Photostimulated Reactions of Potassium Diphenylarsenide with Haloarenes by the $S_{RN}1$ Mechanism[1]

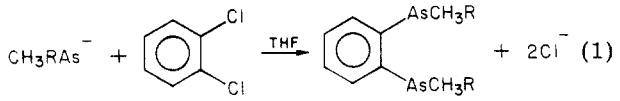
Roberto A. Rossi,* Ruben A. Alonso, and Sara M. Palacios

Departamento de Quimica Organica, Facultad de Ciencias Quimicas Universidad Nacional de Cordoba, Est. 32, 5000 Cordoba, Argentina

Received April 29, 1980

Photostimulated reactions of haloarenes with potassium diphenylarsenide (3) were studied in liquid ammonia. *p*-Chloro-, *p*-bromo-, and *p*-iodotoluenes gave four products: triphenylarsine, *p*-tolyldiphenylarsine, di-*p*-tolylphenylarsine and tri-*p*-tolylarsine. Similarly, with *p*-chloro-, *p*-bromo-, and *p*-iodoanisole as substrates, four arsines were found as products: triphenylarsine, *p*-anisyldiphenylarsine, di-*p*-anisylphenylarsine and tri-*p*-anisylarsine. *p*-Chlorotoluene and *p*-bromoanisole are unreactive in the dark, but with 4-chlorobenzophenone there is a dark reaction, which is accelerated by light and inhibited by *m*-dinitrobenzene and oxygen. With the latter substrate, only the straightforward substitution product is formed. These reactions are believed to occur by the $S_{RN}1$ mechanism, with an extra feature of reversible coupling of aryl radicals with arside ions, which causes the scrambling of aryl rings. It is suggested that the low-lying π^* MO of the benzophenone moiety prevents C–As bond breaking in the radical anion intermediate in that case.

Dialkyl- or diarylarsenide ions are well-known to react readily with halo- and dihalobenzenes. For instance dimethylarsenide[2] and methylphenylarsenide[3] ions react with *o*-dichlorobenzene in THF to give diarsines of type **1** (R = CH_3, Ph) in good yields (eq 1). Diphenylarsenide ion reacts with *p*-dibromobenzene in THF to give the diarsine in 75% yield.[4]



(1)

1

One method to prepare diphenylarsenide ion **3** is via cleavage, with C–As bond rupture, of triphenylarsine **2** by means of alkali metals in THF[5] or dioxane.[6] Anion **3** has also been prepared by reaction of **2** with metals in liquid ammonia (eq 2).[7] It was shown to react with alkyl halides or dihalides to give the substitution or disubstitution products.[8]

$$\underset{\mathbf{2}}{Ph_3As} + 2K \xrightarrow{NH_3} \underset{\mathbf{3}}{Ph_2As^-K^+} + NH_2^-K^+ + PhH \quad (2)$$

In 1971 Felthan and Metzger[9] reported that **3** reacts with 2-chloroquinoline in liquid ammonia to give, after 12 h of reaction, (2-quinolyl)diphenylarsine.

The facts that detailed mechanistic studies of the reaction of **3** with haloarenes had not been reported and that diphenylphosphide ion, which belongs to the same group of elements, reacts by the $S_{RN}1$ mechanism[10] prompted us to undertake an investigation of the reaction of **3** with haloarenes in liquid ammonia.

Results and Discussion

Methods. Nucleophile **3** was prepared by the method shown in eq 2, and the concurrently generated amide ion was neutralized with *tert*-butyl alcohol. The addition of an excess of methyl iodide yielded, after workup, 85% of isolated diphenylmethylarsine **4** (eq 3), and 2–4% of **2**,

$$\mathbf{3} + MeI \rightarrow \underset{\mathbf{4}}{Ph_2MeAs} + I^- \quad (3)$$

determined by GC. The small amount of **2** found is probably starting material that escaped reaction with potassium metal, for example, by lodging on the wall of the flask above the solution surface.

To a solution of **3** prepared by this procedure, *p*-chlorotoluene (**5**) was added as substrate, and after 60 min of irradiation, we found the expected *p*-tolyldiphenylarsine (**6**) in 61% yield, accompanied by **2** (15%), di-*p*-tolylphenylarsine (**7**, 15%), and tri-*p*-tolylarsine (**8**, 2%) (eq 4).

$$\underset{\mathbf{5}}{ToCl} + \mathbf{3} \xrightarrow{h\nu} \mathbf{2} + \underset{\mathbf{6}}{Ph_2ToAs} + \underset{\mathbf{7}}{PhTo_2As} + \underset{\mathbf{8}}{To_3As} \quad (4)$$

To = *p*-tolyl

The reaction time was standardized at 60 min, but the reaction was probably completed much sooner, because the orange color of the solution of **3** turned light yellow after about 10 min of irradiation.

