Locked Aryl Rotation in *cis*-Diarylacenaphthenes, Torsionally Rigid Analogues of *cis*-1,2-Diarylcyclopentanes[1]

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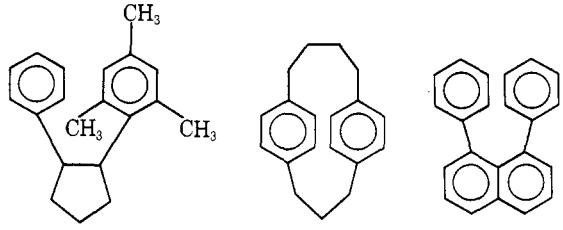
Abstract: Hydrocarbon homologues *cis*-1-phenyl-2-mesitylacenaphthene (**1**) and *cis*-1-phenyl-2-(2,4,6-triisopropylphenyl)acenaphthene (**2**), torsionally rigid analogues of *cis*-1,2-diarylcyclopentanes, were prepared by Birch reduction of corresponding *trans*-diarylacenaphthenols, which were obtained via a high-yield, three-step sequence from acenaphthenequinone. Unlike the cyclopentane system, at ambient temperature both **1** and **2** exhibit locked aryl rotation on the NMR time scale. At 200 °C, **1** displays slow internal rotation, the rate being bracketed by a DNMR technique as $10 < k_{200\,°C} < 195\ s^{-1}$, which corresponds to a free energy of activation of $23 < \Delta G^{\ddagger}_{200\,°} < 26$ kcal/mol. Since hydrocarbon **2** exhibits no line broadening at 200 °C, its rotational barrier exceeds 26 kcal/mol. The higher barriers in the acenaphthenes are interpreted as arising from a greater localization of deformations in the activated complex. Equilibration of the "inside" rotamer of a bromo derivative of **1** indicated an equilibrium constant of $K_{eq} = 0.63 \pm 0.01$ and a forward rate constant of $k_1 = 6 \pm 1 \times 10^{-4}\ s^{-1}$ at 76 °C, which corresponds to $\Delta G^{\ddagger} = 25.6 \pm 0.3$ kcal/mol.

Internal rotation of the face-to-face aromatic rings in *cis*-1,2-diarylcyclopentanes is surprisingly facile. In the parent compound, *cis*-1,2-diphenylcyclopentane, rotation remains fast on the NMR time scale even at −60 °C,[3] and the upper limit for the free-energy barrier to rotation is probably no more than 10 kcal/mol[4] at that temperature. In *cis*-1-phenyl-2-mesitylcyclopentane[5] (A), rotation is still very rapid,



A B C

the rotational half-life being only 4 ms at the −44 °C coalescence temperature. This corresponds to a free-energy barrier of only 11 kcal/mol. That 11 kcal/mol is a small rotational barrier for adjacent aromatic rings, even unsubstituted rings, is indicated by model systems [4.3]paracyclophane (B), $\Delta G^{\ddagger}_{160°} \simeq 33.5$ kcal/mol,[6,7] and 1,8-diphenylnaphthalene (C), $\Delta G^{\ddagger}_{25°} = 16$ kcal/mol.[7,8] Although the ground-state ring separations for the three systems are similar,[9] what would appear to be a more important variable, namely, the *change* in ring separation required for rotational activation, is undoubtedly greatest in A since it must accommodate a methyl group between the orthogonal, activated rings. In view of this, it is interesting that the rings of A nonetheless rotate faster than those of B by a factor of 10^{16} at room temperature.

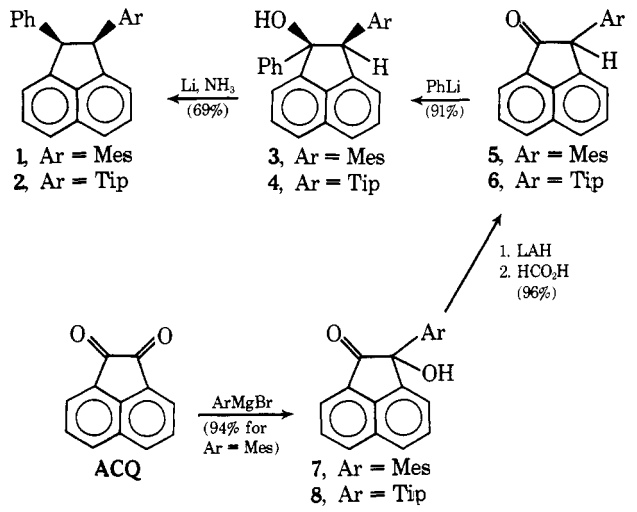
Since bond bending (rather than stretching or orbital compression) is the dominant mode of steric relief in rotation-activated complexes,[12] the low barriers in the diarylcyclopentanes appeared likely to arise from the aliphatic ring's torsional flexibility, which would allow facile expansion of the dihedral angle θ separating the aryl rotational axes. The factor of ultimate relevance to the observed low barriers is not that the aromatic rings are somewhat staggered in the rotational ground state, but that the five-membered ring is torsionally soft; it is this torsional softness that is then responsible for both the staggered ground state and, more importantly, the more staggered transition state. The low energy requirements for torsional flexibility in cyclopentanes are indicated computationally,[13] and experimental evidence can be derived from thermochemical and kinetic data for related cis and trans bicyclic systems: Heat of combustion data[14] demonstrate that the angle strain in *trans*-pentalane (C_{2h} symmetry)[15] is only 6.4 kcal/mol above that of the cis isomer (C_s symmetry). If the strain were delocalized[13] completely over the ten C-C-C angles undergoing deformation, then approximately half of 6.4 kcal/mol should equal the energy required to transform C_s cyclopentane with a torsional angle $\theta = 40°$[16] into C_2 cyclopentane with $\theta = 70°$.[17] Since C_s cyclopentane is 0.5 kcal/mol[18] lower in energy than the C_2 form, the same transformation might require less than 3 kcal/mol if it maintained C_2 symmetry. Solvolysis rate data[19] for bridgehead-substituted derivatives of cis- and trans-fused bicyclo[3.2.0]heptane indicate that the trans-fused isomer is strained 8–9 kcal/mol more than the cis-fused isomer. An argument similar to that applied to the pentalanes suggests that θ in cyclopentane rings can be increased to approximately 90° with an enthalpy increase of only 6–7 kcal/mol. Evidently, facile θ expansion (and concomitant rapid rotation in the *cis*-1,2-diarylcyclopentanes) arises from the capability of the aliphatic ring to distribute the resulting strain over all of its ring bonds.[13] That such delocalization of strain over a number of angles should lower the potential energy for a given aryl-axis deflection is suggested by the mechanics of an ideal helical spring, whose energy for a given displacement varies inversely as the number of turns.[20]

