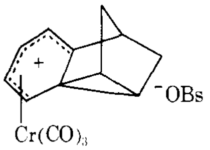
on those offered to explain the unusual stability of ferrocenylcarbinyl cations,[3] the "hyperconjugation"[9a,b] and the "direct interaction"[9c,d] mechanisms. Two similar mechanisms can be proposed for the stabilization of homobenzylic cations which would account for the rapid rate of solvolysis of the syn-exo-2 isomer. If



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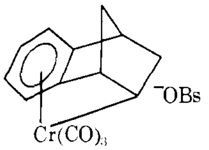

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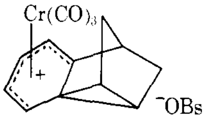

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the "homoconjugation" mechanism operates, which is analogous to the hyperconjugation mechanism, resonance structure **5** would be relatively stable and an important contributor to the structure of the transition state. However, if the direct interaction mechanism operates, structure **6** would be stable and important. The relatively slow rate of solvolysis of the anti-exo-2 isomer indicates that resonance structure **7** of its transition state is not unusually stable. Therefore we prefer to accept the direct interaction mechanism to explain the rate enhancement of the syn-exo-2 isomer rather than the homoconjugation mechanism which requires that the π electrons on the side of the metal atom are much more available to adjacent cations than the π electrons on the opposite side of the metal atom. However, our data do not exclude the latter possibility and an explanation for the greater availability of the π electrons on the side of the metal atom than those on the opposite side has been offered.[10]

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(10) J. A. Mangravite and T. G. Traylor, *Tetrahedron Lett.*, 4461 (1967).

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Evidence for a Radical Mechanism of Aromatic "Nucleophilic" Substitution[1]

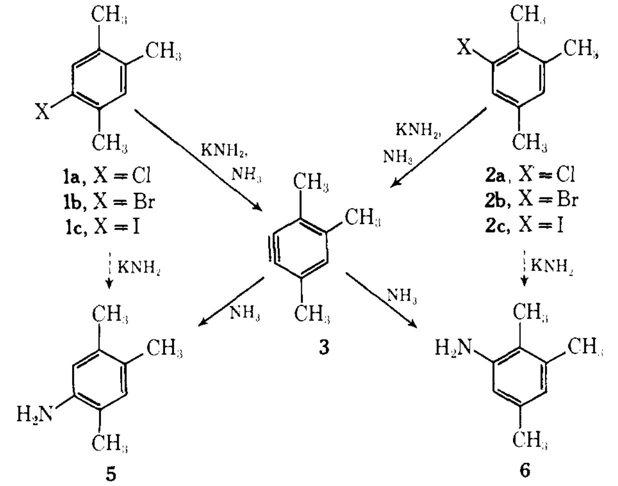
Sir:

According to the aryne mechanism,[2] the reactions of 5- and 6-halopseudocumenes (**1** and **2**, respectively) with KNH_2 in liquid ammonia should proceed *via* the same aryne intermediate (**3**) and form 5- and 6-pseudocumidine (**5** and **6**, respectively) in identical proportions. Neither the identity of the halogen nor its location (5 or 6 position) should affect the product ratio.

These expectations are fulfilled insofar as reactions of bromo compounds **1b** and **2b** and chloro compounds **1a** and **2a** are concerned. With KNH_2 in NH_3, these afford **5** and **6** in high yield and with a **6**:**5** product ratio varying from 1.45 to 1.55. This variation is within experimental error. However, from iodo compounds **1c** and **2c**, the **6**:**5** product ratios were 0.63 and 5.86, respectively (with 0.29 *M* KNH_2). Pseudocumene (**4**) was formed in significant amounts as a by-product in reactions of **1c** and **2c**.

The fact that each of the iodo substrates forms some cine-substitution product indicates that each reacts in part *via* the aryne mechanism. However, the wide divergences of the pseudocumidine **6**:**5** ratio from the "aryne ratio" of about 1.5 demonstrate that some other mechanism also plays a major role. Inasmuch as the divergences are both in the direction of retention of the original orientation, the additional mechanism must be a nonrearranging one.

Scheme I



It is unlikely that the nonrearranging pathway is straightforward aromatic nucleophilic substitution, such as encountered in reactions of *o*- and *p*-halonitrobenzenes[3] and often symbolized SNAr. Aryl iodides generally are somewhat *less* reactive in SNAr reactions than their chloro or bromo analogs, whereas they are generally *more* reactive than the corresponding chlorides in aryne formation and only slightly less reactive than the corresponding bromides.[4] Thus, a change of the halogen from chlorine to iodine would be expected strongly to favor the aryne mechanism in competition with SNAr, while a change from bromine to iodine might slightly favor or slightly disfavor it.

Evidence in Table I indicates the nonrearranging mechanism to be radical in character. This table also gives details on experiments mentioned above. When the reaction of **1c** or **2c** is carried out in the presence of 2-methyl-2-nitrosopropane[5] or tetraphenylhydrazine, both of which are radical-trapping agents (the latter *via* dissociation into diphenylamino radicals[6] or *via* radical displacement on nitrogen), the **6**:**5** pseudocumidine ratio is in both cases shifted toward the "aryne ratio." A shift in the same direction is realized

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(1) Support from the National Science Foundation is gratefully acknowledged.

