Starting with the α-deuterium effect in the propyl group, it is found that a reduction of the reactant H–C–H (2-propyl) bending constant by 20% satisfactorily reproduced that isotope effect. The reasonable assumption that the other bending constants, associated with the 2-propyl carbon atom, are also undergoing a reduction of 20% upon conversion to the transition state, is also made. Moreover, this same relative change is incorporated into the 2-propyl carbon–nitrogen stretching constant. If now, it is assumed that almost complete rupture of the benzylic C–N bond ensues, the nitrogen isotope effects can be reproduced by strengthening the nitrogen–nitrogen stretching constant by 20%.

Undoubtedly, other force fields can be used that might lead to almost as good a fit as shown in Table VI, but it would seem that these might not be as internally self-consistent. As a first approximation then it appears from this study that, for small normal or inverse secondary α-deuterium isotope effects, the relative change in the H–C leaving group bending force constant from reactant to transition state, reflects the same change in the C leaving group stretching force constant.

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Organic Photochemistry. XXVII.[1] Electronically Excited State Structures

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Abstract: A series of 4,4-disubstituted cyclohexadienones, differing in the electronegativity of the 4 substituents, was synthesized and the triplet energies were determined. It was found that electronegative substituents served to lower the triplet energy. This was taken to indicate an enhanced β-carbon electron density in the excited triplet relative to the ground state. A small but significant shift of 0–0 emission to higher energy was found on proceeding to glasses of progressively greater polarity and hydrogen bonding ability. The triplet lifetimes at 77°K were similar for 4,4-diphenylcyclohexadienone and 4-methyl-4-trichloromethylcyclohexadienone. The vibrational structure for the series of dienones was of the same type and characteristic of n–π^* emission. The triplet emission was found to be parallel to singlet absorption suggesting an n–π^* assignment to the triplet. Configuration interaction calculations were carried out including the p_y orbital system for a series of ketones. A good correlation of theory with observation was found for the energies of the n–π^* singlets, the π–π^* singlets, the n–π^* triplets, and the π–π^* triplets. The excited state electron distributions are discussed for the four states of photochemical interest.

One critical point in organic photochemistry is the identification and description of electronically excited species involved in reactions. Once these have been achieved a starting point for correlating electronic configuration with observed photochemical behavior is available. For example, where the triplet state is the reacting species, it would be of considerable help to know the relative energies of the triplet excited states of differing configuration. Thus, although the lowest energy singlet state of dienones and enones is n–π^*, as evidenced by absorption data,[3] this is not necessarily true for the corresponding triplets.[5]

A second point of interest is the electron distribution and the electronic properties in general of different electronically excited states, n–π^* and π–π^*; the triplets are of particular interest. While it is well known that the π–π^* singlets of conjugated carbonyl compounds are usually more electron rich in the carbonyl group than is the ground state[4] and similarly that the n–π^* singlets are less electron rich[6] at oxygen than in the ground state, similar information is not available about the triplet configurations.[7,8] The present study describes some results bearing on these two aspects.

One approach to the problem utilized the four disubstituted dienones: 4,4-dimethylcyclohexadienone (**1**),[9] 4,4-diphenylcyclohexadienone (**2**),[8,10] 4-methyl-4-

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(1) For paper XXVI note H. E. Zimmerman and J. O. Grunewald, *J. Am. Chem. Soc.*, **89**, 3354 (1967).

(2) (a) National Science Foundation Predoctoral Fellow, 1962–1966; (b) Research Associate, University of Wisconsin, 1963–1965; (c) Woodrow Wilson Fellow, 1960–1961; National Institutes of Health Fellow, 1961–1964.

(3) R. S. Mulliken, *J. Chem. Phys.*, **3**, 564 (1935); H. L. McMurry, *ibid.*, **9**, 231, 241 (1941); M. Kasha, *Discussions Faraday Soc.*, **9**, 14 (1950); note also ref 4.

(4) E. M. Kosower and D. C. Remy, *Tetrahedron*, 281 (1959), and related papers for enones.

(5) A triplet of given configuration will in general have a lower energy than the corresponding singlet. This singlet–triplet splitting is small for n–π^* states (note J. W. Sidman, *J. Chem. Phys.*, **27**, 429 (1957)) compared to π–π^* splitting and thus for a given molecule with the lowest excited singlet being n–π^*; it is still possible for the energy decrease on going from the π–π^* singlet to the π–π^* triplet to be sufficient to result in the π–π^* triplet being the lower energy state.

(6) H. McConnell, *J. Chem. Phys.*, **20**, 700 (1952).

(7) It was noted[8] that to a first approximation one might anticipate the electron distribution in n–π^* singlets and triplets to be similar but that the same could not be assumed true of the π–π^* configurations.

(8) H. E. Zimmerman and D. I. Schuster, *J. Am. Chem. Soc.*, **84**, 4527 (1962).

(9) F. G. Bordwell and K. M. Wellman, *J. Org. Chem.*, **28**, 1347 (1963).

(10) H. E. Zimmerman and D. I. Schuster, *J. Am. Chem. Soc.*, **83**, 4486 (1961).

