nection has been established between reactions that occur under the "normal" conditions of acid catalysis and solvolysis on the one hand and in superacid solutions on the other.

I wish to thank my co-workers K. Ranganayakulu, Rollin Haseltine, Alan Jones, Normal Wong, and Eileen and Lucy Huang. I am grateful to the National Research Council of Canada for financial support.

Solvolysis of α-Arylvinyl Derivatives

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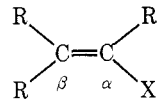
Following the pioneering work of Grob and Cseh, who showed that α-bromo-para-substituted styrenes solvolyze via the SN1 route[1] (eq 1), the solvolysis of vinylic

$$ArC(Br)=CH_2 \xrightarrow{80\%\ EtOH,\ Et_3N} Ar\overset{+}{C}=CH_2 \longrightarrow ArCOCH_3 \quad (1)$$

compounds has flourished in recent years. Work in the field has been extensively reviewed.[2]

Although it is recognized that solvolyses of vinylic and saturated compounds show qualitative similarities, there are differences between the two systems, especially in regard to aryl-substituted substrates in hybridization, conjugation, and steric effects, in stereochemistry and in the presence of potentially alternative reaction centers. Either of these factors alone, or their interaction, gives vinylic solvolysis some special characteristics.

The sp^2 hybridization of the vinylic carbon of a vinyl compound (1) increases its electronegativity,



1

X = leaving group

strengthens the bond to the leaving group, and infers a lower inherent solvolytic reactivity for vinylic than for saturated systems. A compensation is that highly activating substituents may be used, enabling observation of phenomena which may escape observation in the solvolysis of highly reactive sp^3 derivatives.

The double bond can transmit electronic effects of β substituents, and it is also a potential reaction center by itself. These features, as well as the acidity of the vinylic hydrogens, may favor competing reaction routes such as E2 elimination and electrophilic and nucleophilic addition–elimination pathways over the SN1 route.

Depending on structure, the double bond conceivably may conjugate with any or all the four substituents on the vinylic carbons. Conjugation with the leaving group or with an α-aryl group will reduce the ground-state energy, and the solvolytic reactivity will be lower than that of saturated compounds. Conjugation with β-aryl groups may be important in their rearrangement across the double bond. Obviously, any conjugation with aryl groups is highly dependent on the planarity of the system and hence on the steric interactions of the double bond substituents.

The double bond is shorter than a single bond and all the vinylic substituents are in the same plane. Both effects increase the crowding of the substituents compared with the saturated analogues. This should be reflected in phenomena which are sensitive to steric effects, such as steric acceleration and steric inhibition of solvation.

A stereochemical difference exists between the vinylic and the saturated systems. The *R* and *S* enantiomers of an sp^3-substituted system solvolyze at identical rates and the derived sp^2 cation captures nucleophiles from both sides of the vacant orbital at identical rates. The *E* and *Z* sp^2 isomers solvolyze at different rates, and the vinyl cation captures nucleophiles from the two sides of the vacant orbital at different rates.

One purpose of this Account is to show that these facts lead to quantitative differences between the solvolysis of saturated and α-arylvinyl derivatives, especially in those substituted by bulky β substituents. Consequently, the use of criteria for assigning the detailed mechanism and for estimating the polarity of the transition state, which are applicable to saturated systems, may give the wrong answer in vinylic systems. This is demonstrated by the ambiguity of several mechanistic criteria when applied to solvolysis of the trianisylvinyl system $An_2C=C(X)An$, where An represents a *p*-methoxyphenyl group. The low sensitivity to solvent and leaving group effects, as reflected by the Winstein–Grunwald *m* value of 0.34 when X = Br,[3a] and a k_{OTs}/k_{Br} ratio of 32,[4] suggest a solvent assisted (k_s)[5] or a neighboring group assisted (k_Δ)[5] solvolysis. How-

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(1) C. A. Grob and G. Cseh, *Helv. Chim. Acta*, **47**, 194 (1964).

(2) (a) M. Hanack, *Acc. Chem. Res.*, **3**, 209 (1970); (b) C. A. Grob, *Chimia*, **25**, 87 (1971); (c) G. Modena and U. Tonellato, *Adv. Phys. Org. Chem.*, **9**, 185 (1971); (d) P. J. Stang, *Prog. Phys. Org. Chem.*, **10**, 205 (1973); (e) L. R. Subramanian and M. Hanack, *J. Chem. Educ.*, **52**, 80 (1975).

(3) Z. Rappoport and A. Gal: (a) *J. Am. Chem. Soc.*, **91**, 5246 (1969); (b) *J. Org. Chem.*, **37**, 1174 (1972).

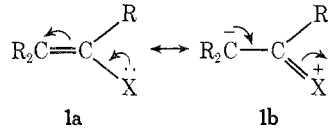
(4) Z. Rappoport and J. Kaspi: (a) *J. Am. Chem. Soc.*, **92**, 3220 (1970); (b) *J. Chem. Soc., Perkin Trans. 2*, 1102 (1972).

(5) P. v. R. Schleyer, J. L. Fry, L. K. M. Lam, and C. J. Lancelot, *J. Am. Chem. Soc.*, **92**, 2542 (1970).

ever, the high sensitivity to substituent effects, as reflected by the ρ values of ca. -4[3b] and 1.91[4] for substituent changes in the α-aryl group and in the arylsulfonate leaving group, respectively, indicate an unassisted k_c route[5] via a highly polar transition state. The latter indication is supported by the high stability of the trianisylvinyl cation which shows an extensive degenerate β-anisyl rearrangement in 2,2,2-trifluoroethanol (TFE)[6a] and high selectivity between the leaving group and the solvent.[7]

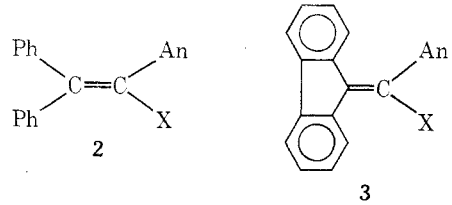
We will show that coupling between steric and conjugation effects and the accumulation of several bulky groups in a confined space result in the unique behavior of some solvolyzing vinylic systems. However, the possible conjugation with the leaving group and the intervention of competing mechanisms will be discussed first.

Conjugation with the Leaving Group. The low solvolytic reactivities of vinylic compounds were recently ascribed mainly to the sp^2 hybridization.[8] An n–π ground state conjugation between the leaving group X and the double bond (cf. **1**), which was earlier invoked,[9] should be manifested by substituent effects. However,



1a **1b**

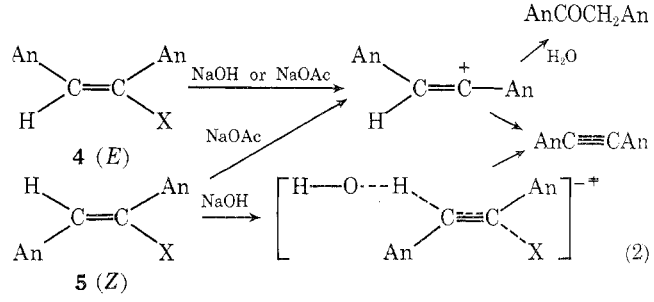
the resemblance of the rate ratios between the acetolysis rates of triphenylvinyl trifluoromethanesulfonate (OTf) and tosylate on the one hand and the k_{OTf}/k_{OTs} ratios for saturated compounds on the other argues that structure **1b**, X = OSO_2R', R = Ph, is unimportant; otherwise the ratio would be higher in vinylic systems.[8b] The only 6–7.5-fold higher reactivity of the α-anisyl-β,β-diphenyl system **2** (X = Br, OTs) compared with the fluorenylidene system **3**[3,4] leads to a similar conclusion.



