Hz, H-10_a); UV (cyclohexane) 260 nm (ϵ 2150), 270 (2070); mass spectrum, m/e 130 (M^+).

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Dehydrobromination of Secondary and Tertiary Alkyl and Cycloalkyl Bromides with 1,8-Diazabicyclo[5.4.0]undec-7-ene. Synthetic Applications

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The alkene proportions from the dehydrohalogenation of eight secondary and six tertiary aliphatic bromides, four 1-bromo-1-alkylcycloalkanes, three dibromobutanes, and 2-hexyl chloride and iodide with the hindered amidine 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) have been determined. For secondary bromides, the ratios of the more substituted alkene (Saytzeff product) to less substituted alkene (Hofmann product) are on the order of 9:1; for tertiary bromides, the corresponding ratios are 2–3:1 for aliphatic systems and >6:1 for cycloalkyl systems. The presence of a tertiary or benzylic β-H favors the Saytzeff product. Chain branching or elongation of the tertiary aliphatic bromides has only a small effect upon the regioselectivity. Activation of the β-H with a bromine atom considerably reduces the regioselectivity. For 2-halohexanes, the proportion of Saytzeff product increases in the order chloride < bromide < iodide, while the trans/cis ratio increases in the same order from 4.9 to 9. Reduced regio- and stereoselectivities were observed when 2-hexyl p-toluenesulfonate was treated with DBU. The thermolysis of the same compound gave a mixture of 1-, 2-, and 3-hexene.

The formation of a carbon–carbon double bond by β elimination (eq 1) is an ever-important operation in organic

$$\mathrm{RR'CHCHXCH_3} \xrightarrow[-\mathrm{HX}]{} \underset{\text{Hofmann}}{\mathrm{RR'CHCH{=}CH_2}} + \underset{\text{Saytzeff}}{\mathrm{RR'C{=}CHCH_3}}\ (\mathrm{R} \neq \mathrm{R'},\ \text{cis/trans}) \quad (1)$$

chemistry[1] and has been the object of extensive research both for synthetic purposes and also for gaining mechanistic information aimed at obtaining an understanding of the factors which affect and determine alkene proportions.[2] Numerous conditions in which the base and solvent have been varied have been examined to determine the effects on regioselectivity (the proportions of Saytzeff and Hofmann products that are formed) and stereoselectivity (in the case of geometrical isomers that are formed).

While 1-alkenes may be formed from primary alkyl bromides and t-BuOK in *tert*-butyl alcohol,[3] it is clearly much more difficult to find simple conditions which provide high regioselectivity and stereoselectivity with good yields in eliminations from secondary or tertiary substrates. Thus treatment of 2-bromopentane with EtOK in refluxing ethanol afforded 74% total yield of 1- and 2-pentene, respectively, in a ratio of 1:2 and with a trans/cis ratio of the latter of 2.8;[4] the regioselectivity could be reversed, however, by using instead of ethoxide the highly hindered t-BuOK.[5,6] Ag^+-promoted eliminations of 2-bromoalkanes were found to proceed with a very high regioselectivity (Saytzeff products preferred) and with trans/cis ratios ranging from 1.1 to 2.8.[7] Ultrahigh regioselectivity favoring the Saytzeff product can be achieved when 2-alkyl bromides or sulfonate esters are treated under E2C-like conditions with a very weak (and soft) base.[6,8] From a preparative viewpoint, these reactions are associated in general with disadvantages such as tedious isolation procedures, moderate yields (in part due to competitive substitution reactions[3]), and long reaction times.[9]

It is thus clear that a method which combines regioselectivity and stereoselectivity with an easy isolation procedure and good yield is needed. Highly hindered tertiary amines are finding an increasing use in synthetic work;[10]

