PROJECT ADMINISTRATION DATA SHEET

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Title: Cation Effects in Organoalkali Metal Chemistry; Organocesium Chemistry

ADMINISTRATIVE DATA

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REstrictions

See Attached NSF Supplemental Information Sheet for Additional Requirements.

Travel: Foreign travel must have prior approval — Contact OCA in each case. Domestic travel requires sponsor approval where total will exceed greater of $500 or 125% of approved proposal budget category.

Equipment: Title vests with GIT

COMMENTS:

This is a continuing grant. Previous project number was G-33-670/Grovenstein.

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Project Director(s): Dr. Erling Grovenstein, Jr.

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☐ None

☒ Final Report (FCTR)

☐ Closing Documents

☒ Final Report of Inventions (if positive)

☐ Govt. Property Inventory & Related Certificate

☐ Classified Material Certificate

☐ Other

Continues Project No: G-33-670

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Form OCA 60:1028
TO: Dr. Kenneth G. Hancock  
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FROM: Dr. Erling Grovenstein, Jr.  
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SUBJECT: Brief Technical Report upon "Cation Effects in Organoalkali Metal Chemistry; Organocesium Chemistry."

NSF Grant No. CHE-8009810
For Period: July 21, 1981 - July 15, 1982

The following articles on work completed under the present NSF Grant have been accepted for publication (preprints have been mailed to the Foundation):

The M.S. thesis of Randall Lee Hughes on "Cation and Substituent Effects upon Migratory Aptitudes in Rearrangements of Carbanions" was completed June, 1982. Captain Hughes' work was partially supported by the present grant (chemicals and supplies); the remainder of his support was from the United States Military Academy, West Point, New York, which sent Captain Hughes to the Georgia Institute of Technology for advance training in Chemistry prior to a teaching assignment at the Academy. In a continuation of prior work Hughes finds that the reaction of trans-5-chloro-4,4-diphenyl-2-pentene with lithium in diethyl ether at -78°C gives (according to the
products of carbonation) the expected 1 (49%) and 2 (10%) and, surprisingly, 34% of an unknown lithium compound (UNKI). When the reaction mixture is warmed to +35°C for 4 hrs., both 1 and UNKI nearly disappeared and the yield of 2 increases to 89%. Evidently both 1 and UNKI rearrange to 2:

\[
\begin{align*}
\text{Ph}_2\text{C} & \quad \text{CH}_2\text{Cl} \\
\text{Li, } -78°C & \quad \text{Et}_2\text{O} \\
\quad & \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad
\end{align*}
\]

Since the rearrangement of 1 to 2 is thought to proceed by way of the addition product 3 whose carbonation product is 4, the synthesis of 4 (as methyl ester in above) 85:15 mixture of diastereomers) was accomplished by a Simmons-Smith addition of CH₂ to methyl 4,4-diphenyl-2-methyl-3-butenoate. However, the carbonation product of UNKI was different from either of the synthetic diastereomers of 4. It is currently hypothesized that UNKI is the alternative cyclobutane derivative 5 which is formed stereospecifically by syn-addition and presumably returns to 1 by syn-elimination prior to stereospecific migration (retention of trans geometry of propenyl group) to give 2.
The organolithium compound 1 when formed in THF at -78°C gave upon warming the solution to 10°C about equal amounts of 2 and the phenyl migration product 6 (M = Li). When the organolithium compound 1 is allowed to react with K⁺ in THF at -78°C, the resultant organopotassium compound rearranged with almost exclusive formation of 6 (M = K). This carbanion rearrangement therefore has large solvent and cation effects.

The possibility of [1,3] migration of phenyl in competition with [1,2] migration has been studied in 2,2,3-triphenylpropyl-1,1-d₂ alkali compound 7 prepared from 1-chloro-2,2,3-triphenylpropane-1,1-d₂ (see Scheme I). Reaction of this halide with lithium in THF at -78°C gave 7 (M = Li) containing 0.7% or less of [1,3] phenyl migration product 8 (M = Li). Conversion of this organolithium compound into the potassium compound by reaction with KO-t-Bu at -78°C in THF gave benzyl migration (9 + 10) and [1,2] phenyl migration (11) in a ratio of 2.2 : 1.
The benzyl migration product contained 4.6% of product (2) which had undergone [1,3] phenyl migration. Repetition of this experiment but with CsO-t-Bu in place of K-O-t-Bu gave benzyl migration and [1,2] phenyl migration in a ratio of 0.39 : 1. The benzyl migration product contained 4.3% of product which had undergone [1,3] phenyl migration or about the same as with KO-t-Bu. Reaction of the halide with potassium metal in THF at 65°C gave chiefly product of [1,2] phenyl migration. The benzyl migration product contained 7.1% of product which had undergone phenyl migration. In contrast the organolithium compound 2 when warmed to 50°C gave only the product of benzyl migration containing no product which had undergone [1,3] phenyl migration. Thus [1,3] phenyl migration increases with temperature as well as along the series Li⁺ << K⁺ = Cs⁺ and parallels [1,2] phenyl migration. However [1,2] phenyl migration greatly exceeds [1,3] phenyl migration in carbanions just as it does for rearrangements of carbonium ions and free radicals.

In another area Dr. Jagvir Singh has continued with study of the reaction of 9-chloromethyl-9-tert-butylfluorene with alkali metals. The product from lithium after carbonation gives a typical distribution of acids as shown below:

Hence the major product at -75°C is the expected organolithium compound 16 accompanied by minor amounts of 17 and 18.
When the reaction mixture from 12 is warmed to 0°C for 1.75 hr the yield of 15 rises to 78% or after 3.0 hr to 88% along with 3% of 12, 5% of 15, and 6% of a new acid 20 which arises from 19.

In summary, the organolithium compound 16 when warmed to 0°C in THF two rearrangements as summarized below in an overall yield from chloride 12 of about 80%.

The major rearrangement is by Path A. As to the mechanism of this rearrangement the following isotope labeling experiment establishes that the methyl group of 16 arises from the CH₂Li group of 16.
The source of the proton of the CD$_2$H group is at present unknown but is assumed to arise from the tert-butyl group; in studies to be undertaken in the near future, the tert-butyl group will be replaced by tert-butyl-d$_9$ to check this postulate.

In studies aimed at testing the generality of rearrangement of 9-alkyl lithiomethylfluorene compounds, the 9-ethyl compound 22 has been prepared from the chloride 21 in a yield of some 73% along with 2 to 5% of 23. When 22 was allowed to warm to 0°C for 3 hr (under conditions similar to those for 16), the yield of 22 decreased to about one-third of its initial value, the yield of 23 doubled, and the yield of 9-ethyl-9-methylfluorene rose from 5% to 25%. Thus 22 undergoes neither of the two rearrangements of the tert-butyl derivative 16. The unusual rearrangements of 16 seem to depend upon the existence of steric strain within 16 which is released (steric acceleration) upon rearrangement.

