**Reduction of *anti*-7-Methoxytricyclo[2.2.1.0$^{2,6}$]heptan-3-one (8).** Lithium aluminum hydride reduction of pure **8** gave a mixture of **16** and **17** in 89% yield.

**Reduction of *syn*-7-Methoxytricyclo[2.2.1.0$^{2,6}$]heptan-3-one (18).** Lithium aluminum hydride reduction of pure **18** gave pure **15**. Identification was made by a comparison of infrared spectra and vpc retention times.

**Reaction of 7,7-Dimethoxybicyclo[2.2.1]hepta-2,5-diene (6) with Methanolic Sulfuric Acid.** The ketal **6** (194 mg) was treated with 10% methanolic sulfuric acid for 21 hr at room temperature. Hydrolytic work-up as described for reactions of **4** gave benzene and no residue after removal of ether and benzene by distillation at reduced pressure.

**Equilibration of 3,3-Dimethoxytetracyclo[2.2.0.0$^{2,7}$.0$^{4,6}$]heptane (4) with Ethanol *via* Acid Catalysis.** A sample of 177 mg of **4** was dissolved in 249 mg of dry ethanol (distilled from magnesium ethoxide). The nmr spectrum was recorded and showed the spectrum of **4** superimposed on the spectrum of ethanol. The triplet observed for ethanol's hydroxyl proton demonstrated that the sample was acid free.

A solution was prepared from 19 mg of sulfuric acid and 3.34 g of dry ethanol, and 86 mg of this solution was added to the nmr tube containing **4** and ethanol. The tube was shaken vigorously and the nmr spectrum was recorded (total elapsed time 100 sec).

In addition to showing the simplified ethanol spectrum (due to acid-catalyzed exchange of the hydroxyl proton), the spectrum showed a drastic decrease in the relative intensity of the absorption due to the dimethyl ketal and the presence of a new absorption due to methanol. This spectrum of equilibrated material did not undergo further change on rerunning.

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# The Solvolysis of Triaryliodoethylenes. Structure and Selectivity of Vinyl Cations

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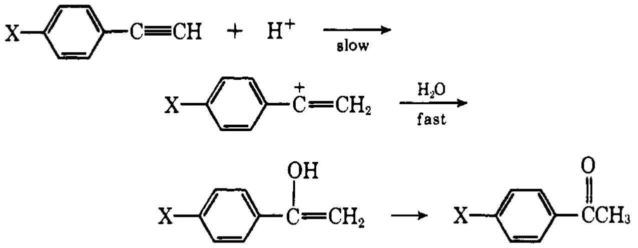
**Abstract:** Several triaryliodoethylenes have been synthesized from the triaryl olefins *via* bromination to the triarylbromoethylenes, followed by the formation of the vinyl Grignard reagent and reaction of this reagent with iodine. In aqueous dimethylformamide it is found that these vinyl iodides solvolyze to iodide ion and the substituted benzhydryl phenyl ketone by an SN1-type mechanism. The rate of appearance of iodide ion was (1) directly dependent on initial reactant concentration, (2) approximately first order in reactant, (3) not enhanced by added nucleophiles, (4) depressed in one case by the addition of a common ion iodide salt, (5) sensitive to substituents on the $\alpha$-phenyl group. For the solvolysis of 2,2-diphenyl-1-anisyliodoethylene, $\Delta H^{\ddagger} = 23.5$ kcal/mol, $\Delta S^{\ddagger} = -16.3$ eu, and $k_{-1}/k_2$ (for rate depression by iodide at 130.5°) was approximately 40. A $\rho = -3.6$ was computed from the rates of solvolysis of 2,2-diphenyl-1-aryliodoethylenes at 189.5 and $\sigma^+$ constants. These data are consistent with formation of an intermediate vinyl cation with extensive delocalization of the positive charge into the $\alpha$-phenyl ring. A comparison of the rates of 1,2,2-triphenyliodoethylene and 1,2-diphenyl-2-anisyliodoethylene shows little acceleration by the *p*-methoxy group. This and other data suggest that a structure of the type $R_2C^+\ddot{C}R$ is a relatively unimportant resonance contributor to the structure of the triphenylvinyl cation. Depression of the 2,2-diphenyl-1-anisyliodoethylene solvolysis rate by iodide ion is indicative of a relatively stable and selective intermediate cation. Reactant stabilization is, therefore, suggested as the major reason for the notoriously slow solvolysis of vinyl halides compared to alkyl halides.

Vinyl cations have been proposed as intermediates in a number of organic reactions. One reaction type for which these proposals have been substantiated is electrophilic addition to acetylenic or allenic bonds,[2-7] as in hydrations, brominations, and addition of hydrogen halides.

$$E^+ + RC{\equiv}CH \longrightarrow R\overset{+}{C}{=}CHE$$

$$E^+ + CH_2{=}C{=}CH_2 \longrightarrow ECH_2\overset{+}{C}{=}CH_2$$

Typical mechanistic results implicating vinyl cation intermediates were found, for example, in a thorough investigation of the sulfuric acid catalyzed hydration of phenylacetylene.[6] Noyce and coworkers measured secondary hydrogen isotope effects and the influence of substituents and the acidity of the medium on the rate of hydration. The data were consistent with a mechanism involving a rate-determining protonation of the terminal acetylenic carbon. The vinyl cation formed in this step is then rapidly trapped with water, leading to the enol of acetophenone and, hence, acetophenone itself.



