In all cases except 5,5-dimethylbicyclo[2.1.0]pentane, the direction of charge transfer was essentially along the line connecting the bridgehead carbons with the attacking proton. In this case, however, a large component was found to lie along the bond from the bridgehead carbon to the CMe_2 carbon, and this probably accounts for the change in which bond is broken.

The nature of these reactions may then be summarized as follows. Proton transfer is rate determining, and the rate of proton transfer depends on the ease of polarization of one (or more) of the carbon–carbon bonds. The reaction proceeds toward the more stable carbocation, but at the product forming activated complex, the structure has not relaxed to a large degree as indicated by the small role of strain relief. The products are formed in major extent by capture of the protonated species before it becomes an open carbocation, leading to stereoselective capture by the nucleophile, and stereoselective hydrogen migration or loss.

Experimental Section

Materials. The *cis*-bicyclo[*n*.1.0]alkanes were prepared by the addition of methylene to the corresponding cycloalkene.[14] *trans*-Bicyclo[5.1.0]octane and *trans*-bicyclo[6.1.0]nonane[15] were prepared by using published procedures. In each case, the compound was purified by preparative scale gas chromatography. Acetic acid was dried as described previously.[1]

Kinetics. A solution of 0.4740 g of *p*-toluenesulfonic acid monohydrate and 5.623 g of chlorobenzene (internal standard) in acetic acid containing 1% acetic anhydride was prepared. Solutions of the cyclopropanes in this solvent were prepared and small aliquots were sealed into ampules. The ampules were placed in a thermostat and were allowed to equilibrate for 5–10 min. The timer was started, and ampules were removed at appropriate intervals and cooled in ice. They were opened and quenched with sodium acetate in acetic acid. Analysis was performed by GC using either a 50-ft Carbowax 20M or a 30-ft Squalene column and a flame ionization detector. The ratio of unchanged hydrocarbon to internal standard was determined by using a H-P digital integrator.

Isotope Effect. [3.2.1]Propellane reacts with acetic acid at 25 °C with a half-life of about 5 s.[4] Therefore, it was not practical to determine the solvent isotope effect by separate rate measurements. A small sample of **13** was added to a mixture of 48% HOAc and 52% DOAc. The product, 1-bicyclo[3.2.1]octyl acetate was examined by ^{1}H and ^{2}H NMR spectroscopy which indicated 79% d_0 and 21% d_1. The mass spectrum, using chemical ionization, was consistent with this analysis.

Calculations. The ab initio calculations were carried out by using the program GAMESS[16] and standard basis sets.[17] The integration of the wave functions to give electron populations was carried out as previously described.[18]

Registry No. 1, 75-19-4; **2**, 594-11-6; **3**, 1630-94-0; **4**, 4127-47-3; **5**, 185-94-4; **6**, 17065-18-8; **7**, 285-58-5; **8**, 286-08-8; **9**, 16526-90-2; **10**, 21370-66-1; **11**, 13757-43-2; **12**, 39124-79-3; **13**, 19074-25-0; **14**, 38325-64-3; **15**, 53797-19-6; **16**, 27621-61-0.

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Stable Simple Enols. 8.[1] Synthesis and Keto $\rightleftharpoons$ Enol Equilibri of the Elusive 2,2-Dimesitylethanal and 1,2,2-Trimesitylethanone. Conformations of 1,2,2-Trimesitylethanone and 1,2,2-Trimesitylethanol

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Abstract: 2,2-Dimesitylethanal (**2**) and 1,2,2-trimesitylethanone (**4**) were prepared by pyridinium dichromate oxidation of 2,2-dimesitylethanol (**5**) and 1,2,2-trimesitylethanol (**7**), respectively. For **4**, ϵ = 11 000 in hexane at 250 nm, $\delta(^{13}C{=}O)$ = 204.65 ppm, and ν_{CO} = 1688, 1695 cm^{-1}, indicating a substantial conjugation between the α-mesityl and the C=O moieties. The calculated dihedral angle Mes–CO θ is 39° and the observed value in the solid is 48°. Other triarylethanones show similar effects. Consequently, bulky β substituents on crowded α-aryl ketones can reduce, rather than increase, the Mes–CO angle. The conformation of **4** is "bisected" with a H–C–C–O angle of ca. 180°, and the three rings adopt a propeller conformation. At 210 K the two β-mesityl groups of **4** are magnetically equivalent, but the α ring *o*-Me and *m*-H protons and the corresponding carbons are anisochronous. A DNMR study suggests that the rapid rotational process which equalizes the β-mesityl groups is a two-ring flip with $\Delta G_c^{\ddagger} < 9.5$ kcal mol^{-1}. The coalescence of diastereotopic groups on the α-ring gives $\Delta G_c^{\ddagger}$ = 13.8 kcal mol^{-1} for rotation around the Mes–CO bond. Equilibration of **2** and **4** with their enol isomers was followed from both sides in hexane at 353.6 K. The enols consist of >95% in the mixtures and K_{enol} = [enol]/[carbonyl compound] values are 20 ± 1 for **2** and 79 ± 7 for **4**, which are the highest values known for simple enols. They are 9 and 11 orders of magnitude higher than the values for acetaldehyde and acetone. Conformational studies showed that **7** exists in $CDCl_3$ at 223 K as a 1:1.4 mixture of the ap and the sc conformers, whereas X-ray diffraction shows that the solid has the ap conformation. **7** undergoes a dynamic process at room temperature which was briefly studied.

In a keto $\rightleftharpoons$ enol equilibria of simple carbonyl compounds (i.e., those substituted only by aryl and/or alkyl groups or hydrogen), the keto compounds are usually much more stable. The concentrations of the enols are usually so low that they have to be determined indirectly.[2] Several of the simpler enols, including vinyl alcohol, were recently prepared under kinetic control,[3] but

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(2) (a) For a recent review, see: Toullec, J. *Adv. Phys. Org. Chem.* **1982**, *18*, 1. (b) For a review on stable enols, see: Hart, H. *Chem. Rev.* **1979**, *79*, 515.

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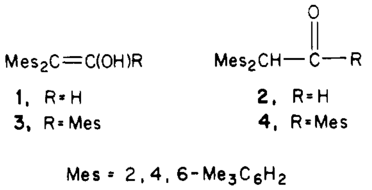
they rapidly rearrange to their carbonyl tautomers.

The relative thermodynamic stability of the enols increases when the double-bond substituents are bulky aryls such as mesityl groups, and stable crowded diaryl- and triarylethenols were prepared a long time ago by Fuson and co-workers.[4] Qualitative[5] and quantitative[6] studies on Fuson's and on closely related enols[7] showed that several of them have similar or even higher stabilities than their isomeric carbonyl compounds. A situation reminiscent of the other extreme side of the keto ⇌ enol equilibria is that highly crowded mesityl-substituted enols of both aldehydes and ketones, e.g., 2,2-dimesitylethenol (**1**)[4a–c] and 1,2,2-trimesitylethenol (**3**),[4d] are the only compounds known of the keto–enol pairs.



$\mathrm{Mes_2C{=}C(OH)R}$ $\quad$ $\mathrm{Mes_2CH{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}R}$

1, R = H $\quad$ **2**, R = H

3, R = Mes $\quad$ **4**, R = Mes

Mes = 2,4,6-$\mathrm{Me_3C_6H_2}$

Indeed, some of the methods used for the preparation of **1**, e.g., the acid-catalyzed pinacol rearrangement of MesCH(OH)CH(OH)Mes, should lead to the corresponding aldehyde, 2,2-dimesitylethanal (**2**). An attempted ketonization of **1** in ROH/HCl gave the 2,2-dimesityl-1-enol ethers rather than **2**, and it was reported that "there is, in particular, no evidence of the presence of the aldehyde in solution of the enol".[4b] Oxidation of the saturated alcohol 2,2-dimesitylethanol (**5**) gave rearranged 1,2-dimesitylethane and ethene derivatives, but not **2**.

Likewise, trimesitylethenol (**3**) could not be ketonized by acid or by base to 1,2,2-trimesitylethanone (**4**).[4d] Condensation of dimesitylacetyl chloride with mesitylmagnesium bromide or with mesitylene, and other synethetic methods, failed to give **4**. Very recently it was suggested that the photoproducts formed by irradiation of **3** arise from its initial isomerization to **4**,[8] but **4** was not detected.

Our previous studies on the keto ⇌ enol equilibria of crowded polyaryl systems[6] suggested that **2** and **4** should be less stable than **1** and **3**, but that they may be detected and even isolated from the equilibrium mixtures with the enol isomers. Moreover, the high kinetic barrier to enolization of related compounds[6] suggested that once **2** and **4** are formed they will be relatively stable to enolization and hence could be isolable. We were successful in preparing these elusive carbonyl derivatives; their synthesis, the keto ⇌ enol equilibria, and the conformation of **4** and its DNMR behavior, as well as the conformations of 1,2,2-trimesitylethanol (**7**), the precursor of **4**, are described below.