To test this postulate the 9-neopentyl-9-lithiomethylfluorene 25 prepared in some 60% yield from the chloride 24. When 25 is warmed to 0°C for 1..., some 60% of 25 rearranges to an isomer which is thought to be structure 26 based on the GC mass spectrum of the product of carbonation. When this rearrangement was allowed to proceed in the presence of a commercial sample of α-butyllithium, some 27%
of the rearrangement product contained a butenyl group (evidently from presence of C₄H₇Li in the commercial sample of n-butyllithium) in place of a neopentyl group. Hence the rearrangement of 25 is analogous to the minor Path B for rearrangement of the tert-butyl compound. Tentatively we formulate this rearrangement:

![Chemical structure diagram]

The rearrangements reported here of compounds 16 and 25 are new for organolithium compounds containing only C, H, and Li; however, the rearrangement of 16 by Path A is analogous to the a',β fragmentations of nitrogen ylides and Path B to some Wittig rearrangements of ethers. Perhaps the most similar known rearrangement (Path B) is that of compound 27 which was shown by Grovenstein and Westworth (1963) to rearrange via:

\[ \text{Ph}_2\text{CCH}_2\text{Li} \quad 27 \quad \xrightarrow{0^\circ \text{THF}} \quad \text{[Ph}_2\text{C=CH}_2 + \text{PhCH}_2\text{Li}] \quad \rightarrow \quad \text{Ph}_2\text{CCH}_2\text{CH}_2\text{Ph} \quad \text{Li}^+ \quad 28 \]

The rearrangement of 27 involves intervention of resonance stabilized benzyllithium while that of 16 (Path B) and 25 evidently involve tert-butylithium and neopentylithium respectively. The mechanisms of all these rearrangements including the Wittig ether rearrangement are in some doubt. Our new work demonstrates for the first time that a saturated alkyl group can undergo [1,2] migration in an organolithium compound containing only C, H, and Li or that such an organolithium compound may undergo fragmentation analogous to an a',β elimination of ylides.
Finally Dr. A. M. Bhatti has continued to study reactions of aromatic compounds with Cs-K-Na alloy:

\[
\text{ArH(THF)} + \text{Cs-K-Na (liq. alloy)} \rightarrow \text{ArH}^+, \text{Cs}^+ \text{ (solid)}
\]

\[
\text{ArH(THF)} + \text{Cs-K-Na (liq. alloy)} \rightarrow \frac{1}{2} (\text{ArH})^{2-}, 2 \text{ Cs}^+ \text{ (solid)}
\]

The equilibrium constant for both of these reactions may be written as

\[
K = \frac{1}{(\text{ArH}) \text{ (atom fraction of Cs in Cs-K-Na alloy)}}
\]

where the concentrations in parenthesis represent equilibrium values. These concentrations are obtained from their initial values and measurement of the extent of reaction as given by the amount of products from quenching with water. Since the quantity of products, starting with the reactants, can approach but not exceed the equilibrium value, the maximum value of \( K \) (for which good analytical data are available) is taken to approximate the equilibrium value. Unfortunately equilibrium is attained slowly in the present system (3 to 6 hours is the normal reaction time), likely because of the low solubility of Cs in THF and also perhaps because of the slow rate of precipitation of the ionic products.

At \(-45^\circ C\) in THF the following values of \( K \) were obtained (the ± value represents the deviation from the average with the next largest value of \( K \)):

\[
\begin{align*}
\text{Si(CH}_3)_3 & \quad > \quad \text{Si} & \quad > \quad \text{CH}_3 & \quad > \quad \text{CH}_3 \quad > \quad \text{CH}_2\text{CH}_3 \\
19,000 \pm 9,000 & \quad > \quad 1,000 \pm 200 & \quad > \quad 672 \pm 5 & \quad > \quad 465 \pm 60 & \quad > \quad 160 \pm 1
\end{align*}
\]

At \(-75^\circ C\) in THF the following values of \( K \) were similarly obtained:

\[
\begin{align*}
\text{CH}_2\text{CH}_3 & \quad > \quad \text{CH}_3\text{CH}_(CH}_3)_2 & \quad > \quad \text{CH}_3 \quad > \quad \text{CH}_3 \quad > \quad \text{C(CH}_3)_2 \\
1700 & \quad > \quad 930 & \quad > \quad 770 \pm 200 & \quad > \quad 740 & \quad > \quad 350 \pm 50 & \quad > \quad 35
\end{align*}
\]
The measured values are in fair qualitative accord with the relative values\(^1\) \((K_{\text{ArH}}/K_{\text{PhH}})\) as measured by \(K_{\text{equil}} \times 1000\) for the following homogeneous reaction in 1:1 (v/v) of THF-DME at -100°C (K\(^+\) as counterion, Na-K alloy reactant):

\[
\begin{align*}
\text{PhH}^+ + \text{ArH} & \rightleftharpoons \text{PhH} + \text{ArH}^- \\
1000 & > 230 \pm 50 & > 110 \pm 10 & > 45 \pm 6 & > 25 \pm 6
\end{align*}
\]

\[
\begin{align*}
& > \text{CH}_3 \\
20 \pm 5 & > 9 \pm 2 & > 1.1 \pm 0.2
\end{align*}
\]

Detailed comparison shows that our value at -45°C for ethylbenzene comes after rather than before m-xylene and at -75°C our value for p-xylene comes after isopropylbenzene rather than before ethylbenzene. Our values at -45°C are more compressed (benzene giving 6 fold more reaction than ethylbenzene) than the values in THF-DME at -100°C (benzene giving 22 fold more reaction than ethylbenzene); however, our values at -75°C show about the same relative extent of reaction as the literature values at -100°C. We think that the general parallel between our data with Cs-K-Na alloy and the literature data for K-Na alloy establishes the general validity of our experimental technique (chemical analysis by GC as oppose measurements for the literature values).

The striking thing about our work with Cs-K-Na alloy (cesium as counter cation) as opposed to K-Na alloy (potassium as likely counter cation) is the much greater extent of reaction with the cesium alloy. Thus with Cs-K-Na in THF at -45°C, we

have measured an extent of reaction of benzene as high as 94%; while with K-Na alloy in 2:1 (v/v) THF:DME, benzene is converted to radical anion only to about 0.1%.

An important experimental observation during the past year is the discovery that the reaction with Cs-K-Na alloy has a negative temperature coefficient; the extent of reaction is greater at -75°C than at -45°C. Thus ethylbenzene gave 69% reaction at -45°C but gave 97% reaction at -75°C. More striking, when unable to get appreciable reaction of isopropylbenzene, p-xylene, and tert-butylbenzene at -45°C (isopropylbenzene gave 2% reaction in 5.5 hr), these hydrocarbons gave yields as high as 91, 87, and 88% respectively at -75°C.

Finally, the products of reaction of aromatic hydrocarbons with Cs-K-Na alloy have been indicated above to be a mixture of radical anions and dimers of radical anions. For benzene the ratio of dimer to monomer varies widely from 0.11 to 4.2, for toluene from 1.1 to 5.4. For the other compounds studied this ratio has been about constant within a factor of 2 or less. For benzene and toluene, the black monomeric product (ArH\(^-\), Cs\(^+\)) appears to be quite insoluble in THF and evidently equilibrates very slowly with the yellow dimer [(ArH)\(^2-\), Cs\(^+\)]. The product ratio appears to be dependent upon the relative rate of formation of the black versus the yellow product; thus thermodynamic equilibrium between the yellow and black products is not attained (for two pure solid product phases, only one is expected to persist at equilibrium according to the phase rule as applied to the present system).

