(BSF), Jerusalem, Israel, to which we are grateful.

Registry No. 1, 26905-20-4; **13**, 87871-28-1; **14**, 87871-29-2; **18**, 38659-55-1; **19**, 87871-30-5; **20**, 87871-31-6; **25**, 80062-28-8; 2-bromomesitylene-*methyl*-d_9, 87871-32-7; dimesitylacetic acid, 5740-42-1; dimesityl ketene, 87871-33-8; mesitylene-*methyl*-d_9, 15690-50-3; 1-bromo-2,6-dimethylbenzene, 576-22-7; 9-bromoanthracene, 1564-64-3.

Supplementary Material Available: Tables S1–S3 giving the crystallographic data for compound **18** (3 pages). Ordering information is given on any current masthead page.

Highly Specific Reciprocal Methyl/Hydrogen Transfer Reactions Preceding Some Unimolecular Dissociations of Crowded Enol Cation Radicals in the Gas Phase as Examples for Conformationally Controlled Processes

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Abstract: The molecular ions of α-(*o*-methyl)-substituted triarylethenols contain in their metastable ion (MI) mass spectra signals for radical losses that are derived from highly site specific reciprocal CH_3/H migrations. The study of analogues, including some deuterium-labeled isotopomers, reveals the following unusual features: The ortho position of the α-aryl ring is the migration origin, and the ipso position of the β-ring (cis to it) is the terminus of the formal [1,5]-CH_3 migration. The hydrogen transferred back to the α-ring stems exclusively from the migrating CH_3 group. Other methyl rearrangements, from the β- to the α-ring or between the β- and the β′-rings, resulting in the eventual loss of a radical were not observed. No evidence was obtained for the operation of hydrogen scrambling processes. For the overall reaction, i.e., CH_3/H transfer and radical loss, a kinetic isotope effect is not operative. The rearrangement is facilitated by the proximity of the migration origin and terminus in the propeller conformation of the crowded enols. The stereochemical and electronic properties of the C_β-aryl groups exert a directing influence on the direction of the CH_3 transfer. Steric and electronic effects in the products generated apparently determine the detailed course of the reaction in that the elimination of the β-aryl ring together with the transferred "CH_2" unit as a benzyl-type radical results exclusively in the generation of an α-aryl-substituted vinyl cation **20**, whereas a similar elimination of the α-aryl ring will generate the less stable isomeric ion **24**. When the cation resulting from the rearrangement is unstable, e.g., that obtained from the substituted indene **32**, the reciprocal CH_3/H migration followed by radical loss is of minor importance.

The gas phase chemistry of ionized keto/enol forms is a subject of very intense current research activity.[2] Whereas the thermodynamic and kinetic stabilities of most simple enols are quite low in comparison to their tautomeric keto forms,[3,4] the opposite usually holds when their ions are generated in the gas phase. MO calculations[5] and thermochemical studies demonstrate[6] that simple enol cation radicals are substantially more stable than their corresponding keto forms. Moreover, collisional activation (CA) mass spectrometric measurements reveal the existence of stable noninterconverting keto/enol ions, which must be separated by substantial energy barriers.[7] For decomposing ions it was shown that ionized ketones dissociate directly to closed-shell ions, in distinct contrast to the more complicated unimolecular pathways of enol ions. Some enol ions isomerize to the keto ions prior to dissociation, and others are known to rearrange to reactive intermediates of unusual structural properties before decomposing.[5]

Crowded enols differ in many respects from their more simple analogues. For example, ketone **1** is *less* stable than the enol form **3** by 0.6–1.1 kcal mol^{-1}, whereas **2**, following qualitatively the general trend of stability order, is more stable than **4** by 0.5–1.0 kcal mol^{-1}.[2a] For the corresponding ions it was observed that **3**$^{+\cdot}$ is more stable than **1**$^{+\cdot}$ by 14.4–14.9 kcal mol^{-1},[2a] in line with data for other keto/enol ions, where the ionized enol is more stable by 14–31 kcal mol^{-1}.[4b,6] Surprisingly, the ΔH°_f values for **2**$^{+\cdot}$ and **4**$^{+\cdot}$ are almost identical.[2a] However, the ionization of **2** and **4** does not lead to a common ion structure since the CA mass spectra

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(1) (a) Hebrew University. (b) Technische Universität Berlin.

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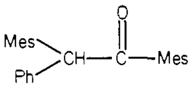
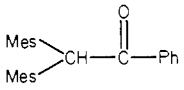


1



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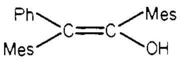

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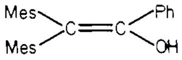
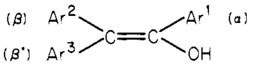


4

Mes = 2,4,6-$(CH_3)_3C_6H_2$

of **2**$^{+\cdot}$ and **4**$^{+\cdot}$ are distinctly different and contain signals derived from structure-specific fragmentation processes as revealed by investigating the deuterated isotopomers.[8] Similarly, the enol isomers **3**$^{+\cdot}$ and **4**$^{+\cdot}$ can easily be differentiated by their CA mass spectra.[8]

Crowded triarylethenols **5** and some related compounds exhibit



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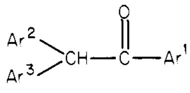


