The Oxidation of Toluene by Cobalt–Copper–Bromide System. A Side-chain Acetoxylation

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The liquid-phase oxidation of toluene catalyzed by the cobalt(II) ion and the bromide ion in the presence of the copper(II) ion has been studied. Benzyl acetate was obtained in a good yield (50—70%) with mixed catalysts of metal acetates and sodium bromide in acetic acid at 100—150 °C, accompanied by small amounts of benzaldehyde and benzoic acid. The product distribution was greatly dependent on the NaBr concentration, which can be explained in terms of the high oxidizing ability of the copper(II) ion coordinated by the bromide ion. A synergistic effect was found on the yield of benzyl acetate upon the addition of copper(II) acetate with a high NaBr concentration, the maximum yield being obtained at the Co:Cu:NaBr ratio of 1:1:5—10. A change in the oxygen partial pressure also varied the product distribution, suggesting that the competitive reaction of the copper(II) ion with the oxygen molecule for the benzyl radical was simultaneously taking place at a diffusion-controlled rate. Benzyl acetate was considered to result from the oxidation of the benzyl radical by copper(II) bromide and the subsequent solvolysis by acetic acid. The addition of acetic anhydride had a negative effect on the formation of benzyl acetate.

The transition metal ion-catalyzed autoxidation of alkylbenzenes, especially with the cobalt(II) ion and the bromide ion, in acetic acid has been widely studied.[1–6] The autoxidation of *p*-xylene catalyzed by the cobalt(II) ion and the bromide ion to terephthalic acid is important from the viewpoint of the petrochemical industry. The oxidation products, however, are mainly acids or carbonyl compounds, although in rare cases in the presence of acetic anhydride,[2,3] they also include acetoxylated compounds.

Hay[2] has reported that methylbenzenes were converted to the acetoxylated compounds in the oxidation catalyzed by the cobalt(II) ion and the bromide ion in the presence of acetic anhydride, *e.g.*, the oxidation of toluene gave benzyl acetate in a 44% yield, but not in the absence of acetic anhydride. On the other hand, copper(II) acetate is well known to act as an inhibitor[9] in the cobalt(III) ion-catalyzed autoxidation and to behave as an oxidizing reagent for alkyl radicals.[8]

We previously suggested that the deactivation of cobalt(III) acetate by copper(II) acetate in the oxidation of toluene is due to the formation of a binuclear complex.[9] Therefore, it seems difficult to obtain benzyl acetate by the oxidation of toluene, which has a relatively high ionization potential, by copper(II) acetate. Recently, Imamura reported the oxidation of 1,2,3,4-tetrahydronaphthalene catalyzed by copper(II) acetate with a high LiCl concentration; in this case, the copper(II) ion, bearing the Cl ion, was considered to be a monomer species that is capable of oxidizing 1,2,3,4-tetrahydro-1-naphthyl hydroperoxide.[10]

We attempted to obtain benzyl acetate by means of the oxidation of toluene in the presence of cobalt–copper catalysts and found that a side-chain acetoxylation of toluene occurred and that the yield was dependent on the reaction conditions.

Experimental

Materials. The acetic acid, copper(II) acetate, cobalt(II) acetate, and other metal acetates were used without further purification. The sodium bromide were dried under a vacuum at 150 °C for 5 h. The toluene was purified by the usual method: distillation after washing with concentrated sulfuric acid, an aq alkaline solution, and water and drying over ($CaCl_2$ and sodium metal).

Procedure. The oxidation was carried out with two methods.

Method A: A 200 ml three-necked round-bottomed flask equipped with a gas inlet, a thermometer, and a condenser was used. Oxygen was blown onto the surface of the reaction mixture.

Method B: A 200 ml autoclave made of Ti was used. The reaction was carried out with a batch method; the total pressure of the mixed gas was 40 kg/cm^2.