Results and Discussion

Synthesis of 2 and 4 from the Saturated Alcohols. Both **2** and **4** were prepared by oxidation of the corresponding alcohols. Since both acid and base were assumed to isomerize them to **1** and **3**, the key for the success of the syntheses was the use of a neutral oxidation reagent—pyridinium dichromate (PDC).[9]

Reduction of dimesitylacetyl chloride (**6**) with $\mathrm{LiAlH_4}$ in THF yielded 2,2-dimesitylethanol (**5**). Oxidation of **5** with PDC in $\mathrm{CH_2Cl_2}$ for 48 h yielded **2** in 70% yield (eq 1). The aldehyde

$$\underset{\mathbf{6}}{\mathrm{Mes_2CHCOCl}} \xrightarrow{\mathrm{LiAlH_4}} \underset{\mathbf{5}}{\mathrm{Mes_2CHCH_2OH}} \xrightarrow{\mathrm{PDC/CH_2Cl_2}}$$

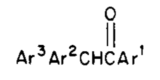
$$\underset{\mathbf{2}}{\mathrm{Mes_2CHCHO}} \xrightarrow{\mathrm{MesLi/THF}} \underset{\mathbf{7}}{\mathrm{Mes_2CHCH(OH)Mes}} \xrightarrow{\mathrm{PDC/DMF}} \underset{\mathbf{4}}{\mathrm{Mes_2CHCOMes}} \quad (1)$$

2 is the precursor of **4**. Reaction of **2** with a molar equivalent of mesityllithium at 0 °C yielded 1,2,2-trimesitylethanol (**7**), the saturated analogue of **3**. Oxidation of **7** with PDC in DMF at room temperature for 4 days gave **4** in 82% yield (eq 1).

Since the dynamic NMR study of **4** and **7** required an unequivocal assignment of the signals of the α-mesityl group, the α-mesityl-*methyl*-d_9 analogues **8** and **9**, containing 98.4% deuterium at the methyl groups as determined by NMR, were synthesized in an analogous way to eq 1, by using mesityl-*methyl*-d_9-lithium. The less crowded related ketones **10**–**13** were prepared by known methods.[10]

$$\underset{\mathbf{8}}{\mathrm{Mes_2CHCH(OH)Mes^*}} \qquad \underset{\mathbf{9}}{\mathrm{Mes_2CHCOMes^*}}$$

$$\mathrm{Mes^*} = 2,4,6\text{-}\mathrm{(CD_3)_3C_6H_2}$$



$\mathrm{Ar^3Ar^2CH\overset{\overset{\displaystyle O}{\|}}{C}Ar^1}$

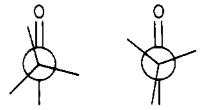
10, $\mathrm{Ar^1 = Ar^2 = Ar^3 = Ph}$

11, $\mathrm{Ar^1 = Ph;\ Ar^2 = Ar^3 = Mes}$

12, $\mathrm{Ar^1 = Mes;\ Ar^2 = Ar^3 = Ph}$

13, $\mathrm{Ar^1 = Ar^2 = Mes;\ Ar^3 = Ph}$

Spectral Properties and Conformations of Triarylethanones. Two main questions related to the conformation of **4** and related ketones are the torsional HC–CO and Mes—C=O angles and the possibility of a propeller arrangement of the three mesityl rings. The structures of aliphatic ketones are discussed in terms of two conformations.[11] The conformation of not very bulky ketones is **14**, where the carbonyl group is eclipsed by a C–H or a C–R bond. In contrast, the carbonyl group of hindered ketones is bisected by the α-bulky group, as shown in **15**. However, a search of the Cambridge Structural Data Base showed that no X-ray diffraction study of any 1,2,2-triarylethanone was yet reported,[12] and we are unaware of a conformational analysis of these ketones in solution. Consequently, we used four probes for determining the conformation of **4** and other triarylethanones.



14 **15**

X-ray Crystallography. This method answers simultaneously all the conformational questions, and its only drawback is that the information is for the solid-state conformation. The structures of **4** and **13** were therefore determined by X-ray diffraction, and although the details will be given elsewhere,[13] the following features are relevant. (i) The three rings are all twisted in the same sense; i.e., they are in a "propeller" arrangement.[14] (ii) The solid-state

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(8) Hart, H.; Giguere, R. J. *J. Am. Chem. Soc.* **1983**, *105*, 7775.

(9) PDC: pyridinium dichromate: Corey, E. J.; Schmidt, G. *Tetrahedron Lett.* **1979**, 399. See warning in the experimental section.

(10) Compound **10**: Staudinger, H. *Ber.*, **1907**, *40*, 1145. Compound **11**: ref 5. Compound **12**: Fuson, R. C.; Armstrong, M. D.; Fischer, C. H.; Rabjohn, N.; Ullyot, G. E.; Wallace, W. E. *J. Am. Chem. Soc.* **1946**, *68*, 343. Compound **13**: Fuson, R. C.; Armstrong, L. J.; Kneisley, J. W.; Shenk, W. J. *Ibid.* **1944**, *66*, 1464.

(11) Dubois, J.-E. *Pure Appl. Chem.* **1977**, *49*, 1029.

(12) This search was conducted by Dr. M. Kaftory from the Technion in Haifa, Israel.

(13) Kaftory, M.; Biali, S. E.; Rappoport, Z. *J. Am. Chem. Soc.*, in press.

(14) The torsional angles are defined by the H–C–$\mathrm{C_{ipso}}$–$\mathrm{C_{ortho}}$ atoms for the β rings, and by the O–C–$\mathrm{C_{ipso}}$–$\mathrm{C_{ortho}}$ atoms for the α ring (cf. ref 44 for a similar definition in tetraarylethanes).

Table I. Some Spectroscopic Data Relevant to the Conformation of Triarylethanones and Related Compounds

compd	λ_{max}(hexane), nm (ϵ)	δ(^{13}C=O) (CDCl$_3$), ppm	ν_{CO}(CCl$_4$), cm^{-1}	θ,[c] deg	θ,[d] deg
10	217 sh (14 000)[a] 245 (11 000)[b]	198.16	1694		32
11	231 (23 400)[a] 245 sh (13 600) 270 (4100)	201.28	1692		19
12	248 (7600)[a]	207.00	1699, 1703		50
13	240 (13 200)[a]	204.68	1699, 1703	67	32
4	250 (11 000)[a,e]	204.05	1688, 1695	48	39
2	220 (19 100) 268 (1200)	199.32	1714, 1729		
5	219 (17 800) 260 (800)				
7	219 (26 300) 256 (1400)				

[a] λ_{max} values below 216 nm are not given. [b] λ_{max}(EtOH) 248 nm (13 500): Rinderknecht, H. *J. Am. Chem. Soc.* **1951**, *73*, 5770. [c] Torsional angle of the α-mesityl ring as determined by X-ray diffraction. [d] Torsional angle calculated from Braude's equation.[15] [e] λ_{max}(MeOH) 221 nm (24 300), 252 (10 200).

conformation is **15**,[11] with an HC–CO torsional angle near 180°. (iii) The Mes—C=O torsional angles are 67° for **13**, but only 48° for **4**.[11]

Assuming that the preferred conformation in solution is identical with that in the solid, i.e., **15**, the degree of conjugation between the carbonyl and the α-mesityl group was studied in solution using three different techniques: UV spectra, and ^{13}C and IR spectra of the C=O group. The related ketones **10–13** were investigated both as references and in order to find a relationship between the bulk of the aryl groups and the spectral properties. The data are summarized in Table I.

UV Spectra. The UV spectrum of **4** is of special interest. In a classical work Braude and co-workers[15] had shown that the ϵ values of the K band of substituted benzaldehydes and acetophenones decrease strongly with the increased *o*-methyl substitution. After calculating the expected ϵ value (ϵ_0) for the hypothetical planar system by correction for the increase in ϵ by the electronic effect of the methyl groups, the ratio of the observed to calculated ϵ's was used to calculate the torsional angle between the aryl and the C=O planes from the equation $\epsilon/\epsilon_0 = \cos^2 \theta$.[15] This angle was calculated to be 22° for mesitylaldehyde (ϵ = 14 000 for PhCHO and 14 500 for MesCHO), but 63° for acetylmesitylene, since ϵ/ϵ_0 was equal to 0.20.

A remarkable result is that ϵ for **4** at 250 nm in hexane is 11 000, a much higher value than for acetylmesitylene and higher than ϵ for 2-methylacetophenone, in spite of the expected higher steric hindrance to planarity caused by the very bulky Mes$_2$CH moiety. For an approximate calculation of θ, the contributions to ϵ by the Mes$_2$CH and by the *o*- and *p*-methyl groups of the α-mesityl ring should be evaluated. Following Braude, a contribution to the ϵ of 1000 L mol^{-1} cm^{-1} by each methyl group was taken, whereas the contribution of the Ar$_2$CH group to the ϵ was taken as 1200 L mol^{-1} cm^{-1} (i.e., ϵ_0 = 18 200).[16] Consequently, ϵ/ϵ_0 = 0.60 and θ = 39°. In order to obtain the calculated θ value of 48° from the UV data ϵ_0 should have the unreasonable high value of 24 600; i.e., each methyl will have to contribute 3000 L mol^{-1} cm^{-1} to the ϵ.