Therefore gusseting the five-membered ring (rather than further increasing the rotor size) was predicted to increase dramatically the rotational barrier of adjacent aryl groups on a five-membered ring. To test this experimentally, we have prepared a torsionally rigid analogue of cyclopentane A, namely, *cis*-1-phenyl-2-mesitylacenaphthene (**1**), utilizing the partially aliphatic five-membered ring of the tricyclic acenaphthene system. The crystal structure[21] of acenaphthene itself indicates eclipsed, bisectional aliphatic bonds of essentially normal lengths and angles; the system's torsional rigidity has been discussed elsewhere.[22]

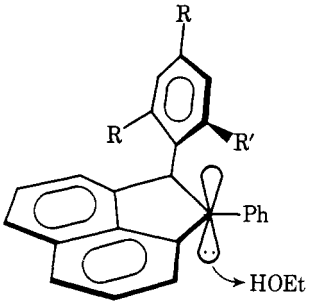
Results and Discussion

The high-yield, four-step synthesis of cis hydrocarbon **1** from acenaphthenequinone (ACQ) is summarized in Scheme I.[23] The method's general applicability to crowded *cis*-1,2-diarylacenaphthenes (as well as analogous systems) was demonstrated by the preparation of the overcrowded homologue *cis*-1-phenyl-2-tipylacenaphthene (**2**) (tipyl = Tip = 2,4,6-triisopropylphenyl).[25] The final and key step of the synthesis provides the desired cis hydrocarbons via a Li/

Scheme I



Na-alloy variation of the Birch reduction[26] of the corresponding trans benzyl alcohols. Reduction by the less reactive sodium metal proved unusable because of facile epimerization of the kinetically controlled cis product to the thermodynamically favored trans product, which is readily prepared by epimerization of the pure cis hydrocarbon. As was predicted, protonation of the intermediate carbanion provides predominantly the cis hydrocarbon as the kinetic product; this transpires because the carbanion is protonated preponderantly trans to the aryl group since the carbanion's cis side is shielded by aryl's "inside" ortho substituent R′.



According to the Hammond postulate, for a highly exothermic reaction the transition state will be reactant-like (carbanion-like here), and thus crowding of the incipient cis aryl groups will not yet have significantly begun in the activated complex.

In contrast to *cis*-1,2-diarylcyclopentane A, cis hydrocarbons **1** and **2** exhibit locked aryl rotation on the NMR time scale at ambient probe temperature. Hydrocarbon **1** displays three sharp methyl proton singlets: a signal at δ 1.07 is assigned to the "inside" methyl, which lies over the naphthalene nucleus and therefore in its shielding region; a signal at δ 2.08, whose line width is temperature independent, is assigned to the para methyl; and one at δ 2.51 is assigned to the "outside" methyl, which resides outside of the periphery of the acenaphthene system but in the plane of the naphthalene ring and therefore in its deshielding region. The inside meta mesityl ring proton is observed as an isolated singlet at δ 6.28. Hydrocarbon **2** exhibits the 10 methyl proton signals characteristic of a locked tipyl rotor; since the methyl groups of each ortho isopropyl group are diastereotopic due to the asymmetry of their magnetic environment, spin–spin splitting by their respective methine protons results in a total of four sets of doublets, or eight lines, each doublet having a relative area of 3 H. The para isopropyl group displays only a six-proton doublet, its methyl groups not being observably diastereotopic. It is of interest that one of the inside methyl doublets of this molecule is centered at δ −0.12, i.e., upfield of Me_4Si. The inside meta ring proton resonates as a doublet at δ 6.60, whose coupling constant, J = 2 Hz, is of the magnitude expected for meta spin–spin coupling in an aryl ring.[27]

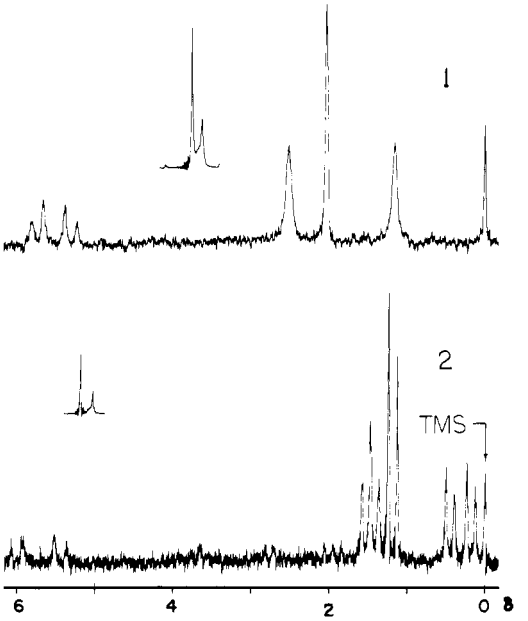
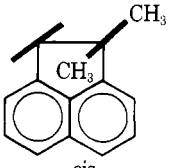
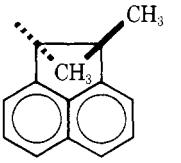


Figure 1. NMR spectra at 500-Hz sweep width of hydrocarbons *cis*-1-phenyl-2-mesitylacenaphthene (**1**) and *cis*-1-phenyl-2-tipylacenaphthene (**2**) in TCB solution at 200 °C (Me_4Si internal reference, ethylene glycol temperature calibration).

