

SMALL RING COMPOUNDS—XXX¹

HOMOLYTICAL AROMATIC SUBSTITUTION AND HYDROGEN ABSTRACTION REACTION WITH CYCLOPROPYL RADICAL

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Abstract—Homolytic aromatic substitution and hydrogen abstraction reactions with cyclopropyl radical were carried out to determine the reactivity and ionic character of cyclopropyl radical by examination of the orientation effect, partial rate factor and influence of substituents. By thermal decomposition of biscyclopropaneformyl peroxide in a series of substituted benzenes, the corresponding cyclopropylated benzene derivatives (the mixture of *ortho*, *meta* and *para* isomers) were obtained in moderate yield. In view of the orientation effect and the partial rate factor, the cyclopropyl radical seems to be fairly free from polar effect, and to resemble the phenyl radical more than the common alkyl radical although the cyclopropyl radical has a slightly higher reactivity than the phenyl radical. The relative reactivity of the 2-phenylcyclopropyl radical in the hydrogen abstraction reaction toward the benzylic position of ring-substituted toluenes gave good Hammett's correlation with the slope of +0.20 suggesting little ionic character in the transition state. This result was in good agreement with the conclusion obtained from homolytic aromatic substitution reaction and with the chemical reactivity to be expected from the non-planar nearly sp^2 -hybridized conformation of the cyclopropyl radical.

INTRODUCTION

The stereoconfigurational stability of the cyclopropyl radical has received much attention²⁻⁴ and although the pyramidal configuration of this radical has been proposed by Walborsky³ and Ando⁴, only little is known concerning character and reactivity.^{5a,b}

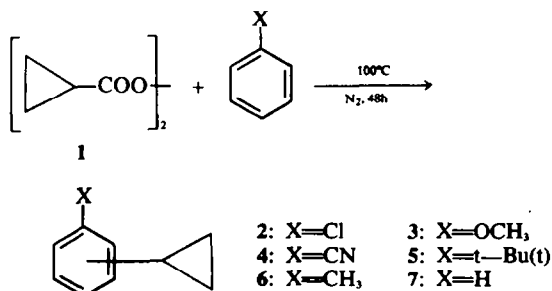
It has been suggested⁶⁻¹¹ that the increase in *s*-character of the orbital occupied by the odd electron of a radical makes its nature in homolytic aromatic substitution more electrophilic. Thus, it may be expected that the ionic character and reactivity of the cyclopropyl radical are analogous to those of the vinyl radical rather than common alkyl radical, since the hybridization state of cyclopropane C-H bond has been proposed to be rather sp^2 than sp^3 . Therefore, in the present study, the homolytic aromatic substitution and hydrogen abstraction reaction with respect to the cyclopropyl radical were carried out.

RESULTS

Homolytic aromatic substitution reaction

Biscyclopropaneformyl peroxide (1) was thermally decomposed in a series of substituted benzenes at 100° for about 2 days and the corresponding cyclopropylated benzenes 2-7 were obtained in moderate yields. Determination of the distribution of the positional isomers (*ortho*, *meta* and *para*) in each product was accomplished by gas chromatographic analysis. (Golay Column; MBMA-45m)

The distribution of each isomer and the yield of



all of the cyclopropylated benzenes are summarized in Table 1, in which the distributions reported in the similar reactions of cyclohexyl radical⁷ and phenyl radical⁹ are indicated for comparison. All of the products were isolated by a preparative gas chromatography and identified by spectroscopic and elemental analyses. Furthermore, some of them were characterized by comparison of their spectroscopic and gas chromatographic behaviour with those of authentic samples.¹³ The low yield of cyclopropylated toluene (6) was rationalized by the existence of the competitive hydrogen abstraction reaction of cyclopropyl radical from the benzylic position of toluene. The *meta/para* ratios in homolytic aromatic cyclopropylation were calculated from the isomer distributions shown in Table 1 and are indicated in Table 2 together with the corresponding data of phenylation⁷ and cyclohexylation.³ Furthermore, the relative reactivities of the

Table 1. The distribution of the positional isomers in homolytic aromatic substitution

