molecular weight can be found. Similarly, no adducts of structure **2** can be detected for $Y = CH{=}CH_2$ (thioacrolein). However, in this case we do find a thioacrolein self-condensation product, **4** (24%).[7b,8] An earlier claim of thioacrolein generation by pyrolysis of diallyl sulfide does not mention the formation of any specific sulfur-containing products.[3a,k]

The regioselectivity of activated thioaldehyde Diels–Alder additions favors **2** over **3**, the same general pattern as observed with other thiocarbonyl dienophiles.[1c,9] By comparison with the analogous cyano or α-oxo dithioesters,[1c] the thioaldehydes are somewhat less selective as might be expected from their enhaced reactivity. Minor adducts **3** have been detected in all cases where a thorough search has been made.

Thianes of general structure **2** are of interest as synthetic precursors to a variety of ring systems. Ramberg–Backlund sulfur extrusion to form cyclopentane derivatives is already known.[10] A brief survey of other possibilities appears in Scheme II, with adducts of phenylthioglyoxal ($C_6H_5COCH{=}S$) or thiopyruvaldehyde ($CH_3COCH{=}S$) in representative examples. From the adduct **2a**, a simple sequence of alkylation ($CH_3OSO_2CF_3$, CH_3CN) and treatment with DBU afford the alkenyl cyclopropyl ketone **6**, 66%.[7c,8] The mechanism is presumed to involve the 2,3-sigmatropic shift of the ylide intermediate **5**.[11]

Treatment of **2b** with salt-free $CH_2{=}PPh_3$ followed by dilute acid affords ketone **7**. After methylation ($Me_3O^+BF_4^-$) and deprotonation (DBU, 0 °C) **7** is converted into a stabilized ylide which rearranges to cycloheptenone **8**[7d,8] (47% yield; 2,3-shift) together with a trace of **9** (Stevens rearrangement).[12] At higher temperatures, better mass balance is observed but the reaction produces significant amounts of dimeric products and more of **9** as might be expected from literature precedent.[13]

Similar alkylation–deprotonation of the diketone **10** apparently generates the ylide intermediate **11**, which rearranges to the cyclic enol ether **12** (66%).[8] The structure is established by NMR spectroscopy and by desulfurization to **13**[7e,8] with nickel boride.[14] The rearrangement from **11** to **12** can be viewed as a 2,3-shift involving benzoyl C=O in the migrating three-atom component. Formation of **12** is closely analogous to the rearrangement leading to **8** and also has precedent in reactions of other keto ylides.[15]

Of particular concern in our laboratory is the possibility of converting Diels–Alder adducts **2** into large ring sulfides by 2,3-sigmatropic ring expansion.[16] This reaction can be surprisingly facile. For example, treatment of **7** with $(CH_3)_3O^+BF_4^-$ followed by KO-*t*-Bu (instead of DBU as in preparation of **8**) produces the thiacyclononene **14** as the major product (32%) via the kinetically favored methylide and **8** (11%) derived from the carbonyl-stabilized ylide. Under conditions more carefully selected to promote ring expansion to a thiacyclononene, excellent yields can be achieved. Thus, **15** (available from thiopyruvaldehyde, Table I, entry g)[17] can be treated with EtO_2CCH_2OTf followed by DBU to give **16**,[7f,8] 87%.

Thioaldehydes are promising intermediates for carbon bond formation under extremely mild conditions. We will describe specialized applications of thioaldehyde chemistry to more complex synthetic problems in future publications.

Acknowledgment. This work was supported by a grant (CA 17918) from the National Institute of Health.

