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PHOTOELECTRON SPECTRA, REACTIONS AND STRUCTURES OF SOME ACYCLIC 2-AZADIENE SYSTEMS

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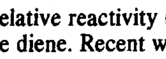
Abstract—A series of substituted 2-azadiene systems has been prepared and characterized by reactivity, structure, and photoelectron-spectroscopic studies. An attempt has been made to employ photo-electron spectroscopy as a tool for predicting sites of chemical reactivity for these azadiene systems. Although such correlations can be tenuous, they seem to be useful in this limited study.

Recent work has been focused upon applications of ultraviolet photoelectron spectroscopy (UPS) to specific chemical problems, such as determination of molecular conformations of molecules which can not be studied by dynamic NMR because of temperature limitations.[1] Another possible application of UPS which is of interest to us is the prediction of reactive sites in complex organic molecules. In other words, if one can deduce from the photoelectron spectrum the nature of the highest occupied molecular orbital (HOMO), will this deduction enable one to correctly predict the types of chemical reactions which the molecule should undergo?

The aza-butadiene conjugated systems (**1** and **2**) are examples of structures to which such UPS analysis could profitably be applied. The structural systems of **1** and **2** hold significant potential as synthons of a variety of nitrogen heterocycles provided that cycloadditions of the [4 + 2] (and [2 + 2]) type can be directed to the π electron system, and that a diverting reaction of the "dienophile" at the competing n-electron site can be avoided. Thus, in addition to the factors of the relative energies of the HOMO and LUMO involved and the accesibility of the diene s-*cis* conformation, [4 + 2]cycloaddition chemistry of **1** and **2** includes a third complicating factor, that of the relative reactivity (energy) of the nb and π electrons of the diene. Recent work by Vocelle *et al.*[2] has reported on the UPS analysis of an example of structure **1**. In this paper we discuss the UPS of certain acyclic examples of structure **2** and the reactions of **2** with certain dienophiles. In this work we have begun an attempt to use UPS results to predict reactive sites in azadienes and to assist in the design of future examples of structure **2** which will be successful synthons of 6-membered *N*-heterocycles.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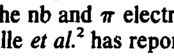
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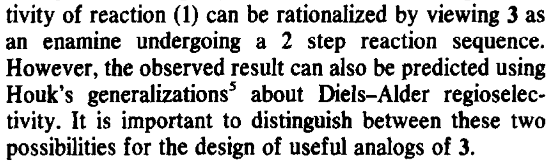
Amongst the wealth of literature on the Diels–Alder reaction there are a few scattered examples of successful [4 + 2] cycloadditions to examples of structure **2**.[3,4] With the exception of reaction (1),[4] in previous examples the 2-aza-butadiene system was cyclic (e.g. an oxazole) or, if acyclic, was in an aromatic system (e.g. *N*-benzylidine-benzenamine).[19] In the case of reaction (1), amidine **3** and a homolog reacted with dienophiles to yield examples of the pyridine, dihydropyridine, tetrahydroquinoline and 2-aza-anthracen-9,10-dione systems.[4]



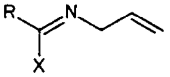
3

These recent results illustrate the promise for heterocyclic synthesis using acyclic 2-aza-dienes. The regioselectivity of reaction (1) can be rationalized by viewing **3** as an enamine undergoing a 2 step reaction sequence. However, the observed result can also be predicted using Houk's generalizations[5] about Diels–Alder regioselectivity. It is important to distinguish between these two possibilities for the design of useful analogs of **3**.

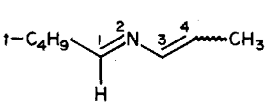
Selection and synthesis of aza-dienes

The series **4a** and **5a** were prepared and studied by UPS to allow a comparison with previous work by Heilbronner which compared π ionizations in olefins and imines.[6] Also UPS analysis of this series would give good indication of the "inherent" nb vs π level ordering in structure **2**. The series **4b**, **5b** and **6** were prepared to allow a test of the effect of phenyl conjugation on the nb/π level ordering. The series **4c** and **5c**, in which the conjugated diene should strongly prefer the *s*-trans conformation, was prepared for comparison of reactivity with analog **3** and to determine the effect of a strong n-electron donor on the energy and ordering of the π system.

