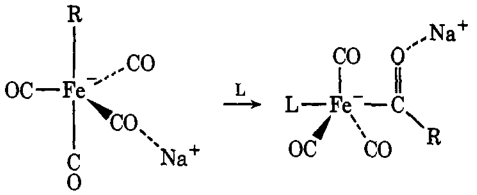
suggests that Lewis acids might be found to accelerate alkyl–acyl migrations.



I

The existence of ion paired structures in THF solution has been inferred by Edgell from ir studies of $NaCo(CO)_4$. The $Co(CO)_4$ anion had C_{3v} symmetry with the sodium ion adjacent to a single carbonyl group.[6] Our structure is written in accord with these findings.

This ion-pairing hypothesis is fortified by all of our observations. The added solvents MP and HMPA are thought to act by competitively solvating the ion pair to form a solvent-separated species which is apparently unreactive (eq 3). Such a solvation equilibrium would lead to an inverse rate dependence on the added solvent. Plots of $(Kk_2)^{-1}$ *vs.* the concentration of MP or HMPA are linear at low concentrations of added solvent. At higher concentrations the plots become strongly nonlinear, evidence of multiple solvation of the cation probably leading to free ions.[7] The fit of experimental points in the pseudo-first-order kinetic curves is excellent at the low concentrations of MP and HMPA, indicating that the ions are present as solvent-separated pairs rather than free ions. HMPA is more effective at depressing the rate than MP.

$$Na(RFe(CO)_4) + S \rightleftharpoons \{Na^+\}S\{RFe(CO)_4^-\} \qquad (3)$$

Addition of the sodium complexing dicyclohexyl-18-crown-6 polyether to **1** in THF dramatically inhibited the migration rate to the point of 1:1 equivalence after which more crown ether had negligible effect (Table I). The conductivity of **1** in THF is a linear function of concentration down to 10^{-4} *M* suggesting that the ion-pair dissociation is small (tight binding) even at this low concentration. The conductivity of $Na(RFe(CO)_4)$ in THF increases linearly upon addition of the crown ether with a sharp break at the equivalence point, suggesting that the crown complex is present as free ions. In a future publication we will describe the equally dramatic effect of ion pairing on the alkylation of the tetracarbonylferrate(−II).

Acknowledgment. We are indebted to R. Komoto, W. Siegl, and S. Winter for counsel and technical assistance. This work was supported by the National Science Foundation, Grant No. GP 20273X.

---

[6] W. F. Edgell in "Ions and Ion Pairs in Organic Reactions," M. Szwarc, Ed., Vol. 1, Wiley, New York, N. Y., 1972; W. F. Edgell and J. Lyford, IV, *J. Amer. Chem. Soc.* **93**, 6407 (1971).

[7] Behavior of this type has been observed in solutions of ketyl ion pairs in similar solvents: K. S. Chen, S. W. Mao, K. Nakamura, and N. Hirota, *J. Amer. Chem. Soc.*, **93**, 6004 (1971).

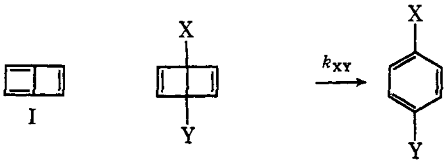
James P. Collman,* James N. Cawse, John I. Brauman
Department of Chemistry, Stanford University
Stanford, California 94305

Received March 27, 1972

Unsymmetrical Substituent Effects on the Antiaromatic Transition State for the Rearrangement of Bicyclo[2.2.0]hexadiene to Benzene

Sir:

In the course of approaches[1,2] to butalene (I) we have prepared 1-chlorobicyclo[2.2.0]hexadiene (II) (chloro(Dewar benzene)) and 1,4-dichlorobicyclo-[2.2.0]hexadiene (III) (dichloro(Dewar benzene)). A notable difference between II and III was immediately apparent. Compound II is thermally quite unstable at room temperature with respect to rearrangement to chlorobenzene, while compound III requires heating for a similar rearrangement to dichlorobenzene. Since it was reported[3] that parent Dewar benzene itself (IV) rearranges only on warming, the observations suggested that there is a striking unsymmetrical substituent effect on the ease of rearrangement of Dewar benzenes.