Registry No. 1a, 80737-85-5; **1c**, 2461-80-5; **1e**, 80737-86-6; **1f**, 36615-92-6; **1g**, 6581-69-7; **2a**, 73496-60-3; **2b**, 80737-87-7; **2c**, 80737-88-8; **2d**, 80737-89-9; **2e**, 80737-90-2; **2f**, 80737-91-3; **2g**, 80737-92-4; **2h**, 80737-93-5; **4**, 80028-57-5; **6**, 80737-94-6; **7**, 80737-95-7; **8**, 80737-96-8; **9**, 80737-97-9; **10**, 80737-98-0; **12**, 80737-99-1; **13**, 80738-00-7; **14**, 80738-01-8; **15**, 80738-02-9; **16**, 80738-03-0; $PhCOCH_2SCH_2POPh_2$, 80738-04-1; 2-ethoxy-1,3-butadiene, 4747-05-1; 2-*tert*-butyldimethylsilyloxy-1,3-butadiene, 80738-05-2; 2-methyl-1-trimethylsilyl-1,3-pentadiene, 80738-06-3; 6-acetoxy-4-6-dimethyl-2,4-heptadiene, 80738-07-4; 2,3-dimethyl-1,3-butadiene, 513-81-5; 3,5-dimethyl-6-diphenylphosphinyl-2-trimethylsilyl-2,5,6-trihydrothiopyran, 80738-08-5; 2-(1-acetoxyethyl)-3,5-dimethyl-6-diphenylphosphinyl-2,5,6-trihydrothiopyran, 80738-09-6; 3,4-dimethyl-6-phenylcarbonyl-2,5,6-trihydrothiopyran, 80738-10-9; 6-acetyl-3,4-dimethyl-2,5,6-trihydrothiopyran, 80738-11-0.

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(17) The adduct of 2-*tert*-butyldimethylsiloxy)butadiene and thiopyruvaldehyde was treated with salt-free $CH_2{=}PPh_3$, dilute acid, $Et_3BH^-K^+$, and acetic anhydride to prepare **15**.

Ionization Energies of *p*-Quinodimethane and 2,5-Dimethyl-*p*-quinodimethane

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Some years ago Koenig et al.[1,2] reported ultraviolet photoelectron spectra (UV-PES) for *p*-quinodimethane (**1**) and its 2,5-dimethyl derivative (**2**), these being formed in situ by flash vacuum thermolysis of their dimers (e.g., **3**). Each spectrum showed three π-type bands (B_{1-3}) with comparable areas in the region below 11.5 eV, which would normally be assigned to the first three π ionizations. The fourth π ionization and the σ ionizations are expected to appear at higher energies. The spectrum of **2** also showed a broad, weak band (B_x) with much structure centered at 9.8 eV, while B_2 in **2** had a somewhat larger area than B_1 (ratio 1.2:1[3]), due to a tail at the high-energy side. Features such as this would usually be attributed to byproducts formed during the pyrolyses, particularly for **2**, which contains labile methyl groups.

Koenig et al.,[1,2] however, claimed that B_2 in **1** corresponds to superimposed π ionizations, I_2 and I_3, on the basis of SR[4] and INDO[5] calculations. They inferred that B_x in **2** then corresponds to I_3, shifted out of coincidence with I_2 by the methyl substituents. The low intensities of these extra bands would normally rule out any such assignment. However, Koenig et al. suggested that this might be due to configurational mixing between the ion corresponding to I_3 and an ion formed by loss of one electron from the HOMO of **2** combined with excitation of the other to the LUMO.[6] It is well-known[7] that similar mixing of the second and third π→π* excited configurations of an alternant hydrocarbon (AH) results

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Table I. Calculated Types and Energies of Orbitals and Observed Ionization Energies