2 **3**

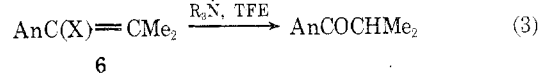
An = *p*-$MeOC_6H_4$

Competing Solvolysis Routes. Several substitution (or elimination) routes at vinylic carbon may compete with the SN1–E1 route in formation of the solvolysis products. This competition is highly sensitive to the identity of substituents and the base and to the geometry of the system. An example is the solvolysis–elimination of **4** and **5** (X = Br) in 80% EtOH: it is SN1–E1 in the presence of NaOAc, but in the presence of the stronger base NaOH **4** reacts also via SN1 but the *Z* isomer with the favorable trans geometry reacts via E2 (eq 2).[10] Another example is the acyl-oxygen cleavage rather than the vinyl-oxygen cleavage of compounds **6**,



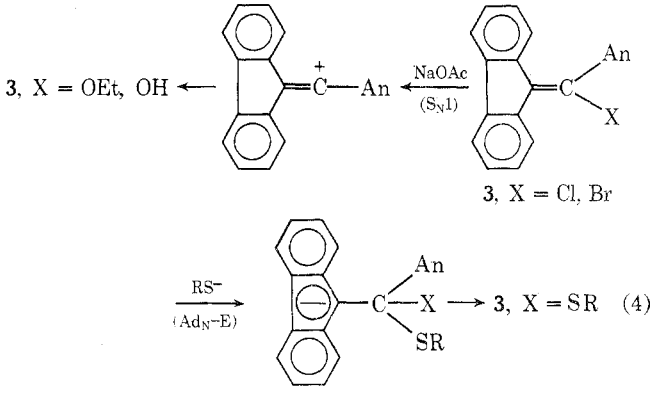
4 (*E*) **5** (*Z*) (2)

X = $OCOCF_3$, $OCOC_6H_3(NO_2)_2$-3,5, with strongly basic amines in TFE (eq 3).[11]



6 (3)

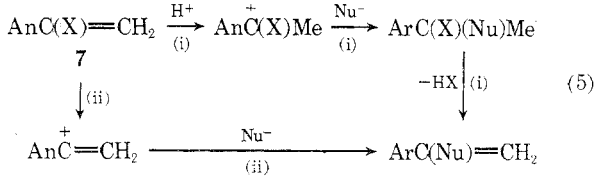
Competition of SN1 solvolysis with the nucleophilic addition–elimination route (AdN-E) is of interest. Formally, this is the vinylic analogue of the SN2 mechanism, but it differs in that the nucleophilic attack proceeds from the direction of the π cloud, gives an intermediate carbanion, and leads to retention, while the SN2 reaction proceeds with inversion and the carbon atom does not acquire a high negative charge. Competition between the vinylic SN1 and the AdN-E routes was observed in only one case. α-Anisyl-β,β-diphenylvinyl halides (**2**) react in 80% EtOH containing either NaOAc or thiolate ions via SN1. However, the fluorenylidene analogues **3** react with NaOAc via SN1, but with thiolate ions via the AdN-E route (eq 4).[3b] Ap-



3, X = Cl, Br (4)

parently, in system **3**, which is capable of negative charge dispersal, a change from a moderate (AcO^-) to a powerful (RS^-) nucleophile changes the mechanism from a rate-determining C–X bond cleavage to a rate-determining C–nucleophile bond formation.[3b]

An electrophilic addition–elimination (AdE-E) route[12] via a rate-determining electrophilic addition to the double bond is demonstrated for the reactions of α-chloro- and α-bromo-4-methoxystyrenes (**7**-Cl and **7**-Br) in eq 5.[12d]



(i) AdE-E; (ii) SN1; Nu^- = Nucleophile (5)

(6) (a) Y. Houminer, E. Noy, and Z. Rappoport, *J. Am. Chem. Soc.*, in press; (b) Z. Rappoport, E. Noy, and Y. Houminer, *ibid.*, **98**, 2238 (1976).
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(8) (a) L. L. Miller and D. A. Kaufman, *J. Am. Chem. Soc.*, **90**, 7282 (1968); (b) W. M. Jones and D. D. Maness, *ibid.*, **92**, 5457 (1970).
(9) E. D. Hughes, *Trans. Faraday Soc.*, **34**, 185 (1938); **37**, 603 (1941).
(10) Z. Rappoport and M. Atidia: (a) *Tetrahedron Lett.*, 4085 (1970); (b) *J. Chem. Soc., Perkin Trans. 2*, 2316 (1972).
(11) Z. Rappoport and J. Kaspi, *Israel J. Chem.*, **12**, 989 (1974).
(12) (a) W. M. Schubert and G. W. Barfknecht, *J. Am. Chem. Soc.*, **92**, 207 (1970); (b) Z. Rappoport, T. Bässler, and M. Hanack, *ibid.*, **92**, 4985 (1970); (c) C. A. Grob and H. R. Pfaendler, *Helv. Chim. Acta*, **53**, 2130 (1970); (d) Z. Rappoport and A. Gal, *J. Chem. Soc., Perkin Trans. 2*, 301 (1973).

Table I
Structure and Mechanism in the Acetolysis of $ArCX{=}CR_2$

Ar	R	X	k_{AcOH}/k_{AcOD}	Mechanism	Ref	Ar	R	X	k_{AcOH}/k_{AcOD}	Mechanism	Ref
Ph	Ph	OSO_2F	1.04	SN1	8b	An	H	Cl	1.94	SN1 + AdE-E	12d
Ph	Ph	OTs	0.93	SN1	8b	An	Me	$OCOCF_3$	5.90	AdE-E	11
An	H	Br	1.45	SN1(+AdE-E?)	12d	An	H	OAc	3.45	AdE-E	12d

Table II
Relative Solvolysis Rates of Compounds 12 in Aqueous EtOH

R^1	R^2	Rel k_1	R^1	R^2	Rel k_1	k_E/k_Z	Ref
H	H	1.0					
Me	H	6.9	H	Me	0.83	7.65	19
t-Bu	H	1362	H	*t*-Bu	0.83	1640	19
An	H	5.45	H	An	0.12	49	10