6

several unusual structural properties and chemical reactivities both in the solid state[9] and in solution:[10] (i) In solution the acid-catalyzed isomerization **5** ⇌ **6** is slow compared with that of simple enols. (ii) Depending on the solvent, **5** can exist in two distinct conformations at room temperature, with syn and gauche arrangement of the hydroxyl group in respect to the C=C double bond.[10c] (iii) In both the solid state and solution **5** prefers a chiral propeller conformation,[9,10a,b] where the aryl substituents on C_α and C_β, and those attached to C_β, are very close in space to one another. This is revealed by inspection of space-filling models and by X-ray analysis,[9] and it has unique consequences for the properties of **5** under electron impact. It is the distinct behavior of **5**$^{+\cdot}$ compared with that of other enol cation radicals that prompted the detailed investigation that is described below.[11]

Experimental Section

Compounds **3**,[12a] **4**,[12b] **7**,[12c] **8**,[12c] **11**,[12d] **29**,[12a] and **30**[12a] were prepared according to Fuson's methods. The geometrical structures of **3**, **29** and **30** were determined by X-ray crystallography.[9,10c] The preparations of **9**, **12**, **13**, **14**, and **25** are described in the accompanying paper.[10b] Compounds **15**, **16**, and **28** were prepared by the addition of the appropriate Grignard reagent to the appropriate aryl D_9-mesityl ketene.[10c] In all the deuterated compounds the 2,4,6-$(CD_3)_3C_6H_2$ ring was >98.4% deuterated in the methyl positions. Compound **26** was prepared in an analogous way to the preparation of **3**, except that the D_5-phenyl-labeled mesitylphenyl acetic acid was used as a precursor for the ketene,[10c] instead of the unlabeled acid. Substitution of OD for OH giving **10** from **7** and **27** from **3** was carried out in the inlet system of the mass spectrometer. Preparation of **31** will be given elsewhere.[10c]

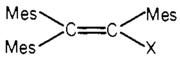
The metastable ion (MI) mass spectra were obtained with the use of a Varian MAT 311A double-focusing mass spectrometer, in which ions pass through the magnetic field (B) before entering the electric field (E). Samples were introduced into the ion source by use of a direct insertion mode (temperature approximately 130–150 °C). The source temperature was 180 °C, the ionizing energy of the electron beam 70 eV, the accelerating voltage 3 kV, and the emission current 0.3 mA. The magnetic and electric fields were adjusted to transmit exclusively the ions of interest. Spectra were obtained by a simultaneous scanning of the magnetic and electric fields (linked B/E scan[13]). The data were recorded on an XY recorder and normalized to the sum of the fragment ion intensities. Signal intensities were not corrected for reduced multiplier response. The data (given in percent fragment ion current, FIC) are mean values of at least three independent measurements.

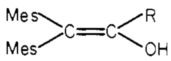
Results and Discussion

The metastable ion **7**$^{+\cdot}$ generated either via direct ionization of neutral trimesitylethenol (**7**) or ionization of trimesitylvinyl acetate (**8**) (via loss of ketene by a four-center rearrangement[2a,14]) eliminates $CH_3\cdot$ (43% FIC) and $C_{10}H_{13}\cdot$ (33%).[15] In contrast to the known $CH_3\cdot$ elimination of aryl-substituted alkene cation radicals,[16] the abundant loss of $C_{10}H_{13}\cdot$ is most unexpected since a $C_{10}H_{13}\cdot$ unit that can be split off directly is not present as such in **7**. On the contrary, elimination of $C_{10}H_{13}\cdot$ requires a formal "CH_2" transfer onto one mesityl ring (C_9H_{11}), which on structural grounds is unfeasible in **7**. Whereas complex rearrangements involving ortho hydrogens take place in stilbene,[16] analogous processes are impossible in **7**. However, reciprocal methyl/hydrogen migrations followed by eventual elimination of the CH_2 unit together with the ring on which transfer has taken place would also result in a corresponding mass shift in the MI spectrum. The following questions should then be ansered: (i) Which aryl ring (α, β, or β') is the migration origin of the CH_3 group, and which ring and at what position is the migration terminus? (ii) What site of the rearranged molecular ion is involved in the reciprocal hydrogen transfer? If it is a methyl group, is it the one which migrates initially or does the hydrogen stem from other parts of the ion? (iii) Are the CH_3/H migrations site specific or not, and does hydrogen scrambling occur? (iv) To what extent is the formal CH_2 transfer dependent on the number, nature, and position of the substituents? (v) Does rotation around the C=C bond precede and/or accompany the rearrangement processes? (vi) What is the mechanism for this unusual reciprocal CH_3/H migration and is it connected with the unique properties of the crowded enol neutrals? (vii) Does this reciprocal migration take place in other crowded systems?

In order to answer these questions we analyzed the MI mass spectra of several triarylethenols, one 2,2-diarylethenol, their derivatives, and some of their isotopomers.

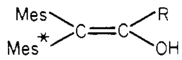
The migration may involve a reciprocal CH_3/H migration between the β- and the β'-rings, in either direction. This is excluded by studying compounds **4**, **11**, and **12**, which share a Mes_2C_β unit, but where α-substituents differ in their character and bulk and do not contain a methyl group. If such transfer takes place, a $C_{10}H_{13}\cdot$ loss from **4**$^{+\cdot}$, **11**$^{+\cdot}$, and **12**$^{+\cdot}$ should be observed, but in their MI mass spectra $C_{10}H_{13}\cdot$ loss amounts to <1% (FIC), and the spectra are dominated by abundant signals for $CH_3\cdot$ loss, in contrast with the spectra of **7**$^{+\cdot}$ and **13**$^{+\cdot}$.[17] A reciprocal CH_3/H transfer from the β-ring to the α-ring should give signals corresponding to abundant losses of $C_7H_7\cdot$ from **4**$^{+\cdot}$, $C_{15}H_{11}\cdot$ from





7, X = OH
8, X = OAc
9, X = Cl
10, X = OD

4, R = Ph
11, R = H
12, R = 9-anthryl
13, R = 2,6-$(CH_3)_2C_6H_3$
14, R = Mes*



15, R = Mes (1/1 *E*/*Z* mixture)
16, R = Mes* (1/1 *E*/*Z* mixture)

[Mes* = 2,4,6-$(CD_3)_3C_6H_2$]

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[8] Depke, G.; Schwarz, H., unpublished results.

