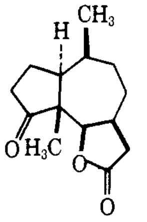
reflux), mp 102.5–105.0°, in 98% yield. Treatment of **10** with ethyl formate and sodium hydride in ether solution (23 h at room temperature) followed by reduction with sodium borohydride in methanol at 0°, hydrolysis with 3 M hydrochloric acid, and reaction with *p*-toluenesulfonyl chloride in pyridine at 0° produced a 36% yield of tosylate **11**, mp 162.5–164.5°.



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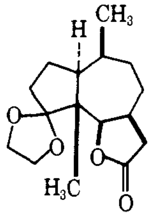
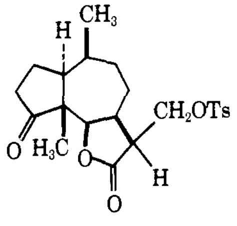


10



11

Tosylate **11** was heated under reflux in pyridine [9]for 5 h to give a 74% yield of (±)-damsin (**1**), mp 124–126°. The ir ($CHCl_3$) and NMR spectra as well as the TLC behavior of the synthetic material were identical with those of naturally occurring damsin (**1**).

Acknowledgment. The authors are grateful to Professor J. Romo for a sample of natural damsin and to the National Science Foundation for partial support of this work.

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Richard A. Kretchmer,* Wayne J. Thompson[10]
Department of Chemistry, Illinois Institute of Technology
Chicago, Illinois 60616
Received February 2, 1976

A Molecular Orbital Model for Bridging Regioselectivity in Di-π-methane Rearrangements

Sir:

Paquette and co-workers have recently reported several examples of regiospecificity in the di-π-methane rearrangements of benzonorbornadienes substituted by electron donor or acceptor groups.[1] While Zimmerman and co-workers have suggested a method for the rationalization of regioselectivity in hydrocarbon di-π-methane rearrangements,[2] the method is not readily extended to heteroaromatic systems. We wish to report a simple molecular orbital model, supported by CNDO/S-CI excited state calculations, which adequately accounts for the substituent effects observed in rearrangements of this type.

Paquette and co-workers found that the rearrangement of a donor-substituted benzonorbornadiene (**1**, D = MeO) gives mainly the di-π-methane product arising from meta bridging, while several acceptor substituted cases (**2**, A = CN or CO_2Et) give the di-π-methane products resulting from para bridging.

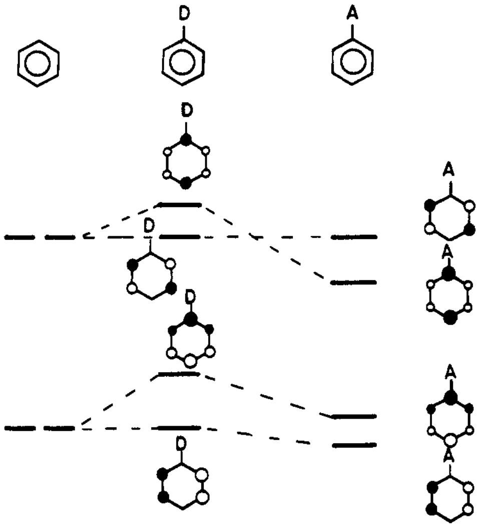
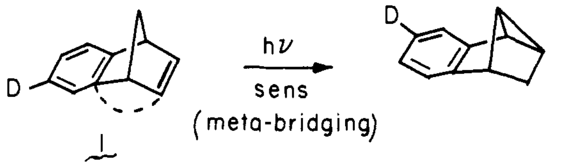
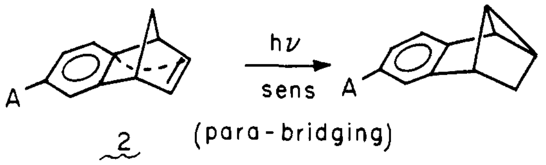


Figure 1. The degenerate HOMO's and LUMO's of benzene and energy changes upon donor (D) or acceptor (A) substitution.



