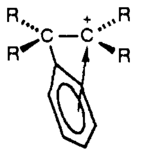
state leading to rearrangement.[75] Detailed studies also suggest that formation of π-bridging structures, **15**, are important in these rearrangements.[76,77]



15

1,2-Phenyl migration is a more favorable process than the corresponding 1,2-hydrogen migration for carbenium ion **8**. Although the thermodynamics of the products are not known, all three migration processes, reactions 8a–c, are probably highly exothermic. The facile nature of 1,2-phenyl migration in **8** is consistent with the $AlCl_3$ induced rearrangement of $(p\text{-}XC_6H_4)(CH_3)_2SiCH_2Cl$, where exclusive aryl migration is observed.[3] Phenyl migration is probably facilitated by initial interaction of the π electrons of the phenyl group with the developing empty 2p orbital on the carbon atom yielding a complex similar to **15**. Formal 1,2-phenyl migration then completes the process. 1,2-Hydrogen migration may precede formation of the π-bridging structure.

The results for carbenium ions, **5–8**, suggest the following relative migratory aptitude: phenyl > hydrogen ≫ methyl. Several factors, however, may contribute to the observed migration distribution. For example, the orientation of the neutral organosilane as the elimination of chloride occurs may be important. The overall thermodynamic stability of the products may also be important. Both of these effects will contribute to the observed migration distribution, but they are not part of the *intrinsic* migratory aptitude of a group.

Conclusions

The unimolecular rearrangement of simple nascent α-silyl-substituted carbenium ions in the gas phase has been explored. These incipient carbenium ions undergo 1,2-migration from silicon to carbon to yield a more stable (thermodynamically) silylenium ion with the following relative migratory aptitude: phenyl > hydrogen ≫ methyl. These results, together with recent theoretical[20-22] and experimental[18,19,21,22] findings, suggest that α-silyl-substituted carbenium ions and the corresponding silylenium ions may be important intermediates in solvolytic rearrangements of α-functionalized silanes. We are currently extending these studies to investigate the relative migratory aptitude of various groups including ethynyl, ethenyl, ethyl, *n*-propyl, isopropyl, *tert*-butyl, CH_2Cl, $p\text{-}XC_6H_4$, etc., in order to obtain a deeper understanding of these simple rearrangements in the gas phase.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, the Society for Analytical Chemists of Pittsburgh, and the VG Corp. for partial support of this research.

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Homoconjugation and Transannular Orbital Interactions Detected by Photoelectron and ^{13}C-NMR Spectroscopy. Bicyclo[3.3.1]nona-3,7-diene-2,6-dione and Bicyclo[3.3.1]nonane-2,6-dione

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Contribution from the Organisch-Chemisches Institut der Universität Heidelberg, D-6900 Heidelberg 1, Federal Republic of Germany, and the Department of Chemistry, University of Nevada, Reno, Nevada 89557-0020. Received September 6, 1991

Abstract: Transannular orbital interactions between two ketone carbonyl groups located at positions 2 and 6 on the bicyclo[3.3.1]nonane carbocyclic framework were detected by ^{13}C-NMR and photoelectron spectroscopy (PES). Thus, an ~4.4-ppm shielding of the $\delta_{C=O}$ is observed in the ^{13}C-NMR spectra of the saturated diones (**1** and **3**) relative to the monoketones (**7** and **9**), and in the PE spectra, an ~0.15-eV splitting of the n-orbitals of the diones is detected. In the bis-enone analogues (**2** and **4**) the shieldings (relative to the corresponding mono-enones, **8** and **10**, respectively) are more than doubled, to ~10 ppm, and significant splittings are observed in the PE spectra for both n-orbitals (~0.1 eV) and π-orbitals (~0.3 eV). The origin of the electronic interaction would appear to come from orbital interaction through space and through σ-bonds.

Introduction

The phenomenon of electron delocalization through homoconjugation was described 20 years ago by Hoffmann[2] in terms of direct ("through-bond") and indirect ("through-space") interactions from localized sets of orbitals or chromophores. Orbital interactions through a framework of σ-bonds have been studied in nonconjugated ketones, dienes, and a variety of other functional groups by photoelectron (PE)[3] and electron transmission (ET)[3c,4]

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[1] (a) University of Heidelberg. (b) University of Nevada.

[2] (a) Hoffmann, R.; Imamura, A.; Hehre, W. J. *J. Am. Chem. Soc.* **1968**, *90*, 1499–1509. (b) Hoffmann, R. *Acc. Chem. Res.* **1971**, *4*, 1–9.

[3] Reviews: (a) Gleiter, R. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 696–701. (b) Paddon-Row, M. N. *Acc. Chem. Res.* **1982**, *15*, 245–251. (c) Paddon-Row, M. N.; Jordan, K. D. In *Modern Models of Bonding and Delocalization*; Liebman, J. F., Greenberg, A., Eds.; Verlag Chemie: Weinheim, 1988; pp 115–194. (d) Martin, H.-D.; Mayer, B. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 283–310. (e) Gleiter, R.; Schäfer, W. *Acc. Chem. Res.* **1990**, *23*, 369–375.

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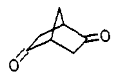
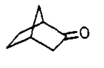
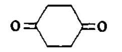
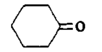
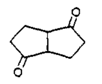
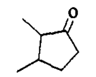
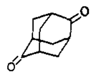
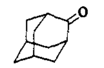
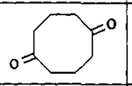
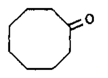
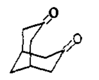
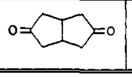
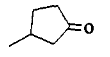
Table I. Influence of Homoconjugation on the ^{13}C-NMR Chemical Shifts[a] of Cyclic Ketones

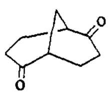
	Orbital Interaction Through n Bonds	Dione	$\delta_{C=O}$	Ketone	$\delta_{C=O}$	$\Delta\delta^b$	r,(Å)[c]
(a)	3		212.3[d]		218.1[d]	-5.9	2.9
(b)	3		208.4[e]		212.1[e]	-3.7	3.0
(c)	3		220.3[f]		220.9[g]	-0.6	3.4
(d)	4		213.4[d]		218.3[d]	-4.9	3.4
(e)	4		213.2[d]		217.7[d]	-4.5	4.1
(f)	4		208.6[d]		212.5[d]	-3.9	2.7-4.0
(g)	4		218.0[f]		218.7[g]	-0.7	4.3

[a] Measured in $CDCl_3$ at 25 °C, δ in ppm downfield from $(CH_3)_4Si$. [b] Dione minus ketone. [c] Interchromophoric nonbonded distances from Dreiding Models. [d] Data from ref 7. [e] Data from J. E. Gurst, University of West Florida. [f] Data from the following: Whitesell, J. K.; Matthews, R. S. *J. Org. Chem.* **1977**, *42*, 3878-3882. [g] Data from the following: Stothers, J. B.; Tan, C. T. *Can. J. Chem.* **1974**, *52*, 308-314.