For ethylbenzene, isopropylbenzene, tert-butylbenzene, m-xylene, and trimethylsilylbenzene the ratio of dimer to monomer is 1.7 or greater (up to 32 for trimethylsilylbenzene). Also all monoalkylbenzenes give > 99% of the product:

(This orientation was explicitly established for toluene, ethylbenzene, and tert-butylbenzene). In contrast, as noted in last year's progress report, trimethylsilylbenzene gives dimer containing only the para-para' product. While at -75°C meta-xylene gives a good yield (75%) of the 3,3',5,5'-tetramethyl dimer:

along with 18% of the monomeric radical anion, para-xylene gives a good yield of the monomeric radical anion (86%) but less than 0.7% of dimer (if any). Similarly ortho-xylene gives 20% of monomeric radical anion and less than 0.01% of dimer.

The above orientations and extents of reaction can be qualitatively explained on the basis that alkyl groups destabilize and trimethylsilyl groups stabilize carbanions in condensed phases (solutions or solids) and that large alkyl groups destabilize carbanions more than small alkyl groups (steric effect). To avoid this destabilization, radical anions of alkylbenzenes condense so as to locate the alkyl group on a carbon carrying little negative charge (hence on the meta position). For ortho- and para-xylene any dimer would have one methyl group on a carbon bearing much negative charge and hence no appreciable dimer is formed. The lower reactivity of ortho-xylene than of para-xylene can be attributed to a similar for these xylenes the degenerate Hückel MO's \( \psi_4 \) and \( \psi_5 \) have their degeneracy broken by interaction with the methyl groups. For para-xylene the antisymmetric orbital is more stable while for ortho-xylene the symmetric orbital is more stable and so are the occupied orbitals. Their symmetry and charge distributions are sketched below as obtained from simple HMO theory:
By occupying the orbitals shown the radical anion of para-xylene can more n-escape the destabilizing effect of methyl groups than that of ortho-xylene and therefore is formed to a larger extent at equilibrium. meta-Xylene should be similar to ortho-xylene at the level of HMO theory. The explanation in the present work as to why the meta isomer reacts to about the same extent as the para isomer with cesium is, in part, that much of the product from meta-xylene escapes destabilization from the methyl groups by formation of the dimer whose structure is given above. Thus it must be emphasized that our equilibrium constants $K$ pertain to formation of radical anions and/or dimers of radical anions, generally to both in likely a metastable equilibrium.
I. **Rearrangements of Organoalkali Metal Compounds**

A. **Propenyl vs. Phenyl Migration in (Z)- and (E)-2,2-Diphenyl-3-pentenyl Alkali Metal Compounds.** - Reaction of the cis-halide 1 with lithium in diethyl ether at -75°C gives the corresponding organolithium compound 2 which when warmed to 35°C rearranges to 4 largely with retention of geometry as deduced from the products of carbonation. The trans-halide 6 behaves similarly except that reaction with lithium at -75°C gives now both 7 and an unknown, likely 8; both 7 and 8 rearrange at 35°C to give 10. That the unknown is not 9 was shown by synthesis of the acid 11 (as an 85:15 mixture of diastereomers) which was different from the carbonation product of the unknown. Also in the solvent tetrahydrofuran (THF) at +10°C the lithium compound 7 again undergoes [1,2] propenyl migration to 10 with 98±2% retention of configuration; however in THF the product of carbonation also contains...
25% of \(\text{12}\) which results from a competing \([1,2]\) migration of phenyl. The organolithium compound \(\text{7}\) in THF at \(-75^\circ\text{C}\) upon cation exchange with KO-t-Bu undergoes exclusive phenyl migration.

The present work exemplifies a considerable cation effect in organo-alkali metal chemistry: the properties of a "carbanion" are modified by the nature of the counter cation and by the ligands which lie within the coordination sphere of the cation. The essential retention of configuration during \([1,2]\) migration of propenyl in lithium compounds \(\text{2}\) and \(\text{7}\) is of theoretical and practical interest; it contrasts with the report of Maercker and Streit\(^9\) that \([1,2]\) migration of the propenyl group in Grignard reagents is NOT stereospecific. Our work suggests that configuration is maintained in the likely intermediates \(\text{3}\) and \(\text{9}\) during rearrangement and for prolonged periods of time in \(\text{8}\) in ethereal solvents. Also no precedent exists for formation of a four-membered ring as in \(\text{8}\) from a reactant such as \(\text{7}\) which might more readily have formed a three-membered ring as in \(\text{9}\). Work is continuing in this interesting area.

**B. \([1,3]\) vs \([1,2]\) Migration of Phenyl in 2,2,3-Triphenylpropyl Alkali Metal Compounds.**

The possibility of \([1,3]\) migration of phenyl in competition with \([1,2]\) migration has been studied\(^8\) in 2,2,3-triphenylpropyl-1,1-d\(_2\) alkali compound \(\text{13}\) prepared from 1-chloro-2,2,3-triphenylpropane-1,1-d\(_2\) (see Scheme I). Reaction of this halide with lithium in THF at \(-78^\circ\text{C}\) gave \(\text{17}\) (\(M = \text{Li}\)) containing 0.7% or less of \([1,3]\) phenyl migration product \(\text{14}\) (\(M = \text{Li}\)). Conversion of this organolithium compound into the potassium compound by reaction with KO-t-Bu at \(-78^\circ\text{C}\) in THF gave benzyl migration \((\text{13} + \text{16})\) and \([1,2]\) phenyl migration \(\text{17}\) in a ratio of 2.2:1. The benzyl migration product contained 4.6% of product \(\text{15}\) which had undergone \([1,3]\) phenyl migration. Repetition of this experiment but with CsO-t-Bu in place of K-O-t-Bu gave benzyl migration and \([1,2]\) phenyl migration in a ratio of 0.30:1. The benzyl migration product contained 4.3% of product which had undergone \([1,3]\) phenyl migration or about the same as with K-O-t-Bu. Reaction of the halide with potassium metal in THF at \(65^\circ\text{C}\) gave chiefly product of \([1,2]\) phenyl migration. The benzyl migration product contained 7.1% of product which had undergone \([1,3]\) phenyl migration. In contrast the organolithium compound \(\text{13}\) when warmed to \(0^\circ\text{C}\) gave only the product of benzyl migration containing no product which had undergone \([1,3]\) phenyl migration. Thus \([1,3]\) phenyl migration increases with temperature as well as along the series Li\(^+\) \(<\) K\(^+\) \(<\) Cs\(^+\) and parallels \([1,2]\) phenyl migration. However, \([1,2]\) phenyl migration greatly exceeds \([1,3]\) phenyl migration in carbanions just as it does for rearrangements of carbonium ions and free radicals.

**C. Rearrangements of 9-Alkyl-9-Lithiomethylfluorenes.**

In conformity to the published report\(^10\) for 9-methyl-9-lithiomethylfluorene, 9-ethyl-9-lithiomethylfluorene (\(\text{18}\)) in THF does not undergo skeletal rearrangement to \(\text{20}\) likely because the expected spiro intermediate (\(\text{19}\)) is highly strained; instead at \(0^\circ\text{C}\) \(\text{18}\) undergoes protonation by the solvent to give 9-ethyl-9-methylfluorene.
In contrast, 9-tert-butyl-9-lithiomethylfluorene (21) undergoes two rearrangements:

The mechanism of the major rearrangement to 9-methylfluorenyl anion has been determined by isotope labeling experiments. Thus the methyl group of 22 arises from the lithiomethyl group since 24 yields 25. Also the required additional proton for the new methyl group comes from the tert-butyl group since 26 yields 28. The rearrangement is believed to proceed via the transition state 27. This mechanism is analogous to

that proposed for the decomposition of ylides (α , β mechanism), sulfoxides, and amine oxides. Like the latter two decompositions the decomposition of 26 proceeds with an abnormally large isotope effect (k_H/k_D > 20 at 0°C) which is likely due to quantum-mechanical tunneling in the transition state 27. Efforts are currently underway to measure this isotope effect with greater precision and at several temperatures.
Finally 9-neopentyl-9-lithiomethylfluorene 29 has been found to rearrange to a product which is tentatively assigned the structure 30 based on the mass spectrum and $^1$H NMR spectrum of the product of carbonation.

