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# Kinetics and mechanism of the dehydrohalogenation of Ar<sub>2</sub>CHCX<sub>3</sub> and Ar<sub>2</sub>CHCHX<sub>2</sub> by strong N-bases

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#### Abstract

The kinetics and mechanism of the elimination reactions of 1,1,1-trifluoro-, 1,1,1-trichloro-, 1,1,1-tribromo-, 1,1-dichloroand 1,1-dibromo-2,2-bis(4-nitrophenyl)ethanes and two strong N-bases: 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) and 7methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD) are discussed. © 1999 Elsevier Science B.V. All rights reserved.

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### 1. Introduction

In the last years very strong N-bases with small nucleophilicity were synthesized and used for the deprotonation reactions of C-H and N-H acids. Amidines (1,8-diazabicyclo[5.4.0]undec-7-ene, DBU, and 1,5-diazabicyclo[4.3.0]non-5-ene, DBN [1]), guanidines (tetramethylguanidine, TMG [1], 1,5,7-triazabicyclo[4.4.0]dec-5-ene, TBD [2], 7methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene, MTBD [3], and pentaisopropylguanidine [4]), proton sponges (1,8-bis(dimethylamino)naphtalene [5-7] and 1,2bis(dimethylaminomethyl)benzene [8]), cryptands (cryptand 111 [9]) and so called Schwesinger bases (phosphazene base P<sub>1</sub>-<sup>t</sup>Bu, phosphazene base P<sub>2</sub>-Et and phosphazene base  $P_4$ -<sup>t</sup>Bu ( $P_4$ -<sup>t</sup>Bu)) belong to such very strong N-bases [10–13].

In previous papers some strong N-bases (TMG and

DBU) were also used for kinetics investigations (isotope effect) of the dehydrohalogenation reactions from various halogenocompounds [2, 14–19]. The results obtained in the case of 1,1,1-trifluoro-2,2-bis(4-nitrophenyl)ethane have demonstrated that the multistep mechanism is realized. They indicate that E1cB mechanism in acetonitrile as a solvent and an E2H or mixed E1cB–E2H mechanism in less polar solvents such as tetrahydrofuran and hexane takes place (Scheme 1). The same results were reported for 1,1,1-trichloro- and 1,1-dichloro-2,2-bis(4-nitrophenyl)ethane promoted by DBN in a series of aprotic solvents [14, 19].

In this paper we studied the mechanism of the dehydrohalogenation reaction of five halogeno-2,2-bis(4nitrophenyl)ethanes (1,1,1-trifluoro-, 1,1,1-trichloro-, 1,1,1-tribromo-, 1,1-dichloro- and 1,1-dibromo-2,2bis(4-nitrophenyl)ethane) by N-bases with guanidine-like character. As N-bases we used two, TBD and MTBD (Scheme 2).

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E1cB mechanism



X = H, Cl or Br

## E2H mechanism

Scheme 1.



Ar<sub>2</sub>CHCF<sub>3</sub>



### 2. Experimental

1,1,1-Trifluoro-2,2-bis(4-nitrophenyl)ethane (Ar<sub>2</sub>CHCF<sub>3</sub>), 1,1,1-trichloro-2,2-bis(4-nitrophenyl)ethane (Ar<sub>2</sub>CHCCl<sub>3</sub>), and 1,1-dichloro-2,2-bis(4-nitrophenyl)ethane (Ar<sub>2</sub>CHCHCl<sub>2</sub>) were prepared according to the previously described procedures [19-21], using as substrates corresponding haloaceto-phenones.

Generally, syntheses of 1,1,1-tribromo-2,2-bis(4nitrophenyl)ethane (Ar<sub>2</sub>CHCBr<sub>3</sub>) and 1,1-dibromo-2,2-bis(4-nitrophenyl)ethane (Ar<sub>2</sub>CHCHBr<sub>2</sub>) were carried out by mixing tri- or di-bromoacetic aldehydes and benzene in sulfuric acid. A typical procedure was described for the well-known pesticide DDT [22]. Then the obtained tri- and di-bromodiphenylethanes analogues were nitrated by nitric acid at  $-30^{\circ}$ C following the procedure given in ref. [23]. MTBD and TBD were purchased from Aldrich and used without any purification.

#### 2.1. Kinetic measurements

The kinetic runs were carried out using a stoppedflow spectrophotometer (Applied Photophysics) with the cell block thermostated to  $\pm 0.1^{\circ}$ C. The kinetic runs were completed under pseudo-first-order conditions with large excess of the base concentration. The observed rate constants were calculated from the traces of absorbance versus time. The spectrophotometric measurements were carried out at 320 nm. The concentration of haloethanes was  $5 \times 10^{-5}$  M.

