

steric factors are concerned, in a  $\beta,\gamma$  chelate containing  $D_2O$ -mediated metal-to-N binding either  $N_1$  or  $N_7$  can function with ease either as the ligand atom in a 1:1 complex or as the ligand atom of the inner nucleotide in a 1:2 complex, and any one of the three adenine nitrogens can be the ligand atom of the outer nucleotide in the 1:2 complex. Because of the differences in the bond angles in the two adenine rings of an adenine nucleotide, the  $H_2$  atom would probably be significantly closer to the metal if  $N_1$  were the ligand atom than  $H_8$  would be if  $N_7$  were the ligand atom. Thus, on the average,  $T_{2M}^{-1}$  and, consequently,  $(fT_{2p})^{-1}$  might be expected to be larger for  $H_2$  than for  $H_8$ , as we have found at pD 5.4. However, the competition study at pD 5.4 points to  $\tau_M$ , rather than  $T_{2M}$ , as the factor responsible for the large  $H_2$  broadening.

The four line-broadenings measured in the equimolar competition study at pD 5.4 (Figure 5) are 6.90, 3.05, 11.95, and 11.95 Hz for the ATP  $H_8$ , AMP  $H_8$ , ATP  $H_2$ , and AMP  $H_2$  signals, respectively. Their relative values are 2.3:1.0:3.9:3.9. Since AMP cannot function as the inner nucleotide of a 1:2 complex when an equal concentration of ATP is present, and since the

two  $H_2$  signals appear to be equally broadened, we conclude that AMP and the ATP  $N_1$  (and  $N_8$ ) function primarily as outer ligands while ATP  $N_7$  functions both as inner and outer ligand. As explained earlier, one would expect the  $Mn^{2+}-H_8$  distance to be approximately the same whether the  $N_7$  is inner or outer ligand and whether the  $H_8$  belongs to ATP or AMP. Consequently, one would estimate that the broadening of the inner ATP  $H_8$  signal is only 3.85 Hz (*i.e.*, 6.90–3.05 Hz) in this experiment. One cannot account for such a small value, considering the magnitude of the sum of the broadenings of the other three signals, by invoking the dependence of  $T_{2M}$  on  $r$ . On the other hand, this large difference between inner and outer broadenings could result if the outer ligand exchanged much faster than the inner ligand, *i.e.*, according to case III(i) with  $\tau_{M,o} < \tau_{M,i}$ . This suggests that the fundamental cause for the drastic changes in the line broadenings seen in Figure 2 between pD 5.4 and 6.4 when  $[ATP]_t = 0.25 M$  might possibly be a change in the ligand exchange mechanism from case III(i) to case II accompanying the structural changes as the pD increases above pD 5.4.

## The Sense of Cleavage of Substituted Benzenes on Reaction with Solvated Electrons, as Determined by a Product Criterion<sup>1</sup>

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**Abstract:** Many compounds of type  $C_6H_5X$ , in which the first atom of substituent X represents diverse elements, are cleaved by potassium metal in ammonia. It is possible to tell whether the immediate fragment from cleavage is phenyl radical or phenyl anion by conducting cleavage in the presence of acetone enolate ion. Phenyl radical is trapped by the enolate ion, as recognized by the formation of phenylacetone, 1,1-diphenyl-2-propanone, and/or 1-phenyl-2-propanol, often in high total yield. Phenyl anion does not arylate the enolate ion, and merely takes a proton from the solvent to appear as benzene. The sense of scission of compounds of the type  $PhY$ ,  $Ph_2Y$ , or  $Ph_3Y$ , where Y is an element of group VII, VI, or V, correlates with the electronegativities of the elements. Phenyl radical is formed when Y is F, Cl, Br, I, O, or S, and phenyl anion when Y is P, As, Sb, or Bi, and both competitively when Y is Se.  $Ph_2I^+$ ,  $PhNMe_3^+$ ,  $(PhO)_3PO$ , and  $PhOPO(OEt)_2$  also cleave to phenyl radical, while  $Ph_2SO$ ,  $Ph_2SO_2$ ,  $PhSO_2Me$ , and  $PhSO_3^-$  are cleaved to phenyl anion. Cleavage of  $Ph_3S^+$  is complex. Some compounds are unaffected, or cleave in other ways.

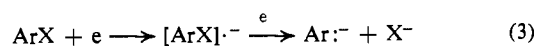
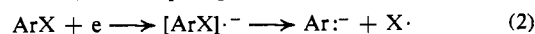
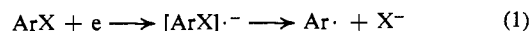
Many substituents are cleaved from benzene rings when electrons are supplied, as solvated electrons, from electrodes, or from other donors. There has been interest in the mechanism of cleavage, especially as to whether one or two electrons are required and as to what are the immediate products of bond rupture. Opinions have differed, and some uncertainty still prevails.<sup>3-6</sup>

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(2) Grateful recipient of a fellowship from the Consejo Nacional de Investigaciones Científicas y Técnicas, Argentina.

(3) (a) A. J. Birch, *Quart. Rev., Chem. Soc.*, **4**, 69 (1950); (b) P. J. Elving and B. Pullman, *Advan. Chem. Phys.*, **3**, 1 (1961); (c) H. Smith, "Organic Reactions in Liquid Ammonia," Wiley, New York, N. Y., 1963, pp 164-206, 279-285; (d) C. L. Perrin, *Progr. Phys. Org. Chem.*, **3**, 165 (1965); (e) A. J. Birch and G. Subba Rao, *Advan. Org. Chem.*, **8**, 1 (1972).

