was achieved via a combination of repeated fractional crystallization (ca. 25 times from EtOH gave **22b**) and partial solvolysis (4–5 times in aqueous acetone gave **22a**); purity was readily monitored by ^{13}C NMR spectroscopy. The stereochemical assignments were made on the basis of the comparative line shapes of the ^1H NMR spectra of **22** and 5.[13] Deuteration of **22a** and **22b**, unsuccessful with diimide, was achieved by using Wilkinson's catalyst.[14] From mass spectral studies, the deuterium incorporations[15] were as follows. **13a** (containing 0–2% **13b**): 1.6% d_1, 98.4% d_2; **13b** (sample 1, containing 4-6% **13a**): 2.5% d_1, 95.7% d_2, 1.9% d_3; **13b** (sample 2, containing 6.6% **13a**): 2.9% d_1, 95.1% d_2, 2.1% d_3. From ^{13}C NMR spectra, it was obvious that essentially only one (different) type of carbon in each of **13a** and **13b** bore deuteriums; the location of the deuteriums is secure, as those carbons (3,5) resonate >8 ppm upfield from the others (1,2,4,6). However, it was not possible to determine much regarding minor amounts of scrambling, except that the **13b** samples contained 2–4% d_1 at C_2.

Hydrolysis and acetolysis of **13**-d_0 have been described. In addition to the silver-assisted hydrolysis to **18–21**, we wanted to study the unassisted solvolysis. Conveniently, heating **13** in 96% aqueous HOAc (NaOAc buffer) at 115 °C afforded **18–21**. In the case of the deuterated samples, the following was found (yields are isolated):

$$\mathbf{13a} \xrightarrow[\text{80\% aq acetone}]{\text{5 equiv of AgClO}_4} \underset{38\%}{\mathbf{18}} + \underset{26\%}{\mathbf{20}} \tag{1}$$

$$\mathbf{13b}\text{ (sample 1)} \xrightarrow[\text{80\%aq acetone}]{\text{5 equiv of AgClO}_4} \underset{34\%}{\mathbf{19}} + \underset{23\%}{\mathbf{21}} \tag{2}$$

$$\mathbf{13b}\text{ (sample 2)} \xrightarrow[\text{NaOAc, 115 °C}]{\text{96\% aq HOAc}} \underset{31\%}{\mathbf{19}} + \underset{9\%}{\mathbf{21}} + \text{others} \tag{3}$$

Monocyclic ketones **18** and **19** were analyzed by ^{13}C NMR spectroscopy: the undeuterated **9b** displayed the 11 expected peaks, whereas **18** and **19** each showed only 9 (the 2 carbons bearing deuterium appeared as small, nonintegrable triplets), where the 2 "missing" resonances in the spectrum of **18** were different from those in **19**. However, it was not possible to assign C_3 and C_4 vs. C_8 and C_9, so the above result does not distinguish between gross retention (i.e., as written above) and gross inversion (i.e., **13a** → **19**, etc.). On the other hand, the degree of stereospecificity could be calculated by comparison of the integrated areas of the ^{13}C NMR resonances in **9b**, **18**, and **19** (taking into account the small amounts of **13b** in **13a** and vice versa): (a) eq 1, 98 ± 3.6% sterospecific (**18** should have contained 0–2% **19** and was calculated to contain 2.6 ± 3.6% **19**), (b) eq 2, 100% sterospecific (**19** should have contained 4–6% **18** and was calculated to contain 4 ± 1.7% **18**), (c) eq 3, 100% sterospecific (**19** should have contained 6.6% **18** and was calculated to contain 6.4 ± 0.6% **18**).

The distinction between retention and inversion was made on the basis of mass spectral analyses of **20** and **21**. The key to the analysis is the loss of a C_3H_6 fragment to give the base peak; this loss is of C_4, C_5, C_6.[16] Thus the base peak ion for 20 (eq 1) was at *m/e* 122 (no deuteriums), while that for **21** (eq 2, 3) was at *m/e* 124. This information served to establish the steroretentive nature of both the assisted and unassisted solvolyses. **In conclusion, neither 14 and 15 nor 16 and 17 interconvert, nor does a perpendicular olefin (1) intervene in these reactions.**[17] While the precise structure of **16** (**17**) remains uncertain, a rehybridized structure appears to be the most reasonable alternative.[18]

Acknowledgment. This work was partially supported by the National Science Foundation, in the form of an energy traineeship to R.F.P.

