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Homolytic Chlorination of Aliphatic Compounds. III.[1] Photochlorination of 1-Substituted Propanes; Steric Effects

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We have recently discussed the relative reactivities of aliphatic compounds in liquid-phase photochlorination and found that in CH_3–X type compounds inductive effect of the substituents X was the principal factor controlling the reactivities.[1-3] A linear free energy relationship was found between the reactivities of methyl hydrogens and Taft's σ^* constants[4] of the substituents X (X: CH_2Cl, CCl_3, CH_2CHCl_2, CH_2CMe_2Cl, CH_2CN).

In this note we wish to describe remarkable deviations from the relationship that were observed in photochlorination of 1-substituted propanes bearing ethyl groups on 1-position. The deviations are considered to be due to steric hindrance by the substituents. Table 1 lists the results obtained in the competitive photochlorination of the series of 1-substituted propanes.

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[1] Part II: M. Kosugi, K. Takeuchi and T. Migita, This Bulletin, **42**, 3242 (1969).

[2] T. Migita, M. Kosugi, Y. Tanaka and Y. Nagai, *Yukigosei Kagaku Kyokaishi (J. Soc. Org. Synth. Chem. Japan)* **25**, 908 (1967).

[3] T. Migita, M. Kosugi and Y. Nagai, This Bulletin, **40**, 920 (1967).

[4] M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley & Sons Inc., New York (1956), p. 619.

Table 1. Relative reactivities[a)] of 1-substituted propanes 40°C

CH_3-CH_2-CH_3 — —	CH_3-CH_2-CH_2Cl[b)] 21 58	CH_3-CH_2-$CHCl_2$[b)] 11 14
CH_3-CH_2-CMe_3[b)] 44 206	CH_3-CH_2-CMe_2Cl 25 90	CH_3-CH_2-$CMeCl_2$ 15 26
CH_3-CH_2-CEt_3[c)] 27 39	CH_3-CH_2-CEt_2Cl[c)] 9.3 19	CH_3-CH_2-$CEtCl_2$[c)] 4.4 7.2

a) The values are relative to the reactivity of a C–H bond of 2,2-dichloropropane and average of several runs.
b) See Ref. 2.
c) Carbon tetrachloride was used as solvent.

Table 1 shows that the successive introduction of chlorine substituent in 1-position of propane derivatives deactivates, and introduction of methyl groups in the 1-positions enhances the reactivities of C–H bonds on the 2- and 3-positions. This tendency is explainable in terms of inductive effects of chlorine and methyl substituents. However, when ethyl groups were introduced in 1-position, the reactivities of 2- and 3-position were found to be definitely lowered. For example, in substituted 1-chloropropane series, the reactivities of C–H bonds of 2- and 3-position decreases in the order:

$$CH_3CH_2CMe_2Cl > CH_3CH_2CH_2Cl > CH_3CH_2CEt_2Cl$$

Similar trends were observed in the other series of compounds. This is not expected from inductive effect of an ethyl group. Figure 1 shows the Hammett plot of the data in Table 1.

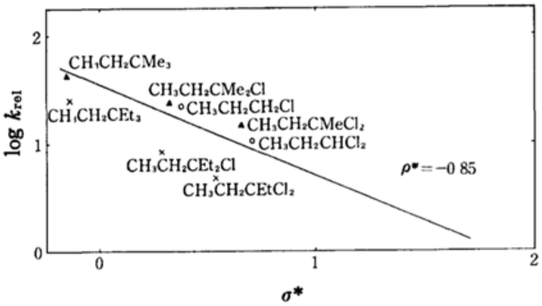
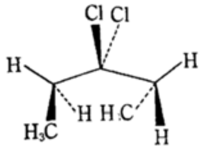


Fig. 1. Hammett plot for CH_3–X.
(σ^* values for X were estimated as described in the previous paper.)

The straight line in Fig. 1 represents the Hammett relationship obtained in our previous study,[2)] ρ^* value being −0.85. As shown in Fig. 1, methyl groups in 1,1,1-triethylpropane (3,3-diethylpentane), 1-chloro-1,1-diethylpropane (3-chloro-3-ethylpentane) and 1,1-dichloro-1-ethylpropane (3,3-dichloropentane) are less reactive than expected from the relationship, while those of the other compounds have expected reactivities. This indicates that ethyl substituent on 1-position of propane derivatives causes the deactivation of the molecule, but methyl substituent does not.

Russell[5)] reported that the methine hydrogens of 2,4-dimethylpentane and 2,2,4-trimethylpentane possessed unusually low reactivities toward the free or complexed chlorine atom, and explained that result in terms of the preferred conformation in which methine hydrogen atoms were protected from attack of the chlorine atom along the axis of C–H bond. A similar situation may be considered to be the deactivating factor in our cases. For example, for 3,3-dichloropentane, the presence of two chlorine atoms on 3-position will make the following conformation preferable.