A reaction of **3** with **5** was carried out under identical conditions but in the dark, methyl iodide was added after 60 min of reaction, and only **4** was formed as determined by GC and NMR.

We suggest that this reaction occurs by the photostimulated $S_{RN}1$ mechanism[11] with a propagation cycle as depicted in Scheme I.

Radical anion intermediate **12**, formed in eq 7 by coupling of *p*-tolyl radical **11** with **3**, undergoes three competitive reactions, namely, reversion to starting materials, fragmentation to *p*-tolylphenylarsenide (**13**) and phenyl

(1) Research supported in part by the Consejo Nacional de Investigaciones Cientificas y Tecnicas and the Secretaria de Ciencias y Tecnologia, Argentina.

(2) Felthan, R. D.; Silverthorn, W. *Inorg. Synth.* **1967**, *10*, 159.

(3) Henrick, K.; Wild, S. B. *J. Chem. Soc., Dalton Trans.* **1975**, 1506.

(4) Zorn, H.; Schindlbauer, H.; Hammer, D. *Monatsh. Chem.* **1967**, *98*, 731.

(5) (a) Wittenberg, D.; Gilman, H. *J. Org. Chem.* **1958**, *23*, 1063. (b) Aguiar A. M.; Mague, J. T.; Aguiar, H. J.; Archibald, T. G.; Prejean, G. *Ibid.* **1968**, *33*, 1681 and references cited there in.

(6) Tzschach, A.; Lange, W. *Chem. Ber.* **1962**, *95*, 1360. Morris, T. L.; Taylor, R. C. *J. Chem. Soc., Dalton Trans.* **1973**, 175. Dubois, T. D.; Smith, F. T. *Inorg. Chem.* **1973**, *12*, 735.

(7) Mann, F. G.; Pragnell, M. J. *J. Chem. Soc.* **1965**, 4120. Tzschach, A.; Voigtländer, W. *Z. Anorg. Allg. Chem.* **1973**, *396*, 39. Ellerman, J.; Schössner, H.; Haag, A.; Schödel, H. *J. Organomet. Chem.* **1974**, *65*, 33.

(8) Brill, T. B.; Parris, G. E.; Cong, G. G.; Bowen, L. H. *Inorg. Chem.* **1973**, *12*, 1888.

(9) Felthan, R. D.; Metzger, H. G. *J. Organomet. Chem.* **1971**, *33*, 347.

(10) Swarts, J. E.; Bunnett, J. F. *J. Org. Chem.* **1979**, *44*, 4673.

0022-3263/81/1946-2498$01.25/0

Scheme I[a]

$$\underset{5}{ToCl} + \underset{3}{Ph_2As^-} \xrightarrow{h\nu} \underset{9}{(ToCl)^-\cdot} + \underset{10}{Ph_2As\cdot} \quad (5)$$

$$\underset{9}{(ToCl)^-\cdot} \longrightarrow \underset{11}{To\cdot} + Cl^- \quad (6)$$

$$\underset{11}{To\cdot} + \underset{3}{Ph_2As^-} \rightleftharpoons \underset{12}{(Ph_2ToAs)^-\cdot} \rightleftharpoons \underset{13}{PhToAs^-} + \underset{14}{Ph\cdot} \quad (7)$$

$$\downarrow \text{electron transfer}$$

$$\underset{6}{Ph_2ToAs}$$

$$\underset{11}{To\cdot} + \underset{13}{PhToAs^-} \rightleftharpoons \underset{15}{(PhTo_2As)^-\cdot} \rightleftharpoons \underset{16}{To_2As^-} + \underset{14}{Ph\cdot} \quad (8)$$

$$\downarrow \text{electron transfer}$$

$$\underset{7}{PhTo_2As}$$

$$\underset{11}{To\cdot} + \underset{16}{To_2As^-} \rightleftharpoons \underset{17}{(To_3As)^-\cdot} \xrightarrow{\text{electron transfer}} \underset{8}{To_3As} \quad (9)$$

$$\underset{14}{Ph\cdot} + \underset{3}{Ph_2As^-} \rightleftharpoons \underset{18}{(Ph_3As)^-\cdot} \xrightarrow{\text{electron transfer}} \underset{2}{Ph_3As} \quad (10)$$

[a] To = *p*-tolyl.

radical **14**, and electron transfer to substrate **5** to give product **6**.

