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Ground States of Molecules. 61.[1] Relative Stabilities of *o*-, *m*-, and *p*-Benzyne

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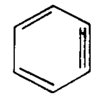
Abstract: Calculations are reported for the three isomeric benzynes (dehydrobenzenes, C_6H_4), using MNDO, UMNDO, and MNDO/CI. The results agree with an earlier MINDO/3 study in predicting *o*-benzyne and *m*-benzyne to be comparable in energy, the para isomer being appreciably less stable. Both *m*- and *p*-benzyne are predicted to occur in isomeric forms, a bicyclohexatriene and a phenylene biradical, the latter being the lower in energy in each case. The bicyclic species are separated from the biradicals by appreciable barriers (meta, 9; para, 3 kcal/mol). Both seem to have been identified as intermediates in reactions. Studies of the formation of benzynes by loss of chloride ion from chlorophenyl anions imply that derivatives of all three benzynes should be obtainable by dehydrochlorination of suitable precursors. The degenerate rearrangement of 3-hexene-1,5-diyne is found to involve *p*-benzyne as a stable intermediate. Published data for the rearrangement of 3,4-dipropyl-3-hexene-1,5-diyne lead to a lower bound for the heat of formation of *p*-benzyne.

While *o*-benzyne (**1**) has long been known as a reaction intermediate, and while it has indeed recently been observed in matrices at low temperatures,[2] the status of its meta (**2**) and para (**3**) isomers is much less certain. Until recently it was taken for granted that **1** must be much the most stable of the three isomers, on the grounds that **2** and **3** must exist as biradicals (**4**, **5b**) or possess exceptionally strained rings.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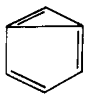
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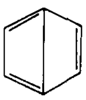
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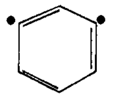
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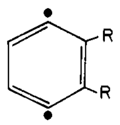
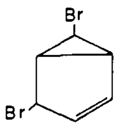

5 a, R = Pr
b, R = H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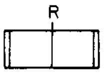
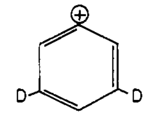

7a, R = Cl
b, R = NMe2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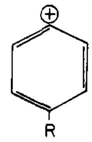
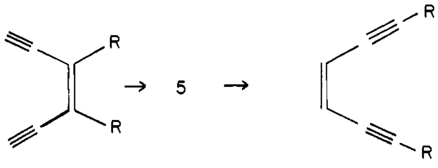

12a, R = D
b, R = T

Recently, however, a MINDO/3[3] study[4] led to the surprising conclusion that the meta isomer is similar to **1** in stability, the bicyclic structure (**2**) being unexpectedly stable. This prediction was subsequently confirmed by Washburn[5] who showed that **2** is involved as an intermediate in the reaction of 1,5-dibromobicyclo[3.1.0]hex-2-ene (**6**) with lithium dimethylamide.

The results from the MINDO/3 calculations for the para isomer were also unexpected. While the most stable form was indeed found to be the biradical (**5b**), the bicyclic species (**3**) was found to correspond to a second minimum on the potential surface, separated from **5b** by an appreciable barrier. This prediction was also subsequently confirmed by Breslow et al.[6] who presented evidence for the intervention of **3** as a stable intermediate in the reaction of lithium dimethylamide with 1-chlorobicyclo[2.2.0]hexa-2,5-diene (**7a**).

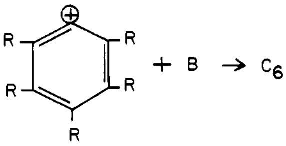
The calculations also implied that the more stable biradical form (**5b**) of *p*-benzyne is not much higher in energy than **1** or **2**. This prediction again seems to have been supported by recent studies[7] of the rearrangements of derivatives of hex-3-ene-1,5-diyne, e.g., **8a** → **9a**, which suggest that the reactions take place via a stable intermediate, presumably **5a**.



8 a, R = Pr
b, R = H

9

Pollack and Hehre[8] have recently tried to determine the heats of formation of the three benzynes by measuring their proton affinities, using ion cyclotron resonance (ICR) spectroscopy to study the loss of deuterons from deuterium derivatives of the phenyl cation (**10**) on treatment with bases of varying strengths, see eq (2). They assumed that the perdeuteriophenyl cation (**10b**) would give **1** and that 3,5-deuterio- (**11**) and 4-deuteriophenyl (**12a**) cation would give **2** (**4**) and **3** (**5b**), respectively. The deuteron affinities found in this way were, however, identical, leading to the same estimate (118 kcal/mol) for the heat of formation of the benzyne in each case. Thus, either the deuterium in **11** and **12a** must have undergone scrambling prior to reaction with base or the rates of dedeuteration in all three positions of **10b** must be similar. Pollack and Hehre favored the former



$$\mathbf{10} + B \rightarrow C_6H_4 + BR^+ \qquad (2)$$

10 a, R = H
b, R = D

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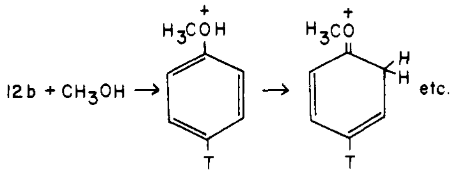
explanation, assuming that an *o*-benzyne (e.g., **1**) was formed in each case and that loss of deuterium indicated that the deuterium had been scrambled into the ortho position.

