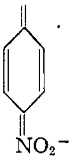
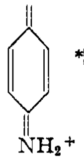
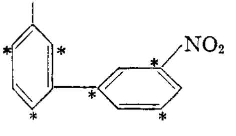
as the benzyl ions (IV) and (VI). Here $+E$ substituents stabilize the anions (*e.g.*, IV) more efficiently, and the cations (*e.g.*, VI) less efficiently than do analogous $\pm E$ (hydrocarbon) substituents (such a pair being the $+E$ formyl group and the isoelectronic $\pm E$ vinyl group), the effect being much more marked if the substituent is attached to an active atom. $-E$ substituents (*e.g.*, NH_2) show exactly the opposite effect. These conclusions also agree with resonance theory, it being possible to write unexcited ionic resonance structures (*e.g.*, VII, VIII) only if the substituent is attached to an active carbon atom.



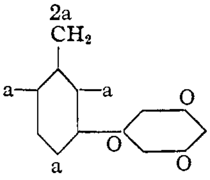
VII



VIII



IX



X

From this follows the rule for mutual conjugation of substituents, mutual conjugation being the condition in which the resonance energy of an even AH is increased more by attaching two substituents than one would anticipate from additivity of their individual effects. The previous correspondence with resonance theory ensures that here too both treatments should lead to similar conclusions. Thus mutual conjugation occurs only when the two substituents are of opposite types (one $+E$, one $-E$) and when they are attached to positions of opposite parity (*e.g.*, *o* or *p* in benzene; *cf.* (I)).

This rule for mutual conjugation is necessary but not sufficient. If the $-E$ substituent is S and the even AH R, then RS will be isoelectronic with an odd AH anion RS′; if the NBMO does not cover all the active atoms in this, RS′ is cross-conjugated and attachment of a $+E$ group at inactive starred atoms in RS′, or at equivalent atoms in RS, will not lead to mutual conjugation. This effect is seen well in 3-nitro-3′-aminobiphenyl (IX); the NO_2 and NH_2 groups are attached to atoms of opposite parity in biphenyl, but the NO_2 is attached to an atom inactive in the analogous *m*-biphenylmethyl anion (X) (the NBMO coefficients are as indicated). The resonance theory leads to similar conclusions, the condition for mutual conjugation given here being equivalent to the condition that an unexcited structure $S^+{=}R{=}T^-$ can be written. It follows that both treatments lead to similar conclusions concerning the qualitative charge distributions in neutralized, or mutually conjugated, systems; and both to similar general definitions of $+E$ and $-E$ substituents.

The present treatment differs from resonance theory, however, in the possibility it offers of estimating all these effects semi-quantitatively within its limitations.[1] The introduction of ionic structures in resonance theory rests almost entirely on qualitative reasoning and intuition, and their importance cannot be estimated in any given case except by appeal to experiment. Some such applications of the present treatment to the prediction of $+E$ and $-E$ activity of substituents are indicated above; others will appear in subsequent papers of this series when definite chemical problems are studied.

NOTRE DAME, INDIANA

[CONTRIBUTION FROM THE UNIVERSITY OF NOTRE DAME]

A Molecular Orbital Theory of Organic Chemistry. IV.[1] Free Radicals

BY M. J. S. DEWAR[2]

RECEIVED SEPTEMBER 13, 1951

The methods of the preceding papers[1] are applied to the study of free radicals. Their reactivity and their stabilization by substituents are discussed.

Free radical chemistry has proved something of a stumbling block to existing qualitative theories, since the latter were designed mainly to analyze charge distributions in even systems. The extension to radicals has involved an unusually large proportion of *ad hoc* explanations. Here the methods previously used[1] will be applied to the study of radicals and the effect of substituents, etc., on their stability. The notation used is that of Parts (I)–(III),[1] and the discussion will be limited to alternant Kekulé radicals.

Theorem 58. The total π-electron energy of two odd AH radicals is normally greater than that of the two even AH's obtained by transfer of one active atom (*i.e.*, the even AH's are the more stable). This result follows at once from theorems 18 and 19 of Part (II).[1] The rise in energy on separating the active carbon from one radical is $< \beta$, and the decrease in energy when that atom is added to the other radical is $> \beta$.

