J. Org. Chem. 1982, 47, 1955–1958

Table XI

$[Et_3N]$, M	0	0.007	0.013	0.026	0.046	0.066	0.109
ϕ_r	0.16	0.25	0.31	0.38	0.40	0.39	0.38

Table XII

$[Et_3N]$, M	ϕ_r	% light absorbed by Et_3N	% singlets quenched by Et_3N
0	0.25	0	0
0.022	0.26	3	4
0.027	0.26	4	5
0.056	0.26	8	9
0.111	0.27	14	17
0.167	0.28	19	23
0.174	0.28	21	24
0.223	0.30	24	29
0.347	0.30	34	38
0.521	0.26	45	48
0.694	0.21	50	56

Acknowledgment. I thank the Natural Sciences and Engineering Research Council for financial support. Mr. Luis Ravanal prepared the dimethylamino derivative 3, Mr. Jim Gallacher helped prepare some of the solutions for the deuteration studies, and Mr. Stewart McKinnon ran the mass spectrometer.

Registry No. 3, 27107-82-0; 2,2′,5,5′-tetrachlorobiphenyl, 35693-99-3; 4-chlorobiphenyl, 2051-62-9; 1-chloronaphthalene, 90-13-1; chlorobenzene, 108-90-7; 1-(*p*-chlorophenyl)-3-(dimethylamino)-1-propanol, 16254-21-0; 1-(*p*-chlorophenyl)-3-(dimethylamino)-propene,, 81012-73-9.

Supplementary Material Available: Original kinetic data (Table III) and deuterium incorporation data (Table VI) for the photolysis of 4-chlorobiphenyl and of 1-chloronaphthalene with aliphatic amines are available (5 pages). Ordering information is given on any current masthead page.

Photolysis of Aryl Chlorides with Dienes and with Aromatic Amines

Nigel J. Bunce* and James C. Gallacher

Department of Chemistry, University of Guelph, Guelph, Ontario, Canada N1G 2W1

Received June 16, 1981

Simple dienes quench the fluorescence of 1-chloronaphthalene and 4-chlorobiphenyl with a concurrent singlet-state photochemical reaction, which does not involve dechlorination. Similar chemistry is brought about when the diene is initially excited. Chlorobiphenyls quench the fluorescence of *N,N*-dimethylaniline with concomitant photodechlorination of the aryl chloride. Attempts to extend this reaction to amines having longer wavelength absorption were unsuccessful.

In the accompanying paper,[1] the photolysis of aryl chlorides in the presence of aliphatic amines was examined. A mechanism was proposed in which initial light absorption by the aryl halide was followed by interaction of the amine with both the singlet and triplet excited states of the halide. While the singlet-state process led to fluorescence quenching, the triplet-state interaction was mainly responsible for the amine-assisted photodechlorination. At least two pathways were involved in the later steps of the reaction; following electron transfer to the aryl halide, both hydrogen abstraction from the solvent and, where possible, proton transfer were responsible for the formation of the reduced product (Scheme I).

Scheme I

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

$${}^1\mathrm{ArCl} \rightarrow \mathrm{ArCl}$$

$$\mathrm{R_3N} + {}^1\mathrm{ArCl} \rightarrow {}^1(\mathrm{R_3N}\cdot\mathrm{ArCl}) \rightarrow \mathrm{R_3N} + \mathrm{ArCl}$$

$${}^1\mathrm{ArCl} \rightarrow {}^3\mathrm{ArCl}$$

$${}^3\mathrm{ArCl} \rightarrow \mathrm{ArCl}$$

$$\mathrm{R_3N} + {}^3\mathrm{ArCl} \rightarrow {}^3(\mathrm{R_3N}\cdot\mathrm{ArCl}) \leftrightarrow (\mathrm{R_3N}^{+\cdot}\ \mathrm{ArCl}^{-\cdot})$$

$$\mathrm{ArCl}^{-\cdot} \rightarrow \mathrm{Cl}^- + \mathrm{Ar}\cdot \xrightarrow{\mathrm{RH}} \mathrm{ArH}$$

$$(\mathrm{H}^+) + \mathrm{ArCl}^{-\cdot} \rightarrow \mathrm{ArClH}\cdot \rightarrow \mathrm{ArH} + \mathrm{Cl}\cdot$$

In this paper we extend our studies to dienes and to aromatic amines.