Insofar as the aryl fragment of cleavage is concerned, the two principal possibilities are the aryl radical and the aryl anion. The former may arise by reaction 1, and the latter by either reaction 2 or reaction 3. The



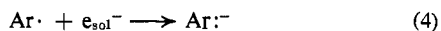
(4) (a) J. W. Sease, F. G. Burton, and S. L. Nickol, *J. Amer. Chem. Soc.*, **90**, 2595 (1968); (b) W. E. Wentworth, R. S. Becker, and R. Tung, *J. Phys. Chem.*, **71**, 1652 (1967); D. E. Durbin, W. E. Wentworth, and A. Zlatkis, *J. Amer. Chem. Soc.*, **92**, 5131 (1970); (c) T. C. Cheng, L. Headley, and A. F. Halasa, *ibid.*, **93**, 1502 (1971).

(5) E. Grovenstein, Jr., and R. W. Stevenson, *J. Amer. Chem. Soc.*, **81**, 4850 (1959).

(6) D. H. Eargle, Jr., *J. Org. Chem.*, **28**, 1703 (1963); D. H. Eargle, Jr., and W. B. Moniz, *ibid.*, **32**, 2227 (1967); C. G. Screttas, *J. Chem. Soc., Chem. Commun.*, 869 (1972).

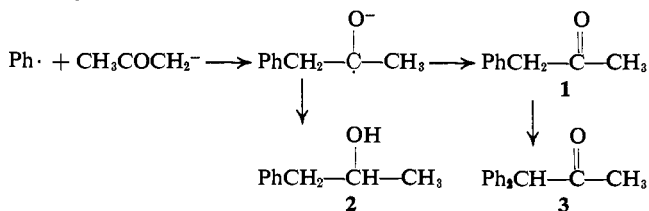
initial product of electron acceptance by a neutral molecule is a radical anion, as represented for the first step of all three reactions, even when the C-X bond is quite labile.<sup>7,8</sup>

The aryl radical produced in reaction 1 may subsequently accept an electron,<sup>9</sup> being reduced to an aryl anion (eq 4).



Product studies sometimes give useful indications of the mechanisms of redox reactions.<sup>10</sup> In the case of the reductive cleavage of ArX species, however, the prominent product under many circumstances is ArH, which does not tell much about the mechanism of cleavage. An aryl anion generated *via* reaction 2 or 3 can form ArH by proton capture from a solvent such as ammonia or 1,2-dimethoxyethane.<sup>9</sup> An aryl radical formed *via* reaction 1 can progress to ArH either by hydrogen atom abstraction (from solvent or other constituent of the medium) or by reduction to aryl anion (eq 4) and finally proton capture.

The high reactivity of phenyl radical with acetone enolate ion to form phenylacetone (1) and related products<sup>11,12</sup> (Scheme I) suits this enolate ion for use to trap Scheme I



phenyl radicals formed according to eq 1. If this enolate ion is present during cleavage of a substituted benzene by solvated electrons, and if phenylacetone (1) and/or 1-phenyl-2-propanol (2) are formed, one may conclude that phenyl radicals were generated as intermediates. This interpretation is grounded on the premise that neither the phenyl anion nor the radical anion [ArX]<sup>·-</sup> reacts with acetone enolate ion to form phenylacetone rapidly enough to compete with alternative processes, if at all. If neither 1 nor 2 is formed, one may conclude that free phenyl radicals were not intermediates.

## Results and General Discussion

The experimental fact is that several substituted benzenes, on being cleaved by alkali metals in liquid ammonia in the presence of acetone enolate ion, afford 1, 2, and 3, whereas cleavage of other substituted benzenes in the presence of this enolate ion fails to produce any 1, 2, or 3, although benzene is formed. Still other substituted benzenes are not cleaved by solvated electrons in ammonia, or undergo alternative reactions. Our experiments are summarized in Table I, which includes some from a previous publication.<sup>11</sup>

(7) E. J. Hart and M. Anbar, "The Hydrated Electron," Wiley, New York, N. Y., 1970, p 139; E. J. Hart, *Surv. Progr. Chem.*, **5**, 172 (1969); M. Anbar, *Advan. Phys. Org. Chem.*, **7**, 125, 129 (1969).

(8) T. J. Kemp and T. J. Stone, *Chem. Soc., Spec. Publ.*, No. 24, 376 (1970).

(9) J. F. Garst, *Accounts Chem. Res.*, **4**, 400 (1971); G. D. Sargent, *Tetrahedron Lett.*, 3279 (1971).

(10) Cf. K. Meyer and J. Roček, *J. Amer. Chem. Soc.*, **94**, 1209 (1972).

(11) R. A. Rossi and J. F. Bunnett, *J. Amer. Chem. Soc.*, **94**, 683 (1972).

(12) R. A. Rossi and J. F. Bunnett, *J. Org. Chem.*, **38**, 1407 (1973).

**Table I.** The Action of Potassium Metal in Liquid Ammonia on Substituted Benzenes in the Presence of Acetone Enolate Ion, at  $-78^\circ$