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Table I. Composition of Alkenes Formed by Dehydrobromination of Secondary and Tertiary Bromides with DBU

expt	R in RBr	composition[a] 1-alkene	2-alkene (trans/cis ratio)[b]	overall yield, %
1	$CH_3CH_2CH_2CHCH_3$	10	90 (8.5)	80
2	$CH_3CH_2CHCH_2CH_3$		100 (6.8)	85
3	$CH_3CH_2CH_2CH_2CHCH_3$	12	88 (5.5)	75
4	$CH_3CH_2CH_2CH_2CH_2CHCH_3$	14	86 (5.7)	80
5	$(CH_3)_2CHCHCH_3$	4	96	70
6	$PhCH_2CHCH_3$	<2	>98 (17)	60
7	$BzCHCH_2CH_3$	6[c]	94[d]	100
8	c-$C_6H_{13}CHCH_3$	30	70	>55
9	$CH_3CH_2C(CH_3)_2$	29	71	95
10	$CH_3CH_2CH_2C(CH_3)_2$	25	75	90
11	$(CH_3)_2CHC(CH_3)_2$	8	92	100
12	$(CH_3)_2CHCH_2C(CH_3)_2$	34	66	85
13	$(CH_3)_3CCH_2C(CH_3)_2$	61	39	95
14	$PhCH_2C(CH_3)_2$	21	79	100
15	1-methylcyclopentyl	6	94	100
16	1-methylcyclohexyl	4	96	95
17	1-ethylcyclohexyl	10	90	65
18	1-methylcycloheptyl	16	84	>50

[a] By ^1H NMR spectroscopy. [b] By ^{13}C NMR spectroscopy (±0.3). [c] $BzCH=CHCH_3$. [d] $PhCH=CHC_2H_5$.

Table II. Composition of Products from Dehydrobromination of Dibromobutanes with DBU

expt	dibromide	products[a] (% yield)	overall yield, %
19	$CH_3CH_2CHBrCH_2Br$[b]	$CH_3CH_2CBr=CH_2$ (57), $CH_3CH_2CH=CHBr$ (43; cis/trans, 1:1)[c]	70
20	*meso*-$CH_3CHBrCHBrCH_3$	$CH_3CBrCH=CH_2$ (<3), $CH_3CH=CBrCH_3$ (>97; cis/trans, 1:1)[c]	75
21	$CH_3CHBrCH_2CH_2Br$	alkylation, no volatile products	0

[a] By ^1H NMR; for peak assignments, see ref 26 and R. Y. Tien and P. I. Abell, *J. Org. Chem.*, 35, 956 (1970). [b] No trace of crotyl bromide was found in this experiment (for GLC, see text). [c] By GLC.

Table III. Composition of Hexenes from Elimination Reactions of Various Substrates under Different Conditions

expt	reaction	temp, °C	% composition 1-hexene[a,b]	2-hexene[b,e]	3-hexene[b]	% composition under E2H conditions[d] 1-hexene	2-hexene[e]
22	$CH_3CH_2CH_2CH_2CHBrCH_3$ + DBN	85	16	4.5		28	3.0
23	$CH_3CH_3CH_2CH_2CHClCH_3$ + DBU	170	19	4.9		33	2.9
24	$CH_3CH_2CH_2CH_2CH_2CH(OTs)CH_3$ + DBU	125	27	3.0		33	1.9
25	$CH_3CH_2CH_2CH_2CHICH_3$ + DBU	90	9[c]	9.1		19	3.6
26	$CH_3CH_2CH_2CH_2CH(OTs)CH_3$	150	14	1.8	15		
27	$CH_3CH_2CH_2CHBrCH_2CH_3$ + DBU	85	0	5.0	58		

[a] By ^1H NMR. [b] By ^{13}C NMR. [c] Total hexene yield = 75%. [d] With sodium methoxide in methanol.[13a,27] [e] Trans/cis mixture.

due to their lack of nucleophilicity, they are used as proton acceptors in many reactions. One of these, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), was reported by Oediger and Möller to dehydrobrominate 2-bromoalkanes with a regioselectivity of 4:1 in favor of the Saytzeff product.[11] In a recent experiment in this laboratory, it was found that DBU converted 2-bromopentane into 1- and 2-pentene in a total yield of 80% and in a ratio of 1:9, with the latter in a trans/cis ratio of 8. In the light of this promising result, an investigation of DBU as a dehydrohalogenating reagent seemed warranted. Herein are reported the yields and proportions of alkenes formed from various secondary and tertiary alkyl and cycloalkyl bromides, dibromobutanes, and some other derivatives.