C ₆ H ₅ X	Cyclohexylation(%)			Cyclopropylation(%)			Y ^a (%)	Phenylation(%)		
	<i>ortho</i>	<i>meta</i>	<i>para</i>	<i>ortho</i>	<i>meta</i>	<i>para</i>		<i>ortho</i>	<i>meta</i>	<i>para</i>
C ₆ H ₅ Cl	54	34	12	59	27	14	29.4	50	32	18
C ₆ H ₅ OCH ₃	67	28	5	70	18	12	26.7	69	18	13
C ₆ H ₅ CN	52	4	44	62	11	27	58.2	60	10	30
C ₆ H ₅ Bu(t)	0	72	28	2	64	34	31.7	24	49	27
C ₆ H ₅ CH ₃	32	43	25	52 ^b		48 ^b	14.3	67	19	14

^ayield: ([moles of cyclopropylated benzene]/2) [moles of 1], yield of 7: 25.8%

^bcalculated from NMR spectrum. The separation of *meta* and *para* isomers was impossible in the present study.

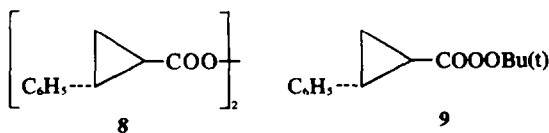
arenes to benzene in the substitution with cyclopropyl radical were determined by a competitive technique.

An appropriate arene-benzene mixture was allowed to react with the cyclopropyl radical and the mixture was analyzed directly by the gas chromatographic technique to determine the relative amount of arylcyclopropane to phenylcyclopropane. From this relative amount, the relative reactivities (K_x^H) of the cyclopropyl radical toward the nuclei of a certain arene to that of benzene may be obtained. The partial rate factors (f_o , f_m , f_p) for the *ortho*, *meta* and *para* positions were calculated from the data in Table 1. Table 3 indicates the relative reactivities and partial rate factors for cyclopropylation together with those of phenylation⁷ and cyclohexylation.⁹

Hydrogen abstraction reaction

Both bis(*trans*-2-phenylcyclopropane) formyl peroxide (8)¹⁴ and *t*-butyl per (*trans*-2-phenylcyclopropane) carboxylate (9)^{2d} were emp-

loyed as precursors of the *trans*-2-phenylcyclopropyl radical.



The reaction products obtained from the thermal decomposition of 8 and 9 in carbon tetrachloride consisted of *trans*- and *cis*-2-phenylcyclopropyl chlorides, (10a and 10b), *trans*-2-phenylcyclopropanecarboxylic acid (11) and a small amount of phenylcyclopropane (7). All the products were identified by comparison of their spectroscopic and gas chromatographic behaviour with those of authentic samples and their yields were determined through gas chromatographic analysis.

The formation of 10a and 10b as major products indicated that both 8 and 9 decomposed homolytically and the resulting cyclopropyl radical abstracted a Cl atom from carbon tetrachloride. As

Table 2. The *meta/para* ratios in homolytic aromatic substitution

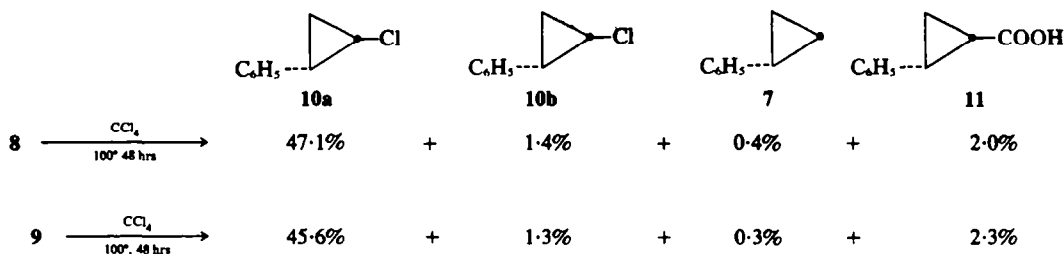
Aromatic	Cyclohexylation	Cyclopropylation	Phenylation
C ₆ H ₅ Cl	2.8	1.9	1.8
C ₆ H ₅ OCH ₃	5.6	1.5	1.4
C ₆ H ₅ CN	0.09	0.43	0.33
C ₆ H ₅ CH ₃	1.7	—	1.4
C ₆ H ₅ Bu(t)	2.5	1.9	1.8

Table 3. Relative reactivity (K_H^X)^a and partial rate factor (f_o , f_m , f_p)^b in homolytic aromatic substitution.