[9] Kaftory, M., unpublished results.

[10] Biali, S. E.; Rappoport, Z. (a) *J. Am. Chem. Soc.* **1981**, *103*, 7350; (b) **1984**, preceding paper in this issue; (c) unpublished results.

[11] For a discussion of the isomerization **5**$^{+\cdot}$ → **6**$^{+\cdot}$, preceding the C_α–C_β bond cleavage of **5**$^{+\cdot}$ in the gas phase, see ref 2a.

[12] (a) Fuson, R. C.; Armstrong, L. J.; Kneisley, J. W. *J. Am. Chem. Soc.* **1944**, *66*, 1464. (b) Fuson, R. C.; Armstrong, L. J.; Chadwick, D. H.; Kneisley, J. W.; Rowland, S. P.; Shenk, W. J.; Soper, Q. F. *Ibid.* **1945**, *67*, 386. (c) Fuson, R. C.; Chadwick, D. H.; Ward, M. L. *Ibid.* **1946**, *68*, 389. (d) Fuson, R. C.; Rowland, S. P. *ibid.* **1943**, *65*, 992.

[13] For details see: (a) Boyd, R. K.; Beynon, J. H. *Org. Mass Spectrom.* **1977**, *12*, 163. (b) Bruins, A. P.; Jennings, K. R.; Evans, S. *Int. J. Mass Spectrom. Ion Phys.* **1978**, *26*, 395. (c) Schwarz, H.; Höhne, G.; Blender, J. M.; Veith, H. J. *Varian Appl. Note* **1979**, *40*, 1.

[14] Kingston, D. G. L.; Hobrock, B. W.; Bursey, M. M.; Bursey, J. T. *Chem. Rev.* **1975**, *75*, 693.

[15] Processes resulting from direct elimination of an aryl radical from all metastable ions **5**$^{+\cdot}$ so far studied are nearly negligible, being always smaller than 1% FIC.

[16] Johnstone, R. A. W.; Millard, B. J. *Z. Naturforsch., A* **1966**, *21A*, 604.

[17] The MI mass spectrum of the molecular ion of **9** displays a very weak signal (<1% FIC) corresponding to $C_{10}H_{13}\cdot$ loss. The spectrum is dominated by the facile eliminations of both Cl· and HCl (22% and 63% FIC, respectively).

$12^{+\cdot}$, and $C_9H_{11}\cdot$ from $13^{+\cdot}$. Again, the corresponding signals amount to <1% (FIC). Consequently, a necessary structural requirement for initiating the CH_3 transfer process is the presence of a methyl group on the α-aryl ring. Reactions commencing with methyl transfer from the β-ring to either of the other two rings or between the β- and the β'-rings contribute negligibly, if at all, to the process.

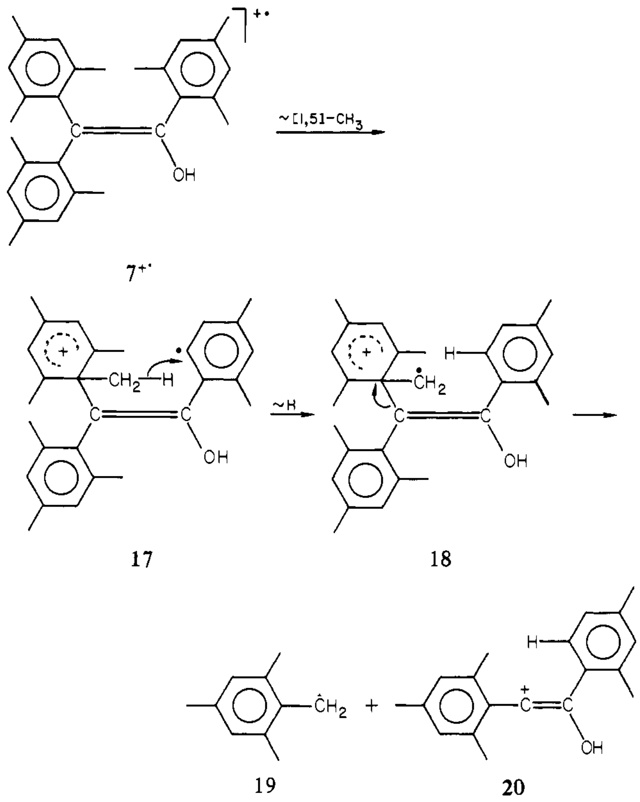
Analysis of **13** is of crucial importance with regard to the questions raised above: its MI spectrum contains a signal for $CH_3\cdot$ loss and an intense peak (18% FIC) corresponding to the elimination of $C_{10}H_{13}\cdot$. Consequently, the CH_3 is transferred from an ortho position of the α-ring, and in the eventual radical elimination only the aromatic ring to which the methyl group has been transferred is eliminated. Hence, the α-ring acts as a CH_3 donor and hydrogen acceptor, whereas either the β- or the β'-ring is involved in the radical elimination reaction.

