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Homolytic Chlorination of Aliphatic Compounds. I. Photochlorination of Chloroethanes

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The effect of the structure on the rate of hydrogen abstraction from chloroalkanes by a chlorine atom has been investigated by carrying out the competitive photochlorination of eight different chloroethanes in the presence of 2, 2-dichloropropane to which the relative site reactivities have been referred. The results show that the successive introduction of a chlorine substituent at the 1-position decreases the reactivity of the 2-position, but that, in some cases, it increases that of the 1-position. A linear free-energy relationship is found to exist between the reactivities of the R group in R-R′ (R=methyl, chloromethyl or dichloromethyl; R′=methyl, chloromethyl, dichloromethyl or trichloromethyl) and Taft's σ^* constants for the R′ group. These facts are elucidated in terms of the inductive and resonance effects of the substituent groups.

The effects of substituents on the reactivities of C–H bonds in an aliphatic chain to photochlorination have received considerable study; the results have traditionally been accounted for in terms of the inductive and resonance effects of the substituents.[1-8] Thus, a chlorine substituent always deactivates the β-position toward chlorination by induction, but its effect on the α-position seems to vary from compound to compound due to the intervention of the resonance stabilization of the radical intermediate.

Tedder and his co-workers found that a chlorine substituent retards the reactivities of the α-positions of primary and secondary butyl chlorides.[3,5] On the other hand, the rate enhancement by an α-chlorine substituent has been reported by several workers. For example, a C–H bond in methyl chloride has been found to be more reactive than that of methane.[9] Henne and Renoll also found that the chlorination of 1, 1, 1-trifluoroethane affords only the dichlorination product.[10] Furthermore, Benoy has pointed out a considerable rate enhancement by an α-chlorine substituent in the consecutive chlorination of trimethylacetic acid.[11]

We have commenced a comprehensive study of the influences of substituents upon the reactivity of each position in aliphatic chains toward the homolytic chlorination. This paper will describe the results of the photochlorination of chloroethanes.

Results

Ethylchloride, ethylene dichloride, ethylidene chloride, 1, 1, 1- and 1, 1, 2-trichloroethane, 1, 1, 1, 2- and 1, 1, 2, 2-tetrachloroethane, and pentachloroethane were competitively photochlorinated in the presence of 2, 2-dichloropropane. The reaction mixtures were then analyzed for chlorinated products by the v. p. c. method.

Since a large excess of the substrate was used in each case, the relative reactivity of the R_1H and R_2H substrates can be calculated from the molar ratio of the R_1Cl and R_2Cl products by the following 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 of R_2H and R_1H, where $[R_2H]_0$ and $[R_1H]_0$ are the initial concentrations of the substrates, and where $[R_2Cl]$ 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 hydrogens of 2, 2-dichloropropane.

The photochlorination of aliphatic compounds is

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[1] C. Walling, "Free Radicals in Solution," John Wiley & Sons, New York (1957), pp. 356—369.

[2] C. Walling and M. F. Mayahi, *J. Am. Chem. Soc.*, **81**, 1485 (1959).

[3] P. C. Anson, P. S. Fredricks and J. M. Tedder, *J. Chem. Sos.*, **1959**, 918.

[4] P. S. Fredricks and J. M. Tedder, *ibid.*, **1960**, 144.

[5] P. S. Fredricks and J. M. Tedder, *ibid.*, **1961**, 3520.

[6] H. Singh and J. M. Tedder, *ibid.*, **1964**, 4737.

[7] E. Muller and E. W. Schmidt, *Chem. Ber.*, **97**, 2614 (1964).

[8] N. Colebourne and E. S. Stern, *J. Chem. Soc.*, **1965**, 3599.

[9] H. O. Pritchard, J. B. Pyke and A. F. Trotman-Dickenson, *J. Am. Chem. Soc.*, **77**, 2629 (1955).

[10] A. L. Henne and M. W. Renoll, *ibid.*, **58**, 889 (1936).