Aromatic	K_H^X	Cyclohexylation			K_H^X	Cyclopropylation			K_H^X	Phenylation		
		f_o	f_m	f_p		f_o	f_m	f_p		f_o	f_m	f_p
C ₆ H ₅ CN	27	42	3.3	72	3.59	5.57	1.03	4.74	3.7	6.5	1.1	6.5
C ₆ H ₅ Cl	3.5	5.6	3.5	2.5	1.78	2.62	1.16	1.26	1.1	1.6	1.0	1.2
C ₆ H ₅ OCH ₃	2.3	4.6	1.9	0.69	1.95	3.38	0.89	1.21	1.7	3.6	0.93	1.3
C ₆ H ₅ CH ₃	0.76	0.73	0.98	1.1	1.03	1.34	—	—	1.2	2.5	0.71	1.0
C ₆ H ₅ Bu(t)	0.28	0	0.60	0.47	0.59	0.04	0.95	1.01	0.64	0.46	0.94	1.0

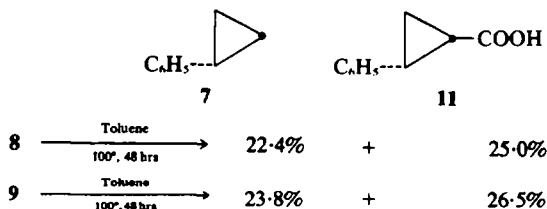
^a $K_H^X = [\text{Arylcyclopropane}]/[\text{Phenylcyclopropane}] \cdot 6/5$

^b $f_o = 5K_H^X \cdot [z]/100 \cdot y$; $y = 1/2$ for *ortho* or *meta* position, $y = 1.0$ for *para* position. The parenthesis [z] represents the distribution of each isomer in cyclopropylated arenes.



was expected, the yield of each product was similar in both cases. The noteworthy formation of 7 may be elucidated by the disproportionation of 2-phenylcyclopropyl radical in solvent cage.³

Phenylcyclopropane (7) was also formed from the thermal decomposition of 8 and 9 in toluene together with a considerable amount of 11.



Thus, the competitive hydrogen abstraction of 2-phenylcyclopropyl radical from the benzylic position of ring-substituted toluenes with chlorine abstraction of the same radical from carbon tetrachloride were carried out at 100° for 48 h using the ampule technique. The relative reactivities of ring-substituted toluenes toward 2-phenylcyclopropyl radical may be estimated through the quantitative analyses of the relative yield of 7 to 10a,b. The relative reactivities (k_H/k_{Cl}), calculated according to the Eq (3)* are summarized in Table 4 and 5.

Table 4. Relative reactivity of ring-substituted toluenes in homolytic hydrogen abstraction reaction with 2-phenylcyclopropyl radical generated from 8^a

$XC_6H_4CH_3$	[7] ^b (%)	10a,b ^c (%)	k_H/k_{Cl} ^d	$\log k_H/k_{Cl}$
<i>m</i> -Cl	11.3	39.9	0.134	-0.873
<i>p</i> -Cl	10.5	41.6	0.120	-0.921
H	10.3	44.4	0.111	-0.955
<i>m</i> -CH ₃	10.1 [*]	45.2	0.106	-0.975
<i>p</i> -CH ₃	10.1 [*]	46.4	0.104	-0.983

^a At 100°, 48 h, [8] initial = 0.1M, [CCl₄]/[XC₆H₄CH₃] = 1/2.

^b Yield of 7 ((moles of 7)/2) [moles of 8]).

^c Yield of 10a,b ((moles of 10a,b)/2) [moles of 8]).

^d Calculated according to Eq 3.

^{*} Corrected for an additional Me group.