Analysis. The reaction mixture, with an internal standard (1-chloronaphthalene), was poured into ice water and then extracted with ether. The extract was submitted to GC analysis after having been washed with water and aqueous Na_2CO_3 and then dried (Na_2SO_4). The benzoic acid was analyzed by GC directly or after esterification with a MeOH–BF_3 reagent. The products were identified by means of IR, NMR, and GC-MS. PhCHO: 9.9 ppm (1H), 7.7 ppm (5H), 2750 cm^{-1}, 1690 cm^{-1}, M$^+$ 106 (*MW* 106). $PhCH_2OCOCH_3$: 7.3 ppm (5H), 5.1 ppm (2H), 2.1 ppm (3H), 1730—1760 cm^{-1}, 1220—1260 cm^{-1}, M$^+$ 150 (*MW* 150). $PhCH_2Br$: M$^+$ 171 (*MW* 171). A gas chromatograph (Shimadzu GC-3BT) was mainly used for the analysis of the products.

Column: PEG 20 M 10% on Celite 545, 1 m, 2 m, 145 °C, 180 °C, He gas, 40 ml/min.

Results and Discussion

Effect of Bromide-ion Concentration on the Co–Cu Catalysis. The effect of the Br-ion concentration on the product distribution in the presence of cobalt(II) acetate and copper(II) acetate was investigated (Fig. 1). The ratio of the bromide ion to the cobalt(II) ion drastically affected the product distribution. At ratios lower than four, the major product was benzoic acid, while benzyl acetate was formed in only a minor amount. When the ratios were higher than five, the major products were benzyl acetate and benzyl bromide.

On the oxidation of alkyl radicals by copper(II) salts, Kochi[8] clarified that there is an equilibrium between the monomeric and dimeric copper(II) ion,

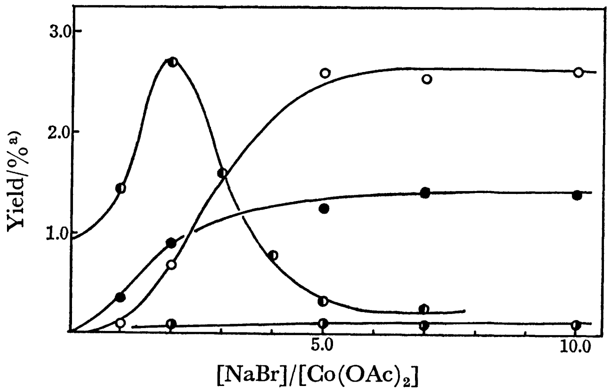

Fig. 1. Oxidation products of toluene catalyzed by Co-Cu-Br as a function of the ratio of [NaBr]/[Co(OAc)$_2$].
Reaction conditions: 100 °C, 20 h, [Co(OAc)$_2$] = [Cu(OAc)$_2$] = 5.71×10^{-2} M, [toluene] = 1.39 M, method A. a) Based on initial toluene.
○: PhCH$_2$OAc, ●: PhCH$_2$Br, ◑: PhCHO, ◐: PhCOOH.

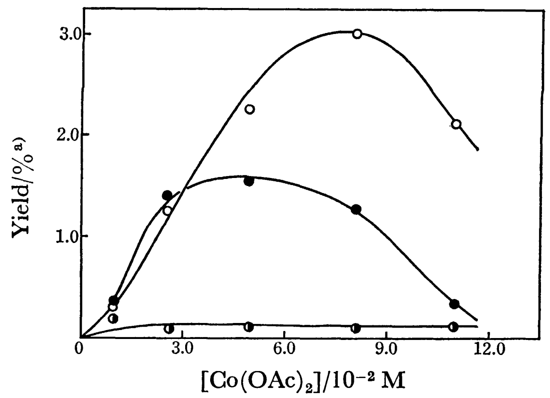

Fig. 2. Oxidation products of toluene catalyzed by Co-Cu-Br as a function of catalyst concentration.
Reaction conditions: 100 °C, 20 h, [Co(OAc)$_2$]: [Cu(OAc)$_2$]:[NaBr] = 1:1:7, [toluene] = 1.39 M, method A. a) Based on initial toluene.
○: PhCH$_2$OAc, ●: PhCH$_2$Br, ◑: PhCHO.