The rearrangement of 21 and 29 and the non-rearrangement of 18 and its 9-methyl analog are thought to arise from steric compressions in 21 and 29. An X-ray diffraction (with collaboration of Dr. Don VanDeveer) upon 9-tert-butyl-9-chloromethylfluorene (the precursor of 21) shows that the tert-butyl group presses against the benzenoid rings of the fluorene such that these exist at an angle of 170.4° to one another in the crystal (rather than the expected 180°).

D. Rearrangements of 2- and 3-p-biphenylalkyl Anions. - Our work upon reactions of 2- and 3-p-biphenylalkyl chlorides with alkali metals with preparation, in favorable cases, of labile spiro anions which can serve as intermediates in rearrangement of the p-biphenyl group has now been completed and published in full.

II. Reactions of Hydrocarbons with Cesium.

A. Benzene and Simple Derivatives. - Cesium (in the convenient form of Cs-K-Na eutectic alloy which is a liquid even at -78°C) reacts with benzene and related aromatic hydrocarbons according to the equation:

$$ \text{ArH (solvent)} + \text{Cs-K-Na (liq. alloy)} \rightleftharpoons \text{ArH}^-, \text{Cs}^+ \text{(solid)} $$

$$ \text{ArH (solvent)} + \text{Cs-K-Na (liq. alloy)} \rightleftharpoons \frac{1}{2} (\text{ArH})_2^-, 2 \text{Cs}^+ \text{(solid)} $$

The equilibrium constant for both of these reactions may be written as

$$ K = \frac{1}{(\text{ArH}) \text{(atom fraction of Cs in Cs-K-Na alloy)}} $$

where the concentrations are obtained from their initial values and measurements of the extent of reaction as given from the products of quenching with water. Equilibrium is attained slowly in the present system likely because of the low solubility of Cs in the ethereal solvent and the slow rate of precipitation of the ionic products. Some check on the attainment of equilibrium, at -45°C is possible by equilibration first at -70°C (where K is larger than at -45°C) and then at -45°C. The results are summarized in Table I which also records relative values as measured for the following homogeneous reaction in 1:1 (V/V) of THF-DME at 20°C with $^+K$ as counterion (Na-K alloy reaction):

$$ \text{PhH}^-, K^+ \text{(THF-DME)} + \text{ArH (THF-DME)} \rightleftharpoons \text{PhH (THF-DME)} + \text{ArH}^-, K^+ \text{(THF-DME)} $$
Table I indicates that the reducing power of Cs-K-Na alloy increases as the temperature is decreased and as the expected solvating power of the solvent increases. These trends are as has been observed with sodium and biphenyl; however with potassium and naphthalene the extent of reduction was independent of temperature and of solvent polarity (indeed no perfectly general order of "solvant polarity" exists for alkali metals - sodium is a more powerful reducing agent than potassium in THF but the order is reversed in 1,3-dimethoxypropane). Apparently the trends in Table I for cesium with changes of temperature and solvent are to be ascribed to increasing solvation of cesium ion in the complex with lowering of temperature and replacement of THF by DME. The effects observed are large and of practical importance. Thus under our experimental conditions, t-butylbenzene in THF reacted only 16% at -45°C but 85% at -75°C; o-xylene at -75°C reacted 27% in THF but essentially 100% in DME/THF.

For intercomparison of our Cs-K-Na alloy reactions with those of K-Na alloy, it should be noted that at -45°C in THF benzene reacts in yields as high as 94% while, with K-Na in 2:1 (v/v) THF:DME at -20° and -83°C, benzene is converted to radical anion only to 0.01 and 0.09% respectively. The observed reactions of benzene and derivatives with K-Na as reported in Table I could be measured only because of the very high sensitivity of esr spectrometry. Our work with Cs-K-Na alloy represents the first practical synthesis of the radical anions of the hydrocarbons listed in Table I. While exceptions exist, the general order of reaction of hydrocarbons in the table with cesium alloy parallels that with potassium alloy especially if the comparisons are made at as similar a temperature as possible.

We conclude that Cs-K-Na alloy in the most powerful reducing agent known for benzenoid hydrocarbons and that the power of this reagent increases to as yet unknown limits as the temperature is decreased and as the number of oxygens increases in solvents of the type \( \text{CH}_3 \text{O(CH}_2 \text{CH}_2 \text{O)}_n \text{CH}_3 \).
hydrocarbons show that the cleavage occurs in a dianion and normally occurs readily at -75°C according to the general process:

\[
\text{Cs-K-Na} \quad \text{THF, 0°C} \quad \rightarrow \quad 2 \text{CH}_2\text{CH}_2^- \quad \text{Cs}^+
\]

provided that the transition state can assume the preferred geometry below which permits the \(\sigma^*\) orbital of the bond undergoing cleavage to interact with the HOMO's of both aromatic rings. The relative rates of cleavage of meta- and para-methyl derivatives of bibenzyl may be correlated with the equilibrium acidities of toluene, \(m\)-xylene, and \(p\)-xylene in a modified Hammett relationship.

The quantitative cleavage of 1,2-diphenylethane and derivatives by Cs-K-Na alloy provides an attractive method of preparation of benzylesium and derivatives of known structure and free of impurities. For example, we have prepared \(o\)-methylbenzyl-\(a,a\)-d\(_2\)-cesium by the reaction:

\[
\text{CH}_3\text{CH}_3 \quad \text{K} \quad \text{CD}_2 \quad \text{CD}_2 \quad \text{THF, -75°C} \quad \rightarrow \quad 2 \text{CH}_3\text{CD}_2^- \quad \text{Cs}^+
\]

This organocesium compound is stable at -75°C but undergoes ready intramolecular \([1,4]\) sigmatropic migration of hydrogen from the \(o\)-methyl group to the methylene group when warmed to near room temperature.

**DESCRIPTION OF PROPOSED RESEARCH**

I. **Organocesium Dianions and Polyanions.**

Much less is known about the chemistry of multiply charged anions than of monoanions\(^{16}\); little is known about such anions with cesium as counter cation. The fundamental tenet of the present proposal is that organocesium dianions and polyanions can be prepared and that their chemical reactions will be novel and useful in synthesis and degradation. Development of this area of organoalkali metal chemistry should be of both theoretical and practical interest. Szwarc and co-workers have noted that in reactions of radical-anions of aromatic hydrocarbons, sometimes it is the trace of dianion in equilibrium with the radical monoanion which is the reactive substrate responsible for the observed product and that such reactions "may change their course if different counterions and solvents are involved in the process."