[11] G. J. Benoy, *Tetrahedron*, **20**, 1567 (1964).

known to proceed by the following chain-propagation steps:

$$Cl\cdot + RH \rightarrow HCl + R\cdot \qquad (1)$$

$$R\cdot + Cl_2 \rightarrow RCl + Cl\cdot \qquad (2)$$

It is assumed in the above method of calculation that all of the R· radicals are consumed by the step (2). In the cases studied, the β-chloroethyl radical derived from the hydrogen abstraction of a chloroethane may undergo the following two side reactions:

$$Cl{-}C{-}C\cdot \rightarrow Cl\cdot + C{=}C \qquad (\beta\text{-scission})$$

or

$$ClCX_2CH_2\cdot \rightarrow \cdot CX_2CH_2Cl \qquad (\text{rearrangement})$$

The second possibility does not complicate the situation, since the rearranged radical should afford the same product through step (2) as the original radical does. The first possibility is unimportant at the reaction temperatures employed, since the β-scission product has been found to form to only a minor extent when benzoyl peroxide is decomposed in chloroethanes near 80°C.[12] Thus, the values obtained as above many indeed be regarded as representing the relative reactivities to hydrogen abstraction by a chlorine atom.

Table 1 shows the relative reactivities of various C–H bonds in chloroethanes. The value for a C–H bond in ethane was calculated from the rate constants of the hydrogen abstraction by a chlorine atom from ethane and ethyl chloride, the rate constants were determined by Pritchard, Pyke, and Trotman-Dickenson.[9]

TABLE 1. RELATIVE REACTIVITIES[a] OF C–H BONDS IN CHLOROETHANES TOWARD HYDROGEN ABSTRACTION BY A CHLORINE ATOM

at 20°C

Substituent R	$-CH_3$	$-CH_2Cl$	$-CHCl_2$	$-CCl_3$
Position attacked				
CH_3-	91[b]	11	0.53	0.05
CH_2Cl-	28	3.4	0.49	0.20
$CHCl_2-$	5.0	0.90	0.36	0.25

at 40°C

Substituent R	$-CH_3$	$-CH_2Cl$	$-CHCl_2$	$-CCl_3$
Position attacked				
CH_3-	68[b]	8.3	0.60	0.07
CH_2Cl-	23	3.0	0.47	0.24
$CHCl_2-$	4.7	0.78	0.43	0.44

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

b) Calculated from the rate constants of chlorination of ethane and ethyl chloride.[9]

Discussion

The second line in Table 1 shows the decreasing reactivity of the methyl group of the CH_3R compounds in the order;

$$CH_3CH_3 > CH_3CH_2Cl > CH_3CHCl_2 > CH_3CCl_3$$

In other words, the successive introduction of a chlorine substituent at the 1-position decreases the reactivity of the 2-position. Quite similar tendencies are also noticed in the third and fourth lines. These deactivations of accumulating chlorine atom in the R substituent may be attributed to two possible effects.

First, the introduction of chlorine atoms into R will increase electron-withdrawing character of the R group; consequently, the reactivity of a C–H bond attached to R toward an electron-seeking chlorine atom will decrease.

$$H{-}C{-}CH_3 > H{-}C{-}CH_2Cl > H{-}C{-}CHCl_2 > H{-}C{-}CCl_3$$

Second, the introduction of chlorine atoms into R will reduce the extent of the C–H hyperconjugative stabilization of the incipient radicals. The diminished possibility of hyperconjugation for the radicals may also be responsible for the tendencies observed.

$$CH_3{-}C\cdot > CH_3Cl{-}C\cdot > CHCl_2{-}C\cdot > CCl_3{-}C\cdot$$

Logarithms of the relative reactivities for the 2-positions are plotted against Taft's substituent constants, σ^*,[13] for substituted methyl groups involving the 1-hydrogens in Fig. 1. For each series