The $\rho$ value determined from a correlation of the re-

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[1] National Aeronautics and Space Administration Trainee, 1967–1969.

[2] D. S. Noyce, M. A. Matesich, and P. E. Peterson, *J. Amer. Chem. Soc.*, **89**, 6225 (1967), and early studies referenced there.

[3] P. E. Peterson and J. E. Duddey, *ibid.*, **88**, 4990 (1966), and the extensive list of papers cited there.

[4] R. C. Fahey and D. J. Lee, *ibid.*, **89**, 2780 (1967).

[5] P. E. Peterson and R. J. Bopp, *ibid.*, **89**, 1284 (1967).

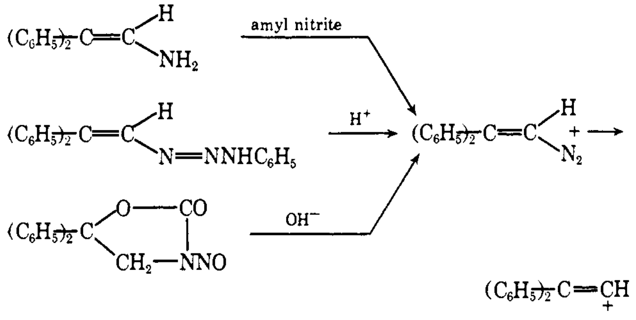
[6] D. S. Noyce and M. D. Schiavelli, *ibid.*, **90**, 1020, 1023 (1968).

[7] R. W. Bott, C. Eaborn, and D. R. M. Walton, *J. Chem. Soc.*, 384 (1965).

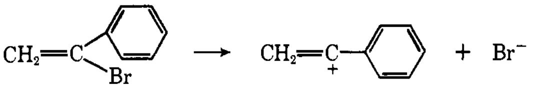
action rates of *para*-substituted phenylacetylenes with $\sigma^+$ was $-3.84$.[6] Similar substituent effects on this reaction were noted by Bott and coworkers.[7]

A second general type of reaction seems to generate vinyl carbonium ions *via* vinyl diazonium ions,[8–11] as in the examples in Scheme I. Although extensive mechanistic studies of these reactions have not been reported, the available evidence is in each case consistent with Scheme I. Finally, there are a number of solvolytic reactions which have been presumed to involve vinyl cations.[12–16] Examples are the solvolysis of sulfonate esters of 3-pentyn-1-ol and 6-heptyn-2-ol where triple bond participation may be involved. Heterolytic cleavage of a group attached directly to the double bond has been investigated in only one instance.[17] A primary reason for this lack of study is the inertness of vinyl halides under solvolytic conditions. For example, the reaction of alkyl bromides with silver nitrate in acetonitrile is conveniently studied at 25° while vinyl bromide is unchanged by this reagent after several days. A more quantitative comparison can be obtained from benzyl bromide and $\alpha$-styryl bromide solvolyses in 80% aqueous ethanol where $k_{\text{benzyl}}/k_{\text{styryl}} \approx 10^6$.

**Scheme I**



The $\alpha$-styryl bromide solvolysis is especially pertinent to the present study because it established that despite the unreactivity of vinyl halides, vinyl cations could be generated solvolytically if an $\alpha$-phenyl group was present. Grob and coworkers were led to propose



an SN1-type ionization for this reaction because the solvolysis rate was independent of the presence of an added nucleophile and very sensitive to substituents on the phenyl ring. The *p*-amino compound, for example, reacted $10^8$ times as fast as unsubstituted $\alpha$-bromostyrene. This study did not, however, offer any satisfying explanations for the unreactivity of vinyl halides compared to alkyl halides. Previous suggestions have invoked reactant stabilization due to increased carbon–halogen bond strengths or unstable vinyl cations to account for this difference. Stabilization of the reactant has been attributed to either partial $\pi$ character in the carbon–halogen bond or increased $\sigma$ bond strength in this bond due to the change in hybridization of carbon from $sp^3$ for alkyl halides to $sp^2$ for their vinyl counterparts. Structural reasons that might account for the special instability of vinyl cations have not been explicitly considered. In fact, as pointed out by Peterson,[3] the closely comparable reactivity of alkynes and alkenes toward protonation by trifluoroacetic or sulfuric acids is consistent with comparable energies for alkyl and vinyl carbonium ions.

Although the previous studies cited allow some insight into the structure of vinyl carbonium ions, several structural questions remain unanswered. One question dealt with in this paper is the possibility[18] of delocalization of positive charge to the adjacent vinyl carbon atom ($\beta$) as in II.