Table I. Triplet Emission of Dienones

Vibrational band	Wavelength, mμ 4,4-DiMe	4,4-DiPh	4-Me-4-$CHCl_2$	4-Me-4-CCl_3
0–0	401.4 ± 0.8	415.2 ± 0.5	421.4 ± 1.0	426.0 ± 0.3
0–1	428.7 ± 0.2	446.4 ± 0.3	452.7 ± 0.6	459.2 ± 1.0
0–2	460.0 ± 0.9	480.9 ± 0.9	489.4 ± 1.0	495.3 ± 0.4
0–3	494.3 ± 1.8	521.6 ± 0.7	530.4 ± 2.0	538.5 ± 0.2
E_{0-0}, kcal	71.2	68.9	67.8	67.0

dichloromethylcyclohexadienone (**3**),[11] and 4-methyl-4-trichloromethylcyclohexadienone (**4**).[12]

The phosphorescence emission spectra of these compounds were run in EPA glass at 77°K. The emission data are recorded in Table I and in Figure 1. We note as one proceeds from 4,4-dimethylcyclohexadienone to dienones with progressively more electron-withdrawing substituents at C-4, the energy of the triplet decreases. This means that the excited triplets emitting are more electron rich near the β end of the dienone moiety than in the ground state. This behavior is reminiscent of that of $n-\pi^*$ singlet bands of unsaturated ketones which shift to longer wavelength as electron-withdrawing substituents are placed near the β-carbon.[5]

Indeed the $n-\pi^*$ portion of the ultraviolet spectra of the present compounds (**1**, **2**, **3**, and **4**) showed the expected shift to longer wavelength as the more electronegative groups were introduced. Here[13] the 0–0 component of the $n-\pi^*$ absorption band was used. Interestingly, the magnitude of the wavelength shift was similar to that of the triplet emission shift noted above. The data are recorded in Table II. This bathochromic shift is in contrast to the behavior of $\pi-\pi^*$ bands which generally show quite different behavior and shift to shorter wavelength when change is observed. In the present instance no appreciable wavelength dependence on substituents was found for the $\pi-\pi^*$ singlet (note Table II).[13] Thus phosphorescence emission gives evidence for a triplet excited state quite different from the $C^+—C=C—O^-$ picture often suggested as photochemically involved. To the extent that the effect of substituents is similar for triplet configurations to that known for singlets, the phosphorescence evidence suggests the emitting triplet to be $n-\pi^*$.

Table II. Singlet Absorption of Cyclohexadienones

Dienone	$n-\pi^*$,[a,c] mμ	$\pi-\pi^*$,[b,c] mμ
4,4-Dimethyl	377	225
4,4-Diphenyl	392	220
4-Methyl-4-dichloromethyl	400	225
4-Methyl-4-trichloromethyl	403	225

[a] 0–0 wavelength. [b] Maximum. [c] In cyclohexane.

A second piece of evidence, related to the substituent effect, is the small but definite shift in the 0–0 phosphorescence emission band on increasing the polarity and hydrogen-bonding ability of the glass employed. It was noted by Yang[14] that shifts to shorter wavelength of up to 5 mμ may be observed for some $n-\pi^*$ emission spectra of ketones on changing from MCIP (methylcyclohexane–isopentane) to EPA (ether–pentane–alcohol). A similar report by Leermakers[15] finds the same effect for $n-\pi^*$ pyruvate ester emission. In our own laboratory,[16] similar results were found for a series of aromatic ketones (note Table III).

Table III. Solvent Effects on Phosphorescence Emission Wavelengths

Compound	Band	MCIP,[a] mμ	$EtOH-Et_2O$,[b] mμ
4,4′-Dimethylbenzophenone	0–0	419.5 ± 0.5	412.9 ± 0.4
	0–1	450.2 ± 0.7	443.2 ± 0.3
	0–2	483.8 ± 0.5	476.5 ± 0.3
	0–3	524.4 ± 1.1	516.4 ± 0.4
4-Chlorobenzophenone	0–0	420.1 ± 0.5	416.1 ± 0.4
	0–1	451.3 ± 0.8	446.7 ± 0.2
	0–2	486.2 ± 0.7	480.8 ± 0.7
	0–3	529.0 ± 1.7	521.3 ± 0.3
Benzophenone	0–0	418.2 ± 0.4	416.6 ± 0.9
	0–1	449.8 ± 0.2	444.8 ± 1.1
	0–2	483.9 ± 0.4	478.2 ± 0.8
	0–3	525.7 ± 0.2	517.0 ± 1.0
Acetophenone	0–0	390.0 ± 0.5	387.3 ± 0.3
	0–1	417.0 ± 0.5	413.9 ± 0.7
	0–2	444.9 ± 0.5	442.6 ± 0.4
4,4-Diphenylcyclohexadienone	0–0	420.3 ± 0.8	415.8 ± 0.5
	0–1	451.9 ± 1.0	446.2 ± 0.9
	0–2	488.3 ± 0.9	481.4 ± 0.7
	0–3	532.1 ± 1.2	523.6 ± 1.1

[a] Methylcyclohexane–isopentane (1:4). [b] $EtOH-Et_2O$ (2:1).

Hence it is noteworthy that a similar shift in emission was found for 4,4-diphenylcyclohexadienone on changing from MCIP to either EPA or ethanol-ether (note Table III). This evidence supports a picture in which the triplet has an oxygen atom which is less electron-rich than in the ground state. The orientation of the solvent seems likely to be that most appropriate to solvating the ground state of the ketone; excitation seems unlikely to appreciably deform the glass molecules. Since polar and hydrogen bonding solvents will selectively stabilize the $C^+—O^-$ dipole of the ground state relative to the inhibited dipole of the $n-\pi^*$ triplet,

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(11) K. V. Auwers and G. Keil, *Ber.*, **35**, 4207 (1902); **36**, 1861 (1903).

(12) T. Zincke and R. Suhl, *ibid.*, **39**, 4148 (1906).

(13) Unfortunately, essentially all of the literature studies dealing with the effect of substituents and solvent describe only the shift in absorption maximum rather than the 0–0 band. Since the same vibrational band may not always be strongest and the 0–0 band may not always be separated from the maximum by the same amount, there is an inherent inaccuracy. However, where vibrational structure cannot be discerned and where the peak shape remains constant, the use of the maximum seems relatively safe.

