Chlorination by Sulfuryl Chloride. III.[1] *The Reactivities of the C–H Bond to Sulfuryl Chloride*

By Mannosuke ARAI

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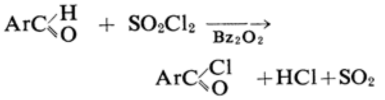
In a previous paper,[2] the author established that the action of sulfuryl chloride, in the presence of peroxide, on aromatic aldehydes with various nuclear substituents other than hydroxyl, resulted in the replacement of aldehydic hydrogen by chlorine, giving the corresponding acid chlorides.



$$\mathrm{ArC}\overset{\mathrm{H}}{\underset{\mathrm{O}}{\lessdot}} + \mathrm{SO_2Cl_2} \xrightarrow[\mathrm{Bz_2O_2}]{} \mathrm{ArC}\overset{\mathrm{Cl}}{\underset{\mathrm{O}}{\lessdot}} + \mathrm{HCl} + \mathrm{SO_2}$$

Aliphatic hydrocarbons and the side chain of aralkyl hydrocarbons have also been established by Kharasch and Brown[3] to undergo a similar chlorination reaction. In order to establish the reactivity of various types of C–H bonding in relation to that of aldehydic hydrogen, the competitive chlorination of benzaldehyde and aralkyl and alicyclic hydrocarbons has now been carried out using sulfuryl chloride. The results are presented in this paper.

Experimental

Materials and Reagents.—Toluene, cyclohexane, cumene and *t*-butyl benzene (all reagent grade) were purified in advance by fractional distillation, and the purified materials were redistilled before use.

Benzaldehyde (reagent grade) was purified by vacuum distillation under a nitrogen atmosphere; freshly-distilled middle-cut was used for the experiment.

Sulfuryl chloride (first grade) was fractionally distilled, stored in a bottle wrapped with aluminum foil, and kept in a desiccator.

General Procedure for Chlorination. — The materials to be chlorinated competitively were placed in a 100 ml. round-bottomed flask equipped with a stirrer, a dropping funnel, and a reflux condenser, to which a calcium chloride tube was attached. After the air in the system had been replaced by dry nitrogen, benzoyl peroxide (0.1% of the weight of the sulfuryl chloride used) was added to the flask and the system was heated to 80±1°C. When sulfuryl chloride was gradually added through the dropping funnel, the evolution of gas was observed after some induction period. Heating was continued until the gas evolution ceased. After cooling, the hydrogen chloride formed was driven off by passing nitrogen through.

Analytical Procedures.—The reaction mixture obtained by the method descrived above was weighed. Any loss of weight during the reaction was distributed to each starting material according to the relative ratio of the vapor pressure.

The total chlorine content was determined by Rauscher's method[4] the reaction mixture (2 ml.) was heated with sodium in xylene for 2 hr. under reflux. *n*-Butanol was used to accelerate the reaction in place of amyl alcohol, which has been reported to contain halogens as impurities.[5] The sodium chloride obtained was determined by Mohr's method, using silver nitrate.

In order to determine the amount of benzoyl chloride produced, the reaction mixture (2 ml.) was decomposed by 80% ethanol at room temperature for 3 hr., thus forming hydrochloric acid, which was then titrated with sodium hydroxide potentiometrically. This method was established by experimentation using known amounts of benzoyl chloride and benzyl chloride in a mixture of toluene and benzaldehyde. It is also known that 2-chloro-2-phenylpropane, the chlorination product of the α-position of cumene, is decomposed quantitatively by 80% ethanol.[6]

Results and Discussion

The relative reactivity of toluene to benzaldehyde was first determined by means of competitive chlorination, using ca. 1/10 mol. of sulfuryl chloride. Under these conditions, the formation of dichlorocompounds can be ignored. The results are shown in Table I.

The relative reactivity is determined by the following scheme, using benzaldehyde as a standard:

$$\mathrm{RH} + \cdot\mathrm{SO_2Cl} \xrightarrow{k} \mathrm{R}\cdot + \mathrm{HCl} + \mathrm{SO_2}$$

$$\mathrm{BzH} + \cdot\mathrm{SO_2Cl} \xrightarrow{k'} \mathrm{Bz}\cdot + \mathrm{HCl} + \mathrm{SO_2}$$

$$\frac{k}{k'} = \frac{\log\left([\mathrm{RH}]_{\mathrm{int}}/[\mathrm{RH}]_{\mathrm{fin}}\right)}{\log\left([\mathrm{BzH}]_{\mathrm{int}}/[\mathrm{BzH}]_{\mathrm{fin}}\right)}$$

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[1] Part II: M. Arai, This Bulletin, 35, 1271 (1962).

