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Homolytic Chlorination of Aliphatic Compounds. II.[1]
Photochlorination of Aliphatic Nitriles

Masanori Kosugi, Kohji Takeuchi and Toshihiko Migita

Department of Chemistry, Gunma University, Kiryu, Gunma

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Acetonitrile, propionitrile, *n*-butyronitrile and pivalonitrile were photochlorinated competitively at 40°C in the presence of an appropriate chlorinated ethane, and relative amounts of the chlorinated products were determined by v.p.c. From the results the relative reactivities of C-H bonds toward hydrogen abstraction by chlorine atom were estimated. A linear free energy relationship was observed between σ^* value of X and the reactivity of CH_3–X toward chlorination (X: $-CN$, $-CH_2CN$, $-CH_2CH_2CN$, $-CMe_2CN$). This indicates that cyano group will affect the reactivities of these C-H bond through its inductive effect.

Orientation of photochlorination of saturated aliphatic nitriles has been studied by Bruylants *et al.*[2] In order to investigate the effect of cyano group on the reactivities of aliphatic chains toward chlorination, we have estimated relative reactivities of acetonitrile, propionitrile, *n*-butyronitrile and pivalonitrile.

Nitriles and the standard substrate were competitively photochlorinated in carbon tetrachloride. The reaction mixture were analyzed for chlorinated products by v.p.c. method. Since a large excess of the substrate was used, the relative reactivities of R_1H and R_2H can be calculated from the molar ratio of R_1Cl and R_2Cl by the equation

$$\frac{k_2}{k_1}=\frac{[R_2Cl]}{[R_1Cl]}\times\frac{[R_1H]_0}{[R_2H]_0},$$

where k_2/k_1 is the ratio of the rate constants for R_2H and R_1H, $[R_2H]_0$ and $[R_1H]_0$ are the initial concentrations of the substrates, and $[R_2Cl]$ and $[R_1Cl]$ are the molar amounts of the chlorinated products. The relative reactivities of C–H bonds were calculated by correcting the relative rate constants for the statistic factors. Unit reactivity was assigned to one of the six available hydrogen atoms of 2,2-dichloropropane. Results are summarized in Table 1.

Table 1. Relative reactivities* of nitriles at 40°C

CH_3—	CN		
0.02			
CH_3—	CH_2—	CN	
1.4	0.98		
CH_3—	CH_2—	CH_2—	CN
3.7	7.7	0.39	
CH_3—	CMe_2CN		
2.7			

* The values are relative to the raeactivity of a C-H bond of 2,2-dichloropropane and average of four runs.

The relative reactivity of acetonitrile toward photochlorination reported by Russell[3] is ten times higher than that we obtained. However, our value is considered to be more plausible. Russell estimated the relative reactivities from the amounts of substrates consumed by competitive reactions. In this technique, considerably high conversions are required. In such circumstances, acetonitrile seems to undergo consecutive chlorination and triazine derivatives formation as shown in the

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[1] Part I: T. Migita, M. Kosugi and Y. Nagai, This Bulletin, **40**, 920 (1967).

[2] A. Bruylants, M. Tits, C. Dieu and R. Gauthier, *Bull. Soc. Chim. Belges*, **61**, 366 (1952).

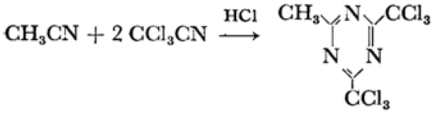
[3] G. A. Russell, *J. Am. Chem. Soc.*, **80**, 4997 (1958).

following equations.[4,5]

$$CH_3CN + Cl_2 \xrightarrow{\text{slow}} (CH_2ClCN)HCl$$

$$(CH_2ClCN)HCl + Cl_2 \xrightarrow{\text{fast}} (CHCl_2CN)HCl + HCl$$

$$(CHCl_2CN)HCl + Cl_2 \xrightarrow{\text{fast}} (CCl_3CN)HCl + HCl$$



We obtained a considerable amount of 2-methyl-4,6-di-trichloromethyl-1,3,5-triazine in the photo-induced chlorination of acetonitrile at a high conversion. Since acetonitrile is consumed not only by chlorination but also by triazine formation, it would be possible that the relative reactivity obtained from the amount of acetonitrile consumed gives an overestimated value. In our method, such consecutive chlorination might lead us to underestimate the reactivity of acetonitrile, since relative reactivities were derived from the relative amounts of the monochlorinated products. However, the conversion was so small (less than 10%) that the possibility of underestimation due to the consecutive reaction may be negligible.

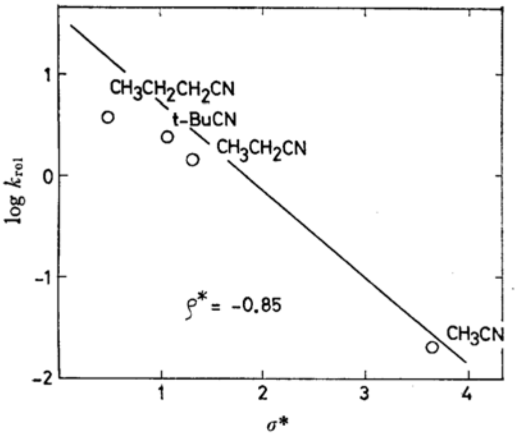


Fig. 1. Hammett plot for CH_3–X. 40°C.