Run no.	Substrate	Method <sup>a</sup>	Major products (yield, %)	Category <sup>b</sup>
1	PhF <sup>c</sup>	B	PhCH <sub>2</sub> COCH <sub>3</sub> (51) <sup>d</sup>	I
2	PhCl <sup>c</sup>	B	PhCH <sub>2</sub> COCH <sub>3</sub> (68) <sup>d</sup>	I
3	PhBr	B <sup>e</sup>	C <sub>6</sub> H <sub>6</sub> (5); PhCH <sub>2</sub> COCH <sub>3</sub> (91) <sup>d</sup>	I
4	PhBr	A <sup>e</sup>	C <sub>6</sub> H <sub>6</sub> (18); PhCH <sub>2</sub> COCH <sub>3</sub> (71) <sup>d</sup>	I
5	PhI <sup>c</sup>	B	PhCH <sub>2</sub> COCH <sub>3</sub> (71) <sup>d</sup>	I
6	Ph <sub>2</sub> I <sup>+</sup> Br <sup>-</sup>	C	C <sub>6</sub> H <sub>6</sub> (20); PhCH <sub>2</sub> COCH <sub>3</sub> (33); PhI (18)	I
7	Ph <sub>2</sub> I <sup>+</sup> Br <sup>-</sup>	B	PhCH <sub>2</sub> COCH <sub>3</sub> (142) <sup>d,f</sup>	See text
8	PhOCH <sub>3</sub>	A	PhOCH <sub>3</sub> (90) <sup>g</sup>	IV
9	Ph <sub>2</sub> O <sup>c</sup>	A	PhCH <sub>2</sub> CH(OH)CH <sub>3</sub> (4.5); Ph <sub>2</sub> O (93)	I
10	PhOPO(OEt) <sub>2</sub> <sup>c</sup>	B	PhCH <sub>2</sub> COCH <sub>3</sub> (46) <sup>d</sup>	I
11	(PhO) <sub>3</sub> PO	B	PhCH <sub>2</sub> COCH <sub>3</sub> (43) <sup>d,h</sup>	I
12	PhSCH <sub>3</sub>	A	PhSH (60); PhSCH <sub>3</sub> (40)	III
13	Ph <sub>2</sub> S <sup>c</sup>	A	PhCH <sub>2</sub> COCH <sub>3</sub> (89) <sup>d</sup> ; PhSH (84)	I
14	Ph <sub>3</sub> S <sup>+</sup> Cl <sup>-</sup>	B	C <sub>6</sub> H <sub>6</sub> (59); PhCH <sub>2</sub> COCH <sub>3</sub> (55) <sup>d,i</sup> ; PhSH (91)	See text
15	Ph <sub>2</sub> SO	B <sup>j</sup>	C <sub>6</sub> H <sub>6</sub> (89); PhSH (81)	II
16	PhSO <sub>2</sub> CH <sub>3</sub>	B	C <sub>6</sub> H <sub>6</sub> (90)	II
17	Ph <sub>2</sub> SO <sub>2</sub>	B <sup>j</sup>	C <sub>6</sub> H <sub>6</sub> (144)	II
18	PhSO <sub>3</sub> <sup>-</sup> Na <sup>+</sup>	B	C <sub>6</sub> H <sub>6</sub> <sup>k</sup>	II
19	Ph <sub>2</sub> Se	B	PhCH <sub>2</sub> COCH <sub>3</sub> (32) <sup>d,l</sup> ; C <sub>6</sub> H <sub>6</sub> (60); PhSeH (68) <sup>m</sup>	See text
20	PhNMe <sub>3</sub> <sup>+</sup> I <sup>-c</sup>	A	PhCH <sub>2</sub> COCH <sub>3</sub> (71) <sup>d</sup>	I
21	Ph <sub>3</sub> P	B	C <sub>6</sub> H <sub>6</sub> (70); Ph <sub>2</sub> PH (78) <sup>n</sup>	II
22	Ph <sub>3</sub> As	B	C <sub>6</sub> H <sub>6</sub> (96); Ph <sub>2</sub> AsH (75) <sup>o</sup>	II
23	Ph <sub>3</sub> Sb	B	C <sub>6</sub> H <sub>6</sub> (97); Ph <sub>2</sub> SbH (85) <sup>p</sup>	II
24	Ph <sub>3</sub> Bi	B <sup>j</sup>	C <sub>6</sub> H <sub>6</sub> (270)	II
25	PhCN	B	<i>g, q</i>	III
26	Ph <sub>3</sub> Si	B <sup>j</sup>	Ph <sub>3</sub> Si (92); <i>g</i>	IV
27	Ph <sub>3</sub> B	B	Ph <sub>3</sub> BNH <sub>3</sub> (80); <i>r</i>	III
28	PhB(OH) <sub>2</sub>	B <sup>j</sup>	<i>g, q</i>	III

<sup>a</sup> A, substrate added to CH<sub>3</sub>COCH<sub>2</sub><sup>-</sup>K<sup>+</sup> and K in NH<sub>3</sub>; B, K added bit-by-bit to substrate and CH<sub>3</sub>COCH<sub>2</sub><sup>-</sup>K<sup>+</sup> in NH<sub>3</sub>, until blue color persisted; C, substrate and CH<sub>3</sub>COCH<sub>2</sub><sup>-</sup>K<sup>+</sup> combined in NH<sub>3</sub>, without K metal, and after 15 min quenched with NH<sub>4</sub>Cl.

<sup>b</sup> Categories I-IV are defined in the text. <sup>c</sup> From ref 11. <sup>d</sup> Yield listed is sum of 1, 2, and 3. <sup>e</sup> CH<sub>3</sub>COCH<sub>2</sub><sup>-</sup>K<sup>+</sup> made from acetone and KNH<sub>2</sub>. <sup>f</sup> PhCH<sub>2</sub>COCH<sub>3</sub>, 112%; PhCH<sub>2</sub>CH(OH)CH<sub>3</sub>, 28%; and Ph<sub>2</sub>CHCOCH<sub>3</sub>, 2%. <sup>g</sup> No C<sub>6</sub>H<sub>6</sub>, 1, 2, or 3 detected as product. <sup>h</sup> PhCH<sub>2</sub>COCH<sub>3</sub>, 6%; PhCH<sub>2</sub>CH(OH)CH<sub>3</sub>, 37%. <sup>i</sup> Ph<sub>2</sub>S<sup>+</sup>Cl<sup>-</sup> (12.8 mmol) afforded 0.9 mmol of PhCH<sub>2</sub>COCH<sub>3</sub>, 6.1 mmol of PhCH<sub>2</sub>CH(OH)CH<sub>3</sub>, 7.5 mmol of C<sub>6</sub>H<sub>6</sub>, and 11.6 mmol of PhSH. <sup>j</sup> Na used instead of K. <sup>k</sup> Identified but not quantified. <sup>l</sup> PhCH<sub>2</sub>COCH<sub>3</sub>, 6%; PhCH<sub>2</sub>CH(OH)CH<sub>3</sub>, 26%. <sup>m</sup> Isolated as PhSePh. <sup>n</sup> Isolated as Ph<sub>2</sub>PO<sub>2</sub>H. <sup>o</sup> Isolated as Ph<sub>2</sub>AsO<sub>2</sub>H. <sup>p</sup> Isolated as Ph<sub>2</sub>SbO<sub>2</sub>H. <sup>q</sup> Several unidentified products formed. <sup>r</sup> Ca. 2% of a substance with glpc retention time of C<sub>6</sub>H<sub>6</sub> was formed.