Table 5. Relative reactivity of ring-substituted toluenes in homolytic hydrogen abstraction reaction with 2-phenylcyclopropyl radical generated from 9^a

$XC_6H_4CH_3$	[7] ^b (%)	10a,b ^c (%)	k_H/k_{Cl} ^d	$\log k_H/k_{Cl}$
<i>m</i> -Cl	11.1	37.1	0.137	-0.863
<i>p</i> -Cl	10.3	38.0	0.121	-0.917
H	9.1	38.7	0.112	-0.951
<i>m</i> -CH ₃	8.9 [*]	39.0	0.108	-0.967
<i>p</i> -CH ₃	8.9 [*]	39.3	0.105	-0.979

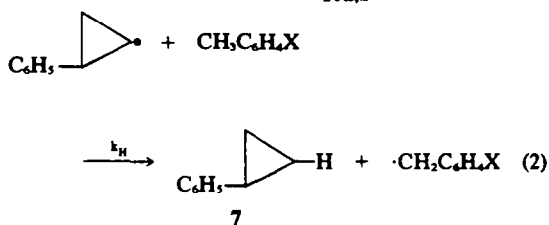
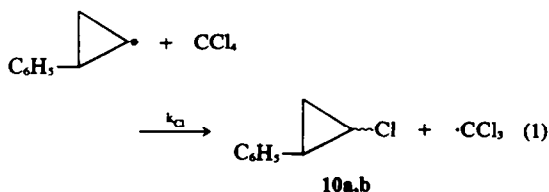
^a At 100°, 48 h, [9] initial = 0.1M, [CCl₄]/[XC₆H₄CH₃] = 1/2

^b Yield of 7 ([moles of 7]/[moles of 9])

^c Yield of 10a,b ([moles of 10a,b]/[moles of 9]).

^d Calculated according to the Eq (3).

^{*} Corrected for an additional Me group.



X = *p*-CH₃, *m*-CH₃, H, *p*-Cl, *m*-Cl

$$k_H/k_{Cl} = \frac{[7] - 0.5}{[10a,b]} \cdot \frac{[CCl_4]}{[CH_3C_6H_4X]} \quad (3)$$

DISCUSSION

As is shown in Table 2, in homolytic substitution reaction, cyclopropylation and phenylation gave a lower *meta/para* ratio than cyclohexylation for the electron-releasing substituents exhibiting *ortho/para* orientation in the common electrophilic aromatic substitution reaction. On the other hand, just the reverse is observed for the strong electron-attracting cyano group. It, thus, may suggest the

*Because of the formation of a small amount of 7 (0.4% from 8 and 0.3% from 9) in carbon tetrachloride, all data were corrected by subtracting 0.5% (as the upper limit) from the yield of 7, as was done for the similar reaction of phenyl radical.¹²

lower nucleophilicity of cyclopropyl and phenyl radicals in comparison with the cyclohexyl radical.

Furthermore, it may be seen from Table 3 that the relative reactivities obtained for cyclopropylation and phenylation varied by less than a factor of 5–6 over the range of the aromatics listed in the Table, while those for cyclohexylation differed by almost a factor of 100. It appears that homolytic aromatic cyclopropylation possesses similar selectivity to that of phenylation and is less selective than cyclohexylation. The correlation of *meta* partial rate factor (f_m) with Hammett's σ -parameters in cyclopropylation is illustrated in Fig 1. A least square analysis of these plots gave a slope of 0.08 (correlation coefficient; 0.756, standard deviation; 0.05). A similar correlation has been recently reported for arylation⁹ ($\rho = 0.05$), cyclohexylation⁷ ($\rho = 1.1$) or silylation¹⁶ ($\rho = 1.4-1.6$).

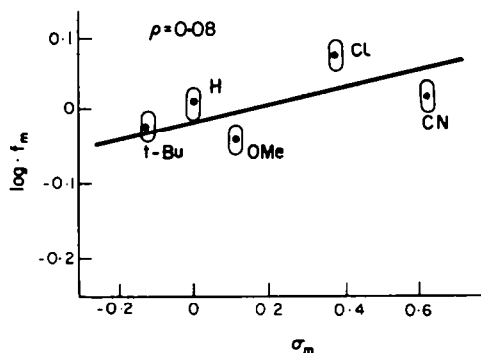


Fig 1. Hammett's correlation for homolytic aromatic cyclopropylation.