Photolysis with Dienes

The effect of dienes on the efficiency of photodegradation of aryl halides is rather confused. Some systems appear to show increased photolability when dienes are present, while for others the reverse effect is observed. In the former category, Smothers, Schanze, and Saltiel[2] have studied the photodechlorination of 9,10-dichloroanthracene assisted by 2,5-dimethyl-2,4-hexadiene; they present evidence for reaction proceeding from a singlet exciplex and triplex, where the complexes have charge-transfer character, diene$^{+\cdot}$...ArCl$^{-\cdot}$.

On the other hand, Ruzo, Zabik, and Schuetz[3] observed that 1,3-cyclohexadiene retarded the photodecomposition of certain polychlorinated biphenyls. They argued that a reactive triplet state was involved and used the method to estimate the triplet lifetimes of the PCB molecules in solution. Later, we found that dienes also quench the singlet states of many PCB molecules;[4] further, in the particular case of 1,3-cyclohexadiene, the diene absorbs the incident light competitively with the aryl halide.[5] If we

---

[1] Bunce, N. J. *J. Org. Chem.*, preceding paper in this issue.

[2] Smothers, W. K.; Schanze, K. S.; Saltiel, J. *J. Am. Chem. Soc.* **1979**, *101*, 1895.

[3] Ruzo, L. O.; Zabik, M. J.; Schuetz, R. D. *J. Am. Chem. Soc.* **1974**, *96*, 3809.

[4] Bunce, N. J.; Kumar, Y.; Ravanal, L.; and Safe, S. *J. Chem. Soc., Perkin Trans. 2* **1978**, 880.

[5] Bunce, N. J.; Bergsma, J. P.; Bergsma, M. D.; DeGraaf, W.; Kumar, Y.; Ravanal, L. *J. Org. Chem.* **1980**, *45*, 3708.

0022-3263/82/1947-1955$01.25/0

Table I. Kinetic Data for Photolyses of Aryl Chlorides with Aliphatic Dienes

substrate	diene	solvent	K_{SV},[a] M^{-1}	slope[b]	intercept[b]	r[c]	P,[d] M^{-1}
1-chloronaphthalene	DMH[e]	CH_3OH	26.7	0.0266 ± 0.0007	0.655 ± 0.049	0.998	24.6
1-chloronaphthalene	DMH	CH_3CN	30.7	0.0153 ± 0.0008	0.422 ± 0.064	0.995	27.6
1-chloronaphthalene	DMH	C_6H_{12}	15.3	0.0316 ± 0.0011	0.547 ± 0.082	0.997	17.3
1-chloronaphthalene	C_5H_8[f]	CH_3OH	2.2	0.0234 ± 0.0097	0.517 ± 0.089	0.997	2.2
4-chlorobiphenyl	C_5H_8	CH_3OH	3.2	0.132 ± 0.018	0.141 ± 0.026	0.972[g]	1.1

[a] Stern-Volmer fluorescence quenching constant. [b] Slope and intercept for the plot of ϕ_r^{-1} against $[\text{diene}]^{-1}$. [c] Correlation coefficient. [d] Intercept/slope. [e] 2,5-dimethyl-2,4-hexadiene. [f] 1,3-Pentadiene, mixture of cis and trans. [g] In order to get most of the light absorbed by the halide, high halide concentrations had to be used. Long irradiation times were required, and the photolyzed solutions were colored.

assumed that the light absorbed by diene did not result in reaction, then it could be shown that after correction for the light absorbed by diene, the effect of the diene was actually to increase photolability rather than to suppress it.[5]

The experiments below were designed to probe the situation further; 1-chloronaphthalene and 4-chlorobiphenyl were chosen as chlorinated substrates; 2,5-dimethyl-2,4-hexadiene and 1,3-pentadiene were the dienes.

The absorption characteristics of 1-chloronaphthalene made it more convenient for most of the experiments. By irradiation at 300 nm (where naphthalene has ϵ 1460 in methanol), it is possible to avoid exciting either of the dienes used and hence to avoid also the mechanistic ambiguity mentioned above. Preliminary experiments in methanol gave a surprising result: almost no photoreduction occurred, even though the aryl halide was consumed. Apparently photoadducts between the chloride and the diene were formed, but their complete structures have not yet been elucidated. This is compatible with work on naphthalene[6] but different from the 9,10-dichloroanthracene system, where cycloaddition is preferred in nonpolar media,[7] and reduction occurs in polar solvents.

