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Vinylation of Aromatic Substrates with Solvolytically Generated Trisubstituted Vinyl Cations[1]

Tsugio Kitamura,[2a] Shinjiro Kobayashi,[2a] Hiroshi Taniguchi,*[2a] and Zvi Rappoport*[2b]

Department of Applied Chemistry, Faculty of Engineering, Kyushu University, Fukuoka 812, Japan, and
Department of Organic Chemistry, The Hebrew University, Jerusalem 91904, Israel

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Vinylations of aromatic compounds by α-aryl-β,β-disubstituted vinyl bromides (**3a–i**) in the presence of silver salts and 2,6-lutidine or 2,6-di-*tert*-butyl-4-methylpyridine proceed with high yields. The silver triflate assisted reaction is preferable to the silver tetrafluoroborate assisted reaction. The reaction of 1-anisyl-2,2-diphenylvinyl bromide gives a ρ^+ value of –4.08 and high intramolecular selectivity with k_o/k_p ratios of 6.2–78. It is suggested that the reaction proceeds via intermediate α-arylvinyl cations and that the inter- and intramolecular selectivities are determined in the same transition state.

Most of the early studies of vinyl cations[3] were concentrated on mechanistic aspects of their generation and behavior. However, in recent years there has been an increasing number of synthetic applications of reactions involving intermediate vinyl cations.[4,5] Some of these reactions, especially those initiated by electrophilic additions to alkynes (e.g., cyclizations[5a]), require mild conditions since the high energy of the intermediate cations is compensated by the high energy of their triply bonded precursors. In contrast, the solvolytic generation of vinyl cations from their vinyl–X precursors (X = Br, Cl, OTs, OTf) is more difficult and requires more severe conditions than the analogous process for the corresponding saturated derivatives.

Friedel–Crafts vinylation of aromatic substrates was achieved with alkynes in the presence of acids,[6] but vinyl esters[7] and vinyl halides[8,9] also gave vinylation in the presence of Friedel–Crafts catalysts. With unactivated vinyl halides the reaction requires rather drastic conditions and proceeds with low yields, as in the $AlCl_3$-catalyzed formation of 1,1-diphenylethene and 1,1-dianisylethene from 1,1-dibromoethene with benzene and anisole, respectively.[9] The reaction conditions are much less severe with α-arylvinyl halides and sulfonates since the intermediate α-arylvinyl cations are relatively stable, and benzofurans,[10a] benzothiophenes,[10b] and benzothiophene dioxides[10c] were formed by internal vinylation of α,β-diarylvinyl sulfonates and bromides in the presence of mild Friedel–Crafts catalysts such as BF_3 or even in the absence of a catalyst. α-Bromostyrene condenses rapidly with toluene in the presence of Al_2Br_6, giving mainly 1-phenyl-1-*p*-tolylethene.[11] Trianisylvinyl chloride and (*E*)-1,2-dianisyl-1,2-dichloroethene react with anisole in the presence of $AlCl_3$ or $SnCl_4$ to give tetraanisylethene, whereas mainly 2,3-dianisylbenzofurans were obtained when one of the β-anisyl groups was replaced by *o*-anisyl.[12]

In spite of these works, very little was known until recently about the mechanistic side of the intermolecular Friedel–Crafts vinylations. Stang and Anderson[13] recently investigated these aspects by using several vinyl triflates as the vinylation precursors in the presence of 2,6-di-*tert*-butyl-4-methylpyridine and obtained high yields in some cases. They found a ρ^+ value of –2.57 for vinylation of five aromatic compounds by 1-phenyl-2-methylpropen-1-yl triflate and a relatively high intramolecular positional selectivity in the aromatic ring. It was suggested that the reaction involves two intermediates, one determining the intermolecular and the other determining the intramolecular selectivity.

The present work aims to extend these mechanistic and synthetic studies in relation to the following questions. (a) Can an aprotic inert solvent be used advantageously in the substitution reaction? (b) Can α-aryl-β,β-disubstituted vinyl bromides, which are frequently more available than the corresponding triflates, be used as vinylation precursors and still give high yields? (c) What is the effect of the anion associated with the vinyl cation on the intermolecular selectivity? (d) What is the effect of increasing the stability of the vinyl cation on the inter- and intramolecular selectivities in the vinylation reaction?

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(1) Part 36 of the series "Vinylic Cations from Solvolysis" from Jerusalem. For Part 35, see: Ikeda, T.; Kobayashi, S.; Taniguchi, H.; Rappoport, Z. *J. Org. Chem. 1982*, **48**, 1916.

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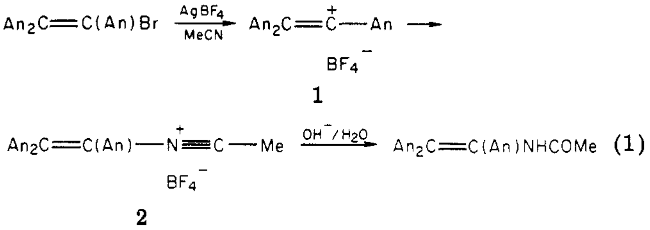
Buffered solvolysis of α-arylvinyl bromides is a relatively slow process.[14] However, the cleavage of the carbon–halogen bond is strongly assisted by silver salts and triarylvinyl sulfonates can be prepared by a short-time reaction of the bromides with silver arenesulfonates in acetonitrile at 120 °C.[15] Consequently, we studied the silver salt assisted vinylation of trisubstituted vinyl bromides with several aromatic compounds.

Results

In a preliminary experiment the reaction of trianisylvinyl bromide with silver tetrafluoroborate was conducted in acetonitrile. It was hoped that trianisylvinyl tetrafluoroborate would be obtained in a form which would be suitable for a rapid vinylation. Reflux in acetonitrile for 30 min gave a high yield of AgBr, but when the mixture was hydrolyzed with NaOH, the product was not the expected trianisylethanone but 1-(acetylamino)-1,2,2-tris(*p*-methoxyphenyl)ethene; i.e., a Ritter-type vinylation on the nitrogen of the solvent took place (eq 1). Since both **1** and **2** may react with the aromatic substrate and thus complicate the mechanistic studies, the vinylations were conducted with the aromatic substrates as the solvents.

