a $\mathrm{p}K_\mathrm{a}$ of 2.42 compared to the predicted value of 2.6 for the neutral species of **3b** and of −0.3 for **1b** is a clear indication that the molecule exists predominantly as **3b** in this equilibrium.

As the pH of a solution of **1b** in dilute $DCl/D_2O$ was lowered by the addition of concentrated DCl (to pH 0.8), the signals for **2b** increased sharply at the expense of those for **4b**. Increased acid concentration can promote the ring closure especially if dehydration of **3b** occurs.[10] The assignment of the signals at $\delta$ 9.06 and 9.23 to **2b** is based on the fact that, at pH 0.8, nearly all of the molecule would be protonated.

A new set of signals appeared at $\delta$ 9.80 and 10.1. It is suggested that these signals belong to **5b**, which must be formed as an intermediate when the molecule is converted from **3b** to **6b**. This, however, is only a transient intermediate. Upon standing at room temperature for several weeks a tan solid separated from the solution. This substance was identified as **6b** on the basis of UV ($\lambda_{max}$ 290 nm at pH 2, 7, 13) and $^1H$ NMR ($\delta$ 9.67 for CHO) spectra. Subsequently, a solution of **1b** in 0.1 N HCl was heated for 3 h. Upon cooling, a solid separated which had spectral properties (UV and $^1H$ NMR) identical with the material isolated above. Furthermore, the product from 0.1 N HCl was identical with an authentic sample of **6b**[16] as determined by UV, $^1H$ NMR, and IR spectra.

Undoubtedly the $\mathrm{p}K_\mathrm{a}$ of 2.42 creates a more complex set of equilibria and reactions which take place over a much longer period than in the case of **1a**. Furthermore, it was not possible to simplify this situation by going directly to a more concentrated acid solution. When this was attempted **2b** precipitated as the chloride salt.

An examination of **1b** in dimethyl sulfoxide, to which both $D_2O$ and $DCl/D_2O$ were added, gave a similar pattern of covalent hydration. No evidence for the formation of **4b** was seen, and the reaction was not monitored long enough to see the eventual formation of **6b**.

While the UV spectrum of 2,4-dioxo-(1*H*,3*H*)-pyrimido[4,5-*d*]pyrimidine (**1c**) bore some resemblance to that of **1b**, $^1H$ NMR studies in dilute $DCl/D_2O$ did not indicate any evidence of covalent hydration comparable to either **1a** or **1b**. The $\mathrm{p}K_\mathrm{a}$ for **1c** was estimated to be at or below zero. This estimate is undoubtedly low because protonation could only be expected to occur in the unsubstituted ring, leaving **2c** an unlikely species. Consequently, acid-catalyzed covalent hydration would require far stronger acid solutions and be less well stabilized by resonance than is the case for either **1a** or **1b**. Indeed, indications are that such strongly acid solutions would very likely promote dehydration[10] due to the decreased activity of water. Even so, the poor solubility of **1c** in aqueous acid solutions prevented any further examination of this species. In dimethyl sulfoxide, **1c** is more soluble but when $DCl/D_2O$ was added no evidence of covalent hydration was observed. As the acid concentration was increased, **1c** precipitated from the aqueous dimethyl sulfoxide solution.

## Experimental Section

All $^1H$ NMR spectra were recorded on a JEOL FX 90Q fourier transform spectrometer in either deuterium oxide (with sodium (trimethylsilyl)propanesulfonate, TPS, or dioxane as internal standard) or dimethyl sulfoxide (with tetramethylsilane as internal standard). Mass spectra were measured on a Varian MAT-CH7. UV spectra were recorded on a Unicam SP 1800 ultraviolet spectrophotometer in aqueous solution. IR spectra were determined on a Unicam SP 1050 infrared spectrophotometer.

**Syntheses of Pyrimido[4,5-*d*]pyrimidines 1a–c.** **1a** was prepared according to literature methods[11] in 79% yield: $^1H$ NMR ($Me_2SO$-$d_6$ + $Me_4Si$), $\delta$ 6.99 (2 H, br s, 4-$NH_2$), 7.91 (2 H, br s, 2-$NH_2$), 8.88 (1 H, sharp s, $H_5$), 9.24 (1 H, sharp s, $H_7$).