Results and Discussion

The alkenes formed were easily separated by distillation, vacuum transfer into a cooled trap, or extraction with ether of the product mixture, which was obtained by heating equimolar amounts of substrate and DBU for 5–20 min after the appearance (3 min) of a white precipitate (or syrup). Tertiary bromides reacted faster than secondary ones. The reported yields correspond to reactions carried out on a 4–10-mmol scale.[12] The results obtained for secondary and tertiary aliphatic and alicyclic bromides are shown in Table I, those for dibromobutanes appear in Table II, and those for 2-hexyl chloride, iodide, and tosylate are in Table III.

The eliminations of secondary aliphatic bromides all proceed with a high regioselectivity favoring the Saytzeff product (expt 1, 3, 4) and which is enhanced when the abstracted β-H is tertiary or benzylic (expt 5–7); the enhancement also prevails when the secondary β-H is benzylic (expt 7). The cyclohexyl group could seem to impose some steric hindrance since an appreciable amount of the Hofmann product was produced (expt 8).

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The regioselectivities observed with DBU and 2-bromoalkanes exceed those previously reported by using alkali alkoxides, which produce the 1-alkene in 26% and with a trans/cis ratio of 3–3.6 for the 2-alkene; typical yields were on the order of 75%.[13] Although treatment of 2-bromopentane with tetrabutylammonium bromide in acetone containing an excess of 2,6-lutidine gives almost exclusively (98%) the Saytzeff product in a trans/cis ratio of 5.3, the method has serious disadvantages for reactions carried out on a preparative scale. When 2-bromo-1-phenylpropane was treated with quinoline, the Hofmann product, allylbenzene, was formed in 41% yield;[14] with DBU, this yield was reduced to 2%.[15]

While chain elongation has no appreciable effect on the regioselectivity, the stereoselectivity decreases on going from 2-pentyl to 3-pentyl and also to 2-hexyl and 2-heptyl; for the pentyl bromides, however, no change was found under E2C-like conditions.[6] On the other hand, it is the reverse of that found for tosylates under E2H conditions (alkoxide/alcohol) where it has been found that 3-pentyl tosylate yields more *trans*-2-pentene than does 2-pentyl tosylate.[16] A small decrease of the trans/cis ratio upon chain elongation seems to be apparent under E2H conditions (cf. ref 13). The conclusion which can be drawn from the present results in the light of the hypotheses put forward by Feit and Saunders,[6,16,17] is that steric hindrance to rotation by the departing bromine seems to be of nearly equal importance for the groups attached at C_α and C_β under DBU conditions.

The Hofmann product formed from the tertiary aliphatic bromides is 2–3-fold greater than that for the secondary ones (expt 9, 10, 12). The regioselectivity increases, however, with the presence of a tertiary or benzylic β-H, but apparently less so in the latter case (expt 11, 14). The high proportion of 2,4,4-trimethyl-1-pentene formed from 2-bromo-2,4,4-trimethylpentane is not a violation of the Saytzeff rule, because the 1-alkene is more stable than the 2-alkene;[18] the proportion of the latter, however, is greater than that reported by using EtOK or pyridine.[19] The alkene composition from 2-bromo-2-methylbutane (expt. 9) is practically the same as that reported by using EtOK or pyridine as the base;[18] with ethyldicyclohexylamine, however, the formation of 2-methyl-2-butene (81%) was reported.[20] The alkene composition from 2-bromo-2-methyl-3-phenylpropane (expt 14) is likewise the same as that reported by using MeONa.[21]