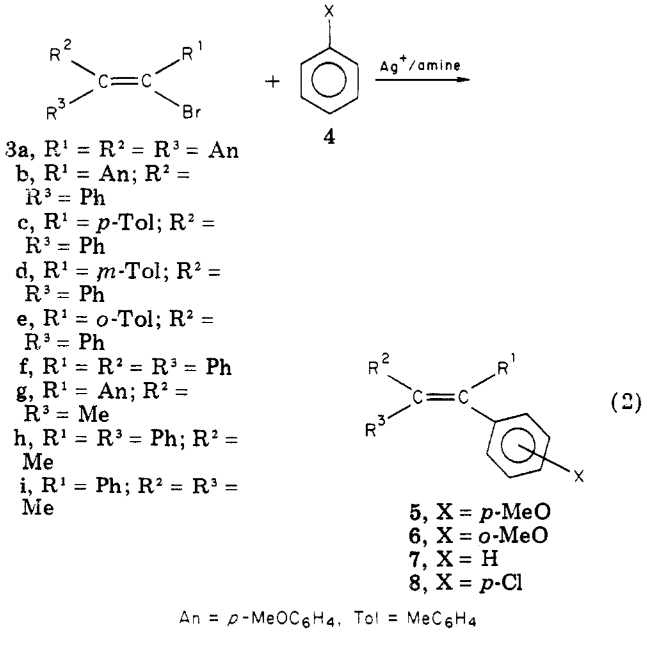


$$\mathrm{An_2C{=}C(An)Br} \xrightarrow[\text{MeCN}]{\text{AgBF}_4} \underset{\textbf{1}}{\underset{\mathrm{BF_4^-}}{\mathrm{An_2C{=}\overset{+}{C}{-}An}}} \longrightarrow$$

$$\underset{\textbf{2}}{\underset{\mathrm{BF_4^-}}{\mathrm{An_2C{=}C(An){-}\overset{+}{N}{\equiv}C{-}Me}}} \xrightarrow{\mathrm{OH^-/H_2O}} \mathrm{An_2C{=}C(An)NHCOMe} \quad (1)$$

An = *p*-MeOC$_6$H$_4$

Reactions of the vinyl bromides **3a–c,f–i** were conducted at 110–150 °C for 24–36 h in the presence of silver tetrafluoroborate (eq 2). Since the vinylation is accompanied by the formation of a strong acid (HBF$_4$) which can add to the double bond,[15] a slight excess of 2,6-lutidine was added. The aromatic substrate was mostly anisole, except for the reaction of 2,2-dianisyl-1-phenylvinyl bromide (**3b**) which was also performed with toluene and benzene. Except for these two reactions the isolated yields were 57–83%, and there was no evidence for other products. The reactions with toluene and benzene gave much lower yields (23% and 13%, respectively) of the vinylation products after 48 h. The major products were not isolated, although they probably contain fluorination products, as reported by Hammen and Hanack for AgBF$_4$-assisted reaction of 1-anisyl-2-methylpropen-1-yl bromide with cyclohexene.[16] Actually, triphenylvinyl fluoride was obtained together with tetraphenylethene (**7f**) in AgBF$_4$-assisted reaction of **3f** with benzene.



3a, R^1 = R^2 = R^3 = An
b, R^1 = An; R^2 = R^3 = Ph
c, R^1 = *p*-Tol; R^2 = R^3 = Ph
d, R^1 = *m*-Tol; R^2 = R^3 = Ph
e, R^1 = *o*-Tol; R^2 = R^3 = Ph
f, R^1 = R^2 = R^3 = Ph
g, R^1 = An; R^2 = R^3 = Me
h, R^1 = R^3 = Ph; R^2 = Me
i, R^1 = Ph; R^2 = R^3 = Me

4

5, X = *p*-MeO
6, X = *o*-MeO
7, X = H
8, X = *p*-Cl

An = *p*-MeOC$_6$H$_4$, Tol = MeC$_6$H$_4$

In order to avoid this side reaction, vinylations by **3b,d–f,i** were conducted in the presence of silver triflate (silver trifluoromethanesulfonate, AgOTf) by using 2,6-di-*tert*-butyl-4-methylpyridine,[17] the nonnucleophilic base used by Stang and Anderson,[13] as the buffering base. The isolated yields were 79–83% and 88–99% when determined by gas chromatography. For example, chlorobenzene, the least reactive aromatic substrate studied, gave 97% yield. The reaction conditions, products, and yields are given in Table I, and physical and spectral properties of the products are given in Table IV.

Intramolecular selectivities were determined in the reactions of **3b** with anisole, toluene, and chlorobenzene. In all the cases the para-substituted isomer was the main product. With anisole the para product was isolated, the ortho product was identified by gas chromatography, and their ratio was determined by gas chromatography. With chlorobenzene, only the para isomer was isolated, and the relative ortho/para ratio was determined by gas chromatography from the appropriate retention times. Since the retention time of an authentic sample of the meta isomer is similar to that of the para isomer, its formation cannot be excluded unequivocally. Since toluene was the only aromatic compound which gave ortho, meta, and para products in the reaction with Me$_2$C=C(Ph)OTf,[13] the product distribution in this case was investigated thoroughly in the presence of AgOTf/2,6-di-*tert*-butyl-4-methylpyridine (DBMP). The *o*-, *m*-, and *p*-1-tolyl-1-anisyl-2,2-diphenylethenes (**5e,d,c**, respectively) were formed in a 3:2:9.3 ratio according to the NMR. The three isomers were obtained independently from the vinylation of anisole with 2,2-diphenyl-1-*o*-, -*m*-, and -*p*-tolylvinyl bromides (**3e**, **3d**, and **3c**, respectively, Scheme I). The NMR spectra suggested the formation of the *o*-methoxy isomers in low yield but further investigations were not conducted.