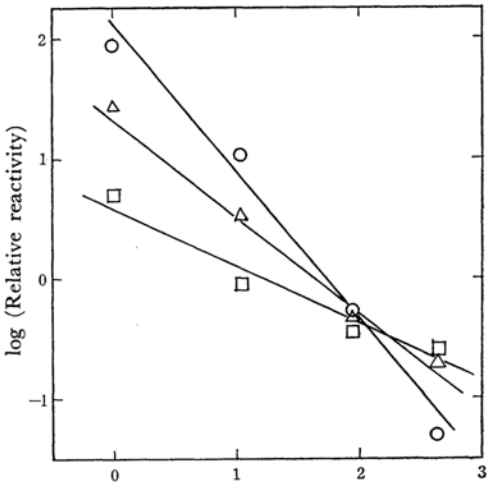

Fig. 1. Plots of logarithms of the relative reactivities of C–H bonds in chloroethanes CH_3R (○) $ClCH_2R$ (△) and Cl_2CHR (□) against Taft's substituent constants of R.

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[12] T. Migita, M. Kosugi, H. Kono and Y. Nagai, *J. Soc. Org. Synth. Chem. Japan,* **24**, 223 (1966).

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

TABLE 2. COMPETITIVE CHLORINATION OF CHLOROETHANES AND 2, 2-DICHLOROPROPANE

i) Ethyl chloride

No.	$\frac{C_2H_5Cl}{Me_2CCl_2}$	Chlorine a) ml	Temp. °C	Molar ratio of products b)		Rel. reactivity c)	
				CH_3CHCl_2	$ClCH_2CH_2Cl$	$ClCH_2$	CH_3
1	0.46	25.0	20	4.47	2.74	29	12
2	0.46	30.0	20	4.15	2.68	27	12
3	0.46	22.5	20	4.19	2.46	28	11
4	0.46	23.0	20	4.13	2.03	27	9
5	0.39	28.0	40	3.27	1.74	25	8.9
6	0.39	25.5	40	3.03	1.63	23	8.4
7	0.39	35.0	40	2.76	1.42	21	7.3
8	0.39	21.5	40	3.01	1.68	23	8.6

ii) Ethylidene dichloride

No.	$\frac{C_2H_4Cl_2}{Me_2CC_2}$	Chlorine a) ml	Temp. °C	Molar ratio of products b)		Rel. reactivity c)	
				CH_3CCl_3	$CH_2ClCHCl_2$	Cl_2CH	CH_3
10	1.09	37.5	20	0.97	0.30	5.3	0.55
11	1.09	29.5	20	0.85	0.27	4.7	0.50
12	1.09	26.5	20	0.92	0.30	5.1	0.55
13	1.09	33.5	20	0.90	0.28	5.0	0.51
14	1.00	45.0	40	0.83	0.28	4.7	0.61
15	1.00	49.0	40	0.84	0.31	4.7	0.67
16	1.00	40.5	40	0.87	0.30	4.9	0.65
17	1.00	36.5	40	0.91	0.31	5.1	0.66

iii) Ethylene chloride

No.	$\frac{C_2H_4Cl_2}{Me_2CCl_2}$	Chlorine a) ml	Temp. °C	Molar ratio of products b)	Rel. reactivity c)	
				$CH_2ClCHCl_2$	$ClCH_2$	CH_2Cl
18	1.00	29.5	20	2.06	3.1	3.1
19	1.00	26.0	20	2.42	3.6	3.6
20	1.00	38.5	20	2.16	3.2	3.2
21	1.00	33.0	20	2.31	3.5	3.5
22 d)	1.00	75.5	40	2.02	3.0	3.0
23 d)	1.00	84.0	40	2.15	3.2	3.2
24	1.00	37.5	40	1.96	2.9	2.9
25	1.00	40.0	40	1.82	2.7	2.7
26	1.00	36.0	40	2.20	3.3	3.3

iv) 1, 1, 1-Trichloroethane

No.	$\frac{C_2H_3Cl_3}{Me_2CCl_2}$	Chlorine a) ml	Temp. °C	Molar ratio of products b) CH_2ClCCl_3	Rel. reactivity c) CH_3CCl_3
27	10.00	28.5	20	0.22	0.04
28	10.00	21.5	20	0.22	0.04
29	10.00	33.5	20	0.29	0.06
30	10.00	29.0	20	0.26	0.05
31	4.98	40.0	40	0.15	0.06
32	4.98	40.5	40	0.16	0.07
33	4.98	34.5	40	0.16	0.06
34	10.00	31.0	40	0.34	0.07
35	10.00	35.0	40	0.36	0.07