In this conformation, one of methylene hydrogens and methyl hydrogens will protect each other from attack of the chlorine atom. In 2,2-dichlorobutane having normal reactivities, however, such crowding at the back of molecule would be reduced.

Experimental

Materials. *3,3-Dichloropentane.* A charge of 917.4 g of phosphorus pentachloride was dissolved in 344 g of diethylketone prepared from propionic acid.[6)] After stirring overnight, the solution was refluxed for one hour. The reaction mixture was subjected to steam distillation followed by fractional distillation. 71 g of 3,3-dichloropropane was obtained, bp 132°C (lit[7)] 127—135°C), n_D^{20} 1.442 (lit[7)] 1.442).

3-Chloro-3-ethylpentane. Ethylmagnesium bromide solution prepared from 164 g of ethyl bromide and 36 g of magnesium in ether was added to 186 g of diethyl ketone. The usual work-up yielded 153 g of triethylcarbinol boiling at 69—72°C/50 mmHg (lit[8)]

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6) D. M. Cowan, G. H. Geffery and A. I. Vogel, *J. Chem. Soc.*, **1940**, 171.

7) A. I. Heune and E. G. De Witt, *J. Am. Chem. Soc.*, **70**, 1548 (1948).

8) H. J. Lucas, *J. Am. Chem. Soc.*, **51**, 248 (1929).

TABLE 2. NMR SPECTRA OF MONOCHLORINATED PRODUCTS

	τ Values	
$\mathrm{CH_3^1CH^2ClC(CH_2^3CH_3^4)Cl_2}$	8.21 (H^1 doublet)	5.75 (H^2 quartet)
	7.65 (H^3 multiplet)	8.80 (H^4 triplet)
$\mathrm{CH_2^1ClCH_2^2C(CH_2^3CH_3^4)Cl_2}$	6.20 (H^1 triplet)	8.80 (H^4 triplet)
	7.65 (H^2 and H^3 multiplet)	
$\mathrm{CH_3^1CH^2ClC(CH_2^3CH_3^4)_2Cl}$	8.36 (H^1 doublet)	5.77 (H^2 quartet)
	8.08 (H^3 multiplet)	8.95 (H^4 triplet)
$\mathrm{CH_2^1ClCH_2^2C(CH_2^3CH_3^4)_2Cl}$	6.42 (H^1 triplet)	9.11 (H^4 multiplet)
	7.3—8.6 (H^2 and H^3 multiplet)	
$\mathrm{CH_3^1CH^2ClC(CH_2^3CH_3^4)_3}$	8.2—8.8 (H^1 and H^3 multiplet)	
	6.02 (H^2 quartet)	9.11 (H^4 multiplet)
$\mathrm{CH_2^1ClCH_2^2C(CH_2^3CH_3^4)_3}$	6.60 (H^1 triplet)	
	8.2—9.4 (H^2, H^3 and H^4 multiplet)	
$\mathrm{CH_3^1CH^2ClCMe_2^3Cl}$	8.35 (H^1 doublet)	5.92 (H^2 quartet)
	8.30 (H^3 singlet)	
$\mathrm{CH_2^1ClCH_2^2CMe_2^3Cl}$	6.34 (H^1 triplet)	7.81 (H^2 triplet)
	8.40 (H^3 singlet)	
$\mathrm{CH_3^1CH^2ClCMe^3Cl_2}$	8.23 (H^1 doublet)	5.75 (H^2 quartet)
	7.78 (H^3 singlet)	
$\mathrm{CH_2^1ClCH_2^2CMe^3Cl_2}$	6.19 (H^1 triplet)	7.35 (H^2 triplet)
	7.82 (H^3 singlet)	

TABLE 3. COMPETITIVE CHLORINATION OF 1-SUBSTITUTED PROPANES

1. Et_2CCl_2 40°C, in 2 m*l* of CCl_4

$\frac{Et_2CCl_2}{Me_2CCl_2}$	Molar ratio of products $\frac{MeCHCl\text{-}CEtCl_2}{CH_2Cl\text{-}CMeCl_2}$	$\frac{CH_2ClCH_2\text{-}CEtCl_2}{CH_2Cl\text{-}CMeCl_2}$	Rel. reactivities $-CH_2-$	CH_3-
0.529	2.37	2.19	6.7	4.1
0.529	2.55	2.30	7.3	4.4
0.529	2.48	2.32	7.0	4.4
0.529	2.69	2.45	7.6	4.6