The NMR spectra allow a detailed analysis of the rotational ground states of these molecules and indicate that arylacenaphthenes preferentially place the largest inside substituent over the cavity of the five-membered ring. If phenyl and mesityl are cis, as in **1**, the sterically dominant mesityl group places its inside methyl over the ring cavity, and phenyl must reside in a less favorable, "parallel" conformation. In this parallel skewed conformation, the phenyl group augments the ring current effect of the naphthalene ring by



cis
"parallel" aryl groups



trans
"orthogonal" aryl groups

shielding the inside and deshielding the outside methyl group. Accordingly, in hydrocarbon **1**, the inside methyl proton signal is shifted upfield, and the outside methyl signal is shifted downfield, relative to the same proton resonances in model compound *cis*-2-mesityl-1-acenaphthenol. However, if phenyl and mesityl are trans, as in the trans hydrocarbon and carbinol **3**, then both aromatic rings can adopt the favored conformation with their inside substituents over the cavity. In this conformation, the "orthogonal" phenyl group opposes both the normal effects of the naphthalene ring. Accordingly, the inside methyl signal is shifted downfield relative to the model, and the outside methyl signal is actually shifted upfield of the para methyl signal.

At 200 °C in trichlorobenzene (TCB) solution, the ortho methyl signals of **1** (see Figure 1) are somewhat broadened by slow site exchange. Clearly, since the line widths at half-height are increased by only a factor of 2, the exchange rate remains considerably below the coalescence rate. The latter

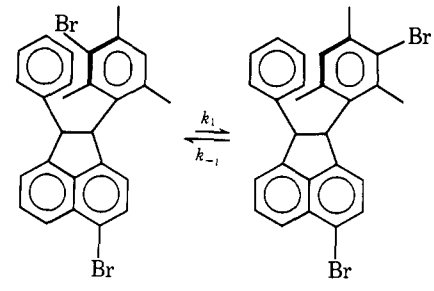
may be estimated from the observed chemical shift difference $\Delta\nu$ and the relation[28] $k_c = \pi(\Delta\nu)/\sqrt{2}$, which gives a value of $k_c = 195\ s^{-1}$. Furthermore, the observation of some broadening indicates an exchange rate greater than 10 s^{-1}.[29] Thus, the rotational rate at 200 °C is bracketed as $10 < k_{200°} < 195\ s^{-1}$. Substitution of these rate limits at 200 °C into the Eyring equation likewise brackets the rotational barrier as $23 < \Delta G^{\ddagger} < 26$ kcal/mol.

An interesting comparison can be made of the half-lives of hydrocarbon **1** and its flexible analogue *cis*-1-phenyl-2-mesitylcyclopentane at a common temperature. The latter's rotational rate at the −44 °C coalescence temperature is approximately $k_c = 170\ s^{-1}$, which corresponds to a half-life of 4 ms. In contrast, assuming a free-energy barrier of at least 23 kcal/mol at −44 °C ($|\Delta S^{\ddagger}|$ is probably small),[29] hydrocarbon **1** would exhibit a half-life of over 40 years.

Hydrocarbon **2** in TCB solution exhibits no line broadening even at 200 °C; therefore, its rotational barrier probably exceeds 26 kcal/mol. However, the 200 °C spectrum did exhibit slightly perturbed chemical shifts for two of the ortho isopropyl methyl doublets: the highest field doublet was shifted 13 Hz downfield, relative to the same doublet in the 44 °C, TCB solution spectrum, whereas the lowest field doublet was shifted 4 Hz upfield. The remaining lines of the spectrum were not significantly changed. The temperature dependence of the chemical shifts is undoubtedly due to the temperature dependence of the ground-state conformer distribution.[3]

We interpret the higher rotational barriers in the acenaphthene analogues as arising from a greater localization of deformations in the activated complex. The potential-energy distribution among the points of a deformed elastic system is such that the energy arising from each point's deformation is inversely proportional to the local force constant.[30] Necessarily, the weakest points will be deformed the most. Therefore, since relatively large force constants for deformation are associated with the acenaphthene ring system because of its geometry and the π-electron system's preference for planarity, most of the activation energy in **1** will be associated with consequent large local deformations of the C(1) and C(2) bonds, the methyl groups, and especially the rotational axes (i.e., bowing back the aryl groups).[31] In contrast, since small force constants for deformation are associated with the cyclopentane ring, much of the activation energy in A will be delocalized around the five-membered ring. That is, the rotational axes will separate via torsional bending of the cyclopentane ring, and, consequently, activation will require less local deformation. As was noted above,[20] the less local is a given deformation, the lower the potential energy.