p-quinodimethane (1)			2,5-dimethylquinodimethane (2)			dibenzo-*p*-quinodimethane (4)				2,4,5-trimethylbenzyl (5)^e		
							energy^b					
type^a	energy^b	I (obsd)^c	type^d	energy^b	I (obsd)^c	type^a	planar	nonplanar	I (obsd)	type	energy^{b,f}	
$B_{1u}(\pi)$	8.18	7.87	$A_2(\pi)$	8.18	7.58	$B_{1u}(\pi)$	8.27	8.44	8.0	π	8.82	
$B_{3g}(\pi)$	9.94	9.7	$B_2(\pi)$	9.76	8.97	$B_{2g}(\pi)$	9.00	9.05	8.7	π	9.79	9.61
					(9.80)^c	$B_{3g}(\pi)$	9.28	9.29	9.1	π	10.50	10.04
$B_{2g}(\pi)$	10.73	11.1	$B_2(\pi)$	10.69	10.70	$A_{1u}(\pi)$	9.46	9.38		σ	12.14	12.12
$B_{1g}(\pi)$	11.76		A_1	11.71		$B_{1u}(\pi)$	10.91	10.81	10.7	π	12.25	12.03
$B_{1u}(\pi)$	12.70		$A_2(\pi)$	12.27	11.7-12.5	$B_{2g}(\pi)$	11.13	10.92				
B_{2u}	13.13	12.2-12.8	A_1	12.72		B_{3g}	11.92	11.97				
A_{1g}	13.16		B_1	12.85		A_{1g}	12.06	12.23				
B_{3u}	14.13		B_1	13.67		$B_{3g}(\pi)$	12.53	12.43				
B_{2u}	14.33	13.6-14.3	A_1	13.91		B_{2u}	12.62	12.63				
B_{1g}	14.48		B_1	13.98		B_{2u}	13.11	13.13				
B_{1g}	16.14		B_2	14.14	13.0-14.0	B_{2u}	13.13	13.16				
A_{1g}	16.69	15.2-16.0	$B_2(\pi)$	14.24		B_{1g}	13.41	13.25				
B_{3u}	16.78		A_1	14.37		$B_{1u}(\pi)$	13.43	13.62				
A_{1g}	21.20		$A_2(\pi)$	14.45								
			A_1	16.14								

[a] Orbital types, D_{2h} symmetry. [b] Orbital energies (eV). [c] Observed ionization energies (eV). [d] Orbital types, C_{2h} symmetry. [e] ΔH_f, 25.9 kcal/mol. [f] First column α spin (→singlet ion), second column β spin (→triplet ion).

in a mixed state to which transition from the ground state is forbidden because of a cancellation of transition moments, leading to weak bands (α or L_a) in the spectra of such compounds.[8] Koenig et al. attribute the weakness of the B_x ionization to a similar cancellation of transition moments, due to mixing of the two excited states of 1^+ or 2^+. Such an effect, if real, would be of much interest, both as an unusual violation of Koopmans' theorem and as the first case where a band in a UV-PES had been ascribed to a state arising from ionization combined with excitation ($I + E$).

This explanation of the weakness of the B_x band is, however, fallacious. Ionization, unlike excitation, involves emission of a free electron. As a result, *no* ionization can ever be forbidden. The wave function of the emitted electron can always be chosen in such a way as to permit ionization. The direction in which the electron is emitted may be restricted, but not in such a way as to interfere with the operation of a conventional ultraviolet photoelectron spectrometer. The assignments suggested by Koenig et al. must therefore be rejected because they do not account for the low intensities of the postulated third ionizations.

It is also difficult to see how the I + E state could be low enough in energy. Cancellation of transition moments occurs only if the interacting states are virtually degenerate (cf. ref 7). The band at 11.1 eV in the UV-PES of **1** would have to be attributed to the second state derived from mixing of I_3 and the $I + E$ state because it is too low in energy to be due to anything else. The energy of the $I + E$ state would then have to be ca. 0.5(9.7 + 11.1) = 10.4 eV, only 2.5 eV above the ground state of the ion. However, it is difficult to see how this difference could in fact be much less than the minimum excitation energy (4.8 eV) of **1** itself, given that the MO's involved are the same in both cases. Indeed, this argument suggests that UV-PES bands due to $I + E$ transitions may in general appear at high energies, in the region obscured by σ ionizations, and that this is why no such bands have been reported.

While these objections seem cogent, the questions raised are important enough to need further study. The obvious line seemed to be calculation of the ionization energies of **1** and **2** by some reliable procedure, and for this purpose MNDO[9] seemed the obvious choice. Very extensive tests[10] using Koopmans' theorem have shown it to reproduce ionization energies of organic molecules always in the right order and usually[11] to within a few tenths of an eV. The calculations can moreover be carried out easily and with full geometry optimization[12] for quite large molecules, while ab initio methods of comparable accuracy are currently restricted to small systems. I have therefore used MNDO to calculate the ionization energies of **1**, **2**, and the dibenzo derivative (**4**) of **1**, whose UV-PES has been reported by Heilbronner et al.[3] Calculations were also carried out for the radical cation (1^+) derived from **1** and for the 2,4,5-trimethylbenzyl radical, for reasons that will appear presently.