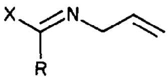
The compounds **4** were prepared by straightforward methods which are recorded in the Experimental. The unconjugated azadienes were readily isomerized to structures **5** (C=C *Z*, *E* mixtures) under basic conditions. For most isomerizations a solution of potassium t-butoxide in dimethyl-sulfoxide at 0° to room temperature was used. Gas chromatography could be used to separate the



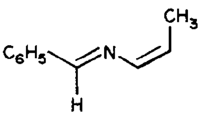
4a: R = tert-C_4H_9, X = H
b: R = C_6H_5, X = H



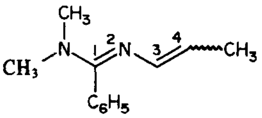
5a



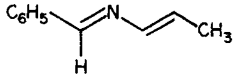
c: R = C_6H_5, X = $N(CH_3)_2$
d: R = C_6H_5, X = $N(C_2H_5)_2$



5b – (*Z*)



5c: (**5d** has X = $N(C_2H_5)_2$)



5b – (*E*)

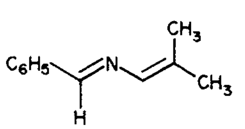


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Table 1. ^1H NMR Chemical shifts, $\delta(Me_4Si)$ of **4** in $CDCl_3$

	Chemical Shift (J, cps)				
Compound	R	X	NCH_2-	=CH-	$=CH_2$
4a	1.2 (s)	7.55 (t,1.3)	4.0 (m)	6.0 (m)	5.2 (m)
4b[a]	7.4,7.2 (m)	8.22 (t,1)	4.25 (m)	6.17 (m)	5.1,5.2 (m)
4c	7.2 (m)	2.75 (s)	3.60 (4.6,1.5)	5.9 (m)	5.0 (m)
4d	7.2 (m)	3.2 & 1.1 (q,6.5 & t,6.5)	3.57 (4.6,1.5)	5.9 (m)	5.0 (m)

[a] Solvent: CCl_4

Z and *E* isomers of **5a** and **5b**, but **5c** and **d** appeared under one peak. The conjugated compounds **5** were readily distinguished from their unconjugated isomers by their NMR (Tables 1 and 2) and UV spectra (Experimental).

The difference in the vicinal vinyl H coupling constants permitted ready determination of configuration about the C=C double bond. The configuration about the imine bond of **4a**, **4b**, **5a**, **5b** and **6** is assigned as *E* as is shown. This is based on analogy with all other structurally similar aldimines (100% *E*) for which the configuration has been determined.[7a] The configuration of the C=N bond of amidines **5c** and **5d** is probably (predominately) *E* as shown. This is consistent with configurations assigned to other N,N-dialkylamidines[7b,c] and with the NMR data of Tables 1–4. Thus, in both ^1H and ^{13}C spectra the NCH_2 group of amidines **4c** and **4d** is at higher field than that of imine **4b** (compare **4b** with **4c** and **d** in Tables 1 and 3). This shielding is also observed when the ^1H and ^{13}C signals of the –NCH= group of **5c** and **d** are compared with **5b** (Tables 2 and 4). The best interpretation is that this effect is due to diamagnetic shielding of the N substituent by a vicinal, tilted phenyl ring, a phenomenon observed in other similarly structured systems.[8] Simple resonance considerations predict that electron donation by the amidine dialkylamino group should shield the =CH– group of **5c** and **d** relative to that of **5b**, but have little effect on the chemical shift of the ^{13}CX and $N^{13}CH$ groups. As can be seen from Table 4, all of the =CX– groups display chemical shifts in the narrow range of 160.1 ± 1.4 ppm while the =CH– group is in fact shielded by 12–13 ppm in **5c** and **d**. Thus, since resonance electron donation in fact does not shield the $=^{13}CX$– group, it is not expected to shield the $N^{13}CH$ group either, and this mechanism cannot be used to explain the observed shielding of the NCH moiety. The UV spectra of **5b**-(*Z*) and **5b**-(*E*) are very similar (λ_{max}

Table 2. ^1H NMR Chemical shifts, $\delta(Me_4Si)$ of **5** in $CDCl_3$

	Chemical Shift (J, cps)				
Compound	R	X	NCH=	C=CH-	CH_3
5a - (Z)	1.2 (s)	7.45 (bs)	6.48 (~6)	5.25 (quint.6.6)	1.39 (6.6,1.3)
5a - (E)	1.2 (s)	7.45 (bs)	6.55 (12.5)	5.90 (12.5,6.6)	1.17 (6.6)
5b - (Z)[a]	7.8,7.5 (m,m)	8.2 (s)	6.80 (7.5,2)	5.5 (quint.7.5)	2.05 (7.5,2)
5b - (E)[a]	7.8,7.5 (m,m)	8.1 (s)	6.85 (13,1)	6.15 (13,7)	1.85 (7,1)
5c - (Z)	7.2 (bm)	2.88 (s)	~6.1[b] (6.5,1.5)	4.63 (quint.6.5)	1.83 (6.5,1.5)
5c - (E)	7.2 (bm)	2.83 (s)	~6.2[b] -	5.43 (12.6,6.5)	1.47 (6.5,1.5)
5d - (Z)	7.3 (bm)	1.11 and 3.33 (t,7.3 and bq, ~7)	~6.1[b] -	4.57 (quint.6.5)	1.84 (6.5,1.5)
5d - (E)	7.3	1.05 and 3.3 (t,7,3 and bq, ~7)	~6.2[b] -	5.35 (13,6.5)	1.50 (6.5,1.5)

[a] Solvent: CCl_4

[b] Overlapping signals

Table 3. ^{13}C Chemical shifts, δ(Me_4Si) of **4** in $CDCl_3$

	Chemical Shifts				
Compound	R	=CX-	NCH_2-	=CH-	$=CH_2$
4b	128.2-136.4	161.9	63.5	136.0	116.0
4c[a]	127.5-139.0	162.8	53.4	139.0	113.2
4d[b]	127.4-135.2	161.6	53.2	139.3	113.0

[a] NCH_3: 38.1.