Kinetic studies were undertaken in order to compare this system with the aryl chloride/aliphatic amine photoreduction[1] investigated previously. The simplest sequence of events is given as Scheme II (D ≡ diene), which is completely analogous to a mechanism proposed by Ohashi et al.[8] for the photoreduction of 4-chlorobiphenyl by triethylamine (D ≡ Et_3N).

Scheme II

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

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

$$\mathrm{D} + {}^1\mathrm{ArCl} \xrightarrow{k_2} {}^1(\mathrm{D}\cdot\mathrm{ArCl})$$

$${}^1(\mathrm{D}\cdot\mathrm{ArCl}) \xrightarrow{k_3} \mathrm{D} + \mathrm{ArCl}$$

$${}^1(\mathrm{D}\cdot\mathrm{ArCl}) \xrightarrow{k_4} \text{products}$$

Scheme II leads to eq 1 and 2 for the dependence of the fluorescence intensity and the reaction quantum yield upon the diene concentration. In these equations ${}^1\tau$ is the singlet lifetime, k_1^{-1}.

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

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

According to eq 1 and 2, the quantity $k_2{}^1\tau$ can be determined in two different ways, from the slope of the Stern–Volmer plot for fluorescence quenching ($k_2{}^1\tau = K_{SV}$) and from the intercept and slope of a plot of ϕ_r^{-1} vs. $[\mathrm{D}]^{-1}$ ($k_2{}^1\tau$ = intercept/slope = P). A test of the mechanism is the consistency between K_{SV} and P.

Table I gives the experimental results for systems where the aryl chloride absorbs the incident radiation. Quantum yields of reactions were calculated by the logarithmic method,[9] eq 3, where $[M_0]$ and $[M]$ are the concentrations

$$\phi_r = ([M_0] \ln (M_0/M))/I_0t \qquad (3)$$

of substrate at the beginning and end of photolysis, and I_0t is the total photon flux absorbed by the solution. Excellent agreement between K_{SV} and P is observed, consistent with Scheme II. This is true in both polar (CH_3OH, CH_3CN) and nonpolar (C_6H_{12}) media.

We contrast these results with those obtained with aliphatic amines.[1] In those experiments, the lack of concordance between K_{SV} and P was a major factor in rejecting Scheme II (D = amine) as a possible reaction mechanism and selecting the more complicated Scheme I instead. Scheme II is a much simplified version of the mechanism proposed by Smothers et al.[2] for the 9,10-dichloroanthracene/2,5-dimethyl-2,4-hexadiene system.

Conditions were also found under which essentially all the light was absorbed by the diene. This allowed us to test whether interaction between the excited diene and the ground-state aryl chloride could lead to chemistry, e.g., according to Scheme III. Then the dependence of ϕ_r upon

Scheme III

$$\mathrm{D} \xrightarrow{h\nu} \mathrm{D}^*$$

$$\mathrm{D}^* \xrightarrow{k_5} \mathrm{D}$$

$$\mathrm{ArCl} + \mathrm{D}^* \xrightarrow{k_6} (\mathrm{D}\cdot\mathrm{ArCl})^*$$

$$(\mathrm{D}\cdot\mathrm{ArCl})^* \xrightarrow{k_7} \mathrm{D} + \mathrm{ArCl}$$

$$(\mathrm{D}\cdot\mathrm{ArCl})^* \xrightarrow{k_8} \text{products}$$

[ArCl] is given by eq 4. Equation 4 represents an ap-

$$\frac{1}{\phi_r} = \left(1 + \frac{k_7}{k_8}\right)\left(1 + \frac{k_5}{k_6[\mathrm{ArCl}]}\right) \qquad (4)$$

---

(6) Yang, N. C.; Libman, J.; Savitsky, M. F. *J. Am. Chem. Soc.* **1972**, *94*, 9226. Yang, N. C.; Neywick, C. V.; Srinivasachar, K. *Tetrahedron Lett.* **1975**, 4313.

(7) Yang, N. C.; Srinivasachar, K.; Kim, B.; Libman, J. *J. Am. Chem. Soc.* **1975**, *97*, 5006. Cf.: Yang, N. C.; Yates, R. L.; Masnovi, J.; Shold, D. M.; Chiang, W. *Pure Appl. Chem.* **1979**, *51*, 173.

(8) Ohashi, M.; Tsujimoto, K.; Seki, K. *J. Chem. Soc., Chem. Commun.* **1973**, 384.