Calculations by both the MINDO/3 and STO-3G[9] models have, however, predicted very high barriers to hydrogen migration in phenyl cation (MINDO/3, 44;[10] STO-3G, 77[11] kcal/mol). While STO-3G admittedly gives erratic results for carbocations, this is an area where MINDO/3 performs especially well.[12] It therefore seems unlikely that deuterium scrambling could have occurred in **11** or **12a** under the conditions of the ICR experiment. It is true that migration of hydrogen has been postulated[13] to occur in *p*-tritiophenyl cation (**12b**) to explain the formation of rearranged products in its reaction with methanol. However, MINDO/3 calculations[14] have suggested an alternative and seemingly more likely mechanism, involving migration of hydrogen (tritium) in ring-protonated anisole (e.g., **14**) formed by migration of hydrogen in the initial adduct (**13**).



13 14 (3)

A possible resolution of this dilemma is provided by the MINDO/3 calculations[4] referred to above, according to which **1**, **2**, and **5b** do indeed have comparable heats of formation, equal within the possible limits of error of MINDO/3. This conclusion has, however, been challenged by Noell and Newton[15] on the basis of a GVB[16] calculation which predicted appreciable differences in energy between the three benzynes, **2** (**4**) and **3** (**5b**) being higher in energy than **1** by 14.5 and 23.3 kcal/mol, respectively.

As we have repeatedly pointed out, there is no reason to trust an ab initio calculation more than one by a parametric procedure, other than on the basis of empirical tests. The errors in energies calculated even by "state-of-the-art" ab initio methods are far too large for any reliance to be placed on them a priori. For example, the energy calculated for **1** by Noell and Newton[15] was too positive by 1120 kcal/mol, plus the vibronic (zero point and thermal) energy (which was not included in the calculation). These errors may cancel in comparisons of energies of isomers, e.g., **1**–**5b**, but there is no reason why they should, let alone to the accuracy needed to make chemically significantly comparisons. There is moreover at least one case[17] where a similar GVB procedure apparently led to an erroneous estimate of the relative energies of two isomeric species, one a biradical and the other a normal molecule. While the lack of empirical tests makes it difficult to assess the likely performance of this approach in the present connection, the difference in energy between **3** and **5b** calculated by Noell and Newton (77 kcal/mol) would make it very difficult to explain the formation[6] of **7b** from **7a** on treatment with lithium dimethylamide. Even if **3** were formed, it would be expected to rearrange immediately to **5b**. Noell and Newton did not even establish that **3** was a minimum on the GVB potential surface.

In the case of MINDO/3, the available evidence indicates that, outside a few areas of specific weakness which have been clearly delineated by the very extensive published[3,22] tests to which MINDO/3 has been subjected, the results for hydrocarbons are comparable with those from high level ab initio procedures. There is no reason to suppose that problems should arise in the case of the benzynes; indeed, the MINDO/3 heat of formation for **1** (118.3 kcal/mol) agrees very nicely with (identical) estimates (118.5 kcal/mol) from two very different experimental studies.[8,23] At the time the MINDO/3 work[4] was carried out, the status of MINDO/3 concerning biradicals was still uncertain. Calculations for several "forbidden" pericyclic reactions where the transition states seem to be biradicals[24] have since indicated that energies calculated by MINDO/3 with 3 × 3 CI are too negative by ca. 15 kcal/mol, due to overestimation of the correlation energy,[25] and the same seems to be true also for biradical-like species in general.[26] If the difference between the MINDO/3 and MINDO/3-CI energies for a molecule is less than 15 kcal/mol, the former is then to be preferred; if greater, the CI value, plus 15 kcal/mol. In the former case, the molecule is best regarded as a closed shell species with some "biradical character", i.e., some tendency to react like a biradical. On this basis the MINDO/3 results,[4] correctly interpreted, lead to heats of formation for **1**, **2**, and **5b**, of 118, 118, and 132 kcal/mol, respectively, and at the same time imply that 1 and **2** are closed-shell species. Thus MINDO/3 agrees with GVB[15] in predicting *p*-benzyne (**5b**) to be significantly higher in energy than **1** but differs in predicting **1** and **2** (**4**) to have similar energies.

