2b and **9b** should lead to increased electron density at the para position in the hybrid, the ^{13}C shift of the γ-carbon atom of pyridine *N*-oxide (in trifluoroethanol) is 10 ppm upfield from that of ion **2** (X = Cl) from **4**, although the shifts of the β carbons are nearly the same (128.9 and 128.3 ppm for **2** and **9**, respectively).

As expected, the influences of hydrogen bonding, **7**, and charge-transfer complex formation, **1**, on the ^{13}C shifts of the β-, γ-, and γ-methyl carbons of the pyridine bases are much smaller than those of ion formation (see Table I).

The changes in the shifts of the α carbons and α-methyl carbons of the bases on complex or ion formation seem to be useful indicators of the type of binding at the pyridine-type nitrogens because they are influenced by two mechanisms having opposite effects on the ^{13}C chemical shifts. One is reduction in electron densities which results in downfield shifts of the resonances, and the other is changes in bond order[19,20] and/or higher excitation energies[21] which produce upfield shifts. Thus, hydrogen bonding, protonation, and the formation of the 1:1 complex **3** cause the ^{13}C resonances of both the α and the α-methyl carbons of **5** and **6** to shift to higher fields, while formation of ions **2** (X = Cl) causes downfield shifts of both carbon resonances. Interestingly, charge-transfer complexation with iodine or iodine chloride, as **1**, shifts the α-carbon resonances upfield and those of the α-methyl carbons downfield.

Experimental Section

The pyridine bases used in this study were commercial materials and were dried for several days over molecular sieves and then used without further purification. Iodine (resublimed, Mallinckrodt) was sublimed again and then stored in a desiccator. All solvents were reagent grade and were dried several days over molecular sieves.

Natural-abundance ^{13}C NMR spectra of 0.8 M solutions of the bases were obtained at about 26 °C, with proton-noise decoupling at 15.1, 25.1, and 45.3 MHz, using a Brukarian DFS, a Varian XL-100, and a Bruker WH-180 spectrometer, respectively. Chemical shifts were measured relative to internal 3% cyclohexane and then converted to parts per million from Me_4Si utilizing $\delta_{(CH_2)_6}(Me_4Si) = 27.0$. Proton spectra were obtained before and after the recording of the ^{13}C spectra, using a Varian EM-390 spectrometer operating at 90 MHz.

Registry No. **4**, 110-86-1; **4**·I_2, 2078-94-6; **4**·$PhCO_2H$, 3427-97-2; **4**·CF_3CO_2H, 464-05-1; **5**, 108-48-5; **5**·I_2, 17210-91-2; **5**·$PhCO_2H$, 3372-55-2; **5**·CF_3CO_2H, 70320-26-2; **6**, 108-75-8; **6**·I_2, 696-90-2; **6**·$PhCO_2H$, 57313-86-7; **6**·CF_3CO_2H, 57313-93-6; bis(pyridine)iodine(1+), 33571-24-3; bis(2,6-dimethylpyridine)iodine(1+), 69417-62-5; bis(2,4,6-trimethylpyridine)iodine(1+), 69417-65-8; 1-iodo-2,6-dimethylpyridinium, 70320-27-3; 1-iodo-2,4,6-trimethylpyridinium, 70320-28-4; I_2, 7553-56-2; ICl, 7790-99-0.

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Reactions of Halobenzenes with Cyanomethyl Anion in Liquid Ammonia by the $S_{RN}1$ Mechanism[1]

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Received February 28, 1979

The reactions of fluoro-, chloro-, bromo-, and iodobenzenes with cyanomethyl anion in liquid ammonia have been studied with regard to the product distribution (1,2-diphenylethane/phenylacetonitrile ratio). All the substrates gave about the same ratio. The addition of good electron acceptors such as naphthalene, anthracene, or pyridine inhibited the photostimulated reactions and gave a slight increase in the yield of 1,2-diphenylethane. In reactions stimulated by electrons the presence of naphthalene or benzoate ion as electron acceptors makes the yield of phenylacetonitrile drop almost to zero, whereas yields of the other products increase. Alternative reaction pathways are suggested.

Bromobenzene and cyanomethyl anion in liquid ammonia react under photostimulation giving 1,2-diphenylethane (DPE) (18% yield) and phenylacetonitrile (PAN) (8% yield) as major products, together with 62% of unreacted starting materials.[2]

This result was explained by the mechanism of Scheme I.

