

티안트렌 양이온 자유라디칼 과염소산염과 큐멘과산화수소의 반응

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Reaction of Thianthrene Cation Radical Perchlorate with Cumene Hydroperoxides

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요 약. 아세토니트릴용액중의 티안트렌 양이온 라디칼 과염소산 염 (1)은 Cumene hydroperoxide (4), *p*-chlorocumene hydroperoxide (2), *p*-nitrocumene hydroperoxide (3) 와 상온에서 반응한다.

이 반응의 공통 생성물로서 티안트렌을 얻었으며 4로부터 5-(4'-hydroxyphenyl)thianthrenium perchlorate (5), 2로부터 5-(5'-chloro-2'-hydroxyphenyl)thianthrenium perchlorate (7)와 5-acetylthianthrenium perchlorate (6), 그리고 3으로부터 6만을 얻었다. 이 반응의 양관계는 1의 2몰이 티안트렌 1몰과 티안트렌이온 염 (또는 염들) 1몰을 생성한다. 1에 대한 친핵성 활성도는 페놀 >> *p*-클로로페놀 ≃ 아세톤 >> *p*-니트로페놀 순서임이 밝혀졌다. Hydroperoxide의 산축매 불균일 분해반응외에도 소량의 균일분해 반응생성물이 3과 4로부터 생성됨을 알았다.

ABSTRACT. Reaction of thianthrene cation radical perchlorate (1) with cumene (4), *p*-chlorocumene (2), and *p*-nitrocumene (3) hydroperoxides in acetonitrile at room temperature afforded, *inter alia*, thianthrene as a common product and 5-(4'-hydroxyphenyl) thianthrenium perchlorate (5) for 4, 5-(5'-chloro-2'-hydroxyphenyl) thianthrenium perchlorate (7) and 5-acetylthianthrenium perchlorate (6) for 2 and 6 for 3, respectively. Stoichiometry of these reactions showed that 2 moles of 1 gave rise to 1 mole of thianthrene and 1 mole of thianthrenium salt (or salts). Nucleophilic reactivity to 1 was found to be in the order of phenol >> *p*-chlorophenol ≃ acetone >> *p*-nitrophenol. Apart from acid-catalyzed heterolytic decomposition of hydroperoxides, small amount of homolytic decomposition products were found from 3 and 4.

INTRODUCTION

Recently one of us reported the results of investigations on the reaction of thianthrene cation radical perchlorate(1) with azobisisobutyronitrile(AIBN)¹ and benzoyl peroxide². These studies revealed, *inter alia*, that radicals gene-

rated thermally from the corresponding radical initiator did not undergo combination reaction with 1. Thus the reaction with the former did not afford either 5-(2-cyanopropyl)thianthrenium perchlorate or 2-cyano-2-propylthianthrene. Likewise, 5-phenylthianthrenium perchlorate, 2-phenylthianthrene, 5-(benzoyloxy)

thianthrenium perchlorate, or 2-thianthrenyl benzoate was not detected in the reaction with the latter. By comparison, the corresponding reaction with cumene hydroperoxide and *p*-substituted cumene hydroperoxide which undergo homolytic cleavage to afford cumyloxy radical and hydroxy radical³ were undertaken. We report here the results of our investigation, which are the unexpected findings.

EXPERIMENTAL

Thianthrene was obtained from Merck (zur syntheses, Art. No. 821109) and was recrystallized from ethanol (mp 156.5~157.5°C). Acetonitrile was Kanto Chemical Co. extra pure and was refluxed with phosphorus pentoxide for three hours, followed by distilling twice. Dried acetonitrile was stored over molecular sieve (Merck 4Å, Art. 5708) in a septum capped bottle. Acetic anhydride was Shinyo Pure Chemical Co. guaranteed reagent and was distilled at 138~139°C. Carbon tetrachloride was Junsei Chemical Co. extra pure and was distilled at 76.5°C. Perchloric acid was Wako Pure Chemical Industries guaranteed reagent (70%). Hexane was Junsei Chemical Co. extra pure reagent. Chloroform was Ishizu Pharmaceutical Co. extra pure reagent. Ethyl acetate was Kanto Chemical Co. extra pure reagent. Cumene hydroperoxide was obtained from Merck (zur Synthesis, Art. 820502) and it was 80% solution in cumene. Thin layer chromatography was carried out with Merck, Kiesel gel 60, PF 254 and chromatogram was visualized by mineral ultraviolet lamp. Column chromatography was performed with Merck, Kiesel gel 60, 70~230 ASTM mesh, 0.0200~0.063 mm (Cat. No. 7734). Eluent solvents are specified in each case. Ultraviolet spectra were obtained using Beckman Model 5720 UV-VIS spectrophotometer. Infrared spectra were obtained with