Chain branching or elongation does not cause a major change in the proportions of 1-alkenes that are formed (expt 9, 10, 12); this is clearly in contrast to the results obtained with EtOK or pyridine,[19] where a significant increase was observed. The apparent eclipsing effect observed in the latter case[22] does not seem to play a role under DBU conditions. A small increase in the relative proportions of Saytzeff product seems to be apparent under E2C-like conditions.[2c]

Internal elimination from the 1-bromo-1-alkylcycloalkanes predominates since the major products are 1-alkylcycloalkenes; a small decrease in the proportion of these products occurs, however, when an external β-H is secondary and with cycloheptyl (expt 17, 18). The results show that elimination with DBU is superior to previously reported methods using alkali alkoxides[23] or dehydration of cycloalkanols with iodine[24] or anhydrous $CuSO_4$.[9]

The dibromobutanes react exothermically with DBU upon mixing, and no external heating for completing the reaction is required. No elimination product, however, was observed for 1,3-dibromobutane. Substitution of a β-H with a bromine atom has a dramatic effect and reveals that elimination from a primary carbon atom (C-1) may occur competitively with normal Hofmann rule elimination (expt 19) and also that the formation of Saytzeff or Hofmann product may be suppressed (expt 19 and 20, respectively). Substitution at a primary carbon atom (by salt formation) predominates over elimination from a secondary carbon in the absence of activation of a β-H (expt 21). The formation of a crotyl bromide from 1,2-dibromobutane (Saytzeff product) cannot be excluded, because it would react with DBU with salt formation, thus lowering the total yield of alkenes, by analogy with the observations for 1,3-dibromobutane and primary alkyl bromides.[25] The cis/trans ratio observed in expt 19 and 20 could be due to the fact that the activation energy of isomerization of the products (vinyl bromides) is small, with $k \simeq 1$.[26]

The reactions of 2-hexyl bromide, chloride, iodide, and tosylate with DBU, and in one case with 1,5-diazabicyclo[4.3.0]non-5-ene (DBN)[10], were investigated in order to determine whether better selectivities could be achieved, the results are given in Table III and they show the following: (i) the elimination with DBN proceeds with both lower regio- and stereoselectivities (expt 3, 22); (ii) both selectivities increase in the order tosylate < chloride < bromide < iodide; a similar order has been observed for reactions carried out under E2H conditions (see Table III).[13a,27] Significantly higher temperatures were required, however, in the cases of dehydrochlorination and dehydrotosylation. For the sake of comparison, the thermolysis of 2-hexyl tosylate was briefly investigated. The low trans/cis ratio for the 2-hexenes, that are formed together with the formation of 3-hexene, clearly indicates that the elimination must proceed under E1 conditions (cf. ref 28).

Conclusion

The elimination from secondary and tertiary bromides with DBU is superior in experimental convenience, and the regio- and stereoselectivities are equal to, or in most cases better than, previously reported methods in solution. The proportion of Saytzeff product formed from 2-bromoalkanes is high and so is the trans/cis ratio. Particularly noteworthy is the finding that the selectivities observed with 2-iodohexane are the highest ever reported for a 2-haloalkane. The proportions of Saytzeff products formed from tertiary aliphatic bromides are smaller than

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(25) Comparison of the NMR spectra of the crude product mixture from the exothermic reaction of crotyl bromide with DBU with that for the product from the action of DBU with 1,2-dibromobutane is not incompatible with the formation of some crotyl bromide in the case of the latter reaction (expt 19).

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for secondary ones but are still equal to or better than those observed by using the more conventional methods; with cycloalkyl bromides they are again very high. Hofmann products may predominate, however, when a terminal β-H is activated with a bromine atom.