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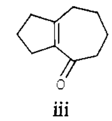
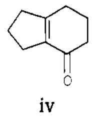
(16) This corresponds to a retro-Diels–Alder-type cleavage. The assignment is supported by observation of the same type loss to give the base peak for iii and a similar loss of C_2H_4 for iv.

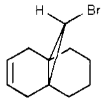


iii

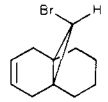


iv

(17) We have also found (M. Ah-King, unpublished results) that the bridgehead olefins derived from v and vi retain their configurations.



v



vi

(18) On the basis of studies of bridgehead olefin formation from **22**, we can exclude the possibility that our results may be explained by conformational properties of the four-carbon bridges in **16**(**17**); these will be detailed in our full paper.

On the Thermochemistry of α-Aminoalkyl Radicals[1]

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Received October 30, 1980

Free radicals are stabilized by conjugative delocalization when the unpaired electron is adjacent to π bonds(s) or electron lone pair(s). Thus, the stabilization energies,[2] E_s, of allyl[3,4] and benzyl[4] radicals are 18 and 16 kcal mol^{-1}, respectively, while those for $\dot{C}H_2OCH_3$[5] and $\dot{C}H_2OH$[6] are 11 and 8 kcal mol^{-1}. However, the stabilizing effect due to a nitrogen lone pair has not been adequately quantified.

Colussi and Benson[7,8] found $E_s(\dot{C}H_2NH_2)$ = 9 kcal mol^{-1} and consequently discounted earlier data[8,9] which suggested that the stabilization energy afforded by an NMe_2 group was 19 kcal mol^{-1}, the premise being that E_s should not be significantly affected by N alkylation. To clarify this situation, we have measured the heats of formation and hence the stabilization energies for $H_2N\dot{C}H_2$, $MeNH\dot{C}H_2$, and $Me_2N\dot{C}H_2$.

The heats of formation of these α-aminoalkyl radicals were obtained from the appearance energies (AE) for the reactions

$$H_2NCH_2{-}CH_2NH_2 + e \rightarrow H_2NCH_2^+ + H_2N\dot{C}H_2 + 2e \tag{1}$$

$$Me_2NCH_2{-}CH_2NHMe + e \rightarrow Me_2NCH_2^+ + MeNH\dot{C}H_2 + 2e \tag{2}$$

$$Me_2NCH_2{-}CH_2NMe_2 + e \rightarrow Me_2NCH_2^+ + Me_2N\dot{C}H_2 + 2e \tag{3}$$

These appearance energies were measured by impact of an en-

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(1) Issued as N.R.C.C. publication No. 19189.

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0002-7863/81/1503-1586$01.25/0

Table I. Thermochemical Data Relating to α-Aminoalkyl Radicals (±2 kcal mol^{-1})

radical	$\Delta H_f(R_2\cdot)$, kcal mol^{-1}	$D(R_2–H)$,[a] kcal mol^{-1}	$E_S(R_2\cdot)$,[b] kcal mol^{-1}	$IP(R_2\cdot)$, eV
$Me_2N\dot{C}H_2$	26	84	20	5.7[c]
$MeNH\dot{C}H_2$	30	87	17	5.9[c]
$H_2N\dot{C}H_2$	36, 37[d]	94	10	6.2[c]
$C_6H_5\dot{C}H_2$	48[e]	87	16	7.2[f]
$CH_2CH\dot{C}H_2$	39[e]	86	18	8.1[f]
$CH_3O\dot{C}H_2$	−3[g]	93[g]	11[g]	6.9[i]
$HO\dot{C}H_2$	−6[j]	96[h]	8	7.6[k]

[a] $D(R_1–H) = \Delta H_f(R_2\cdot) + \Delta H_f(H) - \Delta H_f(R_2H)$. [b] See ref 2. [c] $IP(R_2\cdot) = \Delta H_f(R_2^+) - \Delta H_f(R_2\cdot)$. [d] From ref 7. [e] From ref 3 and 4. [f] From: Houle, R. A.; Beauchamp, J. L. *J. Am. Chem. Soc.* 1978, *100*, 3290–3294. Lossing, F. P. *Can. J. Chem.* 1971, *49*, 357–362. [g] From ref 5. [h] From ref 6. [i] Lossing, F. P. *J. Am. Chem. Soc.* 1977, *99*, 7526–7530. [j] Golden, D. M.; Benson, S. W. *Chem. Rev.* 1969, *69*, 125–134. [k] From $\Delta H_f(HOCH_2^+) = 169$ kcal mol^{-1} (ref i).

