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

Substrate[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 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]

Scheme II[a]

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

$$[ArI]\cdot^- \longrightarrow Ar\cdot + I^- \tag{2}$$

$$Ar\cdot + NH_2^- \longrightarrow ArNH_2\cdot^- \tag{3}$$

$$ArNH_2\cdot^- + ArI \longrightarrow ArNH_2 + [ArI]\cdot^- \tag{4}$$

$$\text{termination steps} \tag{5}$$

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

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 "S_{RN}1," standing for *substitution, radical-nucleophilic, unimolecular*. The mechanism is unimolecular in the same sense as S_N1, 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 S_{RN}1), as sketched in Scheme II of an accompanying communication.[2] From the proposed mechanism, one would anticipate that the S_{RN}1 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 S_NAr 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.

[2] J. K. Kim and J. F. Bunnett, *J. Amer. Chem. Soc.*, 92, 7463 (1970).

[3] M. Szwarc, *Progr. Phys. Org. Chem.*, 6, 379 (1968).

Table I. Reactions with Potassium Metal and/or KNH_2 (or Other Nucleophile) in Liquid Ammonia

Substrate	[Substrate], *M*	[KNH_2], *M*	[K], *M*	Products[a] and yields,[b] %
5-Iodopseudocumene	0.03	0.29	0.13	5-Pseudocumidine, 50 Pseudocumene, 40
6-Iodopseudocumene	0.03	0.29	0.13	6-Pseudocumidine, 54 5-Pseudocumidine, trace Pseudocumene, 30
o-Iodoanisole	0.16	0.85	0.03	*o*-Anisidine, 68 *m*-Anisidine, 17 Anisole, 8
o-Iodoanisole	0.02	0.29	0.12	*o*-Anisidine, 67 Anisole, 11
o-Bromoanisole	0.16	0.85	0.03	*o*-Anisidine, 35 *m*-Anisidine, 39 Anisole, 8
o-Bromoanisole	0.03	0.29	0.15	*o*-Anisidine, 64 Anisole, 16
o-Chloroanisole	0.16	0.85	0.03	*o*-Anisidine, 57 *m*-Anisidine, 26 Anisole, 5
2-Iodo-1,3-xylene	0.02	0.50	0.20	2,6-Dimethylaniline, 64 *m*-Xylene, 25
Diphenyl ether	0.20	0.29		No reaction
Diphenyl ether	0.20		0.40	Aniline, 17 Benzene[c]
Diphenyl ether	0.10	0.64	0.20	Aniline, 53 Benzene[c]
Iodobenzene	0.18	0.34[d]	0.11	Diphenylamine, 10 (19)[e] *o*-Aminobiphenyl, 6 (11)[e] *p*-Aminobiphenyl 6 (11)[e]
Chlorobenzene	0.20	0.40[f]	0.06	Phenylacetonitrile, 36 Toluene, 18 Benzene, 26 Aniline, 3

[a] Products were determined by glpc and identified by retention time analysis and infrared spectra. [b] Based on aryl halide or ether introduced. [c] Detected but not determined. [d] Potassium anilide. [e] Yield based on iodide ion released. [f] Potassium cyanomethylide (KCH_2CN).

afforded 54% 6-pseudocumidine, 30% pseudocumene, and a mere trace of 5-pseudocumidine.

These transformations are intelligible in terms of the SRN1 mechanism of Scheme I, in which (for immediate purposes) Ar is the 5- or 6-pseudocumyl moiety, X is iodine, and Y^- is NH_2^-. Initiation occurs in step 1, and steps 2, 3, and 4 constitute a propagation cycle. Step 5, in which RH may be NH_3 or other hydrogen atom donor, accounts for the substantial amounts of pseudocumene formed.[4] Moreover, if the by-product radical (R·) of step 5 is unsuited to continue the cycle, step 5 is a prelude to termination. All these steps are amply precedented, as discussed elsewhere.[2]