The calculations were carried out by the standard MNDO procedure,[9] geometries being completely optimized by the standard[9] DFP method without making any assumptions. Figure

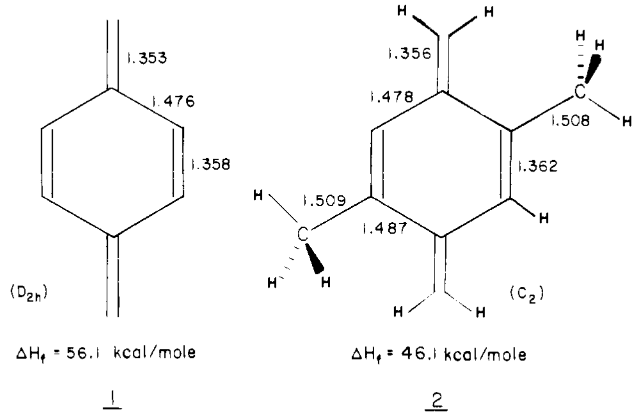

Figure 1. Calculated bond lengths (Å) and heats of formation (ΔH_f) for **1** and **2**.

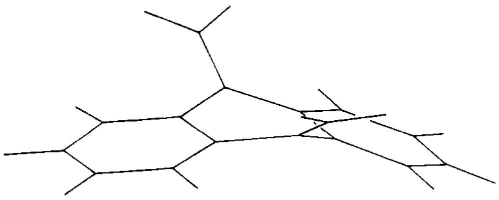

Figure 2. Structure and heat of formation (ΔH_f) calculated for **4**.

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[11] Ionization energies calculated for MO's derived significantly from 2s AO's are too large, due to the neglect of 1s/2s interactions in MNDO.[10]

[12] Geometry optimization is essential if ionization energies are to be calculated properly. Use of "standard" geometries can lead to errors of several tenths of an eV in calculated ionization energies.

1 shows the geometries and heats of formation (ΔH_f) calculated for **1** and **2**. Both are planar, except for the methyl hydrogen atoms in **2**. The indicated (**2**) conformation, with C_{2h} symmetry, was found to be the global energy minimum. While no experimental ΔH_f values are available for comparison, a reasonably reliable estimate can be made for **1** by using the bond-energy scheme of Dewar and de Llano.[13] This (60.5 kcal/mol) is quite close to the MNDO value. **4** was found to be nonplanar (Figure 2), the central ring being bent into a boat geometry as a result of steric interactions. Planar **4** was less stable by 11 kcal/mol. Table 2 lists orbital types and energies calculated for the three molecules, together with the observed[1,2] ionization energies. Values for **4** are given both for a planar geometry (D_{2h}) and for the optimum one (C_{2v}), symmetry designations being for the former. Calculations for $\mathbf{1}^+$ and **5** were carried out by the spin-unrestricted version (UMNDO[16]) of MNDO, which has been found[17] to give good estimates (Koopmans' theorem) of ionization energies of radicals. The ΔH_f calculated for $\mathbf{1}^+$ (227.7 kcal/mol) corresponds to an adiabatic ionization energy for **1** of 7.44 eV, the observed (vertical) value[1,2] being 7.87 eV. Cartesian coordinates are available as Supplementary Material.

According to MNDO, the first two bands in the UV-PES of **1** correspond to π ionizations (B_{1u} and B_{2g}). The third π ionization (B_{3g}) corresponds to the low-energy end of the third band, with a tail at higher energies due to the first σ ionization. The next two bands are each assigned to three superimposed ionizations, an assignment consistent with their position and appearance. The position of the sixth band is also correctly predicted. The published spectrum indicates that, as usual, the sensitivity of the spectrometer fell off at higher ionization energies. The appearance of the sixth band shows that it must also involve, as predicted, several superimposed ionizations.

