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> ORGANIC SYNTHESIS AND INDUSTRIAL ORGANIC CHEMISTRY

## **3-Substituted Thietanes as Effective Inhibitors** of Cumene Oxidation

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Abstract—3-Substituted thietanes were prepared by reaction of 1,2-epithio-3-chloropropane with various nucleophiles in aqueous solutions and were characterized. The inhibiting power of these compounds in cumene oxidation was studied.

Previously we studied antioxidant activity of various thiiranes and thietanes. It was shown that the inhibiting mechanism involves both termination of an oxidation chain by reaction with peroxy radicals with oxidation of the inhibitors by cumyl hydroperoxide (CHP) and formation of substances catalyzing hydroperoxide degradation into molecular products and readily reacting with peroxy radicals.

In this work we synthesized 3-substituted thietanes and studied their antioxidant activity in cumene oxidation.

1,2-Epithio-3-chloropropane (I) was prepared by reaction of epichlorohydrin with thiourea in the presence of methanol [7]. Reaction of I with ammonium thiocyanate in an aqueous solution to form 3-thietanyl isothiocyanate (II) was studied in [8]. 3-Thietanyl-substituted thioureas III and IV were prepared by addition of 3-thietanyl isothiocyanate to benzylamine and morpholine, respectively:



3-Thietanol (V) was prepared by reaction of 1,2-epithio-3-chloropropane with sodium carbonate [9]:



The structure of the resulting compounds was confirmed by IR and 1H NMR spectroscopy and the purity, by elemental analysis and thin-layer and gas– liquid chromatography (GLC).

The IR spectra of 3-thietanyl-substituted thioureas III and IV contain the bands in the range 670-680, 720-730, and 1420-1435 cm<sup>-1</sup>, which are typical for stretching vibrations of the four-membered thietane ring. The band in the range 1500-1520 cm<sup>-1</sup> is assigned to stretching vibrations of the thiourea NHC(S) fragment.

In the range 2.65–3.65 ppm the <sup>1</sup>H NMR spectra of 3-thietanyl-substituted thioureas **III** and **IV** contain a quintet of four protons of two equivalent methylene groups of the thietane ring with the intensity ratio of 1:4:6:4:1. The signal of the single methine proton of the thietane ring appears as a quintet in the range 4.25–4.75 ppm. The broad strong signal of the NH protons of the thiourea skeleton is observed at 7.05–7.65 ppm. The signals of CH<sub>2</sub> protons of the benzyl fragment are observed in the range 2.5– 2.9 ppm. The singlet in the range 6.61–6.89 ppm is assigned to five aromatic protons.

Reactions of II-V with CHP were performed in chlorobenzene under nitrogen at 110°C in a temperature-controlled glass reactor. The CHP content in the samples taken at regular intervals was determined by iodometric titration.

To determine the reaction stoichiometry, CHP was taken in excess. The stoichiometric coefficients calculated by the equation

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$$v = \frac{[CHP]_0 - [CHP]_{\infty}}{[InH]_0},$$

(where  $[CHP]_0$  and  $[CHP]_{\infty}$  are the initial and final CHP concentrations, respectively,  $[InH]_0$  is the initial concentration of the inhibitor) show that products formed from a single molecule of the inhibitors cause several thousand CHP molecules to decompose.

The kinetic parameters of the catalytic decomposition of CHP in the presence of II-V are presented in the table. High stoichiometric coefficients v indicate the catalytic nature of CHP decomposition.

Analysis of the kinetic parameters of reaction of the tested compounds with CHP shows that their activity in this reaction appreciably depends on the nature of the substituent in a thietane molecule.

As in the case of the reaction with cumylperoxy radicals, compound **IV** is the most active in reaction with CHP. The rate constant K and the stoichiometic coefficient v for this compound are higher by an order of magnitude than those for the other compounds.

The study of cumene autooxidation at  $110^{\circ}$ C in the presence of compounds **II**–V showed (Fig. 1) that all these thietanes inhibit the oxidation. To determine their antioxidant power in elementary reactions responsible for inhibition of cumene oxidation, we studied reactions of these compounds with cumylper-oxy radicals and CHP. All the tested compounds (Fig. 2) inhibit initiated oxidation of cumene. The stoichiometric coefficient of inhibition equal to the number of oxidation chains terminated on single inhibitor molecule and products of its conversion was calculated from the induction period  $\tau$  by the equation

$$f = \frac{\tau w_i}{[\text{InH}]_0},$$

where  $\tau$  is the induction period (s),  $w_i$  is the initiation rate (under the conditions studied it is equal to  $2 \times 10^{-7}$  mol l<sup>-1</sup> s<sup>-1</sup>) [10].

