Double-Bond-Stabilizing Abilities of 1-Methyl-2-pyrrolyl, 9-Anthryl, and *o*-Tolyl Substituents[1]

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Equilibrium constants have been determined for the isomerizations of *trans*-PhCH=CHCH$_2$X to *trans*-PhCH$_2$CH=CHX, where X is 1-methyl-2-pyrrolyl, 9-anthryl, and *o*-tolyl. The values (estimated standard deviations) at 30 °C in *tert*-butyl alcohol are 1.53 (0.04), 0.342 (0.022), and 0.407 (0.011), respectively. The equilibrium constant for the 9-anthryl case is only about two-thirds as large as a value reported previously. Steric factors are believed to be the most important reason 9-anthryl and *o*-tolyl groups are poorer double-bond-stabilizing substituents than phenyl groups. Resonance effects are probably decisive in making 1-methyl-2-pyrrolyl substituents better than phenyl but not as good as 2-furyl at stabilizing double bonds. The organolithium compounds formed in the reaction of butyllithium with either *trans*-1-(9-anthryl)-3-phenylpropene (**7**) or *trans*-3-(9-anthryl)-1-phenylpropene (**8**) react with water to give about 11% **7**, 27% **8**, and 58% of what appears to be 9-(3-phenyl-2-propenylidene)-9,10-dihydroanthracene. Similar quenching of organolithium compounds in the *o*-tolyl case gave approximately the equilibrium mixture and in the 1-methyl-2-pyrrolyl case gave almost equal amounts of *cis*-1-(1-methyl-2-pyrrolyl)-3-phenylpropene (37%), *trans*-1-(1-methyl-2-pyrrolyl)-3-phenylpropene (33%), and *trans*-3-(1-methyl-2-pyrrolyl)-1-phenylpropene (30%). The equilibrium constant for the trans-to-cis isomerization of PhCH$_2$CH=CHX at 25 °C is 0.164 (0.011) when X is 1-methyl-2-pyrrolyl, 0.801 (0.027) when X is 9-anthryl, and 0.039 (0.011) when X is *o*-tolyl. *trans*-1-(2-Pyrrolyl)-3-(dimethylamino)propene was prepared but could not be isomerized in the presence of potassium *tert*-butoxide, probably because of anion formation at the pyrrole NH position. In *tert*-butyl alcohol–dimethyl sulfoxide containing potassium *tert*-butoxide, *trans*-1-(1-methyl-2-pyrrolyl)-3-(dimethylamino)propene appeared to isomerize to *trans*-3-(1-methyl-2-pyrrolyl)-1-(dimethylamino)propene with an equilibrium constant of 21 (5), but the evidence for this is incomplete.

For isomerizations of the type shown in eq 1, equilibrium

$$trans\text{-}XCH_2CH{=}CHY \rightleftarrows trans\text{-}XCH{=}CHCH_2Y \quad (1)$$

constants may be correlated by eq 2, in which D_X and D_Y are the double-bond-stabilizing parameters for X and Y and the rest of the right-hand side of the equation is an estimate of the changes in polar interactions across the double bond, with the σ's being Hammett para-substituent constants, τ_v a proportionality constant for interactions across a *trans*-vinylene group, and ΔG_{XY}^{chem} the statistically corrected (if necessary) value of $\Delta G°$ for reaction 1.[2,3]

$$\Delta G_{XY}^{chem} = D_Y - D_X + \tau_v(\sigma_X\sigma_{CH_2Y} - \sigma_Y\sigma_{CH_2X}) \quad (2)$$

The largest D values in the initial compilation were for methoxy and phenyl groups. The double-bond-stabilizing ability of the methoxy substituent was attributed to its ability to donate electrons by resonance; that of phenyl was attributed to conjugation without any major net electron donation or withdrawal. The explanation for the effect of methoxy substituents was supported by the subsequent discovery that the D value for the dimethylamino substituent is about 3 kcal/mol larger than that for methoxy.[4] To combine conjugation with an aromatic ring with resonance-electron-donating ability, we studied the 2-furyl group and found it to have a D value significantly larger than the value for either the methoxy or phenyl substituent.[5] We then decided to study the 2-pyrrolyl substituent, which is an even stronger resonance-electron donor.

Ross and Waight reported equilibrium constants for a number of reactions of the type of eq 3, where Ar is a

$$ArCH_2CH{=}CHPh \rightleftharpoons ArCH{=}CHCH_2Ph \quad (3)$$

polynuclear aromatic radical.[6] For the Ar groups having no *peri*-hydrogen atoms (2-naphthyl, 2-phenanthryl, and 3-phenanthryl) the log K values at 80 °C were all in the range 0.11 ± 0.04; for the Ar groups with one *peri*-hydrogen (1-naphthyl, 1-phenanthryl, and 9-phenanthryl), they were in the range −0.38 ± 0.06. These facts suggest that steric interferences with coplanarity of the double bond with the Ar ring system is the dominant factor in determining $\Delta G°$ for these equilibria. It was therefore surprising that for the 9-anthryl substituent, the only group with two *peri*-hydrogens, log K was reported to be −0.21, larger than any of the values for Ar groups with only one *peri*-hydrogen. However, the equilibrium constant for the 9-anthryl case seemed to be less reliable than their other values. The product of the reaction was not isolated and characterized. The equilibrium constant was determined by UV measurements, with the UV spectrum of the product being estimated by analogy with related compounds. We therefore decided to redetermine the equilibrium constant for reaction 3 in the case where Ar is 9-anthryl.

To broaden our study of the effect of steric interference with coplanarity on D values, we also studied the *o*-tolyl substituent, in which the resonance interaction with the double bond at a given dihedral angle should be about the same as that of a phenyl substituent.

The equilibrium must not be too one sided in order to get a reliable equilibrium constant. Therefore, the X and Y groups used in the reaction of the type of eq 1 should not have D values that differ too much. Because of our expectation that the 2-pyrrolyl group would have a large D value, we decided to study the case where X is 2-pyrrolyl and Y is dimethylamino.

Results

Synthesis of Equilibrium Components. The Mannich reaction of 2-acetylpyrrole with formaldehyde and dimethylamine has been reported to give 2-acetyl-5-((di-

(1) (a) Supported in part by Grant CHE 79 26319 from the National Science Foundation. Part 25 in the series "Structural Effects on Rates and Equilibrium". (b) For part 24 see: Hine, J.; Kanagasabapathy, V. M.; Ng, P. 1982, *47*, 2745. (c) Abstracted largely from the Ph.D. Dissertation of M. J.Skoglund, The Ohio State University, Columbus, OH, 1981.

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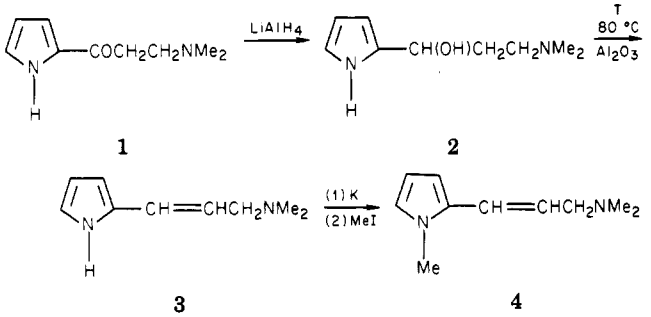
Scheme I

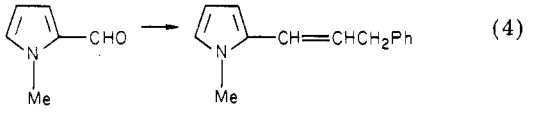


1 2

3 4

methylamino)methyl)pyrrole (after 7-h reaction time)[7] and 2-(3-(dimethylamino)propanoyl)pyrrole (1; under similar conditions but only 10-min reaction time).[8] The latter structure has been referred to as "unlikely",[9] but the literature available to us does not give a structure proof for the product obtained by either group of workers. Since 1 (Scheme I) would be a useful starting material for us, we repeated the reaction. Analysis of the reaction mixture at times ranging from 10 min to 8 h showed little change in composition. The free amine was obtained in 83% yield, and its spectra were in agreement with the structure 1 even though the material was obtained only about 95% pure. The hydrochloride of 1 had a melting point in agreement with the literature value[8] and an appropriate ^{1}H NMR spectrum. In the reduction of 1 to 1-(2-pyrrolyl)-3-(dimethylamino)-1-propanol (2), lithium aluminum hydride was added to 1 to avoid loss of the hydroxy group by overreduction. This procedure was based on Herz and Courtney's preparations of similar compounds,[10] but their dehydration procedure (in our hands) failed with 2. We heated 2 with basic aluminum oxide in benzene to give 1-(2-pyrrolyl)-3-(dimethylamino)propene (3), as the trans isomer, a white solid that decomposed at room temperature. When unsuccessful attempts to isomerize 3 in the presence of potassium *tert*-butoxide suggested that anion formation in the pyrrole ring was interfering, 3 was N-methylated to give *trans*-1-(1-methyl-2-pyrrolyl)-3-(dimethylamino)propene (**4t**).