Since, in general, isomers that are separated by an energy barrier of 17 kcal/mol[12] or greater are physically isolable, if the rotor of **1** or **2** were made asymmetric, two chemically nonequivalent ground states would ensue, corresponding to cis–trans isomerism about a single bond. Bromination of the mesityl ring of **1** proved kinetically noncompetitive with bromination of the naphthalene nucleus; uncatalyzed reaction with molecular bromine afforded 5-bromo-*cis*-1-phenyl-2-mesitylacenaphthene (**9**).[32] Further mild treatment with molecular bromine gave a mixture of "inside" **10** and "outside" **11** rotamers in the approximate ratio of 6:4, respectively. Repeated recrystallization provided the inside rotamer (**10**) in 86% isomeric purity in sufficient quantity to perform a reequilibration experiment monitored by NMR spectroscopy. The equilibrium constant of $K_{eq} = 0.63 \pm 0.01$ indicates that the inside rotamer is the more stable; apparently, placing the bromine-buttressed ortho methyl group over the cavity of the five-membered ring is preferable to placing it over the benzylic hydrogen H_2. The equilibration also provided two kinetic data points from which the rate constants could be determined. The probable error in the rate constant is assessable, and very likely the forward constant lies within the limits of $k_1 = 6 \pm 1 \times 10^{-4}\ s^{-1}$; accordingly, the reverse constant is $k_{-1} = 10 \pm 2 \times 10^{-4}\ s^{-1}$. The corresponding free energies of activation for the forward and reverse processes, respectively, are therefore $\Delta G^{\ddagger} = 25.6 \pm 0.3$ kcal/mol and $\Delta G^{\ddagger} = 25.3 \pm 0.3$ kcal/mol.



10 11

The chemical shift difference $\Delta\nu$ for the ortho methyls of the outside rotamer is greater than $\Delta\nu$ for the same nuclei in the inside rotamer. This is an interesting consequence of the bromine atom's deshielding of its ortho methyl groups to a greater extent than its para methyl group. Considering together the inside methyls of the two rotamers, the methyl of the inside rotamer, being deshielded, should have the lower field methyl signal, and considering the outside methyls, the methyl of the outside rotamer should have the lower field signal. Therefore, since the outside rotamer has the higher field inside methyl signal and the lower field outside signal, $\Delta\nu$ is accordingly larger. In each rotamer, the chemical shift of the methyl not adjacent to bromine is virtually identical with that in bromohydrocarbon **9**, and the magnitude of the relative downfield shifts of the others is close to the 0.15 ppm downfield shift exhibited by the ortho methyls of bromomesitylene. On this view, the para methyls of the two rotamers should be equally deshielded, which is essentially what is observed.

Experimental Section

Melting points were determined on a capillary apparatus at 1–2 °C/min and are corrected. The ir spectroscopy employed 4% solutions in CCl_4 or $CHCl_3$; the uv employed hexane solutions (λ_{max} reported). NMR spectra were recorded at 500-Hz sweep width at concentrations of 100 mg of solute per 450–500 μl of solvent. Chemical shifts are reported in parts per million (δ) from Me_4Si as internal standard. High-temperature runs employed 1,2,4-trichlorobenzene (TCB) as solvent. Temperature determinations were made via peak separations of ethylene glycol,[36] complete thermal equilibrium being assured before a spectrum was recorded. The NMR and ir spectra have been reproduced.[37] Analyses for the elements indicated were correct to within 0.3%.

***cis*-1-Phenyl-2-mesitylacenaphthene (1).** To 400 ml of distilled ammonia at reflux was added dropwise a solution of 3.6 g (10 mmol) of carbinol **3** and 1.7 ml (30 mmol) of dry ethanol in 100 ml of dry THF. To this stirred, essentially homogeneous mixture was added 165 mg (25 mmol) of lithium wire (1% sodium), rapidly cut piecewise and allowed to drop directly into the flask. When the dark purple color had faded to reddish violet (5 min), cautious but rapid dropwise addition of 200 ml of water was commenced. The reaction mixture was worked up, and the nearly colorless pentane solution was evaporated under a stream of nitrogen to give 3.5 g of partly crystalline material. TLC exhibited a single, homogeneous spot. The product was crystallized from methanol–benzene to give 2.4 g (69%) of near-white, highly crystalline material, mp 105–107 °C. Recrystallization from methanol–benzene gave pure, white cis hydrocarbon **1**: mp 108–109 °C; ir (CCl_4) 3060, 3030, 2920, 2860, 1600, 1495, 1450 cm^{-1}; uv 222 (ϵ 62 000), 293 nm (6900); NMR (CCl_4) δ 1.07 (s, 3 H, inside Me), 2.08 (s, 3 H, para Me), 2.51 (s, 3 H, outside Me), 5.28 (d, J = 9 Hz, 1 H), 5.67 (d, J = 9 Hz, 1

H), 6.28 (s, 1 H, inside mesityl ring proton), 6.69–6.97 (outside mesityl ring proton and acenaphthene H_3 proton superimposed on phenyl ring protons, total area 7 H), 6.69 (outside ring proton), 6.83 (phenyl ring protons), 6.97 (acenaphthene H_3 ring proton), 7.20–7.71 (remaining acenaphthene ring protons, total area 5 H); mass (10 eV) *m/e* (rel intensity) 348 (100), 333 (11), 228 (45). Anal. C, H.

Epimerization of **1** afforded the trans hydrocarbon, ***trans*-1-phenyl-2-mesitylacenaphthene.** To a stirred, refluxing solution of 12 ml of distilled ammonia, 2 mg (0.1 mmol) of sodium, and 0.1 ml of a 3:1 (mol/mol) mixture of ethanol–water was added dropwise a solution of 0.1 g (0.3 mmol) of cis hydrocarbon **1** in 3 ml of dry THF. Stirring was continued for 2 h, then 15 ml of water was added dropwise, and the reaction mixture was worked up to give as a yellow syrup the trans hydrocarbon: NMR (CCl_4) δ 1.63 (s, 3 H, inside Me), 1.87 (s, 3 H, outside Me), 2.22 (s, 3 H, para Me), 4.81 (d, J = 5 Hz, 1 H), 5.18 (d, J = 5 Hz, 1 H), 6.72–7.71 (aromatic ring protons), 6.72 (mesityl ring protons), no cis epimer was detectable by the NMR spectrum; mass (12 eV) *m/e* (rel intensity) 348 (100), 228 (30), 118 (34), 116 (32).