The observed rate constant,  $k_{obs}$ , depends on the base concentration and is given by the equation:  $k_{obs} = k[B]$ , where k is the rate constant for the elimination reaction and [B] is the initial base

Table 1 The charge distribution on  $C_{\alpha}$ ,  $C_{\beta}$ ,  $H_{\beta}$  calculated by AM1 (Hyper Chem 3.0) semi-empirical method

Compound	Charge on $C_{\alpha}$	Charge on $C_{\boldsymbol{\beta}}$	Charge on $H_{\boldsymbol{\beta}}$
Ar <sub>2</sub> CHCF <sub>3</sub>	0.418	$\begin{array}{r} - \ 0.063 \\ - \ 0.038 \\ - \ 0.018 \\ - \ 0.017 \\ - \ 0.029 \end{array}$	0.142
Ar <sub>2</sub> CHCCl <sub>3</sub>	0.138		0.131
Ar <sub>2</sub> CHCBr <sub>3</sub>	- 0.274		0.121
r <sub>2</sub> CHCHCl <sub>2</sub>	- 0.251		0.127
r <sub>2</sub> CHCHBr <sub>2</sub>	- 0.118		0.128

concentration. The rate constants for forward (k) reaction were calculated by linear least-squares fit of the variation of  $k_{obs}$  versus base concentration. The activation parameters were calculated by linear least-squares fit of lnk versus 1/T.

#### 3. Results and discussion

TBD and MTBD molecules in acetonitrile are very strong N-bases and their p $K_a$  values are 24.97  $\pm$  0.05 and 24.70  $\pm$  0.05, respectively [12].

The type and quantity of halogen atoms at the  $C_{\alpha}$ atom determines the electronegativity of the  $-CX_3$ group and defines the acidity of  $C_{\beta}$ -H bonds. The electronegativity values for CF<sub>3</sub>, CCl<sub>3</sub>, CBr<sub>3</sub>, CHCl<sub>2</sub>, CHBr<sub>2</sub> groups are 3.29, 2.79, 2.57, 2.63, 2.45, respectively [24].

The values of steric effect described by the Taft equation ( $E_s$ ) for the following substituents, CF<sub>3</sub>, CCl<sub>3</sub>, CBr<sub>3</sub>, CHCl<sub>2</sub>, CHBr<sub>2</sub>, are -1.16, -2.06, -2.43, -1.54, -1.81, respectively [25].

The influence of halo-substituents on charge distribution of the studied molecules was also calculated by semi-empirical method AM1 (Hyper Chem 3.0), and the obtained results are collected in Table 1. The data in this table demonstrate that with increasing electronegativity and quantity of halogen atoms at the  $C_{\alpha}$ atom there is an increase in positive charge on the  $C_{\alpha}$ atom and  $H_{\beta}$ -atom, but simultaneously a decrease in the positive charge on the  $C_{\beta}$ -atom is observed.

All the studied dehydrohalogenation reactions of five halogeno-2,2-bis(4-nitrophenyl)ethanes with TBD and MTBD lead to corresponding halogeno-2,2-bis(4-nitrophenyl)ethenes (Scheme 3).

Kinetic parameters for all these reactions have been calculated and are shown in Tables 2–5.

TBD, in comparison with MTBD, is the more efficient elimination factor because of its basicity. At 25°C the relationship of calculated rate constants for studied reactions between TBD and the followreagents, Ar<sub>2</sub>CHCF<sub>3</sub>:Ar<sub>2</sub>CHCCl<sub>3</sub>:Ar<sub>2</sub>CHCBr<sub>3</sub>: ing Ar<sub>2</sub>CHCHBr<sub>2</sub>:Ar<sub>2</sub>CHCHCl<sub>2</sub>, equals 13:1:6:6:1, while for the reaction with MTBD the relationship is 60:1:3:3:1. For the studied arrangements the large differences of the rate constants values are connected with the differences of the  $\beta$ -hydrogen atom acidity as well as with the character of the leaving halogen atoms. The compound  $Ar_2CHCF_3$  has the highest acidity and a poor leaving group (fluoride ion), whereas Ar<sub>2</sub>CHCBr<sub>3</sub> has a good leaving group (bromide ion) and the lowest acidity in comparison with the other studied trihalogeno-dinitrophenylethanes. A similar observation for corresponding Ar<sub>2</sub>CHCHCl<sub>2</sub> and Ar<sub>2</sub>CHCHBr<sub>2</sub> dihalogenocompounds is found.

All the investigated reactions could be divided into two groups considering their rate constants and reaction parameter values. Reactions between  $Ar_2CHCF_3$ and N-bases belong to the first group, and the other described reactions to the second one. The values of the rate constants for the first group are higher than for the second one. The described arrangements are characterized by difference in entropy–enthalpy



Scheme 3.

