

202. The Mechanism of the Acid-catalysed Hydrolysis of 1-Aryl-2,2,2-trifluorodiazooethanes

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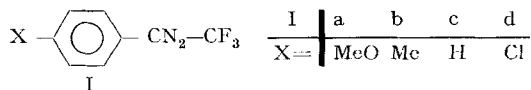
(25. V. 72)

Summary. The rates of the acid-catalysed hydrolysis of a series of 1-aryl-2,2,2-trifluorodiazooethanes Ia–d have been measured in dioxan/water/HClO₄. The results are well correlated with the *Hammett* equation when σ_p substituent constants are used ($\rho_H = -1.74$ and $\rho_D = -1.75$). Kinetic solvent isotope effects, about 2.1, and general acid catalysis indicate that proton transfer is rate-determining (A-S_E2 mechanism). Rate measurements have also been made at pressures up to 1400 atm. The evaluated activation volumes, about $-20 \text{ cm}^3/\text{mole}$, indicate that at least one water molecule is bound in the transition state of protonation. Rate measurements at low water concentrations indicate that no apparent change in mechanism has occurred.

Aliphatic diazo compounds are decomposed in aqueous acidic solutions as follow:



The kinetics and the mechanisms of this reaction have been subject to many studies [1]. Thus the acid-catalysed hydrolysis of primary α -diazocarbonyl compounds ($\text{R} = \text{acyl, aroyl or EtOCO, R}' = \text{H}$) [2] [3] [4] involves fast pre-equilibrium protonation followed by bimolecular rate-determining decomposition of the intermediate diazonium ion (A-2 mechanism; $k_{-p} \gg k_d$). On the other hand, for the corresponding secondary diazo compounds ($\text{R} = \text{acyl or EtOCO, R}' = \text{alkyl}$) [5] [6] protonation is rate-determining (A-S_E2 mechanism; $k_{-p} \ll k_d$). The same mechanism was proved for a series of α -diazo-arylmethane-phosphonates ($\text{R} = \text{aryl, R}' = (\text{EtO})_2\text{PO}$) [7], for diaryl-diazomethanes ($\text{R} = \text{R}' = \text{aryl}$) [1] and for monoaryl-diazomethanes ($\text{R} = \text{aryl, R}' = \text{H}$) [8] [9]. Recently *Jugelt & Berseck* [10] have suggested a borderline A-1/A-S_E2 mechanism for a series of *para* substituted aryl-aroyl-diazomethanes ($\text{R} = \text{aryl, R}' = \text{aroyl}$). Besides, the strongly electron-attracting trifluoromethyl group exhibits the same influence on the reaction mechanism than the carbonyl group. Primary 2,2,2-trifluorodiazooethane ($\text{R} = \text{CF}_3, \text{R}' = \text{H}$) [5] reacts by the A-2 mechanism whereas secondary 1,1,1-trifluoro-2-diazopropane ($\text{R} = \text{CF}_3, \text{R}' = \text{Me}$) [5] reacts by the A-S_E2 mechanism. In order to see if the replacement of the methyl group in 1,1,1-trifluoro-2-diazopropane by the aryl group leads to similar results as for aryl-aroyl-diazomethanes, we have investigated the acid-catalysed hydrolysis of a series of *para* substituted 1-aryl-2,2,2-trifluorodiazooethanes Ia–d.



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Results. – The diazo compounds Ia–d were prepared by treating a suitable α, α, α -trifluoroacetophenone (II) with *p*-toluenesulfonylhydrazine and subsequent alkaline decomposition of the α, α, α -trifluoroacetophenone *p*-toluenesulfonylhydrazone (III)²⁾. The substrates Ia–d were characterized by UV., IR. and NMR. spectroscopy³⁾.

The hydrolyses were performed in dioxan/water with perchloric acid as catalyst and monitored by measuring the decrease of the diazo absorption band at about 266 nm. All rates conformed accurately to a pseudo-first-order rate law.

The acid catalysis of Ic was demonstrated by measurements at different acid concentrations (Table 1), and the second-order rate constant k_2 , given by $k_1 = k_2[\text{H}_3\text{O}^+]$, has a value of $0.127 \text{ M}^{-1}\text{s}^{-1}$. Thus Ic is roughly more reactive than the corresponding phenyl-benzoyl-diazomethane, $k_2 = 0.0022 \text{ M}^{-1}\text{s}^{-1}$ (dioxan/ H_2O 66.6:33.3 v/v, 20.0° , $\mu = 0.10$) [10].