***cis*-1-Phenyl-2-tipylacenaphthene (2).** Conditions analogous to those used in the preparation of mesityl homologue **1** were employed; however, the reaction mixture was not homogeneous. From 0.90 g (2 mmol) of carbinol **4,** 0.9 g of a syrup was obtained. The material was chromatographed on silica gel–pentane to give an oil, which crystallized from chilled methanol to give 0.4 g of hydrocarbon. This was recrystallized twice from methanol–benzene to give pure, highly crystalline, white cis hydrocarbon **2:** mp 124–125 °C; ir (CCl_4) 3060, 3040, 2980, 2960, 2880, 1600, 1390, 1370 cm^{-1}; uv 224 (ϵ 64 000), 293 nm (9000); NMR (CCl_4) δ −0.12 (d, J = 6.5 Hz, 3 H), 0.45 (d, J = 6.5 Hz, 3 H), 1.21 (d, J = 7 Hz, para isopropyl methyls), 1.36 (d, J = 6.5 Hz), 1.53 (d, J = 6.5 Hz), 1.75 (m, J = 6.5 Hz, total area from the δ 1.21 doublet inclusive, 13 H), 2.80 (m, J = 7 Hz, 1 H, para methine proton), 3.58 (m, J = 6.5 Hz, 1 H), 5.40 (d, J = 9 Hz, 1 H), 5.89 (d, J = 9 Hz, 1 H), 6.60 (d, J = 2 Hz, 1 H, inside tipyl ring proton), 6.92–7.78 (aromatic ring protons, total area 12 H), 6.92 (phenyl ring protons); mass (12 eV) *m/e* (rel intensity) 432 (100), 389 (20). Anal. C, H.

***trans*-1-Phenyl-2-mesityl-1-acenaphthenol (3).** To an ice-cold, stirred (Hershberg stirrer) solution of 8.6 g (30 mmol) of ketone **5** in a mixture of 100 ml of dry benzene and 50 ml of *n*-pentane was added dropwise over a 10-min period a 35-ml portion of 1.3 M phenyllithium (45 mmol of PhLi) as prepared by the method of Schlosser and Ladenberger.[38] This resulted in a scarlet (the enolate) solution, which was subsequently titrated with 2 M acetic acid–pentane solution to the yellow end point. The process was then repeated for a total of six complete cycles (i.e., 6 × 45 mmol of PhLi). The reaction mixture was worked up to give a syrup, which crystallized from methanol. The crystalline product was washed with a minimum of cold MeOH and cold pentane to give, after drying in vacuo, 9.9 g (91%) of white product, mp 92 °C (melt evolved a gas). Recrystallization from heptane–pentane gave material of melting point 110–114 °C. Subsequent recrystallization from MeOH gave the highly crystalline material of mp 94 °C (gas evolution). Recrystallization from heptane–pentane gave the following properties: mp 110–114 °C; ir (CCl_4) 3550 cm^{-1}; NMR (CCl_4) δ 1.48 (s, 3 H, inside Me), 1.78 (s, 3 H, outside Me), 2.17 (s, para Me), and 2.22 (s, OH, total area 4 H), 5.50 (s, 1 H), 6.67 (s, 2 H, mesityl ring protons), 6.87–7.73 (aromatic ring protons, total area 11 H); mass (10 ev) *m/e* (rel intensity) 364 (7), 346 (3), 231 (100). Anal. C, H.

***trans*-1-Phenyl-2-tipyl-1-acenaphthenol (4).** The method employed above for preparation of carbinol **3** was analogously applied to ketone **6;** 3.7 g (10 mmol) of ketone **6** gave, after four complete titration cycles, 5.1 g of product. This was dissolved in pentane and placed on a silica gel column, and the column was thoroughly developed with pentane and eluted with benzene. Evaporation of the solvent in vacuo gave a glass, which instantly crystallized upon addition of pentane to give 3.5 g of white solid. Although excellent crystals were obtained from MeOH–water or EtOH–water (mp 110–112 °C) and from heptane–pentane (mp 103–106 °C), repeated recrystallization and subsequent drying in vacuo at 78 °C consistently gave microanalyses slightly low in carbon. The sample, thrice recrystallized from heptane–pentane, exhibited the following properties: mp 103–106 °C; ir (CCl_4) 3545, 1385, 1365 cm^{-1}; NMR (CCl_4) δ 0.52–1.34 (nine methyl signals, one an unresolved doublet, total area 19 H), 2.05–3.14 (OH superimposed on methine protons, total area 4 H), 2.22 (s, OH), 5.77 (s, 1 H), 6.97–7.85 (aromatic ring protons, total area 13 H), 6.97 (tipyl ring protons); mass (12 eV) *m/e* (rel intensity) 448 (14), 430 (3), 406 (20), 405 (64), 231 (100). The exact mass of the *m/e* 448 peak was 448.2762, which corresponds to the correct empirical formula $C_{33}H_{36}O$ (*m/e* = 448.2766).[39]

2-Mesityl-1-acenaphthenone (5). To a boiling, stirred mixture of 350 ml of dry ethyl ether and 3.8 g (100 mmol) of lithium aluminum hydride was added dropwise over a 15-min period a solution of 26.0 g (86 mmol) of hydroxy ketone **7** in 50 ml of dry THF. The mixture was stirred for an additional 15 min, and ethyl acetate (50 ml) was added dropwise. The reaction mixture was poured into saturated aqueous ammonium chloride and worked up to give a colorless syrup. TLC showed a single homogeneous spot having the R_f of diol 2-mesityl-*trans*-1,2-acenaphthenediol (vide infra). The diol was dissolved in 50 ml of hot glacial acetic acid, the temperature was adjusted to approximately 100 °C, and, with stirring, 100 ml of hot formic acid was rapidly added. Hot water was subsequently added to the saturation point, and crystallization was allowed to occur slowly to give 23.7 g (96%) of highly crystalline ketone **5,** mp 149–151 °C. Recrystallization from methylene chloride–heptane gave pure, white ketone **5:** mp 151.5–153 °C; ir (CCl_4) 1722 cm^{-1}; NMR (CCl_4) δ 1.36 (s, 3 H, inside Me); 2.18 (s, 3 H, para Me), 2.47 (s, 3 H, outside Me), 5.14 (s, 1 H), 6.56 (s, 1 H, inside mesityl ring proton), 6.80 (s, 1 H, outside ring proton), 6.95–8.00 (aromatic ring protons, total area 6 H); mass (10 eV) *m/e* (rel intensity) 286 (100), 257 (6), 119 (15). Anal. C, H.