spectroscopy. Through-bond interactions have been detected by chemical reactivity[3,5,6] and ^{13}C-NMR spectroscopy[7,8] and may operate over surprisingly long distances, e.g., 12 σ-bonds (~13.5 Å) as detected by electron-transfer experiments.[9,10] Orbital interaction through space has been detected in anchimeric assistance to solvolysis[6,11,12] and by the spectroscopic methods cited above.[3,4,7,8,13] Through-space interactions are thought to be mainly responsible for the large splittings of the π-orbitals (0.86 eV) and π*-orbitals (1.52 eV) of norbornadiene and the even larger π-orbital splitting (1.26 eV) of *endo,endo*-dimethanonaphthalene and its π*-orbital splitting of 1.45 eV.[13] The very large (1.55-eV) splitting of the two linear combinations from the in-plane MOs of cyclodeca-1,6-diyne is thought to come from orbital interactions through space and through bonds.[14]

Transannular orbital interactions between ketone carbonyl chromophores were predicted and observed to give large splittings between the lone-pair nonbonding orbitals when overlap through skeletal σ-orbitals was possible, as in the 0.75-eV splitting in tetramethyl-1,3-cyclobutanedione[15] and the 0.44 eV splitting in cyclohexane-1,3-dione.[16] Smaller splittings were found in the 1,4-diones, 2,5-norbornanedione (0.16 eV)[17] and 1,4-cyclohexanedione (0.1$_5$ eV),[15] where the overlap between the n-orbitals and the relevant σ-p ring orbitals is poor because of twisting in the six-carbon ring. In the flattened chair geometry of the 1,4-dione, tricyclo[4.2.1.1^{2,5}]decane-9,10-dione, the splitting rises to 0.4 eV,[3d] which is close to that of a *p*-benzoquinone.[15] In addition to the relative orientation of the chromophores, ring skeletal strain also plays a role, as has been demonstrated in a series of bi-, tri-, and tetracyclic compounds incorporating the cyclohexane-1,4-dione unit.[4,18,19] Transannular orbital interactions between ketone carbonyl groups have also been detected by ^{13}C-NMR spectroscopy.[7] Thus, for 1,6-diketones the shift of $\delta_{C=O}$ from 212.5 to 208.6 ppm in going from bicyclo[3.3.1]nonan-3-one to the 3,7-dione is thought to be due to a through-space interaction.[7]

In the following, we present PE and ^{13}C-NMR spectroscopic evidence for the interaction of saturated and α,β-unsaturated 1,6- and 1,3-diones on the bicyclo[3.3.1]nonane framework (**1**–**6**), where **2**, **4**, and **6** are bis-homo *p*- or *o*-benzoquinones.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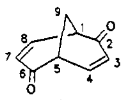

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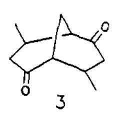
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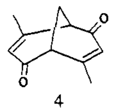
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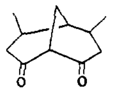
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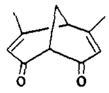
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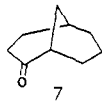
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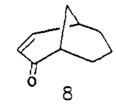
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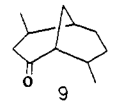
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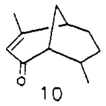
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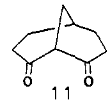
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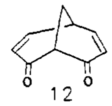
12

Results and Discussion

Synthesis. Diene dione **2** was prepared from the parent dione **1**[20] first by conversion of **1** to its bis-enol acetate with isopropenyl acetate and then allylic bromination with *N*-bromosuccinimide in CCl_4 followed by hydrolysis and dehydrobromination in ethanolic hydrochloric acid. The mono-enone analogue (**8**) was prepared from monoketone **7** by the same procedure, and the latter was prepared from dione **1** by monothioketalization with ethanedithiol followed by Raney nickel desulfurization.[21] Compound **6** was available from the same reaction that produces the isomeric dimethylated diene dione (**4**).[22,23] Thus, **4** and **6** were synthesized by and separated (column chromatography) following acid-catalyzed double intramolecular aldol condensation of the tetraketone, 3,5-diacetylheptane-2,6-dione, which was prepared by condensing 2 equiv of pentane-2,4-dione with 1 equiv of formaldehyde. Saturated diketones **3** and **5** were prepared by catalytic hydrogenation of bis-enones **4** and **6**, respectively, and the configuration

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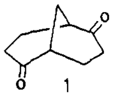
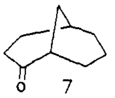
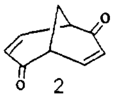
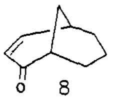
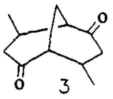
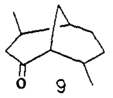
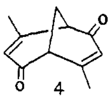
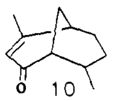
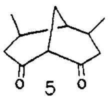
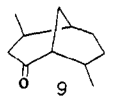
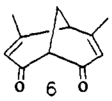
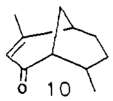
Table II. ^{13}C-NMR Carbonyl Chemical Shifts^a of Mono- and Diconjugated and Unconjugated Bicyclo[3.3.1]nonane Ketones

	Orbital Interaction Through n Bonds	Dione	$\delta_{C=O}$ (ppm)	Ketone	$\delta_{C=O}$ (ppm)	$\Delta\delta^b$
(a)	4	 1	212.5	 7	216.9	-4.4
(b)	2	 2	193.2	 8	203.1	-9.9
(c)	4	 3	208.9	 9	213.3	-4.4
(d)	2	 4	191.1	 10	201.2	-10.1
(e)	2	 5	203.3	 9	213.3	-10.0
(f)	2	 6	193.4	 10	201.2	-7.8

^{a}In ppm downfield from $(CH_3)_4Si$ in $CDCl_3$ at 21 °C. ^{b}Dione minus ketone.

of the methyl groups was thought to be exo. The exo assignment was confirmed by analysis of the ^{1}H-NMR coupling constants between the CH_2 hydrogens at C_3 and the CH hydrogen at C_4 and by an NOE observed between the CH_3 groups and the C_9-CH_2. Saturated dione **3** was converted into monoketone **9** and mono-enone **10** by the procedures (above) used for converting **1** into **7** and **8**.

^{13}C-NMR Detection of Intramolecular Interchromophoric Interaction. Homoconjugative orbital interactions between two ketone carbonyl chromophores have been detected previously by studying C═O ^{13}C-NMR chemical shifts.[7,15,24] Several examples may be seen in Table I, where the dione carbonyl carbon is shifted upfield from that of the parent monoketone. The source of the interaction may have its origins in through-space orbital interactions with $|\Delta\delta|$ being (i) larger with the shorter distance between the carbonyl carbons (interchromophoric distance) (2.9 Å for a, 3.4 Å for d) and (ii) slightly smaller in the monocyclic diones b and e than in the bicyclic diones a and d where the C═O groups are thought to be collinear. Orbital interactions of diketones through the same three or four bonds do not give rise to the large $|\Delta\delta|$ values when there are intervening σ-bonds, even when the C═O are collinear, as in g, or when the C═O groups are not collinear, as in c.