Theorem 59. Combination of an odd AH radical RS, S being an atom, with another radical T to give R–S–T, is more exothermic if S is active. The atom S passes over to sp^3 hybridization in the reaction and is so removed from conjugation with R. If S is active in RS, then R is a normal even AH or a pair of such AH's; if S is inactive, R is either a non-Kekulé AH, or a pair of odd AH radicals. From theorem 29 of Part (II),[1] a non-Kekulé AH is less stable than a Kekulé isomer; and from theorem 58, two odd AH radicals are less stable than an isomeric pair of even Kekulé AH's. Hence the most exothermic modes of addition of T will be those where S is active.

Theorem 60. An odd alternant radical is stabilized by an increase in electron affinity of any atom in it. Let the odd radical be RS, derived from an even AH R and an atom S coulomb term α. Then the resonance energy R_{RS} of RS relative to (R + S), is given[1] by

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[1] For parts (I), (II) and (III) of this series see THIS JOURNAL, **74**, **3341**, **3345**, **3350** (1952).

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$$R_{\mathrm{RS}} = -2\sum^{\mathrm{occ}} \frac{a_{mr}^2\beta^2}{E_m - \alpha} - \sum_m^{\mathrm{all}} \frac{a_{mr}^2\beta^2}{\alpha - E_m} - \sum_m^{\mathrm{occ}} \frac{2a_{mr}^2\beta^2E_m}{E_m^2 - \alpha^2} \tag{1}$$

since R is an even AH. Since $E_m < 0$ for occupied MO's, $R_{\mathrm{RS}} > 0$; and R_{RS} is greater, the greater the numerical value of α, *i.e.*, the greater the electron affinity of S.

Theorem 61. (a) *Odd alternant radicals are stabilized by +E or ±E substituents, the effect being greater if the substituents are attached to active atoms.* Let the odd AH be R and the $\pm E$ substituent be S. Then from Part I[1]

$$R_{\mathrm{RS}} = -2\sum_{m\neq o}^{\mathrm{occ}}\sum_{n}^{\mathrm{unocc}} \frac{a_{\mathrm{mr}}^2b_{\mathrm{ns}}^2\beta^2}{E_m - F_n} - 2\sum_{m\neq o}^{\mathrm{unocc}}\sum_{n}^{\mathrm{occ}} \frac{a_{\mathrm{mr}}^2b_{\mathrm{ns}}\beta^2}{F_n - E_m} - 2\sum_{n}^{\mathrm{occ}} \frac{a_{\mathrm{or}}^2b_{\mathrm{ns}}^2\beta^2}{F_n}$$

$$= -4\sum_{m\neq o}^{\mathrm{occ}}\sum_{n}^{\mathrm{unocc}} \frac{a_{\mathrm{mr}}^2b_{\mathrm{ns}}^2\beta^2}{E_m - F_n} - 2\sum_{n}^{\mathrm{occ}} \frac{a_{\mathrm{or}}^2b_{\mathrm{ns}}^2\beta^2}{F_n} \tag{2}$$

Since $E_m < 0$ for occupied MO's, and $F_n < 0$ for occupied, and $F_n > 0$ for unoccupied MO's, each term in (2) is positive, and so also therefore is the resonance energy R_{RS} of RS relative to (R + S). Also since the mean absolute values of E_m, F_n are of order β, and since $\sum_{m\neq o} a_{\mathrm{mr}}^2 < 1$, it is easily seen that the two sums in (2) are comparable, although the second is the smaller, provided that S is attached to an active atom in R so that a_{or} does not vanish. Hence $\pm E$ substituents stabilize AH radicals, the effect being greater if they are attached to active atoms. The extension to $+E$ substituents follows immediately from theorem 9 of Part II.[1]

Theorem 62. A +E substituent should stabilize radicals more efficiently, the greater its +E activity. This follows from theorems 60 and 61, as a second approximation to the effect of $+E$ groups.

Theorem 63. (a) *A −E substituent should stabilize odd AH radicals;* (b) *the effect should be much greater if it is attached to an active atom;* (c) *the stabilization should be about half that for stabilization of the analogous odd AH cation, and should therefore run parallel to the −E activity of the substituent.* Consider the case of a simple $-E$ substituent S, of coulomb term α, attached to an odd AH radical R. The resonance energy of RS is given[1] by

$$R_{\mathrm{RS}} = -2\sum_{m}^{\mathrm{unocc}} \frac{a_{\mathrm{mr}}^2\beta^2}{\alpha - E_m} - \frac{a_{\mathrm{or}}^2\beta^2}{\alpha} \tag{3}$$