In eq 7 two new intermediates are formed, **13** and **14**. Phenyltolylarsenide ion **13** competes with **3** as nucleophile for **11** to give radical anion **15** (eq 8), which can give **7** by electron transfer to the substrate, revert to **11** and **13** from which it was formed, or fragment to ditolylarsenide ion **16** and radical **14**.

Likewise, **16** can react with **11** to give radical anion **17** (eq 9), which can revert to **16** and **11** or transfer its extra electron to give **8**. Phenyl radicals formed in eq 7 and 8 can compete with *p*-tolyl radical **11** in reaction with **3** to ultimately give triphenylarsine (**2**).

Inasmuch as **13** and **14** are formed through the same radical anion intermediate **12**, their concentrations should be the same (except for a little more **14** from reaction 8) and they should give about the same amount of final products **7** and **2**, respectively. Roughly this is the case. Thus, about 60% of **6** and 15–20% each of **2** and **7** are obtained (Table I). As mentioned before, the amount of **2** that was contributed as a contaminant of the starting material is about 2–4%; it follows that the 15–20% of **2** formed comes mainly from reaction 10.

The ratio of **6** to **2** or **7** indicates that electron transfer from **12** is about 4 times faster than bond rupture to **13** and **14** (eq 7). If the same ratio holds for eq 8, the yield of **8** should be on the order of 2–3%, as observed.

This scrambling of aryl groups was previously observed in the photostimulated $S_{RN}1$ reaction of phenyltelluride ion with *p*-iodoanisole, where the three possible diaryltellurides were all formed (eq 11).[12]

$$PhTe^- + IAn \xrightarrow{h\nu} Ph_2Te + PhAnTe + An_2Te \quad (11)$$

An = *p*-anisyl

According to the mechanism depicted in Scheme I, once coupling product **12** is formed, it may undergo either of three competitive reactions, two of them involving unimolecular breaking of a C–As bond and one bimolecular electron transfer to the substrate. The unimolecular reaction should be independent of substrate concentration, but the bimolecular electron transfer should depend on the concentration and the reduction potential of the substrate. *p*-Bromotoluene (**19**) has a lower reduction potential than **5**;[13] it should therefore be a better electron acceptor, and when it is employed, products derived from the C–As bond rupture should decrease. However, when we used **19** as substrate, we found about the same distribution of products as from **5**. Moreover, similar results were found with *p*-iodotoluene as substrate (expt 3 and 5).

As the *p*-halotoluenes were not completely soluble in liquid ammonia, we suspected that the electron-transfer reaction might be slow due to their low actual concentration in solution. However, a reaction of **19** dissolved in 50 mL of Me_2SO, in which it was completely soluble, afforded the four arsines in similar yields (expt 4).

In the reactions of *p*-chloro-, *p*-bromo-, and *p*-iodoanisoles (**20a–c**), which are soluble in liquid ammonia, with **3**, the four possible arsines **2**, **21**, **22**, and **23** were formed (eq 12).

$$\underset{\substack{\mathbf{20a},\ X = Cl\\ \mathbf{b},\ X = Br\\ \mathbf{c},\ X = I}}{AnX} + 3 \xrightarrow{h\nu} \underset{2}{2} + \underset{21}{Ph_2AnAs} + \underset{22}{PhAn_2As} + \underset{23}{An_3As} \quad (12)$$

With **20b** there was no reaction in the dark, but 100% of reaction was obtained in 5 min of irradiation. The product distribution was similar among the three *p*-haloanisoles, except that the yield of **21** decreases in the order **20c > 20b > 20a**. This trend suggests that the rates of electron transfer from radical anion intermediates to these substrates follow the same order, which is in agreement with the mechanism proposed in Scheme I. However, in an experiment with a tenfold excess of **20b**, which assured a high concentration of electron acceptor throughout the reaction, the yield of **21** did not increase (expt 9).

The constancy of the product distribution when the concentration of **20b** is changed indicates that the molecularity of the reaction leading to the electron transfer is the same as for C–As bond fragmentation.[14a] Similar observations were made regarding the reaction of cyanomethyl anion with halobenzenes by the $S_{RN}1$ mechanism.[14b] It has been suggested that the electron-transfer reaction proceeds through a complex between the radical anion and the substrate.[14b] Similar intermediates were postulated in other systems.[15]

There are other examples in $S_{RN}1$ reactions of the radical anion formed in the coupling of an aryl radical with a nucleophile not only losing its "extra" electron, giving the