Scheme I

$$e_{NH_3}^- + ArX \longrightarrow [ArX]\cdot^- \tag{1}$$

$$[ArX]\cdot^- \longrightarrow Ar\cdot + X^- \tag{2}$$

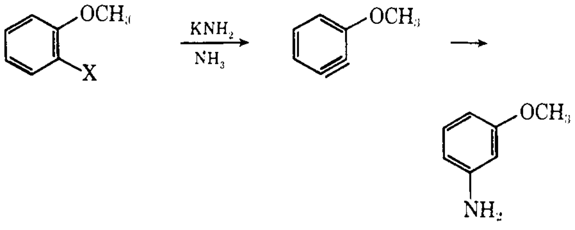
$$Ar\cdot + Y^- \longrightarrow [ArY]\cdot^- \tag{3}$$

$$[ArY]\cdot^- + ArX \longrightarrow [ArX]\cdot^- + ArY \tag{4}$$

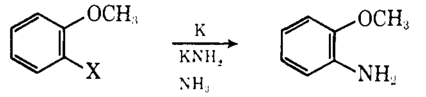
$$Ar\cdot + RH \longrightarrow ArH + R\cdot \tag{5}$$

$$\text{termination steps} \tag{6}$$

The reactions of *o*-haloanisoles with $NaNH_2$ or KNH_2 in ammonia to form *m*-anisidine (eq 7) epitomize cine substitution by the aryne mechanism.[5] When 0.2 g-atom of K metal is furnished per mole of *o*-haloanisole, as well as a fivefold excess of KNH_2, *o*-anisidine is formed in preference to or in amount equivalent to *m*-anisidine; see Table I. When K metal is furnished in excess, together with excess KNH_2, the only anisidine formed is the ortho isomer (eq 8). The experiments with insufficient K metal demonstrate the catalytic effect expected if steps 2–4, Scheme I, are a functioning propagation cycle; the yields of *o*-anisidine obtained range from 175 to 340% based on K metal.



(7)



(8)

2-Iodo-1,3-xylene is unable to react by the aryne mechanism because it has no hydrogen ortho to iodine. However, it reacts with KNH_2 and K metal (both in excess) to form 2,6-dimethylaniline in 64% yield, as well as *m*-xylene (25%). With KNH_2 but no K metal, the same products are formed but in lower yield

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(4) The fact that 30 or 40% of pseudocumene is formed when K metal is present (Table I) in contrast to only 3–11% when it is absent (Table I, ref 2) is in part an obvious consequence of all the reaction going *via* aryl radicals rather than some *via* radicals and some *via* arynes. Also, it is possible that when solvated electrons are abundant, aryl radicals may in part be reduced to aryl anions, which would also form pseudocumene.

(5) H. Gilman and S. Avakian, *J. Amer. Chem. Soc.*, 67, 349 (1945); G. B. R. de Graaff, H. J. den Hertog, and W. C. Melger, *Tetrahedron Lett.*, 963 (1965); J. D. Roberts, D. A. Semenow, H. E. Simmons, Jr., and L. A. Carlsmith, *J. Amer. Chem. Soc.*, 78, 601 (1956).

(12% 2,6-dimethylaniline and 19% *m*-xylene). With or without K metal, the mechanism of Scheme I is apparently followed, except that without K metal the identity of the initial electron donor is uncertain.[2]

The cleavage of diphenyl ether by sodium in ammonia forms benzene and sodium phenoxide.[6] A similar cleavage occurs with potassium metal; a minor product of cleavage is aniline (17%); see Table I. Potassium amide is without effect on diphenyl ether, but the combination of KNH_2 and K metal affords aniline as a major product (53%). The mechanism of Scheme I, in which Ar is phenyl and X is phenoxy, provides interpretation. (The small amount of aniline formed in the absence of KNH_2 perhaps derives from reactions of the amino radical ($H_2N\cdot$) formed in step 5 when RH is ammonia.)

Potassium anilide in ammonia does not react with iodobenzene, but with K metal also present reaction occurs to form diphenylamine (19%) and *o*- and *p*-aminobiphenyl (11% each). Again the SRN1 mechanism provides interpretation. It is noteworthy that the ambident anilide ion nucleophile is about as reactive with phenyl radical at ring carbons as it is at nitrogen.