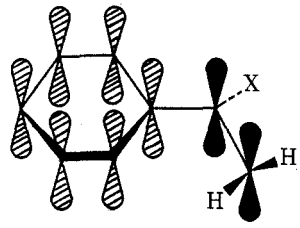
Although the claim that *p*-amino-α-bromostyrene solvolyzes via this route[12a] was later shown to be wrong,[12c] this route cannot be ignored in carboxylic acids or in unbuffered media, and several mechanistic criteria[12b] which distinguish between the AdE-E and the SN1 routes have been applied.[12d,13] For example, strong autocatalysis in the acetolysis of **7**-Br in unbuffered AcOH indicates an AdE-E route involving the HBr adduct.[12d] This route contributes appreciably even in the buffered acetolysis of **7**-Cl, as shown by leaving group, solvent, and solvent isotope effects.[12d]

A strong and a general tool for recognizing the AdE-E route is the solvent isotope effect. k_{RCOOH}/k_{RCOOD} values are 0.85–1.2 for many vinylic SN1 reactions, while the k_{AcOH}/k_{AcOD} ratio of 3.40 found for addition of acetic acid solvent to *p*-methoxystyrene is typical for electrophilic additions.[12d] Table I gives k_{AcOH}/k_{AcOD} values for several $AnCX{=}CR_2$ systems. Notwithstanding the difference in the β substituents, a gradual change from a good leaving group such as fluorosulfonate to a sluggish one such as acetate or trifluoroacetate changes the mechanism from SN1 to AdE-E. The halides are intermediate cases, with **7**-Br reacting via SN1 and **7**-Cl probably via both routes, as suggested above.

The competition between the two mechanisms depends on their relative response to the simultaneous change in the acidity and the ionizing power of the media. In the highly acidic and ionizing trifluoroacetic acid, **6** (X = OSO_2Ar) reacts via SN1, as indicated by the $k_{CF_3COOH}/k_{CF_3COOD}$ ratio of 1.07.[14]

The Effects of the α and β Substituents. The ground state of an unhindered α-arylvinyl system is stabilized by a π(α-Ar)–π(C=C) conjugation. During solvolysis, the developing cationic orbital is perpendicular to the π(C=C) system, and the π(α-Ar)–p(C^+) conjugation which stabilizes the transition state is necessarily accompanied by π(α-Ar)–π(C=C) deconjugation (cf. **8** → **9**).

The ground-state conjugation amounts to several kilocalories/mole as deduced from the comparison of the reactivities of α-halostyrenes (**10**) and their saturated analogues, α-phenylethyl halides (**11**). For the unsubstituted, fully conjugated system (X = Br, R = H), the k_{11}/k_{10} ratio is 2×10^{10},[3a] whereas effective deconjugation by steric interaction of the β-hydrogens with the



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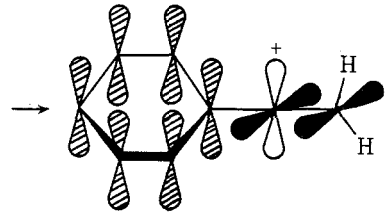

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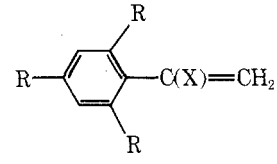
o-methyl groups of **10** reduces the ratio to 1.4×10^6 when X = Cl, R = Me.[15]

The effect of α-aryl substituents at a constant geometry is pronounced. This is inferred from the linearity of plots of log *k* values for the solvolysis of series of α-arylvinyl systems vs. the σ^+ values of the substituents in the aryl group, and from the high ρ values of −3.4 to −6.6 for many vinylic systems.[1,3b,4,8a,16] Lower ρ values are observed when charge dispersal is achieved by overlapping π orbital in the allenyl system $Ph_2C{=}C{=}C(Cl)Ar$,[17] or by β-sulfur participation.[18a]

The effect of a single β substituent on the reactivity of α-anisylvinyl bromides (**12**) is highly geometry dependent (Table II).[10,19] The rate increases telescopically



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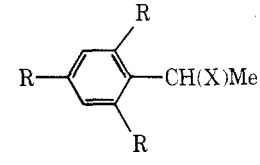

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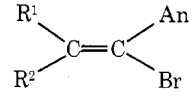

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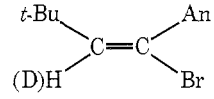
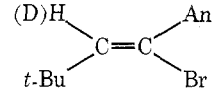
(13) Z. Rappoport and Y. Apeloig: (a) *Tetrahedron Lett.*, 1845 (1970); (b) *J. Am. Chem. Soc.*, **97**, 821 (1975).
(14) Z. Rappoport and J. Kaspi, *Tetrahedron Lett.*, 4039 (1971).
(15) K. Yates and J. J. Périé, *J. Org. Chem.*, **39**, 1902 (1974).
(16) (a) G. Capozzi, G. Modena, and U. Tonellato, *J. Chem. Soc. B*, 1700 (1971); (b) P. Bassi and U. Tonellato, *J. Chem. Soc., Perkin Trans. 2*, 1283 (1974).
(17) M. D. Schiavelli, S. C. Hixon, H. W. Moran, and C. J. Boswell, *J. Am. Chem. Soc.*, **93**, 6989 (1971).
(18) G. Modena and U. Tonellato, *J. Chem. Soc. B:* (a) 374 (1971); (b) 381 (1971); (c) 1569 (1971).

for the E isomers (alkyl group cis to An) and negligibly for the Z isomers as the bulk of the alkyl group increases. Small inductive effects are canceled by taking k_E/k_Z ratios. The increase in rate with the bulk of the alkyl group reflects increase in the ground-state energy of the E isomers. This is due to deconjugation of the double bond from the α-anisyl group by distortion of the latter from planarity owing to interaction with the cis alkyl group.[19] The 5.2-kcal/mol free-energy reduction associated with the *tert*-butyl group indicates nearly complete deconjugation for the E β-*tert*-butyl isomer.

The similarity of the rates of the Z β-alkyl isomers is surprising inasmuch as the transition-state energy should increase for steric reasons as the angle between the bromine and R^2 decreases on the way to the linear cation. A bent transition state, close in structure to the linear cation, in which C–Br bond lengthening compensates for the reduced angle, is plausible. This is supported by the higher β-hydrogen isotope effect when the hydrogen is trans, rather than cis to the leaving group, as demonstrated by the values below.[19,20]



k_H/k_D: 1.10 (50% EtOH)[19]



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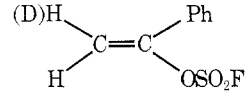
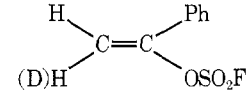
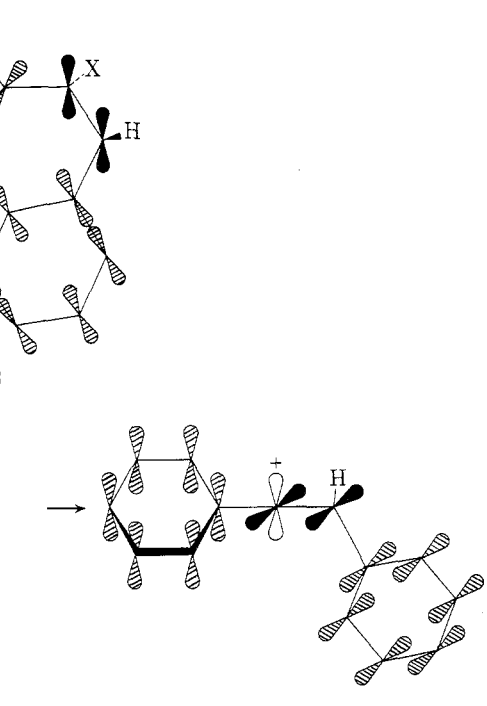


k_H/k_D: 1.57 (AcOH)[20]