TABLE 2. POLAR SUBSTITUENT CONSTANTS

Substituennt	σ^*
CH_3	0.000
CH_2Cl	1.050
$CHCl_2$	1.940
CCl_3	2.65
CH_2CMe_3	−0.165
CH_2CH_2Cl	0.385
CH_2CHCl_2	0.693*
CH_2CCl_3	0.946*
CMe_3	−0.300
CMe_2Cl	0.851*
$CMeCl_2$	1.890*
H	0.490
CN	3.64*
CH_2CN	1.300
CH_2CH_2CN	0.464*
CMe_2CN	1.100*

* Estimated by the following relations:
$\sigma^*(CH_2CHCl_2) = 1/2.8\,\sigma^*(CHCl_2)$
$\sigma^*(CMeCl_2) = \sigma^*(CHCl_2) + \sigma^*(Et)$.
Ref. 7, p. 592.

The orientation patterns of chlorination of propionitrile and *n*-butyronitrile were in good agreement with those obtained by Bruylants *et al.*,[2] except for α-position of *n*-butyronitrile. In our experiments formation of α-chloro-*n*-butyronitrile (at least 3—4% of total chlorinated products) was recognized. The structure of the product was derived from its NMR spectra.

As previously reported,[1,6] a linear free energy relationship was found to exist between the reactivities of methyl hydrogen of CH_3–X and Taft's σ^* constants[7] for the substituents X (X: CH_3, CH_2Cl, $CHCl_2$, CCl_3, CH_2CMe_3, CH_2CH_2Cl, CH_2CHCl_2, CH_2CCl_3, CMe_3, CMe_2Cl, $CMeCl_2$). The straight line in Fig. 1 represents Hammett's relationship we obtained previously,[6] ρ^* value being −0.85. As shown in Fig. 1, the same relationship can approximately hold for the chlorina-

TABLE 3. NMR SPECTRA OF CHLORINATED NITRILES (τ Values)

α-Chloropropionitrile	$CH_3{}^1CH_2{}^2ClCN$	8.15 (H^1 doublet)	5.45 (H^2 quartet)	
β-Chloropropionitrile[9]	$CH_2{}^1ClCH_2{}^2CN$	6.25 (H^1 triplet)	7.10 (H^2 triplet)	
α-Chlorobutyronitrile	$CH_3{}^1CH_2{}^2CH^3ClCN$	8.80 (H^1 triplet)	7.90 (H^2 multiplet)	5.63 (H^3 triplet)
β-Chlorobutyronitrile	$CH_3{}^1CH^2ClCH_2{}^3CN$	8.35 (H^1 doublet)	5.80 (H^2 sextet)	7.25 (H^3 doublet)
γ-Chlorobutyronitrile	$CH_2{}^1ClCH_2{}^2CH_2{}^3CN$	6.37 (H^1 triplet)	7.90 (H^2 multiplet)	7.50 (H^3 triplet)
Chloropivalonitrile[10]	$(CH_3{}^1)_2CH_2{}^2ClCCN$	8.55 (H^1 singlet)	6.48 (H^2 singlet)	

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[4] F. N. Stepanov and N. J. Shirokova, *J. Gen. Chem. U. S. S. R.* **25**, 905 (1955).

[5] G. I. Braz, G. V. Myasnikova, A. Y. Yakubovich, V. P. Bazov and K. I. Sakodyaskii, *Zh. Obshch. Khim.*, **33**, 1939 (1963).

[6] T. Migita, M. Kosugi, Y. Tanaka and Y. Nagai, *Yukigosei kagaku kyohaishi (J. Soc. Org. Synth. Chem. Japan)*, **25**, 908 (1967). Similar tendency was observed in gas phase chlorination of chloroethanes. C. Cillien, P. Coldfinger, G. Huybrechts and G. Martens, *Trans. Faraday Soc.*, **63**, 1631 (1967); W. Mack, *Tetrahedron Letters*, **1967**, 4993.

[7] M. S. Newman, "Steric Effects in Organic Chemistry," Wiley, New York (1956), p. 619.

tion of the nitriles, when σ^* constants noted in Table 2 are used.

It is quite reasonable that reactivities of β- or γ-C–H bonds of nitriles are represented by Hammett's equation, since a cyano group will affect the reactivities of these C–H bonds through its inductive effect. However, it is noteworthy that the relationship holds even in reactivities of α-C–H bonds. This may indicate that resonance stabilizing effect of a cyano group on an intermediate radical $R\dot{C}HCN$ hardly enhances the reactivity of α-C–H bonds of RCH_2CN.

$$R\text{-}\dot{C}H\text{-}C{\equiv}\overline{N} \longleftrightarrow R\text{-}CH{=}C{=}\overline{N}\bullet$$

Experimental

Materials. Acetonitrile and propionitrile (commercial materials) were treated with activated silica gel chromatographically and refluxed over phosphorus pentoxide and then rectified through a Vigreux column. The boiling points were 81°C and 97°C, respectively. *n*-Butyronitrile and pivalonitile were prepared by the dehydration of the corresponding acid amide.[8] The boiling points were 118°C and 105°C, respectively. All the materials were shown by v.p.c. analysis to be pure.

