Schering Corporation, New Jersey, gave us generous samples of **1** and **16.**

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(16) **7** (1 equiv) is added to a solution of the starting material in chloroform (1 mmol in 7 mL) and the solution is stirred in the dark until completion (TLC and/or NMR). Further additions of **7** were usually required. The workup procedure was as previously described by us.[13b]
(17) The two protons at 5.12 ppm[11] disappear giving rise to sharp singlets (at 60 MHz) at 3.49 and 3.54 ppm ascribed to the diastereotopic protons of the iodomethyl group of **9a**.
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(19) We are grateful to Dr. J. Wright of the Schering Corporation for this sample.
(20) ^1H NMR (60 MHz, $CDCl_3$, Me_4Si): 4.22 (d, H-1), 3.22–3.67 (n, H-2, H-5, H-5′), 2.28 (d, H-3), 1.17 (s, CH_3), 2.47 (s, NCH_3), 3.50 ppm (s, OCH_3).

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Mesomeric Stabilization of Carbonium Ions by α-Cyano Groups. A Theoretical Evaluation of Inductive vs. Resonance Effects of the Cyano Moiety

Sir:

Table I. Calculated Bond Lengths and Bond Orders for Acetonitrile and for α-Cyano and β-Cyano Substituted Carbonium Ions

compd or ion	bond length, Å		bond order	
	C-C[a]	C-N	C-C	C-N
CH_3CN (**1**)	1.456	1.155	1.038	2.939
$\overset{+}{C}H_2CN$ (**2**)	1.366	1.197	1.418	2.522
$CH_3\overset{+}{C}HCN$ (**3**)	1.384	1.187	1.310	2.627
$(CH_3)_2\overset{+}{C}CN$ (**4**)	1.401	1.179	1.232	2.707
$(CH_3)_3C\overset{+}{C}(CH_3)CN$ (**5**)	1.401[b]	1.179[b]	1.224	2.705
$\overset{+}{C}H_2CH_2CN$ (**6**)	1.456	1.160	0.977	2.925
$(CH_3)_2\overset{+}{C}C(CH_3)_2CN$ (**7**)	1.456[c]	1.160[c]	0.979	2.927

[a] Refers to the interatomic distance between the α carbon and the carbon of the cyano function. [b] Values not optimized, but taken from **4**. [c] Values not optimized, but taken from **6**.

For generations, students have been taught that mechanisms of organic reactions which require the intermediacy of species having positively charged carbon attached to strong electron-withdrawing groups are to be rigorously avoided. Thus, postulated reaction mechanisms which involve the presence of a carbonium-ion center adjacent to carbonyl, sulfonyl, nitro, trifluoromethyl, or cyano functions are extremely rare. The basis for these teachings is reasonably well founded. Both Hammett[1] and Taft[2] have demonstrated the importance of considering the inductive effect of substituent groups, and Brown[3] has emphasized the importance of these principles when carbonium ions are involved. It is known[4] that placing a cyano function β to an incipient carbonium-ion center provides a rate-retarding effect on ionization of 10^3–10^7. In addition, Koshy and Tidwell have demonstrated that the presence of an α-trifluoromethyl group leads to a H/α-CF_3 rate ratio of 10^6 for the solvolysis of simple sulfonate esters.[5] Using standard extrapolations,[2,6] it might be predicted that the related H/α-CN rate ratio would be somewhere between 10^9 and 10^{18}. Surprisingly, when this H/α-CN rate ratio was measured for three different simple systems, a value of $(2.7 \pm 0.8) \times 10^3$ was observed.[7,8] This discrepancy between expectations and observations prompted us to suggest that α-cyano cations of general formula A are significantly stabilized by charge delocalization through resonance structures such as B, even though this requires a portion of the charge to reside on a divalent nitrogen.[7] In view of the implications of these findings, we have utilized PRDDO[9] and full ab initio calculation in order to evaluate theoretically the implications of our experimental results. We now report the results of these calculations.