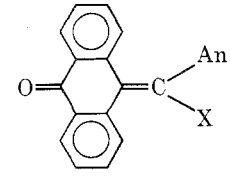


1.10

Decrease in the *cis*-stilbene interaction on the way to the linear cation (cf. **13** → **14**) increases the reactivity of **12**-E, R^1 = An, due to a gain in the $\pi(\beta\text{-Ar})$–π(C=C) conjugation. The combination of this effect, the inductive effect, and the increased deconjugation of the β-aryl cis to X in the transition state leads to a relative insensitivity of rate to β,β-diaryl substitution. Appreciable rate differences are observed only when the geometry at the β carbon is modified: the anthronylidene derivative **15** (X = Br)[21] acetolyzes 49 times faster than the fluorenylidene derivative **3** (X = Br).[22]



13 **14**



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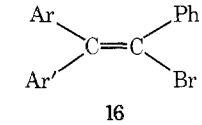

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The effect of β-aryl substituents at a constant geometry is nearly additive.[23,24] For example, in the solvolytic rearrangement of compounds **16** the relative rates in 60% EtOH are 1(Ar = Ar′ = Ph):2.14(Ar = An; Ar′ = Ph):2.44(Ar = Ph; Ar′ = An):5.45(Ar = Ar′ = An).[23] The small rate difference between the two geometrical isomers of **16**, or in the α-anisyl analogues,[24] indicates that β-aryl participation is unimportant; otherwise, much higher reactivity would be predicted for the isomer with anisyl trans to X. In contrast, β-phenyl participation takes place in the solvolysis of (*E*)-α-methyl-β-phenylvinyl triflate.[25]

The Effect of the Leaving Group. Comparison of the solvolysis rates of α-arylvinyl bromides and chlorides gives k_{Br}/k_{Cl} ratios of 20–75.[3,7,12d,22,24,26] When sulfonate leaving groups are compared, the k_{OBs}/k_{OTs} ratios are 2.27–5.70 for system **6** in several solvents and the ρ value is 1.91 for the solvolysis of trianisylvinyl arylsulfonates in 70% acetone.[4] All these values are comparable to or higher than the typical ratios in the solvolysis of saturated compounds and indicate the development of a substantial negative charge on the sulfonate leaving group and a highly polar transition state.

More interesting are the k_{OTs}/k_{Br} ratios. It was suggested for the aliphatic series that high ratios ($>10^3$) indicate a very ionic transition state, and vice versa.[27] Table III indicates that most of the ratios are low and that they decrease from the "normal" value for system **10** (R = Me) to the extreme case of the anthronylidene system **15**, where the ratio is <1.[21] Moreover, the lowest known ratio of 0.157 was found for **15** in TFE.[21] By comparing vinylic and saturated compounds or vinylic compounds among themselves it becomes clear that the vinylic k_{OTs}/k_{Br} ratios do not measure the polarity of the transition state. The low ratios for system **15** cannot reflect transition state of low polarity since the derived ion is highly stable (see below).

A steric explanation for the low ratios is the most plausible. The steric interaction between the leaving

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(20) D. D. Maness and L. D. Turrentine, *Tetrahedron Lett.*, 755 (1973).
(21) Z. Rappoport, J. Kaspi, and Y. Apeloig, *J. Am. Chem. Soc.*, **96**, 2612 (1974).
(22) A. Gal, Ph.D. Thesis, The Hebrew University, 1972.
(23) Z. Rappoport and Y. Houminer, *J. Chem. Soc., Perkin Trans. 2*, 1506 (1973).
(24) Z. Rappoport and Y. Apeloig: (a) *Tetrahedron Lett.*, 1817 (1970); (b) *J. Am. Chem. Soc.*, **97**, 836 (1975).
(25) P. J. Stang and T. E. Dueber, *J. Am. Chem. Soc.*, **95**, 2683, 2686 (1973).
(26) (a) Z. Rappoport and J. Kaspi, *J. Am. Chem. Soc.*, **96**, 586 (1974); (b) *ibid.*, **96**, 4518 (1974); (c) J. Kaspi, Ph.D. Thesis, The Hebrew University, 1975.
(27) H. M. R. Hoffmann, *J. Chem. Soc.*, 6753, 6762 (1965).

Table III
k_{OTs}/k_{Br}, m, α_{app}, and $\alpha_{app'}$ Values for α-Arylvinyl Substrates

System	Solvent	k_{OTs}/k_{Br}	Solvent	m (T, °C) (X = OTs)	m (25 °C) (X = OTs)	α_{app} (X = Br) (AcOH)	$\alpha_{app'}$ (X = Br) 80% EtOH)	Ref
$PhCX{=}CH_2$	40% Me_2CO	64	Aq Me_2CO	0.63 (120)	0.83			26
10, R = Me	80% EtOH	335	Aq EtOH	0.60 (36.5)	0.62			15
$AnCX{=}CH_2$						0	0	1, 12d
$AnCX{=}CMe_2$	80% EtOH	72	Aq Me_2CO	0.51 (60)	0.57	4.3	0	12d, 21, 22, 26
$AnCX{=}CAn_2$	70% Me_2CO	32	Aq Me_2CO	0.41 (75)	0.44	18	~3	7, 21, 26c
3	70% Me_2CO	19				9.5		4b, 22
15	80% EtOH	0.75	Aq EtOH	0.27 (105)	0.34	>32	158	21, 26c, 28

group and the substituent cis to it in the planar vinylic system depends on the bulk of the first atom of the leaving group. Since bromine is larger than oxygen, an increased steric acceleration of the vinyl bromide solvolysis with the increased bulk of the β substituents accounts for the decreased ratios. Indeed, while the crowded space-filling model of **15**-OTs can be built with difficulty, the model of **15**-Br falls apart.

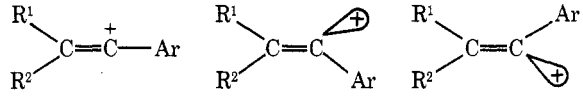
Solvent Effects. Another interesting feature of vinylic solvolysis is the fact that the Winstein–Grunwald m values are lower for solvolysis of α-arylvinyl tosylates[26c] (Table III) and bromides,[3,26c] than for SN1 reactions of saturated compounds.[4b,26c] Again, the m values decrease with the bulk of the β substituents, and m for system **15** is one of the lowest known.