(14) (a) N. C. Yang, *Pure Appl. Chem.*, **9**, 591 (1964); (b) IUPAC International Symposium on Photochemistry, Strasbourg, France, July 1964. (c) Benzaldehyde was reported to show no shift despite its clearly being $n-\pi^*$.

(15) P. A. Leermakers, P. C. Warren, and G. F. Vesley, *J. Am. Chem. Soc.*, **86**, 1768 (1964).

(16) (a) G. A. Zimmerman, Ph.D. Thesis, University of Wisconsin, Jan 1965. (b) These solvent effects are small and are accurately measured only where resolution allows determination of the 0–0 peak.

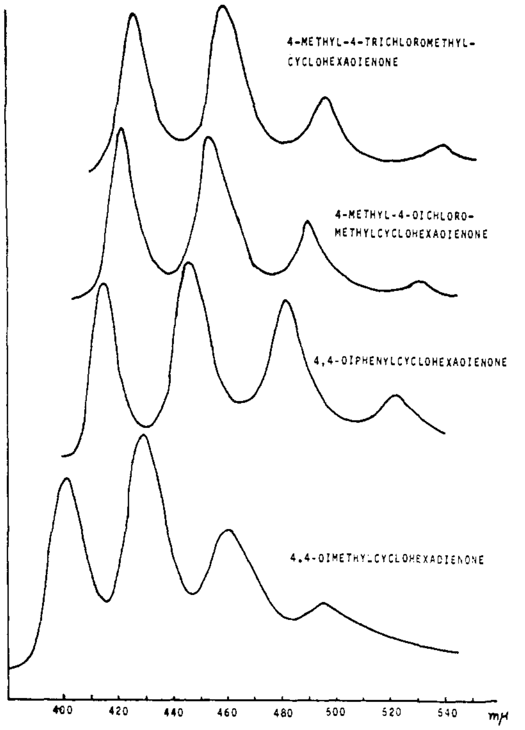

Figure 1. Phosphorescence emission spectra of 4,4-disubstituted cyclohexadienones.

the energy gap is increased with a resulting decrease in wavelength of emission as solvent polarity is increased.

Another method which has been of some use is the measurement of emission polarization. In effect, by determining the plane of polarization of light emitted by a triplet molecule relative to the plane absorbed, it is possible to determine the symmetry possible for the triplet excited state emitting if the symmetry of the singlet absorption is known. In the present case the excitation wavelength was in the n–π^* region; an EPA glass was used. The emission polarization was found to be parallel to the excitation direction. This is a result which is similar to that of benzophenone[17–19] which is well accepted as having its lowest energy triplet of n–π^* configuration. The argument used in the benzophenone example is that absorption is vibronically A_1[18,19] due to an a_2 twisting vibration of the benzene rings; then mixing of the n–π^* singlet with A_1 π–π^* states leads to increased allowedness of absorption. For emission, appreciable intensity results only by virtue of spin–orbit coupling with a strong singlet A_1 band.[17–19] There is a spin–orbit operator (R_z) with the rotational symmetry a_2 which then leads to a ^{3}(n–π^*) to ground-state transition with A_1 vibronic symmetry capable of mixing with an A_1 singlet transition. Thus both n–π^* singlet absorption and n–π^* triplet emission have A_1 symmetry and are parallel.[17–19] In the present instance of 4,4-diphenylcyclohexadienone, the principal question is what a_2 vibration could be involved in giving over-all A_1 symmetry to absorption. We note that anthrone does not have such an a_2 twisting vibration,[19] presumably because the benzene rings are tied together by a methylene group. However, for an n–π^* excited dienone the α–β bonds have a diminished bond order and are not part of an aromatic system. A vibration of the type shown in Figure 2 would have a_2 symmetry and seems reasonable. It should be recognized that this evidence is permissive rather than mandatory for an n–π^* triplet assignment.

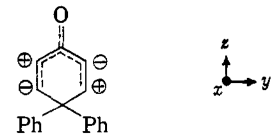

Figure 2. a_2 vibration possible for dienone.

The preceding discussion has described experimental evidence pointing toward an n–π^* configuration for the triplet of 4,4-diphenylcyclohexadienone emitting at 77°K. A parallel approach was theoretical. Not only did it seem worthwhile to compare theoretical prediction of the relative energies of the different configuration triplets available to dienone, but also it seemed of considerable interest to consider in general the matter of different electron distributions characteristic of each of the excited states of various ketones.

Hückel calculations of course do not differentiate between singlets and triplets. Of the two effective approaches, using SCF and configuration interaction calculations, the latter seemed more manageable since no difficulties would arise due to the open-shell nature of the problem.

Configuration interaction calculations were carried out for benzophenone, acetophenone, benzoquinone, 1-acetonaphthone, 2-acetonaphthone, biacetyl, cyclohexenone, formaldehyde, and 4,4-disubstituted cyclohexadienone. Many of the energies of the singlet and triplet excited states were known for these molecules. Hence, to the extent that the treatment was successful in predicting energies for these cases, its results for the unknown states would seem reliable.

Configuration interaction calculations for carbonyl compounds with inclusion of the nonbonding p_y orbital are rare.[20–22] In the studies in the literature carbonyl molecules have been studied individually. The present study attempts to utilize one approach and set of parameters to describe an assortment of ketones, those cited above.

This study began with configurational wave functions (the Ψ's) taken as linear combinations of Slater determinantal functions (the Φ's). The latter, in turn, are constructed from Hückel-like orbitals (the ψ's) derived with the assumption of X-ray geometry. The atomic orbitals are the χ's. Accordingly, the ground configuration prior to configuration interaction is given by

$$^1\Psi_0 = \Phi_0 = \overset{N}{\big|}\psi_1(1)\bar{\psi}_1(2)\psi_2(3)\bar{\psi}_2(4)\ldots$$
$$\ldots\psi_k(i)\bar{\psi}_k(j)\ldots\psi_m(g)\bar{\psi}_m(h)\ldots\bar{\psi}_N(2N)\big| \quad (1)$$

Similarly, each excited singlet configuration has the form

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(17) V. G. Krishna, *J. Mol. Spectry.*, **13**, 296 (1964).