Isomer distributions, partial rate factors, and the relative rate of attack on a para compared with a single ortho position are given in Table II.

The intermolecular selectivities were determined by competition experiments in the reaction of **3b** with a mixture of benzene, toluene, and anisole in the presence of either AgBF$_4$ or AgOTf or with benzene and chlorobenzene in the presence of AgOTf. The log (k_X/k_H) ratios, where k_X is the rate constant for the reaction at a certain position of the substituted benzene and k_H is the rate constant for a single position of benzene were calculated from the initial molar concentrations of the aromatic substrate and the product ratios. The data are given in Table III. The log (k_X/k_H) ratios in the presence of AgOTf

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(14) For example, the half-life of **3b**, the compound most studied by us, is >10 h in AcOH at 120 °C (Rappoport, Z.; Gal, A. *Tetrahedron Lett.* **1970**, 3233–3236). The half-life in a much less ionizing aromatic solvent should be much longer.

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Table I. Silver Salts Assisted Vinylation of Aromatic Compounds C_6H_5X (4) with Vinyl Bromides 3

vinyl bromide[a]	X	silver salt[b]	temp, °C	reaction time, h	product	yield,[c] %
3a	MeO	$AgBF_4$	110	24	5a[h]	75
3b	MeO	$AgBF_4$	120	24	5b,6b	82
	Me	$AgBF_4$	120	48	5c,5d,5e[d]	23[e,f]
		AgOTf	120	48	5c,5d,5e[d]	97[e]
	H	$AgBF_4$	120	48	5f	13[e,f]
		AgOTf	120	37	5f	88[e]
	Cl	AgOTf	120	48	8b[h]	97[e]
3c	MeO	$AgBF_4$	150	24	5c[h]	83
3d	MeO	AgOTf	150	30	5d[h]	99[e]
3e	MeO	AgOTf	150	24	5e[h]	99[e]
3f	MeO	$AgBF_4$	150	36	5f[h]	66
	H	AgOTf	150	42	7f	79
3g	MeO	$AgBF_4$	120	24	5g[h]	79
3h	MeO	$AgBF_4$	150	24	5h[g,h]	57
3i	MeO	$AgBF_4$	150	36	5i[h]	78
	H	AgOTf	150	42	7i	89

[a] Amount of vinyl bromide = 0.58 mmol. [b] Amount of silver salt = 0.80–1.05 mmol. With $AgBF_4$ the reaction mixture contains 0.87 mmol of 2,6-lutidine and with AgOTf it contains 0.83 mmol of 2,6-di-*tert*-butyl-4-methylpyridine. [c] Isolated yield. [d] Mixture of isomers. [e] Determined by gas chromatography. [f] The major product was not identified. [g] A 1:1 mixture of two geometrical isomers. [h] The ortho isomer which could not be isolated was formed in a low yield.

Table II. Isomer Distribution in the Vinylation of C_6H_5X by 3b

		% isomer			partial rate factor			
X	salt/base	o	m	p	${}^of$	${}^mf$	${}^pf$	k_p/k_o
MeO	$AgBF_4$/2,6-lutidine	2.5		97.5	15.8		1230	78
Cl	AgOTf/DBMP[a]	13.2		86.8	0.036		0.48	13.2
Me	AgOTf/DBMP[a]	21	14	65	3.2	2.1	19.5	6.2[b]

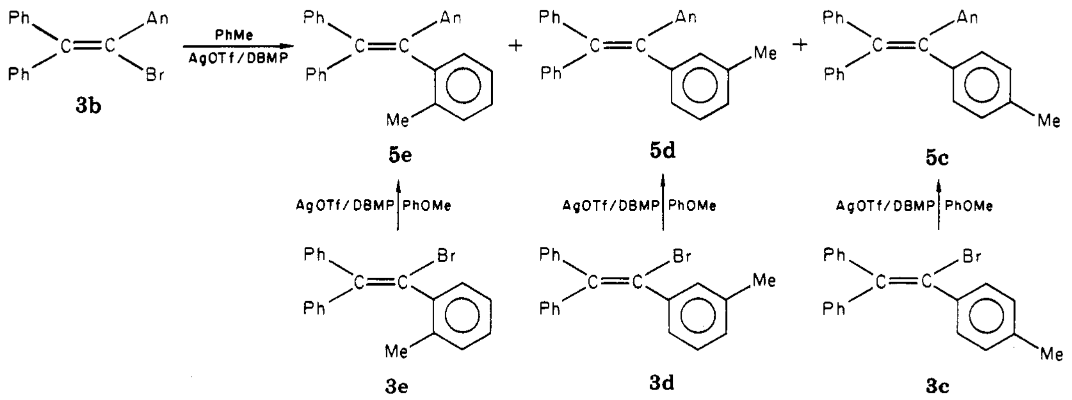
[a] 2.6-Di-*tert*-butyl-4-methylpyridine. [b] $k_p/k_m = 9.3$.

Table III. Competition Reactions of 3b[a] with Aromatic Compounds (4) at 120 °C

no.	added salt (concn, mmol)	C_6H_5X (concn, mmol)	$10^2 \times$ mmol of $Ph_2C{=}C(An)C_6H_4X$-*p*[b]	log (k_X/k_H)
1[c]	$AgBF_4$ (0.77)	C_6H_6 (70.75)	0.663	
		C_6H_5Me (30.32)	1.105	1.35
		C_6H_5OMe (8.90)	17.12	3.09
2[d]	AgOTf (0.67)	C_6H_6 (90.38)	2.063	
		C_6H_5Me (22.04)	1.629	1.29
		C_6H_5OMe (6.11)	41.51	3.25
3[d]	AgOTf (0.67)	C_6H_6 (53.47)	43.08	
		C_6H_5Cl (55.05)	3.595	−0.32

[a] Amount of 3b = 0.46 mmol. [b] Para substitution product. [c] In the presence of 1.17 mmol of 2,6-lutidine; reaction time 28 h. [d] In the presence of 0.82 mmol of 2,6-di-*tert*-butyl-4-methylpyridine; reaction time 48 h.