Acetone enolate ion for most of the experiments of Table I was generated by reaction of acetone with potassium metal in ammonia, a process which, as we later discovered,<sup>12</sup> produces roughly 40% of isopropoxide ion as a by-product. This alkoxide ion is a good hydrogen atom donor to phenyl radical; it has been observed to compete with the enolate ion to form appreciable amounts of benzene as a by-product under conditions not conducive to reduction of phenyl radical to phenyl anion *via* reaction 4.<sup>12</sup> Therefore the production of benzene as a by-product to 1 and/or 2 is for most runs not informative of mechanism. For that reason, and because the benzene yield was not measured in early experiments, it is often not reported.

The acetone enolate ion for runs 3 and 4 was prepared

by reaction of acetone with  $\text{KNH}_2$  and is not accompanied by isopropoxide ion. The production of benzene as a minor by-product of the cleavage of bromobenzene testifies to the generation of some phenyl anions, either directly by reaction 2 or 3 or indirectly by the sequence of reactions 1 and 4. The latter route is suggested by the fact that more benzene was formed when solvated electrons were in excess (run 4) than in overall deficiency (run 3); in the latter case they may have been locally in excess to some extent.

When neither **1** nor **2** is formed, free phenyl radicals cannot have been intermediates and benzene cannot have arisen by radical abstraction of hydrogen atoms from isopropoxide ions or other donors. Phenyl anion is the only other benzene precursor conceivable in this system, and therefore the production of benzene unaccompanied by **1** or **2** is taken as evidence of the intermediacy of phenyl anions not generated *via* reaction 4.<sup>13</sup>

The reactions of Table I are assigned to four categories, as indicated. The basis of assignment is as follows: category I, **1**, **2**, and/or **3** are products; category II, benzene is a product, but not **1**, **2**, or **3**; category III, products of other type are formed; category IV, no evidence of chemical change. Cleavage reactions in category I are judged to occur according to eq 1, and those in category II according to eq 2 or 3. Categories III and IV are of little interest to us.

Many of the substrates studied may be symbolized as  $\text{PhY}$ ,  $\text{Ph}_2\text{Y}$ , or  $\text{Ph}_3\text{Y}$ , where Y is an atom of group VII, VI, or V of the periodic table, respectively. The pattern of cleavage of these substrates correlates rather well with the Pauling electronegativities of the elements Y.<sup>14</sup> With one marginal exception, cleavage occurs to produce phenyl radical intermediates when the electronegativity of Y is greater than or equal to that of carbon, and to produce phenyl anions when the electronegativity of Y is lower. The marginal exception concerns  $\text{Ph}_2\text{Se}$ , the products from which (run 19) suggest scission in part to phenyl radicals and in part to phenyl anions; the electronegativity listed for Se (2.4) is slightly lower than for C (2.5). This correlation suggests that when radical anion  $[\text{PhX}]^-$  ruptures, the "extra" electron tends to go with the fragment which has the first atom of greater electronegativity. An attractive hypothesis thus emerges that phenyl anion in runs 21–24 has its genesis in reaction 2.

### Discussion of Specific Cleavage Reactions

**Halobenzenes.** That halobenzenes are cleaved by electrons in the sense of reaction 1 is widely recognized.<sup>4</sup> Reactions of the halobenzenes with the solvated electron and acetone enolate ion in liquid ammonia were discussed in a previous publication.<sup>11</sup>

**Diphenyliodonium Ion.** It has been known for some time that diphenyliodonium ion brings about the phenylation of carbanions derived from diketones,

(13) A remote possibility is that phenyl radicals produced according to eq 1 are detained in an unreactive complex with the by-product of cleavage or in a solvent cage, thereby being protected from reaction with acetone enolate ion until a further electron can be acquired for reduction to phenyl anion. This would require great specificity of influence by the by-product of cleavage, and no reason for such specificity is evident.

(14) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 93.

esters, etc.<sup>15,16</sup> It was therefore not surprising to find (run 6, Table I) that some phenylation of the acetone enolate ion occurred without stimulation by solvated electrons; 33% of phenylacetone was obtained during only 15 min at  $-78^\circ$ . For reactions of diphenyliodonium ion with carbanions, an electron transfer radical mechanism was proposed in 1962 by Beringer, Galton, and Huang.<sup>15</sup> It resembles the SRN1 mechanism of substitution<sup>11,17</sup> in some respects, but differs in that it is a nonchain mechanism involving radical-radical coupling whereas the SRN1 mechanism involves reaction of radical with nucleophile (*cf.* Scheme I) and is in favorable cases a chain mechanism.