1



2

A simple model to explain these phenomena can be constructed from the molecular orbitals (MO's) of substituted benzenes shown in Figure 1. Substitution of a donor (D) or acceptor (A) group on benzene splits the degeneracies of the highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals. Both types of groups leave the orbitals with a node at the site of substitution (a_2 in C_{2v}) essentially unchanged, but have a relatively large effect on the orbitals with the large coefficient (b_1 in C_{2v}) at the site of substitution. The major difference in the pattern of orbital energies between donor and acceptor substituted benzenes is in the vacant orbitals, the a_2 lying lowest in the former, the b_1 in the latter. A simple rationale for the pronounced regioselectivity in triplet di-π-methane rearrangements of **1** and **2** can be constructed if the triplet states of these molecules involve mainly single configurations with a half-occupied HOMO and a half-occupied LUMO. The interaction of the half-occupied LUMO of the excited aromatic moiety with the vacant LUMO of the ground-state ethylene moiety will lead to preferential meta bonding for the donor-substituted cases and para bonding for the acceptor-substituted compound. Similarly, the preferential α-naphtho-vinyl bridging in 1,2-naphthobarrelene[2a] is explicable on the basis of the larger LUMO density at the α-position of the naphthalene moiety. This explanation is similar to Zimmerman's pioneering discussions of changes in electron densities in the ππ* states of substituted aromatics.[2b] However, the discussion here centers on electron densities in individual orbitals, rather than on total electron densities.

This model can also predict regioselectivity when unsymmetrical alkene substitution is present. Acceptor substituents will cause bridging at the position remote from the acceptor group, since the LUMO of the vinyl moiety has the larger coefficient at the less substituted position.[3] A case of this type

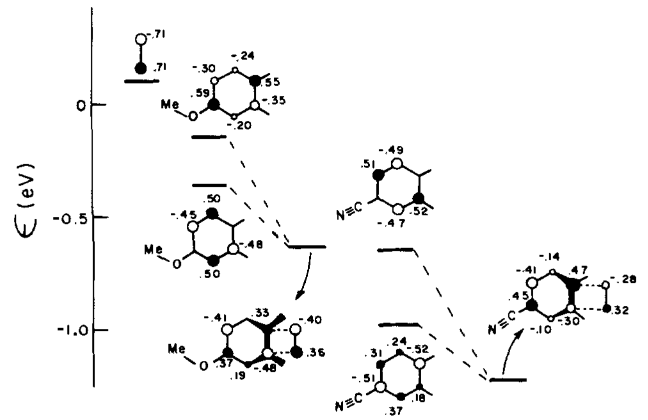
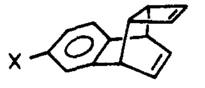


Figure 2. Correlations between the vacant orbitals of ethylene, substituted benzenes, and substituted benzene-ethylene complexes used as models for benzonorbornadienes.

has been reported: 2-cyanobenzobarrelene gives a triplet di-π-methane arrangement product resulting from exclusive benzo-vinyl (C-3) bridging.[4] The case of donor substitution is predicted to give similar regioselectivity, now due to HOMO coefficient differences.

That such an apparently naive model captures the essential origin of the observed regiospecificity has been verified by semiempirical CNDO/S-CI calculations[5] on the excited states of various model systems. In benzene and monosubstituted benzenes, the lowest triplet states (^3L_a or $^3B_{1u}$) are composed of an equal mixture of configurations resulting from a_2 to a_2 promotion and b_1 to b_1 promotion. The introduction of methyls at C-3 and C-4 reduces the molecular symmetry to C_s, perturbing this simple picture. Bringing an ethylene group into the proximity of C-3 and C-4 in a parallel plane further reduces the symmetry of the system, and calculations on the full benzonorbornadiene introduce the additional complication of σ-π mixing. As a result, calculations on benzonorbornadiene give orbitals of unrecognizable shapes, and the triplet state is a complex mixture of configurations. For that reason, we use the substituted *o*-xylene-ethylene complex as an easily understood, yet sufficiently high-order, approximation to the full molecule. Figure 2 shows the relevant vacant orbitals of ethylene, two substituted *o*-xylenes, and of the complexes, where the component molecules are separated by 2.5 Å.[6] The LUMO of the complex may be considered to result from mixing the ethylene LUMO in a bonding fashion with both of the two low-lying orbitals of the aromatic moiety. In the methoxy-substituted aromatic, both of the aromatic orbitals contribute to nearly the same extent, but the resulting LUMO meta and para coefficient magnitudes are dominated by the aromatic LUMO. The cyano-aromatic LUMO mixes most with the ethylene LUMO and dominates the resulting meta and para coefficient magnitudes. Although the situation is more complicated than suggested by the model proposed at the outset of this paper, the simple model contains in it the essential reason for regioselectivity.