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Table I. Reactions of 5- and 6-Halopseudocumenes with Potassium Amide in Liquid Ammonia[a]

Sub-strate[b]	$[KNH_2]_0$, *M*	Added substance, *M*	—Product yields, %— X^-	4	5	6	Ratio, 6:5
1a	0.30		94	0.1	36	53	1.46
2a	0.30		95	0.1	36	52	1.45
1b	0.25		98	0.4	33	51	1.55
	0.44[c]		93	0.3	35	53	1.41
	0.44[c]	0.008[d]	96	0.3	35	53	1.46
2b	0.13		96	0.3	39	56	1.45
1c	0.29		94	6	51	32	0.63
	0.46[c]		92	5	38	46	1.21
	0.45[c]	0.008[d]	98	9	34	47	1.41
	0.30	0.038[e]	97	3	40	46	1.16
	0.30	0.013[d]	95	7	35	45	1.23
	0.29	0.025[f]	98	5	32	30	0.94
	0.15[g]		93	5	45	38	0.86
2c	0.29		95	10	11	65	5.9
	0.44[c]		91	6	23	55	2.4
	0.45[c]	0.012[d]	91	6	27	55	2.0
	0.30	0.002[e]	95	11	16	64	4.1

[a] Reactions at reflux; KNH_2 formation catalyzed by $Fe(NO_3)_3 \cdot 9H_2O$; **4**, **5**, and **6** determined by glpc. [b] *Ca.* 0.02 *M*. [c] Solvent was 50% NH_3–50% diethyl ether (v/v). [d] Tetraphenylhydrazine. [e] 2-Methyl-2-nitrosopropane. [f] 2,4-Dimethylaniline. [g] KNH_2 formation catalyzed by Pt black instead of $Fe(NO_3)_3 \cdot 9H_2O$.

by conducting the reaction in 50% ammonia–50% diethyl ether; the ether solvent component is expected on bond dissociation energy considerations[7] to be a better hydrogen atom donor than ammonia to radicals. Evidently these radical-reactive species interfere with a radical-chain mechanism, so as to favor termination over chain propagation, and by suppressing the radical mechanism allow the aryne mechanism to carry a larger share of the total reaction.

An hypothesis as to the character of the radical mechanism is sketched in Scheme II. The initiation

Scheme II[a]

$$\text{electron donor} + \text{ArI} \longrightarrow [\text{ArI}]\cdot^- + \text{residue} \qquad (1)$$

$$[\text{ArI}]\cdot^- \longrightarrow \text{Ar}\cdot + \text{I}^- \qquad (2)$$

$$\text{Ar}\cdot + \text{NH}_2^- \longrightarrow \text{ArNH}_2\cdot^- \qquad (3)$$

$$\text{ArNH}_2\cdot^- + \text{ArI} \longrightarrow \text{ArNH}_2 + [\text{ArI}]\cdot^- \qquad (4)$$

$$\text{termination steps} \qquad (5)$$

[a] "Ar" stands for the 5- or 6-pseudocumyl moiety.

step is electron transfer from an electron-donor species[8] to the aryl iodide, to form a transient radical anion which quickly undergoes scission of the C–I bond so as to generate an aryl radical and iodide ion.[11] The aryl radical then (step 3) combines with nucleophile to form an arylamine radical anion which quickly transfers an electron (step 4) to the aryl iodide so as to regenerate the aryl radical. Steps 2, 3, and 4 constitute a cycle, and are precedented.[11–14] By analogy with other electron transfer reactions of aryl halides,[14,15] steps 1 and 2 should occur far more readily with iodides than with bromides or chlorides. The mechanism as a whole is substantiated by the fact that nonrearranging substitution is stimulated by the addition of potassium metal to reactions of **1c** or **2c** with KNH_2.[16]

The mechanism of Scheme II resembles electron-transfer radical mechanisms for nucleophilic substitution at saturated carbon proposed by Kornblum,[17] Russell,[18] and their associates. However, no well-defined terminology was developed for this type of mechanism. We propose the designation "SRN1," standing for *substitution, radical–nucleophilic, unimolecular*. The mechanism is unimolecular in the same sense as SN1, except that unimolecular bond fission occurs in a radical anion instead of in a neutral molecule.

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[8] The identity of the electron donor species is obscure. The amide ion (NH_2^-) is unlikely because its ionization potential (27 kcal/mol)[9] is greater than the electron affinity of iodobenzene (13 kcal/mol);[10] the effect of solvation needs however to be taken into account. A substituted anilide ion ($ArNH^-$) is conceptually more attractive, but a run in the presence of 2,4-dimethylanilide ion (Table I) gave *less* reaction by the nonrearranging mechanism than in its absence.

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Alkali Metal Promoted Aromatic "Nucleophilic" Substitution[1]

Sir:

The reactions of 5- and 6-iodopseudocumene with KNH_2 in liquid ammonia occur in part by the aryne mechanism and in part by a nonrearranging substitution route.[2] For the latter, there has been proposed an electron-transfer, radical mechanism (symbolized SRN1), as sketched in Scheme II of an accompanying communication.[2] From the proposed mechanism, one would anticipate that the SRN1 route ought to be stimulated by the addition of superior electron-donor species.

The best electron donor in liquid ammonia solution is the solvated electron itself, as provided by solutions of alkali metals.[3] We now report that, when potassium metal is supplied as well as KNH_2, the aryne mechanism is sometimes totally eclipsed, and substitution occurs virtually without rearrangement. Moreover, we report several other alkali metal promoted substitution reactions of aryl halides with KNH_2 and other nucleophilic reagents in liquid ammonia that defy interpretation by either the aryne or the SNAr mechanism.

Reaction of 5-iodopseudocumene with KNH_2 plus K metal in ammonia afforded 5-pseudocumidine (50%) and pseudocumene (40%), but no 6-pseudocumidine (Table I). Similarly, 6-iodopseudocumene

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[1] This investigation was supported in part by Public Health Service Research Grant No. GM 14647 from the National Institute of General Medical Sciences.

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