(11) Rossi, R. A.; Bunnett, J. F. *J. Org. Chem.* **1973**, *38*, 1407.
(12) Pierini, A. B.; Rossi, R. A. *J. Org. Chem.* **1979**, *44*, 4667.
(13) Sease, J. W.; Burton, F. G.; Nickol, S. L. *J. Am. Chem. Soc.* **1968**, *90*, 2575.
(14) (a) A reviewer has pointed out that the reactivity in the *p*-halotoluenes shows a decrease in the summation of the fragmentation products in the order I > Br > Cl, while in the *p*-haloanisoles this order is in the opposite direction. We think that it is more accurate to compare the yield of the straightforward substitution product $ArPh_2As$ along the series because it is the product formed in greatest yield, and certainly the relative errors are smaller. In this case *p*-chlorotoluene and *p*-bromotoluene gave about the same percentage, while *p*-iodotoluene gave a somewhat smaller yield, but we think that the difference is too subtle to advance an interpretation, and more data and better knowledge of the intimate mechanism of these reactions would be required to determine whether in fact *p*-halotoluenes and *p*-haloanisoles behave differently. (b) Rossi, R. A.; de Rossi, R. H.; Pierini, A. B. *J. Org. Chem.* **1979**, *44*, 2662.
(15) Meyers, C. Y.; Kolb, V. M. *J. Org. Chem.* **1978**, *43*, 1985 and references cited there in. We thank Professor Meyers for pointing this out.

Table I. Photostimulated Reactions of Diphenylarsenide Ion with Haloarenes in Ammonia[a]

expt	ArX[b]	[ArX], M	[Ph_2AsK], M	irradn time, min	yield,[d] % Ph_2AsH[c]	Ph_3As	Ph_2ArAs	$PhAr_2As$	Ar_3As
1	*p*-ClTo	3.42	2.28	60		15	61	15	2
2	*p*-ClTo	3.22	2.15	60[e]	75[f]	3			
3	*p*-BrTo	3.33	2.22	60		21	62	15	1
4	*p*-BrTo[h]	3.53	2.35	60		18	60	19	2
5	*p*-ITo[i]	3.38	2.47	60		20	50	25	4
6	*p*-ClAn	3.42	2.28	60		30	48	19	3
7	*p*-BrAn	3.26	2.17	5	*g*	20	60	22	*g*
8	*p*-BrAn	3.22	2.15	60[e]	83	3			
9	*p*-BrAn	31.8	2.12	60		25	56	19	*g*
10	*p*-IAn	3.46	2.30	5		18	78	5	
11	4-ClB	3.28	2.20	30		1	100		
12	4-ClB	3.52	2.30	30[e]	*g*	*g*	63		
13	4-ClB	3.45	2.30	30[e,j]	*g*	*g*	21		
14	4-ClB	3.58	2.39	30[e,k]	*g*	*g*	0		

[a] Reactions were carried out in 200–250 mL of ammonia. [b] To = tolyl, An = anisyl, 4-ClB = 4-chlorobenzophenone. [c] Reactions were quenched with methyl iodide, and the product was quantified as diphenylmethylarsine. [d] Determined by GC with the assumption of equimolar responses of the arsines. [e] Dark reaction. [f] Isolated yield. [g] Not quantified. [h] Dissolved in 50 mL of Me_2SO. [i] Substrate quite insoluble in liquid ammonia. [j] 20 mol % of *m*-dinitrobenzene. [k] Oxygen bubbled through the solution.

substitution product, but also decomposing by bond-breaking reactions.[16] The reactions of cyanomethyl anion[17] and alkanethiolate ions[18] with phenyl radicals give products derived from C–CN and C–S bond cleavage but only substitution products when the aryl moiety has a low-energy LUMO such as with naphthalene or benzophenone.[19,20]

The photostimulated reaction of 4-chlorobenzophenone (**24**) with **3** afforded a 100% yield of **25** in 30 min of irradiation. It is noteworthy that *only* one arsine was formed, namely, the straightforward substitution product (eq 13).

$$\underset{\mathbf{24}}{4\text{-}ClC_6H_4COC_6H_5} + 3 \xrightarrow{h\nu} \underset{\mathbf{25}}{C_6H_5COC_6H_4AsPh_2} + Cl^- \quad (13)$$

In the dark during the same period of time there was 63% of reaction. The dark reaction was inhibited by *m*-dinitrobenzene and oxygen, which are inhibitors for $S_{RN}1$ reactions[16] (expt 13 and 14) and is therefore judged to be of $S_{RN}1$ character.