[b] NCH_2CH_3: 41.4, 13.5

Table 4. ^{13}C Chemical shifts, δ(Me_4Si) of **5** in $CDCl_3$

	Chemical Shifts				
Compound	R	=CX-	NCH=	=CH-	$=CH_3$
5b - (Z)	128.5 to 136.8	159.2	141.7	125.5	12.6
5b - (E)		158.7	144.0	127.5	15.5
5c - (Z)[a]	128.1 to 134.5	161.4	136.1	112.9	11.6
5c - (E)[a]		161.4	138.1	114.7	15.3
5d - (Z)[b]	128.0 to 134.8	159.9	136.3	112.0	11.7
5d - (E)[b]		159.9	138.3	113.7	15.3

[a] NCH_2: 38.0

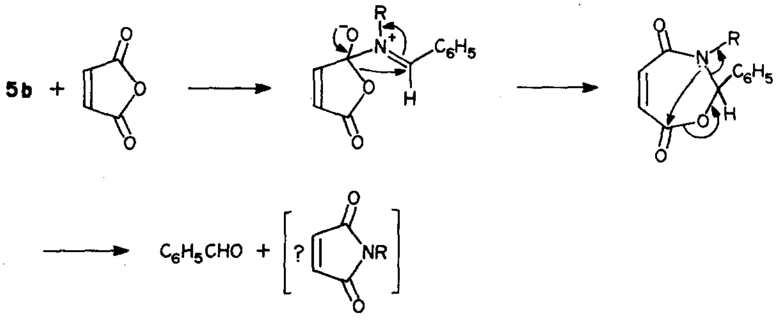
[b] NCH_2CH_3: 41.8, 13.6

280, differing only in log ε) and resemble that of (1*E*, 3*E*)-1-phenyl-1,3-pentadiene (λ_{max} 282, log ε 4.3).[9] All data indicate that the dienes **5** have structures as shown with the chromophore having the *s*-trans conformation.

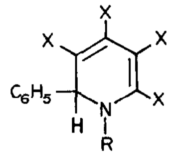
Reactions of the azadienes

Azadiene **5b** reacted with 1 equivalent of maleic anhydride under anhydrous conditions to give benzaldehyde in 47% yield (isolated). Simple imines have been observed to react analogously yielding also maleamic acid derivatives.[10] The reaction must proceed via n-electron attack at the anhydride C=O followed by an eventual N to O transfer to the benzal group (Scheme I). With dimethyl acetylenedicarboxylate (DMA) azadiene **5b** reacted by conjugate n-electron attack to give a product which may or may not incorporate 2 equivalents of the dienophile. This reaction, which gave no completely characterizeable product, was followed by ^1H NMR spectroscopy. In acetonitrile solvent at room temperature **5b** and DMA reacted slowly with preferential destruction of the *E* isomer as evidenced by reduction and eventual loss of the methyl, vinyl and imine proton signals of that isomer. A new Me signal appeared at δ 1.65 which showed both vicinal (6.5 c/s) and allylic (1.3 c/s) coupling. Azadiene **5b**-(*Z*) remained in the reaction mixture. We modeled this reaction using imine **4b** and DMA. As expected[11] this imine gave crystalline **7a** with a UV spectrum almost identical to that reported for **7b**.[11] Based on the above results, we think **5b** and DMA give **7c** as the major product.

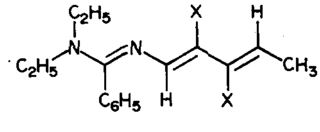
Azadiene **5d** reacted with DMA at room temperature yielding azatriene **8** as a basic, crystalline solid. The structure of **8**, a 1:1 adduct ($C_{20}H_{26}N_2O_4$), was deduced as follows. The $\nu_{C=N}$ of **4d** had been shifted $-50\ cm^{-1}$, from 1600 to 1550 cm^{-1}, by the conjugated double bond in **5d**. Compound **8**, in addition to a strong $\nu_{C=O}$, showed



Scheme 1.