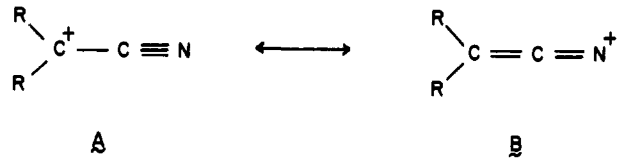

Table I lists the compounds for which PRDDO calculations[9] have been completed. PRDDO is a method which incorporates all electrons in a minimum basis set of Slater-type orbitals. Exponents for atoms were taken from the work of Hehre, Stewart, and Pople.[10] Localized molecular orbitals for the valence space were calculated using Boys' criteria[11] as described previously.[12] Bond orders were calculated according to the procedure of Armstrong, Perkins, and Stewart.[13] All calculations were carried out assuming a planar configuration for the carbonium-ion center. Since we desired to study the changes which might occur in terms of bond lengths and bond orders, we calibrated our calculations by first examining acetonitrile (**1**). The C-H bond lengths were set at 1.10 Å and all angles were set at the tetrahedral value (109° 28′). After optimization, the C_α—C_N and C≡N values derived were 1.456 and 1.155 Å, respectively. When compared with the experimental values[14] of 1.458 and 1.157 Å, our calculated values show excellent agreement. The bond order for the C—C bond was found to be 1.04 and that for the C≡N bond was 2.94. These can be compared with the idealized values of 1.00 and 3.00, respectively.

While some geometry optimization was carried out for most of the molecules studied, the geometry for $^+CH_2CN$ (**2**) was fully optimized.[15] Only the C_α—C_N and C≡N bonds were optimized[16] for **3** and **4**. For **6** the C_α—C_β bond distance and the C_β-C_α-C_N and H-C_β-H angles were also optimized.[17] For **5** and **7**, the C—C and C≡N bonds were taken from **4** and **6**, respectively.[18]

As can be seen from Table I, the C_α—C_N bond length for **2** is considerably shorter than the C_α—C_N bond length of

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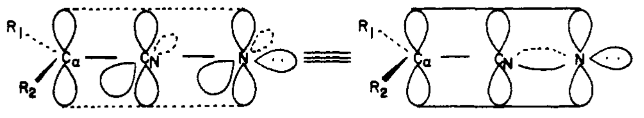

Compound	R_1	R_2	C_α	C_N	N
2	H	H	0·33	1·15	0·52
3	H	CH_3	0·25	1·15	0·60
4	CH_3	CH_3	0·17	1·10	0·72

Figure 1. Localized molecular orbital picture of α-cyano substituted cations showing electron density on C_α, C_N, and N.

acetonitrile. Interestingly, the C_α—C_N bond length of **2** is very similar to a standard C═C double bond (1.366 vs. 1.34 Å).[19] As anticipated the C≡N bond is significantly longer in **2** than in acetonitrile. These changes are also reflected in the bond orders, where a comparison of the C_α—C_N bond order for **2** compared with that of **1** shows a 40% increase, while the corresponding C—N bond order shows an ~40% loss of one bond. Stabilization of the carbonium-ion center by methyl substitution resulted in a lengthening of the C—C bond and a shortening of the C≡N bond. However, even the tertiary cation, **4**, was substantially different from acetonitrile.

As can be seen from Table I, generation of a cationic center β to the cyano moiety had little effect on the C—C or C≡N bond parameters compared with those of acetonitrile. This was expected. However, these calculations permitted direct energy comparison to be made for the isomeric ions **3** and **6**, and **5** and **7**. The α-cyano substituted cation **3** was found to be 15.4 kcal/mol more stable than the β-cyano substituted cation **6**. This suggests that the conversion of **6** into **3** through a 1,2-hydride shift should occur unless there are unusual solvent effects or high activation energy barriers to rearrangement. A similar comparison of tertiary cation **5** with the tertiary cation **7** shows **5** to be more stable by 1.8 kcal/mol. Again, we find α-cyano substitution to be slightly energetically more favorable than β-cyano substitution.[29]