Table 1. *Rate constants of hydrolysis of Ic at various acidities*
(dioxan/ H_2O 60:40 v/v, 25.0° , $\mu = 0.09$)

$[\text{HClO}_4]$	$[\text{NaClO}_4]$	$10^3 k_1 \text{ (s}^{-1}\text{)}$
0.090	–	11.4
0.045	0.045	5.62
0.027	0.063	3.49

The rate constants of the acid-catalysed hydrolysis of Ic were also measured at various temperatures (Table 2), and from the plot of $\log k_2$ against $1/T$ values of $E_a = 14.6 \text{ kcal/mole}$ and $\Delta S^\ddagger = -16 \text{ e.u.}$ were obtained for the activation parameters.

Table 2. *Rate constants of hydrolysis of Ic at various temperatures*
(dioxan/ H_2O 60:40 v/v, $[\text{HClO}_4] = 0.090$)

$T (^\circ\text{K})$	$10^3 k_1 \text{ (s}^{-1}\text{)}$
289.0	5.31
293.0	7.50
298.0	11.40
303.0	17.25

Solvent isotope effects and general acid catalysis. – Rate-determining protonation and general acid catalysis are characterized by solvent isotope effects $k_{\text{H}}/k_{\text{D}} > 1$ whereas pre-equilibrium protonation and specific acid catalysis are associated with solvent isotope effects $k_{\text{H}}/k_{\text{D}} < 1$.

²⁾ Only Ic is described in the literature [11].

³⁾ The ^1H -NMR. spectrum of Ic was also recorded in $\text{SO}_2\text{--HFSO}_3$ at -60° and exhibits a quartet at 5.6 ppm ($J_{\text{H--F}} = 6 \text{ Hz}$) which can be assigned to the 1-aryl-2,2,2-trifluoroethyl-diazonium ion $\text{Ph--CHN}_2^+\text{--CF}_3$ and a singlet at 7.0 ppm due to the phenyl group, the ratio of the integrations being 5:1. With the 2,2,2-trifluoroethyldiazonium ion [12] this is another example of a direct observed stable diazonium ion.

Rate constants of hydrolysis of Ia–d in dioxan/H₂O and in dioxan/D₂O 60:40 v/v are shown in Table 3. The solvent isotope effects of two other trifluoromethyldiazoalcanes are also given in Table 3.

Table 3. Rate constants of hydrolysis of Ia–d in dioxan/H₂O and in dioxan/D₂O 60:40 v/v and solvent isotope effects (25.0°, [HClO₄] = 0.090)

Compound	10 ³ k _H (s ⁻¹)	10 ³ k _D (s ⁻¹)	k _H /k _D	σ _p
Ia (X = MeO)	37.5	17.9	2.09	-0.268
Ib (X = Me)	22.8	11.3	2.02	-0.170
Ic (X = H)	11.4	5.34	2.13	0.000
Id (X = Cl)	5.05	2.43	2.08	+0.227
CF ₃ CN ₂ Me			1.67 [5]	
CF ₃ CN ₂ H			0.25 [5]	

Statistical treatment of the data of table 3 reveals a good agreement with the Hammett equation, $\log k = \log k_0 + \rho\sigma$, when σ_p substituent constants are used. Plots of log k₁ against σ_p for the reactions in light and in heavy water are shown in Fig. 1 and values of ρ_H = -1.74 and ρ_D = -1.75 were obtained for the reaction constant.

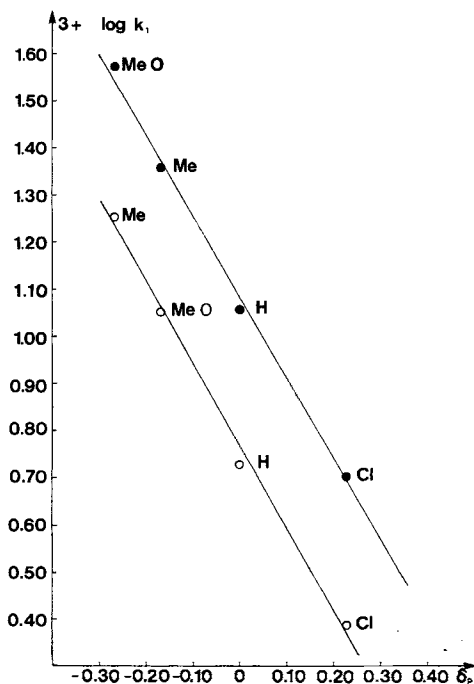


Fig. 1. Correlation of the rate constants for the hydrolysis of Ia–d with the substituent constants σ_p at 25.0° (—●— dioxan/H₂O 60:40 v/v, —○— dioxan/D₂O 60:40 v/v)