**1b** was prepared according to literature methods[12] in 88% yield: $^1H$ NMR ($Me_2SO$-$d_6$ + $Me_4Si$) $\delta$ 7.64 (2 H, br s, 2-$NH_2$), 8.94 (1 H, sharp s, $H_5$), 8.97 (1 H, sharp s, $H_7$); $N_3$-H readily exchanges with $H_2O$ in solvent.

**1c** was prepared according to literature methods[12] in 71% yield: $^1H$ NMR ($Me_2SO$-$d_6$ + $Me_4Si$) $\delta$ 8.96 (2 H, unresolved d, $H_5$ and $H_7$); $N_1$-H and $N_3$-H readily exchange with $H_2O$ in solvent.

**Acknowledgment.** I am grateful to the Australian National University and the Staff of the Medical Chemistry Group, John Curtin School and Medical Research, for the opportunity to conduct this work in their laboratories. Dr. D. D. Perrin was most instrumental in the calculation of $\mathrm{p}K_\mathrm{a}$s based on prediction rules he has formulated. Special appreciation is given to Dr. D. J. Brown for his efforts in providing this opportunity and to the Australian–American Educational Foundation for financial support through a Fulbright Senior Scholar Award. Finally, a very warm thank you is given to Dr. W. L. F. Armarego for his advice and encouragement throughout this study without which this work would not have reached this stage.

**Registry No.** **1a**, 16357-81-6; **1b**, 89890-99-3; **1c**, 89891-00-9; **2a**, 89891-01-0; **2b**, 89891-02-1; **3a**, 89891-03-2; **3b**, 89891-04-3; **4b**, 89891-05-4; **5a**, 89891-06-5; **5b**, 89891-07-6; **6a**, 88075-69-8; **6b**, 88075-70-1.

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## Formation of Alkyl Carbanions by Alkoxide Fragmentation in HMPT

John. S. Lomas and Jacques-Emile Dubois*

*Institut de Topologie et de Dynamique des Systêmes de l'Universitê Paris 7 (associê au CNRS), 1 rue Guy de la Brosse, 75005 Paris, France*

*Received November 7, 1983*

Saturated hydrocarbons are the weakest carbon acids known.[1] The weakest studied to date is isobutane whose $\mathrm{p}K_\mathrm{a}$ is about 13 units higher than that of methane (58 ± 5).[2] No other system giving a tertiary alkyl carbanion has yet been investigated directly. Indirect comparisons of such acids by organolithium exchange[3] are unreliable because of solvation and/or association phenomena that mask the contribution of carbanion stability to the equilibria.

We now report that the fragmentation of tertiary alkoxides, $R^1R^2R^3CO^-Li^+$, in HMPT can be used to study the relative rates of formation of *tert*-butyl and bridgehead tertiary alkyl carbanions by intramolecular competition. By means of molecular mechanics (MM) calculations[4] the steric contribution to these relative rates can be evaluated, revealing discrepancies that are associated with the relative carbanion stabilities.

Tertiary alcohols have been decomposed via the alkoxide ion by Zook,[5] at elevated temperatures, and by Cram,[6] when resonance stabilizing aromatic or cyano groups were

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(1) Reviews on carbon acids: (a) D. J. Cram, "Fundamentals of Carbanion Chemistry", Academic Press, New York, 1965; (b) J. R. Jones, "The Ionization of Carbon Acids", Academic Press, New York, 1973; (c) E. Buncel, "Carbanions: Mechanistic and Isotopic Aspects", Elsevier, Amsterdam, 1975.

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0022-3263/84/1949-2067$01.50/0

**Table I. Normalized Yields and Associated Strain Energy Changes for Tertiary Alkoxide Fragmentation**

| | | | | normalized yields, % | | | | Δ strain, kcal mol$^{-1}$ | | | | deviation, kcal mol$^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| compd | R$^1$ | R$^2$ | R$^3$ | *t*-Bu[a] | Ad[b] | Oc[c] | Nor[d] | *t*-Bu | Ad | Oc | Nor | |
| **1** | *t*-Bu | Ad | Ad | 92.4 | 8.6 | | | 41.23 | 40.88 | | | 1.54 |
| **2** | *t*-Bu | Oc | Oc | 93.7 | | 6.3 | | 39.14 | | 38.80 | | 1.67[e] (1.59) |
| **3** | *t*-Bu | Oc | Nor | 97.4 | | 2.6 | | 33.01 | | 32.84 | 29.57 | 1.96[e] (1.87) |
| **4** | Ad | Ad | Oc | | 73.2 | 26.8 | | | 41.05 | 40.99 | | -0.12 |
| **5** | Ad | Ad | Nor | | 89.7 | | 10.3 | | 35.22 | | 31.89 | 2.46 |
| **6** | Ad | Oc | Oc | | 33.8 | 66.2 | | | 40.52 | 40.57 | | -0.06 |
| **7** | Ad | Oc | Nor | | 38.3 | 50.2 | 11.5 | | 34.05 | 34.26 | 31.00 | -0.05,[f] 2.34[g] |
| **8** | Oc | Oc | Nor | | | 88.5 | 11.5 | | | 33.31 | 30.21 | 2.29[e] (2.21) |