The intermediate diol, **2-mesityl-*trans*-1,2-acenaphthenediol,** was obtained by interrupting the preparation of ketone **5** after the $LiAlH_4$ reduction stage. The syrup was crystallized from *n*-heptane to give 95% of white crystalline diol: mp 128–131 °C; ir (CCl_4) 3610, 3580, 1610 cm^{-1}; NMR (CCl_4) δ 1.16 (s, 3 H, inside Me), 1.68 (d, J = 4 Hz, 1 H, OH), 1.99 (s, 1 H, OH), 2.13 (s, 3 H, para Me), 2.49 (s, 3 H, outside Me), 5.18 (d, J = 4 Hz, 1 H), 6.46 (s, 1 H, inside mesityl ring proton), 6.68 (s, 1 H, outside ring proton), 6.79–7.67 (aromatic ring protons, total area 6 H); mass (10 eV) *m/e* (rel intensity) 304 (76), 286 (63), 184 (93), 147 (100). Discrete OH proton signals in the NMR spectrum preclude hydrogen bonding[22] and therefore the cis configuration.

Reduction of ketone **5** afforded model compound ***cis*-2-mesityl-1-acenaphthenol.** To a stirred solution of borane in THF (10 ml of 1 M) was added 1.0 g of ketone **5.** Stirring was continued for 5 min, followed by dropwise addition of acetone. Work-up gave a colorless oil, which was crystallized and recrystallized from *n*-hexane to give the alcohol: mp 91 °C; ir (CCl_4) 3560 cm^{-1}; NMR (CCl_4) δ 1.40 (s, 3 H, inside Me), 1.71 (d, J = 4 Hz, 1 H, OH), 2.17 (s, 3 H, para Me), 2.40 (s, 3 H, outside Me), 5.18 (d, J = 7 Hz, 1 H, H_2 benzylic proton), 5.56 (d of d, J = 7 Hz and J = 4 Hz, total area 1 H, H_1 benzylic proton), 6.58–7.67 (aromatic ring protons, total area 8 H); mass (10 eV) *m/e* (rel intensity) 288 (100), 270 (53), 255 (10), 168 (11). The high-field resonance for the OH proton indicates the cis configuration.

2-Tipyl-1-acenaphthenone (6). Conditions analogous to those for the preparation of ketone **5** were employed to give, from hydroxyketone **8,** 94% of crystalline ketone, mp 177.5–179 °C. Recrystallization from acetone–water gave pure, snow-white ketone **6:** mp 178–179 °C; ir (CCl_4) 1725 cm^{-1}; uv 202 (ϵ 68 500), 215 (62 900), 256 (20 200), 315 (6400), 336 nm (5600); NMR (CCl_4) δ 0.43 (d, J = 6.5 Hz, 3 H), 0.83 (d, J = 6.5 Hz, 3 H), 1.23–1.46 (overlapping Me signals, total area 12 H), 1.65 (m, J = 6.5 Hz, 1 H), 2.90 (m, J = 7 Hz), 3.36 (m, J = 7 Hz, total area from 2.90 inclusive, 2 H), 5.38 (s, 1 H), 6.87 (d, J = 2 Hz, 1 H, inside tipyl ring proton), 7.06 (d, J = 2 Hz, 1 H, outside ring proton), 7.18–8.10 (aromatic ring protons, total area 6 H); mass (12 eV) *m/e* (rel intensity) 370 (100), 328 (18), 327 (45). Anal. C, H.

Intermediate diol, **2-tipyl-*trans*-1,2-acenaphthenediol,** was obtained by interrupting the preparation of ketone **6** after the $LiAlH_4$ reduction stage to give snow-white solid diol. Recrystallization from *n*-heptane gave the pure diol: mp 170–175 °C; ir (CCl_4) 3600, 3570, 1605, 1383, 1362 cm^{-1}; uv 205 (ϵ 71 900), 227 (102 000), 287 nm (9700); NMR (CCl_4) δ 0.59 and 0.70 (overlapping doublets with apparent J = 7 Hz for both, total area 6 H), 1.18–1.47 (5 methyl signals), 1.57 (d, J = 4 Hz, OH), 1.80 (m, J = 6.5 Hz), 2.00 (s, OH, total area from δ 1.18 inclusive 15 H), 2.8 (m, J = 7 Hz, 1 H), 4.07 (m, J = 6.5 Hz, 1 H), 5.46 (d, J = 4 Hz,

1 H), 6.86 (d, J = 2 Hz, 1 H, inside tipyl ring proton), 7.05-7.83 (aromatic ring protons, total area 7 H); mass (12 eV) *m/e* (rel intensity) 388 (11), 327 (100). Anal. C, H.