Reaction Products. Monochlorinated products were collected by v.p.c. method and their structures were derived from their NMR spectra. The NMR data are given in Table 3.

2-Methyl-4,6-di-trichloromethyl-1,3,5-triazine was isolated from the chlorination mixture of acetonitrile.[5] Mp 94—95°C. NMR 7.0 (H singlet). Found: C, 22.28; H, 1.18%. Calcd for $C_6H_3N_3Cl_6$: C, 21.84; H, 0.92%.

Competitive Chlorination Procedure. The chlorination procedure has already been described.[1] Analysis of the chlorination products were performed by v.p.c. method employing a 1.5 m Carbowax 20M 25% column. Competitive experiments were carried out on the mixtures of nitriles with an appropriate chloroethanes in carbon tetrachloride solution. The reactivities of C–H bonds of nitriles relative to that of 2,2-dichloropropane were calculated from the data thus obtained on the basis of the reactivity values of chloroethanes.[1]

Since acetonitrile has much lower reactivity than 2,2-dichloropropane, competitive experiments with 2,2-dichloropropane have difficulties in gas chromatographical analysis for determination of reliable relative rates. Acetonitrile was made to compete with 1,1,1-trichloroethane. The rate factor was calculated as,

$$f\left(\frac{MeCN}{MeCCl_2Me}\right)=f\left(\frac{MeCN}{MeCCl_3}\right)\times f\left(\frac{MeCCl_3}{MeCCl_2Me}\right).$$

The results of competitive experiments are shown in Table 4.

TABLE 4. COMPETITIVE CHLORINATION OF NITRILES

1. Acetonitrile, 40°C, in 2 m*l* of CCl_4

$\frac{MeCN}{MeCCl_3}$	Molar ratio of products $CH_2ClCN/ClCH_2CCl_3$	Rel. reactivities* CH_3–
3.54	0.717	0.20
3.54	0.663	0.19
3.54	0.635	0.18
3.54	0.650	0.18
	average	0.19

2. Propionitrile, 40°C, in 2 m*l* of CCl_4

$\frac{CH_3CH_2CN}{CHCl_2CHCl_2}$	Molar ratio of products $\frac{CH_2Cl\text{-}CH_2CN}{CCl_3\text{-}CHCl_2}$	$\frac{CH_3CHCl\text{-}CN}{CCl_3\text{-}CHCl_2}$	Rel. reactivities* CH_3–	–CH_2–
0.444	2.43	0.969	3.65	2.18
0.444	2.21	1.11	3.32	2.50
0.444	2.05	0.933	3.08	2.10
0.444	2.25	1.03	3.36	2.22
		average	3.36	2.28

3. *n*-Butyronitrile, 40°C, in 2 m*l* of CCl_4

n-Butyronitrile was chlorinated in carbon tetrachloride at 40°C. Intramolecular reactivity pattern was found to be:

$$\begin{array}{llll} CH_3\text{—} & CH_2\text{—} & CH_2\text{—} & CN \\ 0.48 & 1 & 0.05 & \end{array}$$

Competitive chlorination with 1,1,2-trichloroethane was carried out to find relative reactivity of β-position of *n*-butyronitrile.

$\frac{CH_3CH_2CH_2CN}{CH_2ClCHCl_2}$	Molar ratio of products $\frac{CH_3CHClCH_2CN}{(CHCl_2)_2}$	Rel. reactivities* –CH_2–
0.229	3.60	15.1
0.239	4.65	19.5
0.239	3.71	15.5
0.229	3.63	15.2
	average	16.3

4. Pivalonitrile, 40°C, in 2m*l* of CCl_4

$\frac{t\text{-}BuCN}{CH_2ClCH_2Cl}$	Molar ratio of products $\frac{Me_2CH_2ClCCN}{CHCl_2CH_2Cl}$	Rel. reactivities* CH_3–
0.480	0.977	0.91
0.480	1.01	0.93
0.480	0.958	0.88
0.480	0.941	0.86
	average	0.90

* Relative to a C–H bond of the corresponding chloroethanes.

We are deeply grateful to Professor Y. Nagai for numerous suggestions and discussions concerning assay problems.

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[8] R. E. Kent and S. M. McElvain, "Org. Synth.," Coll. Vol. III. p. 493 (1955).

[9] β-Chloropropionitrile was prepared by addition of hydrogen chloride to acrylonitrile.[11]

[10] Found: Cl, 29.09%. Calcd for C_3H_8NCl: Cl, 30.16%.

[11] R. Stewart and R. H. Clark, *J. Am. Chem. Soc.*, **69**, 713 (1941).