Similar evidence for orbital interaction may be found in the diones of this work. Thus, in Table II, $|\Delta\delta|$ is quite comparable for cases a and c, where orbital interaction passes through four bonds and the interchromophoric distance is ~3.4 Å. As before, through-space interactions would appear to be an important component leading to the carbonyl shieldings of these 1,4-diones. However, when the carbonyl groups are located 1,3, as in e, $|\Delta\delta|$ increases substantially and is comparable to that ($\Delta\delta = -8.9$) found for cyclohexane-1,3-dione (vs cyclohexanone).[25] Evidently through-bond orbital interaction plays an important role in example e of Table II. It also apparently plays a role in the bis-enones.

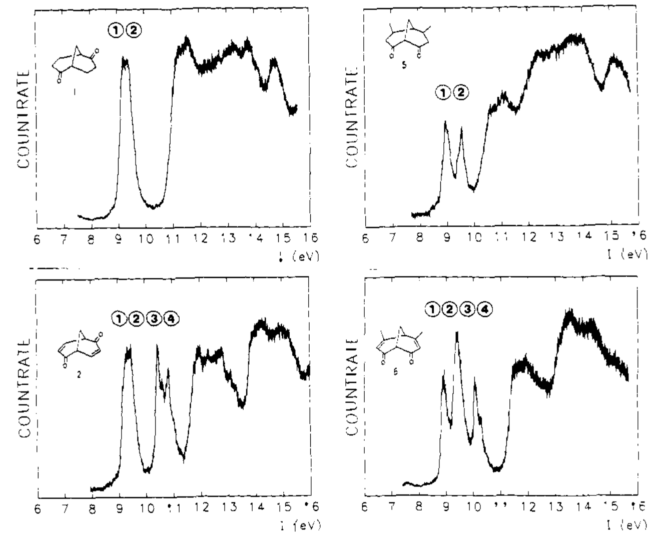


Figure 1. He(I) photoelectron (PE) spectra of ketones **1**, **2**, **5**, and **6**.

Table III. Comparison between the Vertical Ionization Energies ($I_{v,j}$) of **1**-**8** and the Calculated Orbital Energies ($-\epsilon_j$)^a

compd	band	$I_{v,j}$	assignment	$-\epsilon_j$ (MINDO/3)
1	1 2	9.33	n_- n_-	9.63 9.79
2	1 2	9.45	n_- n_+	9.42 9.53
	3	10.49	π_-	10.58
	4	10.86	π_+	10.94
3	1 2	9.22	n_- n_+	9.57 9.69
4	1 2	9.18	n_- n_+	9.29 9.41
	3	9.90	π_-	10.25
	4	10.30	π_+	10.56
5	1	9.05	n_-	9.49
	2	9.58	n_+	10.00
6	1	8.94	n_-	9.31
	2 3	9.43	n_+ π_-	9.76 9.98
	4	10.09	π_+	10.24
7	1	8.94	n	9.45
8	1	9.01	n	9.31
	2	9.80	π	9.98

^{a}All values in electronvolts.

Homoconjugation of C═C and C═O chromophores, as in the β,γ-unsaturated ketone, bicyclo[2.2.1]hept-5-en-2-one, can be detected in the ~2 ppm upfield shift of $\delta_{C=O}$ compared with the saturated analogue.[26] However, in the analogue bicyclo[2.2.2]oct-5-en-2-one, $\Delta\delta$ is only ~−0.2 ppm. These data may be contrasted with those found for homoconjugated bis-enones **2** and **4** where the $\delta_{C=O}$ resonances are shifted upfield by ~10 ppm compared with the parent enones. The isomeric bis-enone **6**, with $\Delta\delta = -7.8$, does not show a comparable shift in $\Delta\delta$ relative to the saturated dione ($\Delta\delta = -10.0$), and the reasons for this are at present unclear.

PE Spectroscopy Detection of Intramolecular Interactions. The photoelectron spectra of **1**-**8** have been recorded. As examples we show in Figure 1 the PE spectra of **1**, **2**, **5**, and **6**. The recorded vertical ionization energies of **1**-**8** are collected in Table III. To interpret the first bands of the PE spectra we make use of the assumption that the recorded vertical ionization energies ($I_{v,j}$) can be set equal to the negative value of the calculated orbital energies (ϵ_j) (Koopmans's theorem[27]). This assumption has proven to be valid for the interpretation of many ketones.[15-19] To calculate

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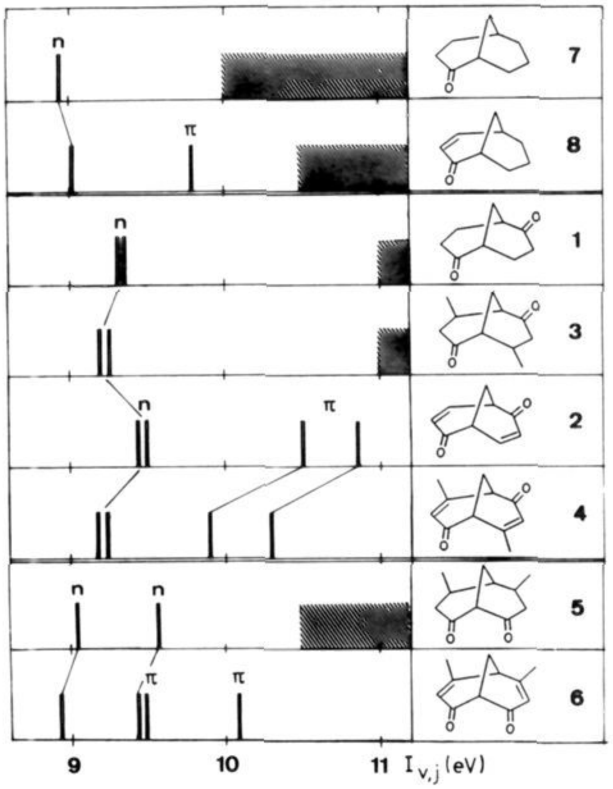

Figure 2. Comparison between the first photoelectron (PE) bands of ketones **1**–**8**.

the orbital energies we rely on the MINDO/3 method[28] because it reproduces the sequence and the values of the MOs of ketones quite well. In addition to the comparison with MO calculations we have correlated the recorded spectra with those of related compounds whose assignment is known.

In Figure 2 we have compared the first bands of the PE spectra of **1**–**8**. The PE spectrum of **7** exhibits a single band near 9 eV which is split by 0.13 eV. This band is clearly shifted from the region of strongly overlapping bands beginning at 10 eV. This single band can be assigned to the ionization of the n-orbital of the oxygen atom by its similarity to the n-orbital ionization of the monocyclic ketones cyclohexanone (9.14 eV[29] and 9.28 eV[30]) and cyclooctanone (9.00 eV[29] and 9.09 eV[30]). The n-orbital ionization of **7** is almost identical to that of its more strained analogue, 2-norbornanone, which exhibits an n-orbital ionization of 8.94 eV.[29]

The PE spectrum of **8** (Figure 2) reveals two distinct bands at 9.01 and 9.80 eV. The bands are very different from a third region of strongly overlapping bands beginning at 10.3 eV. The band at 9.01 eV exhibits a small splitting of 0.07 eV and is more intense than the band at 9.80 eV. Examination of the PE spectrum of **8** reveals an especially interesting observation. One band is shifted strongly toward higher energy compared to the corresponding bicyclic ketone (**7**) and cycloalkenes (cyclohexene, 9.12 eV; cyclooctene, 9.02 eV).[30] This shift may be explained through second-order perturbation theory.[30] Calculations suggest that conjugation of a C=C double bond with a C=O double bond provides a stabilizing interaction between the highest occupied π-molecular orbital (HOMO) with the lowest unoccupied molecular orbital (LUMO). Therefore, in α,β-unsaturated carbonyl compounds, the ionization energy of the n-orbital of the oxygen atom can be expected to lie near that of the saturated ketone, but the first π-ionization energy will be shifted to higher energy. This is exemplified by the PE data reported for 2-cyclohexenone [9.37 eV (n), 10.14 eV (π)][30] and 2-cyclooctenone [9.18 eV (n), 9.80 eV (π)].[30] Applying this reasoning to molecule **8**, the band at 9.01 eV can be assigned to the ionization energy of the n-orbital on oxygen and the band at 9.80 eV can be assigned to the ionization energy of the highest π-MO of the C=C double bond.