Table 1. Effect of sodium salts on the reaction products in the oxidation of toluene by the Co-Cu system

Sodium salts	Products (mol %)[a]
None	—[b]
NaOAc	
NaCl	—
NaBr	PhCH$_2$OAc (64.3)
	PhCH$_2$Br (11.4)
	PhCHO (1.2)
	PhCOOH (23.1)
NaI	PhCOOH (100)

Reaction conditions: Method A, 100 °C, 24 h, [Co(OAc)$_2$] = [Cu(OAc)$_2$] = 5.71×10^{-2} M, [NaX] = 0.4 M, [toluene] = 1.39 M. a) Based on the total amounts of all oxidation products. b) No reaction occurred.

and that the active species in the oxidation is the monomeric one. Upon the addition of the acetate ion[8] or the chloride ion,[10–12] this dimer-monomer equilibrium becomes favorable to the monomer side. In our experiments, this equilibrium may be present, and the monomer with the bromide ion is predominant upon the addition of the bromide ion to the cobalt–copper system at ratios higher than five; thus, the benzyl radical was oxidized by the monomeric copper(II) ion to benzyl acetate and benzyl bromide. On the other hand, Gaevskii[13] recently discussed the active species in the oxidation of ethyl benzene catalyzed by the cobalt(II) ion and the bromide ion; he concluded that cobalt(III) monobromide is an active species, for it has a high stability constant. Accordingly, at a low ratio of the bromide ion to the cobalt(II) ion, the main reaction may be an abstraction of the α-hydrogen of toluene by cobalt(III) monobromide. Figure 1 indicates that the ratio of the amount of benzyl acetate to that of benzyl bromide retains constant, even when the bromide-ion concentration is increased by a factor of two. This fact suggests that the oxidation of the benzyl radical proceeds not through the carbonium ion but through a so-called ligand-transfer reaction.

Effect of Catalyst Concentration. Figure 2 shows the effect on the oxidation of the catalyst concentration at the ratio of Co : Cu : Br$^-$ = 1 : 1 : 7. The maximum yield of benzyl acetate was obtained at the 0.08 M cobalt concentration.

According to Kochi,[8] this ligand-transfer reaction determines the rate of diffusion control. It seems that a higher catalyst concentration is required since the copper(II) ion and oxygen will be competing for the benzyl radical. However, when the concentration of the catalyst was higher than 0.08 M, low yields of benzyl bromide and benzyl acetate were observed. This phenomenon can be explained in terms of an aggregation of metal acetates[14] or a complex formation between metal acetates and hydroperoxide.[15]

As the concentration of a catalyst becomes higher, the ratio of benzyl acetate to benzyl bromide increases, suggesting that the reaction of benzyl bromide with cobalt(II) acetate is playing a part, an idea supported by Hay.[2]

Effect of Sodium Salts. The effect of sodium salts on the product distribution was also investigated. As may be seen from Table 1, it is obvious that the bromide ion is the most effective for the synthesis of benzyl acetate. According to the studies by Imamura[10–12] of the liquid-phase oxidation catalyzed by the Cu–Cl system, the main reaction is a decomposition of hydroperoxide by Cu–Cl compounds and no significant oxidation by the Co–Cu–Cl system seems to occur, since hydrogen abstraction is important in this reaction. The addition of sodium acetate did not change the oxidizing activity of the Co–Cu system and resulted in the recovery of toluene. These results may be attributed to their redox potentials being lower than that of the Co–Cu–Br systems.

When sodium iodide was added to the Co–Cu system, a small amount of benzoic acid was obtained, perhaps for the same reason as in the case of the chloride ion.