A. **Preparation of Organocesium Radical Anions, Dianions and Polyanions.** As Table I (see Resume of Progress to Date) makes clear, Cs-K-Na alloy is an extremely powerful reducing agent in ethereal solvents. Cesium, as judged by its position in the Periodic Table and its first ionization energy, is the most powerful metallic reducing agent in the gas phase. Thanks to its higher solvation energy, lithium is equal to cesium in its standard reduction potential in aqueous solution. The situation with
PART I—PROJECT IDENTIFICATION INFORMATION

1. Institution and Address
Georgia Institute of Technology
225 North Avenue, NW
Atlanta, Georgia 30332

2. NSF Program Chemistry Div. Chemical Dynamics Program

3. NSF Award Number CHE-8009810

4. Award Period From 9-1-80 To 4-1-84

5. Cumulative Award Amount $180,000

6. Project Title
"Cation Effects in Organooalkali Metal Chemistry; Organocesium Chemistry"

PART II—SUMMARY OF COMPLETED PROJECT (FOR PUBLIC USE)

The purpose of this work was to study cation effects in organooalkali metal chemistry and in particular to develop an organometallic chemistry of cesium for comparison with that of lithium. One major topic concerned variation of migratory aptitude of groups in organooalkali rearrangements as the counter cation is varied from lithium to potassium or cesium. Toward this end the rearrangements of 2,2-diphenyl-3-pentenyl, 2,2,3-triphenylpropyl and (9-alkyl-9-fluorenyl)methyl alkali metal compounds have been studied. With (Z)-2,2-diphenyl-3-pentenyl metal compounds, for example, the ratio of propenylophenyl migration was 22:1 with lithium in diethyl ether at +35 °C but was 1:177 with potassium in tetrahydrofuran (THF) at -75°C (or some 1700-fold difference).

A second major topic was study of the almost unique reactions of aromatic hydrocarbons with cesium. Thus Cs-K-Na alloy reacts with benzene in THF at -45°C to give the radical anion of benzene and its dimer in yields as high as 94%, whereas Na-K in 2:1 (v/v) THF:DME at -20° and -83°C reacts to give only 0.01 and 0.09% respectively of the radical anion of benzene. Equilibrium constants for similar reactions of Cs-K-Na alloy with aromatic hydrocarbons in THF at -45°C have been found to decrease in the order: trimethylsilylbenzene > benzene > toluene > m-xylene > p-xylene = ethylbenzene and, at -75°C, ethylbenzene > isopropylbenzene > t-butylbenzene > o-xylene. Under similar conditions 1,1-diphenylalkanes of type (C₆H₅)₂CHY, where Y is a carbanion-stabilizing group, have been found to react with cesium to give carbanionic products with novel [1,2] migration of phenyl, while 1,2-diarylalkanes undergo facile cleavage to benzylic anions.

PART III—TECHNICAL INFORMATION (FOR PROGRAM MANAGEMENT USES)

1. ITEM (Check appropriate boxes) NONE ATTACHED PREVIOUSLY FURNISHED TO BE FURNISHED SEPARATELY TO PROGRAM

a. Abstracts of Theses X
b. Publication Citations X
c. Data on Scientific Collaborators X
d. Information on Inventions X
e. Technical Description of Project and Results X
f. Other (specify) X

2. Principal Investigator/Project Director Name (Typed) Dr. Erling Grovenstein, Jr.

3. Principal Investigator/Project Director Signature

4. Date 4-17-84
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a. ABSTRACTS OF THESES
THE REARRANGEMENT OF
TRANS-2,2-DIPHENYL-3-PENTENYLTHIUM

A THESIS
Presented to
The Faculty of the Division of Graduate Studies
By
John Harold Northrop

In Partial Fulfillment
of the Requirements of the Degree
Master of Science in Chemistry

Georgia Institute of Technology
June, 1981
SUMMARY

The purpose of this research was to synthesize trans-5-chloro-4,4-diphenyl-2-pentene and to study the relative migratory aptitudes of vinyl vs. phenyl groups in trans-2,2-diphenyl-3-pentenyllithium formed by the reaction of the trans-alkyl chloride with lithium metal. In addition, the stereochemistry of the starting material, the precursor to the starting material, the vinyl migration product (trans-2,2-diphenyl-4-hexenoic acid ≅ TR) and the reference acids trans-2-benzyl-2-phenyl-3-pentenoic acid (PM1) and (E)-4,5-diphenyl-2-methyl-3-pentenoic acid (PM2) was studied.

The desired trans-chloride was made by Na-K alloy cleavage of trans-1,1-diphenyl-1-methoxy-2-butene, followed by reaction with methylene chloride. The methyl ether was prepared by reaction of trans-1-chloro-1-propene with lithium metal, followed by reaction with benzophenone and then methyl iodide.

Reaction of the trans-chloride in Et₂O with lithium metal for four hours at -78° gives primarily trans-2,2-diphenyl-3-pentenyllithium, because upon carbonation the reaction mixture is converted chiefly (78%) to trans-3,3-diphenyl-4-hexenoic acid (TU). When the same organolithium compound is warmed to 35° (Et₂O at reflux) and maintained at that temperature for four hours, the principle (89%) product of carbonation is TR, the result of vinyl migration. A small percentage (7%) of phenyl migration is observed. The stereochemistry of the double bond in the product of vinyl migration indicated 98±2% retention of configuration. In THF
the reaction of the trans-chloride with lithium metal for two hours at 
-78° gives, upon carbonation, primarily (84%) TU; this is essentially the 
same result as was observed with Et₂O as the solvent. However, upon 
warming the organolithium compound to 10°, and maintaining that tempera-
ture for four hours, the principle products of carbonation were 37% TR, 
47% PM1 and 12% PM2. The stereochemistry of the double bond in the pro-
duct of vinyl migration indicated 98±2% retention of configuration.

To determine the mechanism of the reaction, two additional experi-
ments were studied. In the first experiment, the organolithium reagent (Et₂O) 
formed at -40° was divided into aliquots. The first aliquot was carbon-
ated and gave primarily TU (58%) and TR (37%). The other aliquot was 
added to n-BuLi at -78°, was warmed to 35°, and was allowed to react for 
four hours at that temperature. Upon carbonation, the second aliquot 
gave primarily TR (91%) and phenyl migration (8%), but no 2,2-diphenyl-
heptanoic acid. In the second experiment, the organolithium compound 
formed at -78° in THF was divided into aliquots. The first aliquot was 
carbonated at -78°. The second aliquot was allowed to react eight hours 
longer at -78° and then was carbonated. Both aliquots gave, within ex-
perimental error, the same product ratios: 80% TU, 5% TR, 11% PM1, and 
3% PM2.
CATION AND SUBSTITUENT EFFECTS UPON MIGRATORY APTITUDES IN REARRANGEMENTS OF CARBANIONS

A THESIS
presented to
The Faculty of the Division of Graduate Studies
By
Randall Lee Hughes

In Partial Fulfillment
of the Requirements of the Degree
Master of Science in Chemistry

Georgia Institute of Technology
June, 1982
SUMMARY

The purpose of this research was threefold. First a study of the relative migratory aptitude of substituents in the reaction of trans-5-chloro-4,4-diphenyl-2-pentene with lithium metal followed by the reaction of the organolithium compound with KO-t-Bu was accomplished. Then a study of an unanticipated product from the organolithium reagent (prior to reaction with KO-t-Bu) which culminated in the synthesis of a possible structure. Finally a search was made for possible [1,3] phenyl migration in competition with known [1,2] phenyl and benzyl migration in 2,2,3-triphenylpropyl alkali metal compounds.

