MINDO/2′ and MINDO/3 Studies of the Electrocyclic Conversion of Dewar Benzene into Benzene[1]

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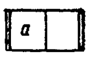
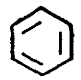
Summary MINDO/3 studies are reported of the electrocyclic conversion of Dewar benzene, and of its 1-chloro- and 1,4-dichloro-derivatives, into benzene, chlorobenzene, and *p*-dichlorobenzene, the calculated activation energies being 114·2, 104·1, and 104·1 kJ mol^{-1} respectively; the transition states of these 'forbidden' reactions show no peculiar features.

The preceding communication[2] described a study of the electrocyclic conversion of bicyclo[2,1,0]pentene into cyclopentadiene. Here we report a similar investigation of the conversion of Dewar benzene (**1**) into benzene (**2**).

Our preliminary studies were carried out using the MINDO/2′ approximation,[3] the geometries being optimized by the SIMPLEX[4] method. Since the system is rather large, we first assumed D_2 symmetry to be retained throughout. Using the length (r) of the interannular bond (a in **1**) as the reaction co-ordinate, the reaction was found to show 'chemical hysteresis,'[5] the forward and backward paths differing. The same was true when the interannular angle (θ in **3**) was used as the reaction co-ordinate. A two-dimensional contour map of energy as a function of r and θ showed the 'two-valley' structure characteristic[4,5] of anti-aromatic reactions, accounting for the 'chemical hysteresis.' The corresponding activation energy (174·0 kJ mol^{-1}) was too high (observed[6], 96·2 kJ mol^{-1}). Removal of the D_2 symmetry restriction led to a similar potential surface but a better estimate (150·6 kJ mol^{-1}) for the activation energy.



(1)



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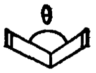

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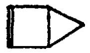

(4)

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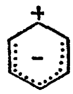
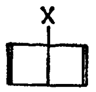
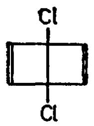


(6)



(7) a; X=Cl
b; X=F



(8)

The high value for the activation energy is not surprising, given that MINDO/2′ is known to underestimate strain energies in small rings. Indeed, the satisfactory value given[2] by MINDO/2′ for the rearrangement of bicyclo [2,1,0]pentene (**4**) to cyclopentadiene (**5**) was probably coincidental, owing to the fact that MINDO/2′ also overestimates the stability of cyclopentadiene. We have therefore re-examined the conversion of (**1**) into (**2**), using MINDO/3 and our new geometry and transition-state programs.[7] The calculated activation energy (114·2 kJ mol^{-1}) now agreed reasonably well with experiment. The calculated geometry of the transition state is shown in the Figure.

It will be seen that the transition state has only C_v symmetry, one of the methine groups having approached its final position more closely than the other. We have recently shown[8] that 'forbidden' electrocyclic reactions tend to proceed *via* biradical intermediates, reached *via* highly unsymmetrical transition states. The transition state for (**4**) → (**5**) appears on the other hand to be symmetrical, owing to the severe geometrical constraints in (**4**). The rearrangement of (**1**) to (**2**) represents an intermediate situation, the transition state being unsymmetrical but corresponding nevertheless to a concerted process. As a result of the asymmetry of the transition state, the HOMO/LUMO crossing in the rearrangement of (**1**) occurs *after* the transition state has been passed. It will be shown elsewhere[9] that this has important consequences concerning the chemiluminescence of the reaction.

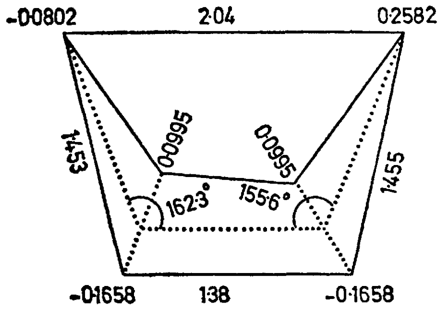


Figure. Calculated (MINDO/3) geometry (distances in Å) and distribution of formal charge in the transition state for conversion of Dewar benzene into benzene.

The calculated distribution of formal charge in the transition state for (**1**) → (**2**) is also shown in the Figure. It will be seen that the structure veers towards the zwitterionic form (**6**). This suggests that an electron-attracting or electron-releasing group at a bridgehead position in (**1**) should accelerate the rearrangement. Breslow *et al.*[6] have indeed found that the 1-chloro-(**7a**) and 1-fluoro-(**7b**) derivatives of (**1**) rearrange much faster than (**1**) itself.

Similar MINDO/3 calculations for the 1-chloro-(**7a**) and 1,4-dichloro-(**8**) derivatives of (**1**) indicated that the reactions should take a similar course, each with an activation energy of 104·1 kJ mol^{-1}. The transition states were similar to that for (**1**) (see Figure) with the chlorine atom in (**7a**) attached to the more negative bridgehead position.

These results account for the fact that (**7a**) rearranges faster than (**1**) and the difference between the calculated activation energies (10 kJ mol^{-1}) agrees with that between the experimental ones (16 kJ mol^{-1}) within the limits of experimental error (standard deviation in each activation energy, 4—8 kJ mol^{-1}). While our calculations also account for the fact that the second chlorine atom in (**8**) does not lead to a further acceleration, the calculated activation energy is too small.†

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† The reported[6] activation energy ($127\cdot6$ kJ mol^{-1}) is probably too high since the corresponding entropy ($\Delta S^\ddagger$) of activation was 12 cal K^{-1} mol^{-1} whereas those for (**1**) and (**7a**) were -5 and -9 cal K^{-1} mol^{-1} respectively. Since the standard deviation in $\Delta S^\ddagger$ was $3\cdot5$—7 cal K^{-1} mol^{-1}, and since all three reactions seem likely to have simila rvalues for $\Delta S^\ddagger$, the activation energy for rearrangement of (**8**) is probably near 113 kJ mol^{-1}. There is, however, no doubt that (**8**) rearranges much more slowly than (**1**).

[1] A preliminary account of this work was given at the Twenty-Third National Organic Chemistry Symposium, Tallahassee, Florida, June 1973.
[2] M. J. S. Dewar and S. Kirschner, preceding communication.
[3] N. Bodor, M. J. S. Dewar, and D. H. Lo, *J. Amer. Chem. Soc.*, 1971, **94**, 5303.
[4] See M. J. S. Dewar, *Fortchr. Chem. Forsch.*, 1971, **23**, 1.
[5] M. J. S. Dewar and S. Kirschner, *J. Amer. Chem. Soc.*, 1971, **93**, 4291, 4292.
[6] R. Breslow, J. Napierski, and A. H. Schmidt, *J. Amer. Chem. Soc.*, 1972, **94**, 5906.
[7] R. C. Bingham, M. J. S. Dewar, and D. H. Lo, *J. Amer. Chem. Soc.* 1975, **97**, 1285.
[8] M. J. S. Dewar and S. Kirschner, *J. Amer. Chem. Soc.*, 1974, **96**, 5244.
[9] M. J. S. Dewar and S. Kirschner, *J. Amer. Chem. Soc.*, in the press.