The initiation step for the photostimulated $S_{RN}1$ reactions is believed to be an electron-transfer reaction from the nucleophile to the substrate promoted by light.[11] However, it is reported that lithium diphenylarsenide in THF spontaneously transfers an electron to benzophenone to give benzophenone radical anion (detected by ESR) and tetraphenyldiarsine (**26**), the coupling product of **10** (eq 14 and 15).[21]

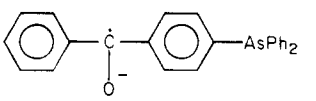
$$PhCOPh + 3 \xrightarrow{THF} (PhCOPh)^{-\cdot} + \mathbf{10} \quad (14)$$

$$2\,\mathbf{10} \rightarrow \underset{\mathbf{26}}{Ph_2AsAsPh_2} \quad (15)$$

Thus it is plain that the initiation step for the reaction of **3** with **24** in liquid ammonia occurs without light stimulation. Nevertheless, light accelerates the reaction since a higher yield was obtained when the reaction was carried out under photostimulation. $S_{RN}1$ reactions that occur without photostimulation are precedented.[10,22]

The fact that in our system **26** could not be detected is probably to be attributed to the chain being long and the propagation cycle efficient.

It is remarkable that with **24** as substrate only one arsine product, **25**, is found, in contrast with the scrambling of aryl rings found in the reactions with *p*-halotoluenes and anisoles. Probably the low-energy LUMO of the benzophenone moiety accommodates the "extra" electron so well that the C–As bond breaking in the intermediate radical anion **27** is greatly retarded.



27

Comparison between Diphenylphosphide Ion and Diphenylarsenide Ion as Nucleophiles in $S_{RN}1$ Reactions. In the photostimulated $S_{RN}1$ reaction of diphenylphosphide ion (**28**) with *p*-bromotoluene (**19**), the only substitution product obtained was *p*-tolyldiphenylphosphine (**29**). There were no products derived from C–P bond fragmentation (eq 16).[10]

$$\underset{\mathbf{19}}{} + \underset{\mathbf{28}}{Ph_2P^-} \rightarrow \underset{\mathbf{29}}{Ph_2ToP} + Br^- \quad (16)$$

This difference in behavior would imply either that electron transfer from *p*-tolyldiphenylphosphine radical anion (**30**) to the substrate is faster than from *p*-tolyldiphenylarsine radical anion (**12**) or that the bond breaking process is faster for **12** than for **30**.

The rates of electron-transfer reactions depend on the difference between the reduction potentials of the species that exchange the odd electron.[23] Inasmuch as the reduction potentials of triphenylphosphine (**31**) and **2** are almost the same (−3.5 and −3.4 V, respectively, vs. Ag/Ag^+ in glyme),[24] it is unlikely that **6** and **29** differ much in reduction potential. If **29** and **6** have about the same reduction potential, the electron-transfer rate to the same

(16) Bunnett, J. F. *Acc. Chem. Res.* **1978**, *11*, 413.
(17) Bunnett, J. F.; Gloor, B. F. *J. Org. Chem.* **1973**, *38*, 4156.
(18) Bunnett, J. F.; Creary, X. *J. Org. Chem.* **1975**, *40*, 3740.
(19) Rossi, R. A.; de Rossi, R. H.; Lopez, A. F. *J. Am. Chem. Soc.* **1976**, *98*, 1252.
(20) Rossi, R. A.; de Rossi, R. H.; Lopez, A. F. *J. Org. Chem.* **1976**, *41*, 3367, 3371.
(21) Busse, P. J.; Irgolic, K. J.; Dominguez, R. J. G. *J. Organomet. Chem.* **1974**, *81*, 45.
(22) Scamehorn, R. G.; Bunnett, J. F. *J. Org. Chem.* **1977**, *42*, 1449.
(23) Dorfman, L. M. *Acc. Chem. Res.* **1970**, *3*, 224.
(24) Dessy, R. E.; Chivers, T.; Kitching, W. *J. Am. Chem. Soc.* **1966**, *88*, 467.

substrate should be about the same (on the order of the diffusion rate if the difference in the reduction potentials of donor and acceptor is >1 V).[25] Therefore, the first alternative can be discarded, leaving the second possibility as the most likely. Although we cannot estimate the rate for the bond-breaking process, we note that the bond dissociation energy for the C–P bond in **31** (70–75 kcal/mol)[26] is about 10 kcal/mol higher than for the C–As bond in **2** (63.8 kcal/mol).[26] It is reasonable that the later should break faster than the former.