(9) Bunce, N. J. *J. Photochem.* **1981**, *15*, 1.

proximation, in that the concentration of ArCl is assumed to be constant, whereas in reality the halide is consumed in the reaction. Conversions of ArCl were therefore kept low.

At 254 nm, 1-chloronaphthalene has ϵ 1900 in methanol, while 2,5-dimethyl-2,4-hexadiene has ϵ 15 000. Suitable adjustment of the concentrations allowed almost all the light to be absorbed by the diene. From the plot of ϕ_r^{-1} vs. $[\mathrm{NpCl}]^{-1}$, the parameter P' ($= k_6/k_5$) was determined to be 360 M^{-1}; this compares with $P = 25$ M^{-1} for the corresponding reaction where 1-chloronaphthalene absorbed the light. Thus, 1-chloronaphthalene is a much more efficient quencher of the reactive excited state of 2,5-dimethyl-2,4-hexadiene than vice versa. If this result is a general one for aryl chlorides and dienes, it becomes clear that the reactions previously studied in the chlorobiphenyl/diene series[3,5] are very complicated systems in which both the halide and the diene absorb light competitively and where each substrate quenches the excited state of the other although with different efficiencies. This makes difficult the interpretation of the results previously[3-5] obtained with such systems.

Photolysis with Arylamines

As mentioned previously,[1] a long-term aim of this work is to explore possible methods for destroying aryl halides photochemically. Alkylamines are unsatisfactory in that the light has to be absorbed by the aromatic halide in order for photodecomposition to ensue; if the halide were present in low concentrations, little light would be absorbed. The finding that photochemistry can result whichever of the partners absorbs light in the halide/diene series suggested that arylamines and aryl halides might prove to be a suitable combination. Our hope was to find systems in which amines would absorb visible light and sensitize the decomposition of the halide. If such systems could be demonstrated to work in homogeneous solution, the final step would be to immobilize the arylamine by attachment to a polymer.

We first studied *N*,*N*-dimethylaniline/chlorinated biphenyl systems, because this amine had already been shown to sensitize the photodecomposition of chlorobenzene,[10] bromobenzene,[11] and dihaloanthracenes.[12] Somewhat related is the action of *N*,*N*-diethylaniline in sensitizing the decomposition of DDT.[13] In all these cases, the results were interpreted in terms of an initial electron transfer from the amine to the halide. The work on dihaloanthracenes[12] differs from the other studies in that the aryl halide was the partner initially excited; in the halobenzene experiments[10,11] light was absorbed by the *N*,*N*-dimethylaniline (DMA), and this was the strategy adopted in our experiments also.

As expected, DMA was able to sensitize the photodecomposition of some representative chlorobiphenyls, with the dechlorinated compound a major product in each case. For 4-chlorobiphenyl, which was studied in a little detail, the quantum yields of reaction were much larger in methanol than in cyclohexane, consistent with a mechanism involving electron transfer. In order to take account of the consumption of the halide substrate, we obtained values of ϕ_r as a function of conversion, and double-reciprocal plots were made of $(\phi_r)_0$, the initial quantum yield, and the initial 4-chlorobiphenyl concentration (see Experimental Section). Fairly comparable parameters were obtained from other experiments where the change in [ArCl] was neglected.

Table II

10^3[DMA], M	$10^3[2,2',5,5'$-$\mathrm{Cl_4Ph_2}]$, M	ϕ_r
5.70	1.05	0.53[a]
5.70	2.10	0.53[a]
5.70	3.78	0.57[a]
5.70	5.25	0.45[a]
5.50	2.08	0.51[b]

[a] Duplicate solutions; ϕ_r evaluated by the "log" method. [b] Time study (cf. ref 9); six solutions in the set; evaluated by the "log" method.

In every case studied, the parameters P' = intercept/slope = k_6/k_5, according to Scheme III, was found to be larger than K_{SV}, the quenching constant for the aryl halide quenching the fluorescence of DMA. This suggests that the chemistry taking place in this system does not occur exclusively from the singlet state. The case of 2,2′,5,5′-tetrachlorobiphenyl/DMA was unusual in that the quantum yield of reaction appeared to be independent of the halide concentration over the concentration range studied. However, the involvement of DMA was shown by the large increase in ϕ_r in this system compared with 2,2′,5,5′-tetrachlorobiphenyl in the absence of amine.