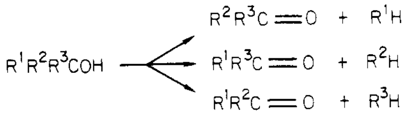
[a] *tert*-Butyl. [b] 1-Adamantyl. [c] 1-Bicyclo[2.2.2]octyl. [d] 1-Norbornyl. [e] Relative to Oc; values relative to Ad in parentheses. [f] Oc/Ad. [g] Nor/Ad.

present. More recently, Arnett[7] has shown that the very congested tri-*tert*-butylcarbinol is decomposed instantaneously by reaction with the strong base, dimsylate anion, in $Me_2SO$. We find that the same reaction can be conveniently performed by generating alkoxides in *n*-butyllithium/hexane and adding HMPT.

$$R^1R^2R^3COH \xrightarrow{n\text{-BuLi}} R^1R^2R^3CO^- \xrightarrow{\text{HMPT}} R^1R^2CO + [R^3]^- \rightarrow R^3H$$

Preliminary experiments indicated that only the most congested tertiary alcohols (**1**, **2**, **4**, and **6**) could be cleaved by $Li^+Me_2SO^-$, whereas in HMPT, whose ability to enhance the reactivity of anions is well-known,[8] otherwise stable compounds (**3**, **5**, **7**, and **8**) were found to react. The solubility of the alkoxides was also greatly improved. Results are given in Table I. The contrast between the present results for alcohol **7** and thermolysis data[9] clearly excludes a radical mechanism for the *n*-BuLi/HMPT-promoted reaction.[10]

According to ab initio calculations the methyl anion, $H_3C^-$, is pyramidal,[12] and experimental evidence generally supports this structure for other $XYZC^-$ species, where X, Y, and Z are nonconjugating substituents.[13] One can therefore assume that a reasonable approximation to the strain energy of the carbanion $R^-$, as described by MM calculations, is that of the corresponding alkane RH. Consequently, one would expect the rates of fragmentation to be governed by the energy difference between the initial alcohol and the ultimate products, ketone and alkane. Thus, from a MM point of view that the *steric* contribution to the relative rates can be expressed by the calculational model:



For each path, Δstrain, the difference between the strain energy of the alcohol and that of the products, is calculated on the basis of Allinger's MM2 force field.[14] It is now assumed that Δstrain reflects the reaction free energy, $\Delta G^*$, i.e., that the $\Delta G^*$ vs. Δstrain plot for the formation of a given anion from various precursors would be linear and have unit slope.[15] Rate ratios for the formation of different anions from each alcohol can then be calculated from the Δstrain values and the statistical weights of the groups.

Comparison of the experimental product ratios (relative to Ad unless stated otherwise) with those calculated leads to the "deviations" listed in Table I. If Ad is taken as the

$$\text{deviation} = RT[\log_e (R^i/R^j)_{\text{exptl}} - \log_e (R^i/R^j)_{\text{calcd}}]$$

norm, the deviations are 1.5–1.9, –0.1, and 2.2–2.5 kcal mol$^{-1}$ for *tert*-butyl, bicyclo[2.2.2]octyl, and norbornyl, respectively. That is, relative to $Ad^-$ and $Oc^-$, both $t\text{-}Bu^-$ and $Nor^-$ are being formed faster than predicted by the estimated steric effect. By analogy with work on bridgehead radicals,[11] the deviations can be considered as representing differences in the energy associated with the hypothetical reaction: $RH \rightarrow R^-$. In the thermolysis of **7** such differences were attributed to extra strain in the radicals formed, there being a slight preference for a near-planar structure in these species.[16] But carbanions are pyramidal, apparently slightly further from planarity than a regular sp$^3$ carbon.[12] If this is a general requirement rather than a peculiarity of the methyl anion, the deviations can be understood on steric grounds: the norbornyl system is already deformed in the right direction and *tert*-butyl is sufficiently flexible to accommodate a reduced C–C–C angle, while Ad and Oc are relatively rigid structures.