When it appeared that **4t** may isomerize almost completely to the enamine isomer, it was decided to pit the 1-methyl-2-pyrrolyl group against a phenyl group, which might have a closer *D* value and which should certainly facilitate isomerization by a carbanion mechanism. The Wittig reaction of 1-methylpyrrole-2-carboxaldehyde with the ylide from (2-phenylethyl)triphenylphosphonium bromide gave 1-(1-methyl-2-pyrrolyl)-3-phenylpropene (**5**),



(4)

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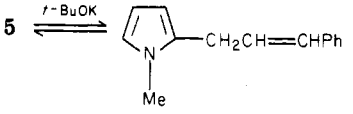
containing 30% of the cis isomer (**5c**) and 70% of the trans isomer (**5t**). Isomerization of this product mixture in *tert*-butyl alcohol containing potassium *tert*-butoxide gave a mixture of **5c**, **5t**, and 3-(1-methyl-2-pyrrolyl)-1-phenylpropene (**6**) that was separated by high-performance liquid chromatography (HPLC). This separation gave pure



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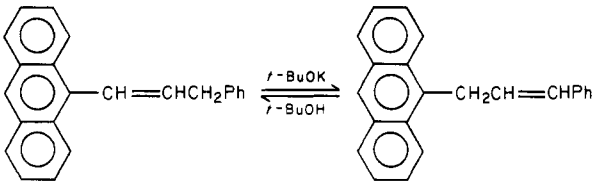
5t and *trans*-**6** (**6t**), but the ^{1}H NMR spectrum of the **5c** fraction revealed the presence of about 10% of an impurity taken to be *cis*-**6** (**6c**). The UV maximum for **5t** (286 nm, ϵ 18000) is similar to that for 1-methyl-2-vinylpyrrole (282 nm, ϵ 11900).[11] The maximum for **5c** is at a shorter wavelength (278 nm) and is less intense (ϵ 14000) than that of **5t**, as would be expected from the increased steric hindrance to resonance.[12]

The synthesis of *trans*-1-(9-anthryl)-3-phenylpropene (**7t**)was a minor modification of the method of Ross and



7 8

Waight. In our hands the vacuum distillation of 1-(9-anthryl)-3-phenyl-1-propanol resulted in complete dehydration to a product mixture from which **7t** was separated. The cis isomer of **7** (**7c**) and both isomers of 3-(9-anthryl)-1-phenylpropene (**8c** and **8t**) were separated by HPLC from the product mixture from the isomerization of **7** by potassium *tert*-butoxide in *tert*-butyl alcohol. They were characterized by their spectra, including vicinal ^{1}H NMR coupling constants across the carbon–carbon double bond of 11.3, 16.0, 11.5, and 16.0 Hz for **7c**, **7t**, **8c**, and **8t**, respectively. The allylic hydrogen atoms of **7c** were strinkingly shielded (δ 3.11), presumably because the 1- and 8-hydrogen atoms of the anthryl group force the carbon–carbon double bond to be approximately perpendicular to the anthryl ring and this puts the allylic hydrogen atoms in the shielding region of the ring.

3-Phenyl-1-*o*-tolylpropene (**9**, *o*-MeC_6H_4CH=$CHCH_2Ph$) and 1-phenyl-3-*o*-tolylpropene (**10**, *o*-$MeC_6H_4CH_2CH$=$CHPh$) were made by the thermolyses of the acetates of 3-phenyl-1-*o*-tolyl-1-propanol[13] and 1-phenyl-3-*o*-tolyl-1-propanol, respectively. The latter alcohol was prepared via the method devised by Rondestvedt[14] in making other unsymmetrical 1,3-diarylpropenes—the Claisen–Schmidt condensation of acetophenone with *o*-tolualdehyde followed by reduction (eq 5).

$$o\text{-}MeC_6H_4CHO + AcPh \rightarrow o\text{-}MeC_6H_4CH{=}CHCOPh \xrightarrow{LiAlH_4} o\text{-}MeC_6H_4CH_2CH_2CH(OH)Ph \quad (5)$$

Preparative VPC gave the trans isomers of **9** and **10** (**9t** and **10t**) in greater than 95% purity. Their trans geometries were established by their infrared spectra and their vicinal vinylene coupling constants of 15.5 and 15.6 Hz, respectively. The positions of the double bonds follow from the methods of synthesis and ultraviolet spectra. Braude and Sondheimer have noted that ortho-substituted styrenes have decreased molar absorptivities at their absorption maxima near 250 nm.[12] The molar absorptivities

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Table I. Results of Equilibration Experiments[a]

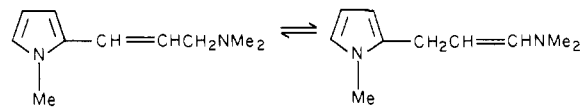
	temp, °C	$10^4 k_2$,[b] M^{-1} s^{-1}	PhCH=CHCH$_2$X[c] trans	PhCH=CHCH$_2$X[c] cis	PhCH$_2$CH=CHX[c] trans	PhCH$_2$CH=CHX[c] cis
1-methyl-2-pyrrolyl	30	3.5	36.1 (0.8)	0.9 (0.5)[d,e]	54.2 (0.8)	8.9 (0.7)
9-anthryl	30	2.0	60.5 (2.4)	2.4 (0.6)[d]	20.7 (1.3)	16.4 (0.6)
	80[f]	g	55.8 (2.0)	2.3 (0.6)[d]	24.9 (1.4)	16.9 (1.0)
o-tolyl	30	8	69.3 (1.1)	1.3 (0.3)[d]	28.2 (0.6)	1.1 (0.3)[d]
	80	100	63.9 (1.1)	1.7 (0.4)[d]	33.1 (0.6)	1.4 (0.3)[d]

[a] In *tert*-butyl alcohol solution. [b] The second-order rate constant for approach to equilibrium in the trans-trans equilibration, assuming that the reaction is first order in potassium *tert*-butoxide. [c] Percent present at equilibrium. The figures in parentheses are estimated standard deviations. [d] This compound was not isolated and characterized. Its identity is based only on certain spectral characteristics and chemical plausibility. [e] This concentration was measured at only one time. Hence it was not assured that this was the equilibrium concentration. [f] Equilibrium approached only from the 7 side. [g] No measurements were made until equilibrium had almost been established.

of **9t** and **10t** at their maxima in this region are 16 600 and 19 400 M^{-1} cm^{-1}, respectively.

Equilibrations. Attempts were made to isomerize **3** by using potassium *tert*-butoxide in *tert*-butyl alcohol. Since pyrrole has a pK_a of 17.5[15] and **3** can give a conjugate base whose negative charge is even more highly delocalized, it seems likely that **3** will be transformed extensively to its conjugate base in the presence of potassium *tert*-butoxide. Isomerization by loss of a second proton from this conjugate base seems an implausible reaction path. If the isomerization involves rate-controlling removal of a carbon-bound proton from **3** by potassium *tert*-butoxide, the rate will be proportional to the concentration of the conjugate base of **3**. If isomerization involves rate-controlling removal of a carbon-bound proton from **3** by the conjugate base of **3**, it will be fastest under conditions where half the **3** has been transformed to its conjugate base. Therefore we used potassium *tert*-butoxide concentrations that were about half the concentrations of **3** in the various runs. After about 48 h at 28 and 43 °C using 0.04 and 0.14 M **3**, respectively, only unchanged starting material could be seen in the reaction solutions. From 0.20 and 0.37 M **3** at about 110 °C for 17 and 48 h, respectively, the only observable products were black tars.

In order to avoid any complications that may have been occurring because of transformation of much of the reactant to its conjugate base, we next studied the *N*-methylpyrrole derivative **4**. It was unchanged after 50 h at 50 °C in *tert*-butyl alcohol containing 0.76 M potassium *tert*-butoxide. However, when 50% (vol) *tert*-butyl alcohol-*O*-*d*–dimethyl sulfoxide-d_6 was used as the solvent for 0.39 M **4** and 0.26 M potassium *tert*-butoxide at 50 °C, the ^{1}H NMR spectral peaks for the pyrrolyl methyl protons (δ 3.55) and dimethylamino protons (δ 2.36) decayed and a new singlet grew at δ 3.43. After a month, equilibrium seemed to have been attained, with the peak at δ 3.43 being about 20 times as large as the reactant peak at δ 3.55. It seems likely that the peak at δ 3.43 comes from *trans*-1-(dimethylamino)-3-(1-methyl-2-pyrrolyl)propene (**11t**),



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the expected product of the isomerization of **4t**. During about the first day of reaction, the reaction was complicated by almost complete exchange of the allylic protons for the deuterons of the solvent. If the 23 points taken after that time are treated as if the reaction was a reversible first-order process, a rate constant of (9.5 ± 0.3) × 10^{-7} s^{-1} for approach to equilibrium and an equilibrium constant of 21 ± 5 for isomerization of **4** to **11** are obtained. Preliminary experiments showed that the reaction product was quite sensitive to many of the procedures that might be used to permit an improved determination of this equilibrium constant. Furthermore, the equilibrium seemed to be much more one-sided than we had anticipated. For this reason we did not try to isolate and characterize **11**. Instead we compared the 1-methyl-2-pyrrolyl substituent with phenyl by isomerizing **5**.

Equilibration of **5t** and **6t** in *tert*-butyl alcohol containing potassium *tert*-butoxide was followed by quenching with water, ether extraction, and HPLC analysis. Starting with both **5t** and **6t** at 30 °C, base concentrations of 0.95 M and 0.3 M were used. Treating the reaction as a two-component equilibration that is first order in a given run gave first-order rate constants for approach to equilibrium that could be divided by the base concentration to give a second-order rate constant (standard deviation) of (3.5 ± 0.3) × 10^{-4} M^{-1} s^{-1}. The HPLC analysis gave a peak for **5c** as well as for **5t** and **6t**. The 200-MHz ^{1}H NMR spectrum of the material from the **5c** peak showed a singlet at δ 2.74 and an ABX_2 type spin system with J_{AB} = 11.3 Hz, each about one-tenth as large as the corresponding peak for **5c**. It was assumed that this came from the cis isomer of **6** (**6c**). In all runs ^{1}H NMR analyses using the pyrrole methyl peaks were carried out on samples obtained after more than 10 half-lives. The **6c** in this sample was at too low a concentration to detect clearly, but it was assumed to be present at one-tenth the concentration of the **5c**, as it had been in the **5c** separated by HPLC. The results of these analyses are summarized in Table I.