Perkin Elmer Model 283 infrared spectrophotometer. All infrared spectra were taken using potassium bromide pellets. ¹H nmr spectra were recorded with Varian EM 360A spectrometer and the data were given in δ units downfield from tetramethylsilane. Gas chromatogram was recorded using G180 Yanaco Gas Chromatograph (Carbowax 20M, column temperature 150°C, He 1.2 kg/cm²). Melting points were taken using a Fisher-Jones melting point apparatus and uncorrected.

***p*-Chlorocumene Hydroperoxide (2).** (a) *p*-Chlorobromobenzene (87% yield, mp 67.5~68°C) obtained from *p*-chloroaniline by Sandmeyer reaction afforded *p*-chlorocumyl alcohol (79% yield, mp 42.5~43°C) by the reaction of its Grignard reagent with acetone. (b) *p*-Chlorocumyl alcohol (5.5 g) saturated in ethyl ether was added in 72 ml of 30% hydrogen peroxide containing 2 ml of conc. sulfuric acid at 0°C and then the mixture was stirred vigorously for 4 hrs, followed by stirring at room temperature for an additional 10 hrs. From the addition of 50 ml of water, followed by the extraction of the aqueous solution with ethyl ether was isolated ether soluble products, which were washed with aqueous sodium hydrogen carbonate and water successively. The ether layer was dried over sodium sulfate and evaporation of the solvent afforded crude product which was purified on silica gel column (15 × 1.5 cm): mp 32~33°C (lit^{4,5} 34°C); IR (KBr) 3400 (OH stretch) and 820 (*tert*-C-O stretch) cm⁻¹; ¹H nmr (CDCl₃) δ 1.57 (*s*, 6H dimethyl), 7.41 (*s*, 4H, aromatic), 7.97 (*s*, 1H, hydroxyl). Yield was 70%.

***p*-Nitrocumene Hydroperoxide (3).** (a) Cumene was prepared from benzene and isopropyl bromide and purified by vacuum distillation. (b) *p*-Nitrocumene was prepared from cumene by nitration with conc. nitric acid and conc. sulfuric acid.⁶ The crude product was purified

by vacuum distillation: bp 122°C/9 torr. (c) Through the mixture of 5g of *p*-nitrocumene and 18 μ l of aqueous sodium hydroxide at 120°C was bubbled for 8 hrs oxygen gas which was passed through a heat reservoir ranged at 105° to 110°C. The reaction mixture was separated on silicagel column (25 \times 1.5cm) and the yield was 20%: mp 37.5~39°C (*lit*⁹ 39°C); IR(KBr) 3440 (OH stretch), 1515 and 1340 (NO₂ stretch), 1160 (C-O stretch), 830 (*tert*-C-O bend) cm⁻¹; ¹H nmr (CDCl₃) δ 1.65 (s, 6H, dimethyl), 7.57~8.32 (q, 4H, aromatic), 7.89 (s, 1H, hydroxyl).

Thianthrene cation radical perchlorate(1). The compound was prepared by the literature method.⁸

Reaction of 1 with Cumene Hydroperoxide

(4). To a stirred solution of 1 (1.256 g, 3.98 mmol) in 35 ml of dried acetonitrile was added 4 (0.593g, 3.90mmol). Reaction occurred immediately and thus the dark purple color of the solution turned brown, along with the formation of white solids. Thin layer chromatography on this reaction mixture performed in benzene showed three spots with *R_f* values, 0.72, 0.45, and 0, which corresponded to thianthrene, phenol, and an unknown, respectively. The solvent was removed and trapped under vacuum at dry-ice temperature. The residue was chromatographed on the silica gel column (1.6 \times 1.5 cm). Elution with hexane (120 ml \times 5) gave 0.437 g (2.02 mmol) of thianthrene. Next elution with benzene (120 ml \times 2) gave 0.127 g of a mixture of which composition was 0.103 g (1.10 mmol) of phenol, 0.006 g (0.05 mmol) of acetophenone, and 0.018 g (0.13 mmol) of cumyl alcohol as determined by ¹H nmr. Finally elution with acetone (120 ml \times 2) gave 1.155 g of brown sticky material which afforded 0.579 g (1.86 mmol) of white solids after being washed with water. Recrystalliza-

