Vinylic Cations from Solvolysis. 42.[1] Cyclization on Methyl, Capture by Solvent, and Degenerate Rearrangement of the Trimesitylvinyl Cation

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Trimesitylvinyl tosylate, prepared in situ from trimesitylethenol (**2**) and tosyl chloride, cyclizes in benzene to 2,3-dimesityl-4,6-dimethylindene (**5**). $AgBF_4$-assisted reaction of trimesitylvinyl chloride (**6**) in the alcohols ROH, R = Me, Et, and *i*-Pr, gives mixtures of **5** and the corresponding alkyl trimesitylvinyl ether **7**, with **7**/**5** ratios of 8.1, 4.6, and 0.32 for R = Me, Et, and *i*-Pr, respectively. Only **5** was formed when R = *t*-Bu. (*Z*)-1,2-Dimesityl-2-phenylvinyl chloride (**8**) gives no indene in *t*-BuOH under similar conditions. A plot of log ([**7**]/[**5**]) is linear with log *k* for the reaction of trianisylvinyl cation with ROH. Reactions of Me-d_3-α- or β-mesityl-labeled **2** with $SOCl_2$ in CH_2Cl_2 gave **6** with statistically scrambled mesityl groups and small amount of **5**. Cyclization of the isotopomeric mixture of labeled **6** gave a mixture of three isotopomeric indenes from which a k_H/k_D isotope effect of 1.6 ± 0.4 for the cyclization was calculated. It is suggested that the rearrangement, the capture by the ROH, and the cyclization proceed via the intermediacy of the trimesitylvinyl cation **3**. Two alternative routes for the unusual cyclization on the saturated β-*o*-Me group are discussed. β-Mesityl rearrangement in **3** is faster than capture by Cl^- which is faster than the cyclization. The capture by ROH is subjected to steric hindrance and is faster than cyclization for R = Me and Et, whereas it is slower than cyclization for the bulkier alcohols, R = *i*-Pr and *t*-Bu.

The bulk of the β-substituents of α-aryl-β,β-disubstituted vinyl halides and tosylates affects several phenomena associated with vinylic solvolysis.[2] The k_{OTs}/k_{Br} reactivity ratios[3] and the Winstein-Grunwald *m* values[2a] decrease on increasing the bulk of the β-substituent and the selectivity of the derived vinyl cation **1** to capture by Br^- vs.

$$\underset{\mathbf{1}}{R_2C{=}C^+{-}Ar}$$

capture by the solvent increases with the bulk of R.[2a,4] These phenomena were ascribed mainly to steric acceleration of the bromide solvolysis, steric hindrance to solvation, and steric hindrance by the bulky β-substituents to capture of the nucleophile.[2-4]

It was therefore of interest to extend the previous studies to more crowded systems. However, a difficulty is that our routine synthesis of triarylhaloethylenes by halogenation-dehydrohalogenation of the triarylethylenes[4c] failed with more crowded systems due both to ring halogenation and to base-catalyzed dehalogenation rather than dehydrohalogenation of the dihalides. Hence, the availability of the stable enol, trimesitylvinyl alcohol **2**,[5] suggested an easy access to precursors of the trimesitylvinyl cation **3**.

$$\underset{\mathbf{2}}{Mes_2C{=}C(OH)Mes} \qquad \underset{\mathbf{3}}{Me_2C{=}C^+{-}Mes}$$

Mes = 2,4,6-$Me_3C_6H_2$

The torsional angles of the β-mesityl group of this ion are likely to be 50-55° as deduced from the known X-ray data of precursor **2**[6a] and of dimesitylketene[6b] which are taken as steric models for the sp^2- and sp-hybridized systems, but even at this geometry nucleophilic approach to the vacant orbital is strongly hindered. This should be reflected in relatively high selectivity of the ion. Another interesting aspect of ion **3** is the presence of *o*-methyl substituents on the β-rings. Systems carrying β-*o*-SMe,[7a] β-*o*-OMe,[7] and β-*o*-NMe_2[8] were found to cyclize to the corresponding five-membered heterocycles, i.e., the substituted benzothiophene, benzofuran, and indole. This intramolecular nucleophilic substitution (k_{cyc}) sometimes occurs in higher preference to the capture by the external nucleophile (k_{Nu}). It was of interest to see whether the presence on the β-rings of the nonnucleophilic *o*-Me groups which lack nonbonding electrons will result in related phenomena. Finally, ions similar to **3** which are substituted by electron-donating aryl groups, e.g., the trianisylvinyl cation, undergo degenerate β-aryl rearrangements across the double bond,[1a,9] and it was of interest to find out if a related process will take place in **3**.

Consequently, formation of **3** and its cyclization, capture, and rearrangement reactions were studied and are described below.

Results

Cyclization of Trimesitylvinyl Cation to 2,3-Dimesityl-4,6-dimethylindene. When sodium trimesitylethenolate, formed from the enol **2** and NaH, was reacted

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(9) (a) For a review of degenerate β-aryl rearrangements in vinyl cations see ref 2a and Lee, C. C. In "Isotopes in Organic Chemistry", Buncel, E., Lee, C. C., Eds.; Elsevier: Amsterdam, 1980; Vol. 5, pp 1-44. (b) Rappoport, Z.; Noy, E.; Houminer, Y. *J. Am. Chem. Soc.* **1976**, *98*, 2238. (c) Houminer, Y.; Noy, E.; Rappoport, Z. *Ibid.* **1976**, *98*, 5632. (d) Lee, C. C.; Cessna, A. J.; Davis, B. A.; Oka, M. *Can. J. Chem.* **1974**, *52*, 2679. (e) Rummens, F. H. A.; Green, R. D.; Cessna, A. J.; Oka, M.; Lee, C. C. *Ibid.* **1975**, *53*, 314. (f) Oka, M.; Lee, C. C. *Ibid.* **1975**, *53*, 320. (g) Lee, C. C.; Oka, M. *Ibid.* **1976**, *54*, 604. (h) Lee, C. C.; Ko, E. C. F. *Ibid.* **1977**, *55*, 2310. (i) Lee, C. C.; Obefami, C. A.; Rappoport, Z. *Ibid.* **1982**, *60*, 3019. (j) Rappoport, Z.; Fiakpui, C. Y.; Yu, X.-D.; Lee, C. C. *J. Org. Chem.* **1984**, *49*, 570. (k) Lee, C. C.; Ko, E. C. F. *Ibid.* **1978**, *56*, 2459. (l) Lee, C. C.; Ko, E. C. F.; Rappoport, Z. *Ibid.* **1980**, *58*, 884, 2369. (m) Lee, C. C.; Obefami, C. A.; Quail, J. W.; Rappoport, Z., *Can. J. Chem.* **1981**, *59*, 2342.