(TABLE 2. Continued)

v) 1, 1, 2-Trichloroethane

No.	$C_2H_3Cl_3$ / Me_2CCl_2	Chlorine[a) ml	Temp. °C	Molar ratio of products[b)		Rel. reactivity[c)	
				CH_2ClCCl_3	$CHCl_2$	Cl_2CH	CH_2Cl
36	2.00	30.0	20	0.30	0.31	0.90	0.47
37	2.00	29.5	20	0.29	0.32	0.87	0.48
38	2.00	28.5	20	0.32	0.32	0.96	0.48
39	2.00	24.0	20	0.29	0.35	0.87	0.53
40	1.98		40	0.27	0.33	0.83	0.50
41	1.98		40	0.27	0.29	0.80	0.44
42	2.00	34.0	40	0.21	0.32	0.71	0.48
43	2.00	30.0	40	0.27	0.35	0.79	0.45

vi) 1, 1, 1, 2-Tetrachloroethane

No.	$C_2H_2Cl_4$ / Me_2CCl_2	Chlorine[a) ml	Temp. °C	Molar ratio of Products[b) $CHCl_2CCl_3$	Rel. reactivity[c) $ClCH_2CCl_3$
44	9.09	30.0	20	0.61	0.20
45	9.09	29.0	20	0.60	0.20
46	9.09	30.5	20	0.64	0.21
47	9.09	24.0	20	0.57	0.19
48	9.98	36.5	40	0.73	0.22
49	9.98	44.5	40	0.85	0.26
50	9.98	35.5	40	0.74	0.22
51	9.98	41.5	40	0.84	0.25

vii) 1, 1, 2, 2-Tetrachloroethane

No.	$C_2H_2Cl_4$ / Me_2CCl_2	Chlorine[a) ml	Temp. °C	Molar ratio of products[b)	Rel. reactivity[c)	
				$CHCl_2CCl_3$	Cl_2CH	$CHCl_2$
52	5.00	27.0	20	0.64	0.39	0.39
53	5.00	24.5	20	0.62	0.37	0.37
54	5.00	28.0	20	0.53	0.32	0.32
55	5.00	31.0	20	0.58	0.35	0.35
56	5.00	35.0	40	0.71	0.43	0.43
57	5.00	36.0	40	0.72	0.43	0.43
58	5.00	36.0	40	0.71	0.43	0.43
59	5.00	29.5	40	0.72	0.43	0.43

viii) Pentachloroethane

No.	C_2HCl_5 / Me_2CCl_2	Chlorine[a) ml	Temp. °C	Molar ratio of products[b) C_2Cl_6	Rel. reactivity[c) Cl_2CHCCl_3
60	10.00	24.0	20	0.38	0.23
61	10.00	34.5	20	0.40	0.24
62	10.00	35.5	20	0.46	0.28
63	10.00	31.5	20	0.40	0.24
64	9.94	43.5	40	0.80	0.48
65	9.94	37.0	40	0.67	0.40
66	9.94	28.0	40	0.69	0.42
67	9.94	32.0	40	0.74	0.44

of compounds, a satisfactory linear relationship is obtained. There facts indicate that the principal factor governing the reactivities is due to the inductive effects of the R substituents.

In the case of the reaction of the series of $CHCl_2R$ compounds, the plots deviate slightly from a straight line, making a concave curve. This may suggest an extra acceleration by the hyperconjugative effects of the R groups.

From the slopes of the lines in Fig. 1, the reaction constants can be calculated to be -1.25, -0.83 and -0.49 at 20°C for the reaction of the CH_3R, CH_2ClR, and $CHCl_2R$ compound series respectively. Evidently, the reactivity becomes less susceptible to the inductive effects of R substituents when chlorine substituents are introduced at the 2-position. Perhaps because of the strong $-I$ effect of the chlorine substituents already present in the 2-position, the additive influence due to the $-I$ effect of the R group will become relatively small.[14]

The second and third columns of Table 1 show decreasing reactivities:

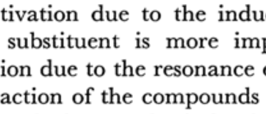
$$CH_3\text{–}R > CH_2Cl\text{–}R > CHCl_2\text{–}R$$

(R: methyl or chloromethyl group).