The small ρ -value in Fig 1 may indicate little ionic character in the transition state of cyclopropylation. Thus, it might be concluded from these experimental results that the cyclopropyl radical is fairly free from ionic character and considerably less selective in comparison with the common alkyl radical (e.g., cyclohexyl or methyl radical).

The nonpolar character of the cyclopropyl radical may also be shown from hydrogen abstraction reactions of 2-phenylcyclopropyl radical. The relative reactivities (k_H/k_{Cl}) of ring-substituted toluenes toward the 2-phenylcyclopropyl radical gave good linear correlation with Hammett's σ -parameters as are shown in Figs 2 and 3. Least square analyses of the plots in Figs 2 and 3 give the same slope of 0.20 (correlation coefficient; 0.980 (Fig 2), 0.977 (Fig 3), standard deviation 0.014 (Figs 2 and 3)).

It would be interesting if a better correlation was obtained with σ rather than $\sigma+$ values in cyclopropylation. The relatively electrophilic radicals such as Br atom¹⁷, trichloromethyl¹⁸ or peroxy radical¹⁹ showed better correlation with $\sigma+$ than with σ , and gave substantially large negative σ -values in the same type of reactions as is shown in Table 6.

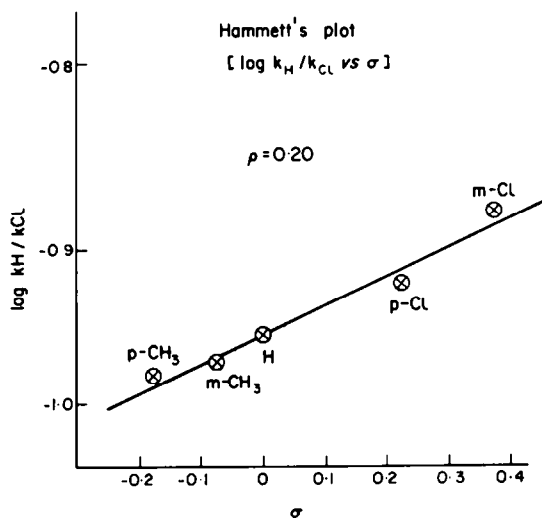


Fig 2. Hammett's plots of the relative reactivities of ring-substituted toluenes with 2-phenylcyclopropyl radical generated from 8.

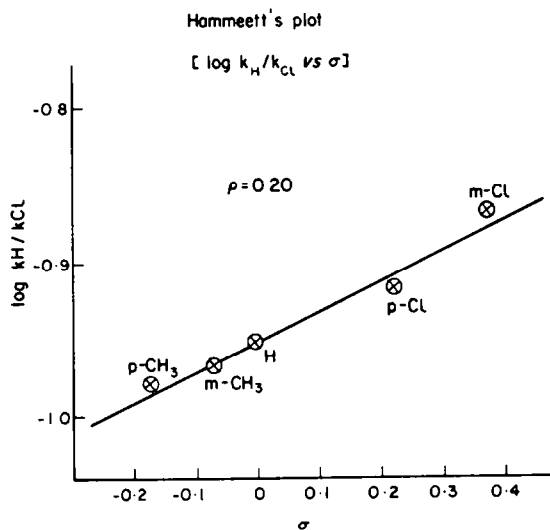


Fig 3. Hammett's plots of the relative reactivities of ring-substituted toluenes in hydrogen abstraction reaction with 2-phenylcyclopropyl radical generated from 9.

Table 6. Polar effect in hydrogen abstraction reactions of various radicals from ring-substituted toluenes

R'	ρ -value	better parameter
Br. ^a	-1.36	$\sigma+$
CCl. ^b	-1.46	$\sigma+$
Cl. ^c	0.66	$\sigma+$ or σ
t-BuO.	-0.32 - 0.39 ^d (-0.75) ^e	$\sigma+$ or σ
Ph. ^f	-0.10	σ
c-Pr.	+0.20	σ

^aRef 17, ^bRef 18, ^cRef 19, ^dRef 20, ^eRef 21, ^fRef 15

The nonpolar character of phenyl radical at the transition state of similar hydrogen abstraction reaction from ring-substituted toluenes ($\rho = -0.1$) was known.¹⁵ Therefore, on the basis of the present study, it seems to be reasonable to propose that the cyclopropyl radical is also almost completely free from polar character and substantially similar to the phenyl radical in reactivity.* This conclusion is in good accordance with the chemical reactivity to be expected from the non-planar nearly sp^2 -hybridized configuration^{3,5b} of the cyclopropyl radical. Finally, these homolytic aromatic cyclopropylation might be of some synthetic utility especially for preparation of cyclopropyl cyanobenzene.