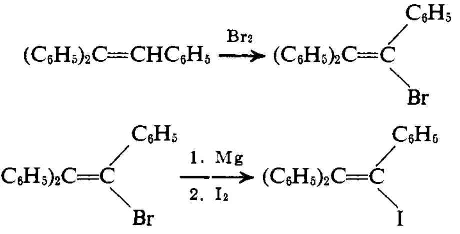
$$R\overset{+}{C}{=}CH_2 \longleftrightarrow R\ddot{C}{-}\overset{+}{C}H_2$$

I II

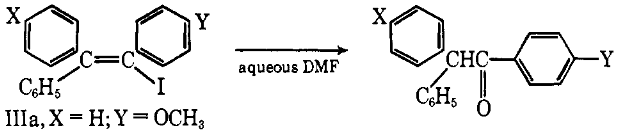
## Results

Several triaryliodoethylenes (III) were synthesized *via* the general Scheme II.[19] These compounds were obtained in 60–78% over-all yield from the corresponding triarylethylene. They were characterized by comparison of their physical properties with literature values or by their spectra and microanalysis. The 2-anisyl-1,2-diphenyliodoethylene was apparently a roughly 4:3 mixture of *cis* and *trans* isomers since it gave a satisfactory analysis and nmr integration but two methoxy peaks in the nmr. Separation of these isomers was not intensely pursued since it was shown that the two methoxy peaks decreased at essentially the same rate during solvolysis.

**Scheme II**



All of the solvolyses were performed in 70% aqueous dimethylformamide (DMF). The products of the solvolysis of 1-*p*-anisyl-2,2-diphenyliodoethylene (IIIa) are iodide ion and *p*-methoxydiphenylacetophenone in essentially quantitative yields. The rates of iodide formation were obtained by potentiometric titration



IIIa, X = H; Y = $OCH_3$
b, X = H; Y = H
c, X = H; Y = Cl
d, X = $OCH_3$; Y = H

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(8) M. S. Newman and A. E. Weinberg, *J. Amer. Chem. Soc.*, **78**, 4654 (1956); M. S. Newman and A. Kutner, *ibid.*, 73, 4199 (1951).

(9) D. Y. Curtin, J. A. Kampmeier, and B. R. O'Connor, *ibid.*, **87**, 863 (1965); D. Y. Curtin, J. A. Kampmeier, and M. L. Farmer, *ibid.*, 87, 874 (1965).

(10) W. M. Jones and F. W. Miller, *ibid.*, **89**, 1960 (1967).

(11) A. C. Day and M. C. Whiting, *J. Chem. Soc., B*, 991 (1967).

(12) J. W. Wilson, *Tetrahedron Lett.*, 2561 (1968).

(13) M. Hanack, J. Haffner, and I. Herterich, *ibid.*, 875 (1965); M. Hanack, *Angew. Chem. Intern. Ed. Engl.*, **5**, 973 (1966).

(14) (a) P. E. Peterson and J. E. Duddey, *J. Amer. Chem. Soc.*, **85**, 2865 (1963); (b) P. E. Peterson and R. J. Kamat, *ibid.*, 88, 3152 (1966).

(15) W. D. Closson and S. A. Roman, *Tetrahedron Lett.*, 6015 (1966).

(16) H. R. Ward and P. D. Sherman, *J. Amer. Chem. Soc.*, **89**, 1963, 4222 (1967).

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

(18) See, for example, S. J. Huang and M. V. Lessard, *J. Amer. Chem. Soc.*, **90**, 2434 (1968).

(19) C. F. Koelsch, *ibid.*, **54**, 2046 (1932).

**Table I.** Kinetics of Solvolysis in 70.4% Aqueous Dimethylformamide

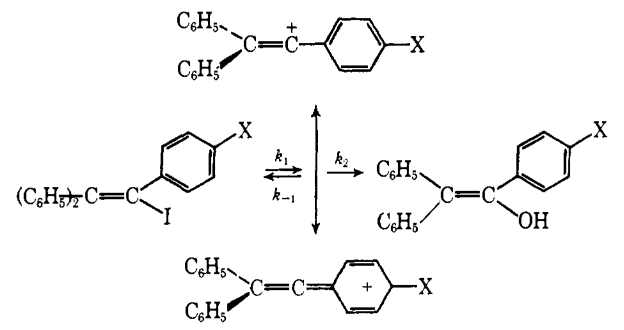
| Compound | $10^5k$,[a] sec$^{-1}$ | Temp, °C | Salt (concn, *M*) |
|---|---|---|---|
| 1-Anisyl-2,2-diphenyliodoethylene (IIIa) | 34.4 | 130.5 | |
| | 10.2 | 114.0 | |
| | 2.49 | 99.0 | |
| | 34.3[b] | 130.5 | |
| | 32.8[c] | 130.5 | |
| | 36.0 | 130.5 | $KNO_3$ (0.01) |
| | 36.0 | 130.5 | KOAc (0.01) |
| | 22.0 | 130.5 | KI (0.01) |
| | 14.0 | 130.5 | KI (0.05) |
| 1,2,2-Triphenyliodoethylene (IIIb) | 2.13 | 189.5 | |
| | 2.13 | 189.5 | KI (0.01) |
| 1-*p*-Chlorophenyl-2,2-diphenyliodoethylene (IIIc) | 1.43 | 189.5 | |
| 2-Anisyl-1,1-diphenyliodoethylene | 2.95 | 189.5 | |
| 1,2,2-Triphenylbromoethylene | 0.84 | 189.5 | |
| 1-Phenylbromoethylene | 3.05 | 189.5 | |
| 1-Anisyl-2,2-diphenylbromoethylene | 9.59 | 130.5 | |
| | 8.68 | 130.5 | KBr (0.01) |