Reaction of trans-5-chloro-4,4-diphenyl-2-pentene in THF with lithium metal for three hours at -78°C reportedly gives trans-2,2-diphenyl-3-pentenyllithium because carbonation gave chiefly (75%) trans-3,3-diphenyl-4-hexenoic acid (TU). When the same organolithium compound is reacted in THF with KO-t-Bu for one hour at -78°C, the main product (64%) of carbonation is trans-2-benzyl-2-phenyl-3-pentenoic acid (PM1) along with 13% of (E) 4,5-diphenyl-2-methyl-3-pentenoic acid (PM2) and 15% of an unknown substance.

Whereas reaction of trans-5-chloro-4,4-diphenyl-2-pentene with lithium metal in diethyl ether at -78°C has been reported to give chiefly trans-2,2-diphenyl-3-pentenyl-
lithium, because carbonation gave 75% yield of trans-3,3-
diphenyl-4-hexenoic acid (TU) along with 23% of trans-2,2-
diphenyl-4-hexenoic acid (TR), in the present work it is
found that carbonation of the same reaction product gives
only some 49% of TU, 34% of an unknown (UNK1), and 10% of TR.
This difference was revealed because of the ability of the
GC column used in the present work to separate TU, TR, and
UNK1. Peculiarly the organolithium compounds which are
precursors of TU and UNK1 both evidently give (E)-1,1-
diphenyl-3-butenyllithium (upon warming to 35°C) because some
89% of the product of carbonation is now TR.

Because cyclopropylcarbinyllithium is known to undergo
ready ring opening to homoallyllithium, the unknown (UNK1)
was thought possibly to be the methyl ester of 2-(2,2-
diphenylcyclopropyl)propanoic acid. The methyl ester of
this acid, in one of its two possible diastereomeric forms,
was synthesized by a Simmons-Smith reaction between methyl
4,4-diphenyl-2-methyl-butenoate and methylene iodide in the
presence of zinc-copper couple. The synthetic methyl ester
had a very different GC retention time and quite different
mass-spectrometric (MS) fragmentation pattern from the methyl
ester UNK1. It is thought unlikely, therefore, that UNK1 is
either of the two diastereomeric methyl 2-(2,2-diphenylcyclo-
propyl)propanoates. The MS fragmentation pattern suggests
that UNK1 is methyl 4-methyl-2,2-diphenylcyclobutane-1-carbo-
xylate but verification must await additional studies.
The study of [1,3] phenyl migration was accomplished by varying the alkali metal cation and temperature in the reaction of 1-chloro-2,2,3-triphenylpropane-1,1-d$_2$ with alkali metals. The reaction of the chloride with lithium metal for four hours at -78°C gave primarily (12%) methyl 3,3,4-triphenyl butanoate-d$_2$ (UN) after carbonation and esterification (0.7% of UN had undergone [1,3] phenyl migration). The reaction of the organolithium compound with KO-t-Bu for 30 minutes at -78°C gave (24%) methyl 2,2,4-triphenyl butanoate-d$_2$ (E?): (5.3% of E? had undergone [1,3] phenyl migration) and (11%) methyl 2,3-diphenyl-2-benzyl propanoate-d$_2$ (P?). The reaction of the chloride with potassium metal for four minutes at +68°C yields primarily (1.3%) methyl 2,3-diphenyl-2-benzyl propanoate-d$_2$ (P?) and to a lesser extent (0.1%) methyl 2,2,4-triphenyl butanoate-d$_2$ (E?): (7.1% of E? had undergone [1,3] phenyl migration). In another run reaction of the chloride with lithium metal for four hours at -78°C gave primarily (19.2%) the unrearranged ester (UN) (none of UN had undergone [1,3] phenyl migration). The warming of the organolithium compound to 0°C for one hour yielded only (1.4%) methyl 2,2,4-triphenyl butanoate-d$_2$ (E?) (none of E? had undergone any [1,3] phenyl migration). The reaction of the original unwarmed organolithium compound with CsO-t-Bu for 30 minutes at -78°C yielded (5.4%) methyl 2,3-diphenyl-2-benzyl propanoate-d$_2$ (P?) and (5.3%) methyl 3,3,4-triphenyl butanoate-d$_2$ (UN) (none
of UN had undergone [1,3] phenyl migration). A smaller amount (2.1%) of methyl 2,2,4-triphenyl butanoate-\(d_2\) (BM) was also observed (4.3% of BM had undergone [1,3] phenyl migration). The data supports the premise that conditions that effect [1,2] phenyl migration will also effect [1,3] phenyl migration in the same manner; however [1,2] phenyl migration always greatly exceeds [1,3] phenyl migration.
A method of synthesis of 5-chloro-4-methyl-4-phenyl-1-pentene in high purity was developed. The reactions of this chloride with lithium, cesium, and Cs-K-Na alloy were studied in order to determine what molecular rearrangements occur.

When 5-chloro-4-methyl-4-phenyl-1-pentene is reacted with lithium at -76°C, the major product is 3-methyl-3-phenyl-5-hexenoic acid which is the unrearranged acid from 5-chloro-4-methyl-4-phenyl-1-pentene. When the temperature is raised to 0°C the major product was still the unrearranged acid but in reduced yield.

When 5-chloro-4-methyl-4-phenyl-1-pentene is reacted with cesium at 35°C the major products are 2-methyl-2-phenyl-5-hexenoic acid, 2,5-dimethyl-2,5-phenyladipic acid, and 3-methyl-2-phenyl-5-hexenoic acid. Upon reaction at -76°C, the major products are 2,5-dimethyl-2,5-diphenyl-adipic acid, 2-methyl-2-phenyl-5-hexenoic acid, and three unknown compounds with a molecular weight of 216, indicating loss of a mole of hydrogen from the expected molecular weight of 218.

Reaction with Cs-K-Na alloy at -76°C. Gave as major products the three previous unknown compounds of 216 molecular weight, an additional unknown compound of molecular weight 216, and 2-methyl-2-phenyl-5-hexenoic acid.
C. DATA ON SCIENTIFIC COLLABORATORS

Principal Investigator: Dr. Erling Grovenstein, Jr., supported 4.5 summer months (or half-time for 3 summers).

Postdoctoral Research Associates:
1. Dr. A. M. Bhatti: 33-1/2 months full time support and 3 months half time support by NSF.
2. Dr. J. Singh: 34 months full time support and 6 months half time support by NSF.

Graduate Students:
Captains John H. Northrop, Randall L. Hughes, and James S. Hansen worked in the area of the present grant for their M.S. Thesis with their stipends paid by the U.S. Army, but with chemicals and equipment supplied by the present NSF grant.