tion of the white solids from ethanol gave white, needle-like crystal, identified as 5-(*p*-hydroxyphenyl)thianthrenium perchlorate (5): mp 256~257.5°C (*lit.*⁹ 256.6~257.5°C); IR(KBr) 1100 and 620 cm⁻¹ (ClO₄⁻); ¹H nmr (DMSO-*d*₆ + CDCl₃) δ 6.92~7.37 (2d, 4H, phenyl moiety), 7.75~8.54 (m, 8H, thianthrene moiety), 10.73 (s, 1H, hydroxyl); UV^{CH₃CN} 316(*br*), 267 (*sh*) nm.

Treatment of the Solvent Trapped with 1. Isolation of 5-Acetylthianthrenium Perchlorate(6). The solvent trapped at dry-ice temperature by distillation using vacuum pump after the reaction of 1 with 4 was treated with 1 (0.394 g, 1.25 mmol). After 1hr, the dark purple solution was quenched by adding enough amount of water. The color of the solution turned pale brown. After the solvent was removed under vacuum, the residue was chromatographed on a silica gel column (9 \times 1.5 cm). Elution with hexane (80 ml \times 9) gave 0.166 g (0.77 mmol) of thianthrene. Elution with benzene(100 ml \times 2), followed by ethyl ether (80 ml \times 4) gave 0.059 g (0.25 mmol) of thianthrene-5-oxide. Elution with acetone gave 0.273 g of yellow sticky material which was crystallized by treating with a mixture of ethanol and ethyl ether to give 0.084 g of pale yellow solid identified as 6: mp 181~182°C (*lit.*¹⁰ 180~181°C); IR(KBr) 1100 and 620 cm⁻¹ (ClO₄⁻); ¹H nmr (DMSO-*d*₆ + CDCl₃) δ 2.21 (s, 3H, methyl), 5.17 (s, 2H, methylene); 7.68~8.36 (m, 8H, thianthrene moiety); UV^{CH₃OH} 290 (*br*), 256 (*br*), 224 nm.

Reaction of 1 with an Equimolar Mixture of Phenol and Acetone. To a stirred solution of 1 (1.025 g, 3.25 mmol) in 30 ml of acetonitrile was added a mixture of phenol (3.013 g, 32.05 mmol) and acetone (1.869 g, 32.20 mmol). The color of 1 turned immediately brown. The reaction mixture was worked up

as usual (18 × 1.5 cm). The first three hexane fractions (300 ml) gave 0.345 g (1.60 mmol) of thianthrene. Next four hexane fractions (400 ml), followed by benzene fractions (400 ml) gave 2.269 g (24.14 mmol) of phenol. Finally acetone fractions (400 ml) gave 0.982 g of a brown sticky material which was identified to be only 5.

Reaction of 1 with 2. To the stirred solution of 1 (1.419 g, 4.50 mmol) in 35 ml of acetonitrile was added 2 (0.678 g, 3.64 mmol). The reaction was continued for 75 min and the color of the solution turned completely dark brown. The reaction mixture was worked up as usual (13 × 1.5 cm). Elution with hexane (120 ml × 6) gave 0.461 g (2.13 mmol) of thianthrene, while elution with benzene (120 ml × 4) gave 0.162 g of translucent solids, identified as *p*-chlorophenol based on IR, UV and mass spectra. Elution with ethyl ether (120 ml × 3) gave 0.015 g of a sticky material and 0.041 g of an inorganic perchlorate salt. Elution with acetone (120 ml × 3) gave 1.161 g of dark brown sticky material from which 0.861 g of pale brown solid was obtained by washing with water. The pale brown solid was a mixture of 0.279 g (0.75 mmol) of 6, 0.083 g (0.39 mmol) of thianthrene, and 0.499 g of an unknown compound as determined on ¹H nmr spectrum. The unknown compound was purified by the recrystallization from ethanol containing ethyl ether and white needle-type crystal was obtained: mp 245~246°C; IR (KBr) 1100 and 620 cm⁻¹ (ClO₄⁻); ¹H nmr (DMSO-*d*₆ + CDCl₃) δ 6.47~7.58 (*m*, 3H, phenyl moiety), 7.71~8.63 (*m*, 8H, thianthrene moiety); UVλ_{max}^{EtOH} (ε × 10⁻⁴) 310.5 (*br.* 0.91), 258 (*sh*, 0.83), 219 (*sh*, 4.05) nm.