The electrochemical reductions of **31** and **2** are also different. The electrochemical reduction of **31** is a one-electron reduction,[27] which means that the radical anion **32** formed has a half-life long enough to diffuse from the electrode surface to the bulk solution before its fragmentation (eq 17–19).

$$Ph_3P + e^- \text{ (electrode)} \rightarrow \underset{\mathbf{32}}{(Ph_3P)^-\cdot} \quad (17)$$

$$\mathbf{32} \xrightarrow{\text{diffusion}} \mathbf{28} + \mathbf{14} \quad (18)$$

$$\mathbf{14} \xrightarrow{SH} PhH + S\cdot \quad (19)$$

On the other hand, the electrochemical reduction of **2** is a two-electron process,[27] which implies that radical anion **18** decomposes rapidly soon after its formation at the surface of the electrode and that **14** is reduced by heterogeneous electron transfer from the cathode to give the observed two-electron reduction (eq 20–23).

$$\mathbf{2} + e^- \text{ (electrode)} \rightarrow \mathbf{18} \quad (20)$$

$$\mathbf{18} \rightarrow \mathbf{3} + \mathbf{14} \quad (21)$$

$$\mathbf{14} + e^- \text{ (electrode)} \rightarrow \underset{\mathbf{33}}{Ph^-} \quad (22)$$

$$\mathbf{33} \xrightarrow{SH} PhH + S^- \quad (23)$$

Concluding Remarks

The facts that the reactions with *p*-halotoluenes and anisoles need photostimulation and that there is a scrambling of aryl rings in the products are hard to explain by known ionic mechanisms of nucleophilic aromatic substitution. However, the $S_{RN}1$ mechanism, which involves a photostimulated initiation step and the formation of arsine radical anion intermediates, which react in part by electron transfer and in part by C–As bond breaking, gives a good account of the observations.

When the substrate has a low-energy LUMO, as in 4-chlorobenzophenone, the radical anion intermediate formed does not decompose, and the straightforward substitution product is obtained. Although there is a dark reaction with this substrate, the reaction is catalyzed by light. Furthermore, it is inhibited by *m*-dinitrobenzene and oxygen, which are known inhibitors of the $S_{RN}1$ mechanism.

Experimental Section

General Methods. The instruments and procedures were as previously reported.[12]

Photostimulated Reaction with *p*-Bromoanisole. The photostimulated reaction of **3** with *p*-bromoanisole is representative. Into a three-necked, 500-mL, round-bottomed flask, equipped with a cold-finger condenser charged with solid CO_2 and acetone, a nitrogen inlet, and a magnetic stirrer was condensed ~250 mL of ammonia. To the ammonia were added triphenylarsine (0.664 g, 2.17 mmol) and then small pieces of K metal until the blue color persisted ~30 min (0.172 g, 4.4 mmol), and an orange solution was formed. Then *tert*-butyl alcohol (2.20 mmol) was added to neutralize the amide ion formed. *p*-Bromoanisole (3.26 mmol) was added, and the mixture was irradiated for 60 min. The reaction was quenched by adding ammonium nitrate in excess, and then the ammonia was allowed to evaporate. Water (100 mL) was added to the residue, and the mixture was extracted three times with 100 mL of diethyl ether. The combined ether extracts were dried over anhydrous Na_2SO_4 and distilled. The residue was submitted to column chromatography on neutral aluminum oxide (Merck) and eluted with petroleum ether; triphenylarsine was isolated and identified by comparison with an authentic sample; *p*-anisyldiphenylarsine was then isolated by elution with petroleum ether–benzene (1:1): NMR (CCl_4) δ 3.72 (3 H, s), 6.66–6.87 (2 H, m), 7.05–7.26 (12 H, m); mass spectrum, *m/e* 336, 259, 258, 257, 229, 228, 227, 184, 183, 182, 153, 152, 77. Di-*p*-anisylphenylarsine was eluted by petroleum ether–benzene (3:7): NMR (CCl_4) δ 3.70 (6 H, s), 6.53–6.73 (4 H, m), 6.97–7.13 (9 H, m); mass spectrum, *m/e* 366, 289, 287, 215, 214, 212, 189, 184, 182, 152, 151. Tri-*p*-anisylarsine was eluted by benzene: NMR (CCl_4) δ 3.68 (9 H, s), 6.53–7.10 (12 H, m); mass spectrum, *m/e* 397, 396, 367, 366, 336, 214, 185, 184, 182, 152, 151.