In view of the fact that some reaction occurs without stimulation by solvated electrons, the proper interpretation to be placed on the results of run 7 is not entirely clear. For one thing, the iodobenzene product of phenylation by diphenyliodonium ion is itself able to phenylate the enolate ion when electrons are supplied, and that explains why more than 1 mol of phenylacetone was obtained per mol of  $\text{Ph}_2\text{I}^+$ . To the extent that the products obtained do represent cleavage of the iodonium salt by solvated electrons, reaction according to eq 1 is indicated. Such an interpretation would be in harmony with evidence from polarographic studies.<sup>18</sup>

**Anisole.** We recovered 90% of anisole after 1 hr of exposure to potassium metal and acetone enolate ion in ammonia at  $-78^\circ$  followed by 3 hr at  $-33^\circ$ , and detected no cleavage products. Birch<sup>19</sup> describes cleavage of anisole to phenol in 27% yield through the action of 2 M sodium metal in ammonia during 7.25 hr at  $33^\circ$ ; that places the reaction in category III.<sup>20</sup>

**Diphenyl Ether.** This cleavage reaction has been known for a long time,<sup>21</sup> but without convincing evidence of its mechanism. Diphenyl ether is cleaved more slowly than most of the other substrates investigated; only 4% of **2** was obtained from 8 min reaction at  $-78^\circ$ , and even during 9 min at  $-33^\circ$  only 14% of **1** and **2** (mainly **2**) was obtained, most of the unreacted diphenyl ether being recovered in both cases. The formation of **2** shows that the first step of cleavage of diphenyl ether to benzene and phenoxide ion by alkali metals in ammonia occurs according to eq 1. This conclusion is also indicated by the formation of aniline in 53% yield through the action of potassium metal and  $\text{KNH}_2$  on diphenyl ether.<sup>17</sup> In the absence of strong nucleophiles, the phenyl radical generated in the initial scission is further reduced to benzene by successive capture of an electron (eq 4) and a proton.

This representation of the cleavage mechanism is in harmony with the mechanism of alkali metal cleavage of dibenzofuran to *o*-phenylphenoxide ion in tetrahydro-

(15) F. M. Beringer, S. A. Galton, and S. J. Huang, *J. Amer. Chem. Soc.*, **84**, 2819 (1962).

(16) F. M. Beringer and P. S. Forgione, *J. Org. Chem.*, **28**, 714 (1963).

(17) J. K. Kim and J. F. Bunnett, *J. Amer. Chem. Soc.*, **92**, 7463, 7464 (1970).

(18) F. M. Beringer and S. Messing, *J. Org. Chem.*, **37**, 2484 (1972).

(19) A. J. Birch, *J. Chem. Soc.*, 102 (1947).

(20) Electron spin resonance studies of the anisole radical anion in ether solvents have detected the appearance of biphenyl radical anion, which suggests scission according to eq 1. On the other hand, efforts to detect biphenyl as a product by glpc or mass spectrometry were unsuccessful: K. W. Bowers in "Radical Ions," E. T. Kaiser and L. Kevan, Ed., Interscience, New York, N. Y., 1968, p 232.

(21) A. L. Kranzfelder, J. J. Verbanc, and F. J. Sowa, *J. Amer. Chem. Soc.*, **59**, 1488 (1937); P. A. Sartoretto and F. J. Sowa, *ibid.*, **59**, 603 (1937); F. C. Weber and F. J. Sowa, *ibid.*, **60**, 94 (1938).

uran solution, deduced by Evans, Roberts, and Tabner<sup>22</sup> from evidence of a wholly different character.

**Phenyl Diethyl Phosphate and Triphenyl Phosphate.** These esters both cleave with Ph-O scission, to afford phenyl radicals in the manner of eq 1. However, in the absence of solvated electrons they react more slowly with the acetone enolate ion in ammonia to yield phenol as a principal cleavage product, probably by nucleophilic attack on phosphorus. Aryl diethyl phosphates are easily prepared in high yield from the corresponding phenols, and the fact that they cleave in the sense of eq 1 is of considerable preparative significance.<sup>11,23</sup>

**Thioanisole and Diphenyl Sulfide.** Whereas diphenyl sulfide undergoes scission in the fashion of eq 1, thioanisole suffers fission of the sulfur-methyl bond. Our results provide no indication of the mechanism of thioanisole cleavage.

**Triphenylsulfonium Ion.** This ion would be expected to be cleaved doubly, first to remove one phenyl group and form diphenyl sulfide, and then to cleave that product, as in run 13. But whereas the reaction of diphenyl sulfide with potassium metal and acetone enolate ion occurs cleanly to form 1 and 2 in high total yield, together with thiophenol, reaction of triphenylsulfonium ion gives under the same conditions only 55% of 1 and 2, 59% of benzene, and 91% of thiophenol (run 14). One might have expected the summed yields of these products to approach 300%, on the basis of 1 mol of product per mol of triphenylsulfonium ion, instead of 205% as found. There was a considerable tarry residue in the reaction flask, which probably accounts for the missing benzene rings.

The fact that 59% of benzene was formed in run 14, in contrast to at most 11% in run 13, suggests that benzene stems from phenyl anions liberated in the first stage of cleavage. This view is strengthened by a further run conducted with enolate ion made from reaction of KNH<sub>2</sub> with acetone, and thus free of isopropoxide ion; the products were benzene (48%), phenylacetone (26%), 1-phenyl-2-propanol (33%), thiophenol (79%), and diphenyl sulfide (5%). The benzene yield was substantial despite the lack of opportunity for phenyl radicals to abstract hydrogen atoms from isopropoxide ions. Moreover, samples of the reaction mixture taken after various amounts of potassium metal had been added showed, at first, that much diphenyl sulfide but relatively little phenylacetone (or 2) had been formed; later 1 and 2 appeared strongly, at the expense of diphenyl sulfide.

These observations suggest that triphenylsulfur, the radical which results from addition of an electron to triphenylsulfonium ion, does not spontaneously split into phenyl radical and diphenyl sulfide at -78°. It can accept a further electron, and then fall apart to diphenyl sulfide and phenyl anion. Alternatively, triphenylsulfur can apparently take part in ill-defined reactions to form tarry products. These may include reaction with phenyl radicals generated by the action of solvated electrons on diphenyl sulfide, in the second stage of cleavage.