Recycling of the Bromide Ion in the Course of the Oxidation. Figure 3 shows the time dependence on the yield of products in the oxidation of toluene in acetic acid at 100 °C. In the early stage of the oxidation, benzyl bromide was primarily formed and benzyl acetate increased gradually. After 20 h, benzyl acetate turned into the major product. Many workers[1—6)] have suggested that the reaction of benzyl bromide with acetic acid proceeds easily at 100 °C. In our study, however, this reaction was very slow, presumably because of the high bromide-ion concentration. The formation of benzyl bromide in the early stage suggests that the ligand transfer by the copper(II) ion is mainly bromide-ion transfer; consequently, the structure of the copper(II) ion might be $CuBr_n^{m-}$. Here, $m=0$—2 and $n=2$—4, according to Imamura.[10—12)] The Br ion concentration decreases in the course of the oxidation; hence, the activity of the copper(II) ion is gradually lost. Under these conditions (method A), benzoic acid and benzaldehyde were minor products, since the oxygen concentration in the reaction media was very low. The dependence of the reaction temperature on the product distribution was also investigated (Table 2).

It was found that the selectivity changes drastically with the reaction temperature and that benzyl bromide disappears at temperatures above 140 °C. As reported by Hay,[2)] the solvolysis of benzyl bromide in the oxidation catalyzed by the cobalt(II) ion and the bromide ion in acetic acid is quite difficult at temperatures lower than 100 °C. In our study, benzoic acid was formed at low reaction temperatures; that is, the oxidizing ability of the cobalt(III) ion was maintained because of the high additional bromide-ion concentration. The amount of products which can be regarded as resulting from the oxidation of the benzyl radical by the copper(II) ion was relatively small because of the deterioration of the copper(II) ion. At low temperatures, the monomeric copper(II) ion gradually turns to a dimer, becoming inactive for the oxidation of the benzyl radical in the course of the oxidation, because the bromide ion in the reaction media decreases because of the slow rate in the solvolysis of benzyl bromide. At 150 °C for 1—5 h, the yield of benzyl acetate was at its maximum. The solvolysis of benzyl bromide may proceed easily at these temperatures.

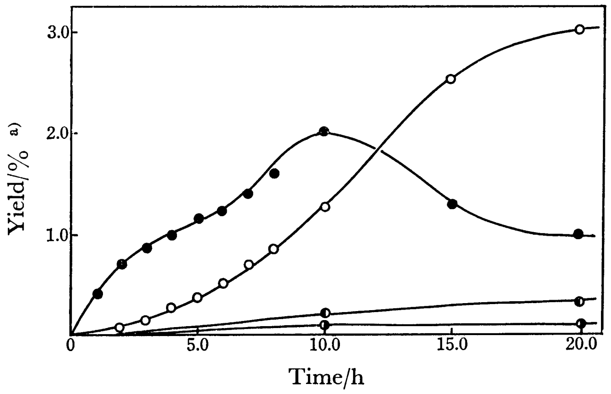

Fig. 3. Oxidation products of toluene catalyzed by Co-Cu-Br as a function of reaction time.
Reaction conditions: 100 °C, $[Co(OAc)_2]=[Cu(OAc)_2]=5.71\times10^{-2}$ M, [NaBr]=0.4 M, [toluene] =1.39 M, method A. a) Based on initial toluene.
○: $PhCH_2OAc$, ●: $PhCH_2Br$, ◑: PhCHO, ◐: PhCOOH.

Therefore, the activity of the catalyst in the oxidation can be maintained. On the other hand, at temperatures higher than 150 °C, the oxidation of benzyl acetate and benzyl bromide can not be ignored, for it results in a lower yield of benzyl acetate.