The selectivities observed with DBU show a close resemblance with those obtained for reactions carried out under E2C-like conditions with a weak base.[6,8,15] It is thus clear that a more detailed investigation of the mechanism is warranted.

Experimental Section

^{1}H and ^{13}C NMR spectra were recorded on a JEOL FX-90 Q spectrometer. GLC analyses were performed on a Hewlett-Packard Model 5840 A by using a OV-101 or Carbowax 20M column.

Materials. DBU and DBN were purchased from EGA-Chemie. ^{1}H and ^{13}C NMR spectroscopy was used to check purity (absence of alkene) and isomeric purity of all substrates. 2- and 3-bromopentane, 2-bromohexane, 2-bromoheptane, and 2-bromo-3-methylbutane were prepared from their corresponding alcohols according to the method of Wiley et al.[29] by using Ph_3P and Br_2 in DMF. The preparation of the last-mentioned bromide was accompanied by alkene formation, and several redistillations were required to obtain a pure sample, bp 40–41 °C (50 mm); the ^{1}H NMR was in accord with that reported.[30] 2-Chlorohexane was prepared by using Ph_3P and CCl_4.[31] 2-Iodohexane (60%) was prepared by using Ph_3P and I_2 (dissolved in DMF) according to Wiley et al.[29] bp 55–56 °C (13 mm) [lit.[27] bp 50.5–51.5 °C (12 mm)]. A slight modification of the method of Baldwin and Tomesch[32] was used for the preparation of 2-bromo-1-phenylpropane from 1-phenyl-2-propanol with pyridine, Ph_3P, and Br_2 in the molar ratio (1:1:1.2:1.125): the cooled solution was decanted and poured into ice/water, and the mixture was stirred for 15 min. The lower phase was separated and extracted four times with pentane, the combined organic phases were washed with H_2O and then dried (Na_2SO_4), and the pentane was removed by evaporation under reduced pressure. Distillation under reduced pressure gave the pure compound: 40%; bp 48–49 °C (0.2 mm) [lit.[33] bp 89 °C (3 mm)]. 2-Bromo-1-phenylbutane (70%) was prepared in a similar manner; bp 58–60 °C (0.2 mm) [lit.[34] bp 111–112 °C (2 mm)].[35] 1-Cyclohexylethyl bromide was prepared as above from 1-cyclohexylethanol [60%; bp 70–80 °C (10 mm) [Lit.[36] bp 85–87 °C (17 mm)]], which was made by reaction of cyclohexylmagnesium chloride and acetaldehyde. Due to poor conversion of the alcohol, several redistillations were required to obtain the pure bromide,[35] bp 78–80 °C (14 mm).

The tertiary bromides were prepared from their corresponding alcohols, which were made from Grignard reactions, with LiBr/HBr.[37] After distillation, they were stored at −20 °C. Yields and boiling points were as follows: 2-bromo-2,3-dimethylbutane, 60%, 131–135 °C; 2-bromo-2-methylpentane, 90% (with PBr_3), bp 50–51 °C (39 mm); 2-bromo-2,4-dimethylpentane, 65%, bp 46–47 °C (19 mm) [lit.[38] bp 46 °C (20 mm)]; 2-bromo-2-methyl-3-phenylpropane, 70%, bp 64–65 °C (2 mm) [lit.[39] bp 57 °C (2 mm)]; 1-bromo-1-methylcyclopentane, 70%, bp 42–43 °C (18 mm) [lit.[40] bp 56–57 °C (36 mm)]; 1-bromo-1-methylcyclohexane, 60%, bp 50–51 °C (10 mm) [lit.[40] bp 78–79 °C (39 mm)]; 1-bromo-1-ethylcyclohexane, 50%, bp 70–73 °C (10 mm) [lit.[41] bp 98–100 °C (40 mm)]; 1-bromo-1-methylcycloheptane, 50%, bp 60–61 °C (1 mm) [lit.[40] bp 106–107 °C (38 mm)]. 2,4,4-Trimethyl-2-pentanol[42] was obtained by adding a solution of acetone in ether to neopentyllithium, which was made from neopentyl bromide[45] and lithium in ether according to Gilman.[46] Hydrolysis of the reaction mixture with saturated NH_4Cl and ice afforded the alcohol: 50% yield; bp 48–50 °C (12 mm). Treatment of the alcohol with LiBr/HBr gave 2-bromo-2,4,4-trimethylpentane (40%). Careful redistillation through a glass helix column gave a pure sample, bp 48–49 °C (10 mm) [lit.[38] bp 61.5 °C (15 mm)]. 1,2-Dibromobutane was prepared from 1-butene (99% purity, Matheson) and Br_2.[47] *meso*-2,3-Dibromobutane was made according to Lucas[48] from Br_2 and *trans*-2-butene (99% purity, Matheson). 1,3-Dibromobutane was purchased from EGA-Chemie and redistilled. 2-Hexyl tosylate was made by a standard method.[49]