The unusually high ϵ value is unlikely to be due to an intramolecular charge transfer between the Mes$_2$CH and the carbonyl moieties as shown by the low ϵ of **2** which also contains both functionalities, and by the lack of any appreciable solvent effect on both λ and ϵ by changing the solvent from hexane to methanol (Table I). Moreover, the low ϵ values at 256 nm for **7** and at 268 nm for **2** indicate that the high ϵ at 250 nm for **4** is indeed due to the MesCO moiety. The UV spectra of the triarylethanones **10–13** (Table I) also display high ϵ values of >7600, which are higher than ϵ for acetylmesitylene.

Assuming that Braude's relationship is valid and that the high ϵ values reflect a lower torsional Ar–CO angle in **4** and **10–13** than in acetylmesitylene, the order of the ϵ values is illuminating. The lowest value is for **12** where the Ar^{3}Ar^{2}C group is the least bulky, while the highest value is for **11** where this group is the most bulky. Consequently, it seems that steric interactions between the aryl groups on C$_\alpha$ and C$_\beta$ result in a decrease of Ar–CO torsional angles, increased coplanarity, and hence increased conjugation.[17]

Calculations similar to those above give the θ values of Table I and show the limitation of the UV method. For example, the θ values for **10** and **13** are similar, although the α-aryl group in **13** is bulkier. Likewise, the higher ϵ for **13** compared with **4** is consistent with the lower calculated θ, in contrast with the results of the ^{13}C and X-ray data (Table I). However, in **13** the band of interest appears as a shoulder, with a consequent large error in ϵ.

^{13}C Carbonyl Chemical Shifts. The extent of conjugation between the α ring and the carbonyl group should also be reflected in the ^{13}C chemical shifts of the latter. It was shown that δ(C=O) values are lower for the more conjugated and delocalized system.[18] Moreover, a linear correlation exists between δ(^{13}C=O) of substituted acetophenones and the $\cos^2 \theta$ values calculated from UV data.[19] The δ(^{13}C=O) values given in Table I for **4** and **10–13** behave qualitatively similarly to the UV spectra. The lowest field carbonyl is for **12**, the ketone with the lowest ϵ, whereas **11** with the highest ϵ shows the second highest δ(^{13}C=O). The δ value for **4** is between the extremes and is close to that of **13**, but small differences (such as between **4** and **13**) will not be discussed since ring currents as well as polar effects could be responsible for them. Comparison of the pairs of ketones **10–11** and **12–4** is interesting. The change β-Ph$_2$C $\rightarrow$ β-Mes$_2$C leads to a 3-ppm downfield shift in the pair **10–11**, but to a similar upfield shift for the **12–4** pair. We ascribe the latter shift to a decrease in the torsional Mes–CO angle in **4** compared with that in **12**.

IR C=O Stretching. The IR stretching frequencies of the carbonyl group reflect conjugation effects, and conjugated ketones absorb at lower wavenumbers than nonconjugated ones. The IR spectra given in Table I were taken in dilute solutions (7.1 mM) in CCl$_4$. Most of the ketones showed two absorptions which are completely resolved only for **2**.[20]

If an average of the two absorptions is taken, the order of ν_{CO} is **11** < **10** < **4** < **12**, **13**. This is the order of decreased conjugation, as obtained from the UV spectra. The lowering of the frequencies of the C=O stretching on increasing the steric crowding around the C=O group finds precedent in the spectra of heavily crowded aliphatic ketones.[11,21]

Consequently, all the spectroscopic evidence points to an interesting conclusion. In contrast with acetylmesitylene where a θ value of 60–90° was calculated by using lanthanide shift reagents,[22] or with 2,4,6-trimethyl-3-pivaloylbenzoic acid where an angle of 89.9° was found by X-ray diffraction,[23] bulky β-aryl substituents in triarylethanones reduce the Ar–CO torsional angle. Specifically in **4**, the steric interactions between the α- and β-aryl

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(15) (a) Braude, E. A.; Sondheimer, F. *J. Chem. Soc.* **1955**, 3754. This article was cited over 220 times in the period 1961–1984. (b) Braude, E. A.; Sondheimer, F.; Forbes, W. F. *Nature (London)* **1954**, *173*, 117.

(16) The use of ϵ = 1200 for the Mes$_2$CH moiety is based on the ϵ of **2**. The ϵ for **7** is somewhat higher because of the α-Mes group. ϵ values of ca. 1000 were found for Mes$_2$CHCOR, R = Me, *i*-Pr (Nugiel, D. A., unpublished results).

(17) In order to find precedents for this unusual behavior, an extensive literature search of the last 14 years was made. No precedents were found.

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Table II. NMR Data (δ in ppm) and Assignments[a] for 4 and the Two Conformers of 7[b]

4, ^{1}H NMR	4, ^{13}C NMR[d]	$-sc$-7, ^{1}H NMR	ap-7, ^{1}H NMR
1.98 (4B)	20.72 (β-p-Me)	1.61 (A)	1.56 (B)
2.00 (A)	21.18 (α-Me)	1.68 (B)	1.72 (A)
2.24 (2D)	21.25 (α-Me)	2.06 (B)	1.89 (B)
2.30 (C)	21.40 (α-Me)	2.13 (B or D)	1.94 (B)
2.36 (A)	22.52 (β-o-Me)	2.24 2.26 } (2B or D and C)[c]	2.15 (A)
5.81 (C*H*CO)	58.30 (CHCO)	2.65 (A)	2.24 2.26 } (3C and D)[c]
6.81 (4F)	128.85 (α-Mes-*C*-H)	2.89 (B)	2.32 (OH)[d]
6.87 (E)	130.19 (α-Mes-*C*-H)	5.17 (C*H*Mes$_2$)[e]	3.00 (B)
6.93 (E)	130.54 (β-Mes-*C*-H)	6.02 (C*H*OH)[e]	4.81 (C*H*Mes$_2$)
	130.30 (β-Mes-C_{ipso})	6.53 (F)	6.16 (C*H*OH)
	134.98 (α-Mes-o- or -p-C)	6.56 (E)	6.69 (E)
	135.92 (β-Mes-p-C)	6.60 (F)	6.76 6.79 } (3F)[c]
	137.47 (β-Mes-o-C)	6.76 6.79 } (F)[c]	6.85 (E)
	138.50 (α-Mes-o- or -p-C)	6.83 (E)	6.93 (F)[c]
	138.90 (α-Mes-C_{ipso})	6.93 (F)[c]	
	140.02 (α-Mes-o- or -p-C)		
	204.05 (C=O)		

[a] A = α-o-Me; B = β-o-Me; C = α-p-Me; D = β-p-Me; E = α-Mes-H; F = β-Mes-H. [b] All the signals are singlets unless otherwise indicated. [c] Overlapping signals. [d] d: ^3J(HCOH) = 10.2 Hz. [e] d: ^3J(HCCH) = 11.5 Hz.

groups are partially relieved by reducing the Mes–CO torsional angle. This is manifested by higher UV absorption and lower $\delta(^{13}C{=}O)$ and ν_{CO} values, as well as in the rotational barrier (vide infra).

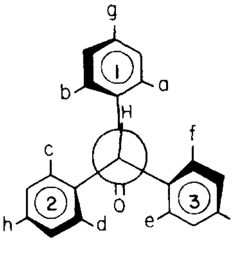
Hence, the broad generalization based on Braude's and related results, as well as on chemical intuition, that the bulkier are the α and β substituents the lower is the Ar–CO conjugation, should not be taken without reservation. The present work shows that when the β-Ar substituents become bulkier, the most stable conformation may be one where Ar–CO planarity is enhanced at the expense of changes in other torsional angles or bond lengths in the molecule.

Dynamic NMR Study of 4. The NMR spectra of the enols **1** and **3** show restricted rotation around the =C—Mes bonds and their DMR's were extensively studied.[24,25] The corresponding rotations in **2** and **5** are not restricted under our experimental conditions since the ^{1}H NMR spectra of both compounds show only one aromatic protons signal and one signal for the o-Me groups even at 210 K in CD_3COCD_3. In contrast, the spectrum of **4** shows temperature dependence and a coalescence phenomenon, and its DNMR behavior was therefore studied. In the following discussion we will assume that the preferred conformation in solution is identical with that of the crystal of **4** and **13**; i.e., the carbonyl group is bisected by the β rings as in **15** and the rings exist in a helical propeller conformation.

