BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 2323—2326 (1969)

Photochemical Reactions of Some Thioparabanates

Teijiro YONEZAWA, Masakatsu MATSUMOTO, Yoichi MATSUMURA and Hiroshi KATO

Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Kyoto

(Received December 23, 1968)

1,3-Disubstituted thioparabanates (I) were reduced with ethanol under the action of light to yield 2-mercaptoimidazolidine-4,5-diones (II) with or without 2-(1-hydroxyethyl)-2-mercapto-imidazolidine-4,5-dione (III). It seems that these reactions may be initiated by the n–π^* transition of the lone pair in the 2-thiocarbonyl group. When dimethylthioparabanate (Ic) was irradiated with a high-pressure mercury arc in a chloroform solution of amylene, a photocycloaddition product, a trimethylene sulfide (IVa), was obtained.

Recently several investigations[1–3] into the photochemical reduction of thiobenzophenone in alcoholic solvents and the photocycloaddition of the same compound with such olefins as 1-butene and 1,3-cyclooctadiene have been made. Its photochemical behavior has been found to be considerably different from that of benzophenone; in the photochemical reduction reaction, the former gave benzhydryl mercaptan, dibenzhydryl disulfide, and a tetrasulfide as reduction products,[1] whereas dibenzopinacol was produced from the latter.[2] In the photocycloaddition reaction thiobenzophenone with olefins gave 1:1 adducts and 2:1 adducts, or olefins formed by the decomposition of these adducts,[3] while it is well known that oxetanes are produced from many carbonyl compounds.

However, the photochemical reactivities of the ureid carbonyl group and the thioureid group have scarcely been studied at all. A purpose of the present work is to compare the photochemical reactions of thioparabanates containing a thioureid group with those of thiobenzophenone and benzophenone.

Results

Electronic Spectra. All the thioparabanates (I) are yellow. The ultraviolet and visible spectra of these compounds are shown in Table 1, together with those of thioparabanic acid, parabanic acid, and tetramethylthiourea. For all the derivatives of thioparabanic acid (I), the electronic spectra in ethanol showed an n–π^* absorption band at 400—440 mμ and a π–π^* absorption band at about 300 mμ. The former is probably due to an n–π^* transition which is mainly localized on the thiocarbonyl group in thioparabanates (I); parabanic acid has an n–π^* absorption band due to the carbonyl group of the oxalyl group at 314 mμ, and thioparabanates (I) are expected to have an n–π^* absorption band of the oxalyl group in the same region. The n–π^* absorption band of the thiocarbonyl group in tetramethylthiourea is at 324 mμ[4] and the imidazolidinetrione molecule is nearly planar,[5] so if the thioparabanic acid molecule has a similar structure, the π orbitals of 2-thiocarbonyl group may overlap with the lone-pair orbitals of N atoms and also with the π orbitals of the oxalyl group. Consequently, the n–π^* absorption band of the thiocarbonyl group is thought to shift longer wavelength region than that of tetramethylthiourea. The results of the ASMO SCF calculation[6] (zero differential approximation) indicate that the singlet-singlet transitions for thioparabanic acid are as follows; the $n_{C=S}$–π^* transition at 341 mμ,

---

[1] G. Oster, L. Citarel and M. Goodman, *J. Am. Chem. Soc.*, **84**, 703 (1962).

[2] *E. g.*, N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, New York (1965), p. 140.

[3] a) E. T. Kaiser and T. F. Wuifers, *J. Am. Chem. Soc.*, **86**, 1897 (1964); b) K. Yamada, M. Yoshika and N. Sugiyama, *J. Org. Chem.*, **33**, 1240 (1968).

[4] M. J. Janssen, *Rec. Trav. Chim.*, **79**, 454 (1960); *Chem. Abstr.*, **55**, 104i (1961).

[5] L. E. Sutton, "Tables of Interatomic Distances and Configuration in Molecules and Ions," Chemical Society, London (1958), p. 144.

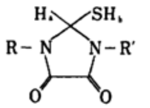
[6] T. Yonezawa, H. Konishi and H. Kato, to be published.

TABLE 1. ELECTRONIC SPECTRA OF THIOPARABANATES (I)

R	R′	π-$\pi^{*a)}$		n-$\pi^{*a)}$	
		λ_{max} (mμ)	ε	λ_{max} (mμ)	ε
H	H	304	10400	416	40
C_6H_5	H	302	13200	422	49
$C_6H_5CH_2$	H	302	12800	415	30
C_6H_5	C_6H_5	305	15300	432	44
CH_3	CH_3	298	13900	402	25
C_2H_5	C_2H_5	301	14600	405	35
C_6H_5	$C_6H_5CH_2$	302	14000	421	38
parabanic acid		—	—	314	40
$((CH_3)_2N)_2C{=}S^{b)}$		—	—	324	$2.41^{c)}$

