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Electron-transfer Reduction of α-Substituted Ketones and 1,2-Diketones with Benzenethiol Mediated by Iron Polyphthalocyanine

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Iron polyphthalocyanine (Fe-poly PC) has been found to act as an electron-transfer reagent in the reductions of α-substituted ketones, α-bromodeoxybenzoin (**1a**), 2-bromopropiophenone (**1b**), α,α-bis(phenylthio)deoxybenzoin (**4**), and 1,2-diketones, benzil (**5**) and 4,5-octanedione (**8**), with benzenethiol. The α-bromo ketones (**1a** and **1b**) have been debrominated to their parent ketones. **4** has been reduced to α-(phenylthio)deoxybenzoin and deoxybenzoin *via* the cleavage of the carbon-sulfur bond, and **5** and **8** to the corresponding α-hydroxy ketones. The ability of Fe-poly PC to perform these reactions is superior to that of iron phthalocyanine (Fe-PC), particularly those reactions in dry benzene. The catalytic action of Fe-poly PC and Fe-PC becomes evident when methanol or 80 vol % aqueous methanol is used as solvent. Furthermore, the reductions of related compounds by the Fe-poly PC-benzenethiol system are described.

Iron polyphthalocyanine (Fe-poly PC) is an electroconductive polymer which has iron(II) ions in a conjugated system.[1] It has been shown that Fe-poly PC is catalytically active for the oxidation of hydrocarbons with oxygen[2] and the reductive dehalogenation of α-halo ketones with 1-benzyl-1,4-dihydronicotinamide.[3] In these reactions, Fe-poly PC assists the transfer of the electron from an electron donor to an electron acceptor to promote the reduction of the electron acceptor coupled to the oxidation of the electron donor. Furthermore, the catalytic effects increase with an increase in the degree of the conjugation of the phthalocyanine polymer. The function of Fe-poly PC may be due to the nature of iron ions bridged with an electron-transferring ligand.[4] Similar phenomena have been observed in the catalytic action of copper polyphthalocyanine on the decomposition of hydrogen peroxide[5] and the exchange reaction between hydrogen and deuterium.[6]

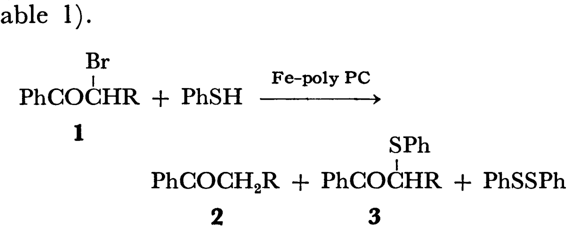
To further explore the catalytic behavior of Fe-poly PC, the reactions of α-substituted ketones and 1,2-diketones (electron acceptors) with benzenethiol (electron donor) have been conducted in the presence of Fe-poly PC. In this paper, the characteristic of Fe-poly PC as an electron-transfer reagent is reported. Some of the results described here have been communicated in a preliminary report.[7]

Results and Discussion

The Properties of Fe-PC and Fe-poly PC. The visible absorption spectrum of Fe-PC and Fe-poly PC using a KBr disk showed absorption maxima at 677 and 725 nm respectively which agrees with previous data.[2] The absorption of Fe-poly PC is shifted towards the longer wavelength by 48 nm at 725 nm compared with Fe-PC. Thus, Fe-poly PC is a stronger electron donor than Fe-PC.

The value of ρ_{20} of the electrical conductivity of Fe-poly PC was 2×10^6 ohm-cm and it is apparent that Fe-poly PC has a better electron-conducting property than Fe-PC ($>10^9$ ohm-cm[8]). Furthermore, the catalytic activity of Fe-poly PC in the oxidation of acetaldehyde ethylene acetal with oxygen at room temperature was similar to that of the previously prepared Fe-poly PC.[2] On the other hand, Fe-PC did not show any activity. In this paper, Fe-PC and Fe-poly PC which have these properties have been used.