This compound was assigned to be 5-(5'-chloro-2-hydroxyphenyl)thianthrenium perchlorate (7) and yield was 50% based on 50% of 1.

Reaction of 1 with *p*-Chlorophenol. To a

stirred solution of 1 (1.258 g, 3.99 mmol) in 35 ml of acetonitrile was added 0.366 g (2.58 mmol) of *p*-chlorophenol. Color of 1 turned yellow in 3 days. The reaction mixture was worked up as usual (13 × 1.5 cm). Elution with hexane (120 ml × 4) gave 0.353 g (1.63 mmol) of thianthrene, while elution with benzene gave 0.081 g (0.63 mmol) of the unreacted *p*-chlorophenol. Elution with acetone (120 ml × 2) gave 1.368 g of brown solid, which was washed with water to give 1.064 g (3.40 mmol) of 7.

Reaction of 1 with an Equimolar Mixture of *p*-Chlorophenol and Acetone. To a stirred solution of 1 (1.213g, 3.84mmol) in 40ml acetonitrile was added a mixture of *p*-chlorophenol (3.253 g, 25.32 mmol) and acetone (1.489 g, 25.67 mmol). Color of 1 disappeared completely in 1 hr. The reaction mixture was worked up as usual (16 × 1.5 cm). The first three hexane fractions (360 ml) gave 0.427 g (1.98 mmol) of thianthrene. Next three fractions (360 ml) of hexane, followed by benzene fractions (100 ml × 5) gave 1.512 g (11.77 mmol) of *p*-chlorophenol. Elution with ethyl acetate (100 ml × 2) gave 0.146 g of inorganic perchlorate salts. Finally elution with acetone (100 ml × 4) gave 1.152 g of sticky brown material which was almost an equimolar mixture of 7 and 6 as determined with ¹H nmr spectrum. Recrystallization from ethanol gave 0.081g (0.22 mmol) of 6 and 0.074 g (0.17 mmol) of 7.

Reaction of 1 with 3. To a stirred solution of 1 (1.577 g, 5.00 mmol) in 40 ml of acetonitrile was added 0.847g (4.30mmol) of 3. Color of 1 turned completely dark in 19 hrs. The reaction mixture was worked up as usual (16 × 1.5 cm). Elution with hexane (120 ml × 6) gave 0.520 g (2.41 mmol) of thianthrene. Elution with benzene (100 ml × 4) gave 0.051 g of pale yellow sticky material, identified as *p*-nitrocumyl alcohol contaminated with a trace amount

of *p*-nitroacetophenone. Elution with chloroform (120 ml \times 3), followed by ethyl ether (120 ml \times 4) gave 0.45 g (3.56 mmol) of *p*-nitrophenol. Elution with ethyl acetate (120 ml \times 2) and acetone (120 ml \times 3) gave 1.181 g of sticky brown solid, which was washed with water to give 0.75 g of brown solid. This solid was a mixture of 0.623 g (1.67 mmol) of **6** and 0.172 g (0.80 mmol) of thianthrene as determined with ^1H nmr spectrum.

Reaction of 1 with *p*-Nitrophenol and Acetone. To a stirred solution of **1** (0.910 g, 2.88 mmol) in 40 ml acetonitrile was added an equimolar mixture of 3.390 g (24.39 mmol) of *p*-nitrophenol and 1.511 g (26.05 mmol) of acetone. Color of **1** turned completely crimson in 70 min. The reaction mixture was worked up as usual (12 \times 1.5 cm). Elution with hexane (120 ml \times 5) gave 0.75 g (1.27 mmol) of thianthrene, while elution with benzene (100 ml \times 3) gave no product, subsequent elution with chloroform (120 ml \times 2) and ether (100 ml \times 3) gave 3.514 g (22.69 mmol) of *p*-nitrophenol. Finally elution with acetone (100 ml \times 2) gave 0.734 g of brown sticky material which was washed with water to give 0.57 g (1.44 mmol) of **6**.