Photostimulated Reaction with *p*-Chlorotoluene. The procedure was as described above. The GLC tracing of the ether extract showed four peaks, the first one with the same retention time as authentic triphenylarsine. To a sample of the ether extract was added 9-bromophenanthrene as internal standard, and the products were quantified on the assumption that all the arsines had the same molar response as triphenylarsine. After distillation of the ether extract, the residue was submitted to column chromatography on aluminum oxide and eluted with petroleum ether, but it was not possible to isolate the constituents in pure form. By GC/MS the first peak showed the same mass spectrum as authentic triphenylarsine: *m/e* 306, 229, 227, 152. The second one showed a mass spectrum that could be attributed to *p*-tolyldiphenylarsine: *m/e* 320, 293, 241, 227, 166, 152, 91, 77. The third one showed a mass spectrum that could be attributed to di-*p*-tolylphenylarsine: *m/e* 334, 241, 182, 181, 168, 167, 166, 152, 91, 77. The last one showed a mass spectrum that could be attributed to tri-*p*-tolylarsine: *m/e* 348, 257, 255, 182, 181, 166, 91.

Dark Reaction with *p*-Chlorotoluene. The procedure was similar to that for the photostimulated reaction, except that the reaction flask was wrapped with aluminum foil to avoid any incident light. After 60 min of reaction, the mixture was quenched by adding methyl iodide. After the workup, the ether extract showed by GC only starting *p*-chlorotoluene, triphenylarsine (3%), and diphenylmethylarsine (88%). After evaporation of the solvent, the residue was submitted to a column chromatography on aluminum oxide and eluted with petroleum ether, and diphenylmethylarsine was isolated: 75% yield; NMR (CCl_4) δ 1.27 (3 H, s), 6.87–7.16 (10 H, m); mass spectrum, *m/e* 244, 229, 228, 227, 167, 153, 152, 91, 77.

Photostimulated Reaction with 4-Chlorobenzophenone. The procedure and workup were as described above. To a sample of the ether extract was added 1-chloronaphthalene as an internal standard. Analysis by GC showed that a 100% yield of the substitution product has been obtained. After distillation of the ether, the residue obtained was recrystallized twice from acetone: 43% yield; mp 131–132 °C; mass spectrum, *m/e* 410, 333, 332, 331, 256, 229, 228, 227, 153, 152, 151, 105, 77.

Dark Reaction with 4-Chlorobenzophenone and *m*-Dinitrobenzene. The procedure was as described, except that 20 mol % of *m*-dinitrobenzene was added to the reaction flask and then 4-chlorobenzophenone. The dark red solution was kept in the dark for 30 min. After the workup, 1-chloronaphthalene was added to the ether extract as an internal standard, and the constituents of the mixture were quantified by GC.

Dark Reaction with 4-Chlorobenzophenone and Oxygen. The procedure was as described, except that pure and dry oxygen was bubbled through the ammonia solution for 30 min in the dark.

(25) The $E_{1/2}$ of **19** is −1.84 (DMF) and −1.96 V (CH_3CN) vs. Ag/Ag^{+} [13] as compared with −3.5 V (glyme) vs. Ag/Ag^{+} [24] for **31**.

(26) Levason, W.; McAuliffe, C. A. *Acc. Chem. Res.* **1978**, *11*, 363.

(27) Wagenknecht, J. H., Ph.D. Dissertation, State University Iowa, 1964, quoted in ref 24.

The reaction was worked up and quantified as before.

Acknowledgment. R.A.A. gratefully acknowledges receipt of a fellowship from the Consejo Nacional de Investigaciones Cientificas y Tecnicas, Argentina. The mass spectra were run at the University of California at Santa Cruz through the courtesy of Professor J. F. Bunnett. We thank Professor Joseph F. Bunnett for critical reading of the manuscript.

Registry No. 2, 603-32-7; 3·K, 21498-51-1; 4, 945-48-2; 5, 106-43-4; 6, 76917-06-1; 7, 76917-07-2; 8, 2896-10-8; 19, 106-38-7; 20a, 623-12-1; 20b, 104-92-7; 20c, 696-62-8; 21, 24579-39-3; 22, 76917-08-3; 23, 35569-46-1; 24, 134-85-0; 25, 76917-09-4; *p*-ITo, 624-31-7.

Kinetic Study of the Homolytic Brominolysis of 1,2-Diarylcyclopropanes[1]

Douglas E. Applequist* and Rick D. Gdanski

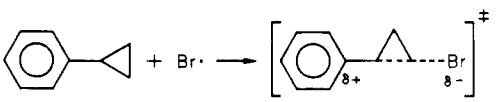
Department of Chemistry, University of Illinois, Urbana, Illinois 61801

Received February 12, 1981

The rate constants for the photolytic brominolysis of 22 *trans*-1,2-diarylcyclopropanes in carbon disulfide relative to an internal standard, *p*-chlorotoluene, have been determined. The products of the brominolysis are 1,3-dibromo-1,3-diarylpropanes. The rate constants range over 5 orders of magnitude, being enhanced by electron-donating substituents on one or both benzene rings. The quantitative size of the substituent effect (ρ) at either involved carbon center is a function of the substituent at the other center. This fact suggests a continuum of transition-state structures with varying degrees of bond breaking and charge separation.