Since $\alpha < 0$, and $Em > 0$ for unoccupied MO's $R_{\mathrm{RS}} > 0$. Also the final term in (3) will be relatively large since α is not large for the usual heteroatoms[3]; therefore R_{RS} is much greater for attachment of active atoms than of inactive ones (where a_{or} vanishes). From Part III,[1] the stabilization energy for the equivalent cation R^+ is given by

$$R_{\mathrm{RS}}^{+} = -2\sum_{m}^{\mathrm{unocc}} \frac{a_{\mathrm{mr}}^2\beta^2}{\alpha - E_m} - \frac{2a_{\mathrm{or}}^2\beta^2}{\alpha} \tag{4}$$

where the important final term is double that for the radical. Also the final terms are less, the more negative α—*i.e.*, the less the $-E$ activity of S (*cf.* theorem 50[1]).

Theorem 64. A −E substituent at an active atom in an odd AH radical raises the charge density at the active atoms, the effect being greater, the greater its −E activity. Consider the case of a simple $-E$ substituent T, of coulomb term α, where α is small. Let the odd AH be S, and the corresponding cation be S^+. Then the highest occupied and lowest unoccupied MO's of $\mathrm{S}^+\mathrm{T}$ were shown (*cf.* theorem 34 of Part III[1]) to involve to a first approximation the AO of T and the NBMO of S^+; and in the highest occupied MO the latter contributed less, so that the active positions in S carried fractional positive charges. It follows that in the lowest unoccupied MO of $\mathrm{S}^+\mathrm{T}$, the NBMO of S makes a large contribution. Now ST differs from $\mathrm{S}^+\mathrm{T}$ only in that one electron now occupies the lowest unoccupied MO of $\mathrm{S}^+\mathrm{T}$; hence the active atoms of S carry negative charges in ST—*i.e.*, the charge density at those atoms is raised by the substituent T. It is easily seen from equations (3) of Part III[1] that the effect should be greater the greater α—*i.e.*, the greater the $-E$ activity of T (theorem 50[1]).

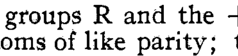
Theorem 65. A +E substituent R and a −E substituent T can conjugate mutually through an odd AH radical S if R, T are both attached to active atoms in S. This theorem is the analog of theorem 49 of Part III[1] for even AH's, and can be proved in exactly the same way; using theorem 64 to determine the charge distribution in ST. Note that the effect of a $-E$ substituent on the charge distribution in an odd AH is opposite to its effect on an even AH, and that the rule for mutual conjugation is likewise opposite.

Theorem 66. The mutual conjugation energy of theorem 65 is greater, the greater the +E activity of R or the −E activity of T. This theorem corresponds to theorem 53 of Part III[1] and the proof is similar.

Discussion

The conclusions from the present treatment agree with current theory as far as the latter goes. Thus the tendency of radicals to react at active atoms (theorem 59), and their stabilization by electromeric substituents of all types when attached to active atoms (theorems 61, 63), are familiar, although it is not easy to explain in terms of current theory why $-E$ substituents should be effective. The latter remark also applies to mutual conjugation, the orientational requirements for radicals being different to those for even alternant systems (theorem 65), and to the facts that $+E$ substituents stabilize radicals more efficiently the greater their $+E$ activity, and $-E$ substituents the greater their $-E$ activity. Finally the effect of heteroatoms in stabilizing radicals (theorem 60) is not predicted by current theory, still less the lack of orientation involved; this prediction is supported by the available evidence, pyridine undergoing phenylation by phenyl radicals very easily, and with no significant orientation effect. Electromeric substituents seem to produce significant "ortho–para" orientation in substitution judging by the rather inclusive evidence available; this orientation is predicted alike by the present treatment and by existing theories. (These points are discussed in more detail in Part VI.)

The rules for mutual conjugation are supported by the available evidence; notably by the stability of radicals of the type (I), which Goldschmidt[4] found to be more stable, the greater the $-E$ activity of R and the greater the $+E$ activity of X. Note that



I

both the $-E$ groups R and the $+E$ group X are attached to atoms of like parity; this is the opposite orientation to that required for mutual conjugation in an even alternant system.

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(3) *Cf.* M. J. S. Dewar, *J. Chem. Soc.*, 2329 (1950).

(4) S. Goldschmidt, *Ber.*, **53**, 44 (1920); *Ann.*, **473**, 137 (1929).