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HETEROSUBSTITUTED VINYL CARBANIONS I. KINETIC ACIDITY OF DI- AND TRISUBSTITUTED HALOETHYLENES.

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In saturated systems, the influence of electronegative substituents on the acidity of hydrogen atoms is well-known. It is especially strong in α-position and, for halogen substituents, it decreases in the order (1) :

$$\mathrm{I} \sim \mathrm{Br} > \mathrm{Cl} > \mathrm{F}.$$

In contrast, the influence of halogen on the acidity of hydrogen on vinylic carbon is little studied and difficult to predict. Thus, for cis- and trans-1-chloro-2-fluoroethylene, it was shown that the kinetic acidity of the hydrogen in α-position to chlorine is greater than that of the hydrogen in α-position to fluorine (2,6). Since furthermore experiments, with lithium organics at low temperature (3), on vinyl chloride and vinyl fluoride revealed that only the former metallated (4), it appeared that also for sp^2 carbon the α effect is predominating in the same order as for sp^3 carbon. In addition to these results, the qualitative comparison of the two above isomers showed, similar to other dihaloethylenes (5), the higher acidity of the cis isomer (2).

These findings have been used for the discussion of the directiochemistry of nucleophilic additions and substitutions on haloacetylenes (6), but more information on the ease of formation of heterosubstituted vinyl carbanions was desirable. Di- and trihaloethylenes were the simplest models for pertinent studies and it is the purpose of this paper to describe our results on the influence of α and β effects (cis and trans) on there kinetic acidity.

We have studied the rate of base-catalyzed hydrogen-deuterium exchange on several di- and trihaloethylenes in sodium methoxide-methanol-O-d solution (7). The rate of exchange was followed by the disappearance of the proton signal in the NMR spectrum (8), using benzene as an internal standard. This technique allows all kinetic runs to be performed directly in the NMR tube at 33 ± 1°.

Pseudo first-order rate constants were determined, using the equation (9) :

$$k_1t = 2{,}303 \log \frac{(H/B)_0 - (H/B)_\infty}{(H/B)_t - (H/B)_\infty}$$

where k_1 is the pseudo first-order rate constant per hydrogen (10), H is the integrated intensity of the vinyl hydrogen peak, B is the integrated intensity of the reference (benzene) peak and the subscripts refer to the reaction time. Second-order rate constants were calculated by dividing k_1 by the base concentration (11).

Table 1 gives the summary of our results. Accordingly, except for products 2 and 8 (see table, footnote j), all olefins undergo base-catalyzed hydrogen-deuterium exchange faster than they undergo HX elimination or nucleophilic halogen substitution (12).
Data from table 1 allow the calculation of the k_H/k_D for carbanion formation on trichloroethylene (4 and 5). Taking into account the greater nucleophilicity of CH_3O^- in CH_3OD than in CH_3OH (by a factor of 1.5 (14)), one finds k_H/k_D = 1.3, at 33°C. This low value is indicative of a highly unsymmetrical transition state, probably placed on the product side as in the case of the haloforms (15).

Some other conclusions may be drawn from examination of table 1. It can be seen that the kinetic acidity of chloroform (1) is greater than that of any of the olefins studied. On the other side, by comparing the rate at which 2, 4 and 10 (see table) undergo the isotope exchange, it is clear that α-halogen substituents facilitate carbanion formation in the same order as that found for the haloforms (1) :

$$Br > Cl > F$$

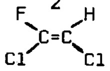
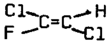
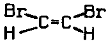
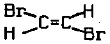
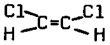
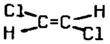
The observed greater acidity of trans-dibromoethylene (9) versus trans-dichloroethylene (12), under our conditions, verify the above sequence (16). The influence of the geometry of the molecule on its acidity is shown by comparison of the data on cis- and trans-dichloroethylene (11 and 12), where the expected (2,5) order (i.e. cis > trans) is found. The same comparison on cis- and trans-dibromoethylene (8 and 9) is impossible, under our conditions(16,17), because a rapid elimination and/or nucleophilic substitution reaction (12) on the cis isomer competes with deuteration.

It is of interest that the α-substituent effect may be dominated by the β-substituent effect (compare 4 and 9, 10 and 11).