Scheme I



and $AgBF_4$ are practically identical. A plot of these values against Brown–Okamoto's σ^+ values for *p*-MeO, *p*-Me, *m*-Me, H, and *p*-Cl is linear (Figure 1) with a slope of −4.08 and a correlation coefficient of $r = 0.999$.

Discussion

The results of Table I show clearly that the silver salt assisted reaction of vinyl bromides with aromatic substrates can be conveniently used as a synthetic method for the formation of 1,1-diaryl-2,2-disubstituted alkenes. Moreover, due to the relatively high ρ^+ vallue and high intramolecular selectivity, relatively pure isomeric products can be obtained by an appropriate choice of the starting materials as shown in Scheme I. We believe that the syntheses, at least those starting from the α-anisyl derivatives,[18] require much shorter reaction times than those

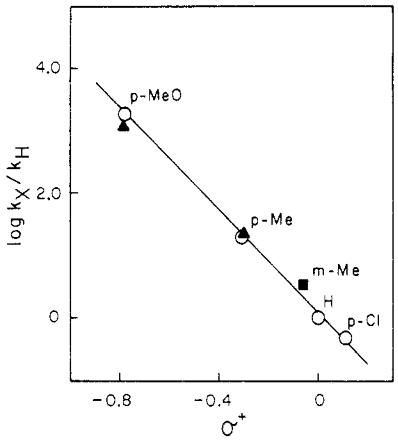
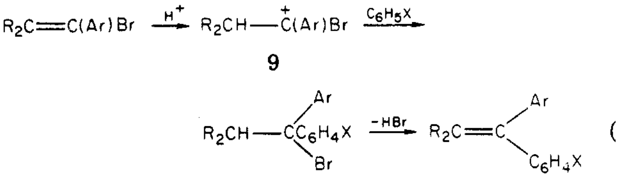


Figure 1. Log (k_X/k_H) vs. σ^+ for the AgOTf-assisted (○, ■) or $AgBF_4$-assisted (▲) reaction of **3b** with aromatic compounds **4**.

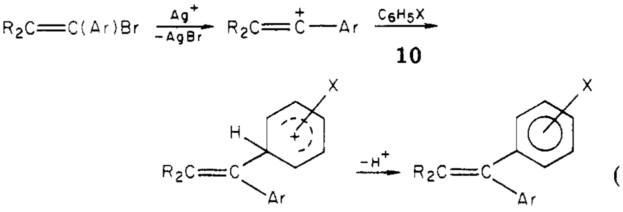
given in Table I, but the longer reaction times were used in order to ensure complete reaction in order to simplify the VPC analysis and enable the detection of the minor products and in order to use comparable conditions for the generation of the α-phenyl- and α-anisylvinyl cations.[18] The anion of the silver salt does not affect the intermolecular selectivities as shown by the similar positions of the points for the $AgBF_4$- and the AgOTf-assisted reactions in Figure 1.

While the effect of the two salts on the reaction rates was not compared, AgOTf was found to be a superior reagent since the BF_4^- anion apparently serves as a fluoride ion donor in the case of the reactive intermediates derived from benzene and toluene, resulting in formation of fluorinated products at the expense of the desired alkenes.

The vinylation products can be obtained by two alternative pathways: (i) by proton addition to the double bond, alkylation of the aromatic compound by **9** (the formed sp^2-hybridized ion), and elimination of HBr (eq 3) or (ii) by silver-assisted ionization, followed by alkylation of the aromatic compound by the vinyl cation **10** (eq 4).



(3)



(4)

The first route can be excluded since the reaction medium is basic both at the beginning and throughout the reaction. The vinyl cation route is favored since the silver salt strongly assists the cleavage of the carbon–bromide bond.

Inter- and Intramolecular Selectivity. Stang and Anderson studied the vinylation of aromatic substrates **4** by the α-phenylvinyl cation **11** and found a linear log (k_X/k_H) against σ^+ plot with $\rho = -2.57$.[13] This low intermolecular selectivity suggested that **11** is highly reactive.

$$\underset{\mathbf{11}}{Me_2C{=}C^+Ph} \qquad \underset{\mathbf{12}}{Ph_2C{=}C^+An} \qquad \underset{\mathbf{13}}{Me_2C{=}C^+An}$$

In contrast, the intramolecular selectivity is high since the reaction with C_6H_5X (X = MeO, Me, F, Cl) gave mainly the para product and appreciable amounts of the ortho isomer, but only in the case of toluene was 8% of a meta product formed. Hence, it was concluded that the inter- and intramolecular selectivities are not determined in the same transition state. The intermolecular selectivity (ρ) is determined by the first transition state which resembles a π complex, whereas the isomer distribution is determined in a second transition state which presumably resembles the σ complex and where the vinyl cation electrophile attacks only activated ring positions.

Our α-anisylvinyl cation **12** differs from **11** both in the α and in the β substituents. However, we believe that the presence of two β-methyl groups in **11** compared with two β-phenyl groups in **12** does not affect the selectivities much, as judged by the selectivities of ions **12** and **13** toward pairs of nucleophiles.[19]

The ρ^+ value for the reaction of **12** is more negative (−4.08) than that for **11** (−2.57). In spite of recent reservations concerning the use of ρ values as a general measure of transition-state structure,[20] we believe that since the ions are structurally similar, comparison of the ρ's is justified if both reactions proceed by the same mechanism with the same rate-determining step. Since **12** is more stable than **11**, the Hammond principle suggests a more advanced transition state for the vinylation in the case of **12**, with a consequent higher intermolecular selectivity as measured by ρ^+. If we accept Stang's mechanism,[13] the higher ρ^+ value for **12** reflects higher stabilities of the π complexes of **12** with the aromatic compounds than of those of **11**.