EXPERIMENTAL

Thermal decomposition of bicyclop propaneformyl peroxide (1) in a series of substituted benzenes

General procedure. In 10 ml of one arene (benzene, anisol, monochlorobenzene, cyanobenzene and *t*-butylbenzene) 1¹² (0.85g; 0.005 moles) was dissolved and the soln was heated in an ampule at 100° for 48 h. Then the excess aromatic solvent was evaporated at ordinary pressure and the residue was distilled at reduced pressure. The distribution of the positional isomers of cyclopropylated benzenes and their yields were determined by the gas chromatographic technique (column: silicon DC 550 5m, PEG 2M 5m and Golay Column MBMA 45m). All were isolated through a preparative gas chromatography and their configurations characterized by spectroscopic methods and elemental analyses. Some of them were identified by comparison of their spectroscopic and gas chromatographic behaviour with those of authentic samples.¹³ The spectroscopic and analytical results of these products are shown in Tables 7 and 8.

Preparation of bis(*trans*-2-phenylcyclopropane)formyl peroxide (8). The title compound was prepared from oxidative coupling of *trans*-2-cyclopropanecarbonyl chloride with sodium peroxide according to a modified procedure.¹² m.p. 119°; yield: 49.6%.

Preparation of *t*-butyl per (*trans*-2-phenylcyclopropane) carboxylate (9). In 100 ml anhyd ether *t*-butyl hydroperoxide (54.0 g; 0.60 moles) and anhyd pyridine (71.0 g; 0.80 moles) was dissolved. To this ethereal soln, a soln of *trans*-2-cyclopropanecarbonyl chloride (36.1 g; 0.20 moles) dissolved in 150 ml of anhyd ether was carefully added dropwise with vigorous stirring under cooling in an ice-water bath. The resulting white-suspended soln stood for 24 h at room temp in the dark. Then the mixture was poured into 500 ml ice-water and extracted with ether 3 times. The combined ethereal layer was washed 3 times with 10% H₂SO₄ aq neutralized with 10% Na₂CO₃ aq, finally washed with distilled water and dried over MgSO₄. After the ether was evaporated under reduced pressure at room temp, the residual white solid was washed with *n*-pentane, m.p. 75–76°; yield: 80.0%; IR(nujor): 1765 cm⁻¹ ($\begin{array}{c} \diagup \\ \text{C=O} \\ \diagdown \end{array}$), 1380 cm⁻¹ (—CH₂); NMR (CCl₄, ppm): $\tau = 2.82$ (doublet, 5H, phenyl ring protons), 7.30–7.67 (multiplet, 1H, a benzylic proton),

7.85–8.90 (multiplet, 3H, cyclopropane ring protons), 8.68 (singlet, 9H, *t*-butyl methyl protons); (Found: C, 71.80; H 7.97. C₁₄H₁₆O₂ requires: C, 71.77; H, 7.74%).

Thermal decomposition of 8 or 9 in toluene. In 50 ml freshly distilled toluene, 8 or 9 (0.05 moles) was dissolved and the soln was heated at 100° for 48 h in an ampule. The mixture was analyzed by the gas chromatographic technique using cumene as an internal standard (column: silicon DC 550 2m). Compounds 7²² and *trans* 11²³ were obtained in almost similar yields (ca 22–25%).

Thermal decomposition of 8 or 9 in carbon tetrachloride. In 100 ml freshly distilled CCl₄, 8 or 9 (0.025 mole) was dissolved and the soln was heated at 100° for 48 h in an ampule. The mixture was cooled to room temp and analyzed by the gas chromatographic technique using *m*-chloroallylbenzene as an internal standard. The products consisted of large amounts of *cis* and *trans* 10a,b²⁴, a small amount of *trans* 11 and a trace amount of 7.