The smallness of the decrease in energy brought about by inclusion of CI is interesting. In the case of a genuine biradical, where the unpaired electrons are effectively isolated from one another, CI lowers the energy by 40–60 kcal/mol. The smaller differences indicate that **4** (**2**) and **5b** are not true biradicals, there being a significant coupling between the "unpaired" electrons. Indeed, as noted above, **4** (**2**) is best regarded on this basis as a closed shell species and the biradical character of **5b** is only a little greater. The coupling between the unpaired electrons in **4** (**2**)

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(17) GVB calculations by Harding and Goddard[18] predicted the biradical ($\cdot OOCH_2CH_2\cdot$) form of the adduct from singlet ($^1\Delta_g$) oxygen and ethylene to be lower in energy by 39 kcal/mol than the isomeric peroxirane. However, Stevenson et al.[19] have shown that the adduct from tetramethylethylene is th e peroxirane not the biradical. Since there is no reason why methyl groups should selectively stabilize the peroxirane, certainly not to the extent needed, it seems clear that the relative energies calculated by Harding and Goddard are in error by at least 30 kcal/mol. MINDO/3 calculations[20] predicted the most stable form of the adducts from most olefins, including ethylene, to be peroxiranes. It should be added that the term "peroxirane" refers here to the geometry of the adduct. Its electronic structure is probably best represented by a π complex formulation,[21] like that of protonated oxirane.

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(23) Gruetzmacher, H. T.; Lohman, J. *Liebigs Ann. Chem.* **1967**, *705*, 81.

(24) See, e.g.: Dewar, M. J. S.; Fonken, G. J.; Kirschner, S.; Minter, D. E. *J. Am. Chem. Soc.* **1975**, *97*, 6750 and papers cited therein.

(25) Inclusion of 3 × 3 CI provides complete compensation for the extreme electron-pair correlation between the unpaired electrons in a biradical. However, since MINDO/3 and MNDO already allow for normal correlation being parametrized to reproduce experimental energies of molecules, the allowance for the unpaired electrons in a biradical is correspondingly overestimated if CI is included.

(26) For example, triplet excited states. Extensive studies of these will be published shortly.

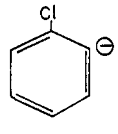
Table I. MNDO-Calculated Heats of Formation of the Isomeric Benzynes (kcal/mol)

compd	RHF	CI	UHF	triplet RHF/HE
1	138.2	125.7,^{a} 125.7^b	119.9	142.0
2	146.7	136.6^a		
3	167.0	157.6^a	155.6	
4		130.9,^{a} 126.6^b	126.5	135.7
5	173.9	131.6,^{a} 128.7^b	117.4	133.7

^{a} Calculated using the standard 3 × 3 CI. ^{b} Calculated using all significant configurations. ^{c} Reference 7.

is probably due largely to a "through-space" interaction, the calculated[4] geometry indicating the existence of a strong attraction between the quaternary carbon atoms. In the case of **5b**, however, the interaction must be via the intervening σ bonds. A similar 1,4 interaction between radical centers in a six-membered ring has been demonstrated for the "chair" Cope rearrangement of 1,5-hexadiene by MINDO/3 calculations.[27]

In view of these uncertainties, we thought it would be of interest to reinvestigate the C_6H_4 system using the MNDO method,[28] which has been found to give good results for a very wide variety of hydrocarbons and for ions and radicals derived from them.[28,29] Comparative tests[30] have shown it to be at least comparable in accuracy with ab initio calculations using a double-ζ basis set. Furthermore, studies of several photochemical reactions[31] have suggested that while the energies calculated for open-shell systems tend to be too negative, the errors are systematic, so that the energies of isomeric open-shell species are well reproduced. We also studied two related reactions, namely the formation of the three benzynes by deprotonation of chlorobenzene to one or other of the three isomeric chlorophenyl anions, **15**, **16**, and **17**, followed



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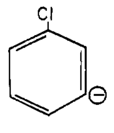

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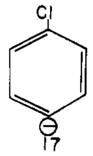

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by loss of chloride ion, and the degenerate rearrangement of hex-3-ene-15-diyne (**8b** **9b**; see eq 1).

Procedure

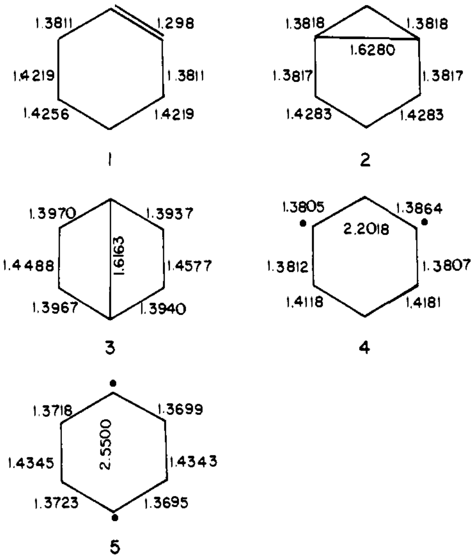

Figure 1. Geometries calculated by MNDO-CI for the five isomeric dehydrobenzenes, **1–5b**.