Comparison of 4 and 6, at one hand, and of 10 and 13, at the other hand, indicates that in our solvent-base system, two fluorine atoms on the β-carbon lower the kinetic acidity of hydrogen on the α-carbon, when compared with two β-chlorine atoms. Similarly, other things being

TABLE 1

Rates of hydrogen-deuterium exchange on substituted ethylenes in CH_3OD/CH_3O^{-}(a)

Nr	Product(l)	CH_3O^{-}(j) $mole.l^{-1}$	$k\ CH_3O^{-}\ .10^{5}\ s^{-1}$	$k.10^{3}\ l.mole^{-1}.s^{-1}$
1	$CHCl_3$	-	-	102(c)
2	$CCl_2{=}CHBr$(b)	-	-	68(c)
3		0.049	147.8	31.2(d)
4	$CCl_2{=}CHCl$	0.0475	116.6	24.15(d)(e)
5	$CCl_2{=}CDCl$(g)	0.062	77.6	12.40(d)(f)
6	$CF_2{=}CHCl$	-	-	9.8(c)(i)
7		0.049	32.8	6.33(d)
8		0.0534	-	-
9		0.0534	6.7	1.24(d)
10	$CCl_2{=}CHF$	0.049	2.81	0.57(d)
11		0.153	2.60	0.16(d)
12		0.153	1.75	0.114(d)
13	$CF_2{=}CHF$	0.05	0.26	0.05(k)

(a) All runs were made at 33 ± 1°. (b) Elimination and/or substitution competes with deuteration. (c) Extrapolated values from runs in a 20 % CH_3OH/CH_3OD solution. (d) Least squares values. (e) Average of 4 runs. (f) Average of 2 runs. (g) Exchange in CH_3OH/CH_3O^{-} solution. (h) Competing elimination and/or substitution reaction consumed the total amount of base in a few minutes. (i) Only the upper limit may be assigned, due to competing methanol addition(13). This side-reaction enhances the apparent k for hydrogen-deuterium exchange. (j) Except for products 2 and 8, base consumption after 30-50 % reaction was no more than 10 % and in general less than 5 %. (k) Qualitative result only, because of the slowness of exchange. (l) Product concentration is about 1,8 $mole.l^{-1}$. for each run equal, only one fluorine substituent in β-trans position relative to hydrogen lowers the acidity of the latter, when compared with one chlorine in the same position (compare **4** and **7**). On the contrary, the reverse seems to be true for one β-cis substituent (F or Cl) relative to hydrogen (see **3** and **4**).

These preliminary results demonstrate the complex influence of the nature, the positions and the orientations of halogen substituents, and their mutual arrangement, on the acidity of ethylenic hydrogens.

The observed kinetic acidity sequence reflects the complicated but interesting interplay of electronegative, mesomeric (18), "d-orbital" (1), geometrical (2,5) and proximity (19) effects.

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(1) J. Hine, N.W. Burske, M. Hine and P.B. Langford, *J. Am. Chem. Soc.* **79**, 1406 (1957).

(2) S.Y. Delavarenne and H.G. Viehe, *I.U.P.A.C. Fluorine Symposium,* Estes Park, Colorado, U.S.A., July 1967.

(3) G. Köbrich, *Angew. Chemie,* Int. Ed., **6**, 41 (1967).

(4) H.G. Viehe and S.Y. Delavarenne, *Symposium on Microcycles,* Louvain, Belgium, september 1967.

(5) S.I. Miller and W.G. Lee, *J. Am. Chem. Soc.* **81**, 6313 (1959).

(6) H.G. Viehe, *Angew. Chemie,* Int. Ed. **6**, 767 (1967).

(7) We thank Prof. J. Jullien for a generous gift of methanol-O-d.

(8) Using a Varian model A-60 spectrometer.

(9) Only the data for the first 30 % of the reaction were used.

(10) C. Rappe, *Acta Chem. Scand.* **20**, 2236 (1966).
C. Rappe and W.H. Sachs, *J. Org. Chem.* **31**, 4127 (1967).

(11) We thank Prof. J. Pecher and Mr. J. Kotel for the base concentration measurements, performed on a Radiometer automatic titrator.

(12) G. Marchese, G. Modena and F. Naso, *Tetrahedron* **24**, 663 (1968).

(13) P. Tarrant and H.C. Brown, *J. Am. Chem. Soc.* **73**, 1781 (1951).

(14) S. Andreades, *J. Am. Chem. Soc.* **86**, 2003 (1964).

(15) J. Hine and N.W. Burske, *J. Am. Chem. Soc.* **78**, 3337 (1956).

(16) See, however, reference 5.

(17) W.K. Kwok, W.G. Lee and S.I. Miller, *J. Am. Chem. Soc.* **91**, 468 (1969).

(18) See, for example, J.A. Pople and M. Gordon, *J. Am. Chem. Soc.* **89**, 4253 (1967).

(19) H.G. Viehe and E. Franchimont, *Berichte* **97**, 602 (1964), and previous papers in the series.