RESULTS

Upon addition of **4** to the solution of **1** in acetonitrile at room temperature, vigorous reaction took place immediately, which was in contrast with the reactions with other radical initiators, *e.g.* AIBN¹, benzoyl peroxide². Reactions with the latter did not proceed at room temperature but at reflux temperature purple color of **1** faded gradually and the rate of disappearance of the color depended on the concentration of the latter. On the other hand, **2** and **3** underwent rather slowly the analogous reactions. The products either isolated or detected in each reaction *vide supra* were thi-

anthrene as a common product and 5-arenethi anthrenium perchlorate for the reactions with **4** and **2**. In addition, **6** was obtained only from the reaction with **2** and **3**. As the decomposed products of each hydroperoxide, phenol, acetone, small amounts of cumyl alcohol, and acetophenone were obtained from **4**, while only *p*-chlorophenol was obtained from **2**. On the other hand, **3** gave *p*-nitrophenol, small amounts of *p*-nitrocumyl alcohol and *p*-nitroacetophenone. The amounts of major products and reactants are tabulated in Table 1. Phenol and acetone were common products derived from each hydroperoxide and the two compounds were likely to participate competitively in the subsequent reaction. So investigation on the reaction of **1** with mixed nucleophiles revealed the following order of reactivity: phenol \gg *p*-chlorophenol acetone \gg *p*-nitrophenol.

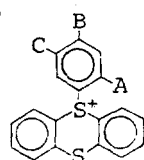
DISCUSSION

It has been well-documented that **4** and its *p*-substituted analogs decompose *via* either ionic or radical mechanism depending on the reaction conditions. For example, **4** undergoes decomposition to lead to phenol and acetone in the presence of 0.01 to 0.2 mole percent of perchloric acid in acetic acid,¹¹ while in the presence of ferrous ion,¹² homolysis is known to be a predominant reaction pathway. Reaction of **1** with either AIBN¹ or benzoyl peroxide² in acetonitrile at reflux temperature gave 5-thianthreniumyl thianthrene perchlorate as a major product of which formation mechanism has not been clarified. No combination products between **1** and any radicals originated from the initiators were found. Surprisingly reaction of **1** with **4** took place immediately and white fume accompanying heat were evolved. The white fume was trapped into a gas cell (10 cm path length) for infrared spectrum. However, the infrared

Table 1. Summary of 1 with cumene hydroperoxides.

| Reactants (mmol) | | Products (mmol) | | | |
|------------------|-----------------------------|-----------------|---------|------|------|
| 1 | | a | b | 6 | c |
| | | Th | | | |
| 3.98 | 4, x=H, 3.90 | 2.02 | 5, 1.86 | 0 | 1.28 |
| 4.50 | 2, x=Cl, 3.64 | 2.13 | 7, 1.13 | 1.14 | 1.26 |
| 5.00 | 3, x=NO ₂ , 4.30 | 2.41 | 0 | 2.47 | 3.84 |

^aThianthrene, ^b

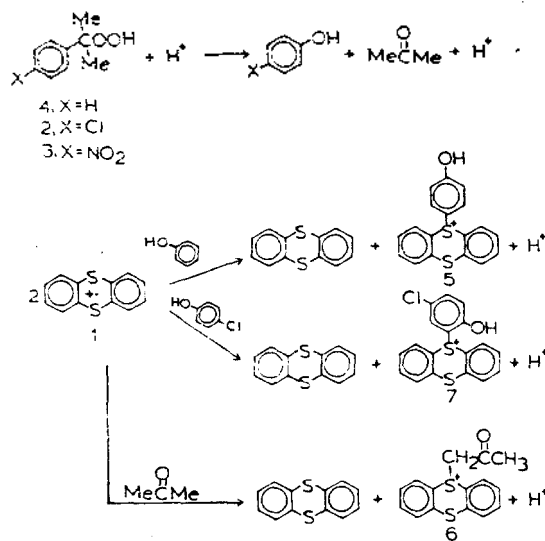


5, A=C=H, B=OH

7, A=OH, B=H, C=Cl

c: Small amounts of the compounds were evaporated in the process of removing the solvent under vacuum.