Additional mechanistic details are provided by the MI mass spectra of the deuterium isotopomers of **7**, i.e., compounds **10** and **14–16**. For example, >96% of the $C_{10}H_{13-x}D_x\cdot$ (x = 0–9) fragments lost from the metastable molecular ion of **14** consist of $C_{10}H_{11}D_2\cdot$. Consequently, CD_3 transfer from the α-ring is followed by a back-transfer of D, and the migrating methyl group is therefore the exclusive source of the reciprocal hydrogen (deuterium) rearrangement. Neither the hydrogen of the hydroxyl group nor hydrogen from any position of either ring β or β' is involved to any significant extent in the overall reaction as shown by studying the following decompositions: The OD-labeled isotopomer **10** eliminates $C_{10}H_{13}\cdot$ but not $C_{10}H_{12}D\cdot$. An ca. 1/1 E/Z mixture of the β-mesityl-labeled isotopomer **15** gives $15^{+\cdot}$, which undergoes unimolecular loss of $C_{10}H_{13}\cdot$ and $C_{10}H_4D_9\cdot$ in a 1.03:1 ratio. The sum of the two reactions corresponds to ≥92% of the total $C_{10}H_{13-x}D_x\cdot$ elimination. Likewise, a ca. 1:1 E:Z mixture of the D_{18}-labeled isotopomer **16** exhibits in the MI spectra elimination of $C_{10}H_{11}D_2\cdot$ and $C_{10}H_2D_{11}\cdot$ in a 0.95:1 ratio, which account to ≥90% of the total $C_{10}H_{13-x}D_x\cdot$ loss.

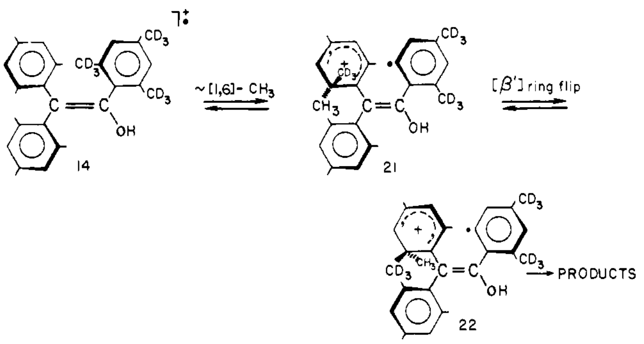
These results lead to the following conclusions: (i) Hydrogen scrambling is not, or at most only to an extremely low extent, occurring in the course of the reciprocal CH_3/H migration.[18] Significant kinetic isotope effects are also not observed and we consider the ratios of the two eliminating $C_{10}H_{13-x}D_x\cdot$ radicals to be equal to unity within the experimental error. (ii) The reaction is highly site specific, and the migrating methyl group originates exclusively from the ortho position of the α-ring. (iii) The migrating methyl group serves as the source for the hydrogen back-transfer.

These results are best described in terms of the reaction sequence outlined in Scheme I. The first step is a [1,5]-CH_3 migration,[19] resulting in a methyl transfer to the ipso position of the β-ring ($7^{+\cdot} \rightarrow 17$). Hydrogen abstraction then generates **18**, the eventual cleavage of which leads to the formation of the stabilized 2,4,6-trimethylbenzyl radical **19** and the stabilized vinyl cation **20**. That the $(M - C_{10}H_{13})^+$ ion generated from $7^{+\cdot}$ is likely to have structure **20** is indicated by the CA mass spectrum of this fragment, which in addition to abundant signals for consecutive methyl losses contains a weak, but structure-indicative, signal at m/z 119 ($C_9H_{11}^+$). In the CA mass spectrum of the $(M - C_{10}H_{11}D_2)^+$ ion generated from ionized **14**, the crucial m/z 119 is not shifted to higher masses, thus suggesting that one β-mesityl group remained intact in the course of the reciprocal methyl/hydrogen migration. CA fragments that would result from hydrogen transfer onto the hydroxyl group are absent. These important results are in perfect agreement with the mechanism outlined in Scheme I.

Scheme I



Scheme II



The preference for methyl transfer to the ipso position is due to the relative thermochemical stabilities of the possible products. Only the ipso attack results after cleavage in the formation of a stabilized benzyl-type radical, i.e., **19**. Attack at any other position, followed by back-transfer of a hydrogen from the migrating methyl group, and cleavage of the C_β–β-Ar bond would give radicals that are certainly higher in energy than **19**. Hence, even if the isomeric species **21** is formed in addition to **17** (cf. Scheme II), the low energy route for the reciprocal CH_3/H transfer and the eventual dissociation will be that of Scheme I.

An alternative mechanistic route is shown in Scheme II. The fact that the migrating methyl group is also the source of the hydrogen back-transfer seems to rule out the ortho positions of the β- or the β'-rings as potential CH_3 acceptor centers. For example, in **14** the migrating $CD_3\cdot$ and one of the o-CH_3 groups of ring β (β') would become structurally equivalent and back-transfer of either hydrogen or deuterium should be observed, eventually resulting in elimination of $C_{10}H_{10}D_3\cdot$ and $C_{10}H_{11}D_2\cdot$, in contrast to the observed elimination of only $C_{10}H_{11}D_2\cdot$. However, a closer inspection shows that this is not the case. The internal transfer of the o-methyl group from one helicity enantiomer of **14** to the ortho position of the β-ring converts this position to a new chiral center (even two identical methyl groups at this position are in a diastereotopic environment, cf. **21**). If internal rotation is restricted before the reciprocal D (or H) return,

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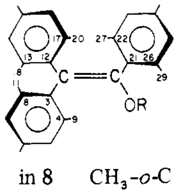
(18) The fact that the sum of $C_{10}H_{13-x}D_x\cdot$ eliminations is less than 100% may be due to the fact that in **7** in addition to the loss of $C_{10}H_{13}\cdot$, elimination of $C_{10}H_{12}\cdot$ is observed (ratio 9:1). Due to the isobaric nature of some of the $C_{10}H_{13-x}D_x\cdot$ and $C_{10}H_{12-y}D_y\cdot$ fragments and the limited resolving power of the instrument used, some arithmetical corrections had to be applied for the deuterated isotopomers, a result of which minor differences are likely to arise.