Rate constants of hydrolysis of Ic in dichloroacetic acid/dichloroacetate buffers in dioxan/H₂O 60:40 v/v at 25.0° and at constant pH* are shown in Table 4.

Table 4. *Rate constants of hydrolysis of Ic in dichloroacetic acid/dichloroacetate buffers* (dioxan/H₂O 60:40 v/v, 25.0°, $\mu = 0.10$)

[CHCl ₂ COOH]	[CHCl ₂ COONa]	[NaClO ₄]	10 ³ k ₁ (s ⁻¹)
0.200	0.100	—	2.68
0.100	0.050	0.050	1.59
0.060	0.030	0.070	1.12

As the reaction is catalysed by undissociated acid, the first-order rate constant k_1 is given by Equation (1).

$$k_1 = k_2[\text{H}_3\text{O}^+] + k_{\text{HA}}[\text{HA}] \quad (1)$$

A method previously described [8], which takes into account dimerisation of the acid HA and association with its anion A⁻, was used to evaluate the catalytic coefficient k_{HA} . A value of $k_{\text{HA}} = 0.0139 \text{ M}^{-1}\text{s}^{-1}$ was obtained by the method of least mean squares.

Pressure effects. – Rate constants of the acid-catalysed hydrolysis of Ib–d in dioxan/H₂O 60.8:39.2 v/v at 20.0° were measured at pressures up to 1400 atm and are shown in Table 4. Plots of log k_2 against p are shown in Fig. 2.

Table 5. *Rate constants of hydrolysis of Ib–d at various pressures and volumes of activation* (dioxan/H₂O 60.8:39.2 v/v, 20.0°, $[\text{HClO}_4] = 1.11 \cdot 10^{-3} \text{ M}$)

Compound	Ib (X = Me)	Ic (X = H)	Id (X = Cl)
p (atm)	10 ⁵ k ₁ (s ⁻¹)		
1	11.2	6.12	2.56
190	—	6.86	—
295	14.2	7.49	3.17
597	17.8	9.14	3.70
798	19.8	10.5	—
1000	22.2	11.8	4.59
1206	25.3	12.8	—
1418	27.7	13.5	5.36
$\Delta V_p^\ddagger$ (cm ³ /mole)	– 20	– 20	– 17

The effect of the pressure on the rate constant at constant temperature is given by Equation (2):

$$\left(\frac{\partial \ln k_2}{\partial p} \right)_T = - \frac{\Delta V_p^\ddagger}{RT} \quad (2)$$

where $\Delta V_p^\ddagger$ is the volume of activation which represents the volume associated with the activation process, i.e. the difference between the partial molar volumes of the activated complex and the reactants. Equation (2) requires that $\Delta V_p^\ddagger$ is obtained from the slope of the plot of log k_2 against p . As the initial and the transition state have often different compressibilities, the plots of log k_2 against p are seldom linear. There-

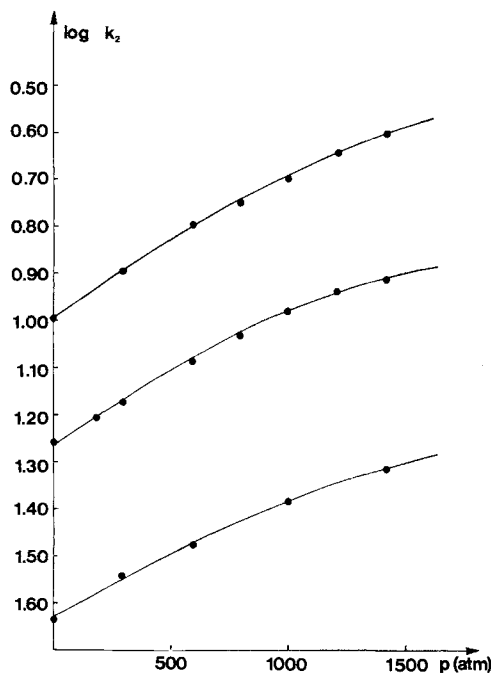


Fig. 2. Correlation of the rate constants for the hydrolysis of Ib–d with the pressures at 20.0° (dioxan/H₂O 60.8:39.2, [HClO₄] = 1.11 · 10^{−3} M)