[2] M. Arai, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), 81, 1450 (1960).

[3] M. S. Kharasch and H. C. Brown, *J. Am. Chem. Soc.*, 61, 2142 (1939).

[4] W. H. Rauscher, *Ind. Eng. Chem., Anal. Ed.*, 9, 296 (1937).

[5] C. Walling and B. Miller, *J. Am. Chem. Soc.*, 79, 4181 (1957).

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

TABLE I. COMPETITIVE CHLORINATION OF BENZALDEHYDE AND TOLUENE AT 80°C[a]

Reactant	mol.	mol.
Benzaldehyde	0.280	0.171
Toluene	0.253	0.326
Sulfuryl chloride	0.040	0.034
Product		
Total chlorides	0.0398	0.0338
Benzoyl chloride	0.0308	0.0211
Benzyl chloride[b]	0.0090	0.0127
Benzaldehyde[c]	0.249	0.150
Toluene[c]	0.244	0.313
Reactivity of toluene	0.305	0.310
Mean	0.31	

a) In the presence of benzoyl peroxide
b) Total chlorides minus benzoyl chloride
c) Initial quantity minus the amount substituted and the amount vaporized

where $[\ ]_{\text{int}}$ and $[\ ]_{\text{fin}}$ denote the initial and the final concentration respectively.

Table I shows the reactivity of toluene to be 0.31 that of benzaldehyde.

Similar experimentation on and calculations of cyclohexane and benzaldehyde lead to the results listed in Table II, which shows the reactivity of cyclohexane to be 3.64 times that of benzaldehyde.

TABLE II. COMPETITIVE CHLORINATION OF BENZALDEHYDE AND CYCLOHEXANE AT 80°C[a]

Reactant	mol.	mol.
Benzaldehyde	0.248	0.339
Cyclohexane	0.261	0.245
Sulfuryl chloride	0.043	0.042
Product		
Total chlorides	0.0416	0.0421
Benzoyl chloride	0.0091	0.0123
Chlorocyclohexane[b]	0.0325	0.0298
Benzaldehyde[c]	0.239	0.327
Cyclohexane[c]	0.228	0.215
Reactivity of cyclohexane	3.65	3.62
Mean	3.64	

a) In the presence of benzoyl peroxide
b) Total chlorides minus chlorocyclohexane
c) Initial quantity minus the amount substituted and the amount vaporized

From the relative reactivity (0.31) of toluene to benzaldehyde, the value of 11.8 was derived as that of cyclohexane vs. toluene. The value thus derived indirectly is somewhat smaller than the value (13.1) obtained by Russell and Brown through the competitive chlorination of cyclohexane and toluene at 80°C directly.[6]

Next, the relative reactivity of cumene vs. benzaldehyde was examined. Since cumene has two kinds of hydrogen—a tertiary hydrogen at the α-position and six primary hydrogens at the β-position—all of which can be subjected to abstraction, it is of interest to determine each of the isomers formed and to see the relative reactivity of these two different hydrogens. Cumene was reacted at 80°C with ca. 1/10 mol. of sulfuryl chloride and benzoyl peroxide; the total amounts of chlorides and α-chloride (2-chloro-2-phenylpropane) in the product were determined separately, the amount of β-chloride (1-chloro-2-phenylpropane) being obtained as the difference between these two figures. The ratio of the isomers in the product is summarized in Table III.

TABLE III. ISOMER DISTRIBUTION OF CUMENE BY CHLORINATION AT 80°C[a]

Reactant	mol.	mol.
Cumene	0.334	0.496
Sulfuryl chloride	0.034	0.062
Product		
Total chlorides	0.0334	0.0622
α-Chloride	0.0270	0.0544
β-Chloride[b]	0.0044	0.0078
α-Chloride/β-Chloride	6.59	7.00
Mean	6.80	

a) In the presence of benzoyl peroxide
b) Total chlorides minus α-chloride

The ratio, 6.80, of α-chloride to β-chloride gives 40.8 per hydrogen at both positions. This value is rather close to the figure obtained by Kharasch[3] in 1939 from a similar reaction