Support for a similar mechanism may be obtained by comparison of the intramolecular selectivities. Formally, the intramolecular selectivities in the reactions of **11** and **12** are similar since a meta-substituted product is obtained in both cases only in the reaction of toluene. However, a more quantitative comparison is achieved when the log ($k_{m\text{-Me}}/k_H$) value, obtained from a combination of the product distribution and the competition experiment in the reaction of toluene with **3b**, is plotted on the Hammett plot of the para substituents. As shown in Figure 1, the point for m-Me is very close to the line determined by the para substituents. The plot for the para substituents predicts the formation of 13% of the meta product, while the observed value is 14%. The high ρ^+ value combined with the large $\sigma^+_{p\text{-MeO}} - \sigma^+_{m\text{-MeO}}$ difference suggests that if attack on the meta position of anisole obeys the same Hammett equation, only 0.084% of the meta product will be obtained under the reaction conditions of Tables II and III, where para substitution gave 97.5% of the product. This value is below the detection limit, and the absence of the meta product cannot be invoked as evidence for

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[18] Judging by the extensive collection of ρ^+ values for the generation of α-arylvinyl cations,[3] α-anisylvinyl cations may be generated 1000 times faster than their phenyl analogues.

[19] Reference 3, Chapter 6. Gal, A. Ph.D. Thesis, The Hebrew University, 1972. A referee raised the possibility that β-phenyl participation in the ionization of **3b** or phenyl bridging in the ion **12** may affect the inter- and intramolecular selectivities. however, kinetic and stereochemical data for (E)- and (Z)-AnC(Ph)=C(Br)An (Rappoport, Z.; Apeloig, Y. *J. Am. Chem. Soc.* **1969**, *91*, 6734–6742; *Tetrahedron Lett.* **1970**, 1817–1820), (E)- and (Z)-PhC(An)=C(Br)Ph (Rappoport, Z.; Houminer, Y. *J. Chem. Soc., Perkin Trans. 2* **1973**, 1506–1518), and p-$CD_3OC_6H_4C(An){=}C(Br)Ph^1$ showed the absence of β-anisyl participation in the transition states leading to the corresponding ions and the absence of bridging in the ions themselves. Since **12** or the transition state for its formation requires less bridging due to the β-anisyl group, it is excluded for these systems.

[20] Johnson, C. D. *Chem. Rev.* **1975**, *75*, 755–765; *Tetrahedron* **1980**, *36*, 3461–3480. However, see: McLennan, *Tetrahedron* **1978**, *34*, 2331–2341.

different inter- and intramolecular selectivities. A similar treatment requires that the percentage of the meta isomer from the reaction of **3b** with chlorobenzene will be 12%. Although this was not observed, we noted above that the possibility of overlap of VPC peaks makes the absence of this isomer inconclusive.

Consequently, the inter- and intramolecular selectivities in the reactions of **12** with aromatic compounds seem to be close, with the possible exception of chlorobenzene. Hence, we see no reason to invoke two intermediates in our system, and a rate-determining formation of a σ complex seems plausible.

A similar analysis was applied to Stang and Anderson's[13] results. Their lower ρ value requires the formation of a higher percentage of the meta products than in our case. If the same Hammett plot is applicable for both the inter- and intramolecular selectivities, the calculated para/meta product ratios for X in C_6H_5X are as follows: MeO, 66; Me 2.1; F, 6.2; Cl, 2.7. Actually, no meta product was observed except for X = Me. While this may be due to its relatively lower concentration when X = MeO, the meta isomer should be easily detected in the reaction with the halobenzenes. Moreover, the observed para/meta ratio of 8 for X = Me is ca. 4 times higher than the ratio calculated on the basis of the intermolecular selectivity. Consequently, Stang's qualitative claim is confirmed, and in more quantitative terms the intramolecular para/meta selectivity is higher than predicted from the intermolecular selectivity.

The difference between the rate-determining steps in the vinylations by **11** and **12** can be rationalized by their different reactivities. The higher reactivity of **11** apparently decreases the energy of the second transition state for σ-complex formation below that of the first transition state for the π-complex formation. With the more stable ion **12**, the relative energy of the second transition state, which involves bond formation, is higher than that of the first transition state. We believe that additional conclusions are premature and that several other systems should be studied before further generalizations are made. We also note that although the direct comparison of the ρ^+'s for the reactions of **11** and **12** is not justified, the conclusion from such a comparison mentioned above, concerning the positions of the transition states, is still valid.

Ortho/Para Ratios. In spite of the availability of two ortho positions, the para isomer is formed 3–39 times in excess in the vinylation with **3b**. The ortho/para ratios in aromatic substitution depend on several factors. Steric effects are important, and less ortho substitution is expected when either the electrophile or the aromatic reaction site becomes bulkier.[21] This effect should be more pronounced for a late transition state. An MO treatment[22] suggests that the electronic factor will favor ortho substitution if the transition state resembles the product σ complex, but since the frontier orbital density is higher at the para position than at the ortho position, the softer the electrophile is the higher the expected amount of para substitution will be. This was experimentally observed in electrophilic reactions of toluene.[21,22] Two additional factors favor para substitution. A para-quinonoid structure, formed by substitution para to a resonatively electron-donating X, is more stable than the ortho-quinonoid structure formed by attack at a position ortho to X. When the field effect is important, the effect of an ortho substituent will be more important as shown by the formation of the lowest ortho/para ratio in the nitration of the halobenzenes when X = F.[22]

The k_p/k_o ratios in the reaction of **12** with C_6H_5X (78, 13.2, and 6.2 for X = MeO, Cl, and Me, respectively) are higher than those of **11** (15.7, 4.7, and 4.6) with the same compounds. This is consistent with all the criteria mentioned above. The more delocalized and stable α-anisylvinyl cation **12** is softer and gives a more advanced transition state than the α-phenylvinyl cation **11**. The lowest ortho/para ratio is obtained for anisole, and OMe is the most resonatively electron-donating substituent of those studied. The difference between the β substituents of **11** and **12** is also consistent with this behavior since methyl is probably smaller than phenyl. However, it should be realized that the spherical symmetry of the methyl group and the ability of the phenyl group to rotate around the phenyl–carbon bond may reverse the actual bulk of phenyl and methyl at the reaction site for the vinylation reaction.