The rate constant of the reaction of the tested inhibitors with peroxy radicals *K* was calculated form the rate of oxygen uptake. For this purpose the kinetic curves of oxygen uptake in the  $\Delta[O_2]$  vs. *t* coordinates were transformed into the  $\Delta[O_2]^{-1}$  vs.  $t^{-1}$  coordinates. From the slope of the straight line

$$\tan \alpha = \frac{fK_7[\text{InH}]_0}{K_2[\text{RH}]w_i}$$

the constant  $K_7$  was calculated by the equation

 $V_{0_2}, \min_{\substack{1.0\\0.8\\0.6\\0.4\\0.2}}$ 

**Fig. 1.** Kinetic curves of cumene autooxidation at  $T = 110^{\circ}$ C in the presence of the tested inhibitors with the concentration [InH] = (1) 0, (2, 3)  $5 \times 10^{-5}$ , and (4)  $5 \times 10^{-6}$  M. ( $V_{\text{O}_2}$ ) Oxygen volume and (t) time; the same for Fig. 2.



**Fig. 2.** Kinetic curves of initiated oxidation of cumene at [AIBN] =  $2 \times 10^{-2}$ ,  $w_i = 2 \times 10^7$  M, and  $T = 60^{\circ}$ C: Inhibitor and concentration, M: (1) none; (2) II,  $1 \times 10^{-4}$  (3) III,  $3 \times 10^{-4}$ , and (4) IV,  $5 \times 10^{-6}$  M.

$$K_7 = \frac{\tan \alpha K_2 [\text{RH}] w_i}{f[\text{InH}]_0}$$

where  $K = 1.51 \ 1 \ \text{mol}^{-1} \ \text{s}^{-1}$  [12], [RH] = 6.9 M.

As seen from the kinetic curves of initiated oxidation of cumene, the oxidation rate in the presence of the inhibitors after the induction period (Fig. 2, curves 2–4) is lower than that in their absence (Fig. 2, curve 1). This indicates that products of reaction of II-V with cumylperoxy radicals are also inhibitors. The kinetic parameters of reaction of II-V with cumylperoxy radicals are presented in the table.

As seen from the table, the stoichiometric coefficient f and the rate constant  $K_7$  for **II**–V range from

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Kinetic parameters\* of reaction of 3-substituted thietanes with cumylperoxy radicals (60°C, [AIBN] =  $2 \times 10^{-2}$  M) and CHP (110°C)

| Com-<br>pound | f    | $\frac{K_7 \times 10^{-4}}{1 \text{ mol}^{-1}}$ | <i>K</i> | ν       |
|---------------|------|---|----------|---------|
| II            | 0.96 | 2.23  | 20       | 53 800  |
| III           | 1.86 | 2.4   | 24       | 68 600  |
| IV            | 34   | 7.05  | 225      | 586 000 |
| V             | 0.24 | 2.0   | 12       | 23 500  |

\* AIBN is azobis(isobutyrolnitrile), f is the stoichiometric coefficient of inhibition,  $K_7$  is the rate constant of reaction of the inhibitors with peroxy radicals, K is the rate constant of the reaction with CHP, and v is the catalytic factor.

0.24 to 34 and from 2.0 to  $7.05 \times 10^{-4} \,\mathrm{l \, mol^{-1} \, s^{-1}}$ , respectively. Analysis of the kinetic parameters of reaction of **II**–**V** with cumylperoxy radicals shows that the reactivity of these compounds strongly depends on the nature of the substituents at the thietane ring. Compound **IV**, unlike the other inhibitors, repeatedly terminates the oxidation chains (f = 34) and exhibits very high reactivity with respect to cumylperoxy radicals ( $K_7 = 7.05 \times 10^{-4} \,\mathrm{l \, mol^{-1} \, s^{-1}}$ ).

Thus, all the tested inhibitors actively decompose CHP in three steps (Fig. 3): the first step is very slow (the induction period), the second is fast and autocatalytic, and the third is the final step of CHP degradation. The first two steps last different times depending on initial concentrations of hydroxperoxide and inhibitor. The induction period shortens with increasing the hydroperoxide concentration. The shape of the curves of CHP autocatalytic decomposition indicates that CHP decomposes under the action of products formed in the first slow step of the reaction



**Fig. 3.** Kinetic curves of CHP decomposition at  $T = 110^{\circ}$ C under the action of V. [InH]  $5 \times 10^{-5}$  M. ([ROOH]) Concentration and (*t*) time.

of the inhibitors with CHP, but not under the action of the initial inhibitors.

## **EXPERIMENTAL**

The IR spectra were recorded in a thin layer on a Specord 75-IR spectrometer. The <sup>1</sup>H NMR spectra were recorded on a Varian T-60 spectrometer operating at 60 MHz, with tetramethylsilane as the internal reference.

Thin-layer chromatography of I-V was performed on Silufol-254 plates using an ethanol-hexane mixture (1:5) as the eluent. In all case a single spot was observed after development with iodine.

**1-Benzyl-3-(3'-thietanyl)thiourea (III).** Benzylamine [10.7 g (0.1 mol)] was mixed with 3-thietanyl isocyanate [13.1 g (0.1 mol)]. The reaction mixture slightly warmed up. Crystalline target product was isolated after the reaction mixture was cooled to room temperature and diluted with benzene. The reaction course was monitored by TLC and IR spectroscopy. The yield of **III** was 24 g (87%), mp 165°C,  $R_f =$ 0.86.

