593. cyclo*Heptatrienone,* cyclo*Pentadienone, and* γ*-Pyrone.*

By R. D. Brown.

Predictions are made of the chemistry of *cyclo*heptatrienone, based on molecular-orbital calculations. The related molecules *cyclo*pentadienone and γ-pyrone are also discussed and in particular the theoretical results are shown to give a complete account of the chemistry of the latter, and the tendency of derivatives of the former to dimerize.

Recently the synthesis of *cyclo*heptatrienone was announced simultaneously from two laboratories (Dauben and Ringold, *J. Amer. Chem. Soc.*, 1951, **73**, 876; Doering and Detert, *ibid.*, p. 876) and speculations were made concerning its electronic structure and chemical properties. In the present paper we communicate the values of various theoretical quantities, calculated by the LCAO molecular-orbital approximation (Coulson and Longuet-Higgins, *Proc. Roy. Soc.*, 1947, *A*, **191**, 39), which may be employed to predict the chemistry of this compound. For comparison the corresponding results for *cyclo*pentadienone and γ-pyrone are also reported. It is also of interest to compare the present results with those for tropolone recently obtained by Dewar (*Nature*, 1950, **166**, 790), which are in good agreement with the known chemistry of this molecule (Doering and Knox, *J. Amer. Chem. Soc.*, 1951, **73**, 828).

In the present calculations we have assumed the following values for Coulomb integrals, α, and resonance integrals, β : $\alpha_O = \alpha_C + 2\beta$; $\beta_{CO} = \sqrt{2}\beta_{CC}$. The overlap integrals have been neglected, and we have not considered any slight perturbations to carbon atoms adjacent to oxygen, since it is not yet certain whether or not these are of significant magnitude. The free valences were computed by assuming $N_{\text{max.}} = \sqrt{3}$. The atomic localization energies were calculated in the standard manner (Wheland, *J. Amer. Soc.*, 1942, **64**, 900), overlap being neglected. Their significance and relation to chemical properties has already been considered in detail (Wheland, *loc. cit.*; Brown, *Trans. Faraday Soc.*, 1950, **46**, 146). It will be observed that the parameters employed differ somewhat from those used by Dewar (*loc. cit.*) but are similar to those of Orgel *et al.* (*Trans. Faraday Soc.*, 1951, **47**, 113).

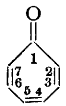
The π-electron densities, q, atom localization energies, A, and free valences, F, for various positions in *cyclo*heptatrienone (I) are listed in Table I. It will be noticed that the charge densities and atomic localization energies (A_e) both predict electrophilic attack to occur at position 2. Likewise the localization energies (A_r) agree with the free valences in attributing also the highest homolytic reactivity to position 2. On the other hand q and A_n are in disagreement as to the position preferentially undergoing substitution by nucleophilic reagents.† If we consider a plot of π-electron energy against motion of the system along the reaction co-ordinate (Glasstone, Laidler, and Eyring, "The Theory of Rate Processes," McGraw-Hill, 1941, Chap. III), then q indicates the relative positions of the plots for each position in the molecule when the reactants are well separated, while A indicates the relative positions at a stage of the reaction after the reactants have passed through the transition state. Consequently the results for nucleophilic substitution indicate that the curves for positions 2, 3, and 4 cross between these two points, and we cannot be sure which will be lowest at the stage corresponding to the transition state. This perhaps indicates the care that must be exercised in predicting relative reactivities from insufficient theoretical data.

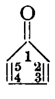
TABLE I.

cyclo*Heptatrienone.*

Position	q	F	$A_e(-\beta)$	$A_r(-\beta)$	$A_n(-\beta)$
O	1·769	—	—	—	—
1	0·771	—	—	—	—
2	0·942	0·494	2·436	2·211	1·987
3	0·884	0·424	2·876	2·508	2·140
4	0·905	0·443	2·644	2·367	2·091

The mobile-bond orders of the *cyclo*heptatrienone bonds, together with the bond localization energies, B (Brown, *Australian J. Sci. Res.*, 1949, **2**, *A*, 564; *J.*, 1950, 3249), for the carbon–carbon ring bonds, are given in Table II. The most interesting point to be deduced from the mobile orders, p, is that, taken in conjunction with the charge densities of Table I, they reveal that (IV) provides quite a faithful picture of the general electronic structure. Both Dauben and Ringold (*loc. cit.*) and Doering and Detert (*loc. cit.*) consider that the properties of *cyclo*heptatrienone so far known are in agreement with such a structure. The bond localization energies indicate that its 2 : 3-bond will be preferentially attacked by, say, ozone, in agreement with the mobile order values, but the product thus formed would be more reactive than the original *cyclo*heptatrienone, so experimental verification of this prediction may prove rather difficult.


(I.)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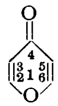
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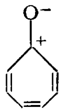
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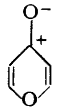
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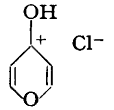
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TABLE II.

Bond orders and localization energies.

Bond	*cyclo*Heptatrienone p	*cyclo*Heptatrienone $B(-\beta)$	*cyclo*Pentadienone p	*cyclo*Pentadienone $B(-\beta)$	γ-Pyrone p	γ-Pyrone $B(-\beta)$
O : 1	0·522	—	0·742	—	—	—
1 : 2	0·530	—	0·289	—	0·565	—
2 : 3	0·709	1·255	0·880	0·549	0·711	1·449
3 : 4	0·600	1·672	0·306	1·086	0·570	—
4 : 5	0·690	1·335	—	—	0·488 *	—

* This value applies to the carbonyl bond, not the ring 4 : 5-bond, which of course is equivalent to the 3 : 4-bond.