The cyanomethyl anion (from acetonitrile) is unreactive with chlorobenzene,[7] but in combination with K metal it affords phenylacetonitrile (36%), aniline (3%), benzene (26%), and toluene (18%). Toluene is evidently a product of degradation of the phenylacetonitrile radical anion; toluene is formed on treatment of phenylacetonitrile with K metal in ammonia.

To date, we have observed catalytic character in respect to K metal (*i.e.*, yields over 100%) only in the aforementioned reactions with *o*-haloanisoles and in reactions of bromo- and iodobenzene with *N*-methylanilide ion that are still under investigation. In order for steps 2, 3, and 4 to function as a propagation cycle, each of them must be rapid in comparison to the various side reactions which may occur with the reactive intermediates involved.

The scope of metal atom promoted aromatic "nucleophilic" substitution is not yet well defined. We expected, in view of evidence that propagation cycles analogous to steps 2, 3, and 4 are quite efficient in certain reactions of nitrobenzylic halides,[8] that nucleophilic substitution at saturated carbon should also be promoted by solvated electrons, and have recently learned that such effects have been observed.[9]

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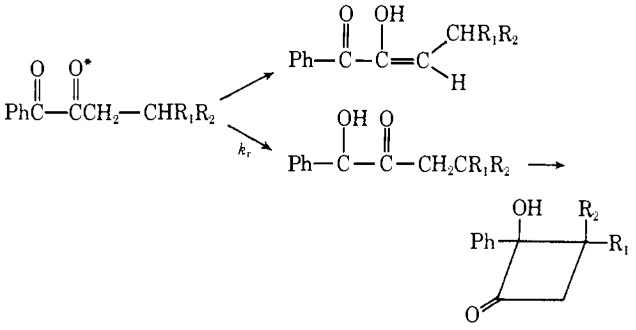
Competitive Photoenolization and Photocyclization of 1-Phenylalkane-1,2-diones

Sir:

Although the photoreduction of 1,2-diones has received a great deal of attention,[1] very few detailed mechanistic studies have been reported. Urry and Trecker found that aliphatic α-diketones, like most carbonyl compounds containing γ C–H bonds, undergo photoinduced intramolecular hydrogen transfer, with exclusive formation of 2-hydroxycyclobutanones.[2] Some quantitative kinetic data on this photocyclization have been reported for aliphatic α-diketones.[3] Because of the interesting behavior of 1-(*o*-alkylphenyl)-1,2-propanediones,[4] we have investigated the excited-state kinetics of several phenyl alkyl α-diketones.[5] We find that photoenolization of the 2-carbonyl is competitive with hydrogen abstraction from a γ-carbon by the 1-carbonyl.



Quantitative data for several diketones are summarized in Table I. All reactions are completely quenchable by pyrene or anthracene and can be sensitized efficiently by benzophenone. These results indicate exclusive triplet-state reactions and high intersystem crossing yields. Product formation was measured at low conversions (<5%) by vpc; diketone disappearance by uv analysis at higher conversions (20–50%).

Although quantum yields for disappearance of phenyl ketones with γ-hydrogens increase to unity in polar solvents,[6] quantum yields for the corresponding phenyl diketones are only slightly greater in acetonitrile than in benzene. The effect of polar solvents on photoelimination of phenyl ketones has been attributed to retardation of the disproportionation of 1,4-biradical intermediates.[6,7] If we assume that with the diketones a small amount of biradical reversal occurs in benzene but is eliminated in acetonitrile, we can divide the calculated triplet state lifetimes into k_r and k_d values, as shown in Table I. Both values turn out to be solvent independent. Importantly, the uniform k_d values for all three reactive diketones attest to the validity of our kinetic assumptions. The previously reported behavior of aliphatic α-diketones[3] unfortunately is not as simple, and the triplet-state rate constants could not be evaluated accurately.

The 2×10^5 sec^{-1} triplet decay rate common to all the phenyl diketones studied not only is faster than that indicated for aliphatic diketones,[3] but apparently involves a chemical reaction. We originally noted that

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(5) All diketones were prepared by the method of N. Kornblum and H. W. Frazier, *J. Amer. Chem. Soc.*, **88**, 865 (1966).

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