The agreement between the MNDO calculations for **2** and its observed UV-PES would be equally satisfactory[14] were it not for the band (B_x) at 9.8 eV. For reasons indicated above, this cannot correspond to a simple ionization because its intensity is too small. The only way it could arise from **2** would be if it were due to an I + E process and were thus analogous to a double excitation. The excitation probability for such a process might well be low. This, however, seems to be ruled out by the small difference in energy (2 eV) between B_1 and B_x since, as noted above, this is unlikely to be much less than the minimum excitation energy of **2**. Support for this argument is provided by the HOMO/LUMO separations calculated here for **1** (7.6 eV) and $\mathbf{1}^+$ (7.1 eV). On this basis the first I + E ionization of **1** should appear at ca. 12.2 eV.

We are therefore forced back to the inherently reasonable suggestion that B_x corresponds to some species other than **2**. While there is no direct evidence concerning the compound responsible, one obvious candidate seems to be the 2,4,5-trimethylbenzyl radical (**5**), which might very well have been formed during the pyrolytic synthesis of **2**. As Table I shows, **5** is indeed predicted to have three ionizations in the range 9.6–10.2 eV. A small amount of **5** could then lead to a broad weak band at 9.8 eV, due to coalescence of bands due to these ionizations.

As Table I shows, the MNDO calculations also reproduce the observed[4] UV-PES of **4** in a satisfactory manner. The first two peaks in this correspond to single ionizations and the third to two overlapping ionizations, as predicted.

There is therefore no reason to suppose that the UV-PES of **1**, **2**, or **4** are in any way abnormal or that any unusual effect operates in the corresponding ions. It would indeed be very surprising if **1**, an apparently normal polyene, showed unique behavior, of a kind that has never been encountered in any of the very many hydrocarbons that have been studied by UV-PES. Very strong evidence would be needed to refute the interpretations given here, which indeed seem to illustrate once again the usefulness of MNDO as an aid in assigning ultraviolet photoelectron spectra.

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Registry No. **1**, 502-86-3; **2**, 63238-49-3; **4**, 3302-51-0; 2,4,5-trimethylbenzyl radical, 15220-27-6.

Supplementary Material Available: Listing of Cartesian coordinates for **1**, **2**, and **4** (1 page). Ordering information is given on any current masthead page.

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(14) Changes in ionization energy due to methyl substitution are systematically underestimated by MNDO[15]. The errors for **2** are just what would be expected from analogy with other compounds[15] and the results for **1**.

(15) Compare the following[10] calculated (observed) differences (eV) in I_1 between methyl derivatives and parent compounds: CH_3NH_2/NH_3, 0.64 (1.04); $PhCH_3/PhH$, 0.11 (0.43); C_3H_6/C_2H_4, 0.21 (0.63); CH_3OH/H_2O, 0.78 (1.66); CH_3CN/HCN, 0.62 (1.39).

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One- and Two-Electron Reduction of Oxygen by 1,5-Dihydroflavins

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Considerable attention has been paid to the mechanism by which molecular oxygen reacts with 1,5-dihydroisoalloxazine molecules.[1] This concern stems from the importance of the reaction in the mechanism of action of the flavoxygenase enzymes. The flavomono- and flavodioxygenase reactions are the only non-metal-ion-requiring oxygen activation reactions in biochemistry. Notable advances in the understanding of the mechanisms of oxygen transfer from intermediate enzyme-bound[2] and model[3] flavin 4a-hydroperoxides to substrate have been made, yet the mechanism of reaction of 1,5-dihydroflavin with $^3O_2$ has not been clarified. Hamilton[1c] considered the problem of spin forbiddeness in the formation of a flavin hydroperoxide by direct reaction of triplet oxygen with singlet dihydroflavin. Spin inversion is not required if the initial step involves a one-electron transfer.[4] The central 1,4-dihydropyrazine ring of the 1,5-dihydroisoalloxazine

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