Conclusion. The silver salt assisted vinylation of aromatic substrates by α-aryl-β,β-disubstituted vinyl bromides proceeds with high yields and with high intra- and intermolecular selectivity.

Experimental Section

General Methods. Melting points are uncorrected. NMR spectra were recorded with a Hitachi R-24B spectrometer. Gas chromatographic analysis was carried out with a Shimadzu GC-6A gas chromatograph equipped with a 0.5 M stainless-steel OV-17 column.

Materials. The vinyl bromides **3a**,[23] **3b**,[24] **3c**,[25] **3f**,[26] **3g**,[27] **3h**,[28] and **3g**[29] were prepared according to known literature methods. The bromides **3d** and **3e** were prepared as follows.

2,2-Diphenyl-1-*m*-tolylvinyl Bromide (3d). (a) Ethyl *m*-tolylacetate was prepared in 81% yield from *m*-methylbenzyl bromide by a Grignard reaction followed by esterification of the acid formed:[30a] ^1H NMR (CCl_4) δ 1.11 (3 H, t, J = 7 Hz, Me), 2.19 (3 H, s, Me), 3.33 (2 H, s, $ArCH_2$), 4.92 (2 H, q, J = 7 Hz, CH_2), 6.86 (4 H, br s, Ar). A solution of ethyl *m*-tolylacetate (5.78 g, 30 mmol) in dry ether (20 mL) was added to an ethereal solution of phenylmagnesium bromide which was prepared from bromobenzene (9.4 g, 60 mmol) and magnesium (1.8 g, 74 mmol) in dry ether (80 mL). After completion of the reaction the mixture was hydrolyzed by 2 N hydrochloric acid and extracted with ether. The organic layer was washed with water and then with saturated sodium chloride solution and dried (Na_2SO_4), and the solvent was evaporated. The crude material was heated in 85% phosphoric acid (50 mL) at 130 °C for 2 h, and the mixture was then poured into water and extracted with ether. The organic layer was washed successively with water and saturated NaCl solution and dried (Na_2SO_4). After evaporation of the solvent, 1,1-diphenyl-2-*m*-tolylethene (4.7 g, 58%) was obtained as an oil: ^1H NMR (CCl_4) δ 2.50 (3 H, s, Me), 6.65–7.08 (15 H, m, Ar). Anal. Calcd for $C_{21}H_{18}$: C, 93.23; H, 6.71. Found: C, 93.16; H, 6.80.

(b) A solution of bromine (0.55 mL, 10 mmol) in CCl_4 (10 mL) was added dropwise at 0 °C to a solution of 1,1-diphenyl-2-*m*-tolylethene (2.7 g, 10 mmol) in CCl_4 (50 mL). After 65% conversion the solvent was evaporated, and the residue was chro-

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Table IV. Physical and Spectral Data of the Products

compd[i]	mp, °C (cryst solv)	formula	analysis				NMR solvent	NMR,[a] δ		
			calcd, %		found, %					
			C	H	C	H		Me	MeO	ArH
5a	182–183[c] ($EtOH-C_6H_6$)						$CDCl_3$		3.68 (4)[b]	6.43–6.89
5b	157–159[d] ($EtOH-C_6H_6$)						$CDCl_3$		3.64 (2)[b]	6.46–6.94
5c	101–103 (EtOH)	$C_{28}H_{24}O$	89.33	6.43	89.15	6.41	CCl_4	2.19	3.62	6.32–6.87
5d	oil	$C_{28}H_{24}O$	89.33	6.43	89.12	6.27	CCl_4	2.09	3.59	6.29–6.87
5e	oil	$C_{28}H_{24}O$	89.33	6.43	89.26	6.40	CCl_4	1.99	3.50	6.25–6.89
5f	139–141 (EtOH)	$C_{27}H_{22}O$	89.47	6.12	89.28	6.14	$CDCl_3$		3.62	6.39–6.92
5g	67–68 (EtOH)[e]						CCl_4	1.72 (2)[b]	3.59	6.43–6.88
5h[f]	oil	$C_{22}H_{20}O$	87.96	6.71	87.55	6.73	CCl_4	2.09, 2.16	3.66	6.55–6.96
5i	oil[g]						CCl_4	1.76	3.56	6.69–7.21
6b	120–122 ($EtOH-C_6H_6$)	$C_{28}H_{24}O_2$	85.68	6.16	85.50	6.16	$CDCl_3$		3.37, 3.91	6.36–7.09
7f	245–247[h] ($EtOH-C_6H_6$)						$CDCl_3$			6.89[h]
7i	oil[g]						CCl_4	1.75 (2)[b]		6.96[g]
8b	184–196 (EtOH)	$C_{27}H_{21}ClO$	81.70	5.33	81.66	5.31	$CDCl_3$		3.46	6.40–6.91

[a] Me and MeO groups appear as singlets and ArH groups as multiplets. The integration is consistent with the given structure. [b] Number of identical groups. [c] Lit. mp 181–182 °C (Gattermann, L. *Chem. Ber.* **1895**, *28*, 2869–2877). [d] Lit. mp 159–160 °C (Staudinger, H.; Kon, N. *Justus Liebigs Ann. Chem.* **1911**, *384*, 38–135). [e] Lit. mp 64 °C (Pfeiffer, P.; Wizinger, R. *Ibid.* **1928**, *461*, 132–154). [f] Mixture of the *E* and the *Z* isomers. [g] Stang, P. G.; Anderson, A. G. *J. Am. Chem. Soc.* **1978**, *100*, 1520–1525. [h] Lit. mp 223.5–224.5 °C (Biltz, H. *Justus Liebigs Ann. Chem.* **1897**, *296*, 219–260).

matographed on alumina. Recrystallization from ethanol gave 2,2-diphenyl-1-*m*-tolylvinyl bromide (**3d**): mp 85–86 °C; 0.733 g (21%); ^1H NMR (CCl_4) δ 2.15 (3 H, s, Me), 6.80–7.11 (14 H, m, Ar). Anal. Calcd for $C_{21}H_{17}Br$: C, 72.22; H, 4.91. Found: C, 72.24; H, 4.89.