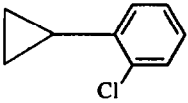
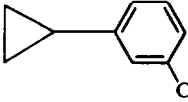
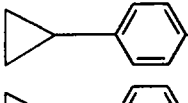
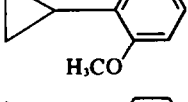
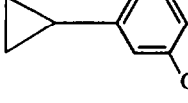
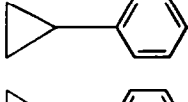
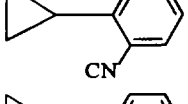
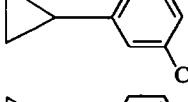
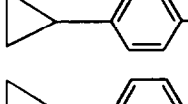
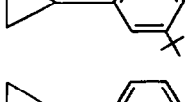
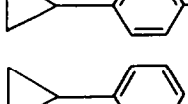
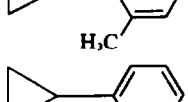
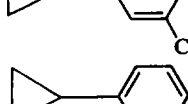
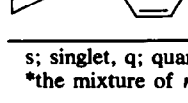
Homolytic competitive abstraction of 2-phenylcyclopropyl radical from the mixture between each of ring-substituted toluene and carbon tetrachloride. In 10 ml of the mixed solvent between 0.05 moles of one of the ring-substituted toluenes (*m*-chloro, *p*-chloro, non-substituted, *m*-methyl, *p*-methyl) and 0.025 mole carbon tetrachloride, 0.001 moles of 8 (or the *t*-butyl perester 9) was dissolved. The soln was heated at 100° for 48 h in an ampule. The mixture was cooled and analyzed by the gas chromatographic technique to obtain the yield of 7 and the total yield of 10a,b. (column: silicon DC 550 5m and PEG 2M 5m). At the same time, a few samples which consisted of various relative amounts of 7 to 10a,b were analyzed by the gas chromatographic technique to get the internal correction curve line. The relative reactivities (k_H/k_{Cl}) of each of the ring-substituted toluenes toward 2-phenylcyclopropyl radical were calculated according to the equation 3.

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*More recently, Stefani¹⁶ suggested the importance of steric effect in addition to that of electronic effect in addition reactions of cyclopropyl radical to a variety of olefines.

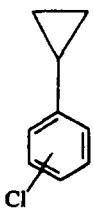
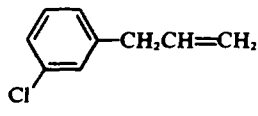
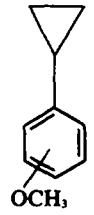
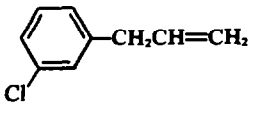
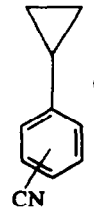
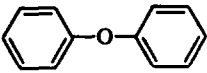
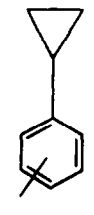
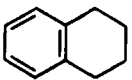
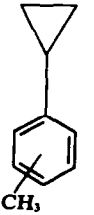
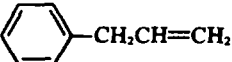
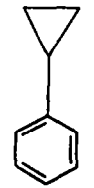
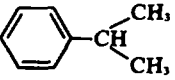
Table 7. The NMR, and IR spectra of the positional isomers of cyclopropyl benzenes