Equilibration of **7** and **8** was complicated by formation of solids in the equilibration mixture after long but variable times. It is suspected that this solid, which is believed to be a polymer, forms sooner when the usual removal of oxygen from the reaction mixture is less complete than normal. In addition, the HPLC analysis showed that all runs gave varying amounts of a material taken to be 1-(9-anthryl)-3-phenylpropane on the basis of its ultraviolet, ^{1}H NMR, and mass spectra.

When either of the *o*-tolyl compounds **9t** or **10t** was treated with potassium *tert*-butoxide in *tert*-butyl alcohol, HPLC analysis showed two peaks in addition to those for **9t** and **10t**. These two peaks showed ultraviolet absorption maxima at 241 and 236 nm, respectively. In view of the similarity of the former maximum to that for *cis*-1-phenylpropene (242 nm, ϵ 12 900),[16] which is shifted to shorter wavelengths relative to styrene (248 nm, ϵ 15 000),[17] the compound with λ_{max} equal to 241 nm is taken to be **10c**.

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Table II. Thermodynamics of Double-Bond Migration and Cis-Trans Isomerization[a]

equil const[b]	K 30 °C	K 80 °C	ΔH, kcal/mol	ΔS, eu
$K_{6t:5t}$	1.50 (0.04)			
$K_{5t:5c}$	0.164 (0.011)			
$K_{6t:6c}$	0.025 (0.015)			
$K_{8t:7t}$	0.342 (0.022)	0.446 (0.025)	1.1 (0.4)	1.6 (1.2)
$K_{7t:7c}$	0.801 (0.027)	0.679 (0.040)	−0.7 (0.3)	−2.8 (0.9)
$K_{8t:8c}$	0.04 (0.01)	0.04 (0.01)	0.0 (1.5)	−6 (5)
$K_{10t:9t}$	0.407 (0.011)	0.518 (0.013)	1.0 (0.2)	1.6 (0.5)
$K_{9t:9c}$	0.039 (0.011)	0.042 (0.009)	0.3 (1.7)	−5 (5)
$K_{10t:10c}$	0.020 (0.005)	0.027 (0.006)	1.3 (1.5)	−4 (5)

[a] In *tert*-butyl alcohol. The figures in parentheses are estimated standard deviations. [b] In $K_{6t:5t}$, for example, **6t** is the reactant and **5t** is the product.

Even more steric inhibition of resonance should give a maximum at an even shorter wavelength and the compound with λ_{max} 236 nm is taken to be **9c**. In the calculation of concentrations both were assumed to have molar absorptivities of 12900 M^{-1} cm^{-1}, like *cis*-1-phenylpropene. The equilibrium results obtained at 30 and 80 °C by using HPLC analysis of samples taken after 10 half-lives are shown in Table I. At 30 °C about 0.15 M base was used. At 80 °C 0.037 M base was used in one run and 0.33 M base in another, with almost identical results.

All the equilibria studied were established by the catalyst potassium *tert*-butoxide, and all were quenched with water or aqueous acid before analysis. If a significant fraction of the reactants had been present as carbanions and if the quenching of these carbanions gave a mixture of the reactants and products in other than their equilibrium ratios, this would produce an error in our results. Because of this, for each of the three equilibrations we varied the base concentration by at least 1.7-fold without any noticeable effect on the composition of the equilibrium mixtures. If the reactants were so acidic that they were transformed almost entirely to carbanions by the excess of base present in each equilibration mixture, the change in base concentration would not change the carbanion concentrations significantly. However, if this had occurred, the equilibrations solutions would have been deeply and characteristically colored. Our equilibration solutions had, at most, a light yellow color, and none had absorption maxima in the visible region of the spectrum. All the carbanions (as the lithium salts, at least) were strongly colored.

The equilibrium constants and enthalpies and entropies of reaction that may be calculated from the results in Table I are listed in Table II, in which $K_{6t:5t}$, for example, refers to the reaction in which **6t** is the reactant and **5t** is the product.

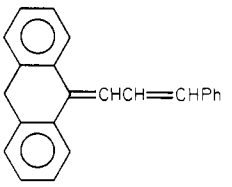
Products of Carbanion Quenching. Having three sets of tautomers of known relative stabilities, we made a brief study of the kinetic products of protonation of the common anions. Excesses of *n*-butyllithium were added to solutions of **5t**, **6t**, **7t**, **8t**, **9t**, and **10t** in tetrahydrofuran. The solutions of **5t** and **6t** became orange-red, those of **7t** and **8t** became green, and those of **9t** and **10t** became red. Each solution was quenched with D_2O, the product mixture was analyzed by HPLC, and the mass spectrum was determined. In each of the three cases both members of the pair of isomers gave the same results. As shown in Table III, the organolithium compound from **9t** and **10t** gave a product mixture that does not differ greatly from the equilibrium mixture. The organolithium compound from **5t** and **6t** is seen to give comparable amounts of **5t** and **6t**, and **5c**. Quenching the organolithium compound prepared from **7t** and **8t** gave a major product whose HPLC peak had not been observed in the equilibration

Table III. Products of Quenching Organolithium Compounds with D_2O

RLi precursor	$PhCH{=}CHCH_2X$[a] trans	$PhCH{=}CHCH_2X$[a] cis	$PhCH_2CH{=}CHX$[a] trans	$PhCH_2CH{=}CHX$[a] cis
5t:6t	33	<5	30	37
7t:8t[b]	27	3	11	1
9t:10t	54	3	41	2

[a] Percent present in product mixture. [b] 58% 9-(3-phenyl-2-propenylidene)-9,10-dihydroanthracene is also believed to be formed.

experiments. This compound has ultraviolet maxima at 248 (ε ~38000) and 343 nm (ε ~80000) and when produced by quenching with protium oxide, an ^1H NMR singlet at δ 3.9 (also not observed in equilibrated mixtures). These properties are consistent with the structure 9-(3-phenyl-2-propenylidene)-9,10-dihydroanthracene (**12**).



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The UV spectrum is similar to that for 1,1,4-triphenyl-1,3-butadiene [λ_{max} 240 (ε 20400) and 335 nm (ε 47900)],[18] and the differences—somewhat longer wavelength maxima and larger molecular absorptivities—are in the direction that would be expected since the two phenyl rings in the dihydroanthracene ring system should be more nearly coplanar with the carbon–carbon double bonds than the corresponding phenyl rings in 1,1,4-triphenyl-1,3-butadiene would be. The mass spectra of the product mixtures from quenching with deuterium oxide in the *o*-tolyl and 1-methyl-2-pyrrolyl cases showed a ratio (M + 1)/M (where M is the parent peak for the undeuterated reactants) that is as large or almost as large as the ratio M/(M − 1) had been in the undeuterated reactant, and an M + 2 peak with essentially the intensity that may be calculated from the intensity of the M + 1 peak and the natural abundances of ^{13}C and deuterium. This is the result that would be expected if the carbanions had been deuteronated in high yield with one deuteron. In the 9-anthryl case, however, both the M + 2 and M peaks of the product of quenching were larger than would be calculated for 100% monodeuteronation. This suggests that during the quenching process some of the initially formed products lost a second proton to reform a carbanion that was again deuteronated.

(18) Nikitina, A. N.; Galanin, M. D.; Ter-Sarkissian, G. S.; Mikhailov, B. M. *Opt. Spektrosk.* **1959**, 354–65; (Opt Spectrosc. (*Engl. Transl.* **1959**, 226–30.

Table IV. D Values

X	D_X, kcal/mol	X	D_X, kcal/mol
1-methyl-2-pyrrolyl	4.74	vinyl	5.89
9-anthryl	3.83	methoxy	4.93
o-tolyl	3.94	dimethylamino	7.46
phenyl	4.48	1-naphthyl	3.91
2-furyl	5.17	2-naphthyl	4.60

This would cause an initially formed kinetic product mixture to change its composition somewhat toward that of the equilibrium mixture.

Discussion

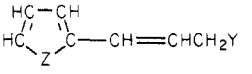
For the reactions of the type of eq 1 presently being considered, the term in eq 2 that allows for polar interactions across the carbon–carbon double bond should be quite small. For the phenyl substituent, σ_X is 0.03 and σ_{CH_2X} is −0.09. For any group with the same values the polar term will be zero. The values of 0.02 and −0.07, used for the 2-furyl and 2-furylmethyl groups, respectively, when X was 2-furyl and Y was phenyl[5] gave an estimated polar interaction of only 0.004 kcal/mol. Partly for this reason and partly because we do not have reliable values for the necessary substituent constants, we have neglected the polar term and used eq 6 to calculate D values. With the

$$\Delta G_{XY}^{chem} = D_Y - D_X \quad (6)$$

K values at 30 °C[19] and a D value of 4.48 kcal/mol for phenyl, obtained from an updated compilation and treatment of the available data,[20] D values of 4.74, 3.83, and 3.94 kcal/mol are obtained for the 1-methyl-2-pyrrolyl, 9-anthryl, and o-tolyl groups. These values are listed in Table IV with other values[20] needed for comparison purposes.

The D value for o-tolyl is seen to be 0.54 kcal/mol smaller than that for phenyl. If the o-methyl substituent affected the phenyl group in the same way that a p-methyl substituent does,[21] the D value would be 0.09 kcal/mol larger than that for phenyl. We attribute the difference, 0.63 kcal/mol, to steric inhibition of resonance. The o-methyl substituent produces a substantial deviation from coplanarity between the aromatic ring and the carbon–carbon double bond with which it is conjugated.