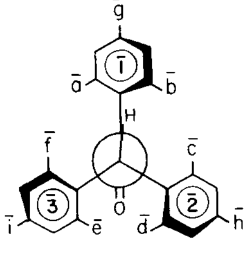
The ^{1}H 300-MHz NMR of **4** in CD_2Cl_2 at 200 K shows five signals in the methyl region in a 4:1:2:1:1 ratio, a methinic proton at δ 5.81, and three aromatic protons signals in a 4:1:1 ratio. An unequivocal assignment of the methyl and the aromatic singlets of the α-mesityl ring was obtained by comparing the spectra of **4** and **9**. The assignments (Table II) are based on the disappearance of the methyl signals of the α ring in the spectrum of **9**, and on the appearance of the α-ring protons of **9** as doublets with J = 2.0 Hz characteristic of meta coupling.[26] The remaining aromatic signals (as well as all the aromatic signals of **4**) appear as somewhat broad singlets due to the additional long-range coupling with the methyl group,[27] a coupling which is removed by deuteration. A noteworthy feature of the ^{1}H NMR spectrum is that all the signals of the α ring are at a lower field compared with those of the β rings. The $\Delta\delta$ of two α-o-Me groups of 0.36 ppm is understood by inspection of space-filling molecular models. In its frozen conformation one o-Me group of the twisted α ring is close to the shielding region of the carbonyl group, while the other o-Me is near the deshielding region of a β-mesityl ring.

The proton noise-decoupled ^{13}C NMR of **4** determined in $CDCl_3$ at 223 K displays 17 signals: 5 in the methyl region, 1 methinic carbon, 10 aromatic carbons, and 1 carbonyl carbon. In the corresponding spectrum of **9** the three central methyl carbon signals vanish because of (i) an increase in the relaxation times of the carbons, (ii) a diminution of the nuclear Overhauser effect, and (iii) the splitting to seven peaks,[28] thus identifying them as methyl carbons of the α-mesityl ring. The relative intensities of the two other methyl signals assign them as due to the p- and the o-β-Me groups. The three higher field aromatic signals are assigned to the C–H carbons, the lower field carbons are due to the α ring, and those in the middle belong to either of the β rings. The broadening of the α-ring signals of **9** compared with those of **4**, and the relative intensities, gave the assignments of Table II.

An important conclusion drawn from both the ^{1}H and ^{13}C NMR spectra is that while each of the four β-o-CH_3 groups, four β-o-C, four β-Mes-H, four β-m-C, two β-p-C, and two β-ipso carbons appear as a singlet, pairs of signals (o-C, m-C, o-CH$_3$, o-CH_3, m-H) corresponding to the α ring remain anisochronous. Hence pairs of signals in the α ring of **4** present at low temperature residual diastereotopism.[29] Consequently, a rapid dynamic process on the NMR time scale averages the signals for the β-mesityl rings, but not those of the α ring. In order to analyze the different processes that could lead to coalescence of the signals of the β-mesityl rings, we label the nine methyls in one enantiomer of **4**, i.e., **4a** by the letters a–i, and the groups in enantionmeric sites



4a



4b

in **4b** by the same letters with an overbar (i.e., $\bar{a}$–$\bar{i}$).

Following Mislow[30] Table III analyzes the different rotational mechanisms (flip and nonflip) and the sites exchanged by each of them. In the "flip" routes,[31] zero, one, two, or all three rings

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[24] Nugiel, D. A.; Biali, S. E.; Rappoport, Z. *J. Am. Chem. Soc.* **1984**, *106*, 3357.

[25] Biali, S. E.; Rappoport, Z. *J. Am. Chem. Soc.* **1984**, *106*, 477.

[26] Günther, H. "NMR Spectroscopy"; Wiley: Chichester, 1980; pp 384–385.

[27] Literature value: ^4J(HMe) $\sim$ 0.75 Hz.[26]

[28] Abraham, R. J.; Loftus, P. "Proton and Carbon-13 NMR Spectroscopy, an Integrated Approach"; Heyden: London, 1978; p 146.

[29] (a) Finocchiaro, P.; Gust, D.; Mislow, K. *J. Am. Chem. Soc.* **1974**, *96*, 3205. (b) Finocchiaro, P.; Hounshell, W. D.; Mislow, K. *Ibid.* **1976**, *98*, 4952.

[30] Gust, D.; Mislow, K. *J. Am. Chem. Soc.* **1973**, *95*, *1535*.

[31] (a) Kurland, R. J.; Schuster, I. I.; Colter, A. K. *J. Am. Chem. Soc.* **1965**, *87*, 2279. (b) Mislow, K. *Acc. Chem. Res.* **1976**, *9*, 26.

Table III. Sites Exchanged by Flip and Nonflip Rotational Routes for **4a**

ring flip route	flipping ring(s)[b]	site exchanged[a]	rotating ring(s)[c]	site exchanged[a]
zero ring	[0]	(ab̄)(bā)(cf̄)(dē)(ed̄)(fc̄)(gḡ)(hī)(ih̄)	[0]	(aa)(bb)(cc)(dd)(ee)(ff)(gg)(hh)(ii)
one ring	[1]	(aā)(bb̄)(cf̄)(dē)(ed̄)(fc̄)(gḡ)(hī)(ih̄)	[1]	(ab)(ba)(cc)(dd)(ee)(ff)(gg)(hh)(ii)
	[2]	(ab̄)(bā)(cē)(df̄)(ed̄)(fc̄)(gḡ)(hī)(ih̄)	[2]	(aa)(bb)(cd)(dc)(ee)(ff)(gg)(hh)(ii)
	[3]	(ab̄)(bā)(cf̄)(dē)(ec̄)(fd̄)(gḡ)(hī)(ih̄)	[3]	(aa)(bb)(cc)(dd)(ef)(fe)(gg)(hh)(ii)
two ring	[1,2]	(aā)(bb̄)(cē)(df̄)(ed̄)(fc̄)(gḡ)(hī)(ih̄)	[1,2]	(ab)(ba)(cd)(dc)(ee)(ff)(gg)(hh)(ii)
	[1,3]	(aā)(bb̄)(cf̄)(dē)(ec̄)(fd̄)(gḡ)(hī)(ih̄)	[1,3]	(ab)(ba)(cc)(dd)(ef)(fe)(gg)(hh)(ii)
	[2,3]	(ab̄)(bā)(cē)(df̄)(ec̄)(fd̄)(gḡ)(hī)(ih̄)	[2,3]	(aa)(bb)(cd)(dc)(ef)(fe)(gg)(hh)(ii)
three ring	[1,2,3]	(aā)(bb̄)(cē)(df̄)(ec̄)(fd̄)(gḡ)(hī)(ih̄)	[1,2,3]	(ab)(ba)(cd)(dc)(ef)(fe)(gg)(hh)(ii)

[a] Letters (a–i, ā–ī) in each bracket indicate the corresponding site-exchanging groups. [b] Numbers in square brackets indicate the flipping ring(s). [c] Numbers in square brackets indicate the rotating ring(s).

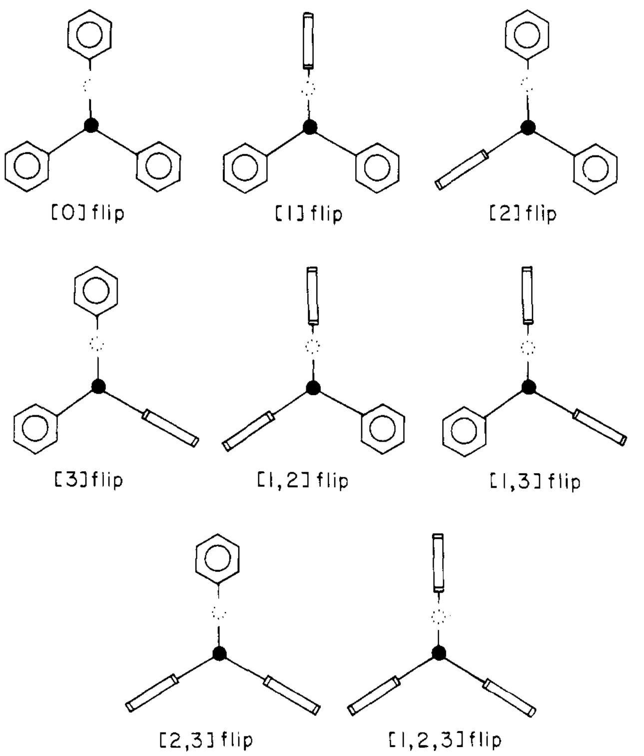
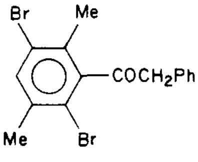


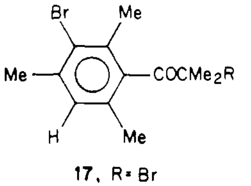
Figure 1. Idealized transition states for the different flip mechanisms for **4**. A solid circle denotes the methinic hydrogen pointing to the observer, and a dotted circle denotes the carbonyl oxygen pointing away from the observer.

flip, i.e., rotate in such a way that the dihedral angle (C_{ortho}–C_{ipso}–C–H or C_{ortho}–C_{ipso}–C=O) passes through 0°, while the nonflipping rings rotate in the opposite direction so that the dihedral angle passes through 90°. The ideal transition states for the different flip mechanisms are depicted in Figure 1. All the flip mechanisms involve helicity reversal while the nonflip routes (which involve rotation of 180° around the C–Mes bond(s)) retain the helicity.