	$k_{\rm obs}~({\rm s}^{-1})$	$k_{\rm obs}~({\rm s}^{-1})$				
Temp. (°C)	0.001 M	0.002 M	0.003 M	0.004 M	0.005 M	$k (M^{-1} s^{-1})$
Ar <sub>2</sub> CHCF <sub>3</sub>						
5	0.09	0.30	0.50	0.79	1.03	$237 \pm 9$
15	0.72	1.25	1.74	2.47	3.08	$594 \pm 24$
25	1.64	3.01	4.63	6.01	7.82	$1536 \pm 42$
35	4.03	8.35	12.51	16.51	20.34	$4078 \pm 56$
45	7.52	15.99	23.77	30.49	38.49	$7640 \pm 161$
Ar <sub>2</sub> CHCCl <sub>3</sub>						
5	0.03	0.07	0.10	0.14	0.18	$37 \pm 1$
15	0.06	0.13	0.26	0.34	0.43	$95 \pm 5$
25	0.27	0.38	0.46	0.61	0.75	$120 \pm 5$
35	0.31	0.75	1.02	1.53	1.83	$382 \pm 20$
45	0.39	1.05	1.83	2.51	3.34	$736 \pm 16$
Ar <sub>2</sub> CHCBr <sub>3</sub>						
5	0.47	0.91	1.32	1.75	2.35	$460 \pm 20$
15	0.61	1.21	1.82	2.34	3.01	$593 \pm 11$
25	0.83	1.64	2.35	3.21	3.97	$785 \pm 11$
35	1.05	1.85	2.89	3.85	4.75	$940 \pm 20$
45	1.20	2.45	3.45	4.51	5.56	$1080 \pm 23$
Ar <sub>2</sub> CHCHBr <sub>2</sub>						
5	0.39	0.78	1.18	1.58	1.97	396 ± 18
15	0.54	1.19	1.79	2.21	2.85	$564 \pm 13$
25	0.72	1.43	2.10	2.85	3.54	$706 \pm 15$
35	0.89	1.65	2.39	3.16	4.01	$775 \pm 18$
45	1.01	1.98	2.82	3.82	4.75	$932 \pm 17$
Ar <sub>2</sub> CHCHCl <sub>2</sub>						
5	0.01	0.04	0.08	0.11	0.14	$33 \pm 2$
15	0.03	0.10	0.19	0.27	0.35	81 ± 3
25	0.17	0.29	0.42	0.52	0.64	$117 \pm 5$
35	0.21	0.47	0.74	1.0	1.25	$261 \pm 13$
45	0.35	1.05	1.65	2.13	2.87	612 ± 19

Table 2 Kinetics parameters (  $\pm$  standard deviation) for reaction between  $Ar_2CHCX_3$  and TBD in acetonitrile

distribution. The difference in  $\Delta G^{\neq}$  values for reactions between Ar<sub>2</sub>CHCF<sub>3</sub> and MTBD or TBD is 5 kJ mol<sup>-1</sup>, while for the other reactions this difference equals 9 kJ mol<sup>-1</sup>. The difference in  $\Delta G^{\neq}$  values for these two groups of reactions demonstrates the different structures of the transition states. The reac-

tions between  $Ar_2CHCF_3$  and N-bases are led by E1cB mechanism, while the other reactions by E2H mechanism. The course of reaction and the structures of the transition states are presented in Scheme 1.

The fluoride anion abstraction from carbanion formated by alkane in the fast reversible step is the

Table 3 Activation parameters (  $\pm$  standard deviation) for reaction between Ar<sub>2</sub>CHCX<sub>3</sub> and TBD in acetonitrile

Compound	$\Delta H^{\neq}$ (kJ mol <sup>-1</sup> )	$\Delta S^{\neq} (\mathrm{J} \ \mathrm{mol}^{-1} \ \mathrm{deg}^{-1})$	$\Delta G^{\neq} (\mathrm{kJ} \mathrm{mol}^{-1})$	
Ar <sub>2</sub> CHCF <sub>3</sub>	62.9 ± 1.9	$27.1 \pm 6.2$	54.8 ± 1.9	
Ar <sub>2</sub> CHCCl <sub>3</sub>	$51.7 \pm 5.6$	$-29.0 \pm 18.8$	$60.3 \pm 5.6$	
Ar <sub>2</sub> CHCBr <sub>3</sub>	$13.6 \pm 1.0$	$-144.6 \pm 3.2$	$56.7 \pm 1.0$	
Ar <sub>2</sub> CHCHBr <sub>2</sub>	$12.6 \pm 1.7$	$-148.9 \pm 5.7$	$57.0 \pm 1.7$	
Ar <sub>2</sub> CHCHCl <sub>2</sub>	$49.0\pm2.0$	$-39.3 \pm 13.6$	$60.7 \pm 4.0$	

