.48, silica, hexanes; δ_H(300 MHz; $CDCl_3$; Me_4Si) 2.01 (3 H, s), 2.30 (3 H), 7.04 (2 H, d), 7.25 (2 H, d); *m*/*z* 130 (M+, 100%), 115 (83).

1-(3-Trifluoromethylphenyl)-prop-1-yne

R_f = 0.40, silica, hexanes; δ_H(300 MHz; $CDCl_3$; Me_4Si) 2.06 (3 H, s), 7.34–7.62 (4 H); *m*/*z* 184 (M+, 100%), 165 (16), 115 (95).

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1-(2-Chlorophenyl)-prop-1-yne [10]

To a flame dried 3-neck flask under N_2 atmosphere 1.757 g (1.5 eq.) of anhydrous zinc bromide was added followed by 15 mL of anhydrous THF. The resulting solution was cooled in an ice bath to 5 °C. The propargyl Grignard solution, 15 mL of a 0.5 M solution in THF (1.5 eq.), was added dropwise to the stirred solution of zinc bromide over a fifteen minute period. The ice bath was removed and the reaction mixture was allowed to warm to room temperature. After 15 minutes at room temperature, 1.233 g (5.17 mmol) of *o*-chloroiodobenzene dissolved in 5 mL of THF was added to the stirred reaction mixture followed by 0.293 g (0.05 eq.) of palladium tetrakis(triphenylphosphine) dissolved in 10 mL of THF. The reaction was allowed to proceed at room temperature for two hours and then was quenched with water. The crude product was extracted with ether, washed with brine and dried over anhydrous sodium sulfate. The solvent was removed by rotary evaporation. The residue was taken up in hexanes and the resulting slurry was filtered to remove the catalyst. Flash chromatography on silica gel with hexanes yielded 0.690 g, 92% yield of a colorless liquid. R_f = 0.50, silica, hexanes; δ_H(300 MHz; $CDCl_3$; Me_4Si) 2.11 (3 H, s), 7.14–7.16 (2 H), 7.17–7.32 (1 H), 7.39–7.42 (1 H); *m*/*z* 150 (M+, 61%), 115 (100).

1-(2-Methylphenyl)-prop-1-yne

R_f = 0.45, silica, hexanes; δ_H(300 MHz; $CDCl_3$; Me_4Si) 2.07 (3 H, s), 2.40 (3 H, s), 7.05–7.14 (3 H), 7.33 (1 H); *m*/*z* 130 (M+, 100%), 115 (84).

Synthesis of all four isomers of phenylbromopropene

1-Phenylprop-1-yne (0.644 g, 5.55 mmol) was cooled in an ice bath. To the stirred reaction 5.5 mL of ice cold 30% HBr in acetic acid solution was added. The reaction was allowed to proceed for fifteen minutes at 5 °C and then was quenched with water. The mixture of products was extracted with hexanes, washed with water, saturated $NaHCO_3$ and brine. ^{1}H-NMR and GC/MS analysis determined the products to be:

(E)-1-phenyl-1-bromoprop-1-ene 3.0%; δ_H(300 MHz; $CDCl_3$; Me_4Si) 1.64 (3 H, d, J 6.8), 6.24 (1 H, q, J 6.8), 7.24–7.53 (5 H); *m*/*z* 198, 196 (M+, 48%), 115 (100);

(Z)-1-phenyl-1-bromoprop-1-ene 20.2%; δ_H(300 MHz; $CDCl_3$; Me_4Si) 1.93 (3 H, d, J 6.6), 6.24 (1 H, q, J 6.6), 7.24–7.53 (5 H); *m*/*z* 198, 196 (M+, 47%), 115 (100);

(E)-1-phenyl-2-bromoprop-1-ene 14.6%, *m*/*z* 198, 196 (M^+, 70%), 115 (100);

(Z)-1-phenyl-2-bromoprop-1-ene 62.1%; δ_H(300 MHz; $CDCl_3$; Me_4Si) 2.48 (3 H, s), 6.68 (1 H, s), 7.24–7.35 (4 H), 7.51–7.53 (1 H); *m*/*z* 198, 196 (M+, 75%), 115 (100).

HBr in acetic acid addition to 1-(2-methylphenyl)-prop-1-yne

^{1}H-NMR and GC/MS analysis determined the products to be:

(E)-1-(2-methylphenyl)-1-bromoprop-1-ene 10.0%; δ_H(300 MHz; $CDCl_3$; Me_4Si) 1.42 (3 H, d, J 7.2), 2.23 (3 H, s), 6.24 (1 H, q, J 7.2), 7.1–7.4 (4 H); *m*/*z* 198, 196 (M+, 48%), 115 (100);

(Z)-1-(2-methylphenyl)-1-bromoprop-1-ene 17.3%; δ_H(300 MHz; $CDCl_3$; Me_4Si) 1.89 (3 H, d, J 6.6), 2.32 (3 H, s), 6.24 (1 H, q, J 6.6), 7.1–7.4 (5 H); *m*/*z* 198, 196 (M+, 47%), 115 (100);

(E)-1-(2-methylphenyl)-2-bromoprop-1-ene 28.0%; δ_H(300 MHz; $CDCl_3$; Me_4Si) 2.23 (3 H, s), 2.28 (3 H, d, J 1.5), 6.90 (1 H, s), 7.1–7.4 (4 H); *m*/*z* 198, 196 (M+, 70%), 115 (100);

(Z)-1-(2-methylphenyl)-2-bromoprop-1-ene 44.7%; δ_H(300 MHz; $CDCl_3$; Me_4Si) 2.23 (3 H, s), 2.46 (3 H, d, J 1.5), 6.66 (1 H, s), 7.1–7.4 (4 H); *m*/*z* 198, 196 (M+, 75%), 115 (100).

HBr in acetic acid addition to 1-(2-chlorophenyl)-prop-1-yne

^{1}H-NMR and GC/MS analysis determined the products to be:

(E)-1-(2-chlorophenyl)-1-bromoprop-1-ene 0.30%, *m*/*z* 198, 196 (M^+, 48%), 115 (100);

(Z)-1-(2-chlorophenyl)-1-bromoprop-1-ene 2.2%, *m*/*z* 198, 196 (M^+, 47%), 115 (100);

(E)-1-(2-chlorophenyl)-2-bromoprop-1-ene 26.8%; δ_H(300 MHz; $CDCl_3$; Me_4Si) 2.35 (3 H, d, J 1.5), 6.97 (1 H, q), 7.1–7.4 (3 H), 7.88–7.92 (3 H); *m*/*z* 198, 196 (M+, 70%), 115 (100);

(Z)-1-(2-chlorophenyl)-2-bromoprop-1-ene 70.7%; δ_H(300 MHz; $CDCl_3$; Me_4Si) 2.51 (3 H, d, J 1.5), 6.77 (1 H, q), 7.1–7.4 (3 H), 7.61–7.66 (1 H); *m*/*z* 198, 196 (M+, 75%), 115 (100).

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