(19) Whether this process is a symmetry-allowed reaction in terms of the Woodward-Hoffmann rules is open to question. For a more recent, thorough, discussion of this topic and for leading references see: Lay, J. R.; Gross, M. L. *Lect. Notes Chem.* **1982**, *31*, 237.

Table I. C–C Distances (in Å) between C–CH_3 and Ipso and Ortho Positions in **7** (R = H) and **8** (R = Ac)



CH_3-ipso	in 7	in 8	CH_3-*o*-C	in 7	in 8
9–12		4.10	9–13		4.22
9–21		4.40	9–22		4.75
11–12	3.05	3.12	11–13	>3.6	3.94
11–21		4.98	11–17	3.36	3.40
18–3	3.04	3.11	11–26		4.72
18–21		4.79	18–4	3.34	3.28
20–3		4.15	18–8	>3.6	3.92
20–21	3.17	3.15	18–22		4.68
27–3		4.52	20–8		4.32
27–12	3.21	3.30	20–22	>3.6	3.89
29–3		4.37	20–26	3.38	3.28
29–12		4.70	27–4		3.85
			27–13	3.44	3.49
			27–17	>3.6	3.94
			29–4		4.39
			29–8		3.97
			29–17		4.55

the geometrical constraints allow only a return of D since only the CD_3 and the radical center face one another (Scheme II). In order to bring the radical and the CH_3 group to such proximity (cf. **22**) helicity reversal involving rotation of both the α- and the β-rings via the C_α–C_β–O plane should take place. In terms of the flip mechanisms[20] of triarylvinyl propellers[10a,b] this can be achieved by a correlated rotation involving a zero-ring flip, a ([β']) one-ring flip or three consecutive ([α,β], [α,β'), ([β,β']) two-ring flips. The flip mechanism of lowest activation energy leading to helicity reversal of **7** in solution is the three-ring flip,[10a,b] but it cannot give **22**. Consequently, if the rotational mechanism for **7** in solution and for $\mathbf{21}^{+\cdot}$ in the gas phase are identical, the reciprocal return will be completely degenerate and will involve only D, i.e., a $\mathbf{21} \rightarrow \mathbf{14}^{+\cdot}$ process. The fact that losses of $C_{10}H_{10}D_3\cdot$ and $C_{10}H_8D_5\cdot$ are insignificant can either reflect that methyl transfer to the β ortho position does not take place or that in such transfer return of the migrating methyl group occurs before diastereomerization to **22** and is therefore hidden.

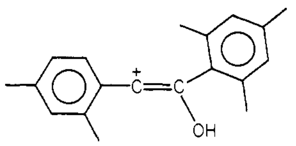
It should be emphasized that the process observed is the cleavage of the rearranged species and not the reciprocal CH_3/H transfer. Consequently, a low-energy reversible CH_3 transfer, e.g., between the β- and the β'-rings (which may scramble the CH_3 and CD_3 groups in **15**), followed by a back-transfer of hydrogen may occur in addition to the above-mentioned process. However, this process is not observable if the following cleavage that involves either the β- or the β'-ring is much higher in energy than the $\alpha \rightarrow \beta$ CH_3/H transfer followed by loss of CH_2 + β-ring.

Three features should be considered when discussing the preferred CH_3/H transfer and cleavage reaction in terms of Scheme I. These are the ground-state conformation of the reacting radical cation and the stabilities of the radical and ionic species formed in the cleavage step. With regard to the stereochemistry, X-ray diffraction data indicate that both **7** and **8** have a propeller conformation in the solid state,[9,10b] and detailed NMR study[10a,b] suggests a similar conformation in solution. Table I gives all the distances in **8** (error ±0.02 Å)[10b] between *o*-methyl groups and ipso and ortho positions on the other rings that are shorter than 5 Å and some relevant distances that are <3.6 Å (error ±0.01 Å) in **7**.[9,21] The numbering of the atoms follows that of ref 10b. The X-ray data, which are similar for both compounds, show that for a given methyl group (except for C-29) the shortest distance to any neighboring aryl carbon is to an ipso position.

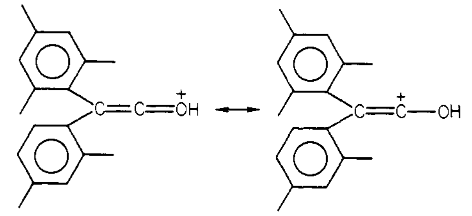
The important point is that although the β- and β'-rings are geminal and the α-and β-rings are vicinal, the angle β-ring-C_β-β'-ring of ca. 120° is much wider than the angle between the C_2 axes of the α- and the β-rings (ca. 60°). Consequently, the distances between the *o*-methyl groups and ipso positions on the neighboring α- and β-rings are similar to the corresponding distances for the β- and β'-rings (3.05–3.21 Å in **7** and 3.11–3.30 Å in **8**). The distances are very short and considering the van der Waals radii of CH_3 (2.0 Å)[22] and aromatic carbon (1.70 Å),[22] the group and site involved in the migration are in a very close proximity in the ground state. Although we cannot rule out any geometrical changes in the course of ionization of **7** or **8**, we strongly believe that due to the congestion of the molecule, the propeller conformation is the lowest in energy and hence the principal features of the steric arrangement of the three aryl groups relative to one another are preserved. The particular stereochemistry and short distances are of a prime importance for the occurrence of the methyl transfer to the ipso position.