II, X = Cl; Y = H
III, X = Y = Cl
IV, X = Y = H
V, X = F; Y = H

This is confirmed by the data in Table I. The thermal rearrangements of Dewar benzenes were followed in tetrachloroethylene solution in a temperature-controlled nmr cavity, and the temperatures were carefully calibrated with a thermocouple. As the relative rate data in Table I show, the monochloro derivative II rearranges considerably faster than does either the parent compound IV or the dichloro derivative III. This is also reflected in the activation parameters;[4] indeed the difference in $\Delta H^{\ddagger}$ between compounds II and III is more than 11 kcal/mol, an enormous effect which is partially compensated by the difference in $\Delta S^{\ddagger}$. We have also prepared the fluoro(Dewar ben-

Table I. Kinetic Data on Rearrangements of Bicyclo[2.2.0]hexadienes to Benzenes

Compd	$k_{XY}(24.3°) \times 10^6$, sec^{-1}	$\Delta H^{\ddagger}$, kcal/mol^b	$\Delta S^{\ddagger}$, eu^b
II	464	19.1	−9.4
III	0.0084^a	30.5	+12.0^c
IV	5.18^a	23.0	−5.0^d
V	1860		

^{a} Extrapolated from data at higher temperatures. ^{b} The standard deviation of $\Delta H^{\ddagger}$ was 1-2 kcal/mol, corresponding to 3.5-7 eu. ^{c} From k_{XY} at 74.0°. ^{d} From k_{XY} at 48.4°.

---

[1] R. Breslow, *Pure Appl. Chem.*, **28**, 111 (1971).

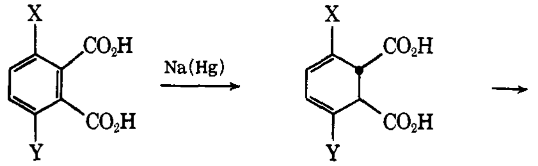
[2] R. Jones and R. Bergman, *J. Amer. Chem. Soc.*, **94**, 660 (1972), footnote 9.

[3] E. E. van Tamelen, S. P. Pappas, and K. L. Kirk, *ibid.*, **93**, 6092 (1971), and earlier publications.

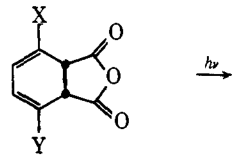
[4] The only previous determination of activation parameters for rearrangement of a Dewar benzene derivative appears to be that of J. F. Oth (*Recl. Trav. Chim. Pays-Bas*, **87**, 1185 (1968)), who found a $\Delta H^{\ddagger}$ of 36.8 kcal/mol and a $\Delta S^{\ddagger}$ of 8.4 eu for the thermal isomerization of the hexamethyl derivative to hexamethylbenzene, and that of H. C. Volger and H. Hoogeveen (*ibid.*, **86**, 830 (1967)), who found $\Delta H^{\ddagger} = 31$ kcal/mol for the same process.

zene) (V), and it rearranges even more rapidly than does compound II.

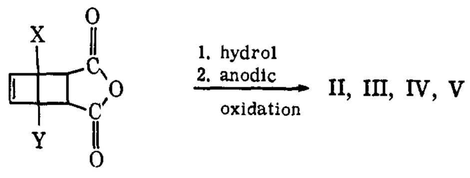
Compound II was prepared by a sequence analogous to that used by van Tamelen[3] for the preparation of IV. Thus, 3-chlorophthalic acid could be converted in 40% yield to *trans*-1,2-dihydro-3-chlorophthalic acid (VI), mp 152–155°, by reduction with 3% sodium amalgam in aqueous acetic acid. This was converted to 3-chloro-*cis*-1,2-dihydrophthalic anhydride (VII), mp 65–67°, in 70% yield by treatment with acetic anhydride. The sublimed anhydride was converted to the tricyclic anhydride VIII, mp 134–135°, in 60–80% yield by photolysis in pentane. Anhydride VIII was converted to II by hydrolysis in aqueous pyridine and electrolytic decarboxylation at −25°, using a clean[5] platinum electrode. Since II is thermally quite unstable, it must be handled and extracted into solvents at temperatures near 0°. In a similar fashion, 3,6-dichlorophthalic acid was converted to the corresponding 3,6-dichloro-1,2-dihydrophthalic acid (IX), mp 212–214°, and this afforded the corresponding *cis*-anhydride X, mp 87–89°. This was also converted to the photoproduct XI, and XI was converted to III on electrolysis, although in this case no special precautions about temperatures were necessary.