The PE spectrum of dione **1** (Figure 1) shows one sharp band at 9.33 eV with a splitting of 0.14 eV and is well separated from a higher energy band at nearly 11.0 eV. The sharp band at 9.33 eV is more intense than the band in the monocarbonyl analogue (**7**) and is assigned to the ionization of the n-orbitals of both oxygen atoms. The splitting of 0.14 eV may be due to an energetic splitting of both n-orbitals, or as in **7**, the splitting could be due to vibrational fine structure. The shift to higher energy for the n-orbital (by 0.39 eV) and the σ-bands (1 eV) compared to that for **7** is attributed to perturbation by the additional carbonyl group.

As one might expect, there is not much difference between the PE spectra of diones **3** and **1**. The 9.33-eV band of **1** is shifted to 9.22 eV in the PE spectrum of **3**, which is assigned to the ionization energy of the n-orbitals of both oxygen atoms. This band does not have any of the fine structure which is present in the PE spectrum of **1**, and the σ-bands beginning at 10.7 eV are also at lower energy by 0.3 eV when compared to **1**.

The PE spectrum of bis-enone **2** (Figure 1) reveals one low-energy band at 9.45 eV and two bands at 10.49 and 10.86 eV followed by a progression of overlapping high-energy bands beginning at 11.7 eV. The 9.45-eV band has twice the intensity of the higher energy bands at 10.49 and 10.86 eV; it is assumed to consist of two overlapping transitions. Comparing the PE spectrum of **2** to the PE spectra of ketone **7** and enone **8**, which have only one functionalized ring, and to the PE spectrum of the saturated dione (**1**), which has both n-orbitals nondifferentiated, the lowest energy band can be assigned to the ionization energy of the oxygen n-orbitals. In contrast to **1** and **7**, however, **2** shows only vibrational fine structure rather than the 0.13-eV splitting of its lowest energy band.

By analogy to enone **8**, the bands at 10.49 and 10.86 eV are assigned to the ionization energies of the π-orbitals of the C=C double bond. (The weaker band of 10.7 eV is presumably revealed only through the loss of its fine structure.) Both bands are separated by a relatively large (0.37-eV) energy gap. The difference between the centers of gravity of the π-bands and the n-bands in **2** amounts to 1.23 eV. This value is 0.44 eV larger than the corresponding separation in **8**. This difference is explained by the presence of additional homoconjugation between the C=C double bond and the additional C=O double bond present in **2**. Bis-enone **2** could also be classified as a β,γ-unsaturated carbonyl group. The PE spectra of β,γ-unsaturated carbonyl compounds typically exhibit a significant shift of their π-orbital band to higher energy by a through-bond interaction via the CH_2 group or CH group located between the C=O and the C=C group.[30] The PE spectra of cyclooct-3-en-1-one (bands at 9.12 and 9.66 eV) and of bicyclo[2.2.1]hept-5-en-2-one (bands at 8.86 and 10.09 eV) agree with this explanation.[30]

The PE spectrum of the dimethyl bis-enone **4** is very similar to that of the parent bis-enone (**2**). Addition of methyl groups causes a shift of all the bands. The n-orbital bands are shifted by 0.27 eV to 9.18 eV, and the π-orbital bands are shifted by 0.59 and 0.56 eV to 9.90 and 10.30 eV. The first σ-band is also shifted by 0.4 eV to 11.3 eV when compared to **2**. Replacing β-hydrogens by methyl groups has its main effect on the ionization energy of the n- and π-bands in the PE spectrum of **4**, which is reduced by 0.31 eV (to 0.92 eV) as compared with the corresponding values obtained for **2**.

The PE spectrum of cisoid dione **5** (Figure 1) exhibits two low-energy bands at 9.05 and 9.58 eV, which are assigned to the ionization of the n-orbitals on oxygen. The average of the two bands is 9.32 eV, which is 0.10 eV higher than the single band observed for the transoid dione **3**. The relatively large splitting (0.53 eV) is within the same order of magnitude as the n-orbital splitting seen in other 1,3-diketones which have a fixed confor-

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(28) Bingham, R.; Dewar, M. J. S.; Lo, D. H. *J. Am. Chem. Soc.* **1975**, *97*, 1285–1301.

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mation, for example, bicyclo[3.2.1]octane-2,4-dione (bands at 9.28 and 9.81 eV, splitting of 0.53 eV) and bicyclo[3.2.2]nonane-2,4-dione (bands at 9.15 and 9.94 eV, splitting of 0.79 eV).[16]

The PE spectrum of the cisoid bis-enone **6** (Figure 1) exhibits three low-energy bands at 8.94, 9.43, and 10.09 eV. The relative intensities of the bands are approximately 1:2:1, which may be due to a double-ionization band at 9.43 eV. This double ionization is shown in Table III. In comparing the cisoid bis-enone **6** to the transoid bis-enone **4**, the bands at 8.94 and 9.43 eV should correspond to the ionization of the n-orbitals on the oxygen atoms. The average of 8.94 and 9.43 eV is 9.19 eV, which is shifted only slightly to lower energy when compared to **4** (9.18 eV), and the 0.49-eV n-orbital splitting is similar to that of the parent dione **5** (0.53 eV).

The π-band ionization of **6** corresponds to the bands at 9.43 and 10.09 eV, consistent with the ionization of the π-orbitals of **4**. The mean (energy) separation of the π-orbital and n-orbital bands of **6** is only 0.57 eV, which is smaller by 0.35 eV than the n–π separation in **4**. The unexpected difference in n–π separation could be due to a lack of homoconjugation between the C=C and C=O double bonds in **4**. The 0.66-eV splitting of the π-bands in **6** is larger than that (0.40 eV) of the π-bands in **4** by 0.26 eV. The larger splitting of **6** is expected because the C=C double bonds are situated closer together, and their contributions to the higher lying π-orbitals are expected to be larger than that of the C=O double bonds.

The experimental ionization energy splitting patterns are generally reproduced well by the MINDO/3 calculations. In general, the calculated orbital energies are a little lower than the experimental orbital energies. The largest deviations for the oxygen n-orbitals in the saturated bicyclic systems range from 0.35 to 0.51 eV. The deviations for the α,β-unsaturated ketones are smaller, ranging from −0.03 to 0.35 eV. The calculations also reproduce the splitting patterns found in the experimental results. For ketone **6**, however, the π-orbital splitting is not reproduced well by the MINDO/3 calculation. Overall, the MINDO/3 calculations agree well with the experimental results obtained and confirm the assignments of the bands made by empirical considerations. According to the MINDO/3 calculations, methyl substitution affords only a small increase in the orbital energies of the highest occupied molecular orbitals (see Table III, **1** and **2**).