However, since several short ipso-*o*-methyl distances are available, this effect alone cannot explain the site specificity of the methyl transfer ($\mathbf{7}^{+\cdot} \rightarrow \mathbf{17}$), since either one of the two reciprocal [1,5]-CH_3/H migrations ($\alpha \rightarrow \beta$; $\beta \rightarrow \alpha$) or the two reciprocal [1,4]-CH_3/H migrations ($\beta \rightarrow \beta'$; $\beta' \rightarrow \beta$) would eventually lead to the elimination of the same 2,4,6-trimethylbenzyl radical. Consequently, whereas other migrations can take place as discussed above, the actually observed site specificity of the $\alpha \rightarrow \beta$ methyl migration should reflect the relative stabilities of the various cationoid species that can be generated in the heterolysis.

Electronic stabilization of the carbocation formed in the cleavage favors $\alpha \rightarrow \beta$ CH_3 transfer over $\beta \rightarrow \beta'$ or $\beta' \rightarrow \beta$ CH_3 transfers. The cleavage that follows the two CH_3/H transfers between the β- and the β'-rings will generate the carbocation **23**.



23



24

It is known that in solution the effect of α-aryl substituents on the stability of vinyl cations is much larger than the effect of β-aryl substituents,[23a] and a similar conclusion is also obtained from MO calculations for isolated ions.[23b] The relative stabilizing effects of the α-mesityl and α-(2,4-dimethylphenyl) group in the reactions leading to the α-arylvinyl cations in solution are known: MesC(OTs)=CH_2 solvolyzes 58–60 times faster in 50% MeOH or in 80% EtOH than 2,4-$(CH_3)_2C_6H_3C(OTs)$=CH_2.[24] The difference in stabilization of the two fully developed ions **22** and **23** in the gas phase should be much larger. In contrast, the effect of β-aryl substituents on the stability of an α-arylvinyl cation is minor and the 2.2 reactivity ratio between the solvolysis rates of AnC(Br)=CAn_2 and *Z*-AnC(Br)=C(Ph)An (An = *p*-$MeOC_6H_4$) in 60% EtOH[25] should be taken as an upper limit for the difference

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[20] For a discussion of definitions and flip mechanisms on molecular propellers see: Mislow, K.; Gust, D.; Finocchiaro, P.; Boettcher, R. J. *Top. Curr. Chem.* **1974**, 1. Mislow, K. *Acc. Chem. Res.* **1976**, *9*, 26.

[21] **7** has two crystalline forms in the solid state. Data for only one of them are given.

[22] Gordon, J. A.; Ford, R. A. "The Chemist's Companion"; Wiley: New York, **1972**; p 109.

[23] Stang, P. J.; Rappoport, Z.; Hanack, M.; Subramanian, L. R. "Vinyl Cations"; Academic Press: New York, 1979; (a) Chapter 6; (b) Chapter 2.

[24] Yates, K.; Périé, J. J. *J. Org. Chem.* **1974**, *39*, 1902.

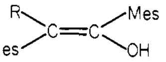
in the electronic effect of the β-Mes and β-[2,4-$(CH_3)_2C_6H_3$] substituents, since the difference in carbocation stabilization between anisyl (An) and Ph is larger than that between Mes and 2,4-$(CH_3)_2C_6H_3$. Steric effects of the different β-aryl groups may somewhat modify the situation, but we believe that the electronic effect dominates in determining this preference for the α → β over the β → β′ CH_3/H fragmentation.

Similar effects operate for the CH_3/H β → α migration. Here the species formed after elimination of the α-mesityl radical is the resonance hybrid of the protonated ketene and α-hydroxyvinyl cation forms **24**. MO calculations[26] at the STO-3G level for the isodesmic reaction of eq 1 give stabilization energies of 37.7 and

$$H_2C{=}C^+{-}R + H_2C{=}CH_2 \rightarrow H_2C{=}C^+{-}H + H_2C{=}CHR \qquad (1)$$

61 kcal mol^{-1} for R = OH[26a] and Ph,[26b] respectively. A β-OH is 2.0 kcal mol^{-1} destabilizing when attached to a vinyl cation[26c] whereas a β-Ph is stabilizing by 15 and 18.8 kcal mol^{-1} when it is perpendicular and in the plane of the double bond, respectively.[26d] Although the difference in energies of the neutral species cannot be ignored, we believe that these values indicate a substantial electronic stabilization of **20** compared with **24**, especially since the calculated heat of formation (MINDO/3) of p-$MeC_6H_4C^+{=}CH_2$ is lower by 8.9 kcal mol^{-1} than that of $PhC^+{=}CH_2$.[26d] The steric effect also operates to make **24** less stable. Heterolysis of **18** to **20** is accompanied by steric relief of the substantial steric interaction of the two mesityl groups on C_β, whereas this interaction, which is larger than the Ar-OH interaction, is mostly retained in ion **24**.