2,2-Diphenyl-1-*o*-tolylvinyl bromide (3e) was prepared in an analogous way to the preparation of **3d** from ethyl *o*-tolylacetate[30b] [^1H NMR (CCl_4) δ 1.09 (3 H, t, *J* = 7 Hz, Me), 2.19 (3 H, s, Me), 3.38 (2 H, s, $ArCH_2$), 4.91 (2 H, q, *J* = 7 Hz, CH_2), 6.88 (4 H, s, Ar)] which gave 80% of 1,1-diphenyl-2-*o*-tolylethene: ^1H NMR (CCl_4) δ 2.23 (3 H, s, Me), 6.60–7.12 (15 H, m, Ar). Anal. Calcd for $C_{21}H_{18}$: C, 93.23; H, 6.71. Found C, 93.19; H, 6.80. Bromination of the ethene gave 30% of 2,2-diphenyl-1-*o*-tolylvinyl bromide (**3e**): mp 94–95 °C (from EtOH); ^1H NMR (CCl_4) δ 2.17 (3 H, s, Me), 6.75–7.12 (14 H, m, Ar). Anal. Calcd for $C_{21}H_{17}Br$: C, 72.22; H, 4.91. Found: C, 72.11; H, 4.96.

1-*p*-Anisyl-1-*o*-anisyl-2,2-diphenylethene (6b). A solution of 4-methoxy-α,α-diphenylacetophenone[31] (1.51 g, 5 mmol) in dry benzene (10 mL) was added to an ethereal solution of *o*-methoxyphenylmagnesium bromide which was prepared from *o*-bromoanisole (930 mg, 5 mmol) and magnesium (112 mg, 5 mmol) in dry ether (20 mL).

After completion of the reaction the mixture was hydrolyzed by 2 N HCl and extracted with ether–benzene. The organic layer was washed successively with water and saturated NaCl solution and dried (Na_2SO_4), and the solvent was evaporated. The residue was heated with 85% H_3PO_4 (10 mL) at 150 °C for 1 h. The mixture was poured into ice–water and extracted with ether which was washed with water and saturated NaCl solution and dried (Na_2SO_4). The crystals obtained after evaporation of the solvent were recrystallized from ethanol–benzene, giving 1-*p*-anisyl-1-*o*-anisyl-2,2-diphenylethene: 901 mg (46%); mp 120–122 °C. The physical and NMR data are given in Table IV.

1-*p*-Anisyl-1-(*p*-chlorophenyl)-2,2-diphenylethene (8b). This compound was prepared in analogy to the preparation of **6b** (see above) from 4-methoxy-α,α-diphenylacetophenone and *p*-chlorophenylmagnesium bromide. The ethene was obtained in 30% yield and was purified by chromatography on alumina. The wide range of the melting point (184–196 °C) suggests the presence of an impurity, but the material gave a single peak in gas chromatography on a 0.5-m OV-17 column at 240 °C.

Reaction of Trianisylvinyl Bromide 3a with $AgBF_4$ in Acetonitrile. A mixture of trianisylvinyl bromide (**3a**; 210 mg, 0.49 mmol) and silver tetrafluoroborate (180 mg, 0.92 mmol) in acetonitrile (10 mL) was refluxed for 30 min. After filtration of the silver salts the solvent was evaporated, and the residue was hydrolyzed with a solution of 1 N NaOH (10 mL). The product was extracted with ether–benzene (50 mL), and the organic layer was washed successively with water and with saturated NaCl solutions and dried (Na_2SO_4). Evaporation of the solvent gave a solid. Recrystallization from ethanol gave 123 mg (62%) of white crystals, mp 138–142 °C. The compound was identified as 1-(acetylamino)-1,2,2-tris(*p*-methoxyphenyl)ethene on the basis of the following data: IR ν_{max} 3230 (NH), 1655 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.78 (3 H, s, Me), 3.66 (6 H, s, MeO), 3.71 (3 H, s, MeO), 4.54 (1 H, s, NH), 6.41–7.20 (12 H, m, Ar H); mass spectrum, *m/e* (relative intensity) 404 (M + 1, 28), 403 (M, 100), 360 (M – MeCO, 40), 345 (M – MeCONH, 19), 227 (An_2CH^+, 36). Anal. Calcd for $C_{25}H_{25}NO_4$: C, 74.42; H, 6.26; N, 3.47. Found: C, 74.25; H, 6.17; N, 3.30.

Vinylation Procedure. A mixture of the vinyl bromide 3 (ca. 0.58 mmol), silver tetrafluoroborate or silver triflate (0.80–1.05 mmol, 1.2–1.5 equiv), 2,6-lutidine (0.87 mmol, 1.5 equiv, for the reaction in the presence of $AgBF_4$) or 2,6-di-t-butyl-4-methylpyridine (0.82 mmol, 1.4 mmol, for the reaction in the presence of AgOTf), and the aromatic compound 4 (10 mL) was heated in a sealed glass ampule in an oil bath at the temperature and for the time given in Table I. At the end of the reaction the ampule was opened, the silver salts were filtered, and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel or alumina. The yields of the isolated tetrasubstituted ethylenic products are given in Table I, and their physical data and ^1H NMR spectral data are given in Table IV.

For example, a sealed ampule containing triphenylvinyl bromide (**3f**; 197 mg, 0.59 mmol), $AgBF_4$ (190 mg, 0.97 mmol), 2,6-lutidine (0.1 mL, 0.87 mmol), and anisole (10 mL) was heated for 36 h at 150 °C. The silver salts were filtered, the solvent was evaporated, and the mixture was chromatographed over alumina, giving 140 mg (66%) of 1-*p*-anisyl-1,2,2-triphenylethene (**5f**), mp 138–141 °C.