TABLE IV. COMPETITIVE CHLORINATION OF BENZALDEHYDE AND CUMENE AT 80°C[a]

Reactant	mol.	mol.
Benzaldehyde	0.182	0.154
Cumene	0.275	0.378
Sulfuryl chloride	0.039	0.039
Product		
Total chlorides	0.0380	0.0392
(HCl)[b]	0.0346	0.0354
Cumene-β-chloride[c]	0.0034	0.0038
Cumene-α-chloride[d]	0.0231	0.0258
Benzoyl chloride[e]	0.0115	0.0096
Benzaldehyde[f]	0.170	0.144
Cumene[f]	0.248	0.348
Reactivity of cumene	1.51	1.23
Mean	1.37	

a) In the presence of benzoyl peroxide
b) The amount of HCl by hydrolysed with 80% EtOH, —— cumene-α-chloride and benzoyl chloride
c) Total chlorides minus (HCl)
d) 6.80 times β-chloride
e) (HCl) minus α-chloride
f) Initial quantity minus the amount substituted and the amount vaporized

in benzene, but it is different from the value, 2.13, derived from the photochlorination using chlorine.[7]

The competitive chlorination of benzaldehyde and cumene was realized, after a consideration of the isomer distribution. The ratio of the reactivity of cumene to that of benzaldehyde is shown to be 1.37 (Table IV); that is, the ratio is 4.43 to toluene. Our direct comparison of the reactivities of cumene and toluene is summarized in Table V.

Table V shows that the cumene vs. toluene ratio is 4.33, which is in good agreement with the value obtained indirectly in Table IV.

TABLE V. COMPETITIVE CHLORINATION OF TOLUENE AND CUMENE AT 80°C[a]

Reactant	mol.
Toluene	0.221
Cumene	0.230
Sulfuryl chloride	0.037
Product	
Total chlorides	0.0373
Cumene-α-chloride	0.0265
Cumene-β-chloride[b]	0.0039
Benzyl chloride[c]	0.0069
Toluene[d]	0.214
Cumene[d]	0.200
Reactivity of cumene	4.33

a) In the presence of benzoyl peroxide
b) (1/6.80) α-Chloride
c) Total chlorides minus cumene α- and β-chlorides.
d) Initial quantity minus the amount substituted and the amount vaporized

TABLE VI. COMPETITIVE CHLORINATION OF BENZALDEHYDE AND *t*-BUTYLBENZENE AT 80°C[a]

Reactant	mol.
Benzaldehyde	0.164
t-Butylbenzene	0.255
Sulfuryl chloride	0.041
Product	
Total chlorides	0.0406
Benzoyl chloride	0.0289
Neophyl chloride[b]	0.0117
Benzaldehyde[c]	0.135
t-Butylbenzene[c]	0.243
Reactivity of *t*-butylbenzene	0.25

a) In the presence of benzoyl peroxide
b) Total chloride minus benzoyl chloride
c) Initial quantity minus the amount substituted and the amount vaporized

The results of a similar reaction of benzaldehyde and *t*-butyl benzene are summarized in Table VI, which shows that the reactivity of the latter is 25% that of the former. The relative value of *t*-butyl benzene to toluene is found from this value to be 0.80, which is again in good agreement with Russell's value,[6] 0.81, derived from the direct competitive reaction.

The results obtained above are summarized in Table VII and in Fig. 1.

TABLE VII. RELATIVE REACTIVITY ON A MOLECULAR AND BOND BASIS

	Molecule[a]		C-H Bond[b]
	A	B	
Benzaldehyde	1.00	3.23	9.7
Toluene	0.31	1.00	1.00
Cumene	1.37	4.42 (4.23)[c]	
t-Hydrogen			11.6
prim-Hydrogen			0.28
t-Butylbenzene	0.25	0.80 (0.81)[c]	0.27
Cyclohexane	3.64	11.8 (13.2)[c]	2.9

a) Reactivity per molecule
b) Reactivity per C-H bond
c) The numerical values in parentheses are based upon the competitive reaction with toluene

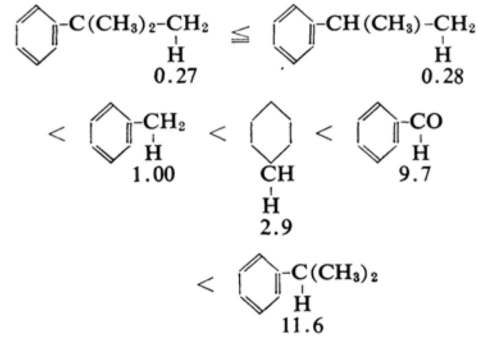

Fig. 1

The results of the chlorination by sulfuryl chloride are listed in Table VIII; those obtained by other halogenation reagents are shown for the sake of comparison.