Reductive Dehalogenation of α-Halo Ketones. Function of Fe-poly PC: In the absence of Fe-poly PC, α-bromodeoxybenzoin (**1a**) and 2-bromopropiophenone (**1b**) did not react under nitrogen with benzenethiol in dry benzene at 80 °C. In 80 vol % aqueous methanol, α-phenylthio ketones (**2a** and **2b**) were obtained in high yields, as Table 1 shows. The reaction of 2-bromoacetophenone (**1c**) with benzenethiol gave 2-(phenylthio)-acetophenone (**3c**) even in dry benzene. In these reactions, the reductive debromination of **1a**, **1b**, and **1c** did not occur. Furthermore, Fe-poly PC did not react under similar conditions with **1a**, **1b**, and **1c**. When Fe-poly PC (iron ion: α-bromo ketone molar ratio = 1 : 1) was suspended in a solution containing α-bromo ketones (**1**) and benzenethiol in dry benzene or 80 vol% aqueous methanol and the solution heated at 80 °C (under conditions similar to those used in the absence of Fe-poly PC), the debromination products (**2**) were produced (Table 1).



$$\mathrm{PhCO\overset{Br}{C}HR} + \mathrm{PhSH} \xrightarrow{\text{Fe-poly PC}} \mathrm{PhCOCH_2R} + \mathrm{PhCO\overset{SPh}{C}HR} + \mathrm{PhSSPh}$$

1 **2** **3**

(**a**, R=Ph; **b**, R=CH$_3$; **c**, R=H)

The product yields decreased in the following order; **2a**>**2b**>**2c**, while those of the α-phenylthio ketones increased inversely. Benzenethiol was oxidized to diphenyl disulfide when the α-bromo ketones were reduced to the parent ketones, respectively. However, the amount of diphenyl disulfide was ambiguous, since benzenethiol was readily oxidized to diphenyl disulfide in air in the presence of Fe-poly PC.

The reaction of **1a** with benzenethiol in the presence of Fe-poly PC conducted at a molar ratio of iron ion to **1a** of 1 : 10 selectively produced **2a**, as shown in Table 1. From this it is apparent that Fe-poly PC acts

TABLE 1. THE EFFECTS OF Fe-POLY PC ON THE REACTIONS OF α-BROMO KETONES WITH BENZENETHIOL[a]

α-Bromo ketone	Solvent[b]	Molar ratio, Fe ion/**1**	Time, h	Yield, %[c] **2**	**3**	Unreacted **1**, %[c]
1a	B	0	24	0	0	89
1a	B	0.1	120	34	0	49
1a	B	1	12	67	0	—
1a	WM	0	1/12	0	96	<1
1a	WM	0.1	2	67	0	23
1a	WM	1	1/12	87[d]	0	—
1b	B	0	24	0	0	100
1b	B	1	96	56	7	22
1b	WM	0	1/12	0	80	20
1b	WM	1	1/2	58	24	0
1c	B	0	24	0	34	66
1c	WM	1	24	16	62	22

a) α-Bromo ketone; 2.8×10^{-2} mol/l. PhSH: α-bromo ketone molar ratio; 4: 1. Solvent; 6 cm^3, 80 °C. b) B; benzene. WM; 80 vol % aqueous methanol. c) The amounts were determined by means of GLC. Based on 1. d) Isolated yield; 70%.

as a catalyst for the reductive debromination. It has been reported that the organic halogen compounds are reduced by iron porphyrins[9] and thiols are oxidized by $\mathrm{Fe(CN)_6}^{3-}$ and iron(III) octanoate to disulfides.[10] Furthermore, the carbon-halogen bond reductions with metals and metal complexes and electrolysis have been explained in terms of an initial conversion of RBr to R· by one-electron reduction.[11] The formation of the ketone (**2**) along with diphenyl disulfide indicates that Fe-poly PC undergoes cleavage of the C–Br bond of the α-bromo ketones (**1**), followed by hydrogen abstraction from benzenethiol to give the parent ketone (**2**). This reaction is coupled to the reduction of the oxidized Fe-poly PC with benzenethiol giving the original Fe-poly PC and diphenyl disulfide. For **1a** and **1b**, the rate of reduction of the C–Br bond

$$\begin{array}{l}\mathbf{1} + \text{Fe-poly PC} \longrightarrow [\text{PhCO}\dot{\text{C}}\text{HR}][\text{Fe-poly PC}]^{\text{Oxd}}\text{Br}^- \\ \qquad\qquad\qquad\qquad\qquad\qquad \downarrow \text{PhSH} \\ \qquad\qquad\qquad\qquad\quad \mathbf{2} + \text{Fe-poly PC} + \text{HBr}\end{array}$$

promoted by Fe-poly PC is considerably faster than that for the formation of the α-phenylthio ketones (**3a** and **3b**).