7: $X = CO_2CH_3$
a: $R = -CH_2-XH{=}XH_2$
b: $R = -CH_2C_6H_5$
c: $R = -CH{=}CH-CH_3$



8: $X = CO_2CH_3$

a strong absorption at 1520 cm^{-1} indicative of further extension of amidine conjugation, and this was consistent with the UV spectral results: λ_{max} 260 nm for **5d**, λ_{max} 330 for **8**. The ^{1}H NMR spectrum showed a vinyl-bound Me group (δ 1.60), vincinally coupled (J = 6.5 c/s) but void of allylic coupling. The vincinal vinyl H partner resonated at δ 6.67 (q, J = 6.5 c/s). A second vinyl H at 6.55 was a sharp singlet, and in addition to the amidine N-Et group signals, the spectrum showed signals for two nonequivalent OMe groups (δ 3.65, 3.75). These features are accomodated by structure **8**. In addition, using the Tobey-Simon empirical rules[12] for calculation of vinyl H resonances, the *Z*, *Z* configuration for the C=C double bonds is tentatively indicated [for the NCH proton at 6.55, the calculated values are 6.81 (*cis* to CO_2CH_3) and 6.49 (*trans* to CO_2CH_3); for the other vinyl H at 6.67, the calculated values are 6.86 (*cis* to CO_2CH_3) and 6.67 (*trans* to CO_2CH_3)]. In a similar fashion, azadiene **5c** gave the N,N-dimethyl homolog of **8**.

The formation of **8** is rationalized in Scheme II. Azadines **5c** and **d** indeed react with the dienophile, but we feel they do so in a stepwise fashion analogous to the Michael addition of enamines to unsaturated systems. Reaction of **5c** and **d** in the *s-trans* conformation yields intermediate **9** which is structurally precluded from ring closure to a 6-membered ring. Instead, ring closure to **11** can occur which, in turn, yields **8** by conrotatory ring opening. Both *Z* and *E* isomers of **5c** and **d** can yield **11** with groups N and Me *trans*, and we've detected no significant differential reactivity between *Z* and *E* isomers. The *s-cis* conformation of **5c** and **d** is required for formation of intermediate **10** which is able to cyclize to a 6-membered ring product.

UPS RESULTS AND DISCUSSION

The 6–12 eV region of the photoelectron spectra of compounds **4a**, **b**; **5a**, **b**, **c**; and **6** are shown in Fig. 1. Band structure above 12 eV is not shown in Fig. 1 because the complex nature of the overlapping bands corresponding to the numerous σ bonding molecular orbitals of these large molecules renders impossible any

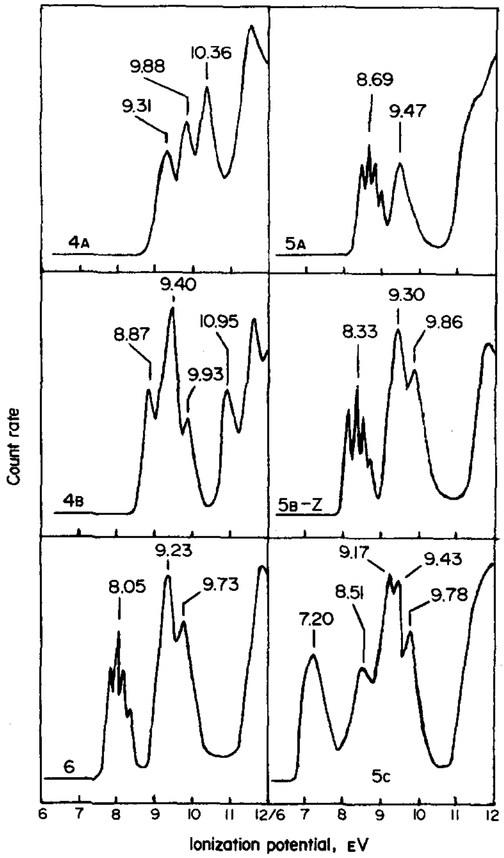
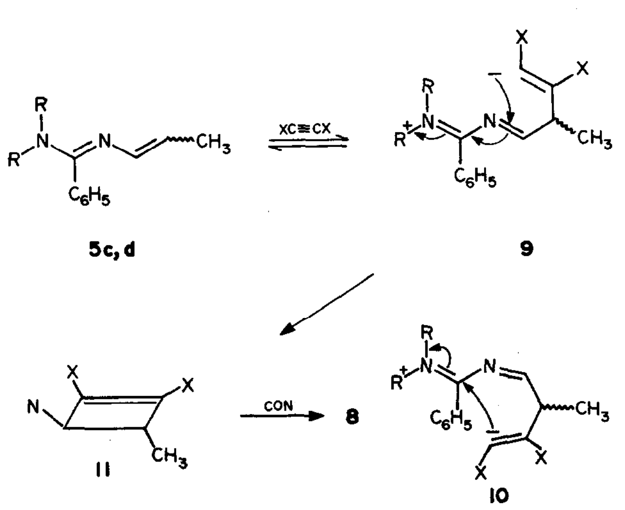
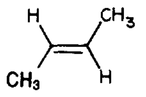


Fig. 1. The photoelectron spectra of some 2-azadienes. The excitation source was the He I resonance line. Spectral noise has been smoothed out of the tracings, and the inert-gas calibration peaks have not been shown.