VI, X = Cl; Y = H
IX, X = Y = Cl
XII, X = F; Y = H



VII, X = Cl; Y = H
X, X = Y = Cl
XIII, X = F; Y = H



VIII, X = Cl; Y = H
XI, X = Y = Cl
XIV, X = F; Y = H

The parent compound IV was prepared as described[3] by van Tamelen, except that anodic decarboxylation was performed using a potentiostat. The compound was extracted into tetradecane, and vacuum transferred into the rearrangement solvent. The very unstable fluoro(Dewar benzene) V was prepared *via* XII (mp 149–151°), XIII (mp 80–82°), and XIV (mp 124–125°).

It is striking that a single halogen substituent makes rearrangement of the Dewar benzene much faster, but that a second halogen more than reverses the effect.[6] A direct disrotatory[7] opening of these bicyclohexadienes to the benzenes involves an antiaromatic transition state.[8] Apparently this transition state can be markedly stabilized by unsymmetrical substitution on the two central carbons, whose electrons should be highly polarizable as the bond breaks. This is in a sense a push-pull effect in an antiaromatic transition state,[9] related to known push-pull stabilization[10] of antiaromatic compounds. An alternative description is that this substitution pattern permits easier mixing[11] of the neutral destabilized transition state with a charge-transfer state which should stabilize it.

Thus, it seems likely that in the transition state for rearrangement of the monohalo(Dewar benzenes) II or V there is appreciable polar charge separation, which is less available for the rearrangements of III or IV. Interpretation of activation parameters in solution kinetics is always hazardous, but the apparently more negative $\Delta S^{\ddagger}$ for II, compared with IV, is consistent with the greater solvation expected for the transition state of II if it is indeed more polar. The large positive entropy of activation for the rearrangement of compound III may indicate substantial solvent release as the originally polar III, with two closely aligned dipoles, rearranges through a transition state with less polarity to *p*-dichlorobenzene which has no macroscopic dipole moment.[12]

---

(5) As the electrode aged, it became an effective catalyst for the isomerization of II to chlorobenzene even at −25°.

(6) The parameters for III are similar to those for hexamethyl(Dewar benzene).[4] Thus, the interesting difference in the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for III and IV may indicate that the parent Dewar benzene IV has a geometry available for rearrangement[7] which is of higher energy with more hindered derivatives.

(7) This is discussed in detail by R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie GmbH, Weinheim/Bergstr., West Germany, 1970, p 174.

(8) The transition state can be thought of as involving a normal cyclic delocalization of four electrons, although the extra double bond cannot be completely ignored. This transition state is to a disrotatory opening of a cyclobutene as butalene (I) is to cyclobutadiene.

(9) R. Gompper and G. Seybold in "Aromaticity, Pseudo-Aromaticity, Anti-Aromaticity" (E. D. Bergmann and B. Pullman, Ed., Israel Academy of the Sciences and Humanities, Jerusalem, Israel, 1971, p 215) describe the fast rearrangement of a probable push-pull substituted Dewar benzene reaction intermediate.

(10) See ref 9, and R. Gompper and G. Seybold, *Angew. Chem.*, **80**, 804 (1968).

(11) N. D. Epiotis, *J. Amer. Chem. Soc.*, **94**, 1924, 1935, 1941, 1946 (1972).

(12) Support of this work by the National Institutes of Health and a postdoctoral fellowship (Arthur Schmidt) from the Deutsche Forschungsgemeinschaft are gratefully acknowledged.

Ronald Breslow,* John Napierski, Arthur H. Schmidt
Department of Chemistry, Columbia University
New York, New York 10027

Received June 12, 1972

The Nature of the 1:1 Adduct of Methylpentaborane(9) with Trimethylamine, $CH_3B_5H_8 \cdot N(CH_3)_3$

Sir:

The formation of the 1:1 adduct of 1-ethylpentaborane(9) and trimethylamine was reported in the literature[1] and the compound was formulated as $(CH_3)_3NH^+C_2H_5B_5H_7^-$. Detailed study of such an adduct formation was thought to yield information valuable in elucidating mechanisms of formation of the diam-

---

(1) W. V. Hough, L. J. Edwards, and A. F. Stang, *J. Amer. Chem. Soc.*, **85**, 831 (1963).