Nevertheless, this is not the only possible explanation. Most of our results are consistent with polar effects: the electron-donor capacity, as expressed by the spectroscopically determined $\sigma_\nu^*$ constants,[17] decreases from Ad (–0.37) to *t*-Bu (–0.30) to Nor (–0.247) and varies linearly with the deviations, the slope corresponding to a $\rho^*$ value of about 19, much higher than that reported for fluorohydrocarbons

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(10) A referee has suggested that, since electrochemical reduction potentials for tertiary radicals[2] and for ketones[11] are very similar, the alkoxide ion could fragment to produce the tertiary radical and the ketyl anion radical. If this were the case, the fragmentation ratios would reflect the strain energies of the tertiary radicals. These, however, increase in the order: *t*-Bu < Ad < Oc < Nor, rather different from what is found in this work: Nor < *t*-Bu < Ad ~ Oc.

(11) D. H. Evans in "Encyclopedia of Electrochemistry of the Elements. Organic Section": A. J. Bard and H. Lund, Eds., Marcel Dekker, Inc., New York, 1978, Vol. XII, pp 1–259. Values for aliphatic ketones in DMF are generally 0.2 to 0.3V more negative than that for the *t*-Bu radical, corresponding to a difference of about 4–6 kcal mol$^{-1}$ in favor of the carbanion mechanism.

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(13) Reference 1c, Chapter 2.

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(15) While there are no kinetic data to support this assumption, the reactivity is qualitatively observed to follow Δstrain: compounds with Δstrain in the range 39–41 kcal mol$^{-1}$ react in minutes, 33–35 kcal mol$^{-1}$ in hours, and other compounds with no Δstrain greater than 29 kcal mol$^{-1}$ did not react at all under the conditions described. If the $\Delta G^*$ vs. Δstrain slope were substantially less than unity, this would have little effect on *t*-Bu, none on Oc, but the "deviations" for Nor would be reduced.

(16) M. N. Paddon-Row and K. N. Houk, *J. Am. Chem. Soc.*, **103**, 5046–5049 (1981).

(17) J. A. MacPhee and J. E. Dubois, *Tetrahedron Lett.*, 2225–2228 (1978); J. E. Dubois, J. A. MacPhee, and N. Jamal, unpublished results. The $\sigma_\nu^*$ value for 1-bicyclo[2.2.2]octyl (–0.283), which puts this point off the correlation, seems anomalously small compared to that of Ad and $Et_3C$ (–0.355).

J. Org. Chem. 1984, 49, 2069-2071

(3.5).[18] The low $\sigma_\nu{}^*$ value of the norbornyl group is presumeably related to the high s character of the very strained bridgehead carbon, to which has been attributed the preference for 1-norbornyllithium in exchange experiments,[3] believed to indicate carbanion stability.

Whatever their cause, the deviations correspond to a $pK_a$ range of less than 2 units. Two conclusions are possible: either (i) the transition state for carbanion formation does not reflect the stability of the carbanion, i.e., the transition state is early, or (ii) the tertiary alkyl carbanion stabilities are similar. If, however, the transition state were early, this would imply incomplete expression of the Δstrain differences. Consequently, the deviation of Nor would be smaller. Yet all the known features of the norbornyl group suggest that the 1-norbornyl anion *should* be the most stable of those studied here. It seems preferable, therefore, to conclude that the relative rates of alkyl group cleavage *do* express the correponding anion stabilities and that the $pK_a$ variation amongst the different tertiary alkanes is indeed small.