ergy-resolved electron beam from an electrostatic electron monochromator, combined with a quadrupole mass spectrometer.[10] The appearance energies for these reactions will, in the limit, correspond to the general relationship

$$AE(R_1^+) = \Delta H_f(R_1^+) + \Delta H_f(R_2\cdot) - \Delta H_f(R_1–R_2) \quad (4)$$

The heat of formation of ($H_2NCH_2^+$) is well established at 178 kcal mol^{-1};[11] $\Delta H_f(Me_2NCH_2^+)$ and $\Delta H_f(MeNHCH_2^+)$ were found to be 158 ± 2 and 166 ± 2 kcal mol^{-1}, respectively,[12] from the AE of reactions analogous to the above in which the neutral fragments were H, $\dot{C}H_3$, and $\dot{C}H_2OH$, whose ΔH_f are known. The resulting thermochemical quantities for $R_2\cdot$ are given in Table I, along with comparable data for $C_6H_5\dot{C}H_2$, $CH_2CH\dot{C}H_2$, $CH_3O\dot{C}H_2$, and $HO\dot{C}H_2$. Heat of formation data for the parent R–H compounds were taken from Cox and Pilcher;[13] those for $R_1–R_2$, were calculated by group equivalents.[14]

It is immediately obvious that α-aminoalkyls have remarkably large stabilization energies which *increase* dramatically with N alkylation. This property must underlie many of the chemical and physical[15] properties of α-aminoalkyls. It is presumably the driving force for reactions such as the Stevens rearrangement[19] which proceeds by a radical-pair mechanism. Moreover, it explains why amines[20] are as reactive as highly conjugated hydrocarbons[21] in H abstractions with *tert*-butoxyl and *tert*-butylperoxyl. These reactions show a stereoelectronic effect[20] which must be a consequence of the conjugative delocalization. That is, H abstraction is most rapid when the C–H bond being broken is aligned with the principal axis of the nitrogen lone pair orbital. We note also that k_5 follows the order tertiary > secondary > primary amine as do the stabilization energies.

$$t\text{-BuO}\cdot + \ {>}CH–N{<} \rightarrow t\text{-BuOH} + \ {>}\dot{C}–N{<} \quad (5)$$

α-Aminoalkyls have low ionization potentials which *decrease* with increasing N alkylation. The observed values are lower than those for the parent amines. In fact, the ionization potential for $Me_2N\dot{C}H_2$ is the lowest thus far reported for any organic species.[11,22] These results correlate with the observation that α-aminoalkyls are powerful one-electron reducing agents.[17,23]

The delocalization which forms the basis of these osbervations can be described in terms of the theory of the "three-electron bond".[24] This predicts that two of the three electrons formally designated by ${>}\ddot{N}–\dot{C}{<}$ will be in a bonding orbital, with the third in an energetically close antibonding orbital. Excitation between the levels should therefore occur at fairly low energies. This is indeed the case; α-aminoalkyls have absorption spectra which "tail" from the UV to the visible region (e.g., for $Me_2N\dot{C}H_2$, ϵ 510 ± 100 M^{-1} cm^{-1} cm^{-1} at 340 nm.[25] These absorptions are considerably red shifted with respect to those of alkyls (e.g., for $Me_2\dot{C}H$, ϵ 1000 ± 50 *M*$^{-1}$ s^{-1} at 220 nm).[26]

We conclude that the thermochemical parameters measured in this work form a basis for understanding the chemical and physical properties of α-aminoalkyls and that these can be modified in predictable ways by changing the extent of N (and C)[22] alkylation.

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Trivacant Heteropolytungstate Derivatives: The Rational Synthesis, Characterization, and ^{183}W NMR Spectra of $P_2W_{18}M_4(H_2O)_2O_{68}^{10-}$ (M = Co, Cu, Zn)

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In addition to the fundamental interest in heteropolytungstates,[1] the preparation of hybrid organometallic–heteropolytungstate derivatives has attracted recent attention.[2] An interesting feature of heteropolytungstates and related iso- and heteropolymetalates is the triangular array of tungsten bridging oxygens present on their surfaces, oxygens which resemble discrete fragments of heterogeneous metal oxide surfaces.[3] We feel that these oxygens,

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