Models show that approach of the solvent to the incipient cationic orbital of the β-unsubstituted compounds is relatively unhindered. However, the accumulation of several bulky groups within a confined space in the tetrasubstituted systems hinders the approach of the solvent to the cationic orbital. This steric hindrance to solvation increases when bulkier β substituents shield the transition-state dipole more effectively, and consequently the m values decrease.

Approach of the solvent from the side of the leaving group is the least hindered and the m values increase when the increase in solvent ionizing power is accompanied by increasing ability of the solvent to assist electrophilically leaving group expulsion. For **6**-OTs the values are "normal" for an SN1 reaction in electrophilic solvents (0.82 in AcOH–HCOOH; 0.78 in TFE–EtOH), while lower values are found in the more nucleophilic solvents (0.48–0.57 in aqueous acetone and aqueous EtOH).[26c] An extreme case is its solvolysis in aqueous TFE.[26a,b] The rate first decreases on addition of water to the TFE, and then increases. This was attributed to a balance of two opposing effects: increase in the water content increases the rate due to the higher dielectric constant of the medium, but decreases it due to reduced electrophilic assistance, since TFE is a better anion solvator. The strong rate increase in highly aqueous mixtures may reflect reduced electrophilic assistance due to hydrogen bonding between TFE and water. Similar phenomena were observed in the solvolysis of other α-anisylvinyl systems.[26]

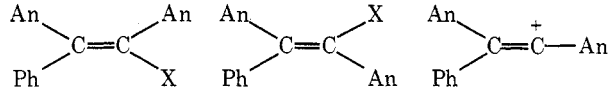
Stereochemistry of the Substitution and Structure of the Ions. Calculations for simple alkylvinyl cations indicate a linear cation with an sp-hybridized α carbon as the most stable configuration,[29a] while the cyclic thiirenium ion is the most stable configuration for ions carrying β-sulfur substituents.[29b] Evidence for the structure of the ions comes from the stereochemistry of the substitution.

It is difficult to distinguish between the linear cation **17** and the rapidly interconverting bent vinyl cation stereoisomers **18a** and **18b**,[30] but the intermediacy of either **17** or **18a** ⇌ **18b** leads to two stereochemical consequences. (a) An identical intermediate will be formed either from the *E* or from the *Z* precursor, and both will give the same product mixture. (b) An ion substituted by different β substituents presents diastereotopic faces to a nucleophile approaching the emtpy orbital. Capture from the sterically more accessible side of the smaller β substituent will be faster, leading to the more hindered product.

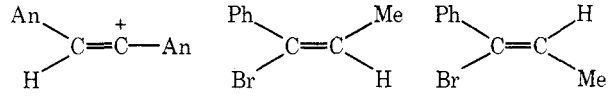


17 **18a** **18b**

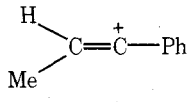
In studies of the α,β-dianisyl-β-phenylvinyl systems **19** and **20**, experiments were performed with three leaving groups (Cl, Br, OMs) and seven nucleophiles (AcO^-, Cl^-, Br^-, OMs^-, $PhCH_2S^-$, p-$MeC_6H_4S^-$, EtOH) in six solvents; in each case the same mixture of nearly 1:1 *E* and Z products[13,24,31] was obtained. Similar results were obtained with β-anisyl-α,β-diphenylvinyl bromides.[23] This result is predicted because of the similar bulk of the β-anisyl and the β-phenyl groups in ion **21**.



19 **20** **21**



22 **23** **24**



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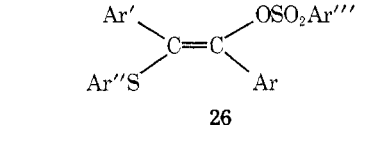
The intermediate ion in unsymmetrical systems is indeed captured preferentially from the side of the smaller group: a 89:11 mixture of the acetates **4**-OAc to **5**-OAc is formed either from **4**-Br or **5**-Br in AcOH via ion **22**.[10] The kinetics indicate the intermediacy of free α-anisylvinyl cations in these systems, and the stereochemistry suggests that they are linear.

(28) Y. Apeloig, Ph.D. Thesis, The Hebrew University, 1974.
(29) (a) L. Radom, P. C. Hariharan, J. A. Pople, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **95**, 6531 (1973); (b) A. S. Denes, I. G. Csizmadia, and G. Modena, *J. Chem. Soc., Chem. Commun.*, 8 (1972).
(30) D. R. Kelsey and R. G. Bergman, *J. Am. Chem. Soc.*, **92**, 228 (1970).
(31) Z. Rappoport and Y. Apeloig, *J. Am. Chem. Soc.*, **91**, 6734 (1969).

Suprisingly, the silver salt assisted acetolysis of (*E,Z*)- and (*Z,Z*)-1-bromo-4-chloro-1,4-diphenylbutadienes gives more of the (*E,Z*)-1-acetoxy-4-chloro-1,4-diphenylbutadiene formed by capture of the ion from its most hindered side.[32] While the retention found in the heterogeneous reaction of **23** and **24** with $AgOCOCF_3$ in pentane was explained by a surface reaction,[33] the excess retention in the homogeneous reaction of **23** in ether was ascribed to a "double inversion" in an intermediate oxonium ion,[33] although retention is the expected outcome for reaction via the linear ion **25.**

Bridging by a β substituent will be favored by the short C=C bond, while the strain in the three-membered unsaturated intermediate and the efficiency of the α-aryl group in positive charge dispersal will disfavor it. Neither β-aryl participation nor evidence for a bridged ion as a product-forming intermediate was observed in the solvolysis of triarylvinyl systems. However, extensive studies by Modena and his coworkers on the solvolysis–cyclization of 1,2-diaryl-2-arylthio-2,4,6-trinitrobenzenesulfonates (**26**) suggest β-sulfur participation in the ionization and product formation from the bridged thiirenium ion **27.** The evidence includes ρ values of -2.85, -1.45, and -1.25 for changes in Ar, Ar′ and Ar″, respectively,[18a] as well as the higher reactivity of **28** compared with **29** (R = Ph).[16a] A symmetrical ion is indicated by the scrambling of the label between the α and the β carbons of the product from α-^{14}C-**28**[34] and by the formation of an identical product mixture starting either from **26,** Ar′ = Ar″ = Ph, Ar = Tol, or from **26,** Ar = Ar″ = Ph, Ar′ = Tol.[18b] β-Oxygen,[35a] β-amino,[35b] and β-chloro[16b] participation were not observed in related systems, but a β-iodo participation and a bridged iodonium ion **30** are indicated by data on the solvolysis of the iodo ester **29,** R = I.[16b]



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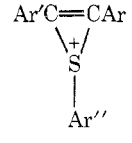

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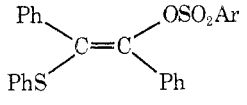

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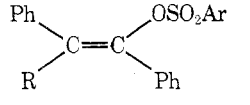

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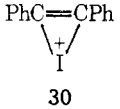