For comparison, the π-electron densities, free valences, and atom localization energies of *cyclo*pentadienone are presented in Table III. As with *cyclo*heptatrienone, the data are consistent in predicting electrophilic attack and radical attack at position 2, but the position of highest nucleophilic activity again is uncertain † owing to crossing of the energy curves. It will be noted that the free valences are appreciably greater, and the localization energies smaller,

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† We have here ignored the most likely course of reaction, *i.e.*, carbonyl addition involving the 2-position. The possibility of a theoretical treatment of carbonyl reactivity will be considered in a forthcoming publication.

than those for the trienone, which may perhaps be taken as an indication that *cyclo*pentadienone is a more reactive molecule.

TABLE III.

cyclo*Pentadienone.*

Position	q	F	$A_e(-\beta)$	$A_r(-\beta)$	$A_n(-\beta)$
O	1·558	—	—	—	—
1	0·560	—	—	—	—
2	1·082	0·563	1·917	1·601	1·286
3	0·859	0·536	2·290	1·849	1·409

The mobile bond orders and bond localization energies of *cyclo*pentadienone are given in Table II. These point to a high reactivity for the 2 : 3-bond. The bond orders indicate that the most important resonance structure is (II) but the charge densities require an appreciable polarization of the carbonyl bond. A structure analogous to (IV) would, however, not be so appropriate for this molecule as for *cyclo*heptatrienone.

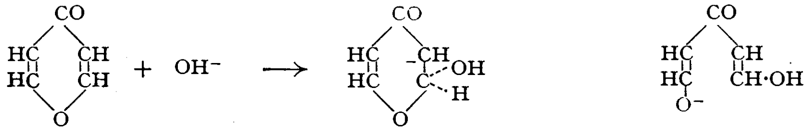
The charges and localization energies for γ-pyrone are listed in Table IV. Both quantities agree in predicting substitution by electrophilic reagents to be most rapid at position 3, and attack by nucleophilic reagents to occur most easily at position 2. The bond orders (Table II) indicate that (V) is the best single representation of the electronic structure of γ-pyrone, and the bond localization energy of the 2 : 3-bond shows that it is probably not so reactive as the mobile order indicates.

These results are in keeping with the known chemistry of γ-pyrone. The general charge distribution suggests that the oxonium salts which γ-pyrone forms with acids have structures such as (VI). The bromination of γ-pyrone giving 3-bromo- and 3 : 5-dibromo-4-pyrone (Feist and Baum, *Ber.*, 1905, **38**, 3562) demonstrates the superior electrophilic reactivity of the 3-position. The high nucleophilic activity of position 2 explains the instability of γ-pyrone in alkaline solution. The resultant ring opening may be formulated as being initiated by attack by nucleophilic reagents at position 2 :

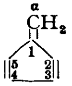
TABLE IV.

γ-Pyrone.

Position	q	$A_e(-\beta)$	$A_r(-\beta)$	$A_n(-\beta)$
1	1·522	—	—	—
2	0·819	3·017	2·749	2·481
3	1·117	2·193	2·432	2·671
4	0·808	—	—	—
O (of CO)	1·796	—	—	—



Finally we may enquire into the possibility of *cyclo*heptatrienone undergoing diene-addition reactions. The Diels–Alder properties of hydrocarbon systems have been discussed in some detail in terms of para-localization energies, *P*, which represent approximations to the variable portion of the activation energy for the diene reaction, by Brown (*J.*, 1950, 691, 2730; 1951, 1612). Para-localization energies for some pairs of positions in *cyclo*heptatrienone and *cyclo*pentadienone are given in Table V, together with corresponding data for fulvene (VII). The para-localization energy for positions 2 : 5 in fulvene lies between the values for the most reactive positions in naphthalene and in anthracene respectively, in keeping with the experimental fact that fulvenes add maleic anhydride fairly readily (*e.g.*, Norton, *Chem. Reviews*, 1942, **31**, 319). The value of *P* for the corresponding positions in *cyclo*pentadienone is appreciably smaller, indicating much greater Diels–Alder reactivity. It is not surprising therefore that the simpler *cyclo*pentadienones dimerize extremely readily, the only reasonably stable compounds being those in which both 2- and 5-positions carry phenyl groups (Norton, *loc. cit.*). It can be shown (Brown, unpublished work) that the effect of such substituents is to increase significantly the localization energy; at the same time the dienophilic activity of the molecule is probably decreased owing to steric



(VII.)

hindrance by the substituents. In spite of this, tetraphenyl*cyclo*pentadienone undergoes the diene reaction with maleic anhydride (Dilthey, Schommer, and Trosken, *Ber.*, 1933, **66**, *B*, 1627; Allen and Sheps, *Canad. J. Res.*, 1934, **11**, 171). These observations confirm the high diene activity of *cyclo*pentadienone itself.

TABLE V.

Para-localization energies.

Compound	Positions	$P(-\beta)$
Fulvene	2 : 5	3·47
*cyclo*Pentadienone	2 : 5	3·04
*cyclo*Pentatrienone	2 : 5	3·79
	2 : 7	3·81
	3 : 6	4·33

In contrast, the smallest localization energy for *cyclo*heptatrienone (for the 2 : 5-positions) is somewhat greater than that for 1 : 4-addition to naphthalene, so it may be predicted that *cyclo*heptatrienone will not be prone to dimerization by a Diels–Alder mechanism, even if it proves to be an effective dienophil.

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