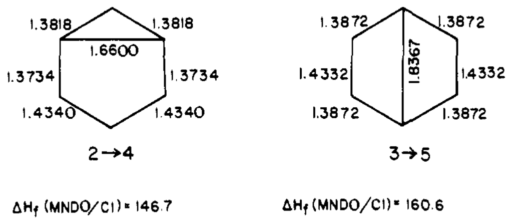

Figure 2. Geometries of the transition states, and activation energies (ΔH_f, kcal/mol), calculated for (a) **4** → **2**; (b) 5b → **3**.

Table II. Comparison of the MNDO-Calculated Relative Energies with Previously Reported MINDO/3 and ab Initio Results

compd	MNDO E_{rel}	MINDO/3 $E_{rel}{}^a$	ab initio $E_{rel}{}^b$
1	0^d	0^d	0
4	8^e	0^{c,d}	14.5
5	9^e	14^e	23.3

^{a} Reference 4. ^{b} Reference 8. ^{c} Actually the MINDO/3 geometry more nearly approximates the bicyclic structure **2**. ^{d} RHF calculation. ^{e} CI calculated energy + 15 kcal/mol.

Table III. MNDO (MINDO/3) Energies^a (kcal/mol) for the Reactants and Activated Complexes

compd	H_f	H_f- (transition state)	E_a
15	40.8 (38.6)	84.0 (78.0)	43.2 (39.4)
16	43.4 (39.9)	100.0 (80.6)	56.6 (40.7)
17	43.6 (41.5)	100.2^b (98.1)	56.6 (56.6)

^{a} RHF calculation. ^{b} CI calculated energy for the transition state located by UMNDO + 15 kcal/mol.

The calculations were carried out using our standard MNDO program[32] and parameters,[28,32] geometries being optimized without making any assumptions by a modified[32] Davidon–Fletcher–Powell[33] procedure. Since the C_6H_4 surface involves biradical-like species (e.g., **4**, **5b**), the calculations were repeated, using the spin-unrestricted[34] version (UMNDO) of MNDO. UMNDO is known[35] to give heats of formation that are too negative by 15–25 kcal/mol, due to overestimation of the correlation energy. Use of 3 × 3 CI[29] is much better but also much more expensive in computer time, due to the cost of calculating derivatives of the energy.[36] This problem was minimized in the present case by using the UMNDO geometries as starting geometries in the MNDO/CI calculations. Reactions were studied by taking an appropriate internuclear distance as the reaction coordinate.[37] The transition states found in this way were refined and characterized by the McIver–Komornicki[38] pro-

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(35) See ref 25. The errors are larger[26] in the case of UMNDO than UMNDOA-CI because the spin-unrestricted treatment provides additional allowance for correlation effects involving the paired electrons.

(36) Since the CI wave function is not variationally optimized, the bond order matrix is not invariant for small changes in the geometry.

(37) The term "reaction coordinate" is used here in its original sense, to denote a geometrical variable that changes during a reaction and whose value at any point along the reaction path can be taken as a measure of the extent to which the reaction has proceeded. The normal coordinate in a transition state, corresponding to translation across it, is better termed the *transition coordinate*.

(38) (a) McIver, J. W.; Komornicki, A. *Chem. Phys. Lett.* **1971**, *10*, 303. (b) McIver, J. W.; Komornicki, A. *J. Am. Chem. Soc.* **1972**, *94*, 2625.

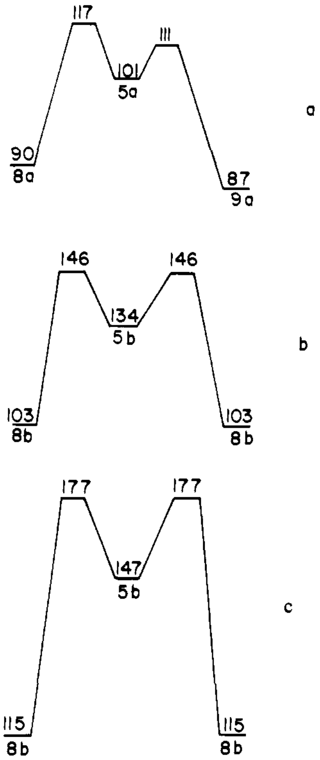


Figure 3. Reaction profiles for the rearrangements of 3-hexene-1,5-diynes: (a) deduced from experiment for **6a**; calculated (b) by MINDO/3, (c) by MNDO, for **6b**.

cedure.[39] We also carried out calculations for some of the biradical-like species using more extensive CI. As expected,[40] the results differed only a little from those with 3 × 3 CI.