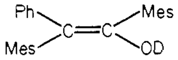
Triaryl-substituted ethenols and their derivatives that are substituted by two different rings on C_β were studied for two reasons. First, we were interested to learn whether prior to or during the reciprocal CH_3/H migrations rotation around the formal C═C double bond might take place. If this is not the case, then the MI mass spectra of *E,Z* isomers substituted by α-mesityl group could be used for determining the geometrical configuration, a problem that is not easily solved by other methods. Second, when migration to two rings is possible, it is of interest to delineate the factors that direct the migrating methyl preferentially to one of the rings. Configurationally different pairs of isomeric enols **5** are not available, but the enol **3** is known only in the *Z* configuration, and a mixture enriched with one isomer was obtained for **25**.[10c] The pure (*Z*)-**3** gives MI mass spectra that contain as a base peak a signal at *m/z* 265 (48% FIC) that corresponds to the loss of $C_7H_7\cdot$, but signals corresponding to the elimination of either $C_8H_9\cdot$ or $C_{10}H_{13}\cdot$ were not observed. Likewise, the isotopomer **26** showed ≥92% loss of $C_7D_5H_2\cdot$, and the isotopomers **27** and **28** exhibited in the MI mass spectra only loss of $C_7H_7\cdot$. This is again consistent with the operation of the mechanism described in Scheme I, provided that rotation around the double bond does not take place. However, if such rotation is possible (see below), the absence of any radical derived from CH_3/H reciprocal transfer to the β-mesityl (or Mes*) group will indicate that the CH_3 group migrates preferentially to the less substituted ring, i.e., to the phenyl ring. When the two rings on C_β are chemically different but comparable in their steric requirements at the reaction site, one should expect that CH_3/H transfer to the two rings will take place if rotation around the double bond is possible, but transfer only to the β-ring will occur when such rotation does not take place. When a 9:1 mixture of the two geometrical isomers of the tert-butyl derivative **25** was investigated, the MI mass spectra contained signals for both losses of $C_{10}H_{13}\cdot$ (i.e., formal transfer of a CH_2 onto the β-mesityl ring) and $C_{13}H_{19}\cdot$ [transfer of a CH_2 to the β-(4-*tert*-butyl-2,6-dimethylphenyl)ring] in a 1.3:1 ratio. This result indicates that rotation around the C═C bond does take place before the reaction and that there is small preference for CH_3 transfer to the less hindered ring. In this case the difference may reflect an electronic effect since the β- and the β′-rings are similar in their steric requirements at the reaction site. We note, however, that one isomer of **25** (the structure of which is yet unknown) undergoes an easy isomerization to the E:Z mixture in solution.[10c] Consequently, isomerization during evaporation of the sample, before the mass spectrum was taken, is likely.



3, R = Ph

25, R = 2,6-$(CH_3)_2$-4-[$(CH_3)_3C$]-C_6H_2 (and isomer)

26, R = C_6D_5



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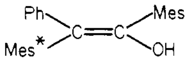
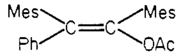


28

Since the question concerning the extent of rotation around the double bond cannot be answered by studying **3** and **25**, we investigated the two pure isomeric enol acetates **29** and **30**. These are stable to mutual isomerization when refluxed for 168 h in acetic acid[10c] and may show a similar stability in the gas phase. When the 70-eV mass spectra of either **29** or **30** were recorded, the main process observed was loss of a C_2H_2O unit. The species formed was shown by kinetic energy release measurements,[2a] as well as by collisional activation spectra,[8] to be identical with the cation radical of the enol **3**. Like $3^{+}\cdot$ it shows a very abundant signal corresponding to $C_7H_7\cdot$ loss. Unfortunately, loss of $C_7H_7\cdot$ from the metastable molecular ion could not be studied due to the very weak $M^{+}\cdot$ signal. Consequently, as yet we have no unequivocal information whether migration of the CH_3 group in our systems is preceded by rotation around the C_α–C_β bond. Since theoretical studies show that the rotational barrier around the double bond of ionized alkenes is substantially lower than the corresponding barrier in their neutral precursors,[27] this route should be considered in future studies of pairs of stable isomeric triarylvinyl derivatives.



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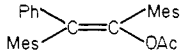

30

In order to exclude the possibility that rotation around the C_α–C_β bond is due to a reversible keto/enol tautomerization $5^{+}\cdot \rightleftarrows 6^{+}\cdot$ prior to the reciprocal CH_3/H migration, we have investigated the enol ether **31** (probably the *Z* isomer), which cannot ketonize. The MI mass spectrum of isomerized **31** is dominated by abundant signals resulting from MeO· and MeOH losses, a weak (2% FIC) but significant one for $C_7H_7\cdot$ elimination, and none corresponding to the loss of $C_{10}H_{13}\cdot$. The loss of $C_7H_7\cdot$ strongly suggests that it is indeed the enol species that undergoes the reciprocal CH_3/H migration in the systems studied here.

$$MesC(Ph){=}C(OCH_3)Mes$$

31

In order to find out whether a reciprocal CH_3/H transfer still takes place when the resulting carbocation is unstable, we investigated the substituted indene **32**. There are two *cis*-mesityl groups in **32** as in **7** although their overall steric environment is different. The two possible carbocations according to Scheme II are cyclopentenyl cation derivatives **33** and **34** (Scheme III), which are extremely unstable in solution.[28] The MI mass spectra of **32** showed mainly a $CH_3\cdot$ loss (68%), some mesityl loss (8%) and also 2% (FIC) of $C_{10}H_{13}\cdot$ loss. Whether the loss of $C_{10}H_{13}\cdot$ is due to some stabilization of **33** or of **34** in the gas phase or to

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(25) Rappoport, Z.; Houminer, Y. *J. Chem. Soc., Perkin Trans. 2* **1973**, 1506.