Found, %: C 55.25, H 5.67, N 11.92, S 27.16.  $C_{11}H_{44}N_2S_2.$  Calculated, %: C 55.42, H 5.92, N 11.75, S 26.90.

Compound **IV** was prepared similarly in a 17.7 g (81%) yield from morpholine [8.7 g (0.1 mol)] and 3-thietanyl isothiocyanate [13.1 (0.1 mol)]; mp 165–166°C,  $R_f = 0.80$ .

Found, %: C 51.21, H 7.75, N 14.85, S 17.37.  $C_8H_{14}N_2OS_2$ . Calculated, %: C 51.58, H 7.58, N 15.04, S 17.21.

Cumyl hydroperoxide was purified by the known procedure [13] with subsequent distillation. Chlorobenzene and cumene were treated with concentrated sulfuric acid [14] to remove impurities. The CHP concentration was determined by iodometric titration [15]. Decomposition of CHP at 110°C in a chlorobenzene solution was studied in glass bubbling reactor under an inert atmosphere. The concentration of CHP and the tested compounds was varied from 0.23 to 0.45 and from  $0.5 \times 10^{-4}$  to  $5 \times 10^{-6}$  M, respectively. Cumene oxidation initiated by AIBN was studied on a manometric unit [10]. The rate constant of the initiation at 60°C is  $K = 1.0 \times 10^{-5}$  s<sup>-1</sup> [11]. The initiator concentration in all experiments was constant (2 ×  $10^{-2}$  M). The concentration of the inhibitors ranged from  $1 \times 10^{-4}$  to  $5 \times 10^{-6}$  M.

## REFERENCES

- Allakhverdiev, M.A., Akperov, N.A., Farzaliev, V.M., et al., Khim. Geterotsikl. Soedin., 1988, no. 12, p. 1619.
- Allakhverdiev, M.A., Akperov, N.A., Farzaliev, V.M., et al., Neftekhimiya, 1988, vol. 28, no. 2, p. 251.
- Allakhverdiev, M.A., Akperov, N.A., Farzaliev, V.M., et al., Zh. Prikl. Khim., 1988, vol. 61, no. 6, pp. 1411– 1443.
- Farzaliev, V.M., Allakhverdiev, M.A., Guseinova, G.M., et al., Abstracts of Papers, V Moskovskaya nauchno-tekhnicheskaya konferentsiya po priborotekhnike i mashinostroeniyu (V Moscow Scientific and Technical Conf. on Instrument Technique and Machine Building), Novgorod, 1991, p. 130.
- Allakhverdiev, M.A., Akperov, N.A., and Farzaliev, V.M., *Khimiya tietanov* (Thietane Chemistry), Baku: Inst. Khimii Prisadok Akad. Nauk Azerbaidzhanskoi Respubliki, Available from VINITI, 1990, no. 369 590.
- Farzaliev, V.M., Allakhverdiev, M.A., Akperov, N.A., and Liksha, V.B., *Neftekhimiya*, 1990, vol. 30, no. 5, p. 706.
- 7. Culvenor, C.C., Davies, W., and Pausacker, K.H., J. Chem. Soc., 1949, no. 11, p. 1050.

- 8. Huretdinova, N.O. and Guseva, F.F., *Izv. Akad. Nauk* SSSR, Ser. Khim., 1976, no. 3, p. 662.
- Adams, E.R., Ayah, N.K., and Queen, A., J. Chem. Soc., 1960, no. 6, p. 2665.
- Denisov, E.T., Kharitonov, V.V., and Fedorov, V.V., Metody transformatsii kineticheskikh krivykh kak sposob otsenki effektivnosti ingibitorov okisleniya (Transformation of Kinetic Curves as a Procedure for Estimating Efficiency of Oxidation Inhibitors), Chernogolovka, 1973.
- 11. Emanuel' N.M., Denisov, E.T., and Maizus, Z.K., *Tsepnye reaktsii okisleniya uglevodorodov v zhidkoi faze* (Chain Reactions of Hydrocarbon Oxidation In Liquid Phase), Moscow: Nauka, 1967.
- 12. Denisov, E.T., Konstanty skorosti gomoliticheskikh zhidkofaznyk reaktsii (Rate Constants of Homolytic Liquid-Phase Reactions), Moscow: Nauka, 1971.
- 13. Karnojitzki, V., *Les peroxides organiques*, Paris: Hermann, 1958.
- Weissberger, A. and Proskauer, E.S., Organic Solvents. Physical Properties and Methods of Purification, Riddick, J.A. and Toops, E.E., Eds., New York: Interscience, 1955.
- Houben–Weyl, Methoden der Organischen Chemie, vol. 2: Analytische Methoden, Stuttgart: Georg Thieme, 1953.