## Experimental Section

**Alcohol Synthesis.** Di-1-bicyclo[2.2.2]octyl ketone was synthesized from 1-bicyclo[2.2.2]octyl nitrile by Hartzler's method.[19] Unsymmetrical ketones were obtained by cuprous chloride catalyzed condensation of acid chlorides with organomagnesium compounds.[20] Alcohol **2** was prepared by the addition of *tert*-butyllithium to di-1-bicyclo[2.2.2]octyl ketone in ether. All other alcohols were obtained by the one-pot Barbier-type addition of alkyl halides to ketones in the presence of lithium metal.[21]

**Alcohol Fragmentation Studies.** In a typical experiment the alcohol (1–2 mg) was dissolved in *n*-butyllithium–hexane (1 N; 0.1 mL) at 20–25 °C. HMPT (1 mL) was then added. After a period ranging from 10 min to 24 h the reaction mixture was quenched with water, and hexane-extracted, and the ketonic products were analyzed by GLC on SE-30. All yields were checked against synthetic mixtures of the pure ketones at approximately the same relative and absolute concentrations in hexane. The results (Table I) are conveniently expressed in terms of the groups that cleaved rather than the ketones formed.

**Registry No.** **1**, 80514-85-8; **2**, 89849-36-5; **3**, 89849-37-6; **4**, 89849-38-7; **5**, 89849-39-8; **6**, 89849-40-1; **7**, 86458-82-4; **8**, 89849-41-2; *t*-Bu$^-$, 65114-21-8; Ad$^-$, 27750-87-4; Oc$^-$, 89849-42-3; Nor$^-$, 89849-43-4; *t*-BuH, 75-28-5; adamantane, 281-23-2; bicyclo[2.2.2]octane, 280-33-1; norbornane, 279-23-2.

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(18) D. Holtz, *Prog. Phys. Org. Chem.*, **8**, 1–74 (1971). In Taft-Ingold correlations the reaction centre is normally outside the group whereas in our work it is one of the atoms of the group; the $\rho^*$ values are therefore not strictly comparable.

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# Synthesis of Aceanthrylene

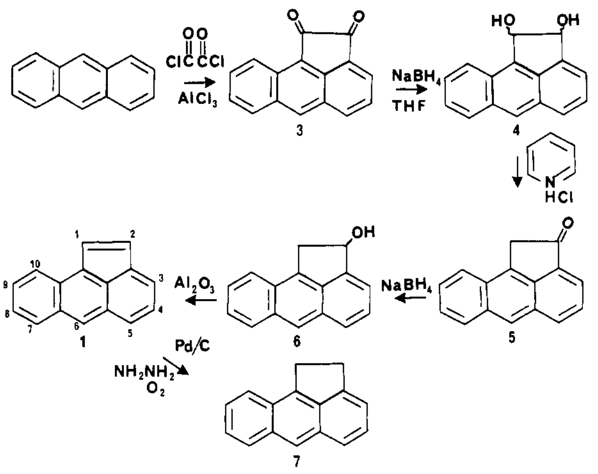
B. F. Plummer,* Z. Y. Al-Saigh, and M. Arfan

*Department of Chemistry, Trinity University, San Antonio, Texas 78284*

*Received December 20, 1983*

Aceanthrylene (**1**) is one of several potentially carcenogenic cyclopenta polycyclic aromatic hydrocarbons (PAH) either known or reputed to be components of diesel soot, carbon black, or of particulates from coal-fired power plants.[1-6] We view these compounds as annelated derivatives of acenaphthylene (**2**) whose derivatives show peculiar luminescent behavior under laser excitation.[7] Cyclopenta[*cd*]pyrene exhibits anomalous fluorescence and its magnetic circular dichroism is interpretable[8] from a paradigm elegantly created by Michl.[9] In accord with our expectations **1** also exhibits a characteristic anomalous fluorescence.[10] The synthesis described herein constitutes a convenient scheme for producing significant amounts of **1**.

Scheme I



## Results and Discussion

One of the major problems encountered in the construction of a cyclopentano PAH is that associated with the intramolecular cyclization of appropriate substituted aryl acetic acid derivatives.[12-14] The preparation of anthracenyl-9-acetic is straightforward,[14] but our attempts to cyclize this compound to aceanthren-2-one failed.[15]

For our approach to the synthesis of **1** we chose to take advantage of the ready preparation of aceanthrenequinone (**3**)[16] (Scheme I). A slight modification of the synthetic procedure for **3** was recently reported[17] in which anthracene is treated with a large excess of oxalyl chloride and anhydrous aluminum chloride in carbon disulfide. Our experience suggests that only a slight excess of oxalyl chloride suffices and thus this constitutes a saving of the more expensive reagent. The synthesis of **3** is achieved in yields of greater than 50% on a routine basis. The quinone is not very soluble in any common organic solvent.

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