Undergraduate or B.S. Students:
1. Miss Karla Black worked for 3-1/2 summer months with stipend paid by present NSF grant.
2. Miss Yvonne M. Heinrich worked for 3 summer months under a stipend paid her as a special summer undergraduate research student under a grant from the Coca-Cola Company; her chemicals and equipment were in part supplied by the present NSF grant.
d. INFORMATION ON INVENTIONS

   Novel preparations, rearrangements, and reactions of organoalkali metal compounds were discovered. It is believed that the scientific community is best served by direct publication of these discoveries in scientific journals; therefore, no patent applications concerning these discoveries are recommended by the principle investigator.
e. TECHNICAL DESCRIPTION OF PROJECT AND RESULTS

Summary of Progress upon "Cation Effects in Organoalkali Metal Chemistry; Organo-cesium Chemistry"

NSF GRANT CHE-8009210 for period November 1, 1980 - April 1, 1984
by Erling Grovenstein, Jr., Principal Investigator

I. Rearrangements of Organoalkali Metal Compounds

A. Propenyl vs. Phenyl Migration in (Z)- and (E)-2,2-Diphenyl-3-pentenyl Alkali Metal Compound

B. [1,3] vs. [1,2] Migration of Phenyl in 2,2,3-Triphenylpropyl Alkali Metal Compounds

C. Rearrangements of 9-Alkyl-9-lithiomethylfluorenes

D. Rearrangements of 2- and 3-p-Biphenylalkyl Anions

II. Reactions of Hydrocarbons with Cesium

A. Benzene and Simple Derivatives

B. 1,2-Diphenylethane and Derivatives

C. 3,3-Diphenyl-1-butene

D. Triphenylmethane
I. Rearrangements of Organoaalkali Metal Compounds

A. Propenyl vs. Phenyl Migration in (Z)- and (E)-2,2-Diphenyl-3-pentenyl Alkali Metal Compounds. Reaction of the cis-halide 1 with lithium in diethyl ether at -75°C gives the corresponding organolithium compound 2 which when warmed to 35°C rearranges to 4 largely with retention of geometry as deduced from the products of carbonation. The trans-halide 6 behaves similarly, except that now the reaction with lithium gives both 7 and an unknown, likely 8; both 7 and 8 rearrange at 35°C to give 10. That the unknown is not 9 was shown by synthesis of the acid

Product 11 (as an 85:15 mixture of diastereomers) which was different from the carbonation product of the unknown. Also in the solvent tetrahydrofuran (THF) at +10°C the lithium compound 7 again undergoes [1,2] propenyl migration to 10 with 98 ± 2% retention of configuration; however in THF the product of carbonation also contains

\[ \text{Reaction scheme and structures} \]
25% of 12 which results from a competing [1,2] migration of the phenyl group. The organo-lithium compound 7 in THF at -75°C upon cation exchange with KO-t-Bu undergoes exclusive phenyl migration.

The present work exemplifies a considerable cation effect in organoalkali metal chemistry: the properties of a "carbanion" are modified by the nature of the counter cation and by the ligands which lie within the coordination sphere of the cation. The essential retention of configuration during [1,2] migration of the propenyl group in lithium compounds 2 and 7 is of theoretical and practical interest particularly since the result contrasts with the report of Maercker and Streit\(^2\) that [1,2] migration of the propenyl group in Grignard reagents is NOT stereospecific. Our work shows that configurations of the suggested intermediates 3 and 9 are maintained during rearrangement and that the configuration of 8 is maintained for a prolonged period of time in ethereal solvents. Also no precedent exists for formation of a four-membered ring as in 7 from a reactant such as 2 which might more readily have formed a three-membered ring as in 9. Work is continuing in this interesting area.

B. [1,3] vs [1,2] Migration of Phenyl in 2,2,3-Triphenylpropyl Alkali Metal Compounds.

The possibility of [1,3] migration of the phenyl group in competition with [1,2] migration has been studied\(^8\) in 2,2,3-triphenylpropyl-1,1-d\(_2\) alkali compound 13 prepared from 1-chloro-2,2,3-triphenylpropane-1,1-d\(_2\) (see Scheme I). Reaction of 13 with lithium in THF at -78°C gave 17 (M = Li) containing 0.7% or less of [1,3] phenyl migration product 14 (M = Li). Conversion of this organolithium compound into the potassium compound by reaction with KO-t-Bu at -78°C in THF gave benzyl migration (15 + 16) and [1,2] phenyl migration 17 in a ratio of 2.2 : 1. The benzyl migration product contained 4.6% of product 15 which had undergone [1,3] phenyl migration. Repetition of this experiment but with CsO-t-Bu in place of KO-t-Bu gave benzyl migration and [1,2] phenyl migration in a ratio of 0.30 : 1. The benzyl migration product contained 4.3% of product that had undergone [1,3] phenyl migration or about the same as with KO-t-Bu. Reaction of the halide with potassium metal in THF at 65°C gave chiefly product of [1,2] phenyl migration. The benzyl migration product contained 7.1% of product which had undergone [1,3] phenyl migration. In contrast, the organolithium compound 13 when warmed to 0°C, gave only the product of benzyl migration. Thus [1,3] phenyl migration increases with temperature as well as along the series.
Li⁺ << K⁺ = Cs⁺ and parallels [1,2] phenyl migration. However, [1,2] phenyl migration greatly exceeds [1,3] phenyl migration just as it does for rearrangements of carbonium ions and free radicals.

C. Rearrangements of 9-Alkyl-9-lithiomethylfluorones. - In conformity with the published report²² for 9-methyl-9-lithiomethylfluorone, 9-ethyl-9-lithiomethylfluorone (18) in THF does not undergo skeletal rearrangement to 20 likely because the expected spiro intermediate (19) is highly strained; instead at 0°C 18 undergoes protonation by the solvent to give 9-ethyl-9-methylfluorone.

\[
\begin{align*}
\text{CH}_3\text{CH}_2 & \quad \text{CH}_2\text{Li} \\
\text{18} & \quad \text{L}^+ \\
\text{CH}_3\text{CH}_2 & \\
\text{19} & \\
\text{CH}_2 & \\
\text{20} & \\
\end{align*}
\]

In contrast, 9-tert-butyl-9-lithiomethylfluorone (21) undergoes two rearrangements:

\[
\begin{align*}
\text{CH}_3\text{C} & \quad \text{CH}_2\text{Li} \\
\text{21} & \quad \text{L}^+ \\
\text{O}^\circ,\text{THF} & \\
\text{22} & \\
\text{CH}_3 & \\
\text{6}^\circ & \\
\text{23} & \\
\end{align*}
\]

The mechanism of the major rearrangement to 9-methylfluorenyl anion has been determined by isotopic labeling experiments. Thus the methyl group of 22 originates from the lithio-methyl group since 24 yields 25. Also, the required additional proton for the new

\[
\begin{align*}
\text{CH}_3\text{C} & \quad \text{CD}_2\text{Li} \\
\text{24} & \quad \text{L}^+ \\
\text{CD}_2 & \\
\text{25} & \\
\end{align*}
\]

methyl group comes from the tert-butyl group since 26 yields 28. The rearrangement is believed to proceed via the transition state 27. This mechanism is analogous to
Finally 9-neopentyl-9-lithiomethylfluorene 29 has been found to rearrange to a product which is tentatively assigned the structure 30 based on the mass spectrum and $^1$H NMR spectrum of the product of carbonation.

The rearrangement of 21 and 29 and the non-rearrangement of 18 and its 9-methyl analog are thought to arise from steric compressions in 21 and 29. An X-ray diffraction (with collaboration of Dr. Don VanDeveer) upon 9-tert-butyl-9-chloromethylfluorene (the precursor of 21) shows that the tert-butyl group presses against the benzenoid rings of the fluorene such that these exist at an angle of 170.4° to one another in the crystal (rather than the expected 180°).