Triphenylsulfur has been implicated as an intermediate

(22) A. G. Evans, P. B. Roberts, and B. J. Tabner, *J. Chem. Soc. B*, 269 (1966).

(23) (a) R. A. Rossi and J. F. Bunnett, *J. Org. Chem.*, **37**, 3570 (1972); (b) *ibid.*, **38**, 2314 (1973).

in photolysis of triphenylsulfonium ion in alcoholic solvents, and in its reactions with alkoxide ions.<sup>24</sup>

**Diphenyl Sulfoxide, Phenyl Methyl Sulfone, Diphenyl Sulfone, and Benzenesulfonate Ion.** The cleavage reactions of these four oxygenated sulfur compounds all fall in category II; phenyl anion is indicated to be an immediate product of cleavage. There is little to indicate whether cleavage occurs according to reaction 2 or 3.

The cleavage reactions of diphenyl sulfoxide and sulfone (runs 15 and 17, respectively) differ in that more than 1 mol of benzene is formed per mol of sulfone but less than 1 mol of benzene per mol of sulfoxide. The by-product of scission of the sulfoxide, presumably PhSO· or PhSO<sup>-</sup>, is further reduced to PhS<sup>-</sup> in good yield. The by-product of diphenyl sulfone cleavage, which is probably PhSO<sub>2</sub>· or PhSO<sub>2</sub><sup>-</sup>, is further cleaved to form phenyl anions without the intermediacy of phenyl radicals. The implication that cleavage of benzenesulfinate ion would fall in category II was not separately investigated.

For cleavage of phenyl methyl sulfone (run 16), two general pathways are conceivable: initial rupture of the phenyl-sulfur bond to generate phenyl anion, or initial rupture of the methyl-sulfur bond and subsequent cleavage of the sulfur-containing fragment, much as in the second stage of the diphenyl sulfone reaction. We have no evidence on which to decide between these possibilities.

The action of sodium metal in ammonia on benzenesulfonate ion was earlier investigated by Kraus and White,<sup>25</sup> who reported formation of benzene in 71% yield, together with sulfite ion and traces of biphenyl. Our results (run 18) indicate cleavage to phenyl anions. Inasmuch as reaction according to eq 3 would in this case suffer a special coulombic disadvantage, the pathway of eq 2 seems more probable.

**Diphenyl Selenide.** The cleavage of this substrate (run 19) is anomalous. First, although 1 and 2 are formed, their yields total only 32%, and they are accompanied by a larger yield (60%) of benzene. The concurrent operation of two cleavage mechanisms is implied: reaction according to eq 1 forming 1 and 2, and reaction according to eq 2 or 3 forming benzene.

On the other hand, the photoinduced condensation of acetone enolate ion with diphenyl selenide in ammonia at -33° affords 1 and 3 in very high yield.<sup>12</sup> The photostimulated reaction is believed to occur by the SRN1 mechanism,<sup>17</sup> an essential feature of which is radical generation as in eq 1.

It is conceivable that the mode of scission of the diphenyl selenide radical anion is different without radiation at -78° from that with 350-nm radiation at -33°. In view of the near-sameness of the Pauling electronegativities of selenium (2.4) and carbon (2.5), a delicate balance between modes of scission is not unreasonable.

Diphenyl selenide is insoluble in liquid ammonia and perhaps for that reason its cleavage was slow, several minutes being required to decolorize the reaction mixture after addition of each bit of potassium metal.

**Phenyltrimethylammonium Ion.** Cleavage occurs

(24) J. W. Knapczyk and W. E. McEwen, *J. Amer. Chem. Soc.*, **91**, 145 (1969); *J. Org. Chem.*, **35**, 2539 (1970).

(25) C. A. Kraus and G. F. White, *J. Amer. Chem. Soc.*, **45**, 768 (1923).

(run 20) according to eq 1, a fact of potential significance to preparative chemistry. The quaternary ammonium ion first accepts an electron to form phenyl-trimethylnitrogen radical, which is probably zwitterionic. The sense of fission of that radical is apparently somewhat solvent dependent: methyl-nitrogen scission is noticeable in water.<sup>26</sup>

**Triphenylphosphine, -arsine, -stibine, and -bismuth.** Our data indicate that these triphenyl derivatives of group VA elements all cleave to phenyl anion intermediates, according to eq 2 or 3. Inasmuch as all four elements are less electronegative than carbon, scission of the initial radical anion in the sense of eq 2 may well occur.

The by-product of cleavage of the triphenyl derivatives of phosphorus, arsenic, and antimony has two phenyl groups attached to the group VA element, as we demonstrated by oxidation with hydrogen peroxide and isolation of  $\text{Ph}_2\text{PO}_2\text{H}$ ,  $\text{Ph}_2\text{AsO}_2\text{H}$ , and  $\text{Ph}_2\text{SbO}_2\text{H}$ , respectively. In preparative work, the diphenylphosphide, diphenylarsenide, and diphenylstibide ions are often formed by cleavage of triphenylphosphine, -arsine, or -stibine with an alkali metal.<sup>27, 28</sup>

In connection with our observation that triphenylbismuth is fully cleaved to give benzene from all three phenyl groups, some reports of Gilman and Yablunsky<sup>29</sup> warrant mention. They obtained sodium diphenylbismuthide in good yield by addition of sodium metal to diphenylbismuth iodide in ammonia solution, using proportions appropriate to the equation:  $\text{Ph}_2\text{BiI} + 2\text{Na} \rightarrow \text{Ph}_2\text{BiNa} + \text{NaI}$ . However, no appreciable amount of  $\text{Ph}_2\text{BiNa}$  was formed when diphenylbismuth iodide was added to a solution of sodium in ammonia; this suggests that the  $\text{Ph}_2\text{BiNa}$  initially formed was further cleaved by excess solvated electrons. Also, their efforts to obtain diphenylbismuthide from the action of sodium in ammonia on triphenylbismuth were unsuccessful.