Scheme I

$$\mathrm{PhBr} + {}^{-}\mathrm{CH_2CN} \xrightarrow{h\nu} (\mathrm{PhBr})^{-}\cdot + \text{residue} \qquad (1)$$

$$(\mathrm{PhBr})^{-}\cdot \rightarrow \mathrm{Ph}\cdot + \mathrm{Br}^{-} \qquad (2)$$

$$\mathrm{Ph}\cdot + {}^{-}\mathrm{CH_2CN} \rightarrow (\mathrm{PhCH_2CN})^{-}\cdot \qquad (3)$$

$$(\mathrm{PhCH_2CN})^{-}\cdot + \mathrm{PhBr} \rightarrow \mathrm{PhCH_2CN} + (\mathrm{PhBr})^{-}\cdot \qquad (4)$$

$$(\mathrm{PhCH_2CN})^{-}\cdot \rightarrow \mathrm{PhCH_2}\cdot + \mathrm{CN}^{-} \qquad (5)$$

$$\mathrm{PhCH_2}\cdot \rightarrow (\mathrm{PhCH_2})_2 + \mathrm{PhCH_3} \qquad (6)$$

A special feature of this reaction, as compared with other

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Table I. Photostimulated Reaction of Halobenzenes with Cyanomethyl Anion in Liquid Ammonia

	PhX		amt of KCH_2CN,	time,[a]	yield,[b] %						
expt	X	amt, mmol	mmol	min	PhX	$PhCH_3$	PAN[c]	DPE[d]	DPM[e]	T_3PE[f]	T_4PF[g]
1	F	6.36	19.4	120	58	4	9	14	2	4	0
2	Cl	9.50	32.4	120	20	4	17	43	2	6	0.5
3	Br	6.89	19.0	30	80	1	4.5	15	1	2	0
4	Br	6.60	19.1	60	32	4	7.5	44	1	2	0
5	Br	5.99	18.1	120	11	5	13	43	1	3.7	0.3
6	Br	7.29	20.8	120	1	6	4	47	3	4	0.3
7	Br	36	108	120	80	1	6	14	0	0	0
8	I	6.75	20.0	120	0	6	7	63	2	*h*	*h*
9	I	7.33	21.8	120	0	3	9	62	3.2	4.5	0.5
10	I	5.33	17.2[i]	90	28		14[j]		2		48
11	I	6.75	18.5[k]	120	*h*	*h*	*h*	(19)[l]	*h*	*h*	*h*
12	CH_2CN	4.25	4.25[i]	120	100	0		0	0	0	0

[a] Irradiated with two 250-W Pyrex-filtered high-pressure UV lamps, Philips Model HTP, refrigerated with water. [b] Determined by GLC, unless otherwise indicated. Benzene was obtained in 0.5–2% yield. [c] Phenylacetonitrile. [d] 1,2-Diphenylethane. [e] Diphenylmethane. [f] 1,1,2-Triphenylethane. [g] 1,1,2,2-Tetraphenylethane. [h] Not quantified. [i] Diphenylacetonitrile. [j] Phenylacetonitrile anion as nucleophile. [k] Valeronitrile anion. [l] Isolated yield of pure 4,5-diphenyloctane.

Table II. Photostimulated Reaction of Halobenzenes with Cyanomethyl Anion and Electron Acceptors in Liquid Ammonia

	PhX		amt of KCH_2CN,			yield,[c] %			
expt	X	amt, mmol	mmol	mol %[a] of E.A.	time,[b] min	PhX	$PhCH_3$	PAN[d]	DPE[e]
1	Br	11.5	35.2	naphthalene, 18[f]	120	40	2	9	21
2	Br	7.03	21.4	naphthalene, 9[g]	120	42[h]	3	7	29
3	Br	9.00	27.5	naphthalene, 2	120	19	4	9	45
4	Br	9.50	28.0	benzophenone, 10	190	6	4	1	71
5	Br	9.50	28.0	benzophenone, 3	120	38	2	3	40
6	Br	5.80	17.2	anthracene, 16[i]	120	10[j]	6	10	47
7	Br	7.60	21.9	iodide, 120[k]	120	21	4	8	48
8	I	8.75	27.0	pyridine, 20	120	15	3	2	71
9	CH_2CN	7.25	7.25[l]	naphthalene, 10	120	100	0		0

[a] Based on halobenzene. [b] See footnote *a*, Table I. [c] See footnote *b*, Table I. [d] Phenylacetonitrile. [e] 1,2-Diphenylethane. [f] 75% recovered. [g] 100% recovered. [h] 1% diphenylmethane, 5% 1,1,2-triphenylethane, and 0.3% 1,1,2,2-tetraphenylethane. [i] Saturated solution, partially insoluble, 100% recovered. [j] 2% diphenylmethane, 6.2% 1,1,2-triphenylethane, and 0.4% 1,1,2,2-tetraphenylethane. [k] Potassium iodide. [l] Phenylacetonitrile anion as nucleophile.