Conclusions

The carbonyl resonances of all of the diones and bis-enones of this work (Table II) are shielded relative to corresponding ketones and enones. This behavior is consistent with earlier observations in other bichromophoric systems with C=O chromophores aligned for transannular orbital interaction (Table I).[7] The origin of this effect would appear to lie in orbital interaction through space as well as through σ-bonds. The through-bond interaction is apparently magnified in bis-enones **2** and **4** and decreased in **6**, all relative to the parent diones and ketones. A more complete analysis of the relative contributions of through-space and through-bond orbital interaction awaits a comparison with appropriate acyclic analogues of the bichromophoric and monochromophoric substances of Tables I and II.

The results from the analysis of the experimental PE spectra and the MINDO/3 calculations can be summarized as follows for the relative orbital energies and the splitting energies of the molecular orbitals of the bicyclo[3.3.1]nonanes examined. (1) The energies of the oxygen n-orbitals are slightly increased by substitution of a β-methyl group. There is no significant change if an α,β C=C double bond acts to lower the energy. (2) Conjugated double bonds have only a small influence on the energy of the oxygen n-orbitals (maximum 0.2 eV), but the energies of the C=C π-orbitals are significantly decreased by conjugation with a carbonyl group. The transoid diketone compounds show this effect more clearly than the cisoid due to the additional homoconjugation between the C=C double bonds and carbonyl group in the former. The energy gap between the n- and π-orbitals is 0.3–0.7 eV larger in the transoid compounds as compared to the cisoid. (3) Methyl substitution of the C=C double bond increases the energy by 0.2–0.6 eV and consequently reduces the gap between π- and n-orbitals. (4) The energies of the n-, π-, and σ-orbitals are all lowered by the presence of a second carbonyl group in the system (from 0.2 to 0.5 eV). (5) In general, bicyclic compounds which are functionalized in both large rings show a significant interaction between both halves of the molecule. This interaction affects the splitting of both the n- and π-orbitals. (6) Transoid (1,6)-diones do not exhibit an energy splitting of their n-orbitals in contrast to the cisoid (1,3)-diones, which show a significant energy splitting (0.5 eV). The splitting of the n-orbitals in the cisoid compounds is not influenced by changes in the remainder of the molecule. (7) The π-orbitals of diones with two olefinic groups show a significant splitting of 0.45–0.65 eV. This splitting is greater in the cisoid bis-enones than in the transoid.

Experimental Section

General Procedures. Infrared (IR) spectra were measured on a Perkin-Elmer Model 1600 FT-IR instrument. Ultraviolet (UV) spectra were recorded on a Cary 219 spectrophotometer or Perkin-Elmer Lambda Array 3840 UV/vis instrument. All nuclear magnetic resonance (NMR) spectra were determined in $CDCl_3$ on a GE QE-300 spectrometer and reported in parts per million downfield from tetramethylsilane, unless otherwise indicated. The PE spectra of **1**–**8** were recorded on a PS 18 photoelectron spectrometer (Perkin Elmer Ltd., Beaconsfield) at room temperature. The spectra were calibrated with Ar (15.76 eV, 15.94 eV) and Xe (12.13 eV, 13.44 eV). A resolution of ca. 20 meV on the Ar line $^2P_{3/2}$ was obtained. All melting points are uncorrected and were determined on a Thomas-Hoover capillary apparatus. Analytical gas chromatography (GC) was performed on a Varian-Aerograph Model 2400 F/I instrument on a 6 ft × $^1/_8$-in.-diameter column of 5% SE-30 on 80/100 Chromosorb-W AW-DMCS. UV spectral data were obtained using spectral grade *n*-heptane (MCB). Other solvents were distilled and dried before use: benzene, pentane, chloroform, and dichloromethane from P_2O_5; acetone from $KMnO_4$; and diethyl ether from $LiAlH_4$ under N_2. The solvents were used freshly distilled or stored over 4-Å molecular sieves (Linde). Column chromatography was accomplished on (60–200-mesh) J. T. Baker silica gel. Combustion analyses were carried out by Desert Analytics, Tucson, AZ.

Bicyclo[3.3.1]nona-2,6-dione (1).[20] Prepared according to a previously reported procedure,[20] the dione had the following data: mp 137–140 °C (lit.[20] mp 145–148.5 °C); IR (film on NaCl), ν 2935, 1697, 1440, 1126 cm^{-1}; UV, $\epsilon_{298}^{\max}$ 36; ^{1}H-NMR, δ 2.0–2.8 (m) ppm; ^{13}C-NMR ($CDCl_3$), δ 212.5 (s, C_2, C_6), 43.6 (t, C_9), 37.1 (t, C_3, C_7), 31.5 (d, C_1, C_5), 26.7 (t, C_4, C_8) ppm.

Bicyclo[3.3.1]nona-2,7-diene-2,6-dione (2).[22] The diene dione was prepared from **1** according to the reported procedure.[22] It had the following data: mp 82–83 °C (lit.[22] mp 81–83 °C); IR (film on NaCl), ν 3040, 2940, 1679, 1606, 1453, 1126, 1024 cm^{-1}; UV, $\epsilon_{393}^{\max}$ 33, $\epsilon_{372}^{\max}$ 217, $\epsilon_{356}^{\max}$ 417, $\epsilon_{330}^{\max}$ 175, $\epsilon_{227}^{\max}$ 6083, $\epsilon_{203}^{\max}$ 4416; ^{1}H-NMR, δ 2.72 (2 H, t, J = 2.84 Hz), 3.30 (2 H, dt, J = 6.72, 2.83 Hz), 5.83 (2 H, d, J = 9.98 Hz), 6.96 (2 H, dd, J = 9.95, 6.79 Hz) ppm; ^{13}C-NMR, δ 34.2 (t, C_9), 45.5 (d, C_1, C_5), 126.0 (d, C_3, C_7), 146.2 (d, C_4, C_8), 193.2 (s, C_2, C_6) ppm.

4,8-Dimethylbicyclo[3.3.1]nona-3,7-diene-2,6-dione (4).[22] The literature procedure was modified accordingly. A mixture of 2,4-pentanedione (200 g, 2 mol), 37% aqueous formaldehyde (formalin) (70 mL, ~1 mol), and absolute ethanol (100 mL) was stirred in a 1000-mL round-bottom flask at room temperature for 3 days. The solvent was removed under reduced pressure with a rotary evaporator, and the resulting oil was distilled (0.075 mmHg) to give 84.4 g of 3,5-diacetylheptane-2,6-dione. It had the following data: ^{13}C-NMR, δ 24.8 (t), 29.0 (q), 64.2 (d), 203.1 (s) ppm. This material was used directly in the next step.