fore the activation volumes were evaluated at zero pressure. Hyne *et al.* [13] have found that the relation between $\log k_2$ and p is generally best described by the second-order polynomial Equation (3):

$$\log k_2 = b_0 + b_1 p + b_2 p^2 \quad (3)$$

which assumes that $(\partial \Delta V_p^\ddagger / \partial p)$ is independent of pressure, and it was pointed out that generally Equation (3) could be employed up to 2000 atm.

We have fitted the data of Table 5 to Equation (3) and calculated the coefficients of this equation by the method of least mean squares. The volumes of activation at zero pressure (Table 5) were calculated from Equation (4) and are approximately constant, about $-20 \text{ cm}^3/\text{mole}$.

$$\Delta V_0^\ddagger = -2.303 b_1 RT \quad (4)$$

Hydrolysis in dioxan-water mixtures of low water content. – In the solvent range from pure water to dioxan containing small amounts of water (about 2 moles per litre) the changes of the rate constant of the acid-catalysed hydrolyses are relatively small. However, when the water concentration is decreased below about 2 moles/l the changes may become very important. As only A-2 and A-1 have been studied in this solvent range [14], we have investigated an A-S_E2 type of hydrolysis. Because of its relative low reactivity, Id was chosen as substrate. The results are shown in Table 6.

From this table it appears that the second-order rate constant increases continuously as the concentration of water in dioxan is decreased. When $\log k_2$ is reported against $\log [H_2O]$ (Fig. 3) a slightly curved plot is obtained. Interpolation for $[H_2O] = 0.124$ in Fig. 3 gives roughly $k_2 = 1.78 \text{ M}^{-1}\text{s}^{-1}$ in light water and with this value a solvent isotope effect of $k_H/k_D \approx 1.3$ (88% D) is calculated.

Table 6. Rate of constants of hydrolysis of *I d* in dioxan/water mixtures of low water content at 25.0°

$10^3 [HClO_4]$	$[H_2O]$	$10^3 k_1 (\text{s}^{-1})$	$k_2 (\text{M}^{-1} \text{s}^{-1})$
8.09	1.517	0.728	0.090
5.70	1.107	0.745	0.131
5.67	0.945	0.892	0.157
5.43	0.784	1.03	0.190
5.43	0.575	1.44	0.265
6.11	0.304	3.42	0.560
5.60	0.175	6.30	1.13
2.35	0.094	5.89	2.51
3.98	0.124 (D_2O)	5.55	1.40

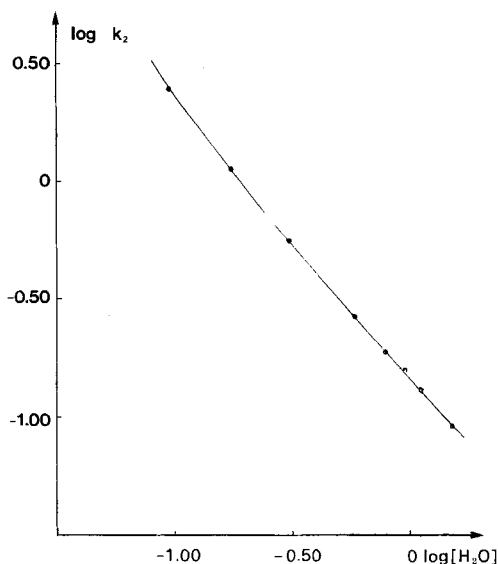


Fig. 3. Correlation of the rate constants for the hydrolysis of *I d* with the water concentrations in dioxan/water mixtures of low water content at 25.0°

Discussion. – A reaction in which a proton transfer occurs in the transition state of the rate-determining step might be expected to proceed more slowly in D_2O than in H_2O and the magnitude of the isotope effect will depend upon the extent of proton transfer in the transition state [15]. From the data of Table 3 it can be seen that the solvent isotope effect is greater than unity and does not vary with increasing electron-withdrawal in the *para* substituent. Thus it can be assumed that protonation is rate-determining ($A-S_E2$ mechanism) and that the degree of proton transfer in the transi-

tion state is practically not affected by substituents in the acid-catalysed hydrolysis of 1-aryl-2,2,2-trifluorodiaoethanes. The catalysis by undissociated dichloroacetic acid, i.e. the general acid catalysis and the rather negative value of the entropy of activation ($\Delta S^\ddagger = -16$ eu) observed for Ic also support the A-S_E2 mechanism.