D. Rearrangements of 2- and 3-π-Biphenylylalkyl Anions. - Our work upon reactions of 2- and 3-π-biphenylylalkyl chlorides with alkali metals and accompanying preparation of labile spiro anions, which can serve as intermediates in rearrangement of the π-biphenyl group, has now been completed and published in full.2,3
where the concentrations are obtained from their initial values and measurements of the extent of reaction as given from the products of quenching with water. The validity of this analytical technique in THF has been corroborated by measurement of the amount of cesium in the alloy phase before and after reaction with aromatic hydrocarbon. Equilibrium is attained slowly in the present system likely because of the low solubility of Cs in the ethereal solvent and the slow rate of precipitation of the ionic products. Some check on the attainment of equilibrium, at -45°C is possible by equilibration first at -70°C (where K is larger than at -45°C) and then at -45°C. The results are summarized in Table I which also records relative values $K_{d}$ (K_{ArH}/K_{PhH}) as measured for the following homogeneous reaction in 1:1 (V/V) THF-DME at -100°C with K^{+} as counterion (Na-K alloy reaction):

$$\text{PhH}^{-},K^{+} (\text{THF-DME}) + \text{ArH} (\text{THF-DME}) \rightleftharpoons \text{PhH} (\text{THF-DME}) + \text{ArH}^{-},K^{+} (\text{THF-DME})$$

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<td>Trimethylsilylbenzene</td>
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<tr>
<td>Benzene</td>
</tr>
<tr>
<td>Toluene</td>
</tr>
<tr>
<td>m-Xylene</td>
</tr>
<tr>
<td>p-Xylene</td>
</tr>
<tr>
<td>Ethylbenzene</td>
</tr>
<tr>
<td>Isopropylbenzene</td>
</tr>
<tr>
<td>t-Butylbenzene</td>
</tr>
<tr>
<td>o-Xylene</td>
</tr>
</tbody>
</table>

$^{a}$DME/THF, 1:1 (v/v); data from ref. 2b.

$^{b}$No detectable reaction
For intercomparison of our Cs-K-Na allow reactions with those of Na-K alloy, it should be noted that, at -45°C in THF, benzene reacts in yields as high as 94% while, with Na-K in 2:1 (v/v) THF:DME at -20° and -82°C, benzene is converted to radical anion only to 0.01 and 0.09% respectively. The observed reactions of benzene and derivatives with Na-K as reported in Table I could be measured only because of the very high sensitivity of ESR spectrometry. Our work with Cs-K-Na alloy represents the most practical synthesis of the radical anions of the hydrocarbons listed in Table I. While exceptions exist, the general order of reaction of hydrocarbons in the table with cesium alloy parallels that with potassium alloy especially if the comparisons are made at as similar a temperature as possible.

In preliminary, more qualitative work with Cs-K-Na alloy, the apparent extent of radical anion formation, as deduced from the yield of hydroaromatic compound upon quenching with ice water, has been measured for p-di-tert-butylbenzene at -75°C as follows: 2.6% in THF, 53% in 3:1 (V/V) DME-THF, 75% in 3:1 diglyme-THF, and 93% in 1:1 triglyme-THF. Since the extent of radical anion formation parallels the expected solubility of the alkali metals, one may question whether the yield of hydroaromatic compound reflects the concentration of radical anion. In other words, in such solutions of alkali metals how can we be certain where the electrons are located? Distribution studies have been made in an effort to answer this question. Thus after 3:1 diglyme-THF was stirred with excess Cs-K-Na alloy at -75°C, the organic phase (after centrifugation) was found to be 0.034 M in dissolved alkali metal. The solution was then made 0.032 M in p-di-tert-butylbenzene and after equilibration with alloy was determined to be 0.075 M in alkali metal. The increased solubility of alkali metal can be explained on the basis that 65% of the p-di-tert-butylbenzene was converted to radical anion; this value agrees approximately with the value of 75% as determined from the yield of hydroaromatic product upon quenching with water.

Our qualitative experiments and those of Table I indicate that the reducing power of Cs-K-Na alloy increases as the temperature is decreased and as the expected solvating power of the solvent increases. Apparently, these trends are to be ascribed to increasing solvation of cesium ion in the complex with lowering of temperature and replacement of THF by DME, diglyme, or triglyme. The effects observed are large and of practical importance. Thus, with Cs-K-Na, t-butylbenzene in THF reacted only 16% at -45°C but 85% at -75°C; p-xylene at -75°C reacted 27% in THF but essentially 100% in DME-THF. These trends are similar to those reported with sodium and biphenyl; however, with potassium and naphthalene the extent of reduction was independent of temperature and solvent polarity (indeed no perfectly general order of "solvant polarity" exists for alkali metals -- sodium is a more powerful reducing agent than potassium in THF but the order is reversed in 1,3-dimethoxypropane).25

We conclude that Cs-K-Na alloy is the most powerful reducing agent known for benzenoid hydrocarbons and that the power of this reagent increases as yet unknown limits as the temperature is decreased and as the number of oxygens increases in solvents of the type \( \text{CH}_3\text{O(CH}_2\text{CH}_2\text{O)}_n\text{CH}_3 \).

B. 1,2-Diphenylethane and Derivatives. - Our studies upon cleavage of 1,2-diphenylethane and derivatives by Cs-K-Na alloy have now been completed and published.4 The product and relative rate studies upon cleavage of some eighteen hydrocarbons show that cleavage occurs as a dianion and normally occurs readily at -75°C according to the general process:
provided that the transition state can assume the preferred geometry below which permits the $\sigma^*$ orbital of the bond undergoing cleavage to interact with the HOMO's of both aromatic rings. The relative rates of cleavage of meta- and para-methyl derivatives of bibenzyl may be correlated with the equilibrium acidities of toluene, $m$-xylene, and $p$-xylene in a modified Hammett relationship.

The quantitative cleavage of 1,2-diphenylethane and derivatives by Cs-K-Na alloy provides an attractive method of preparation of benzylcesium and derivatives of known structure free of impurities. For example, we have prepared $\alpha$-methylbenzyl-$\alpha,d_2$-cesium by the reaction:

This organocesium compound is stable at $-75^\circ C$ but undergoes ready intramolecular [1,4] sigmatropic migration of hydrogen from the $\alpha$-methyl group to the methylene group when warmed to near room temperature.

C. 3,3-Diphenyl-1-butene. - In a continuation of our work upon rearrangement of hydrocarbons with cesium, 3,3-diphenyl-1-butene has been found to react with Cs-K-Na alloy quantitatively according to the scheme:
The new work in conjunction with our previous work upon 5,5-dimethyl-2,2-diphenyl-3-hexyne shows that the acetylenic group of the hexyne may be replaced by a vinyl group without retarding the facile [1,2]-migration of the phenyl group in the dianion.

D. Triphenylmethane. - In view of the above reaction of Cs-K-Na alloy with 3,3-diphenyl-1-butene, we next investigated triphenylmethane to see if replacement of a vinyl group by a phenyl would permit facile [1,2] migration of phenyl to occur. Indeed reaction proceeded as with 3,3-diphenyl-1-butene:

\[
\begin{align*}
\text{Cs-K-Na} & \quad \text{THF, } -75^\circ C \\
\begin{array}{c}
\text{Cs}^+ \\text{H} \quad \text{Cs}^+ \\
\text{Cs}^+ \quad \text{Ph}
\end{array}
\end{align*}
\]

The final product of rearrangement is of novel structure, not readily produced by other known reactions. It also undergoes novel chemistry; thus upon standing at room temperature exposed to light, or more rapidly upon heating in benzene in the presence of a little dibenzoyl peroxide, it decomposes quantitatively to biphenyl and toluene:

\[
\begin{align*}
\text{CH}_2\text{Ph} \\ \\
\text{D}_2\text{O}
\end{align*}
\]
BIBLIOGRAPHY

Publications Based on NSF-Sponsored Research (Since those Listed in the proposal of January 15, 1980)


Other Recent Publications of the Principal Investigation in the Area of the Research


Other References