Results

Table I shows the heats of formation calculated for **1**–**5b** by MNDO, UMNDO, and MNDO/CI. Apart from the MNDO results for **4** and the UMNDO ones for **2**, all five species were predicted to correspond to local minima on the potential surface.

Since MNDO/CI seems the best MNDO-type procedure for open-shell systems, and since it alone reproduces all five isomers, the structures given by it are alone indicated in Figure 1.

The interconversions of **2** with **4**, and of **3** with **5b**, were studied using the length of the transannular bond as the reaction coordinate. The geometries calculated for the transition states, and the corresponding activation energies, are shown in Figure 2.

Table II compares the energies of **2** (**4**) and **5b**, relative to that of **1**, calculated by various procedures.

Table III shows the results of calculations for the isomeric chlorophenyl anions, **15**–**17**, and for their conversion to benzynes.

Figure 3 compares the calculated reaction profiles with those deduced from an experimental study[7] of the rearrangement of **6** (R = H; R′ = $CH_2CH_2CH_3$).

Discussion

MNDO agrees with MINDO/3 in predicting *p*-benzyne to exist in either of two isomeric forms, **3** and **5b**. The barriers to conversion of **3** to **5b**, calculated by both methods, are also similar (MNDO, 3.0; MINDO/3, 4.6 kcal/mol). As noted above, Breslow et al.[6] have presented strong evidence for the existence of the closed-shell form, **3**, as a stable species.

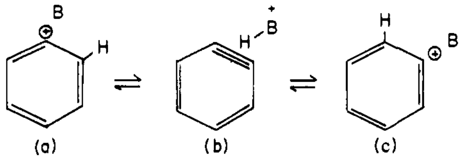
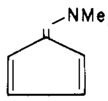


Figure 4. Proposed mechanism for hydrogen migration in phenyl cation. The transformations take place in a relatively long-lived encounter complex.

MNDO, however, differs from MINDO/3 in predicting similar isomerism in the case of *m*-benzyne. The predicted difference in energy between the bicyclohexatriene (**2**) and biradical (**4**) structures is much less than in the case of **3**/**5b** (10 vs. 29 kcal/mol) and the barrier to conversion of **2** to **4** is much larger (9 vs. 3 kcal/mol), the biradical isomer (**4**) being predicted to be again the more stable. As noted above, the bicyclic isomer (**2**) has been shown[5] to occur as an intermediate in a reaction. However, only a small yield of the product (**18**) derived directly from it was obtained. The other products were benzene derivatives which could have been formed from the more stable biradicaloid isomer, **4**. This interpretation is consistent with the MNDO results, according to which **2** should be the product obtained by elimination of HBr from **6** but should rearrange easily to **4**.



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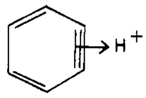

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As noted above, neither MNDO nor MINDO/3 can be used directly to study open-shell systems, in particular biradicals or biradicaloids, because allowance must be made for the unusually large correlation of the motions of the "unpaired" electrons. Since the C_6H_4 system involves such species, the calculations were repeated using UMNDO and MNDO-CI. As in the case of MINDO/3, these procedures give energies for biradicals and biradicaloids that are too negative, by 15–25 kcal/mol (UMNDO) or 10–15 kcal/mol (MNDO-CI). In the case of normal closed-shell molecules, the energies given by MNDO, MNDO/CI, and UMNDO do not differ by more than 2–3 kcal/mol at most. The results in Table I therefore confirm the MINDO/3 conclusion, that all five C_6H_4 isomers, **1**–**5b**, have significant biradical character. With these corrections, the MNDO heats of formation for **1**, **4**, and **5b** are 138, 146, and 147 kcal/mol, respectively. MNDO thus predicts an order of stability similar to that from the GVB calculation[15] but with a smaller spread of energy. This is clearly an area where MNDO performs less well than MINDO/3, as indeed is often the case for hydrocarbons. However, the agreement between the three procedures in predicting a relatively large difference in energy between **1** and **5b** makes it very unlikely that the similar thresholds for deuterium loss from **10**, **11**, and **12a** can be due to the three isomeric benzynes having similar heats of formation. Table II summarizes the results of the various calculations for **1**, **2** (**4**), and **5b**.

The conclusion that *p*-benzyne is significantly less stable than *o*-benzyne is supported by Bergman's[7] study of the rearrangement of **8a** to **9a**. Since the reaction is exothermic, the first step (**8a** → **5a**) must be rate determining if **5a** is indeed a stable intermediate. Now the *n*-propyl groups in **8a** and **5a** are attached in each case to sp^2 hybridized carbon atoms. The difference in energy between **8a** and **8b** should then be the same as that between **5a** and **5b**.[41] The heat of formation of **5a** cannot be much less positive than that of **8a** because otherwise byproducts would have been formed in the rearrangements by polymerization of **5a**. It follows that the heat of formation of **5b** cannot be less than that of **8b**.