It could be readily deduced from Table III that the rapid rotational process at 200 K could not be due to any of the nonflip routes since these routes do not involve helicity reversal, and hence each pair of signals belonging to rings 2 and 3 should show residual diastereotopism.[29] Of the flip mechanisms, the only single-flip routes which could be consistent with the experimental spectrum are the two enantiomeric [1,2] or [1,3] ring flips.[32] A combination of a [1] and a [1,2,3] ring flip is also consistent with the NMR data. Assuming a $\Delta\nu$ value of 20 Hz (under slow-exchange conditions) for a pair of coalescing signals and a coalescence temperature of <190°K, use of the Gutowsky–Holm approximation[33] and the Eyring equation gives an upper limit to the barrier of 9.5 kcal mol^{-1}. The barrier is lower than the barrier reported by Nakamura and Ōki for the internal rotation in the less crowded aryl benzyl ketone **16** ($\Delta G_c^{\ddagger}$ = 12.4 kcal mol^{-1} in pyridine–CS_2).[34]



16



17, R = Br
18, R = Me

The low barrier for the rotational process in **4** (which involves passage through a planar Mes–CO arrangement)[35] can be rationalized in terms of steric effects. The presence of the two β-mesityl rings decreases the Mes–CO torsional angle, thus raising the ground-state energy. A similar explanation was given for the lower barrier of **17**, compared with **18**.[36] The $\delta(^{13}C{=}O)$ values (207 ppm for **17** and 217.4 pm for **18**) are consistent with a lower torsional Ar–CO angle for **17**.[36]

When the temperature was raised, each of the pairs of α-o-Me and α-Mes-H protons coalesced to a singlet. From the coalescence data of the α-mesityl protons ($\Delta\nu$ = 7.8 Hz, T_c = 262 K) and of the ortho methyl groups ($\Delta\nu$ = 142 Hz, T_c = 295 K), a barrier of 13.8 ± 0.1 kcal mol^{-1} for rotation around the Mes–CO bond was calculated. The process observed could be either a [0], [2], [3], or [2,3] ring flip, or any nonflip mechanism involving a 180° rotation of the α ring. Since no information can be extracted from the β-mesityl pattern, we are unable to distinguish between these alternatives.

Keto ⇌ Enol Equilibria. In a preliminary attempt to obtain **2** and **4**, the enols **1** and **3** were equilibrated in hexane in the presence of a catalytic amount of CF_3COOH. Although the keto forms were detected by ^1H NMR[37] (see below), their relative concentrations were so low that attempts for their isolation from the equilibrium mixtures were abandoned when we succeeded to prepare them by the method of eq 1. The availability of both **1** and **2** and **3** and **4** presented a rare opportunity for a quantitative study of the enol ⇌ keto equilibria starting from both precursors and monitoring directly their concentrations. The equilibria were therefore followed from both sides in hexane at 353.6 K until the same equilibrium mixtures were obtained. No catalyst was applied for the **1** ⇌ **2** equilibration, and the equilibrium ratio was obtained after 48 h. However, the **3** ⇌ **4** isomerization was much slower and a catalytic amount of CF_3COOH was necessary in order to obtain the equilibrium mixture in a reasonable reaction time. The

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[32] Since the two β rings are not symmetry equivalent, they should be characterized by different torsional angles. However, since the transition states for the [1,2] and the [1,3] ring flips are enantiomeric, they are of the same energy and therefore they are indistinguishable in an achiral medium.

[33] Gutowsky, H. S.; Holm, C. H. *J. Chem. Phys.* **1956**, *25*, 1228.

[34] Nakamura, N.; Ōki, M. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 2565.

[35] For a Mes–C=O fragment in which the torsional angle differs from 0 and 90°, two different transition states can be envisioned. In one, the carbonyl group passes through a plane perpendicular to the mesityl ring (a 90° barrier), and, in the other, it becomes coplanar with the mesityl ring (a 0° barrier). If the molecule exists in a propeller conformation, our results indicate that the 0° barrier for the correlated rotation is lower than the 90° barrier.

[36] Holík, M.; Mannschreck, A. *Org. Magn. Reson.* **1979**, *12*, 28.

[37] Likewise, by prolonged standing of **3** in the presence of CF_3COOH, a carbonyl absorption that could be due to **4** was detected by IR (H. Hart, personal communication.

composition of the equilibrium mixtures was determined by 300 MHz ^{1}H NMR and was used for calculating the K_{enol} values (eq 2). The values are 20 ± 1 and 79 ± 7 for the **1**–**2** and **3**–**4** pairs,

$$K_{enol} = [\text{enol}]/[\text{carbonyl compound}] \qquad (2)$$

respectively. The corresponding $\Delta G°$ values are -2.1 ± 0.1 and -3.1 ± 0.1 kcal mol^{-1}. The presence of 5% of **2** and 1.2% of **4** in their equilibrium mixtures with the carbonyl compound is consistent with the difficulty in isolating them in the previous work.[4b,d] *These K_{enol} values are the highest known for either simple aldehydes or simple ketones.* It is obvious that the high values are largely due to the presence of the bulky mesityl groups, and four points are noteworthy in this connection. (i) The K_{enol} values were determined in an apolar nonprotic solvent, and they are expected to be higher in a more polar, hydrogen bond accepting solvent (e.g. water), as found for K_{enol} values for closely related species.[7,38] (ii) The K_{enol} values extend enormously the region of known K_{enol} values for simple enols. The ΔK_{enol} for a change from CH_3CHO and CH_3COCH_3 to Mes_2CHCHO and $Mes_2CHCOMes$ are ≥9 and 11 orders of magnitude, respectively, if a moderate increase in K_{enol} by a factor of 10 is assumed for the solvent change hexane → water. (iii) The K_{enol} value for the aldehyde (**1**–**2** pair) is higher than the K_{enol} values for the $MeS_2CHCOR \rightleftharpoons Mes_2C{=}C(OH)R$ equilibria when R = Me, Et, *i*-Pr, *t*-Bu.[39] This is parallel to the behavior of the K_{enol} values of the simpler systems CH_3COR, R = H, Me.[2a] (iv) The sterically hindered 1,2,2-tri(*tert*-butyl)ethanone could not be induced to enolize even under drastic conditions.[40] Similarly, only the aldehydic form of 2,2-di(*tert*-butyl)ethanal is known to date.[41] In the 2,2-dimesityl-1-alkyl systems K_{enol} values decrease with the increased bulk of the alkyl group.[39] Consequently, an apparent difference exists between the effect of bulky aliphatic (*t*-Bu) and aromatic (Mes) groups on K_{enol}. This may be connected with the fact that tetramesitylethylene is a known compound,[42] while tetra(*tert*-butyl)ethylene resisted many synthetic efforts.[40] However, for delineation of the steric and electronic effects on the stabilization/destabilization of the enol/ketone forms, our two K_{enol} values are insufficient, and a larger number of aliphatic and aromatic systems should be studied, as we are presently doing.[38,39]

Conformation of 7. The availability of 1,2,2-trimesitylethanol gave the opportunity to study the conformation of a polymesityl-substituted saturated alcohol and to compare it with that of the vinylic analogue **3**, as well as with that of a less crowded 1,2,2-triarylethanol. The conformation of **7** was therefore studied by NMR and X-ray techniques and its DNMR was briefly recorded.

In contrast with the reported ^{1}H and ^{13}C NMR spectra of 1,2,2-triphenylethanol at room temperature,[43] the 300-MHz ^{1}H NMR of **7** in $CDCl_3$ at 293 K shows extensive signals broadening in the methyl and the aromatic regions. On cooling the solution the signals decoalesce and a well-resolved spectrum, showing a total of 28 signals (14 in the methyl region, 9 in the aromatic region, and 4 at δ 4.81–6.16 (Table II)) is obtained at 223 K. In the latter region three doublets at δ 5.17, 6.02, and 6.16 and one singlet at 4.81 in a 1.4:1.4:1.0:1.0 ratio were observed. It is therefore clear that more than one species is detected since even if the rotation will be completely frozen and all the signals observable, only 18 signals should be observed if a single conformer is present. The spectrum was therefore analyzed in terms of a mixture of two species. None of the signals in the δ 4.8–6.2 region is an OH signal since on shaking the $CDCl_3$ solution with one drop of D_2O none of them disappears. However, the doublet at δ 6.16 ppm (*J* = 10.2 Hz) becomes a singlet, while the rest of the spectrum remains unchanged (Figure 2). Consequently, this signal is assigned to a C*H*OH proton coupled to an OH proton with ^3J(HCOH) = 10.2 Hz. The doublet at δ 6.02 is tentatively assigned an *H*COH proton in the second species because of its similar chemical shift and its relative intensity, while the two signals at δ 5.17 and 4.81 are assigned to the Mes_2CH protons. Decoupling experiments show that the two more intense signals at δ 5.17 and 6.02 are mutually coupled with ^3J(HCCH) = 11.5 Hz, whereas the other two signals do not show any HCCH coupling.