Attempts were now made to use arylamines which would have longer wavelength absorption. DMA absorbs at $\lambda <$ 350 nm, while *N*-ethylcarbazole has absorption in the range $\lambda \approx$ 350 nm, and acridine absorbs out into the visible. These experiments were unsuccessful; decomposition of the halides was extremely slow and could be rationalized in terms of the small amount of direct photolysis of the halide. Correspondingly, the halides failed to quench the fluorescence of these amines.

We conclude that as the absorption wavelength of the amine increases, there becomes insufficient energy for electron transfer to the halide to occur. For a given halide acceptor, and ignoring solvation, the energy of electron transfer from the amine to the halide will be related to a term (IE − $h\nu$), where IE is the ionization energy of the amine and $h\nu$ the excitation energy. For the three amines studied here, ionization energies are all in the range 700–800 kJ mol^{-1} with acridine actually the largest of the three, while the excitation energy changes from ~430 (DMA) to <300 kJ mol^{-1} (acridine). Thus the energy required for electron transfer to the same halide increases by at least 150 kJ mol^{-1} through the series DMA, *N*-ethylcarbazole, acridine. This particular approach to the photolytic destruction of halides such as PCB's was therefore abandoned.

Experimental Section

The photolysis equipment was a Rayonet Model RPR photoreactor equipped with 16 RPR 2537 lamps for photolysis at 254 nm and a Rayonet Model RUL photoreactor equipped with eight RUL 300 lamps for photolysis at 300 nm. Photolyses at 254 nm were carried out in quartz ampules of 8 mm o.d.; these were connected to Pyrex by a graded seal in order to allow evacuation and sealing on the vacuum line. Pyrex ampules of 8 mm o.d. were used for irradiation at 300 nm.

Photolysis of Aryl Chlorides with Dienes. These experiments were carried out in the manner described previously for aryl chlorides and alkylamines[1]; all were carried out at 300 nm except for the reaction of 1-chloronaphthalene with 2,5-dimethyl-2,4-hexadiene when the latter was at high concentration (254 nm).

---

(10) Pac, C.; Tosa, T.; Sakurai, H. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 1169.

(11) Grodowski, M.; Latowski, T. *Tetrahedron* **1974**, *30*, 767.

(12) Soloveichik, O. M.; Ivanov, V. L.; and Kuz'min, M. G. *J. Org. Chem. USSR (Engl Transl.)* **1976**, *12*, 860.

(13) Miller, L. L.; Narang, R. S. *Science* **1970**, *169*, 368.

Table III

10^3[DMA], M	10^3[2,4,6-Cl_3Ph_2], M	ϕ_r
4.56	5.24	0.16[a]
4.56	3.50	0.12[a]
4.56	1.75	0.10[a]
4.56	0.87	0.057[a]
5.5	2.01	0.22

[a] Slope and intercept obtained from plot of ϕ_r^{-1} vs. $[ArCl]^{-1}$. The slope[a] for these four numbers is 0.011 M, and the intercept is 4.7.

Table IV

10^3[4-$ClPh_2$], M	ϕ_r[a]	10^3[4-$ClPh_2$], M	ϕ_r[a]
5.90	0.28	2.36	0.15
4.02	0.21	1.18	0.092

[a] Slope from plot of ϕ_r^{-1} vs. $[ArCl]^{-1}$. Slope = 1.5×10^{-3} M; intercept = 2.2.

Photochemistry of Aryl Chloride/*N,N*-Dimethylaniline Systems. For the fluorescence quenching experiments, the concentration of the chloride was kept very low so that the DMA would absorb the light; consequently, the amount of quenching was always small, and the data were somewhat irreproducible from run to run. The following quenching constants (M^{-1}) were obtained: 4-chlorobiphenyl/DMA/cyclohexane, 36, 32; 4-chlorobiphenyl/DMA/methanol, 40, 61; 2,4,6-trichlorobiphenyl/DMA/cyclohexane, 31; 2,4,6-trichlorobiphenyl/DMA/methanol, 60, 97; 2,2′,5,5′-tetrachlorobiphenyl/DMA/cyclohexane, 31; 2,2′,5,5′-tetrachlorobiphenyl/DMA/methanol, 35, 62. No quenching was observed for any of these halides with *N*-ethylcarbazole or with acridine.

2,2′,5,5′-Tetrachlorobiphenyl/DMA/Methanol. The results shown in Table II were obtained.