Cyclopropylated benzene deriv		NMR spectra (τ -value, ppm, in CCl_4)	IR spectra (cm^{-1})
	(2) <i>ortho</i>	2.66 ~ 3.29 (m., 4 H), 7.56 ~ 8.12 (m., 1 H) 8.87 ~ 9.56 (m., 4 H)	740
	(2) <i>meta</i>	2.85 ~ 3.30 (m., 4 H), 8.00 ~ 8.34 (m., 1 H) 8.87 ~ 9.48 (m., 4 H)	775, 680
	(2) <i>para</i>	2.97 (q., 4 H), 7.96 ~ 8.43 (m., 1 H) 8.85 ~ 9.57 (m., 4 H)	815
	(3) <i>ortho</i>	2.85 ~ 3.50 (m., 4 H), 6.25 (s, 3 H) 7.63 ~ 8.13 (m., 1 H), 8.92 ~ 9.60 (m., 4 H)	740
	(3) <i>meta</i>	2.85 ~ 3.10 (m., 4 H), 6.28 (s, 3 H) 7.90 ~ 8.45 (m., 1 H), 8.93 ~ 9.55 (m., 4 H)	770, 688
	(3) <i>para</i>	3.21 (q., 4 H), 6.28 (s, 3 H) 7.95 ~ 8.55 (m., 1 H), 8.94 ~ 9.57 (m., 4 H)	819
	(4) <i>ortho</i>	2.34 ~ 3.24 (m., 4 H), 7.45 ~ 7.97 (m., 1 H) 8.60 ~ 9.52 (m., 4 H)	755
	(4) <i>meta</i>	2.35 ~ 3.21 (m., 4 H), 7.79 ~ 8.35 (m., 1 H) 8.62 ~ 9.45 (m., 4 H)	792, 675
	(4) <i>para</i>	2.74 (q., 4 H), 7.80 ~ 8.32 (m., 1 H) 8.74 ~ 9.46 (m., 4 H)	810
	(5) <i>meta</i>	2.84 ~ 3.38 (m., 4 H), 8.05 ~ 8.41 (m., 1 H) 8.73 (s., 9 H), 8.87 ~ 9.45 (m., 4 H)	775, 690
	(5) <i>para</i>	2.97 (q., 4 H), 7.90 ~ 8.40 (m., 1 H) 8.69 (s., 9 H), 8.97 ~ 9.46 (m., 4 H)	812
	(6) <i>ortho</i>	2.75 ~ 3.32 (m., 4 H), 7.61 (s., 3 H) 7.76 ~ 8.43 (m., 1 H), 8.90 ~ 9.47 (m., 4 H)	745
	(6) <i>meta</i> *	2.75 ~ 3.32 (m., 4 H) 7.71 (s., 3 H)	770, 690
	(6) <i>para</i> *		

s; singlet, q; quarter, m; multiplet

*the mixture of *meta* and *para* isomers

Table 8. Elemental analyses of cyclopropyl benzenes

Cyclopropylated benzene derivatives	Internal standard material	Yield	Boiling point	Elementary analyses	
				Calculated	Found
(2) 		29.4%	98°–100° /22 mm (lit. ¹³) 113°–115° /35 mm	for C ₉ H ₉ Cl C; 70.83% H; 5.94% Cl; 23.23%	<i>ortho</i> C; 70.57% H; 5.78% Cl; 23.27% <i>meta</i> C; 70.83% H; 5.94% Cl; 23.23% <i>para</i> C; 70.83% H; 5.84% Cl; 23.19%
(3) 		26.7%	145°– 147°/80 mm (lit. ¹³) 103–104° /35 mm)	for C ₁₀ H ₁₂ O C; 81.04% H; 8.16%	<i>ortho</i> C; 81.25% H; 8.13% <i>meta</i> C; 80.80% H; 8.34% <i>para</i> C; 81.12% H; 8.20%
(4) 		58.2%	120°– 122° /20 mm)	for C ₁₀ H ₉ N C; 83.88% H; 6.34% N; 9.78%	<i>ortho</i> C; 83.99% H; 6.32% N; 10.01% <i>meta</i> C; 83.87% H; 6.51% N; 9.75% <i>para</i> C; 83.63% H; 6.15% N; 9.88%
(5) 		31.7%	105°–108° /57 mm	for C ₁₃ H ₁₄ C; 89.59% H; 10.41%	<i>ortho</i> C; 89.75% H; 10.40% <i>meta</i> C; 89.44% H; 10.20%
(6) 		14.3%	87°–89° /30 mm (lit. ¹³) 101–103° /35 mm)	for C ₁₀ H ₁₂ C; 91.61% H; 8.39%	<i>ortho</i> C; 91.37% H; 8.09% <i>meta</i> C; 91.82% <i>para</i> H; 8.18%
(7) 		25.8%	85°–86° /45 mm	(lit. ¹³)	69–70°/21 mm)

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