2-Hydroxy-2-mesityl-1-acenaphthenone (7). The Grignard reagent, prepared from 24.9 g (125 mmol) of bromomesitylene, 50 ml of THF, and 3.5 g (144 mmol) of magnesium chips, was added dropwise over a period of 90 min to a suspension of 18.2 g (100 mmol) of finely powdered acenaphthenequinone (sublimed) in 250 ml of dry, ice-cold diglyme. Stirring was continued at 0 °C for 30 min, and the solution was poured into dilute, iced aqueous acetic acid. The worked-up product was washed with 10% $NaHSO_3$ and with cold CCl_4 to give 28.5 g (94%) of white powder, mp 169 °C dec. Recrystallization from acetone-water gave pure hydroxyketone **7**: mp 174-175 °C (stable melt); ir ($CHCl_3$) 3540, 1727 cm^{-1}; ir (Nujol) 3480, 1708 cm^{-1}; uv 219 (ϵ 59 000), 257 (12 800), 314 (6200), 340 nm (4600); NMR ($CDCl_3$) δ 2.18 and 2.22 (singlets, total area 9 H), 3.19 (s, 1 H, OH), 6.78 (s, 2 H, mesityl ring protons), 7.40-8.15 (aromatic ring protons, total area 6 H); mass *m/e* (rel intensity) 302 (100), 257 (33), 256 (39), 147 (27). Anal. C, H.

2-Hydroxy-2-tipyl-1-acenaphthenone (8). To a mixture of 7.5 g (310 mmol) of magnesium chips and 30 ml of dry ethyl ether was added dropwise over a period of 80 min (maintaining steady reflux) a solution of 28.3 g (100 mmol) of triisopropylbromobenzene and 37.6 g (200 mmol) of ethylene bromide in 100 ml of dry ethyl ether. Stirring, with external heat, was continued for 1 h, and 160 ml of dry benzene was added. This solution was cooled to ca. 15 °C, and, with vigorous stirring, 18.2 g (100 mmol) of finely powdered acenapthenequinone was added as rapidly as possible while keeping the temperature at 20-25 °C and required ca. 3 min. The reaction mixture was stirred for 30 min at 25 °C and was worked up as for the mesityl homologue to give 30.8 g of solid, mp 176 °C dec. The material in methylene chloride (200 ml) was passed through a short neutral alumina column, and the solvent was evaporated to give 28.2 g of solid, mp 185-189 °C dec. Recrystallization from acetone-water gave highly crystalline, white hydroxyketone **8**: mp 193-194 °C; ir (CCl_4) 3550, 1730, 1390, 1360 cm^{-1}; uv 218 (ϵ 82 300), 255 (16 000), 270 (6700), 312 (7600), 337 nm (5900); NMR ($CDCl_3$) δ 0.90 (very broad s) and 1.27 (d, J = 7 Hz, total area 18 H), 2.57-3.03 (complex m, total area 4 H, OH upon methine protons, J = 7 Hz), 7.06 (s, 2 H, tipyl ring protons), 7.54-8.20 (aromatic ring protons, total area 6 H); mass (18 eV) *m/e* (rel intensity) 386 (100), 371 (8). Anal. C, H.

5-Bromo-*cis*-1-phenyl-2-mesitylacenaphthene (9).[32] To a stirred saturated solution of 696 mg (2.0 mmol) of cis hydrocarbon **1** in 6 ml of glacial acetic acid was rapidly added 2.0 ml of a 1.1 M bromine-acetic acid solution. The reaction mixture was kept in the dark and periodically agitated over a period of 2 h, after which 1 ml of water was added portionwise with vigorous agitation. After standing overnight, the crystals were collected and recrystallized from acetic acid-water to afford 558 mg (66%) of highly crystalline material. Recrystallization from acetone-water gave silver needles of brominated hydrocarbon **9**: mp 173-174 °C; ir (CCl_4) 3060, 3020, 2910, 1595 cm^{-1}; NMR (CCl_4) δ 1.07 (s, 3 H, inside Me), 2.12 (s, 3 H, para Me), 2.53 (s, 3 H, outside Me), 5.30 (d, J = 9 Hz, 1 H), 5.60 (d, J = 9 Hz, 1 H), 6.30 (s, 1 H, inside mesityl ring proton), 6.65-7.00 (acenaphthene H_3 ring proton superimposed on outside methyl and phenyl ring protons, total area 7 H), 6.8 (acenaphthene H_3 ring proton), 7.23-7.96 (remaining acenaphthene ring protons, total area 4 H); mass (low eV) *m/e* (rel intensity) 428 (100), 426 (99), 348 (10). Anal. C, H, Br.

5-Bromo-*cis*-1-phenyl-2-(2,4,6-trimethyl-*in*-3-bromophenyl)-acenaphthene[40] (10). To a mixture of bromohydrocarbon **9** in 20 ml of glacial acetic acid and 2.5 ml of chloroform was added 1.0 ml of a 1.1 M bromine-HOAc solution. After being stirred for 10 min, the solution was set aside in the dark. After 5 h solid product was present, and water was added dropwise until cloudiness was reached. The microcrystalline product, 202 mg (40%), was a mixture as indicated by NMR of inside and outside rotamers and starting material in the respective ratio of 72:22:6. Several recrystallizations from acetone-water gave 113 mg of silvery platelets of inside rotamer **10**: mp 157.5-159 °C; ir (CCl_4) 3060, 3030, 2920, 1595, 1450 cm^{-1}; NMR (CCl_4) δ 1.18 (s, 3 H, inside Me), 2.27 (s, 3 H, para Me), 2.54 (s, 3 H, outside Me), 5.35 (d, J = 9 Hz, 1 H), 5.65 (d, J = 9 Hz, 1 H), 6.68-8.00 (aromatic ring protons, total area 11 H); minor methyl proton peaks at δ 1.06, 2.22, 2.75, 6.40 indicated the presence of 14% outside rotamer; mass (10 eV) *m/e* (rel intensity) 508 (62), 506 (100), 504 (53). The exact mass of the *m/e* 504 peak was 504.0083, which corresponds to the correct empirical formula $C_{27}H_{22}Br_2$ (*m/e* 504.0088).