2,4,6-Trichlorobiphenyl/DMA/Methanol. The experiments indicated in Table III were all done in duplicate, except for the last one which was a time study (eight solutions altogether). All ϕ_r values were evaluated by the "log" method.

4-Chlorobiphenyl/DMA/Methanol. The DMA concentration was 5.5×10^{-3} M throughout. All ϕ_r values were obtained by extrapolating back to $t = 0$ from a series of eight ampules each (Table IV).

Table V

10^3[DMA], M	10^3[4-$ClPh_2$], M	ϕ_r[a]
5.95	1.23	0.0040[b]
5.95	3.69	0.0086[b]
5.95	6.14	0.0124[b]
4.95	2.08	0.0091[c]
4.95	5.20	0.0131[c]
5.4	3.77	0.0130[c]
5.4	5.20	0.0165[c]
5.4	1.05	0.0041[c]

[a] Slope and intercept obtained from plot of ϕ_r^{-1} vs. $[ArCl]^{-1}$. [b] Slope[a] = 0.28 M^{-1}; intercept = 36. [c] Slope[a] = 0.21 M^{-1}; intercept = 30.

4-Chlorobiphenyl/DMA/Cyclohexane. The first series of experiments were duplicate analyses and were not extrapolated to time zero. The second series were all extrapolated to $t = 0$ from a series of eight ampules (Table V).

The experiments with 4-chlorobiphenyl were also analyzed by a different method, but with similar results. From Scheme III and on application of the steady-state approximation to ^1D and to $^1(D\cdot ArCl)$, eq 5 is obtained. Integration affords

$$\frac{-d[ArCl]}{dt} = \left(\frac{k_8}{k_7 + k_8}\right)\left(\frac{k_6[ArCl]}{k_5 + k_6[ArCl]}\right)I_{abs} \qquad (5)$$

$$\Delta[ArCl] + \ln([ArCl]_0/[ArCl])/K_{SV} = (k_8/(k_7 + k_8))I_{abs}t \qquad (6)$$

Calling the left-hand side of this equation f(A), a plot of f(A) vs. I_0t gives the slope as $k_8/(k_7 + k_8)$. The value of $(\phi_r)_0$ corresponding to $[ArCl]_0$ can be obtained by substituting back into an equation analogous to eq 4. In practice this method proved more cumbersome and no more effective than the extrapolation of ϕ_r itself.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for financial support.

Registry No. DMA, 121-69-7; DMH, 764-13-6; *cis*-1,3-pentadiene, 1574-41-0; *trans*-1,3-pentadiene, 2004-70-8; 4-chlorobiphenyl, 2051-62-9; 2,4,6-trichlorobiphenyl, 35693-92-6; 2,2′,5,5′-tetrachlorobiphenyl, 35693-99-3; 1-chloronapthalene, 90-13-1.

Notes

Rates of Acid-Catalyzed Geometric Isomerization of Some Compounds Containing a Carbon–Nitrogen Double Bond

James Elver Johnson,* Nancy McPeters Silk,[1] and Mohammed Arfan

Department of Chemistry, Texas Woman's University, Denton, Texas 76204

Received October 19, 1981

We recently reported on the mechanism of the hydrogen chloride catalyzed *E* to *Z* isomerization of *O*-methylbenzohydroximoyl chloride (Scheme I, 1 → 2).[2] Two mechanisms were considered for the isomerization: (a) rotation about the carbon–nitrogen double bond of the conjugate acid of 1 and (b) nucleophilic attack by chloride ion on the conjugate acid of 1 (nucleophilic catalysis). Tracer experiments with $^{36}Cl^-$ showed conclusively that the isomerization of 1 proceeds by nucleophilic catalysis (Scheme I). It was also shown in this work that para substitutents have little effect on the rate of the hydrogen chloride catalyzed isomerization of 1 ($\rho = -0.66$ with σ). The low substituent effect was rationalized in terms of offsetting ρ values for the protonation of 1 ($+\rho$) and the nucleophilic attack of chloride ion on the conjugate acid of 1 ($-\rho$).

The present kinetic study was carried out to determine the effect of para substituents on the rate of hydrogen

---

(1) Taken in part from the M.S. Thesis of N.M.S., Texas Woman's University, May 1978.

(2) Johnson, J. E.; Silk, N. M.; Nalley, E. A.; Arfan, M. *J. Org. Chem.* 1981, *46*, 546.