[a] *k* is an average of two or more runs each at an initial vinyl halide concentration of 0.0083 *M*. [b] In the presence of 0.05 *M* triethylamine. [c] Initial concentration of 0.017 *M*.

with silver nitrate. For IIIb, c, and d satisfactory first-order rate plots were obtained over several half-lives, but with IIIa the rate dropped off significantly with time. As is discussed below, this was due to the increasing free iodide concentration during a run so that for IIIa initial rate constants were calculated by extrapolation to zero time. Using this data it can be determined that for IIIa $\Delta H^{\ddagger} = 23.5$ kcal/mol and $\Delta S^{\ddagger} = -16.3$ eu and a three-point plot of log $(k/k_0)$ *vs.* $\sigma^+$ gives $\rho = -3.6$ (Table I).

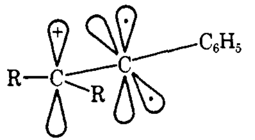
## Discussion

The kinetic results obtained with IIIa and its analogs are clearly most consistent with an SN1-type reaction involving carbon–iodine bond heterolysis. With the exception noted above for IIIa the rates of iodide appearance fit a first-order rate plot and were directly dependent on initial reactant concentration. The rates were not increased by the addition of nucleophiles, but were very sensitive to substituents on the phenyl attached to the $\alpha$-carbon atom. Although a very curved Hammett plot was obtained using $\sigma$ constants, $\sigma^+$ substituent constants[20] gave a nearly linear correlation. The $\rho$ value so obtained is similar to that found for other reactions in which a benzylic vinyl cation is thought to be formed from a neutral molecule. A plot of Grob's data *vs.* $\sigma^+$, for example, gives a curve with $\rho > -4.5$. The hydrations of phenylacetylene and phenylpropionic acid give $\rho = -3.8$ and $-4.8$, respectively. It seems most likely that each of these reactions involves an intermediate of structure IV where the benzylic $\pi$ system is perpendicular to the olefinic bond. The 180° bond angle at the cationic $\alpha$ carbon is presumed since this configuration minimizes steric repulsions and forms the strongest possible $\sigma$ and $\pi$ bonds.

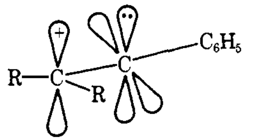


IV

Resonance contributions to vinyl and phenyl cations of the type II have been proposed in the literature.[17] Because of the stereoelectronics of the divalent $\alpha$-carbon atom such delocalization could result in two distinct ways. The first is *via* transfer of an electron into the empty p orbital from the $\pi$ system as in V. This was first suggested by Taft[21] for the phenyl cation. A second reasonable mechanism for achieving structure II is simple polarization of the $\pi$ bond as in VI. The relative rates of triphenyliodoethylene (IIIb) and 2-anisyl-1,2-diphenyliodoethylene (IIId) clearly argue against important contributions from either V or VI. Since the hybridization at the $\beta$-carbon atom is $sp^2$ as in a benzylic carbonium ion, the added *p*-methoxy group should provide a considerable rate enhancement if there were an appreciable electron deficiency at this carbon. A comparison of the solvolyses rates of $\alpha$-bromostyrene and triphenylbromoethylene (VII) substantiates this viewpoint since the $\beta$ phenyls of the latter actually retard the ionization. Here, however, the steric and electronic changes brought about by the substituents are much more complex. It is clear, for example, that the tetrasubstituted olefin, VII, will be destabilized from repulsions between the four large vinyl substituents. Ionization could, therefore, be accelerated by relief of the repulsive interactions of the phenyls on the $\beta$ carbon with the phenyl and bromine on the $\alpha$-carbon atom and from the mutual repulsion of



V



VI

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[20] H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, **80**, 4979 (1958).

[21] R. W. Taft, *ibid.*, 83, 3350 (1961).

the latter two. Steric hindrance to backside solvation at the $\alpha$ carbon could, however, play an equally important role in retarding the ionization rate since the $\beta$ phenyl *trans* to the iodine seriously prohibits nucleophilic push by the solvent. The electronic effects engendered by the addition of $\beta$ phenyls are also complex since inductive destabilization of the transition state and resonance stabilization of both reactant and transition state are feasible. The lack of acceleration of $\beta$ phenyls is, however, consistent with small contributions from a structure like II so that resonance stabilization of the reactant olefin and transition state are of a similar magnitude. It may be noted, that the relative unimportance of II is predicted by theoretical charge densities of 0.25 and 0.06 for the $\alpha$- and $\beta$-carbon atoms of the vinyl cation, $C_2H_3^+$.[22]

It was of considerable interest to find that compound II showed definitely curved first-order rate plots, the rate becoming slower during the reaction. Since the initial rate constant is independent of initial reactant concentration this curvature could only result from reversibility or from a common ion rate depression.[23] The former is unexpected, and is not supported by the infinity titer for iodide or the yield of ketone. The latter is confirmed by the kinetic effects of added potassium iodide and other salts. The added iodide depresses the rate by 40% at 0.1 *M* and tends to linearize the rate plot. The noncommon ion salts have essentially no effect on the rate presumably because the aqueous DMF solvent is quite polar, minimizing normal salt effects.

