

of eq 8 and 9 are negligible and logarithmic plots of $(ct/cc) - 1$ and $(ct/tt) - 1$ vs. T^{-1} are predicted to be linear. The data are plotted in this fashion in Figure 1, with points down to 159°K giving $E_5 - E_{-5} = \Delta H_5 = 324 \pm 22$ cal/mol and $k_6 A_{-5}/k_7 A_5 = k_7 A_5/k_6 A_{-5} = 1.00 \pm 0.01$. The fit of the observations to the mechanism is illustrated by the lines drawn in Figure 1 which were calculated using $E_5 - E_{-5} = 333$ cal/mol, $k_6/A_5 = k_7/A_{-5} = 10^8$, and $E_5 = 3450$ cal/mol. The latter parameters were somewhat arbitrarily selected so that the calculated lines pass close to the low-temperature points for the low-viscosity media. Solvent barriers to interconversion of ³cp and ³tp are expected in temperature regions for which the twisting process is slower than solvent relaxation, and it is likely that a large portion of the activation energies E_5 and E_{-5} is medium derived.¹⁰

Small thermal⁷ and/or solvent barriers to twisting from planar triplets will not affect isomerization quantum yields provided that decay of planar triplets directly to the ground state remains slow relative to twisting, e.g., $k_8 \ll k_4$. Starting with tc in IPMP at 77°K, $\phi_{tc \rightarrow tt}/\phi_{tc \rightarrow cc} = 2.9$. Since these conditions inhibit allyl methylene triplet interconversion, this ratio reflects mainly a preference for twisting of cis over trans double bonds in the planar triplet.

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(10) J. Saltiel and J. T. D'Agostino, *J. Amer. Chem. Soc.*, submitted for publication.

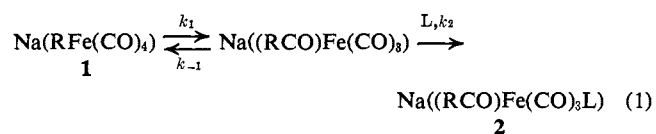
(11) Alfred P. Sloan Foundation Fellow.

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The Role of Ion Pairing in Reactions of Metal Carbonyl Anions. I. Cation-Assisted Alkyl-Acyl Migratory Insertions

Sir:

Disodium tetracarbonylferrate(−II) is an inexpensive, selective reagent converting aliphatic halides into aldehydes¹ and unsymmetrical ketones.² These reactions involve anionic alkyl and acyl intermediates³ **1** and **2**. The fullest synthetic application of these reagents requires a detailed understanding of the reaction mechanisms. We have investigated the alkyl-acyl insertion (eq 1) and found the rate to be dramatically



influenced by the nature of the gegenion and added solvents. We interpret these results as arising from ion pairing and conclude that ion-pairing phenomena

(1) M. P. Cooke, *J. Amer. Chem. Soc.*, **92**, 6080 (1970).

(2) J. P. Collman, S. R. Winter, and D. R. Clark, *ibid.*, **94**, 1788 (1972).

(3) These intermediates have been isolated and characterized: W. O. Siegl and J. P. Collman, *ibid.*, **94**, 2516 (1972).

may have hitherto unrecognized importance in the chemical reactivity of many metal carbonyl anions.⁴

The usual mechanism for alkyl-acyl insertion⁵ involves a reversible migration followed by reaction with a ligand, L, to form the coordinatively saturated product (eq 1). Depending on the relative rate constants k_{-1} and k_2 and [L], such reactions can exhibit rate laws having first, second, or intermediate order. Using the complex **1**, R = *n*-nonyl, the rates of alkyl loss and acyl gain, determined by quenching with acid affording nonane and decanal, respectively (glc analysis), are equivalent within experimental error. Tertiary phosphines were employed as L, usually in tenfold or greater excess, affording pseudo-first-order behavior. The reaction obeyed the second-order rate law (eq 2) which is consistent with either a rapid prior equilibrium (eq 1, $k_{-1} \gg k_2$) or a simple concerted second-order reaction. In accordance with previous observations⁵ we have assumed eq 1. The observed pseudo-first-order rate constant was found to be linearly dependent on the phosphine concentration (0.03–0.4 M), with apparent second-order rate constants $Kk_2 = 0.066$ M^{−1} sec^{−1}, L = triphenylphosphine; and $Kk_2 = 0.23$ M^{−1} sec^{−1}, L = dimethylphenylphosphine; both at 25°, R = *n*-nonyl.