The function of Fe-poly PC accelerating the reductive debromination of **1a** was compared with that of Fe-PC.

TABLE 2. A COMPARISON OF THE CATALYTIC ACTION BETWEEN Fe-POLY PC AND Fe-PC IN THE REDUCTION OF **1a** WITH BENZENETHIOL[a]

Fe-complex	Solvent	Temp, °C	Time, h	Yield, %[b] **2a**	**3a**
Fe-poly PC	B	80	12	67	0
Fe-poly PC	WM	80	1/12	87	0
Fe-poly PC	WM	25	1/2	47	0
Fe-PC	B	80	24	37	17
Fe-PC	WM	80	1/12	59	40
Fe-PC	WM	25	1/2	31	13

a) **1a**; 2.8×10^{-2} mol/l. PhSH: **1a** molar ratio; 4: 1. Fe ion: **1a** molar ratio; 1: 1. Solvent; 6 cm^3. b) The amounts were determined by means of GLC. Based on **1a**.

As Table 2 shows, Fe-PC underwent the reduction of **1a** with benzenethiol to **2a**, but the reduction rate was slower than that in the case of Fe-poly PC. In addition, the reaction was accompanied by the formation of **3a**. Thus, it has been concluded that Fe-poly PC is more effective than Fe-PC as an electron-transfer reagent in the reductive debromination of **1a**.

Acceleration Using Ethyl Iodide: In order to make possible the reduction of **1c** with benzenethiol in dry benzene in the presence of Fe-poly PC, ethyl iodide was added to the reaction system, since the exchange of the bromo substituent with iodine was expected to facilitate the reduction by Fe-poly PC. As is to be expected, after a reaction of 72 h, **2c** was obtained in 88% yield, along with **3c** in 16% yield (**1c**; 2.8×10^{-2} mol/l, PhSH; 1.1×10^{-1} mol/l, the ethyl iodide: **1c** molar ratio; 10: 1, the iron ion: **1c** molar ratio; 1: 1, and 80 °C). The reaction of **1c** with ethyl iodide in the presence of Fe-poly PC without benzenethiol in dry benzene gave 2-iodoacetophenone in a quantitative yield after a reaction time of 6 h (**1c**; 2.8×10^{-2} mol/l, the ethyl iodide: **1c** molar ratio; 10: 1, the iron ion: **1c** molar ratio; 1: 1, and 80 °C). When Fe-PC, Cu-PC, $\mathrm{K_2}$-PC, and $\mathrm{H_2}$-PC were used instead of Fe-poly PC, 2-iodoacetophenone was not obtained under similar conditions. 2-Iodoacetophenone was reduced instantaneously with benzenethiol in the absence of Fe-poly PC at room temperature to give **2c**

$$\mathbf{1c} + \mathrm{EtI} \xrightarrow[\mathrm{C_6H_6}]{\text{Fe-poly PC}} \mathrm{PhCOCH_2I} + \mathrm{EtBr}$$

quantitatively. Thus, Fe-poly PC performs the reduction of **1c** to **2c** by promoting the exchange reaction of the bromo substituent with iodine of ethyl iodide.

$$\mathrm{PhCOCH_2I} + \mathrm{PhSH} \longrightarrow \mathrm{PhCOCH_3} + \mathrm{PhSSPh} + \mathrm{HI}$$

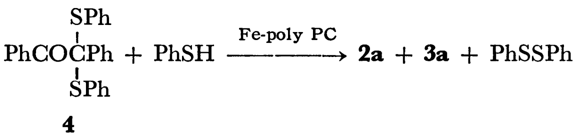
Reductive Cleavage of Carbon-Sulfur Bond of α,α-Bis(phenylthio)deoxybenzoin (4). Fe-poly PC and Fe-PC made possible the reduction of **4** with benzenethiol in dry benzene to give mainly **3a**, as illustrated in Table 3. Furthermore, in the case of Fe-poly PC, **2a** was produced in addition to **3a**, although the yield of **2a** was lower. The ability of Fe-poly PC to form **2a** and/or **3a** was