According to the study by Howard and his coworkers[16)] of the hydrogen abstraction at the α-position of toluene, benzyl bromide, and benzyl acetate by the *t*-butylperoxyl radical at 30 °C, though there is a small difference in the reactivity between the *t*-butylperoxyl radical and cobalt(III) bromide acetate, their rates are 0.012, 0.0075, and 0.006 $M^{-1}\,s^{-1}$ respectively.

Benzyl acetate is oxidized to benzaldehyde *via* benzylidene diacetate. Thus, it is obvious that the optimum reaction temperature is about 150 °C for the synthesis of benzyl acetate.

Effect of the Oxygen Partial Pressure. The dependence of the oxygen partial pressure on the product yields is shown in Table 3. As has been mentioned above, the ligand-transfer is a competitive reaction with the oxygen molecule for the benzyl radical. Therefore, when a low oxygen partial pressure was used, the yield of benzyl acetate was high. However, it should be mentioned that the oxidant in this reaction

TABLE 2. EFFECT OF THE REACTION TEMPERATURE ON THE REACTION PRODUCTS IN THE OXIDATION OF TOLUENE BY THE Co-Cu-Br SYSTEM

Temperature	Toluene conversion	Products (mol %)[a)]			
°C	%	$PhCH_2OAc$	$PhCH_2Br$	PhCHO	PhCOOH
80	12	2	9	34	54
100	54	17	12	49	20
120	66	42	2	29	26
140	64	44	—[b)]	23	43
150	77	49	—	15	33
170	61	48	—	21	30

Reaction conditions: method B, 5 h, total pressure, 40 kg/cm², $(O_2/N_2=1/3)$, $[Co(OAc)_2]=[Cu(OAc)_2]=5.71\times10^{-2}$ M, [NaBr]=0.4 M, [toluene]=1.39 M. a) Based on toluene consumed. b) Not detected.

Table 3. Effect of the partial pressure of oxygen on the reaction products in the oxidation of toluene by the Co-Cu-Br system

Partial pressure of oxygen	Toluene conversion	Products (mol %)[a)]		
kg/cm^2	%	$PhCH_2OAc$	PhCHO	PhCOOH
20	83	29	13	56
10	77	49	15	33
5	34	60	27	12
0	0	Trace	0	0

Reaction conditions: method B, 150 °C, 5 h, $[Co(OAc)_2]=[Cu(OAc)_2]=5.71\times10^{-2}$ M, [NaBr] $=0.4$ M, [toluene] $=1.39$ M. a) Based on toluene consumed.

Table 4. Effect of the $[Cu(OAc)_2]/([Co(OAc)_2]+[Cu(OAc)_2])$ ratio on the reaction products in the oxidation of toluene by the Co-Cu-Br system

[Cu]/([Co]+[Cu])	Toluene conversion	Products (mol %)		
mol %	%	$PhCH_2OAc$	PhCHO	PhCOOH
0.00	98	6	2	88
0.25	91	25	8	66
0.50	77	49	15	33
0.75	76	45	15	37
1.00	65	38	13	48

Reaction conditions: method B, 150 °C, 5 h, $[Co(OAc)_2]+[Cu(OAc)_2]=1.14\times10^{-1}$ M, [NaBr] $=0.4$ M, [toluene] $=1.39$ M; total pressure, 40 kg/cm^2 ($O_2/N_2=1/3$). a) Based on toluene consumed.

is ultimately oxygen; hence, benzyl acetate was not obtained under a nitrogen atmosphere, that is, the active species could not be generated from the reaction between cobalt(II) acetate bromide and the benzylperoxyl radical.

Effect of the Ratio of [Cu]/([Co]+[Cu]). The effect of the copper(II) acetate concentration in the constant NaBr and metal acetate concentrations on the oxidation was also studied (Table 4).

A remarkable synergistic effect was observed at the [Cu]/([Co]+[Cu]) ratio of 0.5; that is, Co : Cu=1 : 1. With an increase in the concentration of copper(II) acetate, the products changed from benzoic acid to benzyl acetate and the conversion of toluene went down little by little. In the region of [Cu]/([Co]+[Cu])=0—0.5, the benzyl radical may react with the oxygen molecule; consequently, the main product was benzoic acid.