Scheme 2.

definitive interpretation of these bands. However, the interpretations of the bands in the 6–12 eV region which refer to the more important nonbonding and π-bonding molecular orbitals are quite straight-forward. Heilbronner and co-workers have reported the photoelectron spectra for compounds **12** and **13** shown below:[6]



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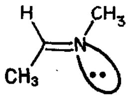

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Upon aza substitution, the π ionization potential increases substantially (9.11 eV for **12**; 10.66 eV for **13**) because the more electronegative nitrogen destabilizes the π ionic state (or stabilizes the ground state π MO). The first ionization band for **13** at 9.49 eV was assigned to ionization of one of the "lone-pair" electrons. By analogy, the first ionization band in the photoelectron spectrum of the nonconjugated **4a** at 9.31 eV must be assigned to ionization of an orbital which is predominantly nonbonding in character. The nb ionization potential of **4a** is lower than that of **13** because of the t-Bu and allyl substituents. The second ionization band in the spectrum of **4a** at 9.88 eV refers to the predominantly C=C π MO, for the first ionization potential of propene[13] is 9.91 eV. The third ionization event at 10.36 eV must then correspond to the predominantly C=N π MO which has been destabilized by the substituents to a greater extent than was the nb MO, as would be expected. Thus, photoelectron spectroscopy would predict that energetically the N in **4a** should serve as a nucleophile in a reaction with dimethyl acetylenedicarboxylate. Although such a reaction was not attempted for **4a**, it does proceed in this manner for the analog **4b**.

For the conjugated **5a**, the photoelectron spectrum contains two clearly resolved bands at low ionization energy (8.69 and 9.47 eV). The first band at 8.69 eV contained well-resolved vibrational structure ($\Delta\nu = 0.17$ eV) and can be assigned to ionization of the highest occupied π MO. The second band at 9.47 eV is due to ionization of the nb MO. The lack of resolved vibrational structure in the second band indicates that the nb MO is extensively delocalized in **5a**. It is interesting to compare **5a** with an example of 1-azadiene (**1**). With (*E,E*)-3-aza-3,5-heptadiene,[2] the n and π levels are unresolved displaying a complex band with some fine structure at 9.4 eV.

The photoelectron spectra of **4b**, **5b**-*Z*, **5c** and **6** are somewhat more complicated due to the accessible π orbitals on the phenyl rings. It is well established that benzene has a first ionization potential of 9.3 eV[14] which corresponds to ionization of the doubly degenerate πMO's (e_{1g}). The eigenvectors corresponding to these degenerate π orbitals are determined by symmetry such that one (ψ_3) has a heavy density contribution at the point of attachment in monosubstitution while the other (ψ_2) has a node at this position. Upon substitution of a phenyl group at the C_1 position of 2-aza-1,4-pentadiene to form **4b**, there should be mixing of the ψ_3 π orbital on the ring with the C=N π orbital on the azadiene moiety, while ψ_2 of the ring should not be affected mesomerically to a first order approximation. Thus, for the photoelectron spectrum of **4b**, the first band at 8.87 eV has been assigned to ionization of the highest occupied πMO in which there is mixing between ψ_3 of the ring and $\pi_{C=N}$. That the interaction is small (*ca* 0.4 eV) is a consequence of the rather large energy separation between ψ_3 at 9.3 eV and $\pi_{C=N}$ at *ca* 10.55 eV and of the angle of rotation of the ring out of planarity with the C=N bond. Haselbach and co-workers have shown that the latter effect is important for benzylideneaniline.[15] The fourth band at 10.95 eV must refer to the bonding combination of ψ_3 and $\pi_{C=N}$. The third band in the spectrum of **4b** at 9.93 eV can be assigned to ionization of the isolated C=C π orbital as was the case for **4a**. This leaves the intense second band at 9.40 eV as being due to $\psi_2(\pi)$ of the ring and the N "lone-pair" orbital. For this molecule, these two processes cannot be resolved. It should be noted that Haselbach, *et al.*,[15] have proposed similar assignments for N-benzylidenemethylamine.

For the conjugated 1-phenyl-2-azadienes (**5b**-*Z* and **6**) the first band (at 8.33 and 8.05 eV, respectively) contained well-resolved vibrational structure ($\Delta\nu = 0.16$ and 0.17 eV, respectively) and must be assigned to ionization of a πMO generated by mixing $\psi_3(\pi)$ and the azadiene πMO in an antibonding manner. The bonding combination in this interaction would then correspond to the bands at 9.86 eV for **5b**-*Z* and 9.73 eV for **6**. The band at 9.30 eV for **5b**-*Z* and 9.23 eV for **6** is again due to the unresolved $\psi_2(\pi)$ and nb orbitals.