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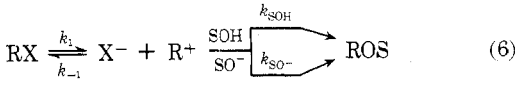
Free Ions and Ion Pairs as Intermediates in Vinylic Solvolysis. *Free Ions.* A most interesting phenomenon in the solvolysis of α-arylvinyl compounds is the occurrence of common ion rate depression by the leaving group.[4,7,13,22,26] This is accounted for by the Ingold-type scheme (eq 6), by external ion return to the



(6)

free vinyl cation R^+. In buffered solution either the solvent SOH or its conjugate base SO^- may compete with the leaving group X^- for R^+, and the first-order rate constant (k_{obsd}) is given either by eq 7 for competition between X^- and SOH or by eq 8 for competition between X^- and SO^-. The corresponding selectivity

$$k_{obsd} = k_1(1 + \alpha_{app}'[X]) \qquad \alpha_{app}' = k_{-1}/k_{SOH} \qquad (7)$$

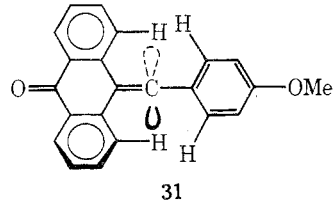
$$k_{obsd} = k_1(1 + \alpha_{app}[X^-]/[SO^-]) \qquad \alpha_{app} = k_{-1}/k_{SO^-} \qquad (8)$$

parameters are α_{app}' (apparent α) and α_{app}, respectively.[13b] There is strong evidence that in RCOOH–$RCOO^-$ the capturing nucleophile is $RCOO^-$ and eq 8 applies,[13b,24b] while eq 7 applies in alcohols buffered by amines.[23,26] Several values of α_{app} and α_{app}' are given in Table III.

The common ion rate depressions are extensive: e.g., k_{obsd} for **15**-Br at half-life is <15% of the initial value. It was calculated from the α_{app} values that >90% of the acetolysis products of many α-anisyl-β,β-disubstituted vinylic derivatives arise from the free vinyl cations.[13b,22,24b,28]

These results are surprising since similar α_{app} values are rare in the solvolysis of saturated substrates. For example, the α_{app}' value of 158 for **15**-Br in 80% EtOH should be compared with the values in 80–85% acetone of 700, 70, and 0.25 for AnCH(Ph)Cl, Ph_2CHBr, and t-BuCl[36] systems which form relatively stable carbonium ions. Moreover, the α_{app}' values for solvolytically formed sp^2-hybridized ions obey the reactivity–selectivity principle: the more stable ion (i.e., that formed faster from its precursor) is more selective (i.e., shows high α_{app}). Apparently, this principle breaks when the slow vinyl halides are compared with the much faster alkyl halides, partially due to different ground-state stabilities. However, the main questions are: why are α-arylvinyl cations much more selective than most of the trigonal ions and why are products mainly formed from the free ions?

Stabilization by the α-anisyl group is only a partial answer since common ion rate depression was not observed for the parent α-bromo-*p*-methoxystyrene (Table III). The increase of α_{app} and α_{app}' with the increased bulk of the β substituents, from 0 for the β-unsubstituted compound to the high values for the crowded anthronylidene bromide **15**-Br,[28] indicate a steric contribution to the high selectivities. Models show that, whereas approach of SOH or SO^- to ion **9** is sterically unhindered, the p orbital of the triarylvinyl cations is sterically shielded to approach of X^-, SO^-, and SOH, as schematically shown for the most selective ion **31.** Consequently, the lifetimes of the ions increase in



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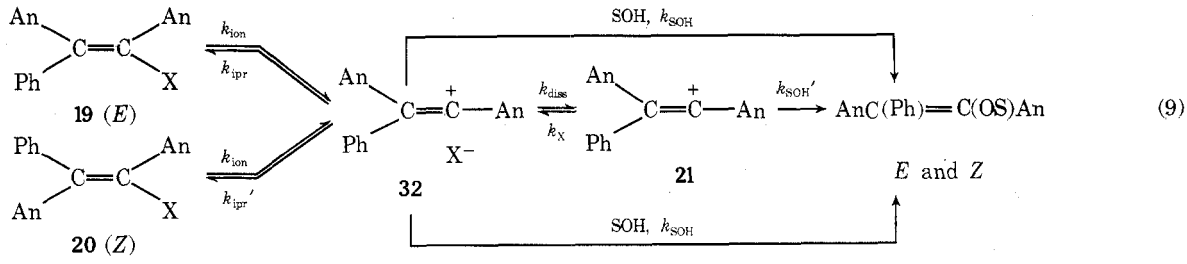
parallel with the bulk of the β substituents and so do the selectivities, since the more polarizable bromide ion captures the ion more effectively than the acetate ion or the solvent.

As a consequence more α_{app} values are known for vinyl cations than for sp^2-hybridized ones. The vinylic

(32) L. I. Reich and H. J. Reich, *J. Am. Chem. Soc.*, **96,** 2654 (1974).
(33) G. F. P. Kernaghan and H. M. R. Hoffmann, *J. Am. Chem. Soc.*, **92,** 6988 (1970).
(34) G. Capozzi, G. Mellŏni, and G. Modena, *J. Chem. Soc. C,* 3018 (1971).
(35) (a) G. Capozzi and G. Modena, *J. Chem. Soc., Perkin Trans. 1,* 216 (1972); (b) G. Capozzi, G. Modena, and L. Ronzini, *ibid.,* 1136 (1972).
(36) (a) C. K. Ingold, "Structure and Mechanism in Organic Chemistry", 2nd ed, Cornell University Press, Ithaca, N.Y., 1969, p 492; (b) T. H. Bailey, J. R. Fox, J. Jackson, G. Kohnstam, and A. Queen, *Chem. Commun.,* 122 (1966).



(9)

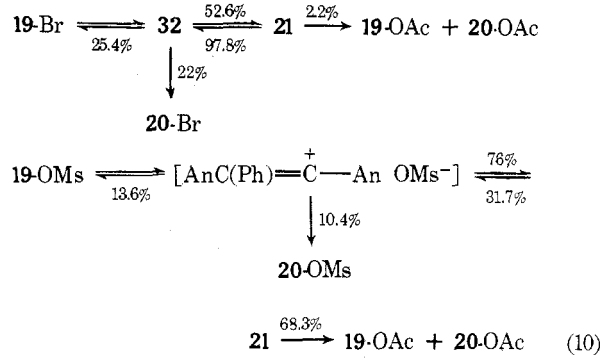
systems can be used advantageously to obtain information about the effects of structural and medium parameters on the α_{app} values. For example, Ritchie had shown that for the reaction of nucleophiles with highly stable free ions the relative rates of two nucleophiles are independent of the cation.[37] This is not the case for α-anisyl-β-substituted vinyl cations which show different selectivities. The selectivities also decrease on decreasing the charge dispersal ability of the α-aryl substituent: α_{app} values are much higher for $Ph_2C{=}C(I)Ar$ when Ar = An than when Ar = Ph,[8a] or for **15**-Br than for its α-*p*-tolyl analogue.[38] A curved selectivity–stability plot for the reaction of carbonium ions with nucleophiles, with a plateau at high stabilities, may be indicated by these data.