**Benzonitrile.** Arapakos, Scott, and Huber<sup>30</sup> report obtaining, from the action of sodium in ammonia on benzonitrile, a 60% yield of benzene as well as 40% recovery of unreacted nitrile.<sup>31</sup> In an experiment very similar to that of Arapakos, *et al.*, except that we used potassium instead of sodium, we got a complex mixture of products. Among these there was nothing with the glpc retention time of benzene.<sup>32</sup> There was a peak at approximately the retention time of benzonitrile, representing about 11% of the nitrile introduced, but it was not otherwise identified.

The action of lithium metal in ethylamine on benzo-

(26) P. Groenewoud and R. Robinson, *J. Chem. Soc.*, 1692 (1934).

(27) D. Wittenberg and H. Gilman, *J. Org. Chem.*, **23**, 1063 (1958); A. M. Aguiar, J. Beisler, and A. Mills, *ibid.*, **27**, 1001 (1962); W. Hewertson and H. R. Watson, *J. Chem. Soc.*, 1490 (1962); Y. Matsumura and R. Okawara, *J. Organometal. Chem.*, **25**, 439 (1970).

(28) G. O. Doak and L. D. Freedman, "Organometallic Compounds of Arsenic, Antimony and Bismuth," Wiley, New York, N. Y., 1970, pp 152, 376.

(29) H. Gilman and H. L. Yablunsky, *J. Amer. Chem. Soc.*, **63**, 212 (1941).

(30) P. G. Arapakos, M. K. Scott, and F. E. Huber, Jr., *J. Amer. Chem. Soc.*, **91**, 2059 (1969).

(31) L. A. Walter and S. M. McElvain, *J. Amer. Chem. Soc.*, **56**, 1614 (1934), report reaction of benzonitrile with sodium metal in an ethanol-toluene medium to form 84% of NaCN and 7% of benzylamine; apparently they did not seek benzene as a product.

(32) Previously, Dr. Jong Kook Kim investigated, in these laboratories, the action of potassium metal on benzonitrile in ammonia. He observed no formation of benzene or cyanide ion, but did obtain "an orange goo."

nitrile is reported to give a 47% yield of cyclohexanemethylamine, as well as tars.<sup>33</sup>

Treatment of benzonitrile with potassium metal in the presence of acetone enolate ion afforded a complex product mixture with glpc behavior similar to that of the products formed from the action of potassium metal on the nitrile in the absence of the enolate ion. No benzene, 1, 2, or 3 could be detected among those products.

From exposure of benzonitrile to a solution of the enolate ion but without alkali metal, the nitrile was recovered to the extent of 95%.

It is probable that potassium metal in ammonia brings about reduction of the cyano group and/or the aromatic ring. There are many conceivable reduction products, which is consistent with our observation that many products are formed.

**Tetraphenylsilane and Tetraphenyl Derivatives of Other Group IV Elements.** We find tetraphenylsilane to be unaffected by potassium metal in ammonia. In this respect it resembles tetraphenylmethane, which is also unreactive.<sup>34</sup>

On the other hand, tetraphenylgermane is cleaved by sodium in ammonia to furnish benzene and sodium triphenylgermide.<sup>35</sup> Tetraphenylstannane is similarly cleaved.<sup>36</sup> We have not applied our product criterion of cleavage mechanism to these cases.

**Triphenylborane and Benzeneboronic Acid.** In our experimental system, triphenylborane underwent a trivial reaction: formation of a coordination complex with ammonia.<sup>37</sup> The latter is described<sup>38</sup> as forming a salt,  $\text{Ph}_3\text{BNH}_2\text{Na}$ , on reaction with sodium in ammonia; such a salt would be reprotonated to regenerate  $\text{Ph}_3\text{BNH}_3$  upon acidification with  $\text{NH}_4\text{Cl}$ , as in our experimental procedure. The radical anions formed by reaction of sodium with triarylboranes are known to be stable.<sup>39</sup>

The action of sodium metal on benzeneboronic acid in the presence of acetone enolate ion afforded no benzene, 1, 2, or 3, and thus no evidence of cleavage. Obtained instead was, in 68% yield, a mixture of two substances. The major of these, on the basis of elemental analyses and spectral evidence, is perhaps a cyclic boronate ester with 2-methyl-2,4-pentanediol. This diol plausibly is formed from acetone under basic, reducing conditions.

**Reactions with Acetone Enolate Ion without Solvated Electron Stimulation.** With one exception, all substrates listed in Table I as giving cleavage reactions in category I and/or II were also exposed to acetone enolate ion in ammonia without addition of alkali metal. Exposure was usually for 15 min at  $-78^\circ$ . Except as mentioned below, no reactivity with acetone enolate ion was found. The one substrate not directly tested in this sense was diphenyl selenide, but observations after short irradiation times in the photostimu-

(33) R. A. Benkeser, C. Arnold, Jr., R. F. Lambert, and O. H. Thomas, *J. Amer. Chem. Soc.*, **77**, 6042 (1955).

(34) C. B. Wooster and N. W. Mitchell, *J. Amer. Chem. Soc.*, **52**, 688 (1930).

(35) C. A. Kraus and L. S. Foster, *J. Amer. Chem. Soc.*, **49**, 457 (1927).

(36) R. F. Chambers and P. C. Scherer, *J. Amer. Chem. Soc.*, **48**, 1054 (1926).

(37) E. Krause, *Ber.*, **57**, 813 (1924).