(18) (a) F. Dörr and J. Dehler, *Tetrahedron Letters*, 189 (1965); (b) J. Dehler and F. Dörr, *ibid.*, 2155 (1965).

(19) R. Shimada and L. Goodman, *J. Chem. Phys.*, **42**, 790 (1965).

(20) T. Anno, I. Matubara, and A. Sado, *Bull. Chem. Soc. Japan*, **30**, 168 (1957), have studied *p*-benzoquinone.

(21) K. Inuzuka and T. Yokota (*Bull. Chem. Soc. Japan*, **37**, 1224 (1964); **38**, 1055 (1965)) have investigated the case of benzaldehyde.

(22) J. M. Parks and R. G. Parr, *J. Chem. Phys.*, **32**, 1657 (1960).

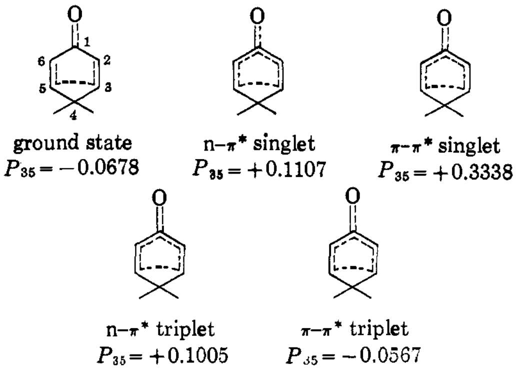

Figure 3. 3,5-Bond orders of the electronic states of 2,5-cyclohexadienones.

$$^{1}\Psi_k{}^l = (1/\sqrt{2})\{\overset{N}{|}\psi_1(1)\bar{\psi}_1(2)\ldots\bar{\psi}_k(i)\psi_l(j)\ldots\bar{\psi}_N(2N)| - \overset{N}{|}\psi_1(1)\psi_1(\bar{2})\ldots\psi_k(i)\psi_l(\bar{j})\ldots\psi_N(\bar{2}N)|\} = (1/\sqrt{2})\{\Phi_k{}^l - \overset{\curvearrowright}{\Phi}_k{}^l\} \quad (2)$$

and each triplet configuration is represented by

$$^{3}\bar{\psi}_k{}^l = (1/\sqrt{2})\{\Phi_k{}^l + \overset{\curvearrowright}{\Phi}_k{}^l\} \quad (3)$$

Here k and m are bonding MO's while l and n are antibonding, the small N over the Slater determinant indicates normalization, and $\curvearrowright$ connotes permutation of spin functions.

Thirteen configurations were allowed to interact where this number was available; these comprised the ground state configuration and singly excited configurations involving promotion from one of the four highest filled MO's to one of the three lowest vacant MO's. The matrix interaction elements between singly excited configurations are given by

$$^{1,3}F_{km}{}^{ln} = \int {}^{1,3}\Psi_k{}^l \mathfrak{F}\, {}^{1,3}\Psi_m{}^n \mathrm{d}\tau = \delta_{km}\delta_{ln}E_0 + \delta_{km}F_{ln} - \delta_{ln}F_{km} + {}^{1,3}G \quad (4)$$

$$F_{ln} = I_{ln} + 2\sum_{w}^{N} G_{wlwn} - \sum_{w}^{N} G_{wlnw} \quad (5)$$

$$^{1,3}G = G_{knlm} - G_{knml} \pm G_{knlm} \quad (6)$$

Here I_{ln} is the core integral between MO's l and n, and G's are MO repulsion integrals, E_0 is the ground-state configuration energy, and the plus or minus sign in eq 6 is determined by whether the matrix element is between singlet or triplet configurations, respectively.[23] The matrix interaction element between the ground-state configuration and singlet singly excited configurations is $^{1}F_{0k}{}^l = \sqrt{2}F_{kl}$; this would be zero if self-consistent field MO's were used as a basis. Elements between singlet and triplet configurations are zero. The mode of evaluation of the core and repulsion integrals is given in the section on calculations.

The configuration interaction calculations afforded energies of both the singlet and triplet states as well as electron distributions predicted for each of these. The calculated energies are compared with experimental ones in Table IV. We note that the agreement with the literature and with unambiguously assigned transitions of the present study is quite satisfactory. For example, there is general agreement in the literature that the lowest energy triplet of benzophenone is n–π*. The calculations not only predict this but give a reasonable fit to the observed 0–0 emission energy. The same is true of acetophenone, biacetyl, benzoquinone, and formaldehyde. Similarly, the fit of the singlet excited states is generally good. Strikingly, we note that the calculations predict that the lowest energy triplets of the 1- and 2-acetonaphthones should be π–π* in accord with currently accepted[24,25] assignments; the agreement with observation is again good. Thus it is of interest that the lowest enone triplet is calculated to be of n–π* configuration. In the case of the cross-conjugated dienones, the energy difference between n–π* and π–π* configurations is small compared with experimental error although the n–π* configuration is lower. The previously discussed evidence[26] points to the n–π* assignment. Especially interesting is the calculation of 3,5-bond orders, P_{35}, for the 2,5-cyclohexadienone moiety in its various electronic states. These are given in Figure 3. Inspection of the bond orders reveals that the one excited state which is not β,β bonding is the π–π* triplet. Since the bond order affords a measure of the energy to be gained by increased overlap,[27] the π–π* triplet (and the ground state as well) encounters a rise in its potential energy surface as β,β bonding ensues. However, such bonding is predicted to be energetically favorable for the π–π* singlet, the n–π* singlet, and the n–π* triplet. From another viewpoint, we noted that evidence has been presented earlier[26,28,29] in the case of dienones that it is a triplet which is involved in the type-A rearrangements,[30] and one is left with a choice between the n–π* and π–π* triplets as the rearranging excited state. However, only the n–π* triplet, because of its positive β,β bond order, accords with the experimental observation of β,β bonding in the type-A photochemical rearrangement of 4,4-disubstituted dienones.[31]