TABLE 3. THE REDUCTION OF **4** WITH BENZENETHIOL IN THE PRESENCE OF Fe-POLY PC OR Fe-PC IN DRY BENZENE (24 h)[a]

Fe-complex	Temp, °C	**2a** %[c]	**3a** %[c]	Unreacted **4** %[c]
None	14—16	0	0	98
Fe-poly PC	14—16	0	19	75
Fe-poly PC	80	15	84	0
Fe-PC	14—16	0	16	83
Fe-PC[b]	80	0	46	53

a) The concentation of **4**; 5×10^{-2} mol/l, Fe ion: **4** molar ratio; 1:1; and the PhSH: **4** moar ratio; 10:1. b) Time of 72 h; **3a** and **2a**: 93 and 0. c) Isolated yields. Based on **4**.

superior to that of Fe-PC. When the reaction was conducted using methanol as a solvent, however, **2a** was not produced even in the presence of Fe-poly PC (**3a** was obtained in 48% yield after a reaction of 24 h at 14—16 °C). In these reactions, benzenethiol was oxidized to diphenyl disulfide. Fe-poly PC and Fe-PC acted as a catalyst in reactions conducted in an iron ion: **4** molar ratio of 1: 10 in methanol.

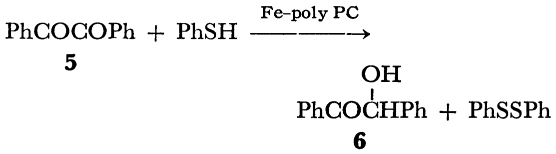


$$\underset{\mathbf{4}}{\mathrm{PhCO}\overset{\mathrm{SPh}}{\underset{\mathrm{SPh}}{\mathrm{C}}}\mathrm{Ph}} + \mathrm{PhSH} \xrightarrow{\text{Fe-poly PC}} \mathbf{2a} + \mathbf{3a} + \mathrm{PhSSPh}$$

In an analogy with α-halo ketones, the reaction proceeds *via* the reductive cleavage of the carbon-sulfur bond of **4** by Fe-poly PC or Fe-PC, followed by the reaction with benzenethiol to give **3a**.

$$\mathbf{4} + \text{Fe-poly PC} \longrightarrow [\mathrm{PhCO}\dot{\mathrm{C}}(\mathrm{SPh})\mathrm{Ph}][\text{Fe-poly PC}]^{\mathrm{oxd}}\mathrm{PhS}^{-} \xrightarrow{\mathrm{PhSH}} \mathbf{3a} + \mathrm{PhSSPh} + \text{Fe-poly PC}$$

Reduction of 1,2-Diketones and Their Related Compounds. Benzil (**5**) was reduced with benzenethiol in the presence of Fe-poly PC (the iron ion: **5** molar ratio; 1: 1) in dry benzene at 80 °C to afford benzoin (**6**) as the reduction product. The amount of **6** produced increased slowly with time until an almost constant value. The maximum yield of **6** was 70% with Fe-poly PC and 16% with Fe-PC. This phenomenon was not observed when methanol was substituted for benzene where the reaction proceeded much more rapidly than in benzene. As Table 4 illustrates, results at the iron ion: **5** molar ratio of 1: 10 indicate that Fe-poly PC and Fe-PC act as catalysts for the reduction of **5** with benzenethiol in methanol. The rate of the formation of **6** catalyzed by Fe-poly PC was faster by a factor of about 25. Furthermore, the reduction of **5** by the Fe-poly PC- or Fe-PC–benzenethiol system in dry benzene was promoted by triethylamine, as shown in Table 5.



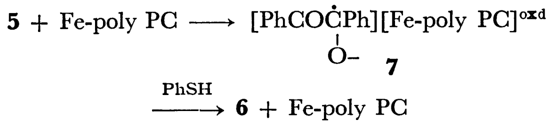
$$\underset{\mathbf{5}}{\mathrm{PhCOCOPh}} + \mathrm{PhSH} \xrightarrow{\text{Fe-poly PC}} \underset{\mathbf{6}}{\mathrm{PhCO}\overset{\mathrm{OH}}{\mathrm{C}}\mathrm{HPh}} + \mathrm{PhSSPh}$$

TABLE 5. THE EFFECT OF TRIETHYLAMINE ON THE REDUCTION OF **5** BY THE Fe-POLY PC OR Fe-PC–BENZENETHIOL SYSTEM[a]