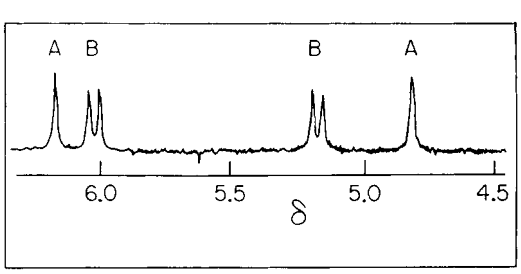
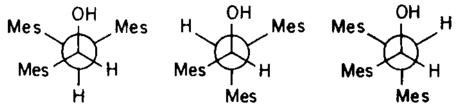


Figure 2. ^{1}H 300-MHz spectrum of the $C_\alpha H$–$C_\beta H$ region of **7** in $CDCl_3$ after treatment with D_2O. The two mutually coupled B protons belong to -*sc*-**7**, and the A protons belong to *ap*-**7**.

By comparing the spectra of **7** and **8** both the α-ring methyls (absent in the spectrum of **8**) and the α-ring protons were assigned, as described for **4**. Coupled with the relative intensities, this led to the assignments given in Table II.

Similarly, the ^{13}C NMR spectrum of **7** in $CDCl_3$ at 223 K shows 10 methyl signals, 21 aromatic carbon signals, and two pairs of signals at δ 49.43 and 50.80 and at 70.39 and 73.01 in a ca. 1.4:1.0 ratio for each pair (see Experimental Section). The first two signals are assigned to the two Mes_2CH carbons and the latter to the two *C*HOH carbons of the two species.

Trimesitylethenol (**3**) differs from its saturated analogue **7** in two respects: (a) the chiral center present in **7** should multiply the number of stereoisomers by a factor of 2; (b) the saturated HC–CHOH bond should allow different orientations of this moiety. Using the Klyne–Prelog nomenclature,[44] the three more probable conformers are *ap*-**7** and ±*sc*-**7**. They are depicted below



ap - **7** -*sc* - **7** +*sc* - **7**

for an arbitrary R configuration of the chiral center.[45]

The +*sc*-**7** conformer should be destabilized compared with the other conformers owing to severe steric interactions between the three juxtapositioned mesityl groups. Consequently, our conformational analysis is in terms of only the *ap*-**7** and the -*sc*-**7** conformers. This is consistent with the X-ray data given below.

Another stereochemical aspect involves the twist angles of the three aryl groups. Extensive analysis of the conformations of Ar_2C moieties, both in saturated[30] and in vinylic systems such as **1** and **3**,[25] indicates a propeller conformation. In order to corroborate this analogy and to determine the solid-state conformation of **7**, a single-crystal X-ray diffraction study was carried out. Several representative bond lengths and angles are given in Table IV, and the positional parameters and a comprehensive list of bond lengths and angles is given in the supplementary Tables S1–S4. The numbering scheme is in Table IV, and a stereoscopic drawing of the molecule is given in Figure 3. The molecule crystallizes in a $P2_{1/c}$ space group having four molecules (related as two pairs of enantiomers) per unit cell.

Figure 3 (and Table IV) shows that in the crystal the molecule has the *ap*-**7** conformation, with a central torsional HCCH angle of 74° and a HCCO angle of 167°. This is in contrast to the

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(38) Nadler, E. N., unpublished results.

(39) Nugiel, D. A.; Rappoport, Z., submitted for publication.

(40) Tidwell, T. T. *Tetrahedron* **1978**, *34*, 1855.

(41) Newman, M. S.; Arkell, A.; Fukunaga, T. *J. Am. Chem. Soc.* **1960**, *82*, 2498.

(42) Zimmerman, H. E.; Paskovich, D. H. *J. Am. Chem. Soc.* **1964**, *86*, 2149.

(43) Rummens, F. H. A.; Green, R. D.; Cessna, A. J.; Oka, M.; Lee, C. C. *Can. J. Chem.* **1975**, *53*, 314.

(44) Klyne, W.; Prelog, V. *Experientia* **1960**, *16*, 521.

(45) Note that the two reference substituents are OH (the substituent of highest priority on C1) and H (on C2).

$Ar_2CH—CHAr_2$
19, Ar = C_6H_5
20, Ar = $2,6\text{-}Me_2C_6H_3$
21, Ar = Mes

tetraarylethanes **19–21** where calculations, as well as X-ray diffraction, show an anti conformation.[46] With regards to the torsional angles of the aryl groups (defined by the $C_{ortho}–C_{ipso}–C–H$ atoms), the two rings of the Ar_2C moiety have the same sense of twist, opposite to that of the 1-mesityl ring. This is in contrast to **21** where the two Mes_2CH propeller moieties have the same helicity. The steric interactions in **20** are reflected in the calculated elongation of the central C–C bond (1.556 and 1.574 Å for **19** and **20**, respectively)[47] and the calculated C(aryl)–C(ethane) bonds (1.533 and 1.554 Å, respectively). These features were corroborated in an X-ray diffraction study of **21**.[48a] For **7** the central C–C bond length is 1.572 (7) Å and the C(aryl)–C(ethanol) bond lengths range from 1.530 (8) (for the 1-mesityl ring) to 1.555 (8) Å (Table IV), values similar to those calculated for **20**. The $C_{15}–C_2–C_{19}$ angle is 116.4 (6)° which compares with the central C–C–C bond angle of 115.9°, found by X-ray diffraction, for trimesitylmethane.[48b]

If both the chiral center and the helicity due to the propeller structure are taken into account in solution, the number of possible stereoisomers of **7** is eight, composed of four enantiomeric pairs.

In contrast with the preferred *ap*-**7** conformation in the solid state, the analysis of the ^1H NMR data in solution at 223 °K is interpreted in terms of the presence of two conformers in a 1.4:1 ratio, i.e., of a free energy difference of $\Delta G°(223\ K) = 150$ cal mol^{-1}. The $^3J(HCCH)$ values are 11.5 and <1 Hz for the major and the minor conformer, respectively, and by using the Karplus relationship between $^3J(HCCH)$ and the HCCH dihedral angle[49] or its Bothner-By modification[50] the major conformer is *ap*-**7** (calculated $^3J(HCCH)$ values for $\theta = 180°$ are 9 or 13 Hz), and the minor conformer is -*sc*-**7** (calculated $^3J(HCCH)$ for $\theta = 74°$ are 0.05 or 2.5 Hz).

The conformations of the OH group are likewise deduced from the observed $^3J(HCOH)$ values and the relationship between them and the dihedral HCOH angle suggested by Fraser and coworkers.[51] For -*sc*-**7** the OH doublet appears at δ 2.32 with $^3J(HCOH) = 10.2$ Hz, whereas the OH signal of *ap*-**7** was not observed, and the CH appears only as a doublet due to coupling with the OH proton. For -*sc*-**7** the calculated dihedral HCOH angle is 160°, and molecular models show that this angle allows the existence of an intramolecular hydrogen bond between the OH group and one of the β-mesityl rings.[52] There are many precedents, including the enol **1** where an OH–π(Ar) hydrogen bonding was suggested.[52] We have no explanation for the absence of the OH signal in *ap*-**7**, although the absence of coupling could point to a rapid exchange or to a conformer in which the coupling is small. Overlap by other signals is another possibility.

In order to evalute the barrier for the *ap*-**7** $\rightleftharpoons$ -*sc*-**7** interconversion, a DNMR experiment was conducted. The number of methyl and aromatic signals in the ^1H and ^{13}C NMR spectra at 223 K (Table II) is smaller than the expected number if each conformer exists in two propeller arrangements of the rings. This is consistent with a dynamic process involving helicity reversal occurring rapidly on the NMR time scale. Hence, no information on this process could be obtained.

By raising the temperature, the pair of signals at δ 4.81 and 5.17 coalesce at 290 K, whereas the pair at δ 6.02 and 6.16 coalesce at 280 K. By using the Gutowsky–Holm approximation as applied for the exchange between nonequally populated sites, barriers ($\Delta G_c^{\ddagger}$) of 13.8 and 14.0 kcal mol^{-1} were calculated for the forward and reverse exchange associated with the ap $\rightleftharpoons$ -sc interconversion.[53] This process is associated with the exchange of the methyl and aromatic protons, as can be seen from the NMR spectrum.

Saturation transfer studies[25,54] carried out by irradiation of one chosen signal (methyl or aromatic proton) show that three more signals show a diminution of intensity. These results mean that the exchange involves four different sites. Further studies to elucidate the DNMR behavior of **7** were not conducted.