$S_{RN}1$ reactions, is that the radical anion formed by reaction of phenyl radical with cyanomethyl anion (step 3) splits, giving benzyl radical and cyanide anion (step 5). This seems to be the main reaction pathway, based on product analysis.

Later on, evidence was found indicating decomposition of alkylphenyl sulfide radical anions in the sense of step 5 to be an important reaction. For instance, the reaction of ethanethiolate ion with phenyl radical gave mainly thiophenoxide anion (eq 7).[3]

$$Ph\cdot + RS^- \rightarrow (PhSR)^{-\cdot} \rightarrow PhS^- + R\cdot \qquad (7)$$

It is remarkable that reactions carried out under conditions similar to those just mentioned, but where the aryl radical was 1-naphthyl, gave alkyl 1-naphthyl sulfides in excellent yield.[4]

Furthermore, the photostimulated reactions of 1-halonaphthalenes and other polycyclic or heterocyclic halo compounds with cyanomethyl anion in liquid ammonia produce the normal substitution products without decomposition in the sense of eq 5.[5]

Molecular orbital considerations led to the suggestion that the difference in behavior implies differences in the nature of the radical anion intermediates, which may be summarized as follows. The predominant radical anion has its extra electron located in the lowest energy unoccupied molecular orbital of the molecule, in the CN moiety in the phenylacetonitrile radical anion and in the aromatic moiety in all other examples (eq 8).[6]

$$ArCH_2(CN)^{-\cdot} \rightleftharpoons \cdot^{-}(Ar)CH_2CN \qquad (8)$$

According to the accepted mechanism, PAN radical anion undergoes two competing reactions: one is bimolecular (eq 4) and one is unimolecular (eq 5). Thus one would expect that the amount of PAN formed would increase when, in eq 4, the substrate is a better electron acceptor.[7]

On the basis of this expectation, we reexamined the reactions of halobenzenes with acetonitrile anion in liquid ammonia to gain more insight into the mechanism of these reactions. Since step 4 leads to PAN and step 5 to DPE, we decided to measure their ratio with the hope that we could obtain the k_5/k_4 ratios for each halobenzene.

Results

All the photostimulated reactions were carried out under the same experimental conditions. Irradiation time and concentration of substrate and nucleophile were kept the same in order to have comparable results.

The reactivity of the four halobenzenes as measured by the amount of substrate consumed in 120 min of irradiation time is in the same order found with other nucleophiles in the $S_{RN}1$ reaction:[8] PhI (100%) > PhBr (90–100%) > PhCl (80%) > PhF (40%). With PhI the

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Table III. Reaction of Halobenzenes with Cyanomethyl Anion and Electron Acceptors Stimulated by Solvated Electrons in Liquid Ammonia

expt	PhX X	PhX amt, mmol	amt of KCH_2CN, mmol	mol %[a] of E.A.	amt of K metal,[b] mmol	yield,[c] % PhX	yield,[c] % PhH	yield,[c] % $PhCH_3$	yield,[c] % PAN[d]	yield,[c] % DPE[e]
1	Br	9.50	30.0	naphthalene, 110[f]	11.7	40	30	24	0	0
2	Cl	9.75	26.0	naphthalene, 120[g]	22.0	1	40	38	0	5
3	Cl	8.75	33.0	biphenyl, 244[h]	15.5	34	*i*	8	34	4
4	Cl	9.75	31.0	benzoate, 190[j]	37.7[k]	0	32	33	6	3
5	CH_2CN	4.15	19.3	naphthalene, 380[l]	16.3	100		0		0

[a] Based on halobenzene. [b] K metal added bit by bit. [c] Determined by GLC. [d] Phenylacetonitrile. [e] 1,2-Diphenylethane. [f] Saturated solution, partially insoluble, 100% recovered. [g] Saturated solution, partially insoluble. [h] To a solution of biphenyl, K metal was added and then PhCl; 93% biphenyl was recovered together with 7% dihydrobiphenyls. [i] Not quantified. [j] Sodium benzoate, saturated solution, partially insoluble. [k] Na metal. [l] To a solution of naphthalene, K metal was added and then phenylacetonitrile.