Steric inhibition of resonance would also be expected with the 1-methyl-2-pyrrolyl substituent. However, the five-membered ring has internal bond angles that average 12° smaller than those of a six-membered ring. This will make the interference with copolanarity considerably less in the case of the 1-methyl-2-pyrrolyl substituent than in the case of o-tolyl. If the only difference in D values between a 1-methyl-2-pyrrolyl and a 2-pyrrolyl substituent arises from steric effects, 4.74 + 0.63 or 5.37 kcal/mol in an upper limit on D for 2-pyrrolyl. Thus, although the 2-pyrrolyl substituent is certainly a more strongly electron-donating substituent by a resonance mechanism than the 2-furyl substituent is, its D value is not significantly larger and may be smaller. For this reason, it is not reasonable to attribute the larger D values of 2-furyl and 1-methyl-2-pyrrolyl substituents, relative to phenyl, largely to their greater resonance-electron-donating abilities. Instead, we suggest that it is mainly a resonance effect. The D value listed in Table IV for vinyl is based largely on heats of hydrogenation and not on equilibration experiments and therefore probably contains more experimental uncertainty than the other values. Nevertheless, we believe that it is probably significantly larger than the values for phenyl, 2-furyl, and 1-methyl-2-pyrrolyl. This value is a measure of the stabilization resulting from conjugation of two carbon–carbon double bonds. Structure **13**, in which



13

Z may be –CH=CH–, –O–, or –NR–, reflects the fact that in the case of phenyl, furyl, and pyrrolyl substituents we are dealing with *cross* conjugation. The "double bond" in the substituent group is now conjugated with Z and the other endocyclic double bond in addition to the double bond at the reaction center. The extent of this cross conjugation can be measured by the resonance energy of the appropriate aromatic ring. In Figure 1 is a plot of D_X vs. the empirical resonance energy of HX for the cases where X is vinyl, 2-furyl, 2-pyrrolyl, and phenyl. The horizontal lines extending from the points cover the range of resonance energies listed by Pauling[22] and Wheland.[23] The vertical lines from the point for 1-methyl-2-pyrrolyl cover the range 4.74–5.37 kcal/mol, which has already been referred to. The four points show a linear correlation that is as precise as the experimental data. Nevertheless, the fact that equilibria of the type of eq 3 where Ar is a meta- or para-substituted phenyl radical[21] follow the Hammett equation with a ρ of −0.45 shows that the polar effects of the heterocyclic substituents must also have a significant effect on the D values.

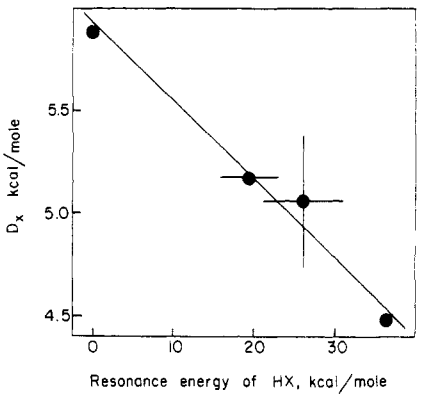


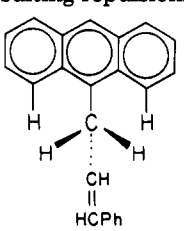
Figure 1. Plot of D_X vs. resonance energy of HX for vinyl, furyl, 1-methyl-2-pyrrolyl, and phenyl groups.

If the D values for 1-methyl-2-pyrrolyl and dimethylamino are used to calculate the equilibrium constant for isomerization of **4t** to **11t** (and the polar term in the equation is taken to be the same as if the groups were phenyl and dimethylamino) the resulting value (25) is in the range we have obtained without isolating and characterizing **11t**. This supports our suggestion that the reaction followed is the equilibration of **4t** and **11t**.

In the 9-anthryl series, the equilibrium constant we have obtained for the isomerization of **6t** to **5t** at 80 °C is only about two-thirds as large as the value reported by Ross and Waight. The main reason for the difference is that Ross and Waight's assumption that the **5** they obtained was almost entirely trans is probably not correct. Our **5**, at

(19) Data obtained as near to 25 °C as possible are used in the correlation.
(20) Hine, J.; Skoglund, M. J. following paper in this issue.
(21) Bushby, R. J.; Ferber, G. J. *J. Chem. Soc., Perkin Trans. 2* **1976**, 1683–8.
(22) Pauling, L. "The Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, NY, 1960; Chapters 6, 8.
(23) Wheland, G. W. "Resonance in Organic Chemistry"; Wiley: New York, 1955; pp 98–9.

least, was about 40% cis at equilibrium at 80 °C. Instead of having a larger D value than aryl groups with one *peri*-hydrogen, as had been concluded previously, the 9-anthryl substituent has a D value (3.83 kcal/mol) in the range (3.78–3.97 kcal/mol) found for such groups. Attributing the D values of the groups with one *peri*-hydrogen, relative to phenyl, largely to steric inhibition of resonance, one could suggest that these groups give such large deviations from coplanarity with an attached double bond that the resonance interaction between the aryl group and double bond was almost zero. The second *peri*-hydrogen atom of the 9-anthryl substituent could then not greatly increase the deviation from coplanarity and not significantly decrease the resonance interaction any further. There is strong evidence that this suggestion is not correct. The 0.63 kcal/mol decrease in D for *o*-tolyl relative to D for *p*-tolyl is almost as large as the ~0.77 kcal/mol decrease in D for polynuclear aryl groups with one *peri*-hydrogen relative to those with no *peri*-hydrogens. Hence it is not plausible that one *peri*-hydrogen produces a much larger deviation from coplanarity in arylethylene derivatives than an *o*-methyl group does. The torsional angle between the carbon–carbon double bond and the ring in *o*-methylstyrene has been estimated to be 31° from UV spectra[17] and 22° from photoelectron spectra.[24] Assuming a $\cos^2\theta$ dependence of resonance interaction on dihedral angle, this deviation from coplanarity should not result in the loss of more than 30% of the resonance interaction. On going from styrene to *o*-methylstyrene to 2,4,6-trimethylstyrene, the introduction of the second *o*-methyl substituent decreases the molar absorptivity much more than the introduction of the first one did.[12] Thus, it seems clear that substantial resonance interactions between the double bond and the aromatic ring will survive the introduction of one *o*-methyl group or one *peri*-hydrogen atom. For the 9-anthryl substituent a large deviation from coplanarity is expected, and indeed, the torsional angle in 9-vinylanthracene has been estimated from dipole moment measurements[25] to be 60 ± 10°. There must be a further loss in resonance interaction between the double bond and the ring on going to the 9-anthryl substituent, but this loss is being offset by some other factor. We believe that this other factor is one that has already been suggested to explain the D value for the *tert*-butoxy substituent[5]—steric destabilization of the isomer in which the substituent is attached to allyl carbon. In both **7t** and **8t** the *peri*-hydrogen atoms probably keep the three-carbon chain attached to the 9-position in a plane nearly perpendicular to the anthryl ring. In **7t** the sp^2 hybridization of the carbon atom attached to the 9-position keeps the hydrogen atom on that carbon in the plane of the three-carbon chain, minimizing its interactions with the *peri*-hydrogen atoms. In **8t**, however, the carbon atom attached to the 9-position is sp^3 hybridized and bears two hydrogen atoms, each of which is aimed somewhat at a *peri*-hydrogen atom as shown in **14**. The resulting repulsions are of the type that cause the anthracene ring in 9-methylanthracene to be distorted from planarity.[26]



14

For the compounds in which the double bond is conjugated with the phenyl substituent, the equilibrium constants for trans-to-cis isomerization are in the expected range. The corresponding equilibrium constant for 1-phenylpropene in dimethyl sulfoxide at 25 °C has been reported to be 0.023.[27] Our values for **6**, **8**, and **10** are within the combined experimental uncertainties of this value. The trans-to-cis equilibrium constants for the compounds in which the double bond is conjugated with a 1-methyl-2-pyrrolyl or a 9-anthryl group are much larger and the value for the *o*-tolyl-conjugated compound may be slightly larger than those for the phenyl-conjugated compounds. It is interesting to compare these values with the corresponding constant for 1-mesityl-2-phenylethylene (0.077), which is 37 times as large as the value for stilbene.[28] The cis isomer of stilbene is destabilized relative to the trans isomer by steric inhibition of resonance. The mesityl group of *trans*-1-mesityl-2-phenylethylene is forced by its *o*-methyl groups so far out of coplanarity with the double bond that it has very little resonance interaction with the double bond. Hence very little resonance interaction between the mesityl group and the double bond is lost on going to the cis isomer. Since the 9-anthryl group contains only sp^2-hybridized carbon, it is thinner than a mesityl group and, when it is perpendicular to the carbon–carbon double bond, it will repell a group cis to it less than a mesityl group would. When perpendicular to the carbon–carbon double bond, the 9-anthryl substituent will extent by only half the width of its π system toward the benzyl group that is cis to it in **7c**. For comparison purposes we note that, according to heats of hydrogenation, the cis isomers of 3-penten-1-yne and 3-decen-1-yne are more stable than the trans isomers, although the differences are not larger than the estimated experimental uncertainties.[29] Similarly, equilibration experiments show that the cis isomer is more stable than the trans isomer of crotononitrile.[30]

The entropies of isomerization of **8t** to **7t** and of **10t** to **9t** are both positive (by 1.6 eu). We attribute this to restriction of rotation resulting from coplanarity between the phenyl substituent and the carbon–carbon double bond in the reactant followed by relatively free rotation around the bond between the phenyl group and the methylene group in the product in both of these isomerizations. In the isomerization of **8t** to **7t** there is probably very little freedom of rotation around the bond between the 9-anthryl group and the rest of the molecule in either reactant or product. The *o*-tolyl group in **10t** cannot become planar with the double bond; hence larger excursions around the bond to the *o*-tolyl group can take place without as much loss of resonance interaction as would occur with a phenyl group. In **9t**, however, there is much less freedom of rotation around the bond to the *o*-tolyl group than there would be if it were phenyl. All the entropies of trans-to-cis isomerization in Table II are negative, as might be expected from increased hindrance to internal rotations in the cis isomers.