Of related interest are the charge densities of the various excited states of dienones and enones. These are given in Figures 4 and 5. The electron densities must be evaluated with caution. While the fit of energies with experiment is quite good, the electron densities derive from the eigenfunctions which are usually less satisfactory. Additionally, no attempt was made to include σ reorganization effects. In the n–π* states one would expect overlap of the nonbonding

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[23] *Cf.* J. N. Murrell and K. L. McEwen, *J. Chem. Phys.*, **25**, 1143 (1956).

[24] G. S. Hammond and P. A. Leermakers, *J. Am. Chem. Soc.*, **84**, 207 (1962).

[25] V. Ermolaev and A. Terenin, *J. Chim. Phys.*, **55**, 698 (1958).

[26] Note also, H. E. Zimmerman and J. S. Swenton, *J. Am. Chem. Soc.*, **86**, 1436 (1964).

[27] Use of the bond order as a measure of energy change on slight increase or decrease in overlap is equivalent to employing first-order perturbation theory. Such approaches may afford erroneous predictions when the energy change following extensive bonding is desired. The use of bond order therefore merely indicates possible energy barriers.

[28] H. E. Zimmerman and J. S. Swenton, *J. Am. Chem. Soc.*, **89**, 906 (1967).

[29] Note also J. Richards and M. Fisch, *ibid.*, **85**, 3029 (1963).

[30] A large number of 4,4-disubstituted dienones are known to rearrange to afford 6,6-disubstituted bicyclo[3.1.0]hex-3-en-2-ones in a process termed (note ref 28 and 31) type A. The presence of a new σ bond between the two carbon atoms originally β to the carbonyl group provides experimental evidence for the tendency for such bonding in some excited state.

[31] H. E. Zimmerman, *Science*, **142**, 1541 (1966).

Table IV. Calculated and Experimental Singlet and Triplet Energies[a]

Molecule	Singlets Calcd	Singlets Obsd	Singlets Config	Triplets Calcd	Triplets Obsd	Triplets Config
1-Acetonaphthone	3.94	*b*	n–π*	2.67	2.47[c]	π–π*
	4.09	3.97[c]	π–π*	3.71	*d*	n–π*
	5.80	5.85[c]	π–π*			
2-Acetonaphthone	3.81	*b*	n–π*	2.82	2.66[c]	π–π*
	4.07	3.70[c]	π–π*	3.57	*d*	n–π*
	4.41	4.43[c]	π–π*			
	5.34	5.06[c]	π–π*			
Acetophenone	3.45	3.43[e]	n–π*	3.19	3.20[e]	n–π*
		(3.34[f])			(3.22[f])	
	4.69	4.50[f]	π–π*	3.40	*d*	π–π*
	5.07	5.20[e]	π–π*			
		(5.32[f])				
	6.13	6.36[f]	π–π*			
Cyclohexenones	3.33	3.32[e]	n–π*	3.06	3.09[e]	n–π*
		(3.71[g])				
	6.15	5.96[g]	π–π*	3.29	*d*	π–π*
		(5.61[e])				
Benzophenone	3.46	3.30[e]	n–π*	3.22	3.00[e]	n–π*
	4.92	4.60[h]	π–π*	4.09	*d*	π–π*
		4.98[i]	π–π*			
Benzoquinone	2.74	2.68[j]	n–π*	2.50	2.3[k]	n–π*
		2.7[k]				
	5.33	5.21[l]	π–π*	3.18	*d*	π–π*
		5.13[j]				
		5.1[k]				
Biacetyl	2.83	2.84[m]	n–π*	2.53	2.65[m]	n–π*
		2.7[n]			2.4[n]	
	7.77	7.51[o]	π–π*	3.41	*d*	π–π*
		7.2–7.6[p]				
Cross-conjugated dienone	3.28	3.28[e]	n–π*	3.02	3.10[e]	n–π*
	5.58	5.50[e]	π–π*	3.05		π–π*
Formaldehyde	3.35	3.50[q]	n–π*	3.07	3.12[q]	n–π*
		4.3[p]				
	8.26	8.05[r]	π–π*	4.00	*d*	π–π*
		7.95[o]				

[a] Energies in ev. [b] Buried under π–π* band. [c] Reference 24. [d] Unknown. [e] This study. [f] Reference 21. [g] K. Inuzuka, *Bull. Chem. Soc. Japan*, **34**, 6 (1961). [h] Estimated from shoulder on 248-mμ band. [i] 248-mμ band. [j] H. McConnell, *J. Chem. Phys.*, **20**, 700 (1952). [k] J. W. Sidman, *J. Am. Chem. Soc.*, **78**, 2363 (1956). [l] G. Scheibe, *Ber.*, **59**, 2617 (1926). [m] S. P. McGlynn, F. J. Smith, and G. Alento, *Photochem. Photobiol.*, **3**, 269 (1964). [n] J. C. D. Brand, *Trans. Faraday Soc.*, **50**, 431 (1954). [o] H. Kon, *Bull. Chem. Soc. Japan*, **27**, 565 (1954). [p] H. L. McMurry, *J. Chem. Phys.*, **19**, 101 (1951). [q] J. C. D. Brand, *J. Chem. Soc.*, 858 (1956). [r] W. C. Price, *J. Chem. Phys.*, **3**, 256 (1935).