Common ion rate depression results from a reversible ionization step[24] and indicates not only that a "free" vinyl cation is reversibly formed (reaction 1), but also that this cation can discriminate against water in favor of reaction with low concentrations of iodide. Such discrimination can be evaluated in terms of $k_{-1}/k_2$ obtained from eq 2. Some typical data are compiled in Table II.

$$k_{\text{obsd}} = \frac{k_1}{1 + (k_{-1}/k_2)(X^-)} \qquad (2)$$

As expected, there is a direct relationship between $k_{\text{solv}}$ and $k_{-1}/k_2$ for the alkyl halides, large values being indigenous to relatively stable carbonium ion intermediates.[26] It seems likely that the cation from IIIa is also relatively stable, perhaps even of comparable stability to a *p*-methoxybenzyl cation. The absence of common ion rate depression of the solvolysis of IIIb demonstrates that the same reactivity–selectivity relationship[27] exists for vinyl carbonium ions as for their alkyl counterparts and that the observed selectivity is not a property of all vinyl carbonium ions. The smaller, but still appreciable, depression noted for 1-anisyl-2,2-diphenylbromoethylene is expected and supports the hypothesis that this selectivity results from the stability of the 1-anisyl-2,2-diphenylethenyl cation. Although the differences in reaction conditions and the inherent reactivities of alkyl and vinyl cations will affect the quantitative nature of this comparison, the dramatic reversal of the $k_{\text{solv}} - (k_{-1}/k_2)$ correlation by the vinyl halides seems incompatible with the postulate that their slow rate is only a result of the special instability of vinyl cations.

**Table II.** Selectivities of Carbonium Ions[a]

| Halide | $k_{1-}/k_2$ | $k_{\text{solv}} \times 10^5$, sec$^{-1}$ |
|---|---|---|
| Triphenylmethyl chloride[b] | ~400 | |
| Benzhydryl chloride | 10–16 | 7 |
| Benzhydryl bromide | 50–70 | 170 |
| *t*-Butyl bromide | 1–2 | 2 |
| IIIa | 30–50 | $\sim 10^{-6}$ [c] |
| IIIb | 0 | $>10^{-7}$ [d] |
| 1-Anisyl-2,2-diphenylbromoethylene | 10 | $\geq 10^{-6}$ [d] |

[a] The alkyl halide data are taken from L. C. Bateman, *et al.*, *J. Chem. Soc.*, 979 (1940), except where noted and refer to 80 or 90% aqueous acetone at 25°. [b] C. G. Swain, C. B. Scott, and K. H. Lomann, *J. Amer. Chem. Soc.*, **75**, 136 (1953). [c] Extrapolated to 25°. [d] Estimated rate at 25°.

It seems worthwhile, therefore, to inquire into the reasons for lethargic vinyl halide solvolyses in terms of reactant stabilization. The two types of stabilization that have been suggested are (1) partial $\pi$ character of the vinyl carbon–halogen bond[28] and (2) a stronger vinyl carbon–halogen $\sigma$ bond due to the different hybridization of the vinyl carbon.[29] A third suggestion[28] utilizes the increased electronegativities of vinyl carbon atoms compared with alkyl carbons. Although this difference will clearly make the carbon–halogen bond less polar, it does not necessarily follow that it must impede ionization. In any case, since an electronegativity difference is primarily a result of the change in hybridization[29] we will consider hybridization effects on $\sigma$ bonds strengths to include both homopolar and dipolar effects.

The validity of reactant stabilization *via* $\pi$ or increased $\sigma$ bond strength can be examined using the bond lengths, bond dissociation energies (BDE) and (electron impact) ionization potentials (IP) in Table III. The reported bond lengths of organic chlorides clearly support the idea of a stronger carbon–halogen bond in vinyl chloride and chlorobenzene than in any alkyl chloride[30] and similar data are available for the bromides and iodides.

The ionization of RX in the gas phase can be approached by dissociation to radicals (BDE) followed by ionization of the radical (IP)

$$RX \longrightarrow R\cdot + X\cdot$$

$$R\cdot \longrightarrow R^+$$

As in solution this (two-step) gas phase ionization is more difficult for vinyl halides than alkyl. Further

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[22] T. Yonezawa, H. Nakatsuji, and H. Kato, *J. Amer. Chem. Soc.*, **90**, 1239 (1968).

[23] Grob[17] noted similar rate effects in bromostyrene solvolyses, but here readdition of hydrogen iodide to initially formed phenylacetylene complicates the kinetics.

[24] The present data gives no information about ion-pair intermediates, although these would seem to be likely intermediates as they are in alkyl halide solvolyses. It has been pointed out[25] that the usual interpretation of common ion rate depression data, as in eq 2, is a gross simplification since it does not take into account ion pairs or specific salt effects.

[25] S. Winstein, M. Hojo, and S. Smith, *Tetrahedron Lett.*, 12 (1960).

[26] T. H. Bailey, *et al.*, *Chem. Commun.*, 122 (1966), have recently investigated the rates and common ion rate depressions for solvolysis of a number of substituted benzhydryl chlorides.