Experimental Section

All reactions were run under argon unless otherwise stated. The benzene, ether, pyridine, triethylamine, tetrahydrofuran, and

(24) Maier, J. P.; Turner, D. W. *J. Appl. Spectrosc.* **1972**, 196–206.
(25) Le Fèvre, R. J. W.; Ritchie, G. L. D. *J. Chem. Soc. B* **1968**, 775–8.
(26) Cox, P. J.; Sim, G. A. *Acta Crystallogr., Sect B* **1979**, *35*, 404–10.
(27) Ela, S. W.; Cram, D. J. *J. Am. Chem. Soc.* **1966**, *88*, 5791–802.
(28) Fischer, G.; Muszkat, K. A.; Fischer, E. *J. Chem. Soc. B* **1968**, 1156–8.
(29) Skinner, H.; Snelson, A. *Trans. Faraday Soc.* **1959**, *55*, 404–7.
(30) Butler, J. N.; McAlpine, R. D. *Can. J. Chem.* **1963**, *41*, 2487–91.

tert-butyl alcohol used were all dried, the latter by distillation from potassium *tert*-butoxide and *tert*-butyl benzoate. HPLC was conducted with a Waters pump (Model 6000A), injector (Model U6K) and μPorasil columns (10-μm mean particle size; 30 cm × 3.9 mm analytical column and 30 cm × 7.8 mm preparative column). Effluent was monitored with a tunable Varian Var-Chrom UV–vis detector and peak areas measured with a Spectra-Physics Minigrator. Retention characteristics are expressed in terms of the capacity factor[31] with CCl_4 as the reference.

Chemical shifts and coupling constants reported for ABX, ABX_2, and A_2B_2 systems were obtained as described by Abraham.[32] Other coupling constants and shifts reported are apparent values. Homonuclear decoupling was routinely used in analyzing ^1H NMR spectra.

2-(3-(Dimethylamino)propanoyl)pyrrole (1). In a modification of the method reported previously,[8] 27.0 g (250 mmol) of 2-acetylpyrrole, 7.4 g (250 mmol) of paraformaldehyde, and 20.2 g (250 mmol) of dimethylammonium chloride in 60 mL of isoamyl alcohol was stirred and refluxed for 12 min. The cooled reaction mixture separated into two phases, and the lower phase solidified after some hours in a refrigerator. The solid was made basic with 100 mL of 1 M NaOH and extracted with ether (3 × 100 mL). The combined dried (K_2CO_3) extracts were concentrated and then distilled to give isoamyl alcohol at 40–50 °C (0.15 mmHg) and 9.0 g of sublimed 2-acetylpyrrole at 85 °C (0.20 mmHg). The residue, about 95% **1** by NMR, was used without purification: IR (CCl_4) 3460 (monomeric NH), 3300 (br, NH), 1635 (C=O), 1545, 1425, 1405, 1110, 1095, 800, 730 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 10.30 (br s, 1, NH), 7.00 (m, 2, pyrrolyl C_3H and C_5H), 6.23 (m, 1, pyrrolyl C_4H), 2.97 (m, 2, A of A_2B_2, J_{AB} = 7 Hz, $COCH_2$), 2.76 (m, 2, B of A_2B_2, CH_2NMe_2), 2.35 (s, 6, $N(CH_3)_2$); ^{13}C NMR ($CDCl_3$, 20 MHz) δ 189.5, 132.2, 125.1, 116.6, 110.5, 55.2, 45.3, 36.4; mass spectrum, *m/z* (rel intensity) 166 (M^+, 7), 122 (4), 121 (4), 109 (3), 94 (15), 80 (4), 72 (4), 66 (6), 59 (4), 58 (100), 57 (7), 44 (6), 43 (9), 42 (7), 39 (6), 26 (3); *m/z* calcd for $C_9H_{14}N_2O$ 166.1106, obsd 166.1110.

Addition of HCl to **1** in ether and recrystallization from absolute EtOH gave **1**·HCl; mp 166–167 °C (lit.[8] mp 168 °C); ^1H NMR (D_2O, 90 MHz) δ 7.23 (m, 2, pyrrolyl C_3H and C_5H), 6.37 (m, 1, pyrrolyl C_4H), 3.51 (m, 2, A of A_2B_2, J_{AB} = 7.0 Hz), 3.39 (m, 2, B of A_2B_2), 2.97 (s, 6, $N(CH_3)_2$).

Refluxing **1**·HCl in isoamyl alcohol for 5 h left it essentially unchanged.

3-(Dimethylamino)-1-(2-pyrrolyl)-1-propanol (2). A solution of 19.7 g (119 mmol) of **1** in 150 mL of dry ether was treated dropwise with a slurry of 5.0 g (132 mmol) of $LiAlH_4$ in ether with stirring. After a period (2.5 h) found by TLC monitoring to maximize the yield, the reaction mixture was quenched with water, the supernatant ether solution was decanted, and the precipitated salts were washed with ether. Concentration of the dried (K_2CO_3) ether layers gave 18.8 g of yellow oil from which 4.3 g (22%) of crude **2** was crystallized by using CCl_4. After elution of the mother liquors through a 7-cm silica gel column with 95% EtOH, another 6.1 g (30%) of **2** was obtained. Recrystallization from CCl_4 gave white crystals: mp 89.5–90.0 °C; IR (KBr) 3240 (br, OH and NH), 1470, 1450, 1410, 1380, 1330, 1290, 1260, 1100, 1090, 1050, 1035 (C–O), 980, 945, 820, 720, 710 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 8.75 (br s, 1, NH), 6.63 (m, 1, pyrrolyl C_5H), 6.08 (m, 1, pyrrolyl C_3H), 6.00 (br s, 1, OH), 5.90 (m, 1, pyrrolyl C_4H), 4.97 [t, 1, *J* = 6 Hz, $CH(OH)$], 2.60 (t, 2, *J* = 7 Hz, CH_2NMe_2), 2.27 [s, 6, $N(CH_3)_2$], 1.84 [m, 2, $CH(OH)CH_2$]; ^{13}C NMR ($CDCl_3$, 20 MHz) δ (multiplicity in off-resonance decoupling) 135.1 (s), 116.6 (d), 108.1 (d), 103.1 (d), 69.6 (d), 58.1 (t), 45.3 (q), 32.9 (t); mass spectrum, *m/z* (rel intensity) 169 (4), 168 (M^+, 33), 150 (3), 106 (5), 96 (4), 94 (8), 93 (6), 92 (4), 80 (4), 73 (4), 72 (5), 59 (5), 58 (100), 45 (8), 44 (8), 44 (8), 42 (8). Anal. Calcd for $C_9H_{16}N_2O$: C, 64.25; H, 9.52; N, 16.65. Found: C, 64.40, H, 9.64; N, 16.97.

***trans*-3-(Dimethylamino)-1-(2-pyrrolyl)propene (3).** Refluxing 1.0 g (5.9 mmol) of **2** and 6.0 g of activated basic aluminum oxide in 150 mL of benzene in the dark for 2.5 h gave 0.1 mL of water in a Dean–Stark trap seeded with a small particle of $CaCl_2$. The cooled reaction mixture was filtered and the alumina washed with 95% EtOH. Room-temperature concentration of the combined filtrates in the dark gave 0.8 g of orange oil that was chromatographed (neutral alumina, 20 cm × 2.3 cm column, $CHCl_3$ eluent) in the dark. After colored materials were discarded, later fractions gave 262 mg (30%) of off-white solid **3** that was crystallized from hexane to give amber crystals, mp 73–74 °C. Alternatively, **3** could be sublimed at 60 °C and 0.02 mmHg to give a white solid: mp 68–70 °C; IR (CCl_4) 3480 (monomeric NH), 3340 (NH), 1630, 1540, 1460, 1410, 1375, 960 (*trans*-CH=CH), 800 cm^{-1}; UV max (hexane) 275 nm; ^1H NMR ($CDCl_3$, 90 MHz) δ 8.97 (br s, 1, NH), 6.60 (m, 1, pyrrolyl C_3H), 6.10 (m, 2, pyrrolyl C_4H and C_5H), 6.29 (dt, 1, A of ABX_2, J_{AX} = 0.4 Hz, J_{BX} = 6.2 Hz, J_{AB} = 15.6 Hz, CH=$CHCH_2$), 5.73 (dt, 1, B of ABX_2, CH=$CHCH_2$), 2.97 (d, 2, X of ABX_2, CH=$CHCH_2$), 2.27 [s, 6, $N(CH_3)_2$]; ^{13}C NMR ($CDCl_3$, 20 MHz) δ (multiplicity in off-resonance decoupling) 130 (s), 127.7 (d), 121.6 (d), 118.8 (d), 109.4 (d), 108.3 (d), 62.3 (t), 45.2 (q); mass spectrum, *m/z* (rel intensity) 150 (M^+, 78), 149 (10), 135 (15), 107 (15), 106 (100), 105 (24), 104 (31), 80 (24), 79 (32), 78 (12), 77 (17), 71 (12), 70 (20), 58 (24), 44 (20), 42 (22); *m/z* calcd for $C_9H_{14}N_2$ 150.1157, obsd 150.1162. Anal. Calcd for $C_9H_{14}N_2$: C, 71.96; H, 9.40; N, 18.64. Found: C, 71.45; H, 9.39; N, 18.44.