p_y orbital and the coplanar (or nearly coplanar) σ bonds with some delocalization of σ bond electrons into the p_y orbital.[32,36] Nevertheless, the present results should be qualitatively useful. We note that the π–π* singlet is polarized δ^+ on the β-carbon and δ^- on oxygen as commonly accepted for π–π* states.[38,40] Similarly the n–π* states, both singlet and triplet, are more electron rich β than in the ground state.[40] Furthermore, the difference in electron distribution between the n–π* singlets and n–π* triplets is small. This was suggested on a qualitative basis earlier[8,34,41] with the

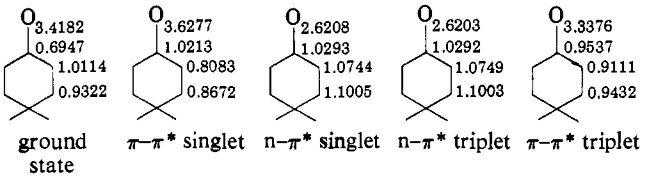

Figure 4. Calculated π electron densities in the electronic states of cyclohexadienones (electron densities at oxygen include p_y contribution).

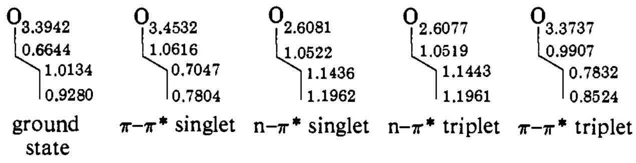

Figure 5. Calculated π electron densities in the electronic states of unsaturated ketones (electron densities at oxygen include p_y contribution).

[32] This overlap and delocalization has been discussed qualitatively in connection with the Norrish Type I fission.[8,28,33–36]

[33] H. E. Zimmerman, 17th National Organic Chemistry Symposium, Bloomington, Ind., June 1961, Abstracts, p 31.

[34] H. E. Zimmerman, *Advan. Photochem.*, **1**, 183 (1964).

[35] Such delocalization is taken into account explicitly by calculations which include orbitals of the σ system, for example, the formaldehyde calculations[36] and the Hoffmann three-dimensional Hückel calculations for saturated ketones.[37]

[36] (a) J. M. Foster and S. F. Boys, *Rev. Mod. Phys.*, **32**, 303 (1960); (b) P. L. Goodfriend, F. W. Birss, and A. B. F. Duncan, *ibid.*, **32**, 307 (1960); (c) note also ref 22.

[37] R. Hoffmann, 1st IUPAC International Photochemistry Conference, Strasbourg, France, 1964, discussion.

[38] Interestingly, most calculations afford a more electron-deficient α-carbon than β-carbon in contrast to intuition derived from Woodward's rules.[39] The slightly greater energy lowering of a β-alkyl group relative to an α one, however, could derive from other effects. One possibility is steric hindrance to excited state solvation by α substituents.

[39] (a) R. B. Woodward, *J. Am. Chem. Soc.*, **63**, 1123 (1941); **64**, 76 (1942); (b) L. Fieser, "Steroids," Reinhold Publishing Corp., New York, N. Y., 1959, p 18.

[40] Note ref 5 for evidence and earlier references cited therein supporting this view of singlet n–π* and π–π* excited-state electron distributions.

[41] H. E. Zimmerman, *Tetrahedron Suppl.*, **2**, 393 (1963).

argument that in n–π^* states the two odd electrons (π^* and n) are more completely separated in space than in π–π^* states with the result that n–π^* singlet–triplet splitting (*i.e.*, the difference between n–π^* singlet and n–π^* triplet energies) tends to be small as experimentally observed (note Table IV) and the electron distribution of the π system electrons should be relatively insensitive to the spin of the nonbonding p_y orbital electron. These predictions of similar n–π^* singlet and triplet charge distributions are in accord with the observed (*vide supra*) similar wavelength effects of γ-electron-withdrawing groups on n–π^* singlet absorption and n–π^* triplet emission.

Most interesting is the π–π^* triplet which in the case of enones is calculated to be intermediate in β-electron density between the ground and π–π^* singlet states. In dienones, this β carbon is actually slightly electron rich relative to ground state. Thus the calculations suggest that the π–π^* triplet is not accurately represented by the structure C^+—C=C—O^- (**5**).[42] This structure seems best reserved for depicting π–π^* singlets.[43]

Experimental Section[44]

4,4-Diphenylcyclohexadienone. This was prepared following the method of Zimmerman and Schuster[8,10,45] and purified by careful sublimation and repetitive crystallization.

4,4-Dimethyl-3,5-cyclohexadienone.[9] 4,4-Dimethylcyclohex-2-enone[46] (13.66 g, 0.11 mole) and 12.8 ml of acetic acid were dissolved in 1250 ml of *t*-butyl alcohol and heated to reflux. Freshly sublimed selenium dioxide was added in small portions during 27 hr until 79 g (0.71 mole) had been added. Reflux temperature was maintained until a total of 45 hr had elapsed. The greenish black solution was filtered through Celite 545 to remove particles of metallic selenium, the *t*-butyl alcohol was removed at atmospheric pressure, and the residue was extracted with ether. The extract was washed with water, 5% aqueous sodium hydroxide, and water, and dried over sodium sulfate. Distillation through a 10-cm Vigreux gave four fractions: 188 mg of pale yellow oil, bp 48–53° (3.7 mm), n^{26}D 1.4761; 127 mg of pale yellow oil, bp 53–55° (3.8 mm), n^{26}D 1.4872; 734 mg of very pale yellow oil, bp 54–56° (3.8 mm), n^{26}D 1.4943; and 556 mg of yellow oil, bp 55° (2.4 mm), n^{26}D 1.4940. The third fraction was identified as 4,4-dimethyl-2,5-cyclohexadienone. An irregularity in the vibrational structure of the n–π^* absorption caused an intensive effort to purify this compound. Preparative vpc techniques on a Ucon LB550 column followed by micro molecular distillation afforded material which still showed strong absorption bands at 333.8, 347.1, 361.9, and 377.6 mμ with weak, but discernible inflections at 330.0, 343.8, 357.9, 372.2, and 388.3 mμ. The similarity of these latter absorptions with the starting enone was noted, but vpc analysis showed the absence of 4,4-dimethylcyclohex-2-enone (under identical conditions the enone had a retention time of 13.1 min and the dienone a retention time of 17.6 min); infrared ($CHCl_3$): 6.01 (s), 6.14 (s), 7.14 (m), 9.06 (m), and 11.61 (s) μ.