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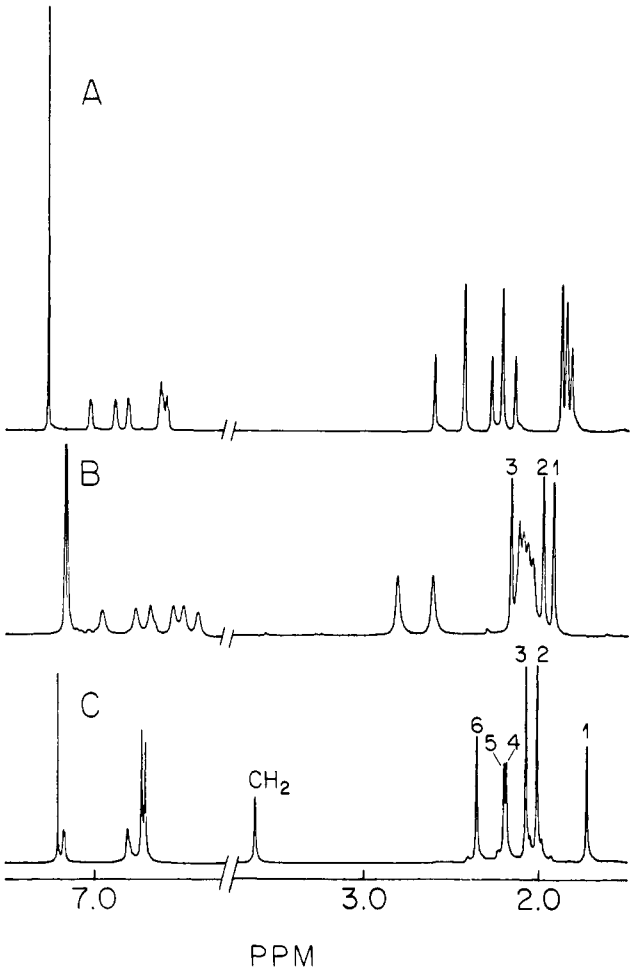
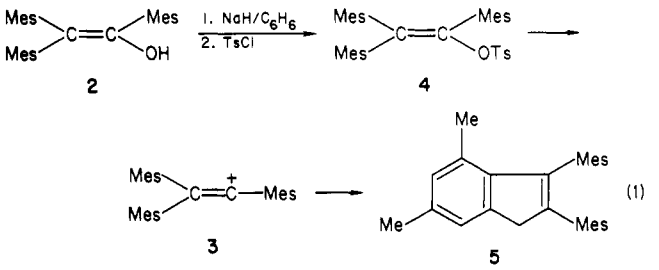


Figure 1. ^{1}H 200 MHz spectra of labeled starting materials and products in $CDCl_3$ (A and C) and in C_6D_6 (B). A: ca, 1:1 *E*/*Z*-Mes(Mes*)C=C(OH)Mes (**2a**). The signals of methyl groups on the β rings appear with half intensity. B: mixture of labeled Mes_2C=C(Cl)Mes (**6a** + **6b** + **6c**) obtained by reacting **2a** with $SOCl_2$ in C_6D_6. A complete scrambling of the label is indicated by the equal integration of the methyls belonging to the three rings (e.g., signals 1, 2, 3 for the *p*-Me groups). Broadening of the *o*-Me and Mes-H protons is due to a dynamic process.[6b] The small peak at 3.57 ppm is due to 4% of **5a** + **5b** + **5c**. C: mixture of labeled indenes (**5a** + **5b** + **5c**) obtained by reacting **6a** + **6b** + **6c** with $AgBF_4$. In the absence of isotope effect the intensities of the Me groups 1, 2, 3, 4, 5, 6 should be 1:2:2:1:1:1. The low relative intensities of signals 2, 3, 4, 5 show visually the isotope effect.

with tosyl chloride in benzene, a single compound was obtained in addition to the recovered **2**. Its ^{1}H NMR spectrum in $CDCl_3$ showed 6 signals in the Me region in a 1:1:1:2:2:1 ratio, a CH_2 singlet that disappeared when the compound was refluxed in $THF/D_2O/NaOD$[10] and four aromatic singlets in a 1:1:2:2 ratio (Figure 1). No broadening of the signals was observed when the solution was cooled to −60 °C. The conversion of one CH_3 to a CH_2 unit and the loss of the distinction between the different *o*-Me and *m*-H's in the two rings which is characteristic for the trimesitylvinyl system (due to hindered rotation on the NMR time scale)[5b] suggested that a cyclization took place. ^{1}H NMR, ^{13}C NMR, and microanalysis are consistent with formation of 2,3-dimesityl-4,6-dimethylindene (**5**) formed by intramolecular cyclization of an intermediate trimesitylvinyl cation **3** on an *o*-methyl group. The structure of **5** was corroborated by X-ray crystallography.[11] The stereoscopic view (Figure 3) and a list of coordinates, bond lengths, and angles are given in the supplementary tables S1–S3 together with the numbering scheme. The indene ring is nearly planar and the two mesityl rings are twisted in the same sense with dihedral angles of 74° (C-2-mesityl) and 69° (C-3-mesityl).

Although trimesitylvinyl tosylate **4** was not observed either by NMR or as an additional spot on a TLC plate of the reaction in progress, the reaction is formulated via both **4** and **3** (eq 1) in analogy with the reactions described



(1)

below. The indene **5** was also obtained when trimesitylvinyl chloride **6** reacted (presumably via **3**) under superacid conditions.[12]

Cyclization vs. Capture by the Solvent. In order to corroborate the suggested reaction course starting from a stable carbenium ion precursor and to evaluate the extent of the cyclization in the presence of added nucleophiles, the silver ion assisted solvolysis of trimesitylvinyl chloride **6** was investigated in several alcohols. We prepared **6** both

$$\underset{\mathbf{2}}{Mes_2C{=}C(OH)Mes} \xrightarrow[CH_2Cl_2 \text{ or toluene}]{SOCl_2 \text{ or } (COCl)_2, \text{ pyridine}} \underset{\mathbf{6}}{Mes_2C{=}C(Cl)Mes} + \mathbf{5} \quad (2)$$

by the previously described reaction[5b] of **2** with thionyl chloride/pyridine except that we used CH_2Cl_2 instead of toluene or from the analogous reaction with oxalyl chloride/pyridine/CH_2Cl_2. In the former reaction, using **2**, **2a**, or **2b** (cf. eq 5) <5% of **5** was detected by NMR.

