cedure. A mixture of 2.2 g (7.8 mmol) of **5a** and 10 ml of acetic anhydride was refluxed for 3.5 h. The solution was cooled and poured into 200 ml of ether and 200 ml of petroleum ether (bp 30–60°) and the resulting solid filtered to give 900 mg (37%) of **6a.** The filtrate was concentrated and the residue refluxed with 20 ml of acetic anhydride for 4 h to give an additional 800 mg (33%) of **6a.** The analytical sample was prepared by recrystallization from acetone–hexane: mp 267–268° (lit.[2] mp 260–262°); ir ($CHCl_3$) 1765, 1700 cm^{-1} (2 C=O).

Anal. Calcd for $C_{17}H_{13}N_3O_3$: C, 66.45; H, 4.26; N, 13.67. Found: C, 66.40; H, 4.36; N, 13.55.

***N*-[(6-Chloro-4-oxo-4*H*-3,1-benzoxazin-2-yl)methyleneamino]-*N*-phenylacetamide (6b).** A mixture of 1.6 g (5 mmol) of **5b** and 25 ml of acetic anhydride was refluxed for 3.5 h, cooled, and poured into ether–petroleum ether. Filtration gave 1.3 g (76%) of **6b.** The analytical sample was prepared by recrystallization from CH_2Cl_2–hexane to give **6b** as colorless needles: mp 266–267°; ir ($CHCl_3$) 1770, 1703 cm^{-1} (2 C=O).

Anal. Calcd for $C_{17}H_{12}ClN_3O_3$: C, 59.79; H, 3.54; N, 12.30. Found: C, 59.73; H, 3.33; N, 12.46.

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Registry No.—**4a,** 57527-44-3; **4b,** 57527-45-4; **5a,** 57527-46-5; **5b,** 57527-47-6; **6a,** 57527-48-7; **6b,** 57527-49-8; anthranilic acid, 118-92-3; chloral, 75-87-6; 5-chloroanthranilic acid, 635-21-2; phenylhydrazine, 100-63-0; acetic anhydride, 108-24-7.

Supplementary Material Available. Tables of the positional and thermal parameters for the structure of **6b** (2 pages). Ordering information is given on any current masthead page.

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An Electron Spin Resonance Study of Kinetics in the SRN1 Reaction of Aryl Halides with Potassium

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The reaction of aryl halides with alkali metals is known to be quite rapid,[1–3] with the anion radical of the aryl halide generally decomposing in less than 1 s, even at very low temperatures. The ESR signal normally obtained after the decomposition is that of the parent hydrocarbon anion radical. We have modified the usual reduction procedure[4] in order to observe the decay of the arene hydrocarbon anion radical in its electron exchange reaction with excess aryl halide (step 4 of Scheme II).

In this modification, a 10^{-3} M solution of the aryl halide in 2:1 THF–DME is only momentarily brought into contact with a potassium mirror at −135°. The solution (removed from contact with the metal) is immediately plunged into a precooled ESR cavity and the ubiquitous[5] arene hydrocarbon signal observed. Under these circumstances, the aryl halide is readily available for electron exchange with the small amount of freshly produced hydrocarbon anion radical.

With the biphenylyl halides what is actually observed then is the decay of the biphenyl anion radical, a special case of the SRN1 mechanism recently recognized by Bunnett et al.[6] and generalized in Scheme I.[7]

Scheme I

$$\text{electron donor} + \text{ArX} \longrightarrow (\text{ArX})\cdot^- \tag{1}$$

$$(\text{ArX})\cdot^- \longrightarrow \text{Ar}\cdot + \text{X}^- \tag{2}$$

$$\text{Ar}\cdot + \text{R}:^- \longrightarrow (\text{ArR})\cdot^- \tag{3}$$

$$(\text{ArR})\cdot^- + \text{ArX} \longrightarrow \text{ArR} + (\text{ArX})\cdot^- \tag{4}$$

The decay of the biphenyl anion radical signal in step 4 follows excellent first-order kinetics,[8] consistent with the SRN1 mechanism. The reaction steps of Scheme II follow the parallel paths of Scheme I, in which the solvent behaves as the "R" donor (steps 3).