Finally, we turn to another aspect of selectivity noted by Paquette and co-workers.[1] In the benzotricyclic systems, **3** and **4**, the direction of preferential di-π-methane bridging is identical with that observed for **1** and **2**; that is, **3** gives a di-π-methane product resulting from para bridging, **4** from meta bridging. However **4** also gives the intramolecular [2 + 2] cycloaddition product, **5**.[1] The kernel of an explanation for these phenomena is contained in Figure 2. Whereas the low-lying nature of the acceptor-substituted aromatic vacant orbitals leads to an excited state more localized on the aromatic moiety, and this leads to aryl-vinyl bridging, donor substituents cause the lowest triplet to be more ethylene $\pi\pi^*$ in nature, increasing the propensity for bridging of ethylene to a second ethylene moiety.



3 (X = CN)
4 (X = OMe)

5

Calculations which validate the last rationale, rationalizations of specificity in ortho-substituted benzonorbornadienes, and extensions of these ideas to photochemical substituent effects in general will be reported in due course.[7]

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(6) Since CNDO/S considers a σ interaction to be 1.71 times stronger than a π interaction for the same overlap, this corresponds, in reality, to a very close approach of ethylene to the aromatic ring. Calculations performed at greater distances give the same results as those reported here, but the amount of mixing is decreased.
(7) Zimmerman's explanation for the relative facility of benzo-vinyl, vinyl-vinyl, and α- or β-naphtho-vinyl bridging, based on the triplet energies of hydrocarbons isoconjugate with the "transition state" for bridging,[2] is, we believe, equivalent to the orbital model we propose here.
(8) Camille and Henry Dreyfus Teacher-Scholar Grant Recipient, 1972-1977; Alfred P. Sloan Foundation Fellow, 1975-1977.

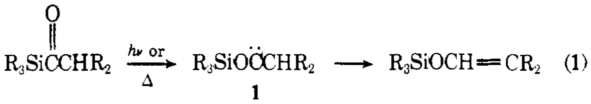
Cielo Santiago, K. N. Houk*[8]
Department of Chemistry, Louisiana State University
Baton, Rouge, Louisiana 70803
Received December 1, 1975

Silicon-Carbon Double Bonds: New Route, New Substituents, New Behavior

Sir:

The transient existence of reaction species which formally are written containing a silicon-carbon double bond is now well established.[1] Since the groups attached to the ends of the bond have generally been restricted to hydrogen, methyl, phenyl, and halogen, the range of compounds reported, and perhaps also their chemical behavior, has been limited. We wish to report a synthetic route to species containing a silicon-carbon double bond which have rather different substituents, and which display previously unreported behavior.

Based on the analogies of the thermal[2] and photochemical[3] rearrangements of acylsilanes to siloxycarbenes,[4] **1** (eq 1),



$$R_3Si\overset{\overset{\textstyle O}{\|}}{C}CHR_2 \xrightarrow[\Delta]{h\nu \text{ or}} \underset{\textstyle 1}{R_3SiO\ddot{C}CHR_2} \longrightarrow R_3SiOCH{=}CR_2 \quad (1)$$

which insert into adjacent C-H bonds to give siloxyalkenes, and the thermal rearrangements of β-ketosilanes to siloxyalkenes[5], **2** (eq 2), the thermolysis of acyldisilanes might be