In these cases chlorine substituents deactivate the α-C–H bond toward the attack of a chlorine atom. The reactivities of the compounds bearing the dichloromethyl substituent, however, are not affected seriously by the introduction of an α-chlorine substituent, as is shown in the fourth column in Table 1. Furthermore, the rate enhancement by the α-chlorine substituent may be seen in the following sequence (see the fifth column in Table 1):

$$H\text{–}CH_2CCl_3 < H\text{–}CHClCCl_3 < H\text{–}CCl_2CCl_3$$

A chlorine substituent will affect the reactivity of the α-C–H bond in two ways. Its $-I$ effect will deactivate the α-C–H bond. Contrary to this, the conjugative effect will accelerate the hydrogen abstraction from the α-C–H bond, for the stabilization of the incipient radical by the following resonance is to be expected:[15]



$$\underset{\text{I}}{R\text{–}\dot{C}\text{–}Cl} \longleftrightarrow \underset{\text{II}}{R\text{–}\overset{(-)}{C}\text{–}\overset{(+)}{\dot{C}l}}$$

The tendencies observed for compounds with a methyl or chloromethyl substituent indicate that the deactivation due to the inductive effect of α-chlorine substituent is more important than the acceleration due to the resonance effect. However, in the reaction of the compounds bearing a dichloromethyl substituent, the inductive effect is almost offset by the conjugative effect. In an extreme case, such an activating resonance effect may surpass the inductive effect, as may be deduced from the reactivity figures of chloroethanes bearing a trichloromethyl substituent.

Thus, the relative importance of the resonance effect of α-chlorine substituent increases with an increase in the electron-withdrawing character of the R substituent. This tendency is not surprising, since the contribution of structure II to the transition state is more important when the electron-withdrawing character of the R substituent increases. The observations of Henne *et al.* and Benoy may be explained in a similar fashion.

An alternative explanation is, however, possible. According to the Hammond postulation,[16] the transition state in a reaction involving a higher activation energy will more closely resemble the products. Russell and Brown[17] have accounted for the difference between toluene and cyclohexane in relative reactivity for chlorination and bromination in terms of this concept.

When the $-I$ effect of the R substituent is not so great, the hydrogen abstraction by a chlorine atom will involve a relatively low activation energy. On the basis of the present data, the activation energies for the reactions of methyl, chloromethyl, and dichloromethyl groups of ethane, ethyl chloride, and ethylidene chloride may be estimated to be approximately 1—3 kcal/mol lower than that for 2, 2-dichloropropane. In these reactions the transition state will resemble the reactants; that is, a C–H bond which is being broken is stretched by only a small amount. Consequently, the resonance contribution of the α-chlorine substituent to the stabilization of the incipient radical will not be important.

On the other hand, when deactivation due to the $-I$ effect of the R substituent is serious, the C–H bond breaking in the transition state will become significant. The activation energy of the reaction of compounds with a trichloromethyl group is estimated to be 2—4 kcal/mol higher than that for the reaction of 2, 2-dichloropropane. In this case, therefore, the C–H bond in the transition state will be extensively broken, so the resonance effect of α-chlorine substituent may contribute to the stabilization of the transition state.

Experimental

Materials. 1, 1-Dichloro, 1, 1, 1-trichloro-, and pentachloroethane were purified by fractionating commercial materials through a Vigreux column. The boiling points were 57°C, 74°C, and 162°C respectively. 1, 2-Dichloro, 1, 1, 2-trichloro-, and 1, 1, 2, 2-tetrachloroethane were purified by treating technical

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[14] J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Company, New York (1962), p. 460.

[15] C. Walling, "Free Radicals in Solution," John Wiley, New York (1957), p. 51.

[16] G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955).