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(39) Transition states are refined by minimizing the scalar gradient of the energy and characterized by calculating and diagonalizing the Hessian (force constant) matrix. This should have one, and only one, negative eigenvalue.

(40) As already noted, introduction of CI in MINDO/3 or MNDO does not lower the energy of a normal molecule by more than 1 or 2 kcal/mol. The exceptionally strong correlation between the "unpaired" electrons in a biradical-like species is moreover completely compensated by use of 3 × 3 CI. Introduction of further CI in a biradical has no more effect than introduction of CI in a normal molecule.

(41) See: Dewar, M. J. S. "The Molecular Orbital Theory of Organic Chemistry"; McGraw-Hill, New York, 1969; Sections 4.11–4.15.

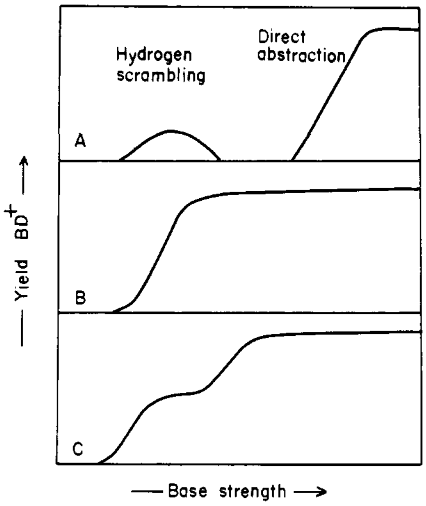

Figure 5. yield of BD^+ from **11** or **12a** as a function of base strength; (A) when ΔH_f for **11** (**12a**) is much greater than that for **1**; (B) when the ΔH_f are similar; (C) when ΔH_f for **11** (**12a**) is somewhat greater than that for **1**.

While the latter has not been measured, it can be estimated[42] to be 133 kcal/mol by assuming group additivity, the bonds in it being localized.[41] This then represents a lower limit to the heat of formation of **5b**, so the difference in heat of formation between *o*- and *p*-benzyne must be at least 12 kcal/mol, subject of course to the rather large uncertainty (~5 kcal/mol) in the heat of formation of **1**.

As a further check we carried out calculations by MNDO, with and without 3 × 3 CI, and by UMNDO, for the degenerate rearrangement of **8b** (→**9b**). In each case the reaction was predicted to take place via **5b** as a stable intermediate, in agreement with the mechanism suggested by Bergman;[7] see Figure 4. The calculated activation energies are greater than that observed for **8a** (27 kcal/mol). The difference may be partly due to hyperconjugative and/or σ-conjugative[43] interactions in the transition state from **8a**, due to the fact that the CC bonds in it are no longer localized and so may interact with the propyl groups.

How then can we explain the results reported by Pollack and Hehre,[8] given that *p*-benzyne, at least, almost certainly has a heat of formation different from that of *o*-benzyne? It is of course possible that phenyl cation was generated in their experiments with enough excess energy to overcome the apparently very high barrier to rearrangement—but this seems very unlikely in view of the relatively low electron energy (10–15 eV) used to generate it and the fact that two such rearrangements would be needed to bring the deuterium in **12a** into a position adjacent to the positive charge. We would like to suggest an alternative explanation which, if correct, may also have implications in other gas-phase rearrangements of ions.

Bimolecular reactions in the gas phase do not normally take place by a single collision between the reactants. Enough kinetic energy is usually converted into vibronic energy for the reactants to remain associated by van der Waals forces until the system reaches the transition state for the reaction, this requiring both a correct geometrical orientation of the reactants and concentration of enough vibrational energy in the appropriate modes. Such encounter complexes should play a much more important role in reactions involving ions because the reactants will be held together much more strongly, by charge/dipole and charge-induced dipole interactions.

Consider now such a complex formed by a base (B) with phenyl cation (**10a**). The base will naturally tend to hover round the positive charge in **10a** (Figure 4a) so it will in any case tend to abstract the adjacent proton, apart from the fact that **1** seems to be the preferred product. If, however, B and **10a** remain in contact for an appreciable time and if B and **1** have similar basicities, the ortho proton may be transferred to and fro between them and such a reversible transfer will of course lead to a 1,2-hydrogen migration in **10a**; cf. Figure 5A–C. This could account for the observation[8] that the critical base strength for abstraction of hydrogen from **10a** is the same for all positions, the 1,2-hydrogen shifts effectively scrambling the position of the positively charged carbon atom in the ring. Naturally if B is a much stronger base than **10a**, the hydrogen transfer may become irreversible, thus inhibiting the scrambling. However, a sufficiently strong base will abstract protons from the meta and para positions directly, so deuterium abstraction from **11** or **12a** would still be observed. This would explain Pollack and Hehre's results, because deuterium would in each case be abstracted from a position ortho to the positively charged carbon atom in **10a**.