If the formation of the transition state in the acid-catalysed hydrolysis of Ib-d can be represented by $RR'CN_2 + H_3O^+ \rightarrow (RR'CN_2 \dots H \dots OH_2)^\ddagger$ a molecule of water is lost by conversion of a *van der Waals* bond into a partial valence bond. *Whalley* [16] has calculated that this change should be accompanied by loss of volume of very roughly 12 cm³/mole. It seems therefore likely that the loss of volume observed in our reactions, which is almost the volume of a water molecule, suggests that the transition state of the rate-determining step contains at least one firmly bound water molecule. Our results can be compared to those obtained in the acid-catalysed hydration of some olefines where protonation is rate-determining, the activation volumes being in the range -13 to -18 cm³/mole [17].

Plots of the logarithms of the rate constants of the acid-catalysed hydrolysis of *para* substituted aryl-aryl-diazomethane and α -diazo-arylmethane-phosphonates against the substituent constants have been found to be linear with slopes $\rho_H = -2.05$, $\rho_D = -2.36$ and $\rho_H = -1.64$, $\rho_D = -1.51$, respectively [7] [10]. These values are comparable to those obtained in the present work, $\rho_H = -1.74$, $\rho_D = -1.75$. As the reaction constant is a measure of the sensitivity of the reaction series to changes in the electron density at the reaction site, the negative value of ρ implies a partial positive charge at the reaction site. The relative high value of ρ confirms that in the transition state of protonation of weak diazoalkane bases proton transfer is far advanced as predicted by the *Hammond* postulate [18]. In other words, the transition state of protonation resembles the diazonium ion.

Our results can be compared to those obtained by *Jugelt & Berseck* [10] for aryl-aryl-diazomethanes. From the variation of the solvent isotope effect they have suggested that the hydrolysis of these diazo compounds may be a borderline reaction between one involving rate-determining C-protonation (A-S_E2 mechanism) and another with fast pre-equilibrium O-protonation (A-1 mechanism)⁴). If this explanation may be correct, we believe that a more probable explanation is a change in the transition state of proton transfer, i.e. in a borderline reaction the substituents in the aryl group have a greater effect on the degree of proton transfer than in a typical A-S_E2 reaction represented by the compounds investigated in the present study.

The hydrolysis rates of Id in presence of perchloric acid as catalyst in dioxan/water mixtures increase rapidly when the amount of water is decreased from about 1.5 mole/l. This indicates that perchloric acid is a much stronger acid in solvent mixtures containing low water concentrations. In other words, at low water concentrations, the concentration of protonated dioxan, which is known to be a stronger acid than the hydronium ion, is increased relative to the concentration of the hydronium ion. However, while the rapid increase of the reaction rate may essentially be due to the increase of the acid strength of perchloric acid, a change in mechanism or more likely a change in the solvation of the intermediate diazonium ion offers an attractive alternative explanation. Thus *Huisgen* [20] has noted that in the reaction

⁴) Recently *Lahti & Kankaanperä* [19] have found A-S_E2 reactions showing k_H/k_D around 0.5.

of diazomethane with benzoic acid in toluene a pre-equilibrium protonation is partially established. Similar results were published by the group of *van der Meerwe* [21]. On the other hand, we have found that neither diazomethane nor diazoethane undergoes H–D exchange in D₂O with perchloric acid as catalyst [22]. Similar observations were made by *Kirmse & Rinkler* [23] in the hydrolysis of diazobutane in MeOD with acetic acid as catalyst. Besides, *Friedman & al.* [24] have studied the influence of solvent on diazoalkane-alkyl diazonium ion equilibria in amine deamination. They have found that as the protonicity of the medium is increased (by addition of acid or change to more protic solvent) deuterium incorporation in the product decreases until none occurs in aqueous solutions. Therefore it may be that at low water concentrations rate-determining protonation competes with pre-equilibrium protonation. Thus with decreasing solvation the intermediate diazonium ion loses nitrogen slower than it can be deprotonated; as the solvation decreases k_{-p} increases relative to k_d . However, at a water concentration of 0.124 M the solvent isotope effect is still larger than unity, $k_H/k_D \approx 1.3$ (88% D), and therefore it can be suggested that protonation is still rate-determining.