4-Methyl-4-trichloromethylcyclohexadienone[12] was prepared using the method of Zincke and Suhl.[12] The product was purified by recrystallization from hexane to give mp 104–105° (lit.[12] 105°).

4-Methyl-4-dichloromethylcyclohexadienone[11] was prepared using the procedure of Auwers and Keil.[11] The product was repeatedly crystallized from hexane with Norit treatment and purified further using liquid–liquid partition chromatography.[8] After recrystallization from hexane the product melted at 52–53° (lit.[11] 55°).

Substituted Benzophenones and Acetophenone. Commercial materials were purified by thorough recrystallization. In the case of acetophenone a center cut of fractionated material was employed.

Emission Measurements. Phosphorescence measurements were made on an Aminco-Kiers spectrophosphorimeter modified with internal baffles to eliminate scatter. Lifetime measurements were determined in an apparatus employing a FX6AU xenon flash lamp fired through a 5C22 hydrogen thyratron by 0.1 to 0.4 μf capacitors charged to 4 kv. The emission was monitored with a short-time constant photomultiplier circuit. Glass filters were used to isolate desired wavelengths of exciting and emitted light. For polarization studies the American Instrument Co. Glan Prism arrangement was used. The degree of polarization was taken as defined by Asumi and McGlynn[47] experimentally to correct for monochrometer polarization.

Emission and excitation spectra were calibrated by use of a low-pressure mercury lamp in each run. Excitation spectra were used to make certain that emission corresponded to the compound under study rather than impurities Solvents were purified by chromatography and subsequent fractionation.

Calculations. A basis set of Hückel-like MO's was used for constructing the Slater determinantal wave functions. For the initial construction the valence state ionization potential of carbon of −11.16 ev and an adjusted oxygen value of −13.56 ev were used as Coulomb integrals. The carbon to carbon resonance integral β_{rs} was taken as −6442 exp(−5.686*r*) ev as suggested by Pariser and Parr,[48] while for the carbonyl group β was taken as −3.000 ev. For nonneighbors, β_{rs} was taken as zero. Neglect of overlap was assumed. These resonance integrals were used for both the initial LCAO MO calculation and in the configuration interaction process. The atomic core integrals were taken as

$$\alpha_{\mathrm{p}} = A - \sum_{q \neq p}^{\substack{\text{charged}\\ \text{atoms}}} Z_q(pp/qq)$$

where

$$A = W_{\mathrm{p}} - \sum_{s \neq p}^{\substack{\text{all}\\ \text{atoms}}} (s/pp)$$

(note Table V). Here *A* was chosen empirically. The necessary repulsion integrals were taken where available from Pariser and Parr[48] for matching geometry. The remaining integrals were obtained empirically and are given in Table V. For distances greater than 1.21 A, the repulsion integrals between a carbon orbital and an oxygen orbital were taken independent of whether the oxygen orbital was π or n. For distances greater than 3.85

Table V. Parameters Used in Configuration Interaction Calculation

Parameter	Distance, A	Value, ev
(11/11)oo	0.00	15.931
(11/*nn*)oo	0.00	11.865
(11/22)co	1.21	8.536
(11/*nn*)oo	1.21	8.036
(11/22)co	2.50	5.6000
(11/22)co	3.00	4.800
(11/22)co	3.85	3.850
A (carbon)	. . .	−11.16
A (oxygen)	. . .	−43.575
Z	. . .	3.25

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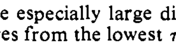
[42] As has been noted by M. J. S. Dewar (18th Reaction Mechanisms Conference, Corvallis, Ore., June 1964, discussion), a structure (*e.g.*, **5**) is not a valid valence bond contributor to a triplet state. However, just as one includes singly excited configurations in valence bond calculations of a ground state, one might conceive of doubly excited structures as



$$C^+—\overset{\cdot\uparrow}{C}—\overset{\cdot\uparrow}{C}—\ddot{\underset{\cdot\cdot}{O}}:^-$$

contributing to a singly excited triplet. Thus, *a priori*, charge separation cannot be ruled out.

[43] The source of the especially large difference between the π–π^* singlets and triplets derives from the lowest π–π^* states in the two cases involving different sets of configurations of different symmetry. The singlet is heavily weighted in the configuration having promotion from the highest bonding π MO to the lowest antibonding orbital while the triplet configurations weighted involve promotion from the highest occupied π MO to the next to lowest antibonding MO and promotion from the next to highest bonding MO to the lowest antibonding MO.

[44] All melting points were taken on a hotstage apparatus calibrated with known compounds.

[45] We thank Dr. John Swenton for this material.

[46] E. L. Eliel and C. A. Lukach, *J. Am. Chem. Soc.*, **79**, 5986 (1957).

[47] T. Azumi and S. P. McGlynn, *J. Chem. Phys.*, **37**, 2413 (1962).

[48] R. Pariser and R. B. Parr, *ibid.*, **21**, 767 (1953).

A, C–O repulsion integrals were approximated by C–C integrals at the same distance.