Table IV. Ratios of Benzyl Radical Derivatives to Phenylacetonitrile Anion Derivatives in the Photostimulated Reactions of Halobenzenes with Cyanomethyl Anion in Liquid Ammonia

X	convrsn, %	$S(PhCl_2\cdot)/S(Ph^-CHCN)$[a]
F	42	1.5
Cl	80	2.0
Br	20	2.6
Br[b]	20	2.5
Br	68	5.2
Br	89	3.2
Br	99	5.5
Br[c]	58	3.2
Br[d]	90	3.4
I	100	4.5

[a] $S(PhCH_2\cdot)$ = summation of products derived from benzyl radicals: toluene, 1,2-diphenylethane, and 1,1,2-triphenylethane. $S(Ph^-CHCN)$ = summation of products derived from phenylacetonitrile anion: phenylacetonitrile, diphenylmethane, 1,1,2-triphenylethane, and 1,1,2,2-tetraphenylethane. [b] Concentrated solution, expt 7, Table I. [c] 9 mol % naphthalene. [d] 16 mol % anthracene.

time necessary to complete the reaction was not determined.

In all these cases the main products were DPE and PAN, but a detailed study of all reaction products showed that small amounts (0.5–6%) of diphenylmethane (DPM), 1,1,2-triphenylethane (T_3PE), and 1,1,2,2-tetraphenylethane (T_4PE) were also formed. These products are not accounted for in Scheme I.

The formation of these products can be explained if the PAN formed in the reaction is deprotonated by the acetonitrile anion in excess and can further react with phenyl radicals. In order to check for this possibility, we did an experiment with PAN anion as nucleophile and PhI. After 90 min of irradiation time, T_4PE was formed in 48% yield and diphenylacetonitrile in 14% yield. These results show that PAN anion can act as initiator and nucleophile in this photostimulated reaction. Thus, Scheme I is incomplete and some steps should be added, as in Scheme II.

Scheme II

$$PhCH_2CN + {}^-CH_2CN \rightarrow Ph^-CHCN + CH_3CN \tag{9}$$

$$Ph\cdot + Ph^-CHCN \rightarrow (Ph_2CHCN)^{-}\cdot \tag{10}$$

$$(Ph_2CHCN)^{-}\cdot + PhX \rightarrow Ph_2CHCN + (PhX)^{-}\cdot \tag{11}$$

$$(Ph_2CHCN)^{-}\cdot \rightarrow Ph_2CH\cdot + CN^- \tag{12}$$

$$Ph_2CH\cdot + PhCH_2\cdot \rightarrow Ph_2CHCH_2Ph \tag{13}$$

$$2Ph_2CH\cdot \rightarrow (Ph_2CH)_2 \tag{14}$$

$$Ph_2CH\cdot \xrightarrow{SH} Ph_2CH_2 \tag{15}$$

In the reactions with acetonitrile anion as nucleophile the yield of T_4PE was always much lower than that of T_3PE, whereas when PAN anion is the nucleophile, it is the main product, but these results are understandable considering that in the former reaction the concentration of diphenylmethyl radical is very low, whereas the concentration of benzyl radical may be relatively high; thus the rate of step 13 should be faster than the rate of step 14.

Obviously if all these reactions occurred, the DPE/PAN ratio is not a good measure of the k_5/k_4 ratio of Scheme I. However, the ratio of the summation of all the products coming from step 4 (PAN, DPM, T_3PE, T_4PE) and the summation of the products coming from step 5 (toluene, DPE, T_3PE) should give us this ratio. Since the yield of DPE is high, the summation of the products coming from step 5 is not modified much. However, the total yield of products derived from step 4 and also the ratio of DPE/PAN change (Table IV).

It can be seen in Table IV that these ratios tend to increase in the series from PhF to PhI. For the first five experiments with PhBr (those without naphthalene present) the mean value of $S(PhCH_2\cdot)/S(Ph^-CHCN)$ is 3.8 ∓ 1.4. Certainly the experimental error is substantial. Nevertheless, if the mean value for PhBr is utilized, this ratio increases steadily from PhF to PhI.

These results are puzzling since PhI has a lower reduction potential than the other halobenzenes, and it is known that electron transfer to substances with more positive reduction potential is faster than to compounds with more negative reduction potential.[7] It should therefore be a better electron acceptor, accelerating step 4, whereas reaction 5 should be independent of the substrate; thus the ratio DPE/PAN should decrease. The fact that PhI is a better electron acceptor for these reactions is demonstrated by the fact that the rates of $S_{RN}1$ reactions are higher with PhI.