The present study was performed during a period spent by the author at the Department of Physical Chemistry of the University of Helsinki. I wish to thank Professor *J. Koskikallio* for his hospitality during this stay and for helpful discussions. The Finnish Minister of Education is acknowledged for a scholarship.

Experimental Part

M.p.'s were obtained from a Dr. *Tottoli* apparatus. UV. spectra were measured on a *Beckman* DK A2 spectrophotometer, IR. spectra on a *Perkin-Elmer* 621 instrument and NMR. spectra on a *Varian* A 60 spectrometer using tetramethylsilane as internal reference ($\delta = 0.00$ ppm).

Syntheses. – α, α, α -trifluoroacetophenones: The procedure described in [25] was used. Slow addition of 0.17 mole (19 g) of trifluoroacetic acid in 50 ml dry ether to the *para* substituted arylmagnesium bromide, prepared from 0.51 mole (12.2 g) magnesium and 0.51 mole of the appropriate aryl bromide in 200 ml dry ether, afforded after one hour at 0° and 15 min at reflux the corresponding α, α, α -trifluoroacetophenone in about 70–80% yield. The IR. spectra (CCl₄) showed bands at about 1720 cm⁻¹ (carbonyl), 1600 and 1500 cm⁻¹ (aromatic) and a series of strong absorbances from 1400 to 1150 cm⁻¹ (CF₃). IIa had b.p. 103–105°/12 Torr, n_D 1.510 (Lit. b.p. 116–117°/16 Torr, n_D 1.5074); IIb had b.p. 76–79°/14 Torr, n_D 1.469 (Lit. b.p. 85–86°/18 Torr, n_D 1.4705); IIc had b.p. 54–56°/12 Torr, n_D 1.461 (Lit. b.p. 60°/17 Torr, n_D 1.4609); IId had b.p. 94–96°/12 Torr, n_D 1.492 (Lit. b.p. 92–93°/12 Torr, n_D 1.4922).

α, α, α -trifluoroacetophenone *p*-toluenesulfonylhydrazone: The liquid carbonyl compound (1 Mol.-equ.) was mixed with one equivalent of *p*-toluenesulfonylhydrazine dissolved in a minimum of ethanol and refluxed for 15 min. After cooling the reaction mixture yielded the white *p*-toluenesulfonylhydrazone which was crystallized from methanol. IIIa had m.p. 124–127°; IIIb had m.p. 129–133°; IIIc had mp. 133–136° (Lit. [11] 134.5–137.5°); IIId had m.p. 151–155°. These materials were deemed sufficiently pure for further reaction.

1-aryl-2,2,2-trifluorodiazethanes: The procedure described by *Closs & Moss* [26] was used. The *p*-toluenesulfonylhydrazone (5 mmoles) was dissolved in 50 ml triethyleneglycol and treated with sodium methoxyde at 60° during 15 min. The resulting red solution was poured into cold water and extracted with pentane. Evaporation of the solvent, chromatography on silica gel (0.05–0.2 mm; CCl₄) and elution with CH₂Cl₂ gave the appropriate deep red diazo compound in about 30% yield and with more than 90% purity as determined by the measured volume of nitrogen liberated when treated with perchloric acid. The spectroscopic data are summarized in Table 7.

Kinetic measurements. – The rates of hydrolysis were measured by following the decrease of the diazo absorption at suitable wavelength. Most experiments were carried out with a *Beckman*

Table 7. *Spectroscopic data of the diazo compounds Ia–d*

Compound	IR. (CCl ₄)	UV. (dioxan)	NMR. (CCl ₄)
	$\nu_{N=N}$	$\lambda_{\max}$ (log ϵ)	
Ia (X = MeO)	2080 cm ⁻¹	269 nm (4.0)	7.05 and 6.85; 3.77
Ib (X = Me)	2087 cm ⁻¹	266 nm (4.2)	7.17 and 6.95; 2.33
Ic (X = H)	2084 cm ⁻¹	265 nm (4.3)	7.08
Id (X = Cl)	2086 cm ⁻¹	266 nm (4.3)	7.35 and 6.98

DU, some with a *Beckman* DK A2 spectrophotometer equipped with a thermostated cell holder and with time scanning. Constant temperature ($\pm 0.1^\circ$) was maintained by circulating water from a thermostat. The temperature of the reaction solution was measured inside of the thermostated cell before and at the end of the run. The first-order rate constants were calculated from the slope of the plots $\log(A_t - A_\infty)$ against t where A_t and A_∞ are the absorbances at time t and at the end of the reaction. The rate constants were averaged over three or more measurements and were reproducible within $\pm 2\%$.