In a 1000-mL round-bottom flask, benzene (500 mL) was heated at reflux overnight to remove H_2O azeotropically using a Dean–Stark trap. Then 3,5-diacetyl-2,6-heptanedione (102 g, 0.48 mol) and *p*-toluenesulfonic acid (5.2 g, 0.027 mol) were added, and the solution was again heated to reflux to remove H_2O azeotropically. When 13 mL of H_2O had been removed, the reaction was cooled to room temperature, and the mixture was washed with H_2O and then dried over $MgSO_4$. Following solvent removal by rotary evaporation, the residual orange oil was chromatographed on a column of silica gel. Elution with 2% ether in benzene gave 2,4-diacetyl-5-methylphenol, then elution with 15% ether in benzene gave **4**, and elution with 75% ether in benzene gave **6**.

Crystallization from methanol gave pure cisoid bis-enone 6. The pure transoid bis-enone **4** was isolated by crystallization in ether. It had the following data: mp 85–86 °C (lit. mp 125–127 °C,[22] 84–85 °C[23]); IR (film on NaCl), ν 3040, 2974, 2938, 1660, 1623, 1433 cm^{-1}; UV, $\Delta\epsilon_{385}^{\max}$ 229, $\epsilon_{365}^{\max}$ 577, $\epsilon_{349}^{\max}$ 819, $\epsilon_{336}^{\max}$ 656, $\epsilon_{235}^{\max}$ 15 310, $\epsilon_{203}^{\max}$ 13 900; ^{1}H-NMR, δ 2.00 (6 H, d, J = 1.4 Hz), 2.64 (2 H, t, J = 2.88 Hz), 3.06 (2 H, t, J

= 2.8 Hz), 5.62 (2 H, d, *J* = 1.38 Hz) ppm; ^{13}C-NMR, δ 22.9 (q), 34.2 (t, C_9), 49.5 (d, C_1, C_5), 121.1 (d, C_3, C_7), 159.4 (s, C_4, C_8), 193.4 (s, C_2, C_6) ppm.

4,6-Dimethylbicyclo[3.3.1]nona-3,6-diene-2,8-dione (6).[22] The crystals isolated above had the following data: mp 151–152 °C (lit.[21] mp 156–158 °C); IR (film on NaCl), ν 3030, 2945, 2910, 1659, 1435 cm^{-1}; UV, $\Delta\epsilon_{396}^{\max}$ 70, $\epsilon_{377}^{\max}$ 100, $\epsilon_{361}^{\max}$ 92, $\epsilon_{350}^{\max}$ 91, $\epsilon_{217}^{\max}$ 10200; ^{1}H-NMR, δ 2.13 (6 H, d, *J* = 1.3 Hz), 2.71 (2 H, t, *J* = 2.8 Hz), 2.90 (1 H, t, *J* = 2.6 Hz), 3.38 (1 H, t, *J* = 2.6 Hz), 5.65 (2 H, d, *J* = 0.6 Hz) ppm; ^{13}C-NMR, δ 24.5 (q), 36.7 (t, C_9), 43.0 (d, C_5), 57.1 (d, C_1), 123.5 (d, C_3, C_7), 163.3 (s, C_4, C_6), 191.1 (s, C_2, C_8) ppm.

Bicyclo[3.3.1]nonan-2-one (7). Monothioketalization[21] followed by Raney Ni desulfurization led to the monoketone as follows. Into a 500-mL three-neck round-bottom flask fitted for magnetic stirring and blanketed with N_2 was placed bicyclo[3.3.1]nona-2,6-dione (1.0 g, 7.25 mmol) dissolved in benzene (110 mL, distilled from CaH_2). Then ethanedithiol (0.62 g, 0.55 mL, 0.6 mmol) and $BF_3 \cdot Et_2O$ (0.5 mL) were added by syringe. The solution was stirred overnight at room temperature and then dried over $MgSO_4$. The solvent was removed by rotary evaporation, and the product was chromatographed on a column of silica gel (60–200 mesh, dried at 175–180 °C). Elution with 10% ethyl acetate in hexane gave 1.18 g of monothioketal as an oil. It had the following data: ^{13}C-NMR, δ 26.6 (t), 29.1 (t), 31.3 (t), 37.3 (t), 37.8 (t), 38.2 (t), 39.1 (t), 40.8 (d), 43.2 (d), 73.8 (s), 214.7 (s) ppm. The monothioketal was used directly in the next step.

Into a 250-mL round-bottom flask equipped with a water condenser and magnetic stirrer were placed the monothioketal from above (1.18 g, 5.18 mmol), Raney Ni[31] (8.2 g), and 95% ethanol (150 mL). The mixture was brought to reflux while being stirred for 6 h. After cooling to room temperature, it was filtered through a 1-cm pad of Celite. The Raney Ni was washed several times with ethanol, and the filtrates were combined and removed by rotary evaporation. The resultant white oily solid was dissolved in acetone (distilled from $KMnO_4$; 20 mL) and cooled to 5 °C. Jones reagent[32] (5 mL) (CrO_3 in aqueous H_2SO_4) was added until an orange-brown color remained, and the mixture was stirred for an additional 20 min at 5 °C. Aqueous $NaHSO_3$ was added until the mixture turned green, and then water was added to dissolve salts. The solution was extracted several times with ether, and the combined extracts were dried over $MgSO_4$ and filtered. After solvent removal by rotary evaporation, the residue was purified by column chromatography using silica gel (60–200 mesh, dried at 175–180 °C). Elution with 10% ethyl acetate in hexane gave 0.33 g of product (46% yield), which was found to be contaminated with unsaturated ketone. Following catalytic hydrogenation in ethyl acetate using Pd(C) catalyst, the solution was filtered through a 1-cm pad of Celite, and the solvent was rotary evaporated to a waxy white solid, 0.30 g (45% yield). The monoketone had the following data: mp 133–135 °C (lit.[33] mp 135–138 °C); IR (film on NaCl), ν 2925, 1708, 1450, 1100 cm^{-1}; UV, $\epsilon_{285}^{\max}$ 35; ^{1}H-NMR, δ 1.52–2.58 (14 H, m) ppm; ^{13}C-NMR, δ 20.0 (t, C_7), 26.1 (t, C_6), 27.4 (t, C_4), 29.7 (t, C_8), 31.9 (d, C_5), 32.5 (t, C_9), 38.9 (t, C_3), 45.0 (d, C_1), 216.9 (s, C_2) ppm.

Bicyclo[3.3.1]non-3-en-2-one (8). Into a 100-mL round-bottom flask fitted with a magnetic stirrer and blanketed with N_2 was placed bicyclo[3.3.1]nonan-2-one (0.29 g, 2.1 mmol) dissolved in 20 mL of isopropenyl acetate. Concentrated sulfuric acid (0.01 mL) was added, and the solution was heated at reflux with stirring for 30 min. The solution was then chilled, diluted with diethyl ether, and washed with 5% aqueous $NaHCO_3$ solution and brine. After drying over $MgSO_4$, the solvent was removed by rotary evaporation. The product was chromatographed on a column of silica gel (60–200 mesh, dried at 175 °C). Elution with 10% ethyl acetate in hexane gave 100 mg of a colorless oil. It had the following data: ^{1}H-NMR, δ 1.2–2.5 (15 H, m), 5.42 (1 H, m) ppm; ^{13}C-NMR, δ 18.41, 20.99, 26.21, 27.44, 30.37, 32.20, 32.83, 33.65, 115.35, 149.25, 169.57 ppm. This material was used directly in the next step.