Since PAN could decompose giving benzyl radical and cyanide ion under our reaction conditions, and thus increase the ratio DPE/PAN through eq 16 → 5, an experiment was designed to answer this question. Equal amounts of PAN and PAN anion were prepared in liquid ammonia and irradiated for 120 min. After workup the mixture was analyzed by GLPC. There was no trace of decomposition products, and nearly all the PAN was recovered unchanged. This experiment clearly shows that PAN survives irradiation under our reaction conditions.

$$Ph^-CHCN + PhCH_2CN \rightarrow Ph\dot{C}HCN + (PhCH_2CN)^{-}\cdot \tag{16}$$

In order to check whether the course of the reaction would be changed by good electron acceptors which could speed up reaction 4 through step 4′, we added 18 mol %

of naphthalene to PhBr and cyanomethyl anion in liquid ammonia.

$$(PhCH_2CN)^{-\cdot} + E.A. \rightarrow PhCH_2CN + (E.A.)^{-\cdot} \quad (4')$$

In 120 min of irradiation time, only 60% of the PhBr reacted, which shows that naphthalene inhibited the reaction, but the ratio DPE/PAN was 2.3. The same reaction in the presence of 9 and 2 mol % of naphthalene gave similar results (experiments 1–3, Table II).

Inhibition of photostimulated $S_{RN}1$ reactions by good electron acceptors has been previously found. As was already suggested, the inhibition of this reaction by naphthalene could be due to the acid–base reaction between PAN and naphthalene radical anion, which acts as a termination step.[5]

To overcome this problem a less basic electron acceptor was needed. We chose benzophenone, since alkoxides are less basic than carbanions. In Table II, experiment 5, we can see that with 3 mol % of benzophenone, 62% of reaction occurred in 120 min of irradiation, with a DPE/PAN ratio of ca. 10. With 10 mol % and 190 min of irradiation, 94% of reaction occurred, with a high yield of DPE. In the study of the products by GLPC it was not possible to detect either benzophenone or benzhydrol (reduction product of the benzophenone); therefore we will not analyze these results further.

In reactions carried out with anthracene, iodide ions, and pyridine, we found a slight inhibition and an increase in the yield of DPE (experiments 6–8, Table II).

In order to determine if the electron acceptor added to the reaction could in some way decompose PAN under our reaction conditions, thus increasing the ratio DPE/PAN, we irradiated for 120 min a solution of PAN and PAN anion in equal amounts, together with 10 mol % of naphthalene. The mixture did not react and no trace of DPE was found by GLPC and NMR analyses.

Reactions Stimulated by Solvated Electrons. The reaction of PhCl with cyanomethyl anion in liquid ammonia, stimulated by solvated electrons, leads to a mixture of benzene, toluene, PAN, and DPE in proportions which change with the experimental conditions.[2]

We chose experimental conditions which lead to the higher yield of PAN (see experiment 6, Table I, ref 2) and ran reactions under these conditions, but in the presence of 120 mol % of naphthalene (saturated solution, since some naphthalene stays undissolved). In this case no PAN was formed; thus in the presence of naphthalene the yield of PAN drops from 24% under the Bunnett and Gloor conditions to 0%. Similar results were obtained when PhBr was used instead of PhCl. Also, similar results were obtained in the presence of benzoate ion as electron acceptor.

When PhCl was added to a solution of cyanomethyl anion and biphenylide radical anion, the product distribution was about the same as when PhCl was added to a solution of cyanomethyl anion and potassium metal dissolved in liquid ammonia.[2]

Discussion

We can summarize the main results of this work as follows:

1. Overall reactivity in photostimulated reactions of halobenzenes with cyanomethyl anion in liquid ammonia decreases in the order PhI > PhBr > PhCl > PhF.
2. The overall rate of reaction decreases in the presence of good electron acceptors.
3. There is apparently some tendency for $S(PhCH_2\cdot)/S(Ph^-CHCN)$, the ratio of products derived from benzyl radical to those derived from the PAN anion, to increase in the series from PhF to PhI.
4. In photostimulated reactions, electron acceptors appear to have little consistent effect on the product ratio.
5. In reactions provoked by solvated electrons, good electron acceptors significantly decrease the proportion of PAN among the products.

Mechanistic Model of Scheme I. Points 1 and 2 are in good agreement with previous findings. The order of reactivity of the halobenzenes is in accord with their rate of reaction with the hydrated electron,[9] which in turn is related to their reduction potentials, or in the order found with other nucleophiles in photostimulated $S_{RN}1$ reactions.[8]

The inhibition of $S_{RN}1$ reactions by good electron acceptors may be due to the fact that they form stable radical anions and act somehow as termination steps as has already been suggested.[10,11]

Points 3–5 cannot be explained by the mechanisms sketched in Schemes I and II. According to these mechanisms, PAN radical anion undergoes two competing reactions, steps 4 and 5. Step 4 is bimolecular and step 5 is unimolecular. The rate of step 4 should increase in the presence of good electron acceptors, whereas step 5 should be independent. Therefore the ratio of total products coming from step 4 to the summation of the products coming from step 5 should decrease as the substrates become better electron acceptors, whereas, if anything, the ratio increases.