[27] See J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley & Sons, Inc., New York, N. Y., 1963, pp 162–168, for a discussion of selectivity–reactivity relationships.

[28] J. D. Roberts and V. C. Chambers, *J. Amer. Chem. Soc.*, **73**, 5034 (1951).

[29] W. Moffitt, *Proc. Roy. Soc.*, *Ser. A*, **202**, 548 (1950).

[30] R. T. Morrison and R. N. Boyd, "Organic Chemistry," 2nd ed, Allyn and Bacon, Inc., Boston, Mass., 1966, p 828.

Table III. Properties of Organic Halides

| Compound (RX) | Bond length, Å[a] | BDE of RX, kcal/mol[b] | IP of R·, eV[c] |
|---|---|---|---|
| $C_2H_5Cl$ | 1.77 | 81.5 | 8.8 |
| $i$-$C_3H_7Cl$ | 1.77 | 81.0 | 8.0 |
| $CH_2{=}CHCl$ | 1.72 | 84 | 9.45 |
| $C_6H_5Cl$ | 1.70 | | 9.9 |
| $C_2H_5I$ | 2.14 | 53 | 8.8 |
| $t$-$C_4H_9I$ | 2.15 | 49.5 | 7.6 |
| $CH_2{=}CHI$ | 2.09 | 55.5 | 9.45 |
| $C_6H_5I$ | 2.08 | 54 | 9.9 |

[a] Tables of Interatomic Distances, Special Publications No. 11 and 18, The Chemical Society, London, 1958 and 1965. [b] S. W. Benson, *J. Chem. Educ.*, **42,** 502 (1965); E. T. Butler and M. Polanyi, *Trans. Faraday Soc.*, **39,** 19 (1943). [c] A. G. Harrison in "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press, New York, N. Y., 1963, p 240; A. Streitwieser, *Progr. Phys. Org. Chem.*, **1,** 1 (1963).

examination of the data in Table III reveals that the relative BDE of alkyl and vinyl halides are very similar, varying less than the BDE of various alkyl-type halides. The difference between alkyl and vinyl instead shows up in the ionization step where an ethyl radical has an IP about 0.7 eV less than the vinyl radical. These data are more easily rationalized in terms of hyrbidizational stabilization than resonance stabilization. The latter should appear as a difference in BDE since it is lost in the cleavage step. It is reasonable to expect, however, that hybridizational stabilization would not be lost in this first step. This would account for both the BDE and the higher IP of the radical.

It is clear that the difference in rates of vinyl and alkyl halide solvolyses provides a complex comparison. Although the above discussion indicates that reactant stabilization *via* hybridizational strengthening of the carbon–iodine $\sigma$ bond is a major reason for this difference, steric hindrance to backside nucleophilic push and changes in the character of other bonds due to the change in carbon hybridization could also be important. It may be noted that $\pi$ character in the cyclopropyl carbon–halogen bond has also often been cited as one reason for slow cyclopropyl halide solvolysis.[28,31] In light of the above discussion this proposal also deserves reexamination. Two other good explanations for the slowness of this reaction are hybridizational (s character of the C–X bond) and increased ring strain in the carbonium ion.

## Experimental Section

All melting points are uncorrected. Spectra were recorded on Varian A-60A and Beckman IR-5 spectrometers. Microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn. and Huffman Laboratories, Wheatridge, Colo.

**2-*p*-Anisyl-1,1-diphenylethylene.** This compound was prepared according to the method of Zimmerman,[32] *via* 2,2-diphenyl-1-anisylethanol. Dehydration yielded the ethylene, which when recrystallized from ethanol gave a crystalline product, mp 83–85° (lit.[32] 83.5–85.5°) in an over-all yield of (42%). The only modification in procedure was to carry out the carbinol dehydration through distillation in the presence of a few drops of 20% sulfuric acid rather than in the presence of sodium bisulfate.

**2-*p*-Chlorophenyl-1,1-diphenylethylene.** This compound was prepared by reacting *p*-chlorobenzylmagnesium chloride with benzophenone.[33] Vacuum distillation of the carbinol, mp 114–116° (lit.[33] 115–116°), in the presence of ten drops of sulfuric acid gave 20 g (91%) of a viscous oil which readily crystallized from ethanol to give a crystalline compound with mp 75–77° (lit.[33] 76–77°).

***cis*- and *trans*-2-*p*-Anisyl-1,2-diphenylethylenes.** These compounds were similarly prepared according to the method of Zimmerman.[32] The total yield of both isomers, obtained as a viscous oil was 11.3 g (78%). No attempt was made to separate the isomers.

**Triphenyliododethylene (IIIb).** This compound was prepared after the method of Koelsch[10] from triphenylethylene *via* the intermediate triphenylbromoethylene. To 5 g (0.0195 mol) of triphenylethylene in 20 ml of glacial acetic was added 3.13 g (0.0195 mol) of bromine. Work-up of the reaction mixture yielded 6.28 g (95%) of triphenylbromoethylene, mp 114.5–116° (lit.[19] 114–115.5°). The bromide (6.28 g, 0.0187 mol) was converted to the Grignard reagent by reaction with magnesium in 150 ml of ether. After refluxing for 3 hr iodine was added as a concentrated ethereal solution until a permanent brown color persisted. The product was worked up by hydrolyzing the Grignard solution by pouring into cold sulfuric acid. The ether layer was separated and dried over $MgSO_4$. Evaporation of the ether on the rotoevaporator left 5.66 g (79%) of a light yellow crystalline product. Recrystallized from ethanol, it melted at 126.5–128° (lit.[10] 125–126°).