Suppose, however, that Noell and Newton's estimates (Table II) of the energies of **4** and **5b**, relative to that of **1**, are correct. A base with a proton affinity ca 15 kcal/mol greater than that of **10a** would then abstract an ortho hydrogen atom essentially irreversibly but would not be strong enough to abstract deuterium from **11** or **12a**. A plot of the deuteron yield (in the form of BD^+) from **11** or **12a** vs. base strength would then be of the form indicated by A in Figure 5, the minimum corresponding to bases too strong to scramble hydrogen but not strong enough to abstract deuterium directly. The second threshold (X) for **11** or **12a** would then lead to an estimate of the proton affinity of **4** or **5b** and hence of its heat of formation.

If, however, the relative energies follow the pattern predicted by MINDO/3, the corresponding plot for **11** should show only a single threshold (see B in Figure 5) because the energies of **1** and **4** would then be similar. The plot for **12a**, however, would be the same as before (i. e., A in Figure 5) because **5b** would be much higher in energy than **1** or **4** (**2**).

Finally, if the energies followed the pattern predicted by MNDO, **4** being higher in energy than **1** but lower than **5b**, the plot for **11** might show an inflection (C in Figure 5), the energies of **1** and **4** being too close together for there to be a true minimum.

Such an investigation would be valuable because the kind of mechanism suggested here may well apply in the case of other gas-phase reactions of ions. It provides a way in which a reversible bimolecular reaction between an ion and a neutral molecule may proceed to equilibrium in the gas phase, even at very low pressures, equilibriation being brought about by a single encounter between the reactants.

Another point of interest concerns the multiplicity of the ground states of the three isomeric benzynes. The ortho isomer would of course be expected to have a singlet ground state, because a normal classical structure can be written for it. This indeed has long been known to be the case. The situation concerning the meta and para isomers is, however, less certain. If they are biradicals, as the classical representations (**4b**, **5b**) indicate, they would be expected to have triplet ground states. The MINDO/3 calculations, however, predicted both of them to have singlet ground states and the same conclusion follows from the GVB calculations[15] and the MNDO ones reported here (Table I). The critical case is clearly **5b**, for which all three procedures predict the singlet–triplet splitting to be the smallest.

Lockhart and Bergman[44] have presented evidence suggesting strongly that the intermediate in the rearrangement of **8a** to **9** is a singlet. It must also exist for quite a long time before undergoing conversion to **9** because it undoubtedly corresponds to quite a deep well on the potential surface. There is therefore little doubt that the singlet structure must be its ground state. Since our calculations confirm its identification[7] as a *p*-benzyne and since there is no reason why the propyl groups in it should have any significant effect on the singlet-triplet separation, there seems little doubt that *p*-benzyne (**5b**) itself must also have a singlet ground

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[42] The difference in heat of formation (ΔH_f) between **86** (ΔH_f, 12.5 kcal/mol[28]) and vinylacetylene (ΔH_f, 72.8 kcal/mol[28]) is 60.3 kcal/mol. Assuming replacement of a second hydrogen in ethylene to have the same effect as that of the first, the heat of formation of **8b** is estimated to be 72.8 + 60.3 = 133 kcal/mol.

[43] Dewar, M. J. S. *Bull. Soc. Chim. Belg.* **1979**, *88*, 957.

[44] Lockhart, T. P.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 4090.

J. Am. Chem. Soc. **1983**, *105*, 3167-3172

state. This would confirm our conclusion that it is in fact a biradicaloid, derived from the biradical by a strong through-bond interaction between the radical centers.

o-Benzyne was originally obtained as a reaction intermediate by dehydrochlorination of chlorobenzene by base. If the meta and para isomers are comparable in stability with *o*-benzyne, as the MINDO/3 calculations[4] and those reported here suggest, may their derivatives also be obtainable by the action of base on suitable precursors? *o*-Benzyne would of course be expected to be formed most easily in this way because the hydrogen atoms adjacent to chlorine in chlorobenzene are the most acidic and because the ortho isomer is probably the most stable. It should, however, be possible to obtain the other isomers in cases where the ortho positions are blocked by suitable substituents. To test this possibility, we calculated the energies of the three chlorophenyl anions, **15–17**, and of the transition states for their conversion to benzynes by loss of chloride ion. As Table III shows, all three isomers are predicted to be formed in this way via intermediates of not too dissimilar energy, so derivatives of all three should indeed be obtainable by the action of base on suitable precursors.