Competition Experiments. Three competition experiments were conducted. A mixture of **3b** (0.46 mmol), silver triflate or tetrafluoroborate (0.67–0.77 mmol), and the substituted pyridine (0.82–1.17 mmol) was heated in a sealed ampule either with a

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(31) Unger, F. *Liebigs Ann Chem.* **1933**, *504*, 267.

mixture of benzene, toluene, and anisole or with a mixture of benzene and chlorobenzene. The aromatic compounds were always in a large excess over **3b**. After the silver salts were filtered, the mixtures were analyzed by gas chromatography with chrysene as an internal standard. No correction for a possible different detector response for the different compounds was introduced. The relative reactivities at the para position of the aromatic compounds were calculated from the relative ratios of the starting materials and the para-substitution products after statistical correction for the presence of six identical positions in benzene; i.e., $\log(k_X/k_H) = \log\ (6[Ph_2C{=}C(An)C_6H_4X\text{-}p]/[Ph_2C{=}C(An)Ph]([C_6H_6]/[C_6H_5X])$. The reaction conditions and the data are given in Table III, and a Hammett plot of $\log\ (k_X/k_H)$ against σ^+ is given in Figure 1.

Isomer Distributions. The ortho/meta/para distribution of the substitution product in the reactions of **3b** was determined with the aid of authentic samples in most cases.

Reaction of **3b**/$AgBF_4$ with toluene gave only two peaks in the gas chromatographic analysis. However, by comparison with authentic samples of the substitution products which were obtained from the reactions of **3c,d,e** with anisole or from the main product isolated from the reaction of **3b** with toluene, it was found that the peaks due to the ortho and meta isomers overlap. Consequently, the distribution was determined by integration of the three separate methyl signals in the ^1H NMR spectrum in CCl_4.

In the reaction of **3b** with anisole the ortho and para isomeric products gave good separation on a OV-17 column at 240 °C. Their ratio was calculated by assuming an identical detector response. A sample of the meta isomer was not available for comparison, but on the assumption that the order of retention times of the isomers is similar to that of the methyl derivatives, no peak for the meta isomer was detected. NMR spectra showed the presence of the *o*-methoxy derivative in the reaction of the other compounds with anisole, in a low yield. No further investigation was conducted on the formation of the ortho isomer.

In the AgOTf-assisted reaction with chlorobenzene, the ortho/para isomer ratio was determined by VPC. There is some overlap between the two peaks, and hence the presence of a meta isomer (whose VPC behavior is unknown) can escape detection.

Reaction of Triphenylvinyl Bromide (3f) with $AgBF_4$ in Benzene. A mixture of **3f**, $AgBF_4$, 2,6-lutidine, and benzene was heated at 150 °C for 48 h in the manner described in the vinylation procedure. After workup of the reaction mixture, triphenylvinyl fluoride (mp 96-99 °C; 82%) was obtained by preparative VPC (column: OV-17, 1 m) and identified by comparison with an authentic sample (mp 103-104 °C).[32] Also, tetraphenylethene was formed in 8% yield.

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Registry No. 3a, 25354-46-5; **3b**, 25354-48-7; **3c**, 83248-27-5; **3d**, 83248-28-6; **3e**, 83248-29-7; **3f**, 1607-57-4; **3g**, 40811-05-0; **3h**, 83248-30-0; **3i**, 5912-93-6; **5a**, 10019-24-6; **5b**, 68161-05-7; **5c**, 83248-31-1; **5d**, 83248-32-2; **5e**, 83248-33-3; **5f**, 70592-05-1; **5g**, 26957-36-8; **5h** (isomer 1), 54186-51-5; **5h** (isomer 2), 54186-52-6; **5i**, 83248-34-4; **6b**, 83248-35-5; **7f**, 632-51-9; **7i**, 781-33-9; **8b**, 83248-36-6; C_6H_5OMe, 100-66-3; C_6H_5Me, 108-88-3; C_6H_6, 71-43-2; C_6H_5Cl, 108-90-7; $AgBF_4$, 14104-20-2; AgOTf, 2923-28-6; ethyl *m*-tolylacetate, 40061-55-0; ethyl *o*-tolylacetate, 40291-39-2; bromobenzene, 108-86-1; 1,1-diphenyl-2-tolylethene, 83248-37-7; 1,1-diphenyl-2-*o*-tolylethene, 72292-01-4; 4′-methoxy-2,2-diphenylacetophenone, 1889-74-3; *o*-bromoanisole, 578-57-4; *p*-chlorophenyl bromide, 106-39-8; 1-(acetylamino)-1,2,2-tris(*p*-methoxyphenyl)ethene, 83248-38-8.

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Regiochemical Control in the Diels-Alder Reaction of Substituted Naphthoquinones. The Directing Effects of C-6 Oxygen Substituents

T. Ross Kelly*[1] and Nitin D. Parekh

Department of Chemistry, Boston College, Chestnut Hill, Massachusetts 02167

Edward N. Trachtenberg

Department of Chemistry, Clark University, Worcester, Massachusetts 01610

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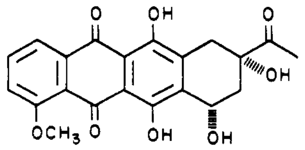
The Diels-Alder reactions of 6-hydroxy-, 6-methoxy-, and 6-acetoxynaphthoquinone with *trans*-1-methoxy-3-methyl-1,3-butadiene have been studied, and the regiochemistry of the adducts has been determined. The results are consistent with the hypothesis that the acetoxy (as well as the hydroxy and methoxy) substituent functions as an electron donor despite Hammett σ constants which would suggest otherwise.

In the course of studies leading to a regiospecific, Diels-Alder-based synthesis of (±)-daunomycinone (1),[2,3] the hypothesis was advanced that the regiochemical outcome of the reaction in eq 1[4] could be rationalized by considering the acetoxy group in 2 as an electron-donating substituent (assuming[4d] a polarized transition state). According to that rationale, resonance donation (2, arrows) from the acetoxy group into the C-4 carbonyl would render



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