Scheme II

$$\text{K}\cdot + \text{ArX} \longrightarrow (\text{ArX})\cdot^- + \text{K}^+ \tag{1}$$

$$(\text{ArX})\cdot^- \longrightarrow \text{Ar}\cdot + \text{X}^- \tag{2}$$

$$\text{Ar}\cdot + \text{solvent-H} \longrightarrow \text{ArH} \xrightarrow[\text{of K}\cdot]{\text{remaining traces}} (\text{ArH})\cdot^- \tag{3}$$

$$(\text{ArH})\cdot^- + \text{ArX} \longrightarrow \text{ArH} + (\text{ArX})\cdot^- \tag{4}$$

It must be noted that Scheme II requires one extra reduction as part of step 3 in which the remaining traces of solvated potassium are used up to produce more biphenyl anion radical. The chain proceeds until the ultimate product is unreduced biphenyl. If the final diamagnetic product is once again subjected to a somewhat longer reduction, the biphenyl signal is produced instantaneously and the signal does not decay.

Following the initial decay of the biphenyl signal from biphenylyl fluoride, a dimerization product, quaterphenyl anion radical, was observed to replace the biphenyl signal after some 90 min at −100°. The dimer probably arises from 2Ar·→ Ar–Ar, followed by reduction via residual ArH·⁻ or K·. Since quaterphenyl was not observed in any of the other reactions, it is possible that a high initial concentration of Ar· from ArF could produce this unique result. The highly reactive ArF would give this high initial concentration.

As may be seen in Table I, we also attempted a similar reduction of 4-nitrilobiphenyl; however, owing to the stabilizing influence of the CN group, we succeeded in obtaining initially only the decay (first order) of the parent anion radical.[9] Upon subsequent reduction at −120°, only the biphenyl signal was found. Evidently, for this system step 2 is quite slow, using up all available solvated metal, and the reaction stops at the step 3 production of biphenyl (unreduced).

We measured the decomposition rates for three of the biphenylyl halides at two temperatures (Table I). Above

Table I
Pseudo-First-Order Kinetics in the Reaction of Biphenyl Radical Anion with Biphenyl 4-Halides

Registry no.	C_6H_5–C_6H_4X X =	Temp, °C	$k \times 10^4$, s^{-1}	ΔH, cal deg^{-1} mol^{-1}
324-74-3	F	−100	2.58 ± 0.5	
2051-62-9	Cl	−40	10.8 ± 0.9	15.4 ± 2.5
		−50	2.43 ± 0.5	
92-66-0	Br	−40	14.4 ± 0.9	22.8 ± 3.7
		−60	1.44 ± 0.5	
1591-31-7	I	−40	422. ± 10	17.8 ± 2.5
		−60	11.6 ± 1.0	
2920-38-9	CN	22	0.0362 ± 0.001	

−40° these materials were highly unstable, and below about −70° the reaction times were rather too long to measure accurately. From these measurements a very rough estimate of the activation energies may be calculated. The value obtained for 4-bromobiphenyl appears rather high, yet considering the error range, all three are somewhat similar. Nevertheless, the reaction rates of the halides Cl, Br, and I at −40° are sucessively more rapid. Since the reaction of 4-fluorobiphenyl with biphenyl·⁻ was too rapid to measure at temperatures higher than −100°, we were not able to attempt an activation energy calculation for it.[10]

We are presently investigating the corresponding naphthyl halide series, and expect to report on them in the near future.

Experimental Section

All compounds and solvents used in this study are available from Aldrich Chemical Co. and were used as purchased (with the exception of solvents—distilled and stored over Na metal). The glass reduction apparatus in its simplest form has been described earlier.[4] The EPR instrument used is a JES-ME-1X (Jeolco) with variable temperature accessory of the Universidad de Los Andes.

A typical kinetic run may be described as follows. The sample tube (in which the K mirror and the ca. 0.3 mg of aromatic compound in 1 ml of 2:1 THF–DME solution are maintained separately) was cooled in a bath consisting of a thick syrup of isopropyl alcohol and liquid nitrogen at −135°. The sample tube was tipped and the solution allowed to contact the metal mirror for almost 1 s. On righting the tube for insertion into the cavity, the solution was agitated a bit in a bulge provided on the tube for mixing. The tube was rapidly wiped of alcohol and inserted into the precooled cavity (−135°). By this time, however, the tube itself was usually ca. −100° (the lowest temperature available for measurement). As soon as an appropriate temperature was reached, the diminution of the nine-line biphenyl signal produced was followed in sweeps of approximately 2.0 min.