In a 100-mL round-bottom flask fitted with a water condenser and magnetic stirrer and blanketed with N_2 were placed 2-acetoxybicyclo[3.3.1]non-2-ene (225 mg, 1.25 mmol), *N*-bromosuccinimide (223 mg, 1.25 mmol), and benzoyl peroxide (0.1 mg) dissolved in 20 mL of CCl_4. This was heated with stirring at 75 °C for 1 h. The solution was cooled to room temperature and filtered. The residue was washed with CCl_4. The filtrates were combined, and the solvent was removed by rotary evaporation. The yellow residue was dissolved in 6 mL of 95% ethanol and 4 mL of 2 N HCl. This solution was heated with stirring at 70 °C for 1 h. The solvents were removed by distillation under reduced pressure (using a plastic aspirator). The residue was dissolved in diethyl ether and then dried over $MgSO_4$. The solvent was removed by rotary evaporation. The product was chromatographed on a column of silica gel (60–200 mesh, dried at 175 °C). Elution with 1:2 ethyl acetate/hexane gave 105 mg (62%) of a white solid, mp 94–96 °C (lit.[34] mp 97.5–98.5 °C). The unsaturated ketone had the following data: IR (film), ν 3020, 2920, 1670, 1450, 1380, 1240 cm^{-1}; UV, $\epsilon_{383}^{\max}$ 11, $\epsilon_{366}^{\max}$ 27, $\epsilon_{350}^{\max}$ 34, $\epsilon_{338}^{\max}$ 32, $\epsilon_{222}^{\max}$ 7200, $\epsilon_{206}^{\max}$ 8200; ^{1}H-NMR, δ 1.2–1.8 (8 H, m), 2.12–2.58 (2 H, m), 6.1–6.2 (1 H, d, *J* = 12 Hz), 6.82–7.0 (1 H, ddd, *J* = 12. 7, 1.5 Hz) ppm; ^{13}C-NMR, δ 17.6 (t, C_7), 25.3 (t, C_6), 28.3 (t, C_8), 31.0 (d, C_5), 34.3 (t, C_9), 43.0 (d, C_1), 132.1 (d, C_3), 152.6 (d, C_4), 203.1 (s, C_2) ppm.

4,8-Dimethylbicyclo[3.3.1]nona-2,6-dione (3). Into a 250-mL round-bottom flask were added 4,8-dimethylbicyclo[3.3.1]nona-3,7-diene-2,6-dione (**4**) (0.5 g, 3 mmol) and methanol (100 mL). The flask was blanketed with argon for 5–10 min; then a small amount of Pd(C) catalyst was added, and the material was hydrogenated with stirring. After hydrogen uptake had stopped, the mixture was filtered through a pad of Celite on a sintered glass funnel, and the solvent was rotary evaporated to leave 0.4 g of product (74% yield). The substance was >99% pure by GC. It had the following data: IR (neat), ν 2957, 2928, 2872, 1705, 1456, 1233, 1124 cm^{-1}; UV, $\epsilon_{299}^{\max}$ 45; ^{1}H-NMR, δ 0.8 (6 H, d, *J* = 6.8 Hz), 1.7–2.7 (10 H, m) ppm; ^{13}C-NMR, δ 19.0 (q), 32.4 (t, C_9), 33.7 (t, C_4, C_8), 47.0 (t, C_3, C_7), 49.4 (d, C_1, C_5), 208.9 (s, C_2, C_6) ppm.

Anal. Calcd for $C_{11}H_{16}O_2$ (180.2): C, 73.30; H, 8.95. Found: C, 73.21; H, 8.89.

4,6-Dimethylbicyclo[3.3.1]nona-2,8-dione (5). As in the preparation of **3** from **4**, 6 was subjected to catalytic hydrogenation on Pd(C) to give >99% pure dione **5**, as determined by GC. It had the following data: 41–42 °C; IR (neat), ν 2955, 2876, 1722, 1694, 1176, 1075 cm^{-1}; UV, $\epsilon_{314}^{\max}$ 34, $\epsilon_{280}^{\max}$ 35, $\epsilon_{211}^{\text{infl}}$ 196; ^{1}H-NMR, δ 1.25 (6 H, d, *J* = 5.7), 2.0–2.5 (9 H, m), 3.39 (1 H, m) ppm; ^{13}C-NMR, δ 21.7 (q), 38.1 (d, C_4, C_6), 38.2 (d, C_5), 38.3 (t, C_9), 47.4 (t, C_3, C_7), 65.7 (d, C_1), 203.3 (s, C_2, C_8) ppm.

Anal. Calcd for $C_{11}H_{16}O_2$ (180.2): C, 73.30; H, 8.95. Found: C, 73.09; H, 8.76.

4,8-Dimethylbicyclo[3.3.1]nonan-2-one (9). Into a 500-mL three-neck round-bottom flask fitted with a magnetic stirrer and blanketed with N_2 was placed 4,8-dimethylbicyclo[3.3.1]nona-2,6-dione (**3**) (1.04 g, 0.006 mol) dissolved in 250 mL of benzene (distilled from CaH_2). Then ethanedithiol (0.57 g, 0.5 mL, 0.006 mol) and $BF_3 \cdot Et_2O$ (0.5 mL) were added by syringe. The solution was stirred overnight at room temperature and then dried over $MgSO_4$. The solvent was removed by rotary evaporation, and the product was chromatographed on a column of silica gel (60–200 mesh, dried at 175 °C). Elution with 10% ethyl acetate in hexane gave an 80% yield of product. It had the following data: ^{13}C-NMR, δ 18.85, 21.89, 32.87, 36.69, 37.20, 38.59, 39.26, 45.73, 48.33, 48.66, 50.37, 72.94, 211.02 ppm. The monothioketal was used directly in the next step.

Into a 250-mL round-bottom flask equipped with a water condenser and magnetic stirrer were placed the monothioketal from above (0.5 g, 1.95 mmol) and Raney Ni[31] (6.0 g) dissolved in 150 mL of 95% ethanol. The mixture was brought to reflux while being stirred for 6 h. After cooling to room temperature, the mixture was filtered through a 1-cm pad of Celite. The Raney Ni was washed several times with ethanol. The filtrates were combined, and the ethanol was removed by rotary evaporation. The resultant oily solid was dissolved in 20 mL of acetone (distilled from $KMnO_4$) and cooled to 5 °C. Jones reagent[32] (5 mL) was added until an orange-brown color remained, and the mixture was stirred for an additional 20 min at 5 °C. Aqueous $NaHSO_3$ was added until the mixture turned green, and then water was added to dissolve the salts. The solution was extracted with diethyl ether (3 × 100 mL), and the combined extracts were dried over $MgSO_4$. After solvent removal by rotary evaporation, the residue was purified by column chromatography using silica gel (60–200 mesh, dried at 175 °C). Elution with 10% ethyl acetate in hexane gave a clear liquid, bp 38 °C (0.025 mmHg). Dimethyl ketone **9** had the following data: IR (film on NaCl), ν 2926, 1704, 1454 cm^{-1}; UV, $\epsilon_{301}^{\max}$ 41, $\epsilon_{283}^{\max}$ 39; ^{1}H-NMR, δ 1.3–2.6 (12 H, m), 1.0 (3 H, d, *J* = 6.6 Hz), 0.78 (3 H, d, *J* = 6.6 Hz) ppm; ^{13}C-NMR, δ 19.71, 20.19, 25.54, 29.87, 32.10, 34.22, 35.58, 35.70, 49.58, 51.81, 213.28 ppm.