Common ion rate depression by other leaving groups was also observed.[4,8a,12d,13,26] From the α_{app} values, the order of reactivities of nucleophiles toward cation **21** in AcOH is Br^-:Cl^-:AcO^-:OMs^- 282:94:6.2:1.[13b] This order is similar to the nucleophilicity order toward a saturated carbon atom, which reflects a combination of basicity, polarizability, and solvation effects. Although the cation **21** is "harder" than a saturated carbon, nucleophile polarizability should be important in attack on the hindered p orbital.

Ion Pairs. The inversion of configuration that occurs in the solvolysis of several α-alkylvinyl triflates[39] and the $LiClO_4$ "special salt effect" in the acetolysis of **26**, Ar = Ar′ = *p*-tolyl, Ar″ = Ph,[18a] indicate ion-pair return. A general method for estimating the extent of ion-pair return in vinylic solvolysis was developed by using cis–trans isomerization concurrent with the solvolysis as a tool.[13b,24b,40] It was applied in several cases, and it is demonstrated in eq 9 for the extensively studied 1,2-dianisyl-2-phenylvinyl system.

The *E* isomer (**19**-Br) ionizes (k_{ion}) to an ion pair **32**, which can either return to **19**-Br (k_{ipr}), dissociate to the free ion **21** (k_{diss}), give products (k_{SOH}), or return to the *Z* isomer **20**-Br (k_{ipr}'). The free ion can either return to **32** (k_X) or give products (k_{SOH}'). Compounds **19**-Br and **20**-Br show extensive common-ion rate depression and isomerization in AcOH. When the reaction profiles in the reaction of **19**-Br were calculated according to eq 6, assuming that isomerization occurs only by return from the free ion **21**, a fit between the calculated and experimental concentration vs. time curves was found for **19**-Br, **19**-OAc, and **20**-OAc, but the observed concentrations of **20**-Br exceeded the calculated values. When the difference was ascribed to ion-pair return from **32** according to eq 9, the calculated and the observed profiles were identical. Other methods verified this mechanism and gave the same values for k_{ion} and for the fraction of ion pairs which returns to covalent RX (symbolized $1 - F$). For example, in solvolysis in the presence of Cl^-, all the free ions **21** are captured, but isomerization via **32** still continues.[13b]

The distribution of the cationic intermediates among the various routes in AcOH are summarized for **19**-Br and **20**-Br[13b] and for the corresponding mesylates[24b] in eq 10, where return to **21** was calculated for the condi-



(10)

tion $[Br^-]$ or $[OMs^-]$ = 1 M. Application of similar analysis to other systems provided rare insight into the effects of structural and solvent parameters on ionization, internal return, and external ion return in the same system, information which is not available for saturated compounds.

For example, in AcOH k_{ion} follows the leaving ability of X, and both $1 - F$ (for X = Br, Cl, OMs, $1 - F$ = 0.47, 0.38, and 0.24) and α_{app} (for X = Br, Cl, OMs, 21, 5.7, and 0.04, respectively) change with the nucleophilicity in a parallel way.[13b] The data reflect the reduced solvation of X^- in the ion pair compared with that of the free X^- anion.

The solvent effects on these parameters are given in Table IV, together with relevant solvent properties. k_{ion} follows the ionizing power *Y* and the extent of internal return is determined both by the dissociation power as measured by the dielectric constant ϵ and by the solvent nucleophilicity. The increase in the α_{app} values in the series AcOH–HCOOH < AcOH < AcOH–Ac_2O parallels the decreased solvation of Br^- by hydrogen bonding, and the consequent increased nucleophilicity.

Capture of the ion pair is sterically hindered in most of the solvents except in trimethylacetic acid. In this solvent dissociation is unfavored due to the low ϵ and products are therefore formed from the hindered ion pair. However, ion-pair return is not hindered and is the dominant process, and >99% of the ion pairs return to covalent RBr.[41] $LiClO_4$ shows a special salt effect, indicating a product-forming solvent-separated ion pair. In contrast, the absence of special salt effect in AcOH indicates that tighter ion pairs are involved in the isomerization.[13b]

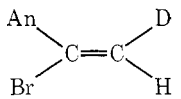
A similar study of (*E*)- and (*Z*)-α-bromo-β-deuterio-*p*-methoxystyrenes **33** and **34** showed that prod-

(37) C. D. Ritchie, *Acc. Chem. Res.*, **5**, 348 (1972).
(38) J. Grinblatt, unpublished results.
(39) R. H. Summerville and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **96**, 1110 (1974); T. C. Clarke, D. R. Kelsey, and R. G. Bergman, *ibid.*, **94**, 3626 (1972); T. C. Clarke and R. G. Bergman, *ibid.*, **94**, 3627 (1972).

Table IV
Parameters for the Solvolysis of 19-Br in Various Solvents

Solvent	Y	ϵ	Rel k_{ion} (120°)	$1-F$ [a]	α_{app}	Ref
80% EtOH	0.00	35.8	4.9	0.32	low	24b
1:1 AcOH–HCOOH	0.76	32.3	5.2	0.46	2.6	24b
AcOH	−1.64	6.2	1.0	0.47	21	13b
1:1 AcOH–Ac_2O	−2.47	15.0	0.53	0.31	27	24b
Me_3CCOOH	−3.6	~2.5	~0.1	>0.99	0	41

[a] $1-F$ is the fraction of ion pairs that return to covalent RX.



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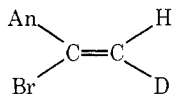

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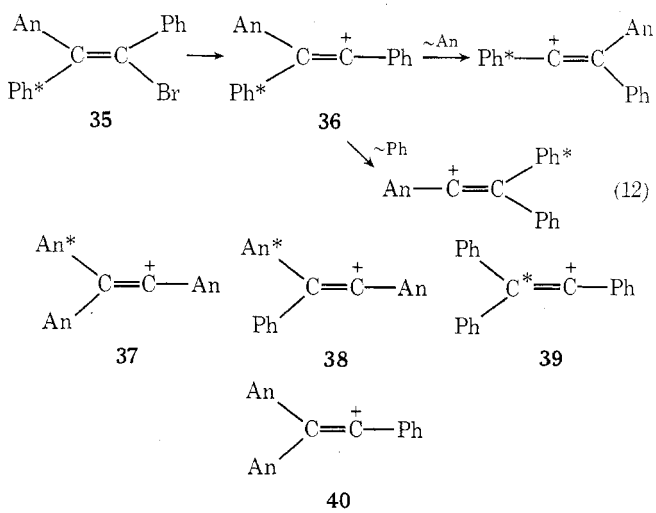
ucts are formed by capture of an unhindered ion pair in both aqueous EtOH and AcOH. Isomerization in AcOH occurs via ion pairs, and 63% of them return to **33** and **34**.[40]