Summary

The previously unknown crowded aldehyde **2** and ketone **4** were prepared. Although they are kinetically relatively stable, they are thermodynamically less stable than their enol isomers. Their K_{enol} values are the highest found for simple enols. Ketone **4** exists in a propeller conformation and the steric interactions of the Mes_2C and the α-Mes ring reduce the Mes–CO dihedral angle to a value lower than in acetylmesitylene. **4** undergoes a rapid dynamic process at 200 K with $\Delta G_c^{\ddagger} < 9.5$ kcal mol^{-1}, and $\Delta G_c^{\ddagger}$ for the coalescence of the α-mesityl diastereotopic groups is 13.8 kcal mol^{-1}. 1,2,2-Trimesitylethanol (**7**) exists in a 1:1.4 mixture of ap and -sc conformers and undergoes a dynamic process at room temperature which was briefly studied.

Experimental Section

General Methods. Melting points are uncorrected. UV spectra were measured with a Bausch and Lomb Spectronic 2000 spectrophotometer, and infrared spectra were taken with Perkin-Elmer 157G and Analect FTIR FX-6200 spectrometers. ^1H NMR and ^{13}C spectra were recorded on a Bruker WH-300 pulsed FT spectrometer operating at 300.133 and 75.460 MHz, respectively. The free induction decay signals were digitized and accumulated on an Aspect 2000 computer (32 K). Temperature measurements were based on the chemical-shift separation of the protons of a methanol sample. The $\Delta G_c^{\ddagger}$ values were determined from the exchange rate constant at T_c. X-ray diffraction of a single crystal of **7** was measured on a PW 1100 Philips four-circle computer-controlled diffractometer equipped with a five-focus Mo X-ray and a graphite crystal monochromator in the incident beam. The crystallographic parameters are given in Table V.

Solvents and Materials. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl under nitrogen immediately before use. CH_2Cl_2 was dried by standing on $MgSO_4$ and filtered, and DMF was dried by standing on alumina and decantation. BuLi (1.55 M in hexane) and PDC were purchased from Aldrich. Dimesitylacetyl chloride was prepared according to the literature,[5] and bromomesitylene-*methyl-d_9* was prepared as described previously.[25]

2,2-Dimesitylethanol (5). A solution of dimesitylacetyl chloride (3.2 g, 10.1 mmol) in THF (15 mL) was reduced at 20 °C with excess $LiAlH_4$ and the mixture was then refluxed for 2 h. The excess $LiAlH_4$ was destroyed by slow addition of ethyl acetate, and the mixture was poured into dilute aqueous HCl, extracted with ether, dried ($MgSO_4$), and evaporated. Crystallization of the residue from petroleum ether (40–60 °C) yielded 2 g (70.2%) of **5**, mp 110–111 °C (lit.[4b] 118–9 °C). ν_{max} (Nujol) 3580, 3430 (OH) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.58 (1 H, t, J = 5.9 Hz, OH), 2.23 (6 H, s, *p*-Me), 2.24 (12 H, s, *o*-Me), 4.22 (2 H, dd, $^3J(HCOH) = 5.9$ Hz, $^3J(HCCH) = 7.4$ Hz, CH_2OH), 4.65 (1 H, t, $^3J(HCCH) = 7.4$ Hz, Mes_2CH), 6.79 (4 H, s, Mes-*H*); ^{13}C NMR ($CDCl_3$) δ 20.54 (*p*-Me), 21.33 (*o*-Me), 49.00 (Mes_2CH), 63.77 ($CHCH_2OH$), 130.86 (Mes_2CH), 135.10 (Mes–C), 135.65 (Mes–C), 137.65 (Mes–C). Mass spectrum: m/z 282 (14%, M), 251 (B, Mes_2CH), 221 (64%, Mes_2CH – 2Me), 206 (39%, Mes_2CH – 3Me), 133 (19%, $MesCH_2$).

Anal. Calcd for $C_{20}H_{26}O$: C, 85.06; H, 9.28. Found: C, 85.28; H, 9.18.

2,2-Dimesitylethanal (2). Warning: PDC is a suspected carcinogen.[55] A solution of 2,2-dimesitylethanol (**5**) (2 g, 7.1 mmol) in dry CH_2Cl_2 (45 mL) was stirred with PDC (4 g, 10.6 mmol) during 48 h. After dilution with ether (300 mL) the chromium salts were filtered and the solvents were evaporated. Recrystallization from petroleum ether (40–60 °C) yielded 1.4 g (70.4%) of **2**, mp 90°C. The UV data are given in Table I. ν_{max} (Nujol) 1700 (C═O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.08 (12 H, s, *o*-Me), 2.26 (6 H, s, *p*-Me), 5.22 (1 H, d, J = 2.0 Hz, MesCH), 6.83 (4 H, s, Mes-H), 9.49 (1 H, d, J = 2.0 Hz, CHO); ^{13}C NMR ($CDCl_3$) δ

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[46] The reference substituents are the two protons.

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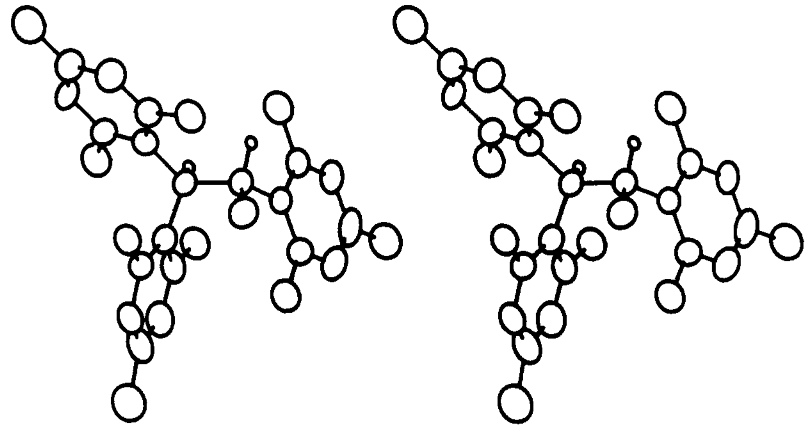
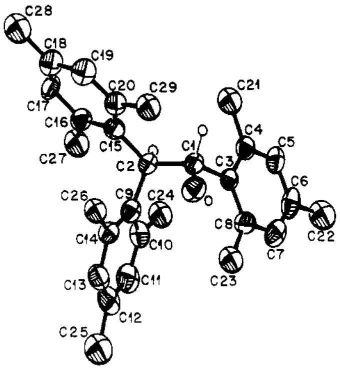


Figure 3. Stereoscopic view of **7**.

Table IV. Several Bond Lengths and Angles for **7**[a,b]



bond	length, Å	angle	deg	angle	deg
O–C(1)	1.438 (7)	O–C(1)–C(2)	110.4 (5)	C(6)–C(7)–C(8)	122.8 (6)
C(1)–C(2)	1.572 (7)	O–C(1)–C(3)	111.8 (5)	C(3)–C(8)–C(7)	118.5 (6)
C(1)–C(3)	1.530 (8)	C(2)–C(1)–C(3)	111.4 (4)	C(3)–C(8)–C(23)	125.0 (6)
C(2)–C(9)	1.535 (7)	C(1)–C(2)–C(9)	110.4 (5)	C(7)–C(8)–C(23)	116.5 (6)
C(2)–C(15)	1.555 (8)	C(1)–C(2)–C(15)	118.3 (5)	C(2)–C(9)–C(10)	119.0 (6)
C(3)–C(4)	1.423 (8)	C(9)–C(2)–C(15)	116.4 (6)	C(2)–C(9)–C(14)	122.5 (5)
C(3)–C(8)	1.415 (8)	C(1)–C(3)–C(4)	116.9 (5)	C(2)–C(15)–C(16)	114.8 (5)
C(4)–C(5)	1.369 (9)	C(1)–C(3)–C(8)	124.5 (6)	C(2)–C(15)–C(20)	127.7 (6)
C(4)–C(21)	1.512 (9)	C(4)–C(3)–C(8)	118.6 (6)	H(1)–C(1)–C(2)–H(2)	74 (1)
C(5)–C(6)	1.39 (1)	C(3)–C(4)–C(5)	120.1 (6)	H(1)–C(1)–C(3)–C(4)	−37 (1)
C(6)–C(7)	1.373 (9)	C(3)–C(4)–C(21)	121.6 (6)	H(1)–C(1)–C(3)–C(8)	145 (1)
C(6)–C(22)	1.52 (1)	C(5)–C(4)–C(21)	118.2 (6)	H(2)–C(2)–C(1)–O	−167 (1)
C(7)–C(8)	1.40 (1)	C(4)–C(5)–C(6)	121.9 (7)	H(2)–C(2)–C(9)–C(10)	23 (1)
C(8)–C(25)	1.512 (9)	C(5)–C(6)–C(7)	118.2 (7)	H(2)–C(2)–C(9)–C(14)	−161 (1)
		C(5)–C(6)–C(22)	119.1 (7)	H(2)–C(2)–C(15)–C(16)	46 (1)
		C(7)–C(6)–C(22)	122.7 (7)	H(2)–C(2)–C(15)–C(20)	−129 (1)

[a] For bond lengths and angles of the β rings, see supplementary tables. [b] Deviation in the least significant digits are given in parentheses.