General Procedure for Dehydrobromination. Equimolar amounts (4–10 mmol) of DBU and substrate (freshly distilled, usually under reduced pressure) were mixed together and heated in an oil bath at 85 ± 5 °C. Heating and stirring were continued for 5–20 min after the appearance (about 3 min) of a white precipitate or syrup. The C_5 alkenes were distilled and collected in a cold trap (dry ice/acetone). The C_6–C_8 alkenes and bromobutenes were collected (liquid air) by vacuum transfer at ca. 1 mm. The higher alkenes were separated from the reaction mixture by extraction with ether followed by evaporation of the solvent. Unchanged substrate amounted to a maximum of 4%.

Control experiments with 2-bromoheptane and DBU (50% molar excess) at 95 °C for 16 h did not show any significant changes (1-heptene to 2-heptene, 14% to 86%); likewise, no changes were observed by using Me_2SO as solvent.

Product Analysis. The product composition was measured from peak areas of ^{1}H NMR spectra and is the average of at least two scans. Trans/cis ratios in C_5–C_7 alkenes were established from peak intensities of C-2 or C-3 in their ^{13}C NMR spectra (decoupled).[50] Appropriate corrections were made for differrent peak responses by comparison with spectra of weighed mixtures of pure isomers (better than 99% pure). The ^{13}C NMR spectra of the C_5–C_7 alkenes could also be used to establish the composition; the agreement was found to be within ±1%. GLC analyses were performed for expt 6, 7, 14, 15, 19, and 20; they varied within ±1.5% of the NMR results.

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Registry No. 2-Bromopentane, 107-81-3; 3-bromopentane, 1809-10-5; 2-bromohexane, 3377-86-4; 2-bromoheptane, 1974-04-5; 2-bromo-3-methylbutane, 18295-25-5; 2-bromo-1-phenylpropane, 2114-39-8; 2-bromo-1-phenylbutane, 81012-82-0; 1-cyclohexylethyl-

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Photolysis of Aryl Chlorides with Aliphatic Amines

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Kinetic arguments show that the aliphatic amine assisted photodechlorinations of chlorides of the benzene, naphthalene, and biphenyl series take place mainly from the triplet excited state. Deuterium labeling studies have been used to determine the origin of the hydrogen atom which replaces chlorine when 4-chlorobiphenyl is photoreduced. Three pathways are inferred: hydrogen abstraction from the solvent and protonation both within the exciplex (or radical ion pair) and by external proton donors.

The photochemistry of chlorinated aromatic compounds has been studied in some detail because of the importance of some of these compounds as environmental pollutants. In some cases, irradiations in the presence of added substances such as amines and dienes have led to enhanced photolability of the halide, as a result of electron-transfer reactions.