Since most of our experiments were carried out at about the same concentration of substrate, one might think that the constancy of the ratio DPE/PAN with varying substrate or electron acceptors is due to the rate of step 4 being diffusion controlled. However, experiment 7, Table I, shows that this is not the case because the ratio is still constant even when the initial substrate concentration changes by a factor of 5.

When naphthalene or other good electron acceptors are present, a significant stationary amount of radical anion may be present; thus the possibility that they react with PAN before it is deprotonated must be considered. Equation −4′ is the reverse of eq 4′.

$$PAN + (E.A.)^{-\cdot} \rightarrow (PAN)^{-\cdot} + E.A. \quad (-4')$$

Electron transfer from naphthalene radical anion to PAN has been reported to yield decyanation products in THF, although deprotonation by the same naphthalene radical anion is the main reaction.[12]

To check for this possibility we performed an experiment in which we added PAN to a solution of naphthalene radical anion and cyanomethyl anion in about equal concentration. After workup PAN was recovered unchanged, and no DPE could be detected by GLC. The experiment shows that the rate of proton transfer to acetonitrile anion is much faster than electron transfer.

The body of our results suggests that the products under consideration (PAN and derivatives and DPE and derivatives) come from reactions of equal molecularity. Steps 4 and 5 in Scheme I do not adequately represent the main pathway for the formation of these products.

A Mechanistic Model with Electron Acceptor in the Transition State. One alternative mechanistic model is eq 17, where E.A. is any electron acceptor, including the substrate PhX.

In eq 17 PAN radical anion and the electron acceptor, which is any electron acceptor present in the reaction

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$$(\mathrm{PAN})^{-\cdot} + \mathrm{E.A.} \rightarrow (\mathrm{PAN{-}E.A.})^{-\cdot} \xrightarrow{k_1} (\mathrm{E.A.})^{-\cdot} + \mathrm{PAN}$$
$$\xrightarrow{k_2} \mathrm{PhCH_2}\cdot + \mathrm{CN}^- + \mathrm{E.A.} \qquad (17)$$

including the halobenzene substrate, form an adduct which then undergoes two competing unimolecular reactions leading to the observed products. The formation of adducts between dianions and electron acceptors before the actual electron-transfer reaction has been demonstrated in other studies.[13]

We also note that a charge-transfer complex was postulated as intermediate in the initiation step of the photostimulated reaction of PhI and diethyl phosphite ion in $\mathrm{Me_2SO}$.[14]

The relative rates of decomposition of the intermediate to give the electron acceptor radical anion and PAN (k_1, eq 17) or benzyl radical and cyanide ion (k_2, eq 17) need not be dependent on the electron acceptor reduction potential.

The increase of the concentration of toluene in the potassium metal stimulated reaction may be attributed to a reaction of this adduct with the solvated electron or the electron acceptor radical anion which are in relatively high concentration (eq 18).

$$(\mathrm{PAN{-}E.A.})^{-\cdot} \xrightarrow{e^- \text{ or } (\mathrm{E.A.})^{-\cdot}} (\mathrm{PAN{-}E.A.})^{2-} \rightarrow$$
$$\mathrm{PhCH_2}^- + \mathrm{CN}^- + \mathrm{E.A.} \qquad (18)$$

Possibility of Electron Release as Solvated Electrons. Another alternative pathway for the photostimulated reactions is shown in eq 19.

$$(\mathrm{PAN})^{-\cdot} \rightarrow \mathrm{PAN} + e^-_{\mathrm{NH_3}}$$
$$\rightarrow \mathrm{PhCH_2}\cdot + \mathrm{CN}^- \qquad (19)$$

In this mechanism PAN radical anion transfers its extra electron to the solvent ammonia or decomposes into benzyl radical and cyanide ions. Both steps have the same concentration dependence and are independent of the substrate and thus can explain our experimental results.

The rate of reaction of acetonitrile with the solvated electron in liquid ammonia has been measured, and the fact that it is very slow ($k_{\mathrm{obsd}} \approx 2\ \mathrm{M^{-1}\ s^{-1}}$) compared with the rate in water ($k_{\mathrm{obsd}} = 3 \times 10^7\ \mathrm{M^{-1}\ s^{-1}}$) led to the suggestion that the overall rate is depressed because k_2 in eq 20 is rate controlling and it is preceded by an unfavorable equilibrium.[15]

$$\mathrm{CH_3CN} + e^-_{\mathrm{NH_3}} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (\mathrm{CH_3CN})^{-\cdot} \xrightarrow{k_2} \text{products} \qquad (20)$$

The low value of K_1 in liquid ammonia is attributed to the high stability of the ammoniated electron which increase k_{-1} relative to k_2 and k_1.