H₂O was distilled over KMnO₄ and NaOH·D₂O contained $> 99.7\%$ D. Dioxan was purified as described in [27]. The mixture dioxan/water was made up by weight. Perchloric acid solutions were prepared from HClO₄ 70% and were titrated. The buffer solutions were prepared as described earlier [8].

Pressure measurements. – The pressure apparatus was similar to that described by *Koskikallio & Whalley* [28]. The reaction was carried out in a 50 ml hypodermic syringe having a tight-fitting glass piston. The syringe was filled with the reaction mixture containing 50 ml thermostated HClO₄ 1.13 10^{-3} M dioxan/H₂O 60:40 v/v and 1 ml of a 10^{-2} M diazoalkane solution in dioxan and placed in the pressure vessel. The pressure was raised to the desired level with a pump and temperature allowed to come to equilibrium. Samples were removed at suitable time intervals through the needle head of a syringe and the absorbance was measured at once. The time for taking a sample and measuring its absorbance was less than 45 s and during this time the reaction did not proceed more than 0.2%. About 9 samples could be removed. The pressure vessel was maintained at $20.0^\circ \pm 0.05^\circ$ in a thermostatically controlled bath. The first-order rate constants were calculated by a least-mean-squares computer program. Except in a very few cases the standard deviations within one run was less than 1%. Two measurements were made at nearly every pressure and the reproducibility was better than $\pm 3\%$.

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203. Utilisation d'ylides du phosphore en chimie des sucres.

XII¹⁾ Dérivés du D-arabino-hexène-1-tétrol-3,4,5,6

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Summary. The preparation of several kinds of derivatives of 1-substituted D-arabino-hex-1-ene-3,4,5,6-tetrols is described. Some of these compounds, having a 'pseudo-formyl' group ($-\text{CH}=\text{CHCN}$, $-\text{CH}=\text{CHSO}_2\text{CH}_3$) are 'pseudo-aldehyde-sugars'. Their ability to react as aldehyde-sugars was examined in light of their ^{13}C -NMR. spectra which provide information on their electron density at C(1) and C(2).

Dans des communications antérieures [2] [3], nous avons examiné l'effet des caractéristiques électroniques et stériques des substituants portés par la double liaison sur les équilibres conformationnels de sucres à insaturation terminale. Indépendamment de leur intérêt comme modèles simples pour l'étude de l'influence encore mal connue des facteurs polaires sur ces équilibres, les sucres vinyliques constituent des intermédiaires de synthèse permettant d'accéder à un grand nombre de groupements fonctionnels [4] [5] [6].

Nous nous proposons dans cette communication de décrire la synthèse et les propriétés d'un certain nombre de ces composés.

Les sulfones **2** et **3** ont été préparées par oxydation d'un mélange des deux isomères géométriques du di-O-isopropylidène-3,4:5,6-méthylthio-1-D-arabino-hexène-1-tétrol-3,4,5,6 (**1**) obtenu par une réaction de Wittig effectuée sur le di-O-isopropylidène-2,3:4,5-aldéhyde-D-arabinose **9** [7] selon une technique que nous avons décrite [4] pour son énantiomère L. Pour cette oxydation, nous avons mis au point une méthode sélective n'affectant pas la double liaison C=C. Nous utilisons une solution de peroxyde d'hydrogène dans l'éther en présence de quantités catalytiques de tétraoxyde d'osmium. Dans ces conditions, les deux sulfones vinyliques **2** et **3** ont pu être isolées par cristallisation fractionnée avec un rendement total de plus de 50%. Ces deux composés sont cristallins mais, alors que le sulfone *cis* est stable, son isomère *trans* s'hydrolyse

¹⁾ XIe communication, v. [1].