The work described in this paper was undertaken with the long-term goal of evaluating whether this increased photolability could be exploited to develop methods for photochemical destruction of chlorinated pollutants of the chlorobenzene, -naphthalene, and -biphenyl series. We now report studies on the mechanism of the aliphatic amine assisted photolysis of some of these substances.

4-Chlorobiphenyl. Ohashi, Tsujimoto, and Seki[1] studied the photoreduction of 4-chlorobiphenyl in acetonitrile, assisted by triethylamine. They observed that the amine both quenched the fluorescence of the halide and also enhanced its photolability. Scheme I was proposed as the mechanism of this photoreduction. Steady-state analysis gives eq 1 and 2 for the influence of amine upon the quantum yields of fluorescence (ϕ_f) and reaction (ϕ_r). In these equations ${}^1\tau$ is the singlet lifetime ($=1/k_1$).

Scheme I

$$\mathrm{ArCl} \xrightarrow{h\nu} {}^1\mathrm{ArCl}$$

$${}^1\mathrm{ArCl} \xrightarrow{k_1} \mathrm{ArCl}$$

$${}^1\mathrm{ArCl} + \mathrm{R_3N} \xrightarrow{k_2} [\mathrm{ArCl}^{-\cdot} \ldots \mathrm{R_3N}^{+\cdot}],\ \mathrm{X}$$

$$\mathrm{X} \xrightarrow{k_3} \mathrm{ArCl} + \mathrm{Et_3N}$$

$$\mathrm{X} \xrightarrow{k_4} \text{products}$$

$$(\phi^0/\phi)_f = (I^0/I)_f = 1 + k_2{}^1\tau[\mathrm{R_3N}] \qquad (1)$$

$$\frac{1}{\phi_r} = \left(1 + \frac{k_3}{k_4}\right)\left(1 + \frac{1}{k_2{}^1\tau[\mathrm{R_3N}]}\right) \qquad (2)$$

According to Scheme I, the quantity $k_2{}^1\tau$ can be evaluated in two independent ways; in acetonitrile solution, Ohashi et al. obtained a value of $k_2{}^1\tau$ of 23 M^{-1} by fluorescence quenching studies and of 20 M^{-1} from a study of the variation of ϕ_r with [Et_3N]. They thus proposed Scheme I as an established mechanism for the amine-assisted photodechlorination of 4-chlorobiphenyl, with electron transfer to the excited aryl chloride as the key step. The intermediate exciplex is not seen to fluoresce in solvents such as acetonitrile but is easily observed in alkane media.[2]

Our initial interest in this reaction was directed toward the events following electron transfer. Ohashi et al. show this as expulsion of chloride ion (eq 3 and 4), precedent

$$\mathrm{ArCl}^{-\cdot} \rightarrow \mathrm{Ar}\cdot + \mathrm{Cl}^- \qquad (3)$$

$$\mathrm{Ar}\cdot + \mathrm{RH} \rightarrow \mathrm{ArH} + \mathrm{R}\cdot \qquad (4)$$

for which is shown by the electroreduction of aryl halides[3] and in one of the chain-propagating steps of the $S_{RN}1$ mechanism for substitution of aryl halides.[4]

Recent work has shown that eq 5–7 could be a plausible

$$\mathrm{ArCl}^{-\cdot} + \mathrm{H}^+ \rightarrow \mathrm{ArClH}\cdot \qquad (5)$$

$$\mathrm{ArClH}\cdot \rightarrow \mathrm{ArH} + \mathrm{Cl}\cdot \qquad (6)$$

$$\mathrm{Cl}\cdot + \mathrm{RH} \rightarrow \mathrm{HCl} + \mathrm{R}\cdot \qquad (7)$$

alternative to the above scheme, because acids can catalyze the photoreduction of aryl halides.[5-7] The intermediate ArClH· is a cyclohexadienyl radical from which aromatization by loss of Cl· should be easy. Since sequences 3 and

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