When a mixture of **6** and $AgBF_4$ in an alcohol ROH (R = Me, Et, and *i*-Pr) was reacted for 48 h at 80 °C, the indene **5** was formed. In addition, a different compound having the trimesitylvinyl skeleton, identified as the corresponding enol ether **7** (eq 3), was formed. The **7**/**5** ratios

$$\underset{\mathbf{2}}{Mes_2C{=}C(Cl)Mes} \xrightarrow[80\ ^\circ C]{AgBF_4,\ ROH} \underset{\mathbf{7}}{Mes_2C{=}C(OR)Mes} + \mathbf{5} \quad (3)$$

were dependent on the bulk of R, being 89:11 for R = Me, 82:18 for R = Et, and 24:76 for R = *i*-Pr (**7**/**5** = 8.1, 4.6, and 0.32, respectively). When the reaction was conducted in *t*-BuOH, only **5** was isolated and the ^{1}H NMR of the crude reaction product in the *t*-Bu region showed that the *tert*-butyl ether (**7**, R = *t*-Bu) consists of <5%, (which is our limit of detection) of the product. No reaction was observed when **6** was left in *t*-BuOH at 95 °C for 48 h in

(10) Although the exchange could be accompanied by an allylic rearrangement to give, at least partially, the isomeric deuterated 1,2-dimesityl-5,7-dimethylindene, we found no evidence for the formation of this isomer.

(11) The material crystallized in the monoclinic $P2_1/n$ space group with four molecules in the cell of dimensions a = 22.401 Å, b = 12.258 Å, c = 8.429 Å, β = 90.46°, V = 2314.5 Å^3. The R factor is 0.070.

(12) At our request, Dr. H.-U. Siehl from the University of Tubingen, to whome we are indebted, tried to generate **3** from **6** under stable ion conditions. To a solution of **6** in a SO_2ClF/SO_2F_2 mixture, SbF_5 was added at −196 °C, and on warming to −125 °C the ^{1}H NMR of the solution displayed only broad peaks, which did not enable analysis. Quenching with EtOH gave a mixture whose NMR showed a mixture of **5**, unreacted **6**, and broad peaks which may be due to a polymeric compound. Signals due to ethyl trimesitylvinyl ether **7**, R = Et were not detected. It is likely that the absence of the latter is due to cyclization to indene before the quenching.

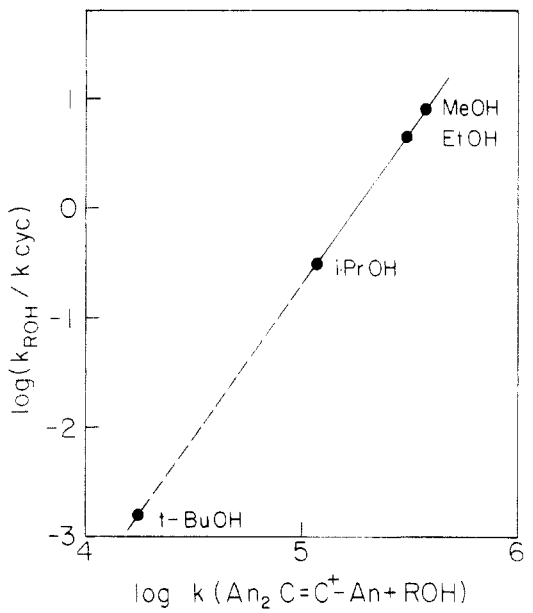


Figure 2. Plot of log [7]/[5] ratio in ROH vs. log k (taken from Figure 4 in ref 10) for the reaction of $An_2C{=}C^+{-}An$ with ROH in MeCN–ROH. The $\log(k_{t\text{-BuOH}}/k_{cyc})$ value is an extrapolated value.

the absence of the silver salt.

Degenerate β-Mesityl Rearrangements during Formation of 6. For studying the cyclization mechanism **6** labeled specifically by o-CD_3 groups on the α- and β-mesityl rings was required. Hence, a ca. 1:1 isotopomeric mixture of the β-Me-d_9 labeled enols E- and Z-1,2-dimesityl-2-(2,4,6-trideuteromethyl)phenylethenols **2a**[13] (Mes* = 2,4,6-$(CD_3)_3C_6H_2$, 98.4% D) and the α-Me-d_9-labeled enol (**2b**)[5b] were reacted separately with thionyl chloride. In each case the integration of the various methyl signals (whose assignment to the α, β, and β′ rings in the ^{1}H NMR of **6** is known),[5b] showed that extensive skeletal rearrangement across the double bond took place. The products from **2a** and **2b** in CH_2Cl_2 were identical and completely rearranged with a statistical distribution of the labeled ring in the three positions of the products (eq 4,

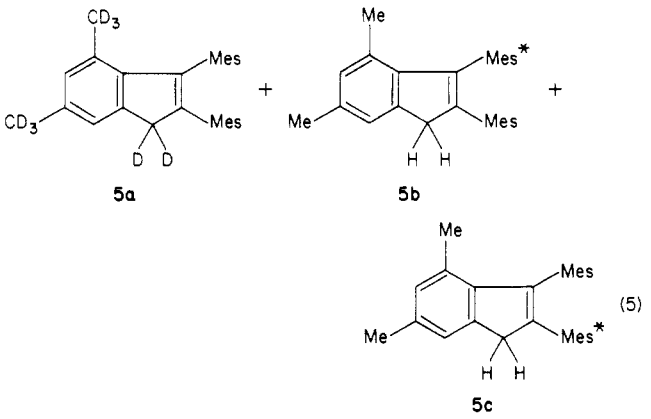
$$\underset{\mathbf{2b}}{Mes_2C{=}C(OH)Mes^*} \xrightarrow[CH_2Cl_2]{SOCl_2,\ pyridine} \underset{\mathbf{6a}}{Mes_2C{=}C(Cl)Mes^*} + \underset{\mathbf{6b}(E)\ +\ \mathbf{6c}(Z)\ (1:1)}{Mes^*C(Mes){=}C(Cl)Mes} \quad (4)$$

Figure 2). A preliminary reaction in toluene gave an extensive, but incomplete β-mesityl rearrangement with a 2.7:1 integration ratio of the methyl groups in the β-rings to the α-ring.

Since the rearrangement presumably proceeds via ion **3**, and since the analogous trianisylvinyl cation can be captured by Br^- before rearrangement[9a,c] capture of **3** by Cl^- before rearrangement was attempted. However, when the reaction of eq 4 was conducted in CH_2Cl_2 in the presence of 0.085 M $PhCH_2N^+Et_3Cl^-$, the same 1:1:1 mixture of the isotopomeric chlorides **6a**:**6b**:**6c** was obtained.