(38) W. B. Robinson, Ph.D. Thesis, Brown University, 1928, quoted by J. E. Smith and C. A. Kraus, *J. Amer. Chem. Soc.*, **73**, 2751 (1951).

(39) E. Krause and P. Nobbe, *Ber.*, **64**, 2112 (1931), and earlier papers; T. L. Chu and T. J. Weismann, *J. Amer. Chem. Soc.*, **78**, 23 (1956); S. D. Darling, O. N. Devgan, and R. E. Cosgrove, *ibid.*, **92**, 696 (1970).

lated reaction<sup>12</sup> indicate that Ph<sub>2</sub>Se is also unreactive with the enolate ion *per se*.

Diphenyliodonium ion reacts with acetone enolate ion without need for provocation by light or solvated electrons; see run 6, Table I, and discussion above. Iodobenzene undergoes a very slow dark reaction with the enolate ion in ammonia at  $-33^{\circ}$ , as reported elsewhere;<sup>12</sup> after 180 min, 94% of the iodobenzene was recovered in one experiment and 83% in another. Several of these substrates react with acetone enolate ion under irradiation with ultraviolet light.<sup>12</sup>

Triphenyl phosphate reacts slowly with acetone enolate ion (and/or with the isopropoxide ion present in preparations of the enolate by the potassium metal method), unless stimulated by solvated electrons; during 15 min at  $-78^{\circ}$ , 28% of phenol was obtained and approximately 70% of triphenyl phosphate was recovered. The formation of phenol suggests a mechanism of nucleophilic attack on phosphorus. The reactivity in run 11, Table I, is of a different character, and is a consequence of much faster reaction with the solvated electron in the sense of eq 1.

In another study<sup>12</sup> we sought to realize photostimulated reaction of phenyl diethyl phosphate with acetone enolate ion to form 1, but obtained only 13% of 1 after 250 min of irradiation at  $-33^{\circ}$ , together with 71% of phenol and 11% of benzene. Again nucleophilic substitution at phosphorus is implied. The high reactivity of this substrate with solvated electrons in ammonia to form benzene in the absence of strong nucleophiles,<sup>23b</sup> to form 1 and 2 in the presence of acetone enolate ion (run 10, Table I, or ref 11), and to form aniline in the presence of amide ion<sup>23a</sup> indicates that cleavage according to eq 1 occurs readily. The competing reaction with the enolate ion and/or isopropoxide ion which releases phenol is relatively slow.

Phenol was formed in substantial amounts during the unstimulated reaction of acetone enolate ion (and/or isopropoxide ion) with phenyl trimethylsilyl ether, diphenyl carbonate, triphenyl phosphite, triphenyl borate, or phenyl benzoate at  $-78^{\circ}$ . The fact that phenol was also formed during exposure of these substances to solvated electrons in the presence of the enolate ion is therefore of uncertain significance.<sup>40</sup> From reaction of

(40) The unstimulated reaction of triphenyl phosphite with acetone enolate ion gave a 95% yield of phenol, but 296% of phenol was obtained when potassium metal was also added. The implication that reductive cleavage of P-O bonds occurred in the latter case is reinforced by the fact that a vile odor suggestive of phosphine was evident during work-up of the reaction mixture.

phenyl benzoate with an enolate ion preparation by the potassium metal method, isopropyl benzoate was obtained in 88% yield. A similar reaction with an enolate preparation by the KNH<sub>2</sub> method afforded none of that ester but a 56% yield of benzamide.

## Experimental Section

**Materials.** The substrates studied were either good commercial samples or were prepared by standard methods; their identities were verified by appropriate physical measurements.

**Cleavage Reactions.** For most runs, potassium acetone enolate was prepared by reaction of potassium metal with acetone in ammonia. In a typical preparation, 6.9 g (0.177 mol) of potassium metal was dissolved in 360 ml of ammonia and, at  $-78^{\circ}$ , an equimolar amount of acetone was added dropwise with stirring. This was almost exactly the amount needed to discharge the blue color. For a few runs, the enolate was made by reaction of acetone with KNH<sub>2</sub>. In a typical preparation, 0.159 mol of KNH<sub>2</sub> was made by reaction of 6.22 g of potassium metal with 350 ml of ammonia, catalyzed by a little ferric nitrate, and acetone (9.23 g; 0.159 mol) was added dropwise with stirring to the resulting solution, at  $-78^{\circ}$ .

In cleavage procedure A, a weighed amount of potassium metal was dissolved in the solution of potassium acetone enolate, and to the resulting solution at  $-78^{\circ}$  the substrate was added, with stirring, as the neat liquid or solid. In procedure B, the substrate was added to the solution of potassium acetone enolate, and to the resulting mixture at  $-78^{\circ}$  was added, with stirring, small pieces of potassium metal, the solution being allowed to decolorize after each addition before the next bit was added. Normally, addition of potassium metal was discontinued when a blue color persisted in the reaction mixture.

After 15 min reaction time (procedure A) or after a persistent blue color was obtained (procedure B), excess solid NH<sub>4</sub>Cl was added followed by 150 ml of diethyl ether. The ammonia was allowed to evaporate, through a condenser held at  $-30$  to  $-20^{\circ}$  when benzene was to be determined quantitatively. Measured amounts of standard substances for glpc analytical purposes (toluene for analysis of benzene, *p*-dichlorobenzene for analysis of 1, 2, and/or 3) were added, followed by water to dissolve inorganic salts, and the ether extract was separated, washed with water, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and analyzed by glpc on a column of 5% Carbowax 20M on Chromosorb P, with thermal conductivity detector. Peak areas were corrected by application of molar response factors.

Details on several runs in Table I appear in another publication.<sup>11</sup>

**Supplementary Material Available.** Experimental details on other runs will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24 × reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-74-112.