Similar results have been found for the reaction of benzene,[16] biphenyl,[19] and fluorobenzene[17] with the solvated electron in ammonia, where it has also been suggested that reversible attachment of an ammoniated electron occurs.

PAN radical anion is not expected to be more stable than acetonitrile radical anion because the lowest unoccupied molecular orbital of the molecule belongs to the cyano group[6] and the phenyl ring is not conjugated with it; thus, PAN radical anion may lose an electron at a rate similar to k_{-1} of eq 20, and electron transfer to the solvent and not to the electron acceptor might be the main reaction pathway under all our reaction conditions (eq 21).

$$(\mathrm{PAN})^{-\cdot} \xrightarrow{k_{21}} \mathrm{PAN} + e^-_{\mathrm{NH_3}}$$
$$\xrightarrow{k_4\,(\mathrm{E.A.})} \mathrm{PAN} + (\mathrm{E.A.})^{-\cdot} \qquad (21)$$

Possibility of Photoejection of Electrons. Also we must consider the effect of the light. It is well-known that radical anions and dianions photoeject electrons on flash photolysis. For instance the pyrenide radical anion photoejects electrons with a pulse of 420-nm light.[18]

In our system we irradiated the solution with a 350-nm UV Pyrex-filtered light (500 W). Considering that pyrene is a better electron acceptor than PAN and the high stability of the ammoniated electron compared to that of the electron solvated by THF, the photoejection of the electron from PAN radical anion could be facilitated (eq 22).

$$(\mathrm{PAN})^{-\cdot} \xrightarrow{h\nu} \mathrm{PAN} + e^-_{\mathrm{NH_3}} \qquad (22)$$

Whether the process is a dark reaction (eq 21) or photostimulated (eq 22) we do not know, but both processes seem reasonable.

The data we have at present are not enough to speculate about which is the mechanism or mechanisms that are operating in our system. However, they clearly indicate that step 4 (Scheme I) is not the main reaction pathway leading to PAN.

Potentialities in Synthesis. As discussed previously,[2] the reactions of aryl halides with alkyl cyanide anions constitute a method for installing an alkyl group on a benzene ring in place of a nucleofugic substituent. With our results some new possibilities are open; one can obtain different products from the same nitrile with choice of appropriate conditions. Thus iodobenzene seems to be a good substrate if one is interested in the symmetrical diphenylalkane of structure PhRCH–CHRPh, since mainly this compound is formed. The formation of aryl-substituted hydrocarbons is easily carried out if benzoate is added, since in this case the main products are benzene and the hydrocarbon. The byproducts of the benzoate reaction with solvated electrons are soluble in alkaline water solution, making the separation and purification of the main product easier.

Experimental Section

General Procedures. Melting points have not been corrected. NMR spectra were recorded on a Varian T-60 nuclear magnetic resonance spectrometer, using $\mathrm{CCl_4}$ as solvent, unless otherwise noted, and the spectra are reported in parts per million relative to $\mathrm{Me_4Si}$ (δ). Mass spectral measurements were obtained with a Hitachi Perkin-Elmer Model RMV-6 mass spectrometer. Thin-layer chromatography was performed on silica gel plates. Gas chromatographic analyses were performed on a Varian Aerograph Series 2400 with a flame ionization detector, using a column packed with 3% FFAP on Chromosorb P, 1.5 m × 3 mm (to quantify benzene, toluene, halobenzenes, phenylacetonitrile, diphenylmethane, and 1,2-diphenylethane), and a column packed with 3% silicon rubber S.E. 30 on Chromosorb P 80–100, 1.5 m × 3 mm (to quantify 1,1,2-triphenylethane and 1,1,2,2-tetraphenylethane). Peak areas were corrected by the detector response, using internal standards. Liquid ammonia was dried over

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Na metal and distilled under nitrogen into the reaction flask. Alkali metals were cut in small pieces and washed free of oil with diethyl ether immediately before adding to the reaction mixtures.

Materials. Acetonitrile (B.P.C., Erba) was purified and dried as described.[5] All the halobenzenes, naphthalene, anthracene, and benzophenone were analytical grade, commercially available products and were used as received. Pyridine was dried over KOH and distilled before use. Phenylacetonitrile[20] and 1,2-diphenylethane[21] were prepared as described. Cyanomethyl anion was prepared in situ as described.[5]

Photostimulated Reactions. The photostimulated reactions were carried out in a photochemical reactor equipped with two 250-W Pyrex-filtered UV lamps, Philips Model HTP, emitting maximally at ca. 350 nm, with water-jacketed refrigeration. The method used was as described.[5]

Potassium Metal Stimulated Reactions. The procedure and the preparation of cyanomethyl anion was done as usual.[5] Then the electron acceptor (sodium benzoate or naphthalene) and bromobenzene were added. After about 10–15 min, the potassium metal was added slowly in small bits. An excess of water was added, followed by 100 mL of diethyl ether, and the ammonia was allowed to evaporate. An internal standard was added and the two layers were separated. The water was twice extracted with ether. The ether extract was twice washed with water and dried over anhydrous Na_2SO_4 and then was analyzed by GLC.