**1-*p*-Anisyl-2,2-diphenyliodoethylene (IIIa).** The bromide was prepared as described in preparation of compound IIIb in 91% yield, 128–130°. The Grignards of all the substituted bromides were more difficult to form than that of the unsubstituted analog and it was found necessary to resort to the addition of magnesium etched with methyl iodide to initiate these reactions. Work-up of the *p*-methoxy reaction mixture gave a yellow crystalline solid with mp 154–156° when recrystallized from ethyl acetate. The over-all yield was 60%. The nmr spectrum showed peaks at $\tau$ 6.26 (singlet, 3 H) and 2.6–3.4 (multiplet, 14 H).

*Anal.* Calcd for $C_{21}H_{17}IO$: C, 61.16; H, 4.12; I, 30.80. Found: C, 64.14; H, 4.2; I, 31.5.

**1-*p*-Chlorophenyl-2-diphenyliodoethylene (IIIc).** The 1-*p*-chloro-2,2-diphenylbromoethylene was formed in 83% yield and gave mp 116–117° when recrystallized from ethanol (lit. 114–115°). The iodide was obtained *via* iodination of the Grignard as light yellow needles upon recrystallization from ethanol, mp 128–129.5°. The over-all yield was 78%.

*Anal.* Calcd for $C_{20}H_{14}ClI$: C, 57.62; H, 3.37; I, 30.47. Found: C, 58.03; H, 3.50; I, 30.91.

***cis*- and *trans*-2-*p*-Anisyl-1,2-diphenyliodoethylenes (IIId).** These isomers were also prepared according to the general method of Koelsch. The intermediate bromides have previously been separated by repeated crystallizations.[34] Following the method of Curtin, recrystallization from isooctane followed by four recrystallizations from ethanol gave very poor separation as judged by only small changes in the relative nmr intensities of the two different methoxyl proton peaks. Thus, further separation of the bromide isomers was abandoned. The iodides were produced as a heavy oil which in ethanol crystallized into a yellow solid. Integration of the two different methoxyl proton peaks (singlets at $\tau$ 6.24 and 6.40 in the nmr) showed the isomers to be present in the ratio of 3:4.

*Anal.* Calcd for $C_{21}H_{17}IO$: C, 61.16; H, 4.12; I, 30.80. Found: C, 61.29; H, 4.01; I, 30.69.

**$\alpha$-Bromostyrene.** This compound was prepared according to the method of Beets[35] in 82% yield.

**Solvolysis Product of 1-*p*-Anisyl-2,2-diphenyliodoethylene.** The iodide IIIa (0.75 g) was dissolved in 50 ml of 70% aqueous DMF and heated in a sealed flask for 16 hr at 130°. By reference to previously obtained kinetic data for IIIa it was seen that quantitative reaction should have occurred within this time. After cooling, the contents of the flask were diluted with a large excess of water rendering the reaction mixture insoluble to ether. The combined ether washings were dried over magnesium sulfate and evaporated to dryness on a rotary evaporator. A white solid weighing 0.52 g remained. An nmr spectrum of this crude product showed only one sharp methoxyl singlet at $\tau$ 6.19 indicating the probability of a single product. Recrystallization of the crude product from ethanol yielded 0.39 g (71%) of *p*-anisylbenzhydryl ketone with mp 128.5–129.5° (lit.[36,37] 128–130°). The nmr spectrum of the re-

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(31) See, for example, J. W. Hauser and N. J. Pinkowski, *J. Amer. Chem. Soc.*, **89,** 6981 (1967).

(32) H. Zimmerman and J. Munch, *ibid.*, **90,** 187 (1968).

(33) W. Tadros, K. Farahat, and J. Robson, *J. Chem. Soc.*, 439 (1949).

(34) D. Curtin, E. Harris, and E. Meislich, *J. Amer. Chem. Soc.*, **74,** 2901 (1952).

(35) M. Beets and E. A. Drukker, *Rec. Trav. Chim. Pays-Bas*, **72,** 247 (1953).

(36) A. McKenzie and A. K. Mills, *Ber.*, **62,** 1792 (1929).

(37) T. Nagano, *J. Amer. Chem. Soc.*, **77,** 1691 (1955).

crystallized product, which was identical with the spectrum of the crude product, had peaks at $\tau$ 6.20 (singlet, 3 H), 2.71 (singlet, 10 H), 3.18 (doublet, 2 H, $J$ = 9 cps), 2.0 (doublet, 2 H, $J$ = 9 cps). The ir spectrum showed dominant peaks at 1675, 1585, 1260, 1154, 815, 740, and 692 cm$^{-1}$.