The initial intensities of all halides were ±10%, and were followed for ca. 10 min at −40° and ca. 50 min at −60° (six to ten points taken). At least three runs were made on each sample and the slopes of each run were within the error range of any single run. The results presented in Table I are the average results of the three runs.

Inasmuch as the error involved in the calculation of the activation energy puts all three halides (Cl, Br, and I) within the same range, we must consider these values as only approximate.

Registry No.—Biphenyl radical anion, 34509-93-8.

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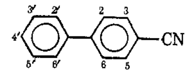
(8) Actually pseudo-first-order, inasmuch as the aryl halide is in large excess in the bimolecular reaction of step 4.
(9) Splitting constants obtained from a McLachlan calculation and experimental values: $a^{N}_{CN} = 5.8$, $a_{3,5} = 2.8$, $a_{2,6} = 0.7$, $a_{2',4',6'} = 0.5$, $a_{3',5'} = 0.2$ G.



(10) Predicting the order of reactivity in various radical reactions of aryl halides has been a rather fruitless task: PhCN > PhI > PhBr (for e_{aq}) (ref 1); ArI < ArBr or ArCl (for KNH_2, NH_3) (ref 6). We too find the practice speculative, and prefer to offer for our system only the observations concerning the CN group and the order of reactivity of the halides at −40° as ArF ≫ ArI > ArBr > ArCl.

Synthesis of Cyanohydrins from Cyanides. Transition Metal Peroxide Reactions

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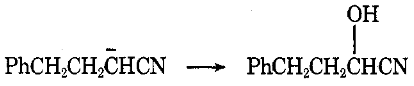
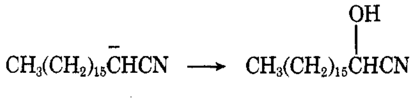
We have previously described the hydroxylation of enolates by the readily available molybdenum peroxide MoO_5·Py·HMPA (MoOPH).[1,2] In this paper, we report the analogous conversion of certain cyanide-stabilized anions to cyanohydrins.

Addition of a solution of 4-phenylbutyronitrile in dry THF to lithium diisopropylamide followed by reaction with MoOPH at −23° gives hydrocinnammaldehyde cyanohydrin in 57% yield (65%, considering recovered starting material) after aqueous work-up. Similarly, 5-cyanonorbornene is hydroxylated in 35–40% yield. Although the yield for this oxidation is poor, the procedure is simple and it becomes possible to convert the acrylonitrile–cyclopentadiene Diels–Alder adduct into an easily hydrolyzed derivative of the ketene–cyclopentadiene adduct.[3] The stereochemistry of the norbornenone cyanohydrin has not been determined, but the MoOPH product is identical with the cyanohydrin obtained by treating norbornenone with acetone cyanohydrin–KCN according to NMR evidence.

Under the usual conditions, stearonitrile affords the cyanohydrin in 55–60% yield and 3,3,3-triphenylpropanonitrile yields 55% cyanohydrin and 10% triphenylacetaldehyde (68 and 12.5%, respectively, considering unreacted starting material). The reaction of diphenylacetonitrile anion with MoOPH gives a mixture of comparable amounts of cyanohydrin and benzophenone in 71% yield (81% based on recovered nitrile) together with 11% of tetraphenylsuccinonitrile, apparently formed by dimerization of diphenylcyanomethyl radicals. Since radical coupling products are not formed in detectable amounts from other MoOPH hydroxylations, we prefer to rationalize cyanohydrin formation via carbanion attack at the peroxide O–O bond of the molybdenum reagent and not by an electron transfer mechanism.



$$PhCH_2CH_2\bar{C}HCN \longrightarrow PhCH_2CH_2CH(OH)CN$$



$$CH_3(CH_2)_{15}\bar{C}HCN \longrightarrow CH_3(CH_2)_{15}CH(OH)CN$$