[17] G. A. Russell and H. C. Brown, *ibid.*, **77**, 4578 (1955).

materials with concentrated sulfuric acid and then distilling them through a Vigreux column. The boiling points were 81°C, 112—113°C, and 146°C respectively.

Ethyl chloride was prepared from ethanol by a method analogous to that used in the preparation of *n*-butyl chloride,[18] bp 12.3°C (yield 90%). 1, 1, 1, 2-Tetrachloroethane was prepared by adding hydrogen chloride to trichloroethylene in the presence of aluminum chloride.[19] The product was purified by vacuum distillation (62°C/100 mg), n_D^{26} 1.4790 (lit.[19] n_D^{25} 1.47941).

2, 2-Dichloropropane was prepared by treating acetone with phosphorus pentachloride, bp 70°C (lit.[20] 70.5°C). Among the authentic samples of chlorination products, 1, 2, 2-trichloropropane was prepared by the photochlorination of 2, 2-dichloroethane, bp 122—123°C (lit.[21] 122.5°C). Hexachloroethane was purified by sublimation, mp 185°C.

The purified samples of ethyl chloride, 1, 1-dichloroethane, 1, 2-dichloroethane, 1, 1, 1-trichloroethane, and 1, 1, 2-trichloroethane were shown by v.p.c. analysis to be essentially 100% pure, no impurities being detected in these cases. The samples of 1, 1, 1, 2-tetrachloroethane, 1, 1, 2, 2-tetrachloroethane, and pentachloroethane were estimated by v.p.c. to be more than 98% pure, the impurities being 1, 1, 1-trichloroethane, 1, 1, 2-trichloroethane, and 1, 1, 2, 2-tetrachloroethane respectively.

Competitive Chlorination Procedure. A 2 m*l* portion of a binary mixture of an appropriate chloroethane and 2, 2-dichloropropane (the molar ratios are shown in Table 2) was introduced into a reaction tube attached to a vacuum line, and the mixture was degassed. A measured amount of chlorine was then condensed in the tube through a gas buret. The tube was sealed and immersed in a thermostat and irradiated with a 200W tungsten lamp until the chlorine color disappeared.

Analyses of the products were carried out by the v. p. c. method employing a 2.5-m. Apiezon L column (90—150°C, He; 0.6 kg/cm^2) which was found to be more suitable for analysis than such other columns as QF-1, Silicon D. C. 550, T. C. P., D. O. P., P. E. G. 6000, and P. M. P. E. Under the conditions employed, an excellent separation of the product peaks was realized by the v. p. c. method.

In a series of v. p. c. analyses each of the chlorination mixtures was put through the v. p. c. in order to check the polychlorination products. This procedure revealed that the consecutive reaction products do not interfere with the analysis to any detectable extent under the experimental conditions. By another series of analyses, the conversion was estimated to be less than 10% in all cases.

The data listed in Table 1 were calculated as follows (See Table 1). In the competitive chlorination of 1, 1-dichloroethane in the presence of 2, 2-dichloropropane (Run 10), $[C_2H_4Cl_2]_0/[Me_2CCl_2]_0$, $[CH_3CCl_3]/[CH_3CCl_2CH_2Cl]$, and $[CH_2ClCHCl_2]/[CH_3CCl_2CH_2Cl]$ values were 1.09, 0.97, and 0.30 respectively. Hence, the rate of the chlorination of 1, 1-dichloroethane compared to 2, 2-dichloropropane is $(0.97+0.30)/1.09$. Relative to only one of the six available positions of the dichloropropane, this becomes $(1.27/1.09)\times 6$. From the above isomer distribution of the chlorination products and the number of available hydrogens the substitution of which can lead to the trichloroethane isomers, the relative rates of chlorination of the 1- and 2-positions of 1, 1-dichloroethane become $(0.97/1.09)\times 6/1=5.3$ and $(0.30/1.09)\times 6/3=0.55$.

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[18] "Organic Syntheses," Coll. Vol. I, p. 142 (1948).

[19] H. J. Prins, *Rec. Trav. Chim.*, **45**, 80 (1926); R. R. Dreisbach and R. A. Martin, *Ind. Eng. Chem.*, **41**, 2875 (1949).

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