β-Aryl Rearrangements across the Double Bond. β-Aryl rearrangements across the double bond (eq 11)

$$\mathrm{Ar''Ar'C{=}C(X)Ar} \longrightarrow \mathrm{Ar''Ar'C{=}\overset{+}{C}Ar} \longrightarrow \mathrm{Ar'\overset{+}{C}{=}CArAr''} + \mathrm{Ar''\overset{+}{C}{=}CArAr'} \quad (11)$$

have been observed,[6,23,42-44] although the transition state for the rearrangement is highly strained. Some specific questions concerning this reaction were answered in studies of four degenerate[6,43] and two nondegenerate[23,44] rearrangements in triarylvinyl systems substituted by phenyl and anisyl groups, which led to the following conclusions: (a) Although conjugation between the migrating group and the double bond is lost in the rearrangement, the order of migratory aptitudes still resembles that in saturated systems. The degenerate β-anisyl rearrangement of **35** via the ion **36** is 76 times faster than the β-phenyl rearrangement (eq 12),[6a] and β-anisyl rearrangement in **37** is >22 times faster in

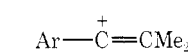


35 36 37 38 39 40

Ph*, An*, C* = labeled groups

TFE than the β-phenyl migration in **38**.[6b] (b) A "windshield wiper" effect of the migrating β-aryl group cannot contribute much to the selectivity of α-anisylvinyl cations: although complete scrambling of the anisyl groups of **37** takes place during trifluoroethanolysis, the ion can be completely captured by Br^- before rearrangement. (c) The similar extents of rearrangement in the *E* and the *Z* isomers of **35** indicate a free linear cation as the intermediate.[6a,23] However, ion pairs are involved in the rearrangement via the ion **39** in RCOOH, as inferred from the similar extents of rearrangement with and without $RCOO^-$,[43a] and in the rearrangement of **40** in trimethylacetic acid, as inferred from the nature of the rearrangement products.[41] (d) The substituent effects on the rearrangement reflect the enhanced charge dispersal ability of the anisyl vs. the phenyl group: the rearrangement is complete for the ion **40** where anisyl groups stabilize both the transition state and the product ion **21**. In degenerate rearrangements, β-anisyl migration between two phenyl-substituted centers is favored over β-phenyl rearrangement between these two centers, while β-phenyl migration between two anisyl-substituted centers is the least favored. (e) Relative reactivity ratios for reactions involving ions **36** and **37** were determined: for **36**, capture by 1 M Br^-: β-phenyl rearrangement:capture by TFE in TFE 97:5.7:1, and β-anisyl rearrangement:capture by solvent:β-phenyl rearrangement 76:19:1 in 60% EtOH, while for **37** capture by 1 M Br^-:β-anisyl rearrangement:capture by TFE in TFE 78:25:1.[6]

Spectroscopically Observable α-Arylvinyl Cations. The selectivity of α-arylvinyl cations suggests that they would be spectroscopically observed. Hanack[45a] and Masamune[45b] and their co-workers reported recently direct observation of the cations **41** (Ar = An, Ph), which were formed from the reaction of **6-F** or of 1-phenyl-2-methylpropen-1-yl chloride in SbF_5–SO_2ClF. The ^1H and ^{13}C NMR spectra showed downfield shift of the aromatic protons and equivalence of the methyl groups as predicted for the linear cation. A substituted α-ferrocenylvinyl cation was formed by protonation of a ferrocenylacetylene.[46]



41

Epilogue. The crowding of several bulky groups in α-arylvinyl systems results in steric hindrance to solvation, steric acceleration of the solvolysis, and shielded cationic orbital. Consequently, several characteristics unusual for a system which solvolyzes via the k_c route

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are observed. Solvent, substituent, and leaving group effects are dependent on the bulk of the β substituents, and product formation and rearrangement proceed in many cases via the free, linear, and selective α-arylvinyl cations. This and the observation of these ions by NMR give them a respectable place in the carbonium ion family.

Thanks are due to the Volkswagen Foundation who supported part of our work. I am privileged to be associated with a group of students whose ideas and enthusiasm contributed much to the work described here. Their names appear in the references. This Account is a memorial to two of them, Dr. Aharon Gal, who pioneered our activity in the area, and Mordechai Thuval, both of whom gave their life in the October 1973 war, so enabling the rest of us to continue our work.

Transition-Metal Dialkylamides and Disilylamides

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For the last quarter of a century the transition metal to carbon bond has tended to dominate inorganic chemistry. The discoveries of sandwich compounds, fluxional organometallic compounds, and stable transition-metal–carbene and –carbyne complexes, together with the development of hydrocarbon catalysis involving these compounds, led to a rapid resurgence of interest in the field of organometallic chemistry.[1] By contrast, the chemistry of the transition metal to nitrogen bond has generated less excitement. Probably the most notable exception to this generalization was the discovery of transition-metal–dinitrogen complexes.[2] This immediately raised hopes that new facile routes to nitrogen fixation would be forthcoming—hopes that for the most part still have to be realized.[3,4] There is, however, an extensive and important chemistry surrounding transition metal to nitrogen bonds. Commonly occurring nitrogen coordinating ligands include amines, pyridines, histidines, nitric oxide, nitrite, nitride, azide, cyanate, thiocyanate, nitriles, Schiff bases, amino acids, peptides, proteins, corrins, and porphyrins. Studies involving nitrogen donor ligands thus range from classical coordination chemistry to the developing field of bioinorganic chemistry.[5,6]

This Account deals with the chemistry surrounding transition metal to nitrogen σ bonds in complexes of the type ML_n where M is a transition metal coordinated by n ligands, L, L = $^-NR_2$ (R = alkyl) or $^-N(SiMe_3)_2$. The coordination chemistry of these compounds reveals the stabilization of unusual coordination numbers and valence states of metal ions, and their reactivity leads to their unique role in the synthesis of many metalloorganic compounds of the transition elements. Also, an interesting comparison exists between the chemistry of transition metal to carbon (alkyl)[7-9] and transition metal to nitrogen (dialkylamide) σ bonds with regard to synthesis, coordination properties, and reactivity.

In addition, the steric requirements of a dialkylamido ligand can dominate the coordination chemistry of transition metals. The use of extremely bulky ligands such as N-i-Pr_2 and $N(SiMe_3)_2$ has allowed the isolation of unusually low coordination numbers and oxidation states for many metals, for example, three- and two-coordinated transition-metal ions. Less bulky ligands such as NMe_2 and NEt_2 allow higher coordination numbers, and in lower valency metal complexes oligomerization may occur either by metal–ligand bridging or by direct metal–metal bonding.

Synthetic Procedures

Although dialkylamides of zinc,[10] sodium,[11] potassium,[11] and lithium[12,13] had been prepared during the 19th century, it was not until 1935 when Dermer and

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Malcolm H. Chisholm received both his B.Sc. and his Ph.D. degrees from Queen Mary College of the University of London, the latter in 1969 under the direction of Professor D. C. Bradley. After 3 years as a postdoctoral fellow at the University of Western Ontario with Professor H. C. Clark, he was appointed Assistant Professor of Chemistry at Princeton University. His research involves the study of structure, bonding, and reactivity of transition-metal organometallic and metalloorganic compounds.

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