2,4,6-Triisopropylbromobenzene. An ice-cold solution of 640 g (4.0 mol) of Br_2 in 600 ml of dimethylformamide,[41] prepared by slowly adding Br_2 to stirred, chilled DMF, was added to a stirred, light-protected ice-bathed solution of 204 g (1.0 mol) of 1,3,5-triisopropylbenzene in 1 l. of DMF. Addition was at such a rate as to maintain the reaction temperature below 30 °C and required 10 min. Stirring was continued for 20 min, and the solution was poured into an iced mixture of 400 g of sodium sulfite and 2 l. of water. The oil was extracted into pentane and worked up to give 282 g (100%) of a nearly colorless oil, whose NMR spectrum indicated was virtually pure aryl bromide (no dibromide and no hydrocarbon were detectable). Two simple distillations in vacuo gave pure aryl bromide: bp 98-100 °C (0.4 mm) (lit.[42] 146-148 °C (18 mm)); NMR (neat) δ 1.20 (d, J = 7 Hz) and 1.22 (d, J = 7 Hz, total area 18 H), 2.80 (septet, J = 7 Hz, 1 H), 3.52 (septet, J = 7 Hz, 2 H), 6.95 (s, 2 H). Anal. C, H, Br.

Bromination of 1 in the Presence of Picric Acid. An examination was made of the possibility of forcing rotor bromination by conducting the reaction in the presence of picric acid, which should preferentially form a charge-transfer complex with the naphthalene nucleus, thereby deactivating it to electrophilic substitution. To the stirred, orange solution of 174 mg (0.5 mmol) of cis hydrocarbon **1** and 160 mg (0.7 mmol) of picric acid in 4.0 ml of glacial acetic acid was added 0.5 ml of 1.1 M Br_2-acetic acid solution. The NMR spectrum of the worked-up product was identical with that for the reaction mixture as prepared above without added picric acid.

1-Phenyl-2-mesitylacenaphthylene.[23] To a solution of 6.0 g (16 mmol) of alcohol **3** in 20 ml of hot glacial acetic acid was gradually added hot formic acid until saturation was reached. The bright orange solution was allowed to crystallize, and the crystals were collected and washed with methanol to give 5.3 g (93%) of olefin, mp 125-126 °C. Recrystallization from absolute MeOH gave analytically pure, golden-yellow olefin: mp 125.5-127 °C; ir (CCl_4) 1610, 1485, 1430 cm^{-1}; uv 203 (ϵ 85 000), 235 (56 000), 328 nm (14 000); NMR (CCl_4) δ 2.03 (s, 6 H), 2.29 (s, 3 H), 6.84 (s, 2 H, mesityl ring protons), 7.11-7.84 (aromatic ring protons, total area 11 H); mass (10 eV) the only observable peak was the parent ion of *m/e* 346. Anal. C, H. This olefin, unlike 1,2-diphenylacenaphthylene,[24] was insoluble in concentrated sulfuric acid, but was soluble in fluorosulfonic acid to give a brilliant magenta solution.

Equilibration of the Inside Rotamer. The sample of inside rotamer containing 13.6 ± 1.1% outside rotamer in CCl_4 solution (containing approximately 20% $CDCl_3$ as cosolvent) was heated in a CCl_4 vapor bath, whose temperature was measured by thermometer as 76 ± 1 °C. After 30-min reaction time, analysis by NMR indicated the presence of 36.8 ± 0.3% outside isomer. The percentage of outside rotamer was determined by measuring the relative areas of the outside methyl signals of the two rotamers. The reported error is the deviation from the mean of two electronic integrations. Equilibration for 24 h at 76 °C indicated, by the average of two integrations, an equilibrium mixture containing 38.6 ± 0.1% outside rotamer; however, the maximum error observed at t = 30 min, i.e., ±0.3%, is also assigned to this determination. With these error limits, the equilibrium constant is calculated as 0.63 ± 0.01.

The rate constants were determined by the relation[43] $\ln x_e - \ln (x_e - x) = (k_1 + k_{-1})t$, in which x_e is the equilibrium relative (percent) peak area of the outside rotamer and x is the relative peak area at time t. Assigning an error of ±1 min to t and the errors indicated above to x and x_e allows calculation of the maximum, the minimum, and the average value for the rate constant. Thus, the computed forward rate constant is $k_1 = 6 \pm 1 \times 10^{-4}$ s^{-1}. Likewise, allowing an error of ±1 °C in the temperature, the Eyring equation[44] gives $\Delta G^{\ddagger} = 25.6 \pm 0.3$ kcal/mol for the forward reaction.

References and Notes

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The Effect of Transient Photoproducts in Benzophenone–Hydrogen Donor Systems

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Abstract: Besides benzpinacol, the photolysis of benzophenone results in the formation of unstable photoproducts whenever a hydrogen donor is present in solution. Benzpinacol has a low quenching constant ($4 \times 10^6\ M^{-1}\ s^{-1}$), but the unstable compounds are diffusion-controlled quenchers so that, although they are minor products, their presence can significantly affect quantum yield determinations. The problem becomes more serious with long triplet lifetimes. Fourier transform NMR is a convenient method for following the photochemistry of dilute ketone solutions even in nondeuterated solvents. The results show that benzpinacol is not formed by the reaction of an unstable photoproduct with ground-state benzophenone as has been suggested.

The photochemistry and photophysics of aromatic ketones and aldehydes have been extensively studied for many years. In solution the bimolecular reactions of hydrogen abstraction,[1] oxetane formation,[2-4] and complex formation[5-10] are well characterized. Recently, the determination of the phosphorescence lifetimes as a function of substrate concentration has afforded a simple direct method for determining the interaction rate constants of a large number of ketones in their triplet states.[11-15] The interaction rate constant can be obtained from