***trans*-3-(Dimethylamino)-1-(1-methyl-2-pyrrolyl)propene (4t).** A solution of 80 mg (0.53 mmol) of **3** in 20 mL of THF was treated with 25 mg (0.64 mmol) of potassium metal at reflux with stirring for 3 h. Into the resulting orange solution, at 0 °C, 5.0 mL of 0.108 M MeI (0.54 mmol) in THF was dropped with stirring. The red product mixture plus brine was extracted with ether. The dried (K_2CO_3) extract was concentrated to 57 mg of brown oil that, upon preparative TLC (neutral alumina, $CHCl_3$), gave 21 mg (24%) of **4** (R_f = 0.3) as a yellow oil: IR (CCl_4) 1635, 1540, 1460, 1410, 960, 800, 700 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 6.50 (m, 1, pyrrolyl C_3H), 6.00 (m, 2, pyrrolyl C_4H and C_5H), 6.32 (d, 1, A of ABX_2, J_{AX} = −0.3 Hz, J_{BX} = 6.7 Hz, J_{AB} = 15.5 Hz, CH=$CHCH_2$), 5.94 (dt, 1, B of ABX_2, CH=$CHCH_2$), 3.02 (d, 2, X of ABX_2, CH=$CHCH_2$), 3.62 (s, 3, pyrrolyl CH_3), 2.36 [s, 6, $N(CH_3)_2$]; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 131.4, 124.9, 123.0, 121.6, 107.9, 106.6, 62.4, 45.2, 34.2; mass spectrum, *m/z* (rel intensity) 165 (11), 164 (M^+, 100), 149 (19), 121 (11), 120 (100), 94 (22), 82 (15), 79 (11), 70 (15), 58 (19), 42 (37); *m/z* calcd for $C_{10}H_{16}N_2$ 164.1313, obsd 164.1317.

Upon standing, **4** decomposed rapidly.

(2-Phenylethyl)triphenylphosphonium Bromide. A mixture of 55.5 g (300 mmol) of $PhCH_2CH_2Br$ and 105 g (400 mmol) of Ph_3P in 500 mL of xylene was stirred at reflux for 6 h. The yellow solid that formed after cooling was dissolved in boiling EtOH, and then benzene was added with stirring, causing a yellow oil to separate. The oil was heated at 0.5 mmHg until vapor evolution ceased (several hours) and then cooled to give 98 g (67%) of the phosphonium bromide as a brittle, light yellow, hygroscopic solid: mp 50–80 °C; ^1H NMR ($CDCl_3$, 90 MHz) δ 7.67 (m, 12, aryl H), 7.00 (m, 8, aryl H), 4.00 (m, 2, Ph_3PCH_2), 3.00 (m, 2, $PhCH_2$).

***cis*- and *trans*-1-(1-Methyl-2-pyrrolyl)-3-phenylpropene (5c and 5t) and *trans*-3-(1-Methyl-2-pyrrolyl)-1-phenylpropene (6t).** To 8.9 g (20 mmol) of a stirred suspension of (2-phenylethyl)triphenylphosphonium bromide in ether at −5 °C was added dropwise 12.9 mL of 1.55 M (20 mmol) *n*-butyllithium in hexane. After 1 h, 2.18 g (20 mmol) of 1-methyl-2-formylpyrrole was added dropwise to the red solution. The resulting slurry was quenched with water and extracted twice with ether. The brine-washed, dried ($MgSO_4$), and combined organic layers were concentrated to 4.7 g of yellow oil that was chromatographed on a 4.5 × 12 cm silica gel column, eluting with 99% benzene–1% Et_3N, to give 2.2 g (56%) of a mixture of 30% **5c** and **5t** (as judged by the methylene peaks in the ^1H NMR spectrum). A solution of 1.0 g (5.0 mmol) of this mixture in 100 mL of 0.3 M *t*-BuOK in *t*-BuOH was kept at 45 °C for 18 h, quenched with water, and extracted twice with ether. The brine-washed, dried ($CaCl_2$), and combined organic layers were chromatographed on a 4.5 × 8 cm silica gel column using hexane containing 1% Et_3N to give 0.8 g of yellow oil containing **5c**, **5t**, and **6t** in the ratio 7:53:40 (NMR). Portions of this sample were separated by preparative HPLC using hexane containing 0.05% Et_3N.

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(32) Abraham, R. J. "The Analysis of High Resolution NMR Spectra"; Elsevier: New York, 1971; Chapter 6.

5c: k' = 3.2; UV max (hexane) 278 nm (ϵ 14 000), 288 (sh, 10 000); ^{1}H NMR (benzene-d_6, 200 MHz) δ 7.16 (s, 5, C_6H_5), 6.48 (dd, 1, X of ABX, J_{AX} = 3.6 Hz, J_{BX} = 1.9 Hz, J_{AB} = 2.6 Hz), 6.32 (br t, 1, A of ABX, pyrrolyl C_4H), 6.28 (dt, 1, B of ABX, pyrrolyl C_5H), 6.15 (dt, 1, A of ABX_2, J_{AX} = 1.8 Hz, J_{BX} = 7.1 Hz, J_{AB} = 11.6 Hz, C**H**=CHCH$_2$), 5.68 (dt, 1, B of ABX_2, CH=C**H**CH$_2$), 3.71 (dd, 2, X of ABX_2, CH=CHC**H**$_2$), 2.85 (s, 3, CH_3); mass spectrum, m/z (rel intensity) 198 (17), 197 (M^+, 100), 196 (37), 120 (33), 115 (29), 109 (16), 108 (14), 105 (13), 94 (74), 91 (23), 78 (10), 77 (23), 65 (11). 53 (11), 51 (19), m/z calcd for $C_{14}H_{15}N$ 197.1204, obsd 197.1209.

5t: k' = 4.0; IR (CCl_4) 1485, 1300, 1260, 1080, 1000, 950 (*trans*-CH=CH), 900, 800, 700 cm^{-1}; UV max (hexane) 286 nm (ϵ 18 000); ^{1}H NMR (benzene-d_6, 200 MHz) δ 7.15 (s, 5, C_6H_5), 6.45 (dd, 1, X of ABX, J_{AX} = 1.8 Hz, J_{BX} = 2.9 Hz, J_{AB} = 2.6 Hz, pyrrolyl C_3H), 6.27 (m, 1, A of ABX, pyrrolyl C_5H), 6.24 (m, 1, B of ABX, C_4H), 6.19 (br d, 1, A of ABX_2, J_{AX} = −1.1 Hz, J_{BX} = 7.0 Hz, J_{AB} = 15.8 Hz, C**H**=CHCH$_2$), 6.01 (dt, 1, B of ABX_2, CH=C**H**CH$_2$), 3.34 (d, 2, X of ABX_2, CH=CHC**H**$_2$), 2.83 (s, 3, CH_3); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 137.5, 131.2, 130.7, 128.5, 127.6, 127.2, 126.2, 121.8, 107.0, 106.8, 33.7, 30.3; mass spectrum, m/z (rel intensity) 198 (10), 197 (M^+, 100), 196 (35), 120 (31), 115 (24), 109 (18), 108 (22), 106 (15), 95 (11), 94 (78), 92 (11), 91 (45), 86 (11), 80 (11), 79 (11), 78 (13), 77 (24), 65 (15), 53 (13), 51 (20); m/z calcd for $C_{14}H_{15}N$ 197.1204, obsd 197.1209.

6t: k' = 4.6; IR (CCl_4) 1495, 1300, 1260, 1080, 1005, 960 (*trans*-CH=CH), 800, 700 cm^{-1}; UV max (hexane) 248 nm (ϵ 30 000), 274 (sh, 9000), 282 (sh, 5600), 294 (sh, 3100); ^{1}H NMR (benzene-d_6, 200 Mhz) δ 7.15 (m, 5, C_6H_5), 6.39 (br t, 1, A of ABX, J_{AX} = 1.8 Hz, J_{BX} = 4.5 Hz, J_{AB} = 2.6 Hz, pyrrolyl C_5H), 6.30 (br t, 1, B of ABX, pyrrolyl C_3H), 6.15 (dd, 1, X of ABX, pyrrolyl C_4H), 6.25 (br d, 1, A of ABX_2, J_{AX} = −0.8 Hz, J_{BX} = 6.0 Hz, J_{AB} = 15.8 Hz, C**H**=CHCH$_2$), 6.14 (dt, 1, B of ABX_2, CH=C**H**CH$_2$), 3.19 (d, 2, X of ABX_2, CH=CHC**H**$_2$), 2.89 (s, 3, CH_3); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 137.5, 131.2, 130.7, 128.5, 127.6, 127.2, 126.2, 121.8, 107.0, 106.8, 33.7, 30.3; mass spectrum, m/z (rel intensity) 198 (12), 197 (M^+, 82), 196 (32), 120 (28), 115 (26), 109 (10), 108 (10), 106 (14), 105 (14), 95 (12), 94 (100), 91 (16), 78 (10), 77 (28), 58 (18), 52 (12), 51 (25), 50 (10); m/z calcd for $C_{14}H_{15}N$ 197.1204, obsd 197.1209.

***trans*-1-(9-Anthryl)-3-phenylpropene (7t).** 1-(9-Anthryl)-3-phenyl-1-propanol[6] (8.82 g) was distilled at 225 °C (0.08 mmHg) to give 4.83 g of yellow oil that was chromatographed on a 6 × 40 cm silica gel column (cyclohexane–toluene) in ~1-g portions. After an anthracene fraction, 1.50 g of 16% **7c** and 84% **7t** (by NMR) was obtained as a waxy yellow solid. Repeated recrystallization from 95% EtOH–toluene gave 1.05 g of **7t** as light yellow needles: mp 96–97 °C (lit.[6] mp 96–97 °C); IR (CCl_4) 1625, 1605, 1500, 1455, 1445, 1160, 1020, 975 (*trans*-CH=CH), 960, 890, 845, 700, 615 cm^{-1}; UV max (hexane) 248 nm (sh, ϵ 94 000), 256 (148 000), 332 (sh, 2800), 350 (5600), 368 (8200), 386 (7400); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.36 (s, 1, anthryl $C_{10}H$), 8.30 (m, 2, anthryl C_1H and C_8H), 7.99 (m, 2, anthryl C_4H and C_5H), 7.45 (m, 9, aryl H), 7.19 (dt, 1, A of ABX_2, J_{AX} = 1.6 Hz, J_{BX} = 6.8 Hz, J_{AB} = 16.0 Hz, C**H**=CHCH$_2$), 6.22 (dt, 1, B of ABX_2, CH=C**H**CH$_2$), 3.85 (dd, 2, X of ABX_2, CH=CHC**H**$_2$); ^{13}C NMR ($CDCl_3$, 20 MHz) δ (multiplicity in off-resonance decoupling) 140.2 (s), 137.7 (s), 133.1, 131.6 (s), 129.7 (s), 129.5, 128.8, 128.7, 127.4, 127.0, 126.4, 126.1, 125.3, 125.1, 40.1 (t); mass spectrum, m/z (rel intensity) 295 (11), 294 (M^+, 44), 215 (12), 204 (15), 203 (100), 202 (38), 191 (4), 189 (4), 178 (4), 91 (15), 77 (4), m/z calcd for $C_{23}H_{18}$ 294.1408, obsd 294.1416. Sublimation at 130 °C (0.10 mmHg) gave analytically pure **7t**. Anal. Calcd for $C_{23}H_{18}$: C, 93.84; H, 6.16. Found: C, 93.77; H, 6.19.