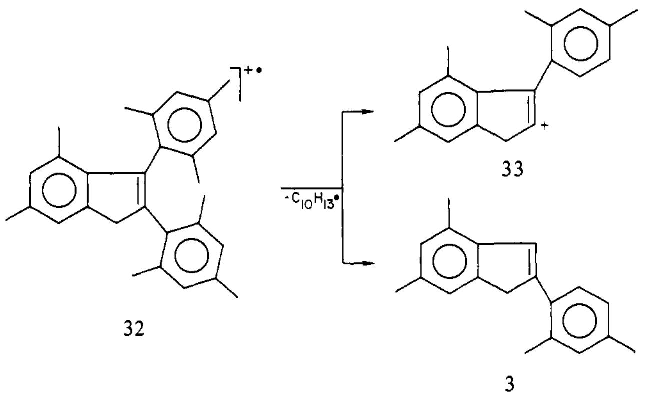
(26) Apeloig, Y.; Schleyer, P. v. R.; Pople, J. A. (a) *J. Am. Chem. Soc.* **1977**, *99*, 1291; (b) *J. Org. Chem.* **1977**, *42*, 3004; (c) *J. Am. Chem. Soc.* **1977**, *99*, 5901. (d) Apeloig, Y.; Franke, W.; Rappoport, Z., Schwarz, H.; Stahl, D. *Ibid.* **1981**, *103*, 2770.

(27) Bellville, D. J.; Bauld, N. L. *J. Am. Chem. Soc.* **1982**, *104*, 294. For exceptions, however, see: Schwarz, H. *Org. Mass Spectrom.* **1980**, *15*, 491.

(28) e.g.: Subramanian, L. R.; Hanack, M. *Angew. Chem.* **1972**, *84*, 714; *J. Org. Chem.* **1977**, *42*, 174.

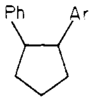
(29) Curtin, D. Y.; Bender, P. A.; Hetzel, D. S. *J. Org. Chem.* **1971**, *36*, 565.

Scheme III

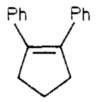


alternative structure(s) of these carbocations is unknown.

The reported 70-eV mass spectra of *cis*-1-mesityl-2-phenylcyclopentane, **35**, and the analogues **36** and **37** also show abundant



35, Ar = Mes
36, Ar = 2,4-$(CH_3)_2C_6H_3$



37

$(M - C_7H_7)^+$ fragments (18%, 92%, and 17% of the base peak, respectively). However, it is doubtful whether these alkyl losses are the result of reciprocal CH_3/H migrations. From field ionization kinetic studies of many substituted cyclopentane derivatives it is known that the molecular ions undergo ring opening followed by hydrogen migration within $t \leq 10^{-10}$ s.[30]

In conclusion, the following features characterize the gas-phase chemistry of ionized triarylethenols. Reciprocal CH_3/H migrations are site specific where the ortho position of the α-ring is the migration origin and the ipso position of the β-ring is the migration terminus. The hydrogen transferred back originates exclusively from the migrating CH_3 group. Other methyl transfer processes or hydrogen scrambling does not take place. The rearrangement is facilitated by the proximity of the migration origin and terminus in the propeller conformation of the crowded olefins,[31] and steric and electronic effects in the generated cation determine the course of the reaction. The stereochemical and electronic properties of aryl groups on C_β may exert a directing influence on the direction of the CH_3 migration. Since the CH_3/H migration may be facilitated by the increased proximity between the α- and β-rings due to buttressing of the β-ring by the β'-ring, it remains to be established if less crowded molecules, such as (*Z*)-2,4,6-trimethylstilbene, or even conformationally rigid saturated systems that are substituted by very close mesityl and aryl groups will display similar behavior.

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Registry No. (*Z*)-**3**, 77787-79-2; (*Z*)-**3** radical cation, 88243-88-3; **4**, 77787-80-5; **7**, 26905-20-4; **7** radical cation, 88200-34-4; **8**, 38659-55-1; **9**, 87871-31-6; **10**, 88180-80-7; **11**, 54288-04-9; **12**, 80062-28-8; **13**, 87871-29-2; **14**, 87871-28-1; **14** radical cation, 88180-81-8; (*Z*)-**15**, 88180-82-9; (*E*)-**15**, 88180-83-0; (*E*)-**16**, 88200-35-5; (*Z*)-**16**, 88180-84-1; **20**, 88180-85-2; (*E*)-**25**, 88180-86-3; (*Z*)-**25**, 88180-87-4; (*Z*)-**26**, 88180-88-5; (*Z*)-**27**, 88180-89-6; (*Z*)-**28**, 88180-90-9; (*E*)-**29**, 77787-81-6; (*Z*)-**30**, 77787-82-7; (*Z*)-**31**, 88200-36-6; **32**, 88180-91-0; mesitylphenyl-d_5-acetic acid, 88180-92-1.

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(30) (a) Borchers, F.; Levsen, K.; Schwarz, H.; Wesdemiotis, C.; Wolfschütz, R. *J. Am. Chem. Soc.* **1977**, *99*, 1716. (b) Levsen, K.; Heimbach, H.; Bobrich, M.; Respondek, J.; Schwarz, H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1977**, *32B*, 880. (c) Schwarz, H.; Wesdemiotis, C.; Levsen, K.; Heimbach, H.; Wagner, W. *Org. Mass Spectrom.* **1979**, *14*, 244.

(31) For other examples of conformationally controlled processes under electron impact conditions see: (a) Longevialle, P.; Milne, G. W. A.; Fales, H. M. *J. Am. Chem. Soc.* **1973**, *95*, 6666. (b) Bohlmann, F.; Friedrich, T.; Köppel, C.; Schwarz, H. *Org. Mass Spectrom.* **1975**, *10*, 158. (c) Longevialle, P.; Asteir, A. *Isr. J. Chem.* **1978**, *17*, 193.