Identification of Products. All products were identified and quantified by comparison of their retention times on both columns with authentic samples. Pure samples of 1,2-diphenylethane and 1,1,2,2-tetraphenylethane were isolated, and their melting points and NMR and IR spectra were identical with those of authentic materials.

4,5-Diphenyloctane was purified by column chromatography on neutral alumina. The mass spectrum has a molecular peak at m/e 266 and peaks at m/e 233, 209, 133, and 91. The NMR spectrum gave δ 0.8 (14 H), 2.7–3.2 (2 H), and 6.8–7.4 (10 H).

Acknowledgments. A.B.P. gratefully acknowledges receipt of a fellowship from the Consejo Nacional de Investigaciones Científicas y Técnicas, Argentina. We thank Professor Joseph F. Bunnett for helpful suggestions and critical reading of the manuscript.

Registry No. PhF, 462-06-6; PhCl, 108-90-7; PhBr, 108-86-1; PhI, 591-50-4; cyanomethyl anion, 21438-99-3; diphenylacetonitrile, 86-29-3; valeronitrile anion, 42117-15-7; toluene, 108-88-3; PAN, 140-29-4; DPE, 103-29-7; DPM, 101-81-5; T_3PE, 1520-42-9; T_4PE, 632-50-8; 4,5-diphenyloctane, 42117-21-5; benzene, 71-43-2; phenylacetonitrile anion, 18802-89-6.

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Strained Heterocycles. Properties of Five-Membered Heterocycles Fused to Four-, Six-, and Eight-Membered Rings Prepared by Base-Catalyzed Rearrangement of 4-Heterohepta-1,6-diynes

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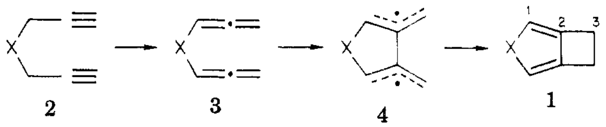
Received November 7, 1978

The base-catalyzed rearrangement of 4-thia-, 4-oxa-, and 4-azahepta-1,6-diynes (**2a–c**) gave the corresponding dimeric 4,5,9,10-tetrahydrocycloocta[1,2-*c*:5,6-*c*′]dithiophene, -difuran, and -dipyrrole (**5a–c**). In contrast, the base-catalyzed rearrangement of the related *tert*-butyl-substituted derivatives **6a–c** gave the monomeric 6,7-di-*tert*-butyl-3-heterobicyclo[3.2.0]hepta-1,4-dienes (**7a–c**). With the nitrogen system **6c** the dimeric cycloocta-1,5-diene **10** could also be obtained by varying the reaction conditions, and a small amount of the tricyclic dimer **9** was obtained on rearrangement of the oxygen system **6b**. Rearrangement of 1,7-diphenyl-4-heterohepta-1,6-diynes **11a–c** gave the corresponding 4,9-dihydro-4-phenylnaphtho[2,3-*c*]heterocycles **18a–c** as primary products and not the naphthalenes **14a–c** as had previously been reported. A unifying mechanism to account for all of these products is described. The ^{13}C NMR spectra of the substituted heterocycles show that annelation by small rings results in an upfield chemical shift of the α-carbon atoms, as previously observed for benzocycloalkenes. The anomalous spectrum of **10** and the chemical shifts observed on oxidizing thiophenes to thiophene 1,1-dioxides are described and discussed.

Following the synthesis of the first benzocyclopropene derivatives,[1,2] there has been a revival of interest in the preparation of aromatic systems strained by annelation of small rings.[3] Most of this work has been directed toward the synthesis of benzenoid systems, but some work has been reported on the preparation of strained heterocyclic compounds.[4,5] We have previously reported the synthesis of 3-thiabicyclo[3.2.0]hepta-1,4-diene (**1**, X = S)[5b] and we now report the preparation of *tert*-butyl derivatives of this thiophene and its pyrrole and furan analogues involving the base-catalyzed rearrangement of the corresponding 4-heterohepta-1,6-diynes.[6] We also describe other base-catalyzed rearrangements which lead to dimeric products, predominantly *syn*-bis(annelated) cyclooctadienes, and to 4,9-dihydronaphtho[2,3-*c*]thiophenes, -pyrroles, and -furans. The mechanisms of these reactions

Scheme I



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