**Kinetics.** The general procedure followed for the kinetic runs is patterned after that of Grob.[19] For reaction vessels at temperatures below 130°, thick-walled Pyrex test tubes were used. For higher temperatures, specially made heavier walled Pyrex tubes were used. Prior to use, all tubes were washed with dilute hydrochloric acid, dilute sodium bicarbonate, thoroughly washed with tap water and distilled water and dried in the oven. Except for runs to test reaction-rate dependence upon concentration, all runs were 0.00833 $M$ in the reactant iodide. DMF was chosen as solvent rather than ethanol because of the much greater solubility of the vinyl iodides in it. Preliminary kinetic runs in DMF with only small amounts of water present showed very slow reaction rates. Thus, it was advantageous to increase the per cent water as much as possible without rendering the compound insoluble. Consequently the following apparently awkward method of filling the tubes was employed. Sufficient compound to make a 0.01 $M$ solution was weighed into the appropriate volumetric. Enough water was added to make the solution 16% aqueous on the basis of the volume with freshly distilled DMF. At this concentration of water, the compounds were still soluble in the solvent system. However, preliminary runs on such solutions still showed inconveniently slow rates. Thus the final method chosen was to place 5 ml of the above-described solutions into each tube along with 1 ml of water making the concentration of the compound 0.0833 $M$ and the solution 29.6% aqueous.

A thermostated oil bath was used which exhibited temperature variations of less than ±1° at 190° and ±0.3° at lower temperatures around 100°. In a given run, all tubes were immersed in the oil bath simultaneously. One tube was removed after 1 min and taken as $t$ = 0. Tubes were then removed at appropriate times and quenched in ice–water. After cooling, the reaction mixture was quantitatively transferred into a beaker with more DMF and six drops of 2 $N$ nitric acid was added. The iodide ion concentration was determined by potentiometric titration with 0.01 $N$ silver nitrate solution. A calomel electrode was used as reference electrode with a silver wire as the indicator electrode. All runs were repeated at least once. Rates were calculated according to the equation $2.303 \log [a/(a - x)] = k$, where $a$ refers to the extent of reaction and was determined from the potentiometric titrations and $x$ refers to the initial concentration of the reactant iodide. For compound IIIa the value of $x$ as determined from the infinity points showed excellent agreement with the initial concentration as calculated from the weighed amount of sample. The value of $x$ for the remaining compounds was determined from weighed amounts of sample only. Attempts to determine infinity points for these less reactive compounds at the long times and high temperatures required led to several explosions of the sealed tubes. It was observed for some long reaction time tubes that a gas had formed, evidently from secondary reactions, and the amount of iodide was about 85% of theoretical. The rate constants were calculated over that portion of the reaction for which first-order kinetics were seen to be valid. For all but compound IIIa, first-order rates could be observed for several half-lives. Sample data are in Table IV.

**Table IV.** Solvolysis of 0.0083 $M$ 1-Anisyl-2,2-diphenyliodoethylene at 114.0°

| Time, min | 0.010 $N$ $AgNO_3$, ml | $10^6k$, sec$^{-1}$ |
|---|---|---|
| 0 | 0.050 | |
| 10 | 0.686 | 98.5 |
| 30 | 1.545 | 85.9 |
| 45 | 2.049 | 84.3 |
| 60 | 2.537 | 83.0 |
| 90 | 3.110 | 76.5 |

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# Formation of 1,1-Dianions of Hydrazones by Certain Bases. N,N-Dialkylation with Halides. Decomposition to Form Hydrocarbons[1]

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**Abstract:** Hydrazones of ketones or aldehydes were converted by 2 equiv of potassium amide in liquid ammonia to 1,1-dipotassio salts, which were dialkylated with halides to form N,N-dialkyl derivatives. Dipotassiobenzophenone hydrazone was allowed to react with 1 equiv of benzyl chloride to form exclusively the mono-N-benzyl derivative, whereas the monopotassio salt of benzophenone hydrazone afforded a mixture of the mono- and di-N-benzyl derivatives. These methods appear preferable to the common type of condensation of ketones or aldehydes with the appropriate mono- or dialkylhydrazines. The dipotassiohydrazones decomposed, evolving nitrogen, on replacing the liquid ammonia with tetrahydrofuran or hexane to form corresponding hydrocarbons. The mechanism evidently involves the intermediate formation of the dipotassio salts of the hydrocarbons. The reaction is related to the Wolff–Kishner reduction, which presumably involves intermediate formation of monoanions of hydrazones and hydrocarbons. Hydrazones were converted by 2 equiv of $n$-butyllithium in tetrahydrofuran–hexane to 1,1-dilithio salts, which were dialkylated or decomposed to form N,N-dialkylhydrazones or hydrocarbons, respectively.

Several active hydrogen compounds have previously been converted to 1,1-dianions by means of bases. Thus, phenylacetonitrile,[2] acetomesitylene,[2] and benzyl phenyl sulfone[3] have been converted to **1**, **2**, and **3**, respectively, by means of $n$-butyllithium, and benzamide

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(1) Supported at Duke University by the Office of Army Research (Durham) and at Duke University and at the University of Missouri by the Petroleum Research Fund, administered by the American Chemical Society.

(2) E. M. Kaiser and C. R. Hauser, *J. Am. Chem. Soc.*, 88, 2348 (1966).

(3) E. M. Kaiser and C. R. Hauser, *Tetrahedron Letters*, 3341 (1967).