The effective nuclear charge on oxygen was adjusted empirically and the value is given in Table V.

Acknowledgment. Appreciation is expressed to the National Science Foundation (Grant GP-1966) and the National Institutes of Health (GM-07487) for support of this research. Support of computing by the National Science Foundation *via* the Wisconsin Computing Center is also appreciated. G. A. Z. gratefully acknowledges Woodrow Wilson and National Institutes of Health Predoctoral Fellowships; R. B. expresses appreciation for a National Science Foundation Predoctoral Fellowship.

Solvent and Salt Effects on the Products from Polar Chlorination of the Linear Pentenes

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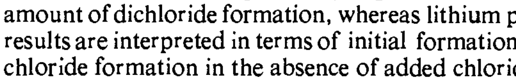
Abstract: Product distributions from chlorination of *cis*-2-, *trans*-2-, and 1-pentene in methanol, ethanol, formic acid, *t*-butyl alcohol, acetic acid, and trifluoroacetic acid have been determined as well as the effects of added lithium chloride, lithium acetate, lithium perchlorate, and lithium formate in acetic acid and lithium chloride in methanol. For the 2-pentenes, addition in each case gives both vicinal dichloride and solvent-incorporated product, each in a stereospecifically *trans* fashion. For the latter product type, both possible positional isomers are formed with a slight preference for attachment of solvent adjacent to the methyl group. For 1-pentene, dichloride is accompanied by both the normal and anti-Markovnikov solvent-incorporated products. For all three olefins, the relative effectiveness of the hydroxylic solvents in diverting intermediates from dichloride formation is in the order listed above. In acetic acid for the 2-pentenes, large concentrations of lithium chloride are required to give modest increases in the amount of dichloride formation, whereas lithium perchlorate has negligible effect on the product composition. The results are interpreted in terms of initial formation of a chloronium ion–chloride ion intimate ion pair. *trans*-Dichloride formation in the absence of added chloride ion occurs by reorientation and collapse of this ion pair. The immediate precursors of solvent-derived products cannot be precisely determined and two possibilities are discussed.

Chlorination of olefins in nonpolar solvents has recently been shown to be a more complex process than previously believed[1] because variations in olefin structure and concentration can lead to reaction through either polar or free-radial intermediates.[2] Use of radical inhibitors allowed isolation and study of the polar process even in nonpolar solvents.[3] Radical reaction can also be avoided by use of polar solvents which support formation of charged intermediates. However, most common polar solvents, such as alcohols and carboxylic acids[4a] as well as many nonhydroxylic solvents,[4b,c] are nucleophilic as well and can divert a portion of the reaction toward formation of products which incorporate solvent. In fact, this observation lent considerable support to the early formulation of a two-step mechanism for halogenation as shown in eq 1 where RCl^+ represents some type of positively charged



$$\begin{array}{l} \rangle\!=\!\langle \; + \; Cl_2 \rightarrow RCl^+ \xrightarrow{Cl^-} RCl\text{–}Cl \\ \qquad\qquad\qquad\quad \xrightarrow{SOH} RCl\text{–}OS + H^+ \end{array} \tag{1}$$

intermediate formed by attack of chlorine on the double bond; RCl–Cl, the dichloride product; and RCl–OS, the solvent-incorporated product.[5a] Significant questions can be asked concerning the attack of chlorine on the olefin which leads to RCl^+, concerning the structure of RCl^+, and concerning the characteristics of the second, product-determining step(s). Considerable direct kinetic evidence in polar solvents (especially acetic acid), albeit for deactivated olefins, has elucidated the electrophilic nature of the first step in some detail;[5] relative reactivity data for simple olefins in nonpolar solvents are also consistent with electrophilic attack, although *via* a rather symmetrical transition state with little development of positive charge on carbon.[3] Evidence as to whether RCl^+ is better formulated as an α-chlorocarbonium ion or as a bridged chloronium ion has appeared more recently. The chloronium ion formulation (or an unsymmetrical version thereof[5a]) has been advanced to explain the formation of significant amounts of anti-Markovnikov products and rearrangement products in several polar chlorinations[6] and to explain certain exclusively *trans* additions.[3,7] Fahey and Schubert,[8] using a stereochemical criterion, have recently shown that RCl^+ may be either bridged or open dependent on the stability of the open ion.

In contrast, knowledge concerning the product-forming steps is meager. Consideration of the reaction

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[1] R. W. Taft, Jr., *J. Am. Chem. Soc.*, **70**, 3364 (1948).

[2] M. L. Poutsma, *ibid.*, **87**, 2161, 2172 (1965).

[3] M. L. Poutsma, *ibid.*, **87**, 4285 (1965).

[4] (a) G. Williams, *Trans. Faraday Soc.*, **37**, 749 (1941); (b) F. C. Weber, G. F. Hennion, and R. R. Vogt, *J. Am. Chem. Soc.*, **61**, 1457 (1939); (c) I. G. Dinulescu, M. Avram, C. T. Jijovici, M. Farcasiu, and C. D. Nenitzescu, *Chem. Ind.* (London), 840 (1964).

[5] (a) See P. B. D. de la Mare and R. Bolton, "Electrophilic Additions to Unsaturated Systems," Elsevier Publishing Co., Amsterdam, 1966, Chapter 6, for a recent review; (b) H. P. Rothbaum, I. Ting, and P. W. Robertson, *J. Chem. Soc.*, 980 (1948), and previous papers.

[6] P. Ballinger and P. B. D. de la Mare, *ibid.*, 1481 (1957).

[7] H. J. Lucas and C. W. Gould, Jr., *J. Am. Chem. Soc.*, **63**, 2541 (1941), and references therein.

[8] R. C. Fahey and C. Schubert, *ibid.*, **87**, 5172 (1965).