***cis*-1-(9-Anthryl)-3-phenylpropene (7c) and *trans*-3-(9-Anthryl)-1-phenylpropene (8t).** A solution of 33 mg of **7t** in 30 mL of 0.74 M *t*-BuOK in *t*-BuOH was kept at 45 °C for 24 h. The reaction mixture was diluted with ether, washed with 1 M HCl and then with brine, dried ($CaCl_2$), and concentrated. Preparative HPLC (hexane) separated portions of the resulting yellow oil into **7c**, **8t**, and 1-(9-anthryl)-3-phenylpropane (?).

7c was a waxy yellow solid: k' = 8.7; UV max (hexane) 250 nm (sh, ϵ 98 000), 256 (150 000), 320 (sh, 1300), 332 (sh, 2500), 348 (6000), 365 (8800), 385 (8500); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.43 (s, 1, anthryl $C_{10}H$), 8.33 (m, 2, anthryl C_1H and C_8H), 8.04 (m, 2, anthryl C_4H and C_5H), 7.49 (m, 4, anthryl H), 7.20 (m, 5, C_6H_5), 7.12 (br d, 1, A of ABX_2, J_{AB} = 11.3 Hz, J_{AX} = 0.7 Hz, J_{BX} = 8.0 Hz, C**H**=CHCH$_2$), 6.44 (dt, 1, B of ABX_2, CH=C**H**CH$_2$), 3.11 (dd, 2, X of ABX_2, CH=CHC**H**$_2$); mass spectrum, m/z (rel intensity) 295 (23), 294 (M^+, 100), 293 (7), 279 (5), 278 (4), 217 (7), 216 (6), 215 (18), 204 (17), 203 (96), 202 (35), 191 (11), 189 (10), 178 (9), 91 (9), 77 (4), m/z calcd for $C_{23}H_{18}$ 294.1408, obsd 294.1416.

Crystallization from 95% EtOH–toluene gave **8t** as yellow needles: mp 76–77 °C; k' = 13.7; UV max (hexane) 250 nm (sh, ϵ 98 000), 256 (150 000), 284 (sh, 3300), 292 (sh, 1500), 318 (sh, 960), 330 (2400), 348 (5400), 365 (8400), 385 (7600); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.41 (s, 1, anthryl $C_{10}H$), 8.30 (m, 2, anthryl C_1H and C_8H), 8.03 (m, 2, anthryl C_4H and C_5H), 7.50 (m, 4, anthryl H), 7.24 (m, 5, C_6H_5), 6.58 (dt, 1, A of ABX_2, J_{AB} = 16.05 Hz, J_{AX} = 5.9 Hz, J_{BX} = 0.8 Hz, C**H**=CHCH$_2$), 6.38 (dt, 1, B of ABX_2, CH=C**H**CH$_2$), 4.54 (dd, 2, X of ABX_2, CH=CHC**H**$_2$); mass spectrum, m/z (rel intensity) 295 (22), 294 (M^+, 92), 293 (6), 279 (5), 278 (4), 217 (6), 216 (5), 215 (17), 204 (15), 203 (100), 202 (32), 191 (10), 189 (8), 178 (8), 91 (8), 77 (4); m/z calcd for $C_{23}H_{18}$ 294.1408, obsd 294.1416.

The material taken to be 1-(9-anthryl)-3-phenylpropane was a waxy yellow solid: k' = 7.6; UV max (hexane) 250 nm (sh), 256, 332, 348, 366, 386; ^{1}H NMR ($CDCl_3$, 90 MHz) δ 8.19 (m, 2, anthryl H), 7.72 (m, 3, anthryl H), 7.46 (m, 4, anthryl H), 7.17–6.88 (m, 5, C_6H_5), 2.63 (t, 2, J = 7 Hz, anthryl CH_2), 2.38 (t, 2, J = 7 Hz, PhC**H**$_2$), 1.10 (m, 2, CH_2C**H**$_2$CH$_2$); mass spectrum, m/z (rel intensity) 297 (11), 296 (M^+, 45), 203 (9), 202 (7), 192 (18), 191 (100), 189 (13), 178 (9), 177 (16).

1-Acetoxy-3-phenyl-1-*o*-tolylpropane. Acetic anhydride (14 mL, 150 mmol) was added to a solution of 10.0 g (44.2 mmol) of 3-phenyl-1-*o*-tolyl-1-propanol in 20 mL of pyridine and stirred overnight. The sodium bicarbonate washed ether extract was dried ($MgSO_4$), concentrated, and distilled to give 11.3 g (95%) of 1-acetoxy-3-phenyl-1-*o*-tolylpropane: bp 130 °C (0.15 mmHg); IR (film) 1740 (C=O), 1605, 1500, 1460, 1380 (acetyl CH_3), 1240 (acetyl C–O), 1050 (C–O), 760, 710 cm^{-1}; ^{1}H NMR (CCl_4, 60 MHz) δ 7.2–6.9 (m, 9, aryl H), 5.87 [t, 1, J = 6 Hz, C**H**(OAc)], 2.50 [m, 2, CH(OAc)C**H**$_2$], 2.20 (s, 3, Ar CH_3), 2.00 (m, 3, PhC**H**$_2$), 1.90 (s, 3, CH_3CO); mass spectrum, m/z (rel intensity) 268 (M^+, <1), 209 (18), 208 (100, M^+ – HOAc), 207 (12), 194 (10), 193 (60), 167 (15), 149 (32), 130 (18), 118 (12), 116 (12), 114 (8), 107 (25), 105 (52), 104 (68), 103 (12), 91 (18), 79 (12), 77 (20), 57 (12), 43 (45).

***trans*-3-Phenyl-1-*o*-tolylpropene (9t).** Flame heating of a flask containing 11.06 g (41.2 mmol) of the preceding acetate was continued until about 80% of the theoretical amount of acetic acid had been collected. Distillation of the residue at 130 °C (0.08 mmHg) gave 8.2 g (95%) of light yellow oil. Portions of this oil were purified by preparative VPC at 270 °C using 10% OV-17 on GAS Chrom Q (80–100 mesh in a 3/8 in. × 12 ft column) to give **9t** as a colorless oil: IR (film) 1650 (C=C), 1605, 1500, 970 (*trans*-CH=CH), 760, 710 cm^{-1}; UV max (hexane) 250 (ϵ 16 000), 288 (1540), 298 nm (870); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.4–7.1 (m, 9, Ar H), 6.87 (dd, 1, A of ABX_2, J_{AB} = 15.5 Hz, J_{AX} = 1.3 Hz, J_{BX} = 7.0 Hz, C**H**=CHCH$_2$), 6.00 (dt, 1, B of ABX_2, CH=C**H**CH$_2$), 3.56 (dd, 2, X of ABX_2, CH=CHC**H**$_2$), 2.32 (s, 3, CH_3); ^{13}C NMR ($CDCl_3$, 20 MHz) δ (multiplicity in off-resonance decoupling) 140.4 (s), 136.7 (s), 135.1 (s), 130.6, 130.2, 129.2, 128.7, 128.5, 127.1, 126.4, 126.2, 125.8, 39.7 (t), 19.8 (q); mass spectrum, m/z (rel intensity) 209 (20), 208 (M^+, 100), 207 (18), 194 (14), 193 (76), 192 (10), 179 (12), 178 (24), 131 (10), 130 (14), 129 (14), 120 (12), 119 (12), 117 (26), 116 (98), 115 (60), 105 (22), 104 (48), 103 (10), 92 (10), 91 (23), 89 (10), 78 (10), 77 (16), m/z calcd for $C_{16}H_{16}$ 208.1256, obsd 208.1256. Anal. Calcd for $C_{16}H_{16}$: C, 92.26; H, 7.74. Found: C, 92.09; H, 7.82.

2-Methylchalcone. A mixture of 23.61 g (196 mmol) of acetophenone, the same amount of *o*-tolualdehyde, 9.92 g (248 mmol) NaOH, 56 mL of 95% EtOH, and 89 mL of H_2O was stirred at about 25 °C for 3 h and left in a refrigerator overnight. The oil layer that separated was combined with an ether extract, washed with HCl and $NaHCO_3$, dried ($MgSO_4$), concentrated, and distilled to give a yellow oil: bp 170 °C (0.30 mmHg); IR (film) 1665 (CH=CHC=O), 1600, 1580, 1490, 1450, 1330, 1285 (aryl C=O), 1020, 985 (*trans*-CH=CH), 755, 700 cm^{-1}; ^{1}H NMR (CCl_4, 60 MHz) δ 8.2–7.0 (m, 11, Ar and vinyl H), 2.30 (s, 3, CH_3); ^{13}C NMR ($CDCl_3$, 20 MHz) δ 190.5, 142.5, 138.4, 134.0, 132.8, 131.0, 130.3, 128.9, 128.7, 128.6, 126.5, 126.4, 123.3, 19.8; mass spectrum, m/z (rel intensity) 223 (11), 222 (M^+, 56), 221 (18), 208 (27), 207 (100),

145 (20), 119 (13), 117 (18), 116 (20), 115 (38), 107 (11), 105 (98), 91 (51), 77 (78), 65 (11), 51 (18), m/z calcd for $C_{16}H_{14}O$ 222.1045, obsd 222.1051.