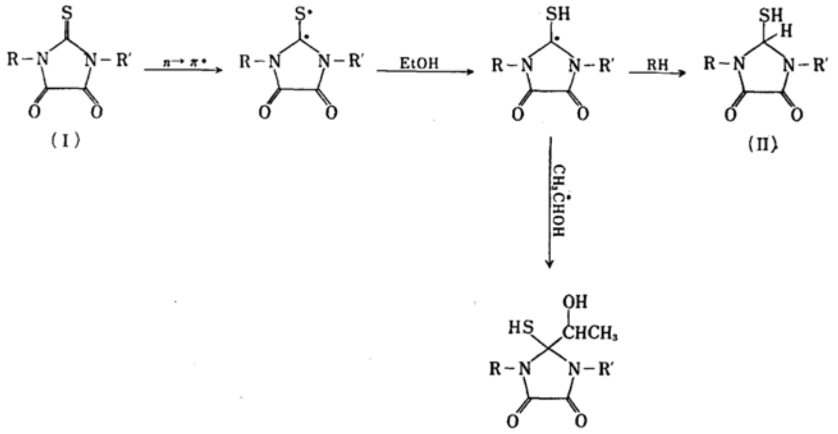
a) Measured in ethanol at 25°C.
b) In diethyl ether.
c) log ε

TABLE 2. PHOTOREDUCTION PRODUCTS OF THIOPARABANATES (II)



	R	R′	Mp (°C)	NMR spectra* (τ)		J_{ab} (Hz)
				H_a	H_b	
(II-a)	Ph	Ph	200	2.50	4.28	9.0
(II-b)	Ph	$PhCH_2$	173	2.53	4.28	9.0
(II-c)	CH_3	CH_3	—	2.82	4.89	9.0
(II-d)	C_2H_5	C_2H_5	—	2.83	4.89	9.0

* in d_6-DMSO solutions



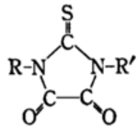
Scheme 1.

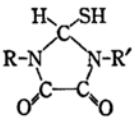
the lowest π-π^* transition at 286 mμ, and a very weak σ-π^* absorption at 436 mμ (though this third transition has never been detected).

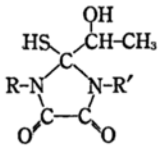
Photoreduction. 1,3-Diphenylthioparabanate (Ia) in an ethanol solution was irradiated under a nitrogen atmosphere with a 200-W high-pressure mercury arc. The yellow color of the solution gradually faded, and the reduction product, 1,3-diphenyl-2-mercapto-imidazolidine-1,5-dione (IIa) was formed in a quantitative yield. As in the case of diphenylthioprarabanate, the irradiation of most 1,3-disubstituted thioparabanates led to the corresponding mercaptans (II). The melting points and NMR parameters of these reduction products are shown in Table 2. In Table 2, when the substituent group is a methyl or an ethyl group, the reduction product (IIc or IId) could not be obtained in a pure form. The mercaptan (IIc) and (IId) were very unstable and were oxidized by air to form the corresponding thioparabanate.

When the substrate had one or two active hydrogen atoms bonded to the nitrogen, the photochemical reactions of these compounds gave complex products. In the case of thioparabanic acid, thiourea, carbon monoxide, and trace of formaldehyde were obtained, while in the case of monoesters, tarry products were obtained. In these photoreductions, active protons bonded to the nitrogen atom may labilize the reduction form (II) of thioparabanate containing an active mercapto proton.*1

In the reduction of diethylthioparabanate, the mercaptan (IId) was obtained, plus 2-(1-hydroxyethyl)-1,3-diethyl-2-mercapto-imidazolidine-4,5-dione (III) as a by-product. The mercaptan (III) can reasonably be assumed to be produced by a combination of the thioketyl radical (A) and the α-hydroxyethyl radical (B). Moreover, the thioketyl radical (A) may be produced from the excited molecule of I resulting from the n–π^* transition of the thiocarbonyl group, but not from a π–π^* transition. Thus, the mechanism of the photochemical reduction of thioparabanates (I) may be considered to be as is shown in Scheme 1.

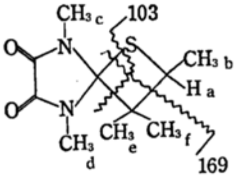

(I)


(II)

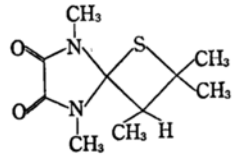

(III)

In the photochemical reduction in ethanol, thioparabanates seem to behave in a considerably different fashion from thiobenzophenone; in the case of thiobenzophenone, it is significant that the benzhydryl-thiyl radical $(C_6H_5)_2CHS\cdot$ is formed through the abstraction of the hydrogen atom from the solvent,[2] while in the case of thioparabanates the ketyl radical seems to be formed through the reaction.