Possibly the most interesting molecule considered in this study is **5c** because its chemical behavior is quite different from other azadienes. The first ionization band at 7.20 eV may be assigned to ionization of one of the lone-pair electrons on the dimethylamine function. The fact that this band is broad (*ca* 0.7 eV width at half maximum) and structureless indicates that this lone-pair is extensively delocalized. This, in fact can explain why electrophilic attack occurs at C-4 for this molecule because delocalization of this lone-pair would substantially increase the electron density at the N-2 and C-4 centers of the diene system, an effect evidenced earlier in the ^{13}C NMR results. The bands at 8.51 eV and 9.78 eV can be assigned to heavily mixed πMO's; the bands at 9.17 eV and 9.43 eV would then correspond probably to $\psi_2(\pi)$ and the delocalized aza N nb orbital.

DISCUSSION AND CONCLUSIONS

The UPS results show that in a 2-aza-1,3-diene system such as that found in **5a** and **b** a π orbital is the highest occupied molecular orbital (HOMO). Sustmann and Schubert[16] used UPS vertical ionization potentials of substituted dienes and electron affinities of two dienophiles (TCNE and maleic anhydride) to estimate the diene-HOMO, dienophile-LUMO energy gaps. Doing this they obtained a quantitative correlation of ΔE with the Diels–Alder reaction second order rate constant. Using this approach one would predict a Diels–Alder reactivity for **5b** not much different from similarly substituted butadienes. Yet, with the dienophiles maleic anhydride and DMA the evidence indicates that **5b** reacted via its nonbonding electron pair. Thus, these pathways have a lower $\Delta G^{\neq}$ than does the [4+2] cycloaddition pathway. Initial studies using **5b** and dienophiles such as phenylacetylene, *p*-methoxystyrene and indene indicate that **5b** is not as reactive as predicted by the approach of Sustmann and Schubert.[16] While the phenyl and Me substitution pattern in **5b** is not optimal for a [4+2] cycloaddition,[17] attainment of the required *s-cis* conformation is (perhaps) precluded only for **5b**-*Z*. We feel, in view of the previous extent to which UPS results have successfully correlated Diels–Alder reactivity,[16] that the present result warrants a further study of the 2-azadiene system with electron rich (diene LUMO-dienophile HOMO controlled) and non-carbonyl-electron poor (diene HOMO-dienophile LUMO controlled) dienophiles. Such a test should employ an azadiene with an easily accessible *s-cis* conformation.

UPS results indicate that **5c**, with its high energy, delocalized HOMO, should be a reactive diene with C-4 being a likely reaction site. If azadienes such as **3** and **5c** react in a "Diels–Alder" fashion, we would expect that **5c**, with the *s-cis* conformation inaccessable, would be unreactive. If **3** and **5c** react in an "enamine" fashion, then **5c** should be reactive but might yield products other than those of [4 + 2] cycloaddition. Examination of models indicates that if intermediate **10** were formed, ring closure to a 6-membered product could proceed. This suggests that availability of the *s-cis* conformation in the ground state could be an important factor regulating [4 + 2] cycloaddition in reactive systems such as **3**.

Considerable additional work needs to be done before photoelectron spectroscopy can be used with confidence as a predictive tool for chemical reaction sites and rates. Also, it should be the most useful for gas-phase reactions, because solvation effects in condensed media can, of course, play an equally important role with energetics and steric effects in determining reaction sites. It would be interesting to examine the photoelectron spectrum of azadiene **3** studied by Ghosez *et al.*[4] which does undergo [4 + 2] cycloaddition to see whether the dimethylamino lone-pair is more or less delocalized than in **5c**.

EXPERIMENTAL

^{1}H NMR spectra were obtained on a Perkin Elmer R-12 spectrometer. ^{13}C NMR spectra were obtained on a Bruker WH-90DS fourier transform spectrometer. Chemical shifts are given as $\delta(CH_3)_4Si$. Vapor phase chromatography was done using a 6 ft × 0.125 in 10% SE30 on Chromosorb W column for analytical work and an 18 ft × 0.25 in 20% SE 30 column for preparative work. M.ps, obtained on a Thomas-Hoover apparatus, are uncorrected. Elemental analyses on C, H and N were performed by Midwest Microlabs, Inc., Indianapolis, Indiana, U.S.A. Analyses obtained on all new compounds were within ±0.3% of the calculated values.

The compounds **4a**, **4b** and N - (benzylidine) - 2 - methyl - 2 - propen - 1 - amine were prepared by methods previously described.[18] See Table 1 and 3 for NMR data for **4a** and **b**.

N-(2-*Propenyl*)-*benzimidoyl chloride*. A soln of 5.1 g (0.032 mol) of *N*-allylbenzamide in dry benzene was added dropwise, at room temp to a soln of 6.4 g (0.03 mol) of PCl_5 in benzene. The mixture was refluxed 3 hr and then concentrated *in vacuo*. Distillation gave 3.5 g (62%) of the title compound, b.p. 65–7° (0.3 mm); NMR (neat) 3.8 (t of d, 2H), 4.7 (m, 2H), 5.5 (m, 1H), 6.8 (m, 3H), 7.6 (m, 2H). The compound was used without further characterization.