	Concentratio	Concentration				
Temp. (°C)	0.001 M	0.002 M	0.003 M	0.004 M	0.005 M	$k (M^{-1} s^{-1})$
Ar <sub>2</sub> CHCF <sub>3</sub>						
5	0.007	0.013	0.019	0.026	0.032	$6.3 \pm 0.1$
15	0.025	0.049	0.078	0.110	0.120	$25.1 \pm 2.0$
25	0.3	0.51	0.72	1.0	1.25	$239.0 \pm 8.0$
35	2.1	3.68	5.55	7.29	9.31	$1803.0 \pm 41$
45	3.64	7.64	11.42	15.41	19.22	$3893.0 \pm 20$
Ar <sub>2</sub> CHCCl <sub>3</sub>						
5	0.001	0.002	0.004	0.005	0.007	$1.5 \pm 0.1$
15	0.003	0.005	0.009	0.013	0.016	$3.4 \pm 0.2$
25	0.008	0.012	0.017	0.020	0.024	$4.6 \pm 0.5$
35	0.010	0.018	0.030	0.039	0.049	$9.9 \pm 0.3$
45	0.021	0.038	0.050	0.062	0.076	$13.4 \pm 0.5$
Ar <sub>2</sub> CHCBr <sub>3</sub>						
5	0.005	0.008	0.012	0.017	0.025	$4.9 \pm 0.6$
15	0.009	0.015	0.025	0.032	0.038	$7.5 \pm 0.4$
25	0.012	0.026	0.035	0.048	0.064	$12.6 \pm 0.6$
35	0.029	0.038	0.075	0.099	0.113	$22.9 \pm 2.4$
45	0.034	0.067	0.096	0.134	0.160	$31.9 \pm 0.9$
Ar <sub>2</sub> CHCHBr <sub>2</sub>						
5	0.003	0.007	0.012	0.017	0.021	$4.6 \pm 0.7$
15	0.006	0.013	0.019	0.025	0.031	$6.2 \pm 0.5$
25	0.008	0.019	0.031	0.042	0.053	$11.3 \pm 0.9$
35	0.020	0.040	0.060	0.086	0.097	$20.0 \pm 1.3$
45	0.028	0.055	0.085	0.112	0.139	$27.9 \pm 1.5$
Ar <sub>2</sub> CHCHCl <sub>2</sub>						
5	0.001	0.002	0.004	0.005	0.006	$1.3 \pm 0.1$
15	0.002	0.004	0.006	0.008	0.011	$2.2 \pm 0.1$
25	0.004	0.009	0.012	0.017	0.020	$4.0 \pm 0.2$
35	0.006	0.014	0.025	0.032	0.039	$8.4 \pm 0.4$
45	0.012	0.025	0.037	0.050	0.062	$12.5 \pm 0.2$

Table 4			
Kinetics parameters ( $\pm$ standar	d deviation) for reaction	between Ar2CHCX3 an	nd MTBD in acetonitrile

rate determining step. The transition state for this slow step is product alkene-like. The HCl or HBr elimination for other arrangements is realized by concerted E2H mechanism. This transition state is strongly polarized.

For the studied reactions the value of activation

enthalpy  $\Delta H^{\neq}$  is determined by the enthalpy–entropy coupling and charge distribution in the transition state.

In conclusion, bases such as MTBD and TBD, demonstrating good basicity and small nucleophilicity, may be applicable to elimination processes and are more efficacious than other weaker N-bases.

Table 5 Activation parameters ( $\pm$  standard deviation) for reaction between Ar<sub>2</sub>CHCX<sub>3</sub> and MTBD in acetonitrile

Compound	$\Delta H^{\neq} (\text{kJ mol}^{-1})$	$\Delta S^{\neq}$ (J mol <sup>-1</sup> deg <sup>-1</sup> )	$\Delta G^{\neq}$ (kJ mol <sup>-1</sup> )	
Ar <sub>2</sub> CHCF <sub>3</sub>	$123.9 \pm 9.4$	215.0 ± 31.7	$59.7 \pm 9.4$	
Ar <sub>2</sub> CHCCl <sub>3</sub>	$37.8 \pm 3.3$	$-104.8 \pm 11.0$	$69.0 \pm 3.3$	
Ar <sub>2</sub> CHCBr <sub>3</sub>	$33.3 \pm 1.7$	$-111.9 \pm 5.7$	$66.7 \pm 1.7$	
Ar <sub>2</sub> CHCHBr <sub>2</sub>	$32.7 \pm 2.5$	$-115.2 \pm 8.0$	$67.0 \pm 2.5$	
Ar <sub>2</sub> CHCHCl <sub>2</sub>	$40.7 \pm 2.1$	$-96.4 \pm 7.0$	$69.5 \pm 2.1$	

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