On the other hand, the product distribution was similarly changed in the ratio of the 0.5—1.0 region. In the copper(II)-ion and bromide-ion system, although the oxidizing ability was small, as has been shown by Shigeyasu,[17)] benzyl acetate was also obtained as well as a large amount of benzoic acid, and precipitates of presumably copper(II) oxide or hydroxide were formed in a manner similar to the oxidation of naphthalene catalyzed by the palladium–copper–chloride system in acetic acid.[18)] The reason for the synergistic effect is not clear, but it might be due to the formation of a binuclear complex between cobalt(III) acetate and copper(II) acetate. In a study of the additive effect of metal acetates to cobalt(III) acetate, Kawai[9)] suggested that the formation of the binuclear complex was caused by the lowering of the activity and the redox potential of cobalt(III) acetate.

We found that toluene can not be oxidized by cobalt–copper system without the bromide ion, although it was easily oxidized to benzyl acetate by the addition of NaBr.

Additive Effect on the Product Distribution. The additive effects of other transition-metal acetates, acetic anhydride, ethyl methyl ketone, and paraacetaldehyde, were also investigated.

No remarkable effects on the product selectivity were found upon the addition of $Ni(OAc)_2$, $Ce(OAc)_3$, $Cr(OAc)_3$, and $Mn(OAc)_2$.

The synergistic effect of Mn^{2+} in the oxidation of alkylbenzenes catalyzed by the cobalt ion and the bromide ion has previously been reported.[5)]

In our study, however, no additive effect of Mn^{2+} on this system was observed, suggesting that the reaction between the peroxyl radical and the metal ion is not very important. Replacing 0.01 part of acetic acid partly with acetic anhydride reduced the yield of benzyl acetate at 150 °C for 5 h. The same effect was observed with ethyl methyl ketone and paraacetaldehyde.

A reaction between these additives and catalyst seems to occur.

Mechanistic Consideration. A plausible mechanism is shown in the Scheme except for the formation of a binuclear complex between cobalt(III) acetate and copper(II) acetate. The present reaction is considered to be substantially a ligand transfer of the benzyl radical with the copper(II) ion based on the studies by Kochi[8)] in Eqs. 6 and 7. Very recently, the oxidation of methylbenzenes with cerium(IV) pyridinium salt was reported by Rol;[19)] a ligand-transfer reaction similar to that in the case of the copper(II) ion occurs and arylalkyl chloride and arylalkyl methoxide were obtained. The active species in a hydrogen abstraction has been proposed by many workers.[2-6)]

One of the present authors[20)] also clarified that the active species, cobalt(III) acetate bromide, produced by the reaction of cobalt(II) acetate bromide with the peroxyl radical has a reactivity similar to that of the Br radical toward various alkylbenzenes (Eqs. 1 and 3).

$$\mathrm{PhCH_3 + Co(III)Br \longrightarrow PhCH_2\cdot + Co(II)BrH} \qquad (1)$$

$$\mathrm{PhCH_2\cdot + O_2 \rightleftharpoons PhCH_2OO\cdot} \qquad (2)$$

$$\mathrm{PhCH_2OO\cdot + Co(II)BrH \longrightarrow PhCHO + Co(III)Br + H_2O} \qquad (3)$$

$$\mathrm{PhCHO + O_2 \longrightarrow PhCOOH + H_2O} \qquad (4)$$

$$\mathrm{[Cu(OAc)_2]_2} + y\mathrm{NaBr} \rightleftharpoons 2\mathrm{Cu(OAc)}_x\mathrm{Br}_y + y\mathrm{NaOAc} \qquad (5)$$