(E) - N^2 - (2 - *Propenyl*) - N^1,N^1 - *dimethylbenzamidine* (**4c**). A soln of 3.5 g (0.02 mol) of the imidoyl chloride (see above) in benzene was cooled in a dry ice-acetone bath. To this was added 4.5 ml (2.7 g, 0.06 mol) of condensed dimethylamine. The mixture was stirred cold for 10 min, slowly brought to room temp., and stirred for 3 hr. The mixture was diluted with ether, washed with water, and dried. Distillation of the solvents and the residue give 2.76 g (73%) of **4c**, b.p. 77° (0.15 mm); IR (neat) 1600 cm^{-1} (s); UV (MeOH) λ_{max} 220 nm (log ϵ 4.2); NMR see Tables 1 and 3.

Illustrative instructions for preparation of **5** *and* **6**. A soln of 3.24 g (0.15 mol) of **4d** in 15 ml of dimethylsulfoxide was cooled to 0°. To this was slowly added 1.68 g (0.015 mol) of solid t-BuOK (prepared by evaporation of t-BuOH from a soln of t-BuOK). The mixture turned brown-red and was stirred at 25° for 1 hr. Dilution with ether, washing with water, drying and distillation gave 2.8 g (86%) of a 3.3 to 2 mixture of (*E*, *Z*) and (*E*, *E*)-**5d**, b.p. 120–3° (1.25 mm); IR (neat) 1550 cm^{-1} (str. br.); UV (CH_3OH) λ_{max} 260 (log ϵ 4.1).

Other *cis-trans* mixtures of conjugated azadienes were prepared in 60–85% yields as above except that only 10 mol % of base catalyst was required for rapid isomerization of the aldimines. NMR data for the azadienes is collected in Tables 2 and 4. Additional physical properties and names for the individual azadienes are listed below.

(E, Z) and (E, E) - N - (2,2 - *Dimethylpropylidine*) - 1 - *propen* - 1 - *amine*, **5a**. Analyt. sample by preparative vpc, column temp. 130°.

(E, Z) - N - (*Benzylidine*) - 1 - *propen* - 1 - *amine*, **5b**-(*Z*), b.p. 40–1° (0.9 mm); IR (CCl_4) 1645 and 1570 cm^{-1}, UV (CH_3OH) λ_{max} 280 nm (log ϵ 4.2); isolated by preparative vpc.

(E, E) - N - (*Benzylidine*) - 1 - *propen* - 1 - *amine*, **5b**-(*E*), b.p. 40–1° (0.9 mm); IR (CCl_4) 1660, 1610 and 1575 cm^{-1}; UV (MeOH) λ_{max} 280 nm (log ϵ 4.2); isolated by preparative vpc.

(E, E) *and* (E, Z) - 1 - *Phenyl* - 1 - *dimethylamino* - 2 - *aza* - 1,3 - *pentadiene*, **5c**; b.p. 97° (0.25 nm); IR (neat) 1550 cm^{-1} (strong, broad); UV (MeOH) λ_{max} 255 nm (log ϵ 3.1).

(E, E) *and* (E, Z) - 1 - *Phenyl* - 1 - *diethylamino* - 2 - *aza* - 1,3 - *pentadiene*, **5d**; b.p. 120–3° (125 nm); UV (MeOH) λ_{max} 260 nm (log ϵ 4.1).

(E) - N - (*Benzylidine*) - 2 - *methyl* - 1 - *propen* - 1 - *amine*, (**6**), b.p. 72° (1.5 nm); UV (MeOH) λ_{max} 290 nm (log ϵ 4.2); ^{1}H NMR ($CDCl_3$) 1.8 (s, 3H, *trans*-CH_3); 2.1 (s, 3H, *cis*-CH_3); 6.6 (m, 1H, vinyl H); 7.3 (m, 3H, *m*, *p*-phenyl); 7.7 (m, 2H, *o*-phenyl), 8.0 (broadened s, 1H, –N=CH).

Reaction of **5b** *with maleic anhydride*. Under strict anhydrous conditions a soln of 290 mg (0.002 mol) of a ~1 : 1 mixture of **5b**-(*Z*) and (*E*) and 200 mg (0.002 mol) of maleic anhydride in benzene was refluxed for 4 hr. At 30 min a brown, viscous material separated from soln and vpc analysis showed the steady production of benzaldehyde. The benzene soln was diluted with ether, washed with water, dried and evaporated to yield 100 mg (47%) of benzaldehyde as identified by its NMR spectrum and vpc retention time. The material that precipitated during the reaction was an amorphous solid (120 mg). It was not characterized.