Cyclization of the Isotopomeric Chlorides. In spite of our failure to obtain an isotopomerically pure **6**, the isotope effect in the cyclization could be obtained by using the 1:1:1 isotopomeric mixture of **6a** + **6b** + **6c**. In order to avoid complications from formation of **7** the $AgBF_4$-assisted solvolysis was conducted in t-BuOH for 48 h. A mixture of the three isotopomeric indenes (**5a**, **5b** and **5c**) was obtained (eq 5) and assignment of the signals of **5a**–**5c** was based on the following observations in the ^{1}H NMR spectrum: (a) The presence of a CH_2 group is associated

$$\underset{\mathbf{6a}}{Mes_2C{=}C(Cl)Mes^*} + \underset{\mathbf{6b}\ +\ \mathbf{6c}}{Mes^*C(Mes){=}C(Cl)Mes} \xrightarrow[24\ h]{AgBF_4,\ 80\ ^\circ C} \quad (5)$$



with cyclization on a non-deuterated ring (i.e., with formation of **5b** and **5c**). Hence the integration ratios of 2:3 of the CH_2 group to two Me groups at δ 1.75 and 2.38 identify the latter as the methyl groups on the indene ring. (b) The other four Me signals appear in a 2:2:1:1 ratio at δ 2.03, 2.09, 2.21, 2.22. Since free rotation of the mesityl groups is evident, the **5b**:**5c** ratio is 1:1. (c) The H-5 and H-7 indenyl protons of the labeled mixture appear in the (resolution enhanced) ^{1}H NMR as two doublets (J_{meta} = 1.61 Hz) corresponding to **5a**, superimposed on the broadened signals of **5b** and **5c**.

The integration ratio of the Me signals of the two mesityls of **5a** is also 2:2:1:1, and the isotope effect k_H/k_D in the cyclization could therefore be calculated in several ways, of which we used two: (i) from the ratio of the CH_2 signal to the sum of all the aromatic signals (In the absence of an isotope effect the ratio will be 2:9 whereas for a very high isotope effect (i.e., **5a** is not formed and $k_H/k_D = \infty$), the ratio will be 1:3.) and (ii) from the ratio of an average of an indenyl-Me signal to the average of a Me signal in the mesityl rings (The ratio will be 1:1 in the absence of isotope effect and 2:1 for a maximal isotope effect.). The differences between the extreme integration ratios indicate that the k_H/k_D value obtained from the ([**5b**] + [**5c**])/[**5a**] ratio will contain a substantial error.

We note that the small steric isotope effect of ca. 1.03 preferring the E isomer of labeled **2a**,[14] and probably preferring **6b** over **6c** should disappear in the labeled linear cations **3**. A steric isotope effect of this magnitude should probably prefer **5b** and **5c** over **5a**.

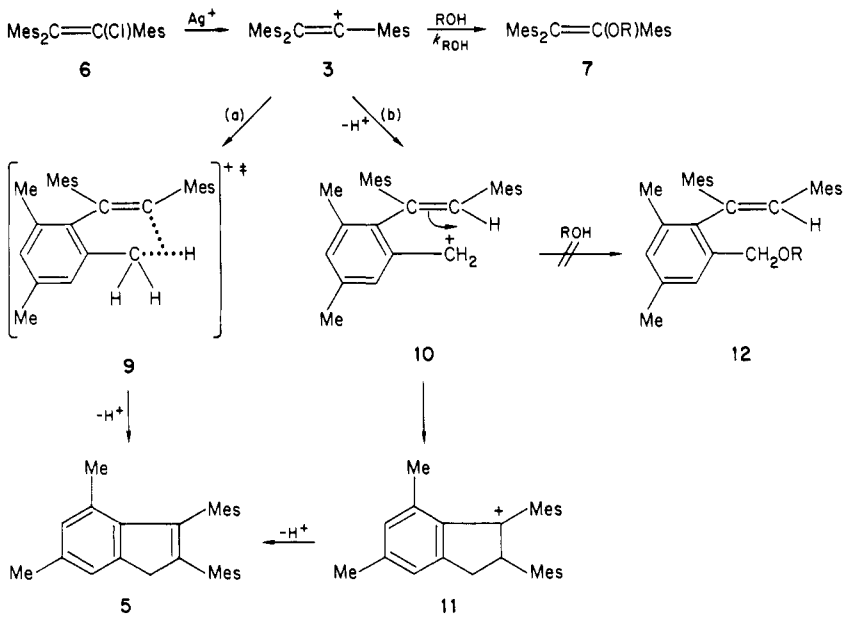
The NMR spectrum of the reaction mixture from **6a** + **6b** + **6c** (Figure 2) leaves no doubt that there is an isotope effect for the formation of **5**. In two different experiments the ratios of the signals by method (i) were 0.24 and 0.25, whereas the ratios were 1.26 and 1.35 by method (ii). The derived k_H/k_D ratios are 1.4 ± 0.1 by method (i) and 1.8 ± 0.2 by method (ii). The average value is taken as k_H/k_D = 1.6 ± 0.4. This result is in contrast with analysis of the sample showed in Figure 2 by chemical ionization mass spectrometry.[15] In this technique the ratio of the molecular ions or the M + 1 ions of the isotopomers, is

(13) Biali, S. E.; Rappoport, Z. *J. Am. Chem. Soc.* **1984**, *106*, 5641.

(14) For a small isotope effect in Me-β-d_9 and Me-α,β-d_{18}-**2** see Biali S. E.; Rappoport, Z.; Hull, W. E. *J. Am. Chem. Soc.* **1985**, *107*, 5450–59.

(15) (a) This experiment was conducted by Prof. H. Schwarz at the Technical University of Berlin. (b) We plan to reinvestigate this question with another sample and instrument.

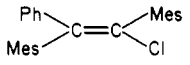
Scheme I



studied, presumably in the absence of isotope effects on mass spectral fragmentation. It was applied by using two ionizing gases. After correcting the observed intensities for the presence of ^{13}C containing species we found that with NO as the ionizing gas, the ratio of the molecular ion peak of **5b** + **5c** at m/z 389 to the molecular ion peak of **5a** at m/z 388 is nearly 2:1. The same is true for the corresponding M + 1 peaks, at m/z 390 and 389 with isobutane as the ionizing gas. Consequently, the [**5b** + **5c**]/[**5a**] ratio calculated from the mass spectra is the statistical ratio of 2:1, i.e., by this analytical technique the cyclization reaction shows no isotope effect.

Although we are unable to reconcile the contrasting results, we believe that the NMR method where inspection of signal intensities shows immediately the presence of an isotope effect is more reliable, whereas the mass spectral method is both "destructive" and involves several assumptions.