Localized molecular orbitals (LMOs) are often extremely useful in examining the bonding characteristics of molecules.[20] Figure 1 shows both the normal delocalized structure (**8**) and the LMO structure (**9**) for **2**, **3**, and **4**. For **2** the basic LMO framework consists of a C—C single bond, two C—N bent single (τ) bonds which reside in the plane defined by the atoms attached to the carbonium ion, and a delocalized π bond which is perpendicular to the plane. The π bond has its dominant density on C_N (1.15e). The remaining density on **2** is divided between N (0.52e) and C_α (0.33e). As methyl groups are added to C_α, the charge density shifts from C_α to N up to the extreme of **4**, where C_α has 0.17e and N has 0.72e. The density on C_N remains reasonably constant (1.10-1.15e).

The centroids of charge (cc) for the π bond show a systematic change for the series **2-4**, with the cc being located at 57% of the distance from C_α to N in **2**, 61% of the distance from C_α to N in **3**, and 66% of this distance in **4**. For **4**, the π bond starts to take on 5-7% 2s character. This is manifested by a slight movement of the centroid of charge off of the C-C-N axis.[21]

A striking feature of the LMO picture is the presence of the delocalized π bond. The Boys criteria, which requires a maximum separation of centroids of charge, is biased against σ-π separations in favor of τ-type bonds.[12,22] The development of the π bond is indicative of the extent of delocalization of the positive charge on C_α by the α-cyano moiety. The presence of the two τ bonds in the plane of the atoms attached to C_α does not place the centroids of charge along the C-N axis. Thus, the centroid of charge for the π bond occurs on the C-N axis resulting in an effective σ-π separation.

We also carried out full ab initio calculations on the simplest ion, $CH_2{}^+CN$, to demonstrate that the use of a minimum basis set was not biasing our results. These calculations were done with a polarized double ζ basis set[23] with geometry optimization via a gradient approach using the program HONDO: version 5.[24] The optimized full ab initio geometry parameters[25] demonstrate that the PRDDO values overestimate the shortening of the C—C bond by 0.02 Å and the lengthening of the C—N bond by 0.03 Å. However, the significant shortening of the C_α—C_N bond observed in the PRDDO results is also seen in the calculations employing this larger basis set. An important comparison between these two sets of calculations is associated with the amount of electron density transferred from the symmetry-unique cyano π bond to the vacant orbital on the carbonium-ion center. The full ab initio p_π densities [C_α (0.25e), C_N (1.13 e), and N (0.60e)] are similar to the PRDDO values given in Table I, although, due to the differences in geometry, more density transfer is found in the PRDDO calculations. Comparison of PRDDO values[26] [C_α (0.29e), C_N (1.13e), and N (0.57e)] calculated at the optimum full ab initio geometry shows good agreement with the full ab initio values. Further PRDDO calculations on **2**, **3**, and **4** were done using scaled C_α—C_N distances and a shorter CN distance.[27] These calculations also show the same trends in the bond orders and in the p_π charge density. Thus, a significant amount of delocalization of the symmetry-unique cyano π bond occurs into the vacant p orbital on the carbonium-ion center. This delocalization is relatively independent of geometry.

In summary, the results of PRDDO and full ab initio calculations compliment and extend our experimental results on α-cyano substituted carbonium ions. In addition to lending credence to our mechanistic interpretation of our experimental findings, these calculations provide insights which will result in a wide variety of new experiments. We are continuing our studies in this area.

Acknowledgment. We are indebted to the National Science Foundation for Grants CHE78-10231 and CHE-7905985 which supported this investigation. We acknowledge the assistance of R. A. Eades in relation to the full ab initio calculations.

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(15) The C—H bond length is 1.104 Å and the H–C–H bond angle is 117.0°.

(16) The C_β—C_α bonds were set at 1.54 Å, C_β—H bonds at 1.10 Å, and H–C_β–H angles at 109° 28′. The C_β–C_α–H angle (**3**) and C_β–C_α–C_β (**4**) angles were set at 120°. The similar C–C–C angle in $(CH_3)_2C^+OCH_3$ has been optimized giving 120.5°: D. A. Dixon and P. A. Charlier, unpublished results.