$$-d[\text{NaRFe}(\text{CO})_4]/dt = Kk_2[\text{L}][\text{Na}(\text{RFe}(\text{CO})_4)] \\ K = k_1/k_{-1} \quad (2)$$

Polar solvents often act⁵ as transient ligands in alkyl-acyl insertions and affect the rate by increasing k_1 . However, in the present case certain solvents produce a different but dramatic effect. For example, addition of a few per cent of *N*-methylpyrrolidone (MP) or hexamethylphosphoric triamide (HMPA) to Na(RFe(CO)₄) in tetrahydrofuran (THF) strongly inhibits the rate. The rate is also remarkably dependent on the nature of the cation, Li⁺ > Na⁺ ≫ (Ph₃P)₂N⁺, spanning a range of at least three orders of magnitude (Table I).

Table I. Effect of Cation on Rate of Allyl Migration^a

Complex	Kk_2 , M ^{−1} sec ^{−1}
LiRFe(CO) ₄	0.24
NaRFe(CO) ₄	0.065
(Ph ₃ P) ₂ NRFe(CO) ₄	<1.5 × 10 ^{−4}
Na(dicyclohexyl-18-crown-6)RFe(CO) ₄	<7 × 10 ^{−4}

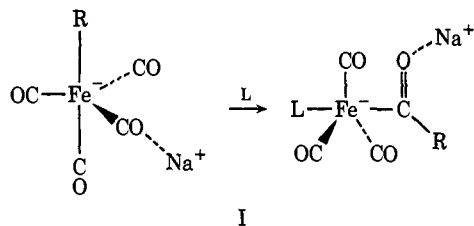
^a Data taken at $T = 25^\circ$, with THF as solvent and R = nonyl.

These results are consistent with a mechanism in which a sodium or lithium ion pair is the kinetically reactive species. Apparently migration of the alkyl to an adjacent terminal carbonyl is facilitated by electrostatic interaction of small polarizing cations which are probably associated with the electron-rich carbonyl oxygens and help stabilize the extra negative charge which accompanies the migrating alkyl group (mechanism I). Larger more diffuse cations or solvent-separated cations are less effective. This mechanism

(4) Ion pairing is known to be of importance in the reactions of carbanions: see for example M. Shinohara, J. Smid, and M. Szwarc, *ibid.*, **90**, 2175 (1968); T. E. Hogen-Esch and J. Smid, *ibid.*, **89**, 2764 (1967).

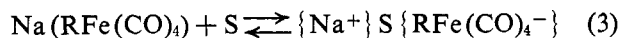
(5) R. W. Glyde and R. J. Mawby, *Inorg. Chem.*, **10**, 854 (1971), and references contained therein.

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



The existence of ion paired structures in THF solution has been inferred by Edgell from ir studies of $\text{NaCo}(\text{CO})_4$. The $\text{Co}(\text{CO})_4$ 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 equi-



librium 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.

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 $\text{Na}(\text{RFe}(\text{CO})_4)$ 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).

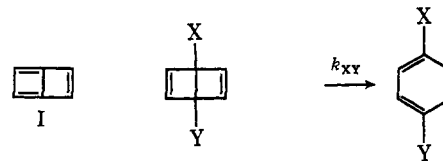
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Unsymmetrical Substituent Effects on the Antiaromatic Transition State for the Rearrangement of Bicyclo[2.2.0]hexadiene to Benzene

Sir:

In the course of approaches^{1,2} to butalene (I) we



II, X = Cl; Y = H

III, X = Y = Cl

IV, X = Y = H

V, X = F; Y = H

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 reported³ 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.

This is confirmed by the data in Table I. The thermal

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

Compd	$k_{XY}(24.3^\circ) \times 10^6, \text{sec}^{-1}$	$\Delta H^\ddagger, \text{kcal/mol}^b$	$\Delta S^\ddagger, \text{eu}^b$
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 ΔH^\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° .

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 ΔH^\ddagger between compounds II and III is more than 11 kcal/mol, an enormous effect which is partially compensated by the difference in ΔS^\ddagger . We have also prepared the fluoro(Dewar ben-

(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 ΔH^\ddagger of 36.8 kcal/mol and a ΔS^\ddagger of 8.4 eu for the thermal isomerization of the hexamethyl derivative to hexamethylbenzene, and that of H. C. Volger and H. Hoogveen (*ibid.*, **86**, 830 (1967)), who found $\Delta H^\ddagger = 31$ kcal/mol for the same process.