$$\mathrm{PhCH_2\cdot + Cu(OAc)}_x\mathrm{Br}_y \longrightarrow \mathrm{PhCH_2OAc + Cu(I)} \qquad (6)$$

$$\mathrm{PhCH_2\cdot + Cu(OAc)}_x\mathrm{Br}_y \longrightarrow \mathrm{PhCH_2Br + Cu(I)} \qquad (7)$$

$$\mathrm{PhCH_2Br + AcO^-} \text{ —— } \mathrm{PhCH_2OAc + Br^-} \qquad (8)$$

$$\mathrm{Cu(I) + O_2 + HX \longrightarrow Cu(II)(OAc)}_x\mathrm{Br}_y \qquad (9)$$

$(\mathrm{HX{=}HOAc,\ HBr.}\ \ x=0,1,2,3,4.\ \ y=0,1,2,3,4.)$

Scheme 1. Oxidation mechanism of toluene catalyzed by Co-Cu-Br.

The coupling reaction between the benzyl radical and the oxygen molecule proceeds at the rate of diffusion control, although it is considered that this reaction may proceed to the reverse side in Eq. 2 and the concentration of the benzyl radical in the reaction media will be high at higher temperatures.[21)]

References

1) D. A. S. Ravens, *Trans. Faraday Soc.*, **55**, 1768 (1959).

2) A. S. Hay and H. S. Blanchard, *Can. J. Chem.*, **43**, 1305 (1965).

3) a) Japan Patent Kokai 51-45572; b) T. Nakayama, E. Nakamura, K. Oguchi, and Y. Kamiya, Presented at the 9th Symposium on Oxidation, Tokyo, Japan, November 25—26, 1975.

4) Y. Kamiya, *Tetrahedron*, **22**, 2029 (1966).

5) Y. Kamiya, "Oxidation of Organic Compounds," Am. Chem. Soc. (1968), Vol. 2, p. 193.

6) C. E. H. Bawn and T. K. Wright, *Discuss. Faraday Soc.*, **46**, 164 (1969).

7) R. Hasegawa and Y. Kamiya, *Bull. Chem. Soc. Jpn.*, **51**, 1490 (1978).

8) a) C. L. Jenkins and J. K. Kochi, *J. Am. Chem. Soc.*, **94**, 856 (1972); b) J. K. Kochi and R. V. Subramanian, *J. Am. Chem. Soc.*, **87**, 4855 (1965).

9) R. Kawai and Y. Kamiya, *Nippon Kagaku Kaishi*, **1974**, 933.

10) S. Imamura, M. Teramoto, T. Sumi, H. Aomi, H. Teranishi, and Y. Takegami, *Bull. Chem. Soc. Jpn.*, **49**, 1650 (1976).

11) S. Imamura, T. Banba, and Y. Takegami, *Bull. Chem. Soc. Jpn.*, **46**, 856 (1973).

12) S. Imamura, T. Otani, and H. Teranishi, *Bull. Chem. Soc. Jpn.*, **48**, 1245 (1975).

13) V. F. Gaevskii, N. P. Evmenenko, and L. I. Budarin, *Kinet. Katal.*, **17**, 307 (1976).

14) K. Kagami, *Bull. Chem. Soc. Jpn.*, **41**, 1552 (1968).

15) J. F. Black, *J. Am. Chem. Soc.*, **100**, 5271 (1978).

16) J. A. Howard, *Ad. Free Radical. Chem.*, **4**, 55 (1972).

17) M. Shigeyasu and M. Inoue, *Kogyo Kagaku Zasshi*, **73**, 1155 (1970).

18) G. G. Arzovmanidis and F. C. Rauch, *J. Org. Chem.*, **38**, 4443 (1973).

19) S. Maini and C. Rol, *J. Org. Chem.*, **43**, 3236 (1978).

20) Y. Kamiya, *J. Catal.*, **33**, 480 (1974).

21) S. W. Benson, *J. Am. Chem. Soc.*, **87**, 972 (1965).