spectrum thus obtained was not identical with either that of methane or ethane which has been known as gaseous product when homolysis of 4 was a predominant reaction. the fume was not identified further. As shown in Table 1, the isolated yields of thianthrene and 5 from the reaction with 4 were approximately 102%, and 93%, respectively based on the stoichiometry in which two moles of 1 gave rise to 1 mole of thianthrene and 1 mole of thianthrenium perchlorate. In the case of the reaction with 2, the isolated yield of thianthrene, 6, and 7 were 95%, 50%, and 50%, respectively. Reaction with 3 did not give 5-(2'-hydroxy-5'-nitrophenyl)thianthrenium perchlorate but gave only 6. The isolated yields of 6 and thianthrene were 99% and 96%, respectively based on the same calculation. These results indicate that 4 and its *p*-substituted analogs (2, 3) undergo the same decomposition reaction in the solution of 1 as an acid catalyzed decomposition. Therefore, the following scheme illustrates the observed results:



According to the scheme, acetone and phenolic products are always formed. However, these two compounds compete with each other for the subsequent reaction with 1. In order to compare the reactivity difference between acetone and phenols, equal molar amounts of two compounds which are 7 to 10 times in excess of the molar amounts of 1 were allowed to react with 1. Table 2 compiles the results.

Table. 2. Reactivity difference between acetone and phenols in the reaction with 1

| Reactants (mmol) | | | Products (mmol) | | |
|------------------|---|---|-----------------|------------------------|--------------------|
| 1 |  |  | Th ^a | 5 | 6 |
| 3.25 | X = H, | 32.05/32.72 | 1.60 | 5 (982mg) ^b | 0 |
| 3.84 | X = Cl, | 25.32/25.67 | 1.63 | | 152mg ^c |
| 2.88 | X = NO ₂ , | 24.39/26.05 | 1.27 | | 1.44 |

a: Thianthrene; b: Some perchloric acid and inorganic perchlorate might be included; c: A mixture of 6 and 7 of which analysis by ¹H nmr demonstrated a mixture of 1 to 1.3.

This data clearly shows that phenol is much more reactive than acetone in these reactions. The observation that no 6 was detected by ¹H nmr technique is in good agreement with the result obtained from the reaction with 4. Reactivity of *p*-chlorophenol, however, was comparable to that of acetone, which was also in accordance with the result from the reaction with 2. As was expected, *p*-nitrophenol was stable in the solution of 1 in acetonitrile. Therefore, only 6 was obtained from the reaction with a mixture of *p*-phenol and acetone. In the meantime, the formation of acetone in the reaction with 4 was successfully demonstrated by distilling the solvent under vacuum, following by the addition of 1 to the trapped the solvent at dry ice temperature to give 6. Apart from the ionic reaction, there are some indications in which radical reaction also intervene in the reaction with 4 and 3. ¹H nmr analysis of benzene fraction from the reaction with 4 showed the formation of small amount of cumyl alcohol (18 mg, 0.13 mmol) and acetophenone (6mg, 0.05mmol). The latter was confirmed by comparison of retention time on gas chromatogram with that of authentic sample. Reaction with 3 also led to the formation of *p*-nitrocumyl alcohol (51 mg) with trace amount of *p*-nitroacetophenone which were identified by ¹H nmr analysis. In the case of the reaction with 2, however, the corresponding

analogous compounds were not detected. The formation of cumyl alcohol can be explained by the hydrogen atom abstraction of cumyloxy radical. Cumene hydroperoxide used in this reaction was 80% solution in cumene. So cumene was likely to act as the hydrogen atom donor. However, one puzzled thing is that the reaction with 3 afforded radical derived products but the reaction with 2 did not. One may rationalize the different behavior in terms of the relative ease of acid-catalyzed decomposition. It has been known that the rate of acid-catalyzed heterolytic decomposition of O-O bond of *p*-substituted cumene hydroperoxides is retarded by the presence of a strong electron withdrawing group. As a result, there may be an increased chance of the involvement of homolytic decomposition. Chlorine is not strong electron withdrawing group as nitro group. Thus acid-catalyzed heterolytic decomposition, followed by the reaction with 1 dominates the formation of radical derived products. To the contrary, 3 undergoes heterolytic decomposition rather slowly and thus formed *p*-nitrocumyloxy radical abstracts a hydrogen from *p*-nitrophenol. This speculation warrants for further study.

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