Fe-complex	Molar ratio Et_3N/Fe ion	Temp, °C	Yield,[b] **6**, %	Unreacted[b] **5**, %
Fe-poly PC	0	r.t.	10	87
Fe-poly PC	5	r.t.	38	60
Fe-poly PC	1	80	85	10
Fe-poly PC	5	80	90	8
Fe-PC	0	r.t.	<3	>97
Fe-PC	5	r.t.	11	89
Fe-PC	1	80	72	27
Fe-PC	5	80	88	12

a) **5**; 0.5 mmol. PhSH/**5** molar ratio; 10. n=1. Solvent; C_6H_6 (10 cm^3). Time; 24 h. b) Isolated yields. Based on **5**.

The catalytic reaction is best rationalized by assuming either a partial or complete electron transfer to form either a charge-transfer complex or the ion radical (**7**), followed by the reaction of **7** with benzenethiol giving **6** and the original Fe-poly PC. The benzenethiolate anion produced by triethylamine facilitates the regeneration of the original Fe-poly PC from **7**.



$$\mathbf{5} + \text{Fe-poly PC} \longrightarrow \underset{\mathbf{7}}{[\mathrm{PhCO}\underset{\mathrm{O}^{-}}{\dot{\mathrm{C}}}\mathrm{Ph}][\text{Fe-poly PC}]^{\mathrm{oxd}}} \xrightarrow{\mathrm{PhSH}} \mathbf{6} + \text{Fe-poly PC}$$

4,5-Octanedione (**8**) and ethyl benzoylformate (**9**) were reduced to the corresponding α-hydroxy carbonyl compounds by the Fe-poly PC–benzenethiol system in methanol at 80 °C (Table 6). The reduction of **9**

TABLE 4. THE REDUCTION OF **5** WITH BENZENETHIOL IN THE PRESENCE OF Fe-POLY PC OR Fe-PC[a]

Fe-complex	Molar ratio Fe ion/**5**	Solvent[b]	Temp, °C	Time, h	Yield,[c] **6**, %	Unreacted[c] **5**, %
Fe-poly PC	1	B	80	72	60	38
Fe-poly PC	1	M	50	3	74	23
Fe-poly PC	1	M	80	24	97	0
Fe-poly PC	0.1	M	80	3	64	30
Fe-PC	1	B	80	168	16	83
Fe-PC	1	M	50	3	20	75
Fe-PC	1	M	80	24	95	0
Fe-PC	0.1	M	80	72	58	36

a) **5**; 0.5 mmol. Solvent; 10 cm^3. PhSH/**5** molar ratio; 10. b) B; C_6H_6. M; MeOH. c) Isolated yields. Based on **5**.

TABLE 6. THE REDUCTION OF **8**, **9**, **10**, AND **11** BY THE Fe-POLY PC–BENZENETHIOL SYSTEM[a)]

Compd	Time, h	Product (Yield, %)[b)]
$C_3H_7COCOC_3H_7$ (**8**)	24	$C_3H_7CH(OH)COC_3H_7$ (69)
$PhCOCOOC_2H_5$ (**9**)	120	$PhCH(OH)COOC_2H_5$(37)
PhCOCH=CHCOPh (**10**)	24	$PhCOCH_2CH_2COPh$(21), $PhCOCH_2CH(SPh)COPh$(73)
PhCO(Ph)C=NPh (**11**)	24	PhCO(Ph)CHNHPh(78)

a) **8**, **9**, **10**, and **11**; 0.5 mmol. Solvent; MeOH (10 cm^3). PhSH/Substrate molar ratio; 10. Fe ion: Substrate molar ratio; 1: 1. 80 °C. b) Isolated yields. Based on substrate.

proceeded very slowly. 1,4-Diphenyl-2-butene-1,4-dione (**10**) was reduced under similar conditions to 1,4-diphenyl-1,4-butanedione in low yield, because of the addition of benzenethiol to the double bond of **10** giving 1,4-diphenyl-1-phenylthio-1,4-butanedione. Furthermore, the Fe-poly PC–benzenethiol system was favorable for reducing the >C=N– bond of the Schiff's base (**11**) of **5**, as illustrated in Table 6.