The possibility that derivatives of *m*- and *p*-benzyne might play a role as intermediates in reactions, comparable in importance with *o*-benzyne, has not been seriously considered until now because it was always assumed that the meta and para isomers would be high-energy biradical-like species, incapable of formation under the conditions used to prepare *o*-benzyne itself. Our calculations suggest that derivatives of *m*-benzyne, and perhaps also of *p*-benzyne, should be obtainable in this way, and exeriments designed to test these predictions are in progress.

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Registry No. 1, 462-80-6; **2**, 1552-99-4; **3**, 1552-98-3; **4**, 1828-89-3; **5b**, 3355-34-8; **15**, 72863-53-7; **16**, 77748-34-6; **17**, 77748-42-6.

Kinetics of Breakdown of the Tetrahedral Intermediate of an O,S-Acyl Transfer Reaction

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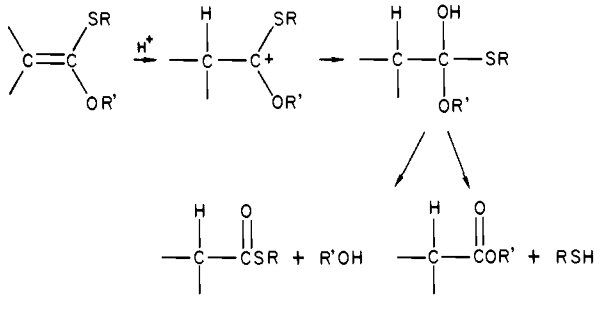
Abstract: The hydrolysis of the ortho thiolester 2-methoxy-2-(4-methoxyphenyl)-1,3-oxathiolane proceeds with an initial exocyclic cleavage producing as intermediates the (4-methoxyphenyl)-1,3-oxathiolan-2-ylium ion (R^+) and the hemiorthothiolester 2-hydroxy-2-(4-methoxyphenyl)-1,3-oxathiolane (ROH). The latter species is the tetrahedral intermediate of the O,S-acyl transfer of the 4-methoxybenzoyl group from one end of 2-mercaptoethanol to the other. These two species are formed in equilibrium as transient intermediates in acid solution, and a kinetic analysis furnishes directly the rate constants for the decomposition of ROH. This occurs in a noncatalyzed reaction ($k_3{}^\circ$) and an H^+-catalyzed reaction ($k_3{}^H$). At pH >2.5 the only product of the hydrolysis is 2-mercaptoethyl 4-methoxybenzoate (O) derived from C–S cleavage of ROH. In more acidic solutions increasing amounts of C–O cleavage product 2-hydroxyethyl 4-methoxythiolbenzoate (S) are observed. This behavior can be analyzed in terms of the noncatalyzed decomposition of ROH producing only O and the H^+-catalyzed decomposition producing only S. This analysis independently reproduces the ratio $k_3{}^\circ/k_3{}^H$ found in the kinetics. These results are compared with those obtained in other systems where hemiorthothiolester type tetrahedral intermediates are formed. The direct kinetic analysis available here verifies the mechanism commonly accepted to explain partitioning behavior. A comparison is also made with the analogous hemiorthoester 2-hydroxy-2-(4-methoxyphenyl)-1,3-dioxolane, the tetrahedral intermediate of an O,O-acyl transfer reaction. The hemiorthothiolester undergoes the noncatalyzed breakdown 5 times more rapidly and the H^+-catalyzed breakdown 100 times more slowly.

Evidence for the presence of a tetrahedral addition intermediate in an O,S-acyl transfer reaction was first presented by Fedor and

$$\mathrm{RC({=}O)SEt} \underset{\nu_{-1}}{\overset{\nu_1}{\rightleftharpoons}} \mathrm{RC(SEt)(OH)OH} \xrightarrow{\nu_2} \mathrm{RC({=}O)OH} + \mathrm{EtSH} \quad (1)$$

Bruice[1] through the observation of a break in the rate–pH profile for the hydrolysis of ethyl trifluorothiolacetate. This was explained by a change with pH in the preferred direction of breakdown of a kinetically significant intermediate, as was subsequently confirmed by Bender and Heck[2] using carbonyl oxygen exchange. The pH dependency for the partitioning of this type of tetrahedral intermediate seems to be general. It is seen in the hydrolysis of other thiolesters[3,4] and is also apparent in the products obtained in the hydrolysis of ketene *O,S*-acetals[3,5] (eq 2) and ethyl thionbenzoate[6] (eq 3). In all these cases[1–6] C–S bond cleavage occurs predominantly if not exclusively in the decomposition at low acidities, while C–O bond cleavage or a mixture of C–O and C–S bond cleavages occurs at high acidities. This has been interpreted in terms of the presence of different forms of the intermediate,



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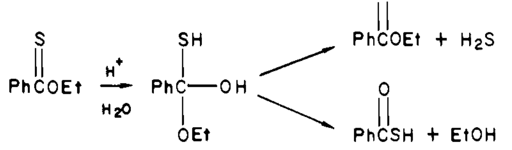

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