2. Et_4C 40°C, in 2 m*l* of CCl_4

$\frac{Et_4C}{CH_2Cl\text{-}CH_2Cl}$	Molar ratio of products $\frac{MeCHCl\text{-}CEt_3}{CHCl_2\text{-}CH_2Cl}$	$\frac{CH_2ClCH_2\text{-}CEt_3}{CHCl_2\text{-}CH_2Cl}$	Rel. reactivities $-CH_2-$	CH_3-
0.249	6.35	6.56	12.8	8.78
0.249	5.60	6.16	11.3	8.24
0.249	6.29	7.20	12.6	9.64

3. Et_3CCl

Since 3-chloro-3-ethylpentane inevitably contains a small quantity of olefin, chlorinations of the compounds were carried out in carbon tetrachloride in the presence of a small amount of bromine, in order to exclude the possibility of addition of chlorine to the olefin. Intramolecular reactivity pattern was found to be:

$$\underset{0.482}{CH_3}—\underset{1}{CH_2}—CEt_2Cl$$

Competitive chlorination with 1,2-dichloroethane was carried out to find the relative reactivity of a methyl group of 3-chloro-3-ethylpentane.

40°C, in 2 m*l* of CCl_4

$\frac{Et_3CCl}{CH_2ClCH_2Cl}$	Molar ratio of products $\frac{CH_2ClCH_2CEt_2Cl}{CHCl_2CH_2Cl}$	Rel. reactivities CH_3-
0.482	2.98	2.75
0.482	3.73	3.44
0.482	2.86	2.64
0.482	3.64	3.36

4. $EtCMeCl_2$

$\frac{EtCMeCl_2}{t\text{-}BuCl}$	Molar ratio of products $\frac{MeCHCl\text{-}CMeCl_2}{CH_2Cl\text{-}CMe_2Cl}$	$\frac{CH_2ClCH_2\text{-}CMeCl_2}{CH_2Cl\text{-}CMe_2Cl}$	Rel. reactivities $-CH_2-$	CH_3-
1.60	0.950	0.779	2.7	1.5
1.60	0.950	0.743	2.7	1.4
1.60	0.950	0.777	2.7	1.5

5. $EtCMe_2Cl$

$\frac{EtCMe_2Cl}{t\text{-}BuCl}$	Molar ratio of products $\frac{MeCHCl\text{-}CMe_2Cl}{CH_2Cl\text{-}CMe_2Cl}$	$\frac{CH_2ClCH_2\text{-}CMe_2Cl}{CH_2Cl\text{-}CMe_2Cl}$	Rel. reactivities $-CH_2-$	CH_3-
1.33	2.54	1.07	8.6	2.4
1.33	2.63	1.09	8.9	2.5
1.33	2.96	1.19	10.0	2.7

72—73.5°C/50 mmHg), $n_D^{20.7}$ 1.4281 (lit[8] 1.4281). Fifty eight grams of this compound was shaken with large excess of concentrated hydrochloric acid and the resulting organic layer was separated. 60 g of desired product was obtained, boiling at 82—82.3°C/100 mmHg (lit[9] 83—83.5°C/100 mmHg), n_D^{20} 1.4332 (lit[9] 1.4334).

3,3-Diethylpentane. Ethereal solution of ethylmagnesium bromide prepared from 109 g of ethyl bromide and 24 g of magnesium was added to 63 g of 3-chloro-3-ethylpentane and the mixture refluxed for 20 hr. The work-up yielded 21 g of 3,3-diethylpentane boiling at 141.5—143°C (lit[10] 139.2°C and 147.6°C), n_D^{20} 1.4201 (lit[10] 1.4203).

2,2-Dichlorobutane. This material was prepared by the reaction of 1000 g of phosphorus pentachloride with 700 g of methyl ethyl ketone. The product was washed with water and purified by fractional distillation. 93 g of 2,2-dichlorobutane was obtained, bp 103—104° (lit[11] 102—104°C), n_D^{20} 1.4273 (lit[11] n_D^{20} 1.4295).

t-Amyl Chloride. t-Amyl alcohol (82 g) was treated with concentrated hydrochloric acid followed by fractional distillation. 59 g of the chloride was obtained boiling at 26°C/85 mmHg (lit[12] 84—86°C), n_D^{20} 1.4040 (lit[12] 1.4052).

Reaction Products. Monochlorinated products were collected by VPC method and their structures were derived from their NMR spectra, are shown in Table 2.

Competitive Chlorination. The chlorination procedure has already been described.[1,2] Analysis of the products of competitive photochlorinations was performed by VPC method. The results are shown in Table 3.

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10) F. C. Whitmore, ibid, **60**, 2539 (1929).

11) B. B. Carson, J. S. Thomas and D. D. Waugh, ibid, **51**, 1950 (1929).

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