Bimolecular homolytic displacements at carbon (S_H2 reactions) remain rare and poorly understood reactions. The best known and most studied example is the ring-opening reaction of cyclopropanes by halogen atoms. This process has been studied with respect to its kinetics,[2-4] stereospecificity,[5,6] and regiospecificity.[7] Cyclobutane rings, in contrast, are opened by halogen atoms only under very special circumstances.[8] On the other hand, bicyclobutanes are more reactive than simple cyclopropanes, being cleaved even by thiyl radicals[9,10] or carbon radicals.[11] Radical attack at tetracoordinate carbon in acyclic systems is almost unknown, except for some extraordinary alkyl-transfer reactions between cobalt atoms,[12] reactions which are at least formally S_H2 processes but which stand in contrast with the scarcity of such processes involving simple free radicals.

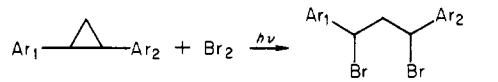
A previous report from this laboratory[4] described competitive homolytic brominolyses of substituted phenylcyclopropanes in carbon disulfide and showed that the process follows a $\rho^+\sigma^+$ relationship, with ρ^+ −1.85. This was interpreted to mean that the S_H2 transition state in this case is polarized with appreciable positive charge on the leaving carbon (eq 1). Such polarization could be a



(1)

consequence of the electronegativity of bromine and have no fundamental significance for the S_H2 process at carbon, or it may offer some clue to the almost unique ability of halogen atoms to perform the cyclopropane ring opening. (Among radicals which will *not* attack the carbon of simple cyclopropanes are methyl,[13,14] methoxyl,[15] and phenyl.[14])

In order to gain a satisfactory understanding of the cyclopropane–halogen atom ring opening, an obvious need was for information on the electronic effects of substituents at the attacked carbon, as opposed to the leaving carbon as studied by Applequist and McKenzie.[4] The present paper is a report of experiments designed to collect the required type of data by competitive brominolyses of 1,2-diarylcyclopropanes. It was already known that the reaction opens the ring at the bond between the two aryl substituents as in reaction 2.[3,7] With substituents on both



(2)

aryl groups there was, therefore, at least a good possibility of observing substituent effects at both leaving and attacked carbons. This expectation has been realized to a great extent.

Results and Discussion

A series of 1,2-diphenylcyclopropanes, variously substituted in the meta and para positions, were synthesized by the conventional route from acetophenones and benzaldehydes by way of the corresponding benzalaceto-

(1) Abstracted from the Ph.D. thesis of R.D.G., University of Illinois, 1980; present address Halliburton Services, Duncan, Oklahoma 73536.
(2) R. A. Ogg, Jr., and W. J. Priest, *J. Chem. Phys.*, 7, 736 (1939).
(3) J. M. Hoffmann, K. J. Graham, and C. F. Rowell, *J. Org. Chem.*, 40, 3005 (1975).
(4) D. E. Applequist and L. F. McKenzie, *J. Org. Chem.*, 41, 2262 (1976).
(5) J. H. Incremona and C. J. Upton, *J. Am. Chem. Soc.*, 94, 301 (1972).
(6) G. G. Maynes and D. E. Applequist, *J. Am. Chem. Soc.*, 95, 856 (1973).
(7) K. J. Shea and P. S. Skell, *J. Am. Chem. Soc.*, 95, 6728 (1973), and references cited therein.
(8) D. E. Applequist and R. Searle, *J. Am. Chem. Soc.*, 86, 1389 (1964).
(9) G. Szeimies, A. Schlosser, F. Philipp, P. Dietz, and W. Mickler, *Chem. Ber.*, 111, 1922 (1978).
(10) P. Dietz and G. Szeimies, *Chem. Ber.*, 111, 1938 (1978).
(11) K. B. Wiberg and R. P. Ciula, *J. Am. Chem. Soc.*, 81, 5261 (1959).
(12) J. Z. Chrzastowski, C. J. Cooksey, M. D. Johnson, B. L. Lockman, and P. N. Steggles, *J. Am. Chem. Soc.*, 97, 932 (1975).
(13) J. R. McNesby and A. S. Gordon, *J. Am. Chem. Soc.*, 79, 825 (1957).
(14) G. S. Hammond and R. W. Todd, *J. Am. Chem. Soc.*, 76, 4081 (1954).
(15) T. Berceš and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 348 (1961).

0022-3263/81/1946-2502$01.25/0