(17) The H–C_α–H angle was set at 109° 28′. The optimized results for C_α—C_β, C_α–C_β–C_N, and H–C_β–H are 1.475 Å, 103.3°, and 116.2°, respectively.

(18) The geometry for **5** was taken from that of **4** with the geometry parameters for the additional methyl groups on C_β as in note 16. The geometry for **7** was taken from **6** with all hydrogens substituted with methyl groups with the parameters given in note 16.

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(25) The optimized full ab initio parameters (within 0.01 Å) are $R(C_\alpha—C_N)$ = 1.384, R(C—N) = 1.165, $R(C_\alpha—H)$ = 1.088 Å; $\theta(HC_\alpha H)$ = 118.6°. The optimized PRDDO parameters are $R(C_\alpha—C_N)$ = 1.366, R(C—N) = 1.197, $R(C_\alpha—H)$ = 1.104 Å; $\theta(HC_\alpha H)$ = 117.0°.

(26) The bond orders evaluated from PRDDO wave functions at the optimum full ab initio geometry are 1.36 and 2.60 for the C_α—C_N and C—N bonds, respectively.

(27) Calculations were carried out using $R(C_\alpha—C_N)$ = 1.456 and R(C—N) = 1.16 Å for the ions and also with $R(C_\alpha—C_N)$ scaled by the ratio $R(C_\alpha—C_N)_{\text{ab initio}}/R(C_\alpha—C_N)_{\text{PRDDO}}$ obtained for **2**.

(28) (a) A. P. Sloan Fellow, 1977–1979; (b) Camille and Henry Dreyfus Teacher–Scholar, 1978–1983; (c) Du Pont Young Faculty Grantee, 1978; (d) Lando Fellow, summer 1979.

(29) NOTE ADDED IN PROOF. Preliminary data indicated that full geometry optimization of **7** and **5** may result in a change in the order of stability such that **7** may be slightly more stable than **5**. This would reflect the difference of an H/α-CN ratio for **6** and **3** vs. a CH_3/α-CN ratio for **7** and **5**.

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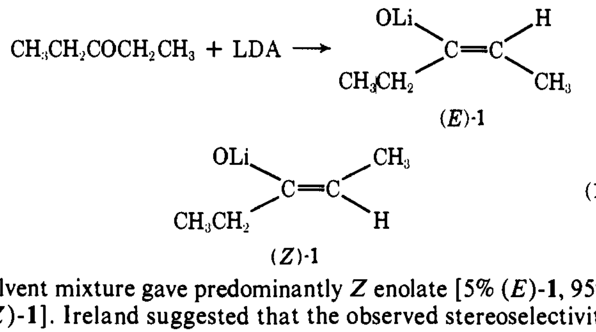
Role of HMPT and TMEDA in Control of Enolate Stereochemistry for Reactions of Lithium Amides with 3-Pentanone

Sir:

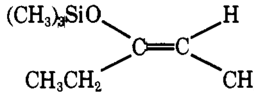
In his pioneering study of the stereochemistry of enolate formation, Ireland reported a remarkable solvent effect of HMPT (hexamethylphosphoric triamide).[1] Deprotonation of 3-pentanone with LDA (lithium diisopropylamide) in THF (tetrahydrofuran) solution gave chiefly the *E* enolate [77% (*E*)-**1**, 23% (*Z*)-**1**; eq 1]. The same sequence in a THF/HMPT solvent mixture gave predominantly *Z* enolate [5% (*E*)-**1**, 95% (*Z*)-**1**]. Ireland suggested that the observed stereoselectivity arises in either case by a kinetically controlled process and that the increased *Z* stereoselectivity is a consequence of the lesser coordinating ability of lithium for carbonyl oxygen in a solvent mixture containing HMPT. Similar effects of HMPT on anion stereochemistry have been reported by Ireland and by other workers for deprotonation reactions of a variety of ketones,[2] esters,[1] hydrazones,[3] and oxazolines.[4]