Reaction of (*Z*)-1,2-Dimesityl-2-phenylvinyl Chloride. In order to investigate whether cyclization can occur in a less sterically hindered system, (*Z*)-1,2-dimesityl-2-phenylvinyl chloride 8 (the assignment is based on analogy



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with the ^1H NMR of (*E*)- and (*Z*)-1,2-dimesityl-2-phenylvinyl acetates)[6b] was prepared and solvolyzed in the presence of $AgBF_4$ in *t*-BuOH. Preliminary analysis showed that several compounds were formed. The major one is (*Z*)-1,2-dimesityl-2-phenylethenol, which is presumably formed by capture of the vinyl cation by *t*-BuOH, followed by loss of isobutene. A compound which by NMR is 1,2-dimesityl-2-phenylvinyl *tert*-butyl ether was also formed but not investigated further. No indene derivative was detected by NMR.

Discussion

The requirement for an electrophilic assistance by the Ag salt, the formation of capture products, the formation of the indene under superacid conditions, and the linearity of Figure 2 discussed below point unequivocally to trimesitylvinyl cation **3** as an intermediate in the cyclization which forms **5**.[16] We therefore discuss below the mechanism of indene formation and the competing reactions in terms of the generation and the reactions of **3**.

Mechanism of Formation of 5. The **3** → **5** conversion is formally an aliphatic S_E process involving electrophilic attack of the carbenium ion center on a β-*o*-Me group with expulsion of a proton. Electrophilic attacks on carbon–hydrogen bonds in super acids are known from the work of Olah and co-workers.[17] Route a of Scheme I is a possible reaction course via transition state **9** where we use Olah's notation for the three-center two-electron bonds. Cyclization on an unactivated methyl group is the formal analogue of cyclization of systems with β-*o*-NMe_2,[8] β-*o*-OMe,[7] and β-*o*-SMe[7a] groups, except that the σ-electrons of the C-H bond rather than the lone pair electrons of the heteroatom are the nucleophilic center. An alternative is route b, where the *o*-Me group first transfers a hydride ion to the carbocation center of **3** to generate the isomeric benzyl cation **10**. This is probably the rate-determining step of this route, since the following intramolecular electrophilic addition of the cation to the proximate double bond to form the protonated indene **11** and loss of proton from **11** should be rapid processes.

At present we are unable to distinguish between the two routes. Since both involve a rate determining cleavage of a C-H bond, a primary isotope effect is expected for both. The magnitude of the isotope effect shows only that the transition state for the proton transfer is unsymmetrical but not whether it is early or late. Intermolecular hydride transfers between secondary and tertiary carbenium ions and alkanes are generally much faster than the alkylation reaction.[17] If the same applies for our intermolecular variant between the cationic part of the vinyl cation **3** and its benzylic hydrogen, route b seems more likely.

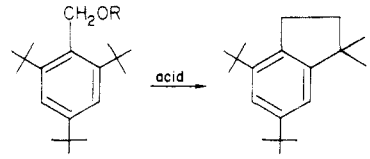
Intermediate **10** may be captured by the nucleophile to give the benzyl ether **12**, but this was not observed. However, capture of **10** requires that the external nucleophilic solvent will compete effectively with the juxta-

(16) Dr. S. Kobayashi from Kyushu University, to whom we are indebted, obtained the spectrum of **3** in MeCN by flash photolysis. It has λ_{max} at 330 and 440 nm with a 2.9 ratio between the corresponding ε values.

(17) E.g., (a) Olah, G. A.; Mo, Y. K.; Olah, J. A. *J. Am. Chem. Soc.* **1973**, *95*, 4939. (b) Olah, G. A.; DeMember, J. R.; Shen, J. *Ibid.* **1973**, *95*, 4952. (c) For a recent review see: Olah, G. A.; Prakash, G. K. S.; Sommer, J. "Superacids"; Wiley-Interscience: Chichester, 1985; pp 270–277.

positioned nucleophilic double bond. Since the latter process may be faster, the absence of **12** cannot serve as evidence against route b.

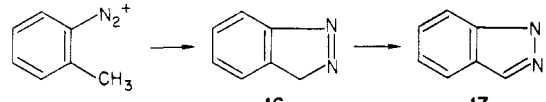
Although the cyclization on the unactivated *o*-Me group is relatively rare, it is not unprecedented. Lewis acids (e.g., BCl_3, HI, or $ZnCl_2$/HCl) catalyze the cyclization of **13**, R = H, Me to the indane **14** (eq 6)[18] in a process which is



(6)

13 **14**

apparently similar to ours. Likewise, the o-methylbenzenediazonium ion **15** cyclizes to the dihydrobenzopyrazole **17** (eq 7)[19] probably via the intermediate **16**, the analogue of **5**. A substituted *o-tert*-butyldiazonium ion first loses nitrogen, and the formed phenyl cation cyclizes on the *tert*-butyl group.[20]



(7)

15 **16** **17**

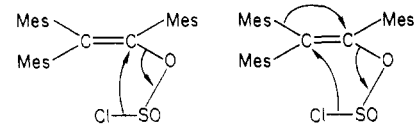
Relative Rates of Cyclization, Capture, and Rearrangement of 3. (a) Capture by ROH vs. Cyclization. The ratio of the capture rate by ROH (k_{ROH}) to the cyclization rate (k_{cyc}) is given by the **7**/**5** ratio. The k_{ROH}/k_{cyc} ratio decreases with the increased bulk of the alcohol. The solvent effect on k_{cyc} should not be large: the positive charge is delocalized on the α-mesityl group and the additional charge delocalization in the transition state of either the hydride transfer or the attack on the C-H bond is not large. Likewise k_{ROH} should not be very sensitive to the solvent polarity since only little extra charge delocalization is achieved in the (presumably) early transition state in the reaction of the carbenium ion with the neutral alcohols. Two additional factors which operate in opposite directions are the solvent nucleophilicity and its bulk. The nucleophilicity of our alcohols in solvolysis reactions changes little, but is higher for the bulkier alcohol as judged by the *N* values of 0.01 (MeOH), 0.09 (EtOH), 0.09 (*i*-PrOH).[21] Steric hindrance to capture, which is important for sterically hindered vinyl cations,[2] should decrease k_{ROH} with the increased bulk of the alcohol. Apparently, this factor is mainly responsible for the decrease of the k_{ROH}/k_{cyc} ratio with the increased bulk of R.