The reaction with sulfuryl chloride is similar to the photochlorination using chlorine, but it has a higher selectivity. The hydrogen abstraction from the C–H bond in toluene would be expected to be accelerated by the formation of a stable benzyl radical in comparison with the case of cyclohexane, where no such acceleration can be expected. However, the reverse has been found to be the case

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[7] G. A. Russell and H. C. Brown, ibid., 77, 4031 (1955).

TABLE VIII. COMPARISON OF RADICAL HALOGENATION AGENTS

	SO_2Cl_2	Cl_2[3]	Br_2[a]	C_4H_9OCl[b]
Toluene	1.0	1.0	1.0	1.0
Cumene				
(*tert.*)	11.6	4.0	>1	6.84
(*prim.*)	0.28	0.31	v. small	0.26
t-Butylbenzene	0.27	0.22	v. small	0.105
Cyclohexane	2.9	2.8	0.004	1.5

a) P. C. Anson, P. S. Fredericks and J. M. Tedder, *J. Chem. Soc.*, **1959**, 918.

b) C. Walling and B. B. Jacknow, *J. Am. Chem., Soc.*, **82**, 6108 (1960).

in the present study. This phenomenon can be rationalized, following Russell's explanation in his photochlorination, in terms of the inductive effect of the phenyl group in toluene. The aldehydic hydrogen in benzaldehyde has, as is shown in Table VII, a higher relative reactivity. This may be explained, together with the case of the tertiary hydrogen in cumene, by the greater stability of the radical formed in its transition state and by the weaker polar effect. However, more extensive studies are necessary before any definite conclusion can be drawn on this point.

The ratio of isomer formation in the chlorination of cumene (*tert/prim*) is 6.80, as has been described, which is far different from the ratio, 3.13, in photochlorination. This difference is of interest and is meaningful in connection with the reaction mechanism of the chlorination by sulfuryl chloride. Two mechanisms have hitherto been proposed for the radical chlorination by the reagent. One is that the chlorosulfonyl radical produced by the initiator decomposes to form the chlorine atom, which is the actual reacting species (equilibrium 1 and reaction 2).

$$SO_2Cl\cdot \rightleftarrows SO_2 + Cl\cdot \qquad (1)$$

$$RH + Cl\cdot \rightarrow R\cdot + HCl \qquad (2)$$

$$RH + SO_2Cl\cdot \rightarrow R\cdot + SO_2 + HCl \qquad (3)$$

$$R\cdot + SO_2Cl_2 \rightarrow RCl + SO_2Cl\cdot \qquad (4)$$

The other, alternative mechanism is that the chlorosulfonyl radical itself is responsible for the hydrogen abstraction (reaction 3). The latter mechanism has been established in the peroxide-catalyzed reaction of sulfuryl chloride with olefins.[8,9] Therefore, the different isomer distributions in the products obtained from cumene by photochlorination and by sulfuryl chloride chlorination is assumed to be based upon the difference between the actions of the chlorine atom and the chlorosulfonyl radical.

Russell[10] has concluded that, as a result of the solvent effect in the radical chlorination reaction, sulfuryl chloride reacts as does chlorosulfonyl radical in the presence of aliphatic solvents, while in aromatic solvents solvated chlorine atoms are the reacting species, as in the case in photochlorination. Since the isomer ratio in the chlorination products of cumene is supported experimentally by Kharasch,[3] an active hydrogen such as tertiary hydrogen in cumene is assumed to be abstracted by the chlorosulfonyl radical, which has greater selectivity than the chlorine atom, even in the aromatic solvent, contrary to Russell's explanation.

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Kawauchi College
Tohoku University
Kawauchi, Sendai

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[8] M. S. Kharasch and A. F. Zavist, ibid., **73**, 964 (1951).

[9] A. Y. Yakubovich and Y. M. Zinovev, *J. Gen. Chem.* (*U. S. S. R.*), **17**, 2028 (1947); *Chem. Abstr.*, **43**, 1248 (1949).

[10] G. A. Russell, *J. Am. Chem. Soc.*, **80**, 5002 (1958).