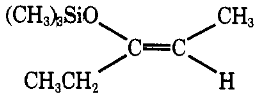
(1)

Because control of enolate stereochemistry is vital to the stereochemical outcome of the aldol reaction,[2,5–6] we have begun a study of the factors which determine the stereoselectivity of enolate formation. We now report evidence that, for deprotonation reactions of 3-pentanone with lithium amide bases, predominant *Z* stereoselectivity is a consequence of thermodynamic control. Under conditions where kinetic control is ensured, predominant *E* stereoselectivity is observed in the presence or absence of HMPT or the related solvent additive, TMEDA (*N,N,N,N*-tetramethylethylenediamine).

Standard solutions of enolates (*E*)-**1** and (*Z*)-**1** were prepared by addition of 3-pentanone to a slight excess (1.1 equiv) of a 1.0 M solution of lithium 2,2,6,6-tetramethylpiperidide (LiTMP) in THF at 0 °C. The enolate content of the solutions was determined by quenching aliquots with trimethylchlorosilane followed by GIC analysis for the corresponding trimethylsilyl ethers, (*E*)-**2** and (*Z*)-**2**. The total yield of enolate was thus established to be 90–100% with an (*E*)-**1**:(*Z*)-**1** ratio of 87:13. The stability of these standard solutions was studied under a variety of conditions. Both enolate total yield and (*E*)-**1**:(*Z*)-**1** ratio did not change over a period of 24 h at 25 °C in the absence of any additive or in the presence of 1.0–4.0 equiv of HMPT or TMEDA. However, addition of 0.2 equiv of 3-pentanone caused a rapid isomerization (complete in 30 min at 0 °C) to an equilibrium mixture of enolates with an (*E*)-**1**:(*Z*)-**1** ratio of 16:84. The rate of this isomerization was appreciably faster (complete in <10 min at 0 °C) in the presence of HMPT or TMEDA. We observed a modest effect of both HMPT and TMEDA on the position of enolate equilibrium at 0 °C: (*E*)-1:(*Z*)-**1** ratio of 10:90 (1.0 equiv of HMPT); 6:94 (4.0 equiv of HMPT); 16:84 (1.0 equiv of TMEDA); 11:89 (4.0 equov of TMEDA).



(*E*)-**2**



(*Z*)-**2**

Although α hydrogen exchange[7] between ketone and enolate would provide a mechanism for enolate isomerization, such a process is probably too slow to account for the rapid isomerization observed at 0 °C. Furthermore, we observe that benzophenone, a ketone without α hydrogens, promotes enolate isomerization about as efficiently as 3-pentanone. We suggest that the most likely isomerization mechanism is reversible aldol condensation:

$$(E)\text{-}\mathbf{1} + R_2CO \rightleftharpoons R_2COLiCH(CH_3)COCH_2CH_3 \rightleftharpoons (Z)\text{-}\mathbf{1} + R_2CO \quad (2)$$

We note that, as a consequence of this rapid isomerization, it is possible to control the deprotonation of 3-pentanone in THF solution alone so as to produce predominantly enolate (*E*)-**1** [87% (*E*)-**1**, by addition of the ketone to 10% excess LiTMP at 0 °C] or predomiantly enolate (*Z*)-**1** [84% (*Z*)-**1**, either by addition of the ketone to a slight deficiency of LiTMP or by addition of a stoichiometric amount of LiTMP dropwise to a solution of the ketone at 0 °C].

Since enolate equilibration occurs only by reaction of enolate with starting ketone, a true kinetically controlled deprotonation of 3-pentanone should be favored by high base/ketone ratios. Accordingly the relative amounts of (*E*)-**1** and (*Z*)-**1** enolates formed by deprotonation of varying amounts of 3-pentanone with fixed amounts of LiTMP[8] in THF solutions containing HMPT or TMEDA was determined and the results are presented in Table I. Addition of 0.9 equiv of 3-pentanone to THF

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