The reaction rate of several α-anisyl-β,β-disubstituted vinyl cations **1**, Ar = An (*p*-$MeOC_6H_4$), with alcohols in acetonitrile was recently studied by Kobayashi, Schnabel, and co-workers by following the decay of the UV spectrum of the vinyl cation.[22] The reactivity order was MeOH > EtOH > *i*-PrOH > *t*-BuOH. A linear relationship was found between the log *k*'s of the reactions of the ions derived from **1**, Ar = R = An and **1**, Ar = An, R = Me. We found that a plot of our log ([**7**]/[**5**]) (which is equivalent to log (k_{ROH}/k_{cyc})) vs. log *k* for the reaction of **1**, Ar = R = An with the alcohols is linear (Figure 2) with a slope of 2.80 and intercept of −14.7 (*r* = 0.9998). This three-points line predicts the absence of *tert*-butyl ether in the reaction of **6** in *t*-BuOH: the extrapolated log ([**7**, R = *t*-Bu]/[**5**]) value is −2.81, leading to predicted [ether]/[indene] ratio of 0.0015 which is below our detection limit.

The linearity of Figure 2 corroborates the assumption of the intermediacy of **3** in the cyclization–capture processes. Although the slope formally indicates that **3** is a more selective intermediate than **1**, Ar = R = An, such a conclusion regarding reactivity–selectivity is unwarranted since the reaction media for the two ions were different.

When the steric hindrance to capture is reduced, as in the 1,2-dimesityl-2-phenylvinyl cation derived from **8**, capture by *t*-BuOH predominates over cyclization.

(b) The Rearrangement, Capture, and Cyclization Rates. The observation of a complete scrambling of the mesityl groups during the formation of **6** from the labeled **2** and $SOCl_2$ excludes a concerted expulsion of SO_2 from the chlorosulfinate ester (transition state **18**) which will not scramble the mesityl groups. Likewise, in a concerted process via chloride attack on C_β (transition state **19**) the



18 **19**

α-mesityl group appears only on C_β of the chloride. Consequently, the migration involves a cationoid intermediate (eq 8). The location of the leaving group is not indicated

$$\underset{\mathbf{3a}}{Mes_2C{=}C^+\text{-}Mes^*} \underset{k_{r(Mes)}}{\overset{k_{r(Mes)}}{\rightleftharpoons}} \underset{\mathbf{3b}}{Mes^*C(Mes){=}C^+{-}Mes} \qquad (8)$$

in this equation since the rearrangement can take place either in the ion pairs $\mathbf{3}\cdot SO_2Cl^-$, $\mathbf{3}\cdot SO_2\cdot Cl^-$, or $\mathbf{3}\cdot Cl^-$ or in the free ion.

There are several examples of degenerate rearrangements in solvolytically generated triarylvinyl cations in protic media.[9] The extent of the rearrangement increases both with the increased electron-donation ability of the aryl groups and with the decreased nucleophilicity of the solvent or of an added nucleophile. A direct comparison of these data with that for **3** is difficult due to the different solvent and conditions for generating the vinyl cation. However, the carbenium ion stabilizing ability of the mesityl group resembles or is even higher than that of the anisyl group, and **3** should be at least as prone to rearrangement as the trianisylvinyl cation, which gives a complete scrambling of the aryl groups in different media.[9a] The effective capture of the trianisylvinyl cation by Br^- which reduces the extent of the rearrangement[9] finds no parallel when **3** was generated in the presence of 0.085 M of Cl^-, although the naked Cl^- in CH_2Cl_2 is presumably more nucleophilic than Br^- in water. We ascribe this behavior to the high steric hindrance to nucleophilic capture by the bulky mesityl substituents. $E \rightleftharpoons Z$ isomerization of the precursor vinyl bromide and common ion rate depression during the solvolysis[2] which indicate capture by Br^- are observed for the trianisylvinyl and the 1,2-dianisyl-2-phenylvinyl cations.[2,23] However, it was not observed for **20** and for **21**, and instead cyclization to the benzo[*b*]furan is observed.[7d] Since a mesityl group should sterically hinder nucleophilic approach more than an *o*-

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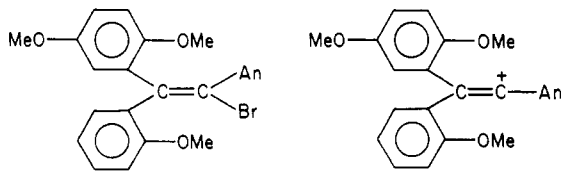

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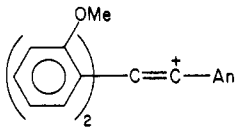

22

methoxyphenyl group the preference for rearrangement (i.e., $k_{r(Mes)}/k_{Cl} \gg 1$) becomes clear.[24]

Although **3** is an intermediate in the formation of **6** < 5% of **5** is observed in the reaction of **2** with $SOCl_2$. Consequently, the hindered capture of Cl^- is still faster than the cyclization, i.e., $k_{Cl} > k_{cyc}$. As shown above, when the weaker nucleophiles than ROH are present, albeit in a large concentration, $k_{ROH} > k_{cyc}$ for the less bulkier alcohols. Consequently, the relative order of the rate constants for processes involving **3** under our conditions is $k_{r(Mes)} > k_{Cl} > k_{ROH} \geq k_{cyc}$.

Comparison of the behavior of the ion **21** or of its analogs such as **22** with that of **3** is therefore of interest. The steric hindrance to capture is lower in **21** and **22** compared with **3**, but the intermolecular oxygen nucleophile is much stronger. Consequently, the following order of rate constants is observed: $k_{cyc} > k_{r(o\text{-}MeOC_6H_4)} > k_{Nu}$ in these species. That cyclization is the fastest process in the *o*-methoxy substituted systems and the slowest for **3** indicates (regardless of whether route a or route b operates) that nucleophilic attack on a juxtapositioned oxygen lone pair is much more favored than attack on the σ C–H bond electrons.

Experimental Section

General Methods. Melting points are uncorrected. The X-ray diffraction of a single crystal of **5** was measured on a PW 1100 Philips four-circle computer-controlled diffractometer equipped with a five focus Mo X-ray tube and a graphite crystal monochrome in the incident beam. ^1H NMR spectra were recorded on a Bruker WH-300 and Bruker WP 200SY pulsed FT spectrometers operating at 300.133 and 200.133 MHz respectively. ^{13}C NMR spectra were recorded on a Bruker WH-300 spectrometer operating at 75.360 MHz. The free induction decay signals were digitized and accumulated on an Aspect 2000 computer.