Anal. Calcd for $C_{11}H_{18}O$ (166.3): C, 79.47; H, 10.91. Found: C, 79.58; H, 10.75.

4,8-Dimethylbicyclo[3.3.1]non-3-en-2-one (10). Into a 100-mL round-bottom flask equipped with a water condenser and magnetic stirrer blanketed with N_2 was placed 4,8-dimethylbicyclo[3.3.1]nonan-2-one (**9**) (0.59 g, 3.5 mmol) dissolved in 25 mL of isopropenyl acetate. Concentrated sulfuric acid (0.01 mL) was added, and the solution was heated at reflux with stirring for 30 min. Then the solution was chilled, diluted with diethyl ether, and washed with 50 mL of 5% aqueous $NaHCO_3$

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solution and 50 mL of brine. After drying over $MgSO_4$, the solvent was removed by rotary evaporation. The product was chromatographed on a column of silica gel (60–200 mesh, dried at 175 °C). Elution with 10% ethyl acetate in hexane gave 0.64 g (85% yield) of a clear oil. It had the following data: ^{1}H-NMR, δ 0.77 (3 H, d, J = 6.9 Hz), 0.92 (3 H, d, J = 7.5 Hz), 1.1–1.35 (m), 1.5–1.78 (m), 1.9–2.05 (m), 1.98 (3 H, s), 5.25 (1 H, d, J = 2.7 Hz) ppm; ^{13}C-NMR, δ 17.36, 20.64, 21.06, 27.43, 27.61, 30.90, 33.41, 34.90, 35.20, 38.85, 121.59, 147.82, 169.17 ppm; MS, [M$^+$] 208 amu. This material was used directly in the next step.

In a 100-mL round-bottom flask equipped with a water condenser and magnetic stirrer blanketed with N_2 were placed 2-acetoxy-4,8-dimethylbicyclo[3.3.1]non-2-ene (0.64 g, 3.1 mmol), *N*-bromosuccinimide (0.55 g, 3.1 mmol), and benzoyl peroxide (0.1 mg) dissolved in 40 mL of CCl_4. This was gently refluxed with stirring for 1 h. The solution was cooled to room temperature and filtered. The residue was washed with CCl_4. The filtrates were combined, and the solvent was removed by rotary evaporation. The yellow residue was dissolved in 12 mL of 95% ethanol and 4 mL of 3 M HCl. The solution was gently refluxed with stirring for 2 h. The solvents were removed by distillation under reduced pressure (using a plastic aspirator). The residue was dissolved in diethyl ether and then dried over $MgSO_4$. The solvent was removed by rotary evaporation. The product was chromatographed on a column of silica gel (60–200 mesh, dried at 175 °C). Elution with 10% ethyl acetate in hexane gave pure product. Enone **10** had the following data: IR (film on NaCl), ν 1666 cm^{-1}; UV, ϵ_{358}^{max} 652, ϵ_{345}^{max} 642, ϵ_{330}^{max} 823, ϵ_{231}^{max} 6563; ^{1}H-NMR, δ 0.80 (3 H, d, J = 6.5 Hz), 1.28–2.63 (9 H, m), 1.96 (3 H, s), 6.08 (1 H, br s) ppm; ^{13}C-NMR, δ 19.5 (q), 22.4 (q), 25.9 (t), 33.0 (d), 35.3 (t), 35.4 (t), 35.7 (d), 47.4 (d), 128.6 (d), 159.0 (s), 200.1 (s) ppm.

Anal. Calcd for $C_{11}H_{16}O_2$ (164.2): C, 80.44; H, 9.82. Found: C, 80.23; H, 9.73.

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Electrospray Mass Spectrometry of Poly(ethylene glycols) with Molecular Weights up to Five Million

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Abstract: Mass analysis has been carried out on ions formed in an electrospray (ES) ion source from poly(ethylene glycols) (PEGs) with molecular weights (*M*s) ranging from 200 to 5 000 000. The number of charges per unit length of oligomer decreases with increasing molecular weight (*M*) in the range below *M* = 20 000. Above that value the number increases until at *M* = 5 000 000 it slightly exceeds the maximum allowed by the electrostatic model previously proposed. This behavior can be understood in terms of the solution properties of PEG and the two mechanisms that have been proposed for the formation of ions from charged droplets.

I. Introduction

Polymers of ethylene oxide have often been the subject of mass spectrometric studies. Comprising linear chains with little or no branching, looping, or cross-linking, they are quite soluble in a variety of solvents including water, and can be had in a wide range of oligomer sizes. The nominal value of molecular weight for commercially available material is that of the most abundant oligomer in a mixture of oligomers having a distribution of sizes that in principle should be Poisson-like but in practice is somewhat broader. Such mixtures of oligomers are known as "poly(ethylene glycols)" or PEGs when the chain lengths are short enough so that the terminal OH groups have a discernible effect on chemical and physical properties. Materials of higher molecular weight are generally referred to as "poly(ethylene oxides)" or PEOs, a name that relates both to the structural unit of the polymer and to the actual starting material from which it is made. The distinction between PEGs and PEOs is not clearly drawn, but custom seems to put the dividing line at a nominal molecular weight value of about 17 500. By this convention the term PEG properly applies to each of the samples used in our earlier study.[1] In order to avoid an unnecessary and perhaps confusing distinction, we will also refer to the subjects of this report as PEGs even though their molecular weights are such that they would ordinarily be called PEOs.

It was a report from our laboratory on mass spectrometric studies with PEGs that first revealed the remarkable ability of electrospray (ES) ionization to produce ions with extensive multiple charging, up to 23 charges per ion in the case of PEG 17 500.[1] In an attempt to identify an upper limit to the number of charges that a PEG oligomer could hold, that paper also proposed a model by which that maximum number could be calculated. The key assumption of the model is that the number of charges on an oligomer ion is at a maximum when the electrostatic repulsion energy (ERE) of the centermost charge equals the energy with which it is bound to its site. The ERE for any charge on such an ion is simply the pairwise sum of potential energies due to Coulomb repulsion between it and each of the other charges on the ion. The ERE of a system comprising two like charges varies inversely as the distance between them. Consequently, in a linear array of charges the ERE is largest for the centermost charge and is at a minimum for the array as a whole when the charges are equally spaced. The intercharge distances needed for this calculation are obtained from the known geometry of a PEG oligomer in its stretched out or "zig-zag" configuration.[2] In addition the charges are assumed to be bound to oxygen atoms at equidistant intervals along the oligomer backbone. In these experiments the charges were Na^+ ions which we assumed are bound to oxygen atoms with an energy of about 2.05 eV, the value that has been measured for Na^+ and dimethoxyethane, the most similar species for which we could find data.[3]

The experimental results of the earlier investigation indicated that the observed ions contained as few as half the maximum

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