Reaction of **5b** *with dimethyl acetylenedicarboxylate*. A soln of 72.5 mg (0.5 mmol) of a mixture of **5b**-(*Z*) and **5b**-(*E*) (ratio ~1 : 9) and 71 mg (0.5 mmol) in 0.2 ml of acetonitrile-d_3 were sealed in an NMR tube and allowed to stand at room temp. in the dark. The reaction was monitored by ^{1}H NMR over a period of several weeks. Gradually, signals at 1.85, 6.15, 6.85 and 8.2 due to **5b**-(*E*) decreased in intensity. The signal at 1.85 was replaced in part by a new Me signal at 1.65 (q, J = 6.5, 1.5 c/s). Also the signal for DMA was slowly reduced in intensity and two new OMe signals appeared at 3.6 and 3.9. At the same time, the spectral region for olefinic H increased in complexity precluding definitive interpretation of that part of the spectrum.

Reaction of **4b** *with dimethyl acetylenedicarboxylate*. A soln of 360 mg (0.0025 mol) of **4b** and 720 mg (0.005 mol) of DMA in 5 ml of toluene was refluxed overnight. Concentration *in vacuo* followed by trituration with ether gave 400 mg (37%) of **7a** as a yellow solid, m.p. 118–19°; recrystallization from benzene-ether gave an analytical sample, m.p. 135–6°; IR ($CHCl_3$) 1709 and 1658 cm^{-1}; UV (MeOH) λ_{max} 228 (log ϵ 4.4), 278 (log 4.4) and 382 nm (log 4.1); ^{1}H NMR ($CDCl_3$) 3.63, 3.67, 3.80, 3.85 (4 singlets with broad base, 14 H, OMe's plus NCH_2); 5.4–5.6 (m, 4H, vinyl plus benzylic H). 7.3 (bs, 5H, phenyl); when sufficient $Eu(fod)_3$ was added the spectrum was resolved as follows: 3.77, 3.99, 4.19 (3s, 3H each, $3OCH_3$), 4.30 (m, 2H, NCH_2), 5.23 (s, 3H, coordinated Me), 5.4–6.0 (m, 3H, typical $-CH{=}CH_2$), 6.65 (s, 1H, benzylic H), 7.3 (m, 3H, *m* and *p*-phenyl), 7.9 (m, 3H, *o*-phenyl).

Dimethyl (Z, Z, E) - 7 - *Diethylamino* - 7 - *phenyl* - 6 - *aza* - 2,4,6 - *heptatrienyl* - 3,4 - *dicarboxylate* (**8**). A soln of 750 mg (0.003 mol) of **5d** and 450 mg (0.003 mol) of DMA in 10 ml of methylene chloride was stirred at 0° for 2.5 hr. The dark mixture was diluted with benzene and extracted with 3N HCl. The acidic aqueous fraction was basified and extracted with benzene. This yellow benzene layer was dried and concentrated to give 400 mg of yellow oil which was triturated with petroleum ether (30–60°) to give 230 mg (21%) of **8**, m.p. 98–104°. Recrystallization from petroleum ether–ether gave an analytical sample, m.p. 102–4°; IR ($CHCl_3$) 1709 (s) and 1519 (s) cm^{-1}; UV (MeOH) 330 nm (log 4.5); ^1H NMR ($CDCl_3$) 1.23 (t, 6H, J = 6.6, CH_3's); 1.60 (d, 3H, J = 6.6, $C{=}CH_3$), 3.45 (bq. 4H, NCH_2's) 3.65, 3.75 (2s, 3H each, 2 OCH_3), 6.55 (s, 1H, NCH=C), 6.67 (q, 1H, J = 6.6, C=CH), 7.3 (m, 5H, phenyl H).

The neutral fraction, 250 mg, was not completely characterized.

Dimethyl (Z, Z, E)-*7-Dimethylamino-7-phenyl-6-aza-2,4,6-heptatrienyl-3,4-dicarboxylate.* As with **5d**, 1.8 g (0.01 mol) of azadiene **5c** was converted to 920 mg (28%) of the title compound, m.p. 98–110°; several recrystallizations from petroleum ether-benzene gave 520 mg of an analytical sample, m.p. 127–8°; IR ($CHCl_3$) 1719 (s) and 1544 (s) cm^{-1}; UV (MeOH) 328 nm (log 4.4); ^1H NMR ($CDCl_3$) 1.51 (d, 3H, J = 7, C=CMe), 3.03 (bs, 6H, NMe_2), 3.55, 3.65 (2s, 6H, 2 OMe), 6.50 (s, 1H, NCH=C), 6.59 (q, 1H, J = 7, C=CH), 7.3 (m, 5H, phenyl H).

Photoelectron spectra. The photoelectron spectra were recorded by a Perkin-Elmer PS-18 photoelectron spectrometer. In all cases the excitation source was the He I resonance line, and xenon and argon were employed as internal calibrants.

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[19] A referee has pointed out that Kondragt'eva and Dol'skaya have reported that 1-ethyl-4-methyl-2-azabutadiene undergoes Diels–Alder addition with both acrolein and ethyl vinyl ether (G. Y. Kondragt'eva and Y. S. Dol'skaya, *Zh. Org. Khim.* **6**, 2200 (1970)). The referee suggested that some of this early work should be repeated in view of the current contrasting results.