Solvents and Materials. Benzene was dried by distillation from sodium. The MeOH, EtOH, *i*-PrOH, and *t*-BuOH were analytical reagents. Trimesitylethenol (**2**),[5b] its Me-d_9-α-[5b] and β-[13] analogues, trimesitylvinyl chloride (**6**),[5b] and isopropyl trimesitylvinyl ether (**7**, R = *i*-Pr)[5b] were described previously. Methyl trimesityl vinyl ether (**7**, R = Me) (^1H NMR ($CDCl_3$): δ 1.83, 1.85, 1.87, 1.92, 2.12, 2.22, 2.24, 2.38, 2.57 ((27 H, 9 s, 9Me), 3.24 (3 H, s, OMe), 6.54, 6.60, 6.62, 6.72, 6.87, 6.97 (6 H, 6s, Mes-H) was previously described by Bailey and co-workers,[25] and 1,2-dimesityl-2-phenylethenol was prepared by Fuson.[26]

2,3-Dimesityl-4,6-dimethylindene (5). To a solution of trimesitylethenol (700 mg, 1.76 mmol) in dry benzene (100 mL), 50% NaH in paraffin (100 mg, 2.08 mmol) was added and the mixture was stirred for 3 h under nitrogen. A pink color was developed. Tosyl chloride (400 mg, 2.10 mmol) was added and the stirring was continued for 30 min. The solvent was evaporated and the residue was chromatographed on a silica Woelm column (40 g) using 70% petroleum ether (60 – 80 °C)–30% toluene as the eluent, giving trimesitylethenol (200 mg) and 2,3-dimesityl-4,6-dimethylindene (130 mg, 40% based on reacted **2**). Two crystallizations from petroleum ether 60–80 °C gave the indene as a colorless solid, mp 192–194 °C. ^1H NMR ($CDCl_3$): δ 1.75 (3 H, s, Me in indene), 2.03 (6 H, s, *o*-Me of Mes), 2.09 (6 H, s, *o*-Me of Mes), 2.21, 2.22 (6 H, 2 s, 2 *p*-Me of Mes), 2.38 (3 H, s, indene–Me), 3.65 (2 H, s, CH_2), 6.74 (2 H, s, Mes–H), 6.76 (2 H, s, Mes–H), 6.84, 7.20 (2 H, 2 s, indene–H). The only change in the spectrum when the mixture was cooled to –60 °C was accidental isochronicity of the signals at δ 2.21 and 2.22. ^{13}C ($CDCl_3$): δ 18.15 (Me), 20.81 (2 Me), 20.88 (Me), 21.02 (Me), 21.08 (2 Me), 21.20 (Me), 42.85 (CH_2), 122.24, 128.17, 128.33, 128.61, 130.03, 131.39, 133.86, 133.95, 134.02, 136.17, 136.40, 136.66, 141.01, 141.53, 142.98, 143.71. MS: *m/z* 380 (B, M), 365 (31%, M – Me), 245 (30%, M – Me – MesH).[27] Anal. Calcd for $C_{29}H_{32}$: C, 91.52; H, 8.47. Found: C, 91.84; H, 8.70%.

1,1-Dideuterio-2,3-dimesityl-4,6-dimethylindene (5-*1,1-d*$_2$). To a solution of **5** (15 mg) in THF (1 mL), was added D_2O (2 mL) to which sodium (100 mg) had been previously added. After 39 h reflux the solvent was evaporated and the organic residue was dissolved in C_6D_6 (0.5 mL). The ^1H NMR spectrum was identical with that of **5**, except for a complete absence of the CH_2 signal, indicating a complete exchange of the methylene protons.

Trimesitylvinyl Chloride (6). To a solution of trimesitylethenol (20 mg, 0.05 mmol) in CH_2Cl_2 (6 mL), was added oxalyl chloride (0.2 mL, 2.3 mmol) at room temperature. On addition of one drop of pyridine an immediate evolution of gas was observed. The reaction was followed by TLC and NMR and after 39 h the reaction was complete. After evaporation of the solvent, the ^1H NMR in C_6D_6 was identical with that of trimesitylvinyl chloride, obtained previously from the reaction with thionyl chloride.

Isotopomeric Trimesitylvinyl Chlorides. To α-(2,4,6-tris(deuteriomethyl)phenyl)-β,β'-dimesitylethenol **2b** (15 mg, 0.038 mmol) in CH_2Cl_2 (5 mL), was added thionyl chloride (0.2 mL, 2.7 mmol) and pyridine (0.05 mL, 0.6 mmol), and the yellow mixture was stirred for 15 h at room temperature, after which the reaction was complete by NMR and TLC. A 1:1:1 mixture of the isotopomers **6a:6b:6c** was observed by NMR, together with signals of <5% for isotopomeric **5**. When the reaction was repeated in the presence of benzyltriethylammonium chloride (100 mg, 0.44 mmol) the same 1:1:1 distribution of the isotopomers and of a **6/5** ratio was obtained.

Ethyl Trimesitylvinyl Ester (**7**, R = Et). To a solution of NaOH (5 g, 125 mmol) in water (5 mL) was added trimesitylethenol (150 mg, 0.38 mmol), benzyltriethylammonium chloride (50 mg, 0.22 mmol), and ethyl bromide (5 mL), and the mixture was stirred for 48 h at room temperature. Ether (15 mL) was added, the phases were separated, and the organic phase was washed with water, dried ($MgSO_4$), and evaporated. Crystallization from ether–ethanol gave 132 mg (81%) of ethyl trimesitylvinyl ether, mp 178 °C, with an ^1H NMR identical with that of the compound obtained from cyclization. ^1H NMR ($CDCl_3$): δ 1.12 (3 H, t, J = 7.1 Hz, $MeCH_2$), 1.82, 1.84, 1.86, 1.91, 2.12, 2.22, 2.25, 2.36, 2.56 (27 H, 9 s, 9 Me), 3.34 (2 H, q, J = 7.1 Hz, CH_2Me), 6.52 (1 H, s, Mes–H), 6.60 (2 H, s, Mes–H), 6.71, 6.84, 6.95 (3 H, 3 s, Mes–H).

It is noteworthy that the two diastereotopic methylene protons of the ether give a single quartet, probably indicating an accidental isochronicity. Anal. Calcd for $C_{33}H_{30}O$: C, 87.27; H, 8.98. Found: C, 87.45; H, 8.96.

(*Z*)-1,2-Dimesityl-2-phenylvinyl Chloride (8). To a solution of (*Z*)-1,2-dimesityl-2-phenylethenol (1 g, 2.8 mmol) in toluene (50 mL) thionyl chloride (8 mL, 0.11 mmol), and pyridine (0.2 mL, 2.4 mmol) were added. The solvent was evaporated after 15 h and the residue was dissolved in hot petroleum ether. Recrystallization from petroleum ether gave (*Z*)-1,2-dimesityl-2-phenylvinyl chloride (0.5 g, 48%) mp 148 °C. ^1H NMR ($CDCl_3$): δ 2.29, 2.32, 2.33 (18 H, 3 s, 6 Me), 6.83 (2 H, m, Ph–H), 6.87, 6.95

(24) An extra steric hindrance from one side of **3** can be due to the SO_2 molecule, provided that rearrangement takes place in the $3\cdot SO_2\cdot Cl^-$ species.