A Characteristic of Fe-poly PC. As described above, Fe-poly PC and Fe-PC assisted the transfer of an electron from benzenethiol to the electron-accepting group at the α-position in the carbonyl group. However, Fe-poly PC differed from Fe-PC in the following respects:

(1) The electron-transfer reduction by Fe-poly PC proceeded more smoothly than by Fe-PC and in particular, a remarkable difference in reactivity was observed in the reduction of the 1,2-diketone **5** in aprotic solvents such as benzene.

(2) Fe-poly PC showed higher selectivity than Fe-PC for the reductive debromination of the α-bromo ketone **1a** giving the parent ketone **2a**.

(3) The reduction of **4** with the benzenethiol–Fe-poly PC system gave **2a** in addition to the α-phenylthio ketone **3a**, while, in the case of Fe-PC, **2a** was not obtained.

The last observation, (3) cannot be explained by the difference in oxidation-reduction potential between Fe-poly PC and Fe-PC. In the case of Fe-poly PC, there is the possibility that the reduction of **4** and the oxidation of benzenethiol may occur on a separate iron site with the assistance of the electron-transfer between iron ions bridged by the conjugated ligand. This probable function of Fe-poly PC may permit the reduction of **4** to **2a**.

Experimental

Materials. α-Bromo ketones (**1**), α-phenylthio ketones (**3**), **4**, **8**, **10**, **11**, and Fe-PC were prepared as described in the literature.[12)] **5** and **9** were purchased. Fe-poly PC was prepared by the method described in a previous paper[2)]: C, 53.16; H, 2.72; N, 17.71; Fe, 6.6%: λ_{max} (KBr method); 725 nm: ρ_{20}; 2×10^6 ohm-cm. Powdered Fe-poly PC and Fe-PC, reprecipitated from sulfuric acid solution with water, were used for the above reactions.

General Procedure for Reaction and Isolation of Product. All reactions were performed similarly in reaction tubes (90-cm^3 total capacity). A typical reaction is described: a solution of a mixture of **5** (0.105 g; 0.5 mmol) and benzenethiol (0.551 g; 5 mmol) in dry benzene (10 cm^3) was placed in the reaction tube and cooled with liquid nitrogen; the air was removed under a reduced pressure of 1 mmHg and, after melting the tube, was filled with nitrogen gas. The replacement by nitrogen gas procedure was repeated 4—5 times. The resulting solution was cooled with liquid nitrogen and to the frozen solution. Fe-poly PC (432 mg) corresponding to 0.5 mmol of Fe was added under nitrogen and degassed under a reduced pressure of 1 mmHg. After the reaction tube was sealed, the solution was melted and vigorously stirred at 80 °C. After a reaction time of 72 h, the Fe-poly PC was filtered and washed with dry benzene. The filtrate was extracted with a 10% sodium carbonate solution, dried over magnesium sulfate, and the benzene removed. The residue was submitted to chromatography on silica gel. Elution with benzene and chloroform gave 0.143 g of diphenyl disulfide (mp 58—59 °C), 0.040 g (38% recovery) of **5** (mp 94—95 °C), and 0.017 g (60%) of **6** (mp 131—132 °C). When methanol was used instead of benzene as a reaction solvent, and excess of benzene was added to the filtrate and the resulting solution worked up in a similar manner to that described for benzene.

The reactions of **1** with benzenethiol in the absence or presence of Fe-poly PC and Fe-PC in 80 vol % aqueous methanol were conducted as follows. Benzenethiol was added under nitrogen to degassed 80 vol % aqueous methanol dispersed by Fe-poly PC or Fe-PC. The resulting solution was frozen, the α-bromo ketones (**1**) added the reaction tube sealed. After the reaction, the products were isolated in a manner similar to that described above.

Analyses. The determination of the products and the unreacted materials in most experiments were conducted by means of GLC, using a silicone HV grease, 80—100 mesh column. After the Fe-poly PC or Fe-PC was removed by filtration, the filtrate was treated with a 10% sodium carbonate solution and submitted to GLC analysis, with biphenyl or 1,2-diphenylethane as an internal standard. The amounts of the products derived from **4**, **5**, **8**, **9**, **10**, and **11**, respectively, were determined satisfactorily by means of chromatography on silica gel. The products were eluted with carbon tetrachloride, benzene, and chloroform, and identified by comparing the IR and NMR spectra with that authentic specimens.

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