1-Phenyl-3-*o*-tolyl-1-propanol. A slurry of 5.90 g (155 mmol) of $LiAlH_4$ in 200 mL of ether was added dropwise to a stirred solution of 35.44 g (155 mmol) of 2-methylchalcone in 250 mL of ether. After 3 h at reflux, the solution was quenched with water and then 5% HCl until it was acidic. The brine-washed, dried ($MgSO_4$) ether layer was concentrated and distilled to give 31.0 g (88%) of the alcohol: bp 155 °C (0.25 mmHg); IR (film) 3350 (br, OH), 1605, 1500, 1460, 1050 (C-O), 760, 700 cm^{-1}; ^1H NMR (CCl_4, 60 MHz) δ 7.10 (s, 5, C_6H_5), 6.93 (s, 4, *o*-MeC_6H_4), 4.43 [t, 1, J = 6 Hz, C**H**(OH)], 2.90 (br s, 1, OH), 2.50 [m, 2, CH(OH)C**H**$_2$], 1.85 (t, 2, *o*-tolyl CH_2); mass spectrum, m/z (rel intensity) 226 (M^+, 8), 209 (11), 208 ($M^+ - H_2O$, 60), 193 (16), 130 (10), 119 (20), 117 (10), 115 (10), 107 (100), 105 (42), 104 (43), 103 (12), 92 (11), 91 (31), 79 (55), 78 (10), 77 (44), 51 (15), 18 (39), 17 (26); m/z calcd for $C_{16}H_{18}O$ 226.1358, obsd 226.1351.

1-Acetoxy-1-phenyl-3-*o*-tolylpropane. This acetate was made from the corresponding alcohol by the same method used to make 1-acetoxy-3-phenyl-1-*o*-tolyl-propane. The product was a colorless oil: bp 150 °C (0.20 mmHg); IR (film) 1740 (C=O), 1605, 1500, 1460, 1380 (acetyl CH_3), 1240 (acetyl C-O), 1050 (C-O), 760, 710 cm^{-1}; ^1H NMR (CCl_4, 90 MHz) δ 7.25 (s, 5, C_6H_5), 6.98 (s, 4, MeC_6H_4), 5.68 [t, 1, J = 6 Hz, C**H**(OAc)], 2.45 [m, 2, CH(OAc)C**H**$_2$], 2.18 (s, 3, Ar C**H**$_3$), 2.00 (m, 2, Ar CH_2), 1.90 (s, 3, CH_3CO); mass spectrum, m/z (rel intensity) 268 (M^+, <1), 208 (M^+ - HOAc, 26), 193 (12), 131 (12), 121 (15), 119 (11), 118 (12), 117 (52), 116 (23), 115 (11), 105 (25), 104 (100), 103 (11), 92 (17), 91 (63), 90 (12), 79 (11), 78 (11), 77 (14), 65 (14), 59 (15), 51 (12), 43 (46).

***trans*-1-Phenyl-3-*o*-tolylpropene (10t).** The preceding acetate was thermolyzed in essentially the same way used to prepare **9t**, yielding **10t** as a colorless oil: bp 130 °C (0.10 mmHg); IR (film) 1650 (C=C), 1605, 1500, 1460, 970 (*trans*-CH=CH), 750, 700 cm^{-1}; UV max (hexane) 252 nm (ϵ 19 400), 282 (1640), 292 (1020); ^1H NMR ($CDCl_3$, 300 MHz) δ 7.4-7.1 (m, 9, Ar H), 6.3-6.4 (m, 2, AB of ABX_2, δ_A 6.36, δ_B 6.33, J_{AB} = 15.6 Hz, J_{AX} = -1.5 Hz, J_{BX} = 7.1 Hz, CH=CH), 3.53 (m, 2, X of ABX_2, CH=CHC**H**$_2$); ^{13}C NMR ($CDCl_3$, 20 MHz) δ (multiplicity in off-resonance decoupling) 138.3 (s), 137.7 (s), 136.4 (s), 131.0, 130.3, 129.3, 128.5, 127.0, 126.5, 126.2, 36.9 (t), 19.4 (q); mas spectrum, m/z (rel intensity) 209 (20), 208 (M^+, 100), 207 (18), 194 (15), 193 (78), 192 (10), 191 (10), 179 (12), 178 (24), 130 (18), 129 (12), 117 (24), 116 (21), 115 (75), 105 (18), 104 (66), 103 (12), 91 (36), 89 (10), 78 (10), 77 (15), 65 (10); m/z calcd for $C_{16}H_{16}$ 208.1252, obsd 208.1256. Anal. Calcd for $C_{16}H_{16}$: C, 92.26; H, 7.74. Found: C, 92.22, 91.90; H, 7.82, 7.75.

Equilibration of Propenes 5-10. The propene (3-20 mg) was placed in a tared Schlenk tube either directly or by concentration of a solution. The argon-purged tube was sealed and transferred to a drybox containing an atmosphere of N_2. A measured amount (10-30 mL) of freshly prepared (from metallic K) *t*-BuOK in *t*-BuOH (0.03-1.1 M) was added to the opened tube, which was resealed, removed from the drybox, purged with argon, and sealed again. The tube was then kept at constant temperature, and during sampling, argon was added to maintain a positive pressure. Aliquots were removed by syringe and analyzed by HPLC or NMR.

Generation and Quenching of Lithio Derivatives of 5-10. The propene (5-21 mg) was placed in a tared 25-mL Schlenk tube that had been washed with D_2O and dried under vacuum at 150 °C. The tube was purged with argon and sealed. Freshly distilled THF (10 mL) was added by syringe, followed by 1.0 mL of 1.55 M (an excess) of *n*-butyllithium in hexane, with the immediate formation of an intense color. The spectrum of the orange-red color obtained with **5t** and **6t** was not determined, but the products from **7t** and **8t** had a maximum at 675 nm, and the product from **9t** and **10t** had a maximum at 470 ± 20 nm. Addition of 1.0 mL of 99.96% D_2O (an excess) discharged the color. the quenched mixture was combined with ether and brine. The ether layer was dried ($CaCl_2$) and concentrated, and the residue was analyzed by HPLC and mass spectral measurements.

In a similar run using 44 mg (0.15 mmol) of **7t**, ^1H NMR ($CDCl_3$, 90 MHz) analysis showed, in addition to peaks characteristic of 28% **8t** and 11% **7t**, the following: δ 8.20 (m, 2), 7.90 (m, 2), 7.55 (m, 4), 7.4-7.1 (m, 6), 6.8-6.3 (m, 2), 3.87 (s, 2). Separation of this mixture by HPLC gave as the main component, for which the structure 9-(3-phenyl-2-propenylidene)-9,10-dihydroanthracene is suggested, a compound with the following UV max (hexane): 248 nm (ϵ 37 000), 343 nm (78 000). Molar absorptivities were estimated from HPLC (256 nm) and NMR comparisons using **8t** as an internal standard.

Registry No. **1**, 83135-65-3; **1**·HCl, 83135-67-5; **2**, 83135-66-4; **3**, 83135-59-5; **4t**, 83135-60-8; **5c**, 83135-56-2; **5t**, 83135-53-9; **5/6** Li, 83135-62-0; **6c**, 83135-72-2; **6t**, 83135-52-8; **7c**, 83135-57-3; **7t**, 5738-43-2; **7/8** Li, 83135-63-1; **8c**, 83135-73-3; **8t**, 83152-05-0; **9c**, 83135-58-4; **9t**, 83135-54-0; **9/10** Li, 83135-64-2; **10c**, 83135-74-4; **10t**, 18916-11-5; **11t**, 83135-61-9; **12**, 83135-55-1; $PhCH_2CH_2Br$, 103-63-9; Ph_3P, 603-35-0; 1-(9-anthryl)-3-phenylpropane, 74387-95-4; 2-acetylpyrrole, 1072-83-9; dimethylammonium chloride, 506-59-2; paraformaldehyde, 30525-89-4; (2-phenylethyl)triphenylphosphonium bromide, 53213-26-6; 1-methyl-2-formylpyrrole, 1192-58-1; 1-(9-anthryl)-3-phenyl-1-propanol, 50688-75-0; 1-acetoxy-3-phenyl-1-*o*-tolylpropane, 83135-68-6; 3-phenyl-1-*o*-tolyl-1-propanol, 83135-69-7; (*E*)-2-methylchalcone, 14182-01-5; acetophenone, 98-86-2; *o*-tolualdehyde, 529-20-4; 1-phenyl-3-*o*-tolyl-1-propanol, 83135-70-0; 1-acetoxy-1-phenyl-3-*o*-tolylpropane, 83135-71-1.

Effects of 57 Substituents on the Stabilities of Carbon-Carbon Double Bonds[1]

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Literature data on equilibria in which *trans*-$XCH_2CH{=}CHY$ is transformed to *trans*-$XCH{=}CHCH_2Y$ have been collected to expand a previous correlation of ΔG^{chem} values for reactions of this type. For 11 substituents in an overdetermined set of 30 equilibria the observed data are fitted with a standard deviation of 0.29 kcal/mol. In addition to the double-bond-stabilizing parameters (D values) for these substituents, D values are listed for 46 substituents that were each involved in only one equilibrium.

A correlation of equilibrium constants for double bond migration reactions of the type shown in eq 1 was described some time ago.[2] A simple correlation could be made in

trans-$XCH_2CH{=}CHY \rightleftarrows$ *trans*-$XCH{=}CHCH_2Y$ (1)

terms of eq 2, in which ΔG_{XY}^{chem} is the change in chemical free energy[3] and D_X and D_Y are the double bond stabilizing

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