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(4 H, 2 s, Mes-H), 7.02 (3 H, m, Ph-H). C_6D_6: δ 2.07, 2.21 (6 H, 2 s, *p*-Me), 2.40 (6 H, s, *o*-Me), 2.42 (6 H, s, *o*-Me), 6.70 (2 H, s, Mes-H), 6.80 (3 H, m, Ph-H), 6.89 (2 H, s, Mes-H), 7.06 (2 H, s, Ph-H). Anal. Calcd for $C_{26}H_{27}Cl$: C, 83.29; H, 7.26. Found: C, 83.03; H, 7.41.

Solvolysis-Cyclization of Trimesitylvinyl Chloride in Alcohols. In an aluminum foil covered ampoule a mixture of trimesitylvinyl chloride (50 mg, 1.25 mmol) and $AgBF_4$ (50 mg, 0.25 mmol) in ROH (R = Me, Et, *i*-Pr, *t*-Bu) (10 mL) was dissolved by heating, and the ampoule was kept at 80 °C for 48 h. The mixture was then poured into water (20 mL) and extracted with $CHCl_3$ (2 × 10 mL), and the organic phase was dried and evaporated. The residue was dissolved in $CDCl_3$ and the **5**/**7** ratio was determined by the relative integration of the indene-CH_2 signal to the methyl group(s) of the alkyl residue of **7**.

In addition, the reaction in *i*-PrOH was conducted on a larger scale: **5** (200 mg, 0.5 mmol) and $AgBF_4$ (200 mg, 1 mmol) in *i*-PrOH (20 mL) were heated in the dark to 110 °C for 24 h. After workup as above, 180 mg of a 85:15 **5**:**7**, R = *i*-Pr (by NMR) was obtained. On a silica TLC plate the R_f's with petroleum ether were 0.3 (**5**) and 0.11 (**7**).

Chromatography on a preparative TLC plate gave **5** (81 mg, 42%), mp 185 °C, and isopropyl trimesitylvinyl ether (17 mg, 8%), mp 167 °C, which was identical with the sample prepared previously by the phase transfer catalysis alkylation of **2**.[5b]

When the reaction of **6** (25 mg, 0.06 mmol) in *t*-BuOH (10 mL) was conducted in the absence of $AgBF_4$ for 96 h at 95 °C, the starting material was recovered unchanged.

Solvolysis of 8 in *tert*-Butyl Alcohol. To a solution of **8** (100 mg) in CCl_4 (0.5 mL) $AgBF_4$ (100 mg) and *t*-BuOH (10 mL) were added, and the mixture was heated in an ampoule in the dark at 95 °C for 48 h. The solvent was evaporated and the residue was dissolved in $CHCl_3$. The organic layer was washed with water, dried, and evaporated. ^1H NMR of the crude reaction mixture showed unreacted **8** and formation of several products. The main product was (*Z*)-1,2-dimesityl-2-phenylethenol[26], identified by ^1H NMR spectrum. The other minor compounds, including one which may be the *tert*-butyl ether (by NMR) were not investigated.

Acknowledgment. We are indebted to Prof. H. Schwarz and Prof. C. Lifshitz for the Cl Mass Spectra of the isotopomeric indenes, to Dr. H.-U. Siehl for the reaction of **6** in superacid, to Dr. S. Cohen for the X-ray diffraction of **5**, to Dr. S. Kobayashi for the UV spectrum of **2**, and to Prof. H. Zollinger for discussions. This work was supported by a grant from the United States-Israel Binational Science Foundation (BSF), Jerusalem, Israel, to whom we are grateful.

Registry No. **2**, 26905-20-4; **5**, 100702-07-6; **5**-*1,1-d*$_2$, 100702-08-7; **6**, 87871-31-6; **7** (R = Et), 100702-09-8; **7** (R = *i*-Pr), 87871-30-5; **8**, 100702-10-1; T_4Cl, 98-59-9; D_2, 7782-39-0; (*Z*)-1,2-dimesityl-2-phenylethenol, 77787-79-2.

Supplementary Material Available: Tables S1-S3 giving the complete list of bond lengths, angles, and positional parameters for carbons of compound **5** and Figure 3 giving the stereoscopic view of **5** (4 pages). Ordering information is given on any current masthead page.

Polydentate Ketal Coronands Containing 2,6-Pyridino and/or 6,6′-(2,2′-Bipyridino) Subunits: Synthesis, Characterization, Structural Aspects, and Conformational Changes upon Complexation

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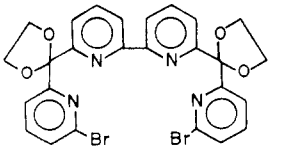
Coronands were formed from 6,6′-bis[2″-(6‴-bromo-2‴-pyridyl)-1″,3″-dioxolan-2″-yl]-2,2′-bipyridine (**1**) and then hydrolyzed to the corresponding diketonic coronands. Comparative data from the X-ray crystal structures of the diketal coronand of bis(2-mercaptoethyl) ether and its Co(II) complex demonstrate that the same conformational preferences are embraced by the ketal assembly in both, but that the bipyridine moiety changes from anti in the coronand to syn in the complex. The Co(II) complex exhibited medium range interactions of *both* ketals *with* the metal and thus a bis-capped tetrahedral geometry.

Introduction

The immediate attachment of an oxygen or sulfur atom to the heteroaromatic ring of a pyridyl coronand subverts the ability of these compounds to engage in metal ion coordination.[1,2] Not only does the presence of an electron-withdrawing group in an α position on the pyridine ring vitiate the donor properties of the nitrogen[1,3] by virtue of the imidate (or thioimidate) function that results,[4] but approach to the N-lone pair is somewhat restricted sterically. The inclusion of a tetrahedral carbon atom between the pyridine and the first bridge heteroatom was envisioned as a solution: flexibility and basicity would be reinstated.[5] 6,6′-Bis[2″-(6‴-bromo-2‴-pyridyl)-1″,3″-dioxolan-2″-yl]-2,2′-bipyridine (**1**)[6] was utilized as the starting material for the construction of the macrocycles, as it contained 2,2′-bipyridine subunit which is a well-known chelating agent.[7] It has been noted in many 2,2-



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