Table V. Crystallographic Data for **7**

a, Å	12.131	μ(Mo Kα), cm^{-1}	0.34
b, Å	9.553	no. of unique reflections	3032
c, Å	21.318	reflections with $I \geq 2\sigma(I)$	2107
β, deg	105.59	*R*	0.094
V, Å^3	2379.6	scan mode	ω/2θ
Z	4	Δω, deg	1.0
space group	$P2_{1/c}$	total background (s)	20
μ calcd, g cm^{-3}	1.118	θ_{max}, deg	22.5

20.72 (*p*-Me), 21.68 (*o*-Me), 60.23 (CHCO), 130.50 (Mes*C*H), 131.50 (Mes–C$_{ipso}$), 136.91 (Mes–C$_{para}$), 137.53 (Mes–C$_{ortho}$), 199.32 (C═O). Mass spectrum *m/e* 280 (53%, M), 251 (B, Mes$_2$CH), 147 (49%, MesCO).

Anal. Calcd for $C_{20}H_{24}O$: C, 85.67; H, 8.63. Found: C, 85.61; H, 8.62.

1,2,2-Trimesitylethanol (7). Bromomesitylene (0.28 g, 1.4 mmol) was dissolved in dry THF (10 mL). The solution was cooled in an ice bath, and a solution of BuLi (1 mL, 1.55 M in hexane) was added under argon atmosphere. After stirring for 5 min a solution of dimesitylethanal (280 mg, 1 mmol) in dry THF (10 mL) was added and the mixture was stirred under argon at 0 °C for 2 h. After the mixture was poured onto ice (100 g), the aqueous phase was extracted with ether (2 × 40 mL), and the organic phase was dried (MgSO$_4$) and evaporated. Recrystallization from ethanol yielded 110 mg (28%) of **7**, mp 204 °C.

ν_{max} (Nujol) 3520 (sharp), 3360 (broad) (OH) cm^{-1}; ^{13}C NMR (CDCl$_3$, 223 K) δ 20.00, 20.29, 20.53, 20.79, 21.60, 21.80, 21.99, 22.21, 22.43, 24.53 (Me–C), 49.43 (Mes$_2$*C*H, ap), 50.80 (Mes$_2$*C*H, sc), 70.39 (*C*HOH, ap), 73.01 (*C*HOH, sc), 128.65, 129.46, 129.61, 130.00, 134.77, 135.25, 135.38, 135.56, 136.00, 136.30, 136.58, 136.98, 137.76, 137.94, 138.16, 138.95, 139.38, 139.56, 139.71 (Mes–C). Mass spectrum: *m/z* 382 (31%, Mes$_2$C═CHMes), 280 (52%, Mes$_2$CHC(OH)), 251 (B, Mes$_2$CH), 147 (89%, MesCO).

Anal. Calcd for $C_{29}H_{36}O$: C, 86.95; H, 9.06. Found: C, 86.77; H, 9.00.

1,2,2-Trimesitylethanone (4). Warning: PDC is a suspected carcinogen.[55] A mixture of 1,2,2-trimesitylethanol (160 mg, 0.4 mmol) and PDC (480 mg, 1.28 mmol) in dry DMF (2.2 mL) was stirred at room temperature for 4 days, during which the starting material dissolved completely but slowly. The mixture was poured into water and filtered, and the solid obtained was recrystallized from ethanol giving 130 mg (82%) of **4**, mp 142 °C. The UV data are given in Table I.

ν_{max} (Nujol) 1680 (C═O) cm^{-1}. CI mass spectra (isobutane): *m/z* 399 (16%, MH), 279 (86%, Mes$_2$CHCO), 251 (B, Mes$_2$CH), 147 (25%, MesCO), 121 (11%, MesH), 75 (43%). EI spectra: *m/z* 398 (70.5%, M), 372 (4%), 287 (9%), 251 (9%, Mes$_2$CH), 147 (100%, B). High

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(55) Many chromium compounds are designed in OSHA category I – reported in *Chem. Eng. News* **1978**, July 31, p 20.

resolution EI spectra: observed m/z 398.260442; calcd 398.26095. A metastable peak at m/e 176.4 corresponds to a 398 → 265 cleavage due to a reciprocal CH_3/H transfer, followed by a $C_{10}H_{13}\cdot$ loss.[1,56]

Anal. Calcd for $C_{29}H_{34}O$: C, 87.39; H, 8.60. Found: C ,87.39; H, 8.41.

1-(2,4,6-Tri(methyl-*d*$_3$)phenyl)-2,2-dimesitylethanol (8). Starting from bromomesitylene-*methyl*-d_9 (0.22 mL, 1.4 mmol, (98.4% D) and **2** (280 mg, 1 mmol), **8** (50 mg, 12%), mp 208 °C, was obtained by the procedure described for the preparation of **7**.

1-(2,4,6-Tri(methyl-*d*$_3$)phenyl)-2,2-dimesitylethanone (9). Starting from **8** (20 mg, 0.05 mmol) and PDC (60 mg, 0.16 mmol) in DMF (0.3 mL), 15 mg (74%) of **9**, mp 142 °C, was obtained by the procedure described above for formation of **4**.

Acknowledgment. We are indebted to Professor H. Schwarz for the mass spectrum of compound **4**, to Dr. S. Cohen for the X-ray diffraction of compound **7**, to Dr. M. Kaftory for the X-ray data of compound **4** and for assistance with the Cambridge Structural Data Base, to Dr. D. Cohn for assistance with the IR measurements, and to Professor E. M. Kosower for helpful discussions. This work was supported by a grant from the United States–Israel Binational Science Foundation (BSF), Jerusalem, Israel, to which were are grateful.

Registry No. 2, 94203-58-4; **4**, 87902-64-5; **5**, 94203-59-5; **6**, 94203-61-9; **7**, 94203-60-8; **8**, 94203-62-0; **9**, 94203-63-1; **10**, 1733-63-7; **11**, 77787-78-1; **12**, 1889-68-5; **13**, 77787-77-0; bromomesitylene, 576-83-0; (bromomesitylene)methyl-d_9, 87871-32-7; mesityllithium, 5806-59-7.

Supplementary Material Available: Tables S1–S4 giving the crystallographic data for compound **7** (5 pages). Ordering information is given on any current masthead page.

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Carbocation Behavior in Norbornyl–Fused Norbornyl Systems. The Kinetic and Chemical Consequences of Fusing Two Norbornane Units Across Framework Bonds of Various Type

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Abstract: The nature of the *syn,endo*-tetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodec-2-ylium cation was probed both solvolytically and by direct examination (^1H and ^{13}C NMR) in superacid solution. This most sterically congested ion is produced in aqueous acetone 3500000 times more rapidly than the *tert*-butyl cation and shows no tendency for skeletal rearrangement. Only a propensity for symmetrization via degenerate 2,3-hydride shifting and for conversion to the alkene has been detected. The response of its benzologue **16a** to solvolysis has also been examined. A 1250-fold rate deceleration was determined, and unrearranged products were likewise obtained. The protonation of **8** as an entry to the *anti*-tetracyclo[4.4.0.1^{1,4}.1^{7,10}]dodec-6-ylium cation was investigated in media of increasing acid strength. In contrast to the above, fusion of two norbornyl systems in this matter introduces a propensity for a cascade of cationic rearrangements. The entire range of these isomerizations has been elucidated. The exo/endo rate ratio exhibited by the epimeric *p*-nitrobenzoates **25**-OPNB and **27**-OPNB is the largest yet determined experimentally. The probable causative factors underlying this reactivity extreme and that of the other carbocationic rearrangements are outlined.

The opportunity to uncover fascinating and intricate transformations of heretofore unknown molecular types is customarily not bypassed by organic chemists. In the past, the lure of the unusual structures has yielded notable dividends in new facts that have been of major importance in the building of organic chemistry as a science. When ready access was recently gained in this laboratory to different types of norbornyl-fused norbornyl compounds, a detailed examination of their cationic behavior was undertaken. Our expectation was that these tantalizing structures would contribute in a meaningful way to our knowledge of this class of reactive intermediates.[1]

Recent years have witnessed development of a greatly enhanced appreciation for the special ability of norbornyl carbon atoms to enter into through-space[1a] and through-bond interactions.[2] The unusual reactivity of the norbornene π bond[3] and its outward deformation have been dealt with from the theoretical[4,5] and experimental vantage points.[6,7] The extent of pyramidalization becomes significantly more pronounced within *syn*-sesquinorbornenes.[8] Whereas distortion angles of 16–18° are commonplace in simple derivatives such as **1**,[9] the bending is still more accen-

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