Photocycloaddition. The photochemical addition reaction of dimethylthioparabanate (Ic) with amylene was attemtped in chloroform with a 200-W high-pressure mercury arc under a nitrogen atmosphere. A 1 : 1 addition product (IV) of dimethylthioparabanate and amylene was obtained as colorless crystals melting at 136.0—137.0°C. The mass spectrum of the adduct (IV) gave fragment ions at m/e 169.098 ($^{12}C_8{}^1H_{13}{}^{14}N_2{}^{16}O_2$ requires 169.0982) and m/e 103.058 ($^{12}C_5{}^1H_{11}{}^{32}S$ requires 103.0576). The NMR spectrum showed a quartet (a-methyne proton, 1H, J=6 Hz) at τ=6.54, a doublet (b-methyl protons, 3H, J=6 Hz) at τ=8.71, and four singlets, due to c-, d-, e-, and f-methyl protons, at τ=6.63, 6.78, 8.70, and 8.95. From these results, the adduct (IV) was identified as a trimethylenesulfide (IVa). The fragmentation patterns in the mass spectrum exclude the isomer (IVb) as a product since the fragment, C_3H_6S, coming from the C–S and C–C bond fission could not be detected.



(IVa)


(IVb)

In the cases of the other thioparabanates, no photocycloaddition reaction occurred.

Experimental

Materials. The thioparabanates (I) were prepared by the treatment of a ethylene dichloride solution of the corresponding thiourea with oxalyl chloride.[7] The thiourea were obtained from the reaction of the corresponding isothiocyanate and amine. The thioparabanates were purified by recrystallization from ethanol.

Amylene was prepared by treating t-amyl alcohol with concentrated H_2SO_4. This was purified by fractional distillation; bp 37.0—38.5°C.

Spectra. The visible and ultraviolet spectra were measured in an ethanol solution at 25°C using a Shimadzu UV50M spectrophotometer.

Irradiation of Diphenylthioparabanate (Ia). A solution of 7.0 g (0.025 mol) of the ester (Ia) in 500 ml of absolute ethanol was purged with nitrogen for 1 hr and then irradiated under nitrogen with a 200-W high-pressure mercury arc. The yellow solution of Ia completely faded within 15 hr. From the reaction mixture, ethanol was evaporated *in vacuo;* then the white residue was recrystallized from benzene, giving 1,3-diphenyl-2-mercapto-imidazolidine-4,5-dione (IIa) as silky crystals melting at 200.0°C; yield, 98%. The infrared spectrum in KBr showed the absorption of the oxalyl group at 1745 cm^{-1}. The NMR spectrum in hexadeuterio-dimethyl sulfoxide (d_6-DMSO) showed one proton at τ=2.51 as a sharp doublet (J=9.0 Hz), one proton at τ=4.28 (a sharp doublet, J=9.0 Hz), and a complex absorption (10H) centered at τ=2.75. Upon the addition of D_2O, the doublet at τ=2.51 disappeared and the doublet at τ=4.28 turned into a singlet at τ=4.28.

Found: C, 63.38; H, 4.26; N, 9.86; S, 11.26%. Calcd for $C_{15}H_{12}O_2N_2S$: C, 63.60; H, 4.04; N, 9.79;

---

*1 Most α-aminomercaptans, $-NH\overset{|}{\underset{|}{C}}SH$, like these analogs, *gem*-diols and α-hydroxymercaptans, are unstable and have never been isolated.

7) T. Yonezawa, M. Matsumoto, S. Tanimoto and H. Kitano, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **89**, 784 (1968).

S, 11.01%.

Irradiation of Benzylphenylthioparabanate (Ib). A solution of 7.4 g (0.025 mol) of the ester (Ib) in absolute ethanol (500 m*l*) was irradiated under a nitrogen atmosphere for 15 hr. In this case the solution was not faded. After irradiation the solvent was evaporated from the reaction mixture *in vacuo*. The oily residue was chromatographed on alumina in benzene, thus giving 1-benzyl-3-phenyl-2-mercapto-imidazolidine-4,5-dione (IIb) (5.9 g), mp 173.0°C after crystallization. The NMR spectrum showed complex absorption due to two phenyl groups centered at $\tau=2.61$ (11H), containing a signal of the mercapto proton, a sharp doublet at $\tau=4.28$ (1 H, $J=9.0$ Hz), and a singlet at $\tau=6.82$ (2H).

Found: C, 65.68; H, 4.59: N, 9.11%. Calcd for $C_{17}H_{14}O_2N_2S$: C, 65.80; H, 4.55; N, 9.03%.

Irradiation of Dimethylthioparabanate (Ic). A 0.05 mol/*l* solution of the ester (Ic) in ethanol (500 m*l*) was irradiated under a nitrogen atmosphere for 2 hr. Then the solution was concentrated under nitrogen at reduced pressure. The almost colorless oily residue was used for the measurement of its NMR spectrum. In this case the expected mercaptan (IIc) was very unstable and was easily oxidized by air to form the starting materials. The mercaptan (IIc) was characterized only by its spectroscopic properties, the NMR spectrum of the oil described previously showed a mercapto proton (a sharp doublet, $J=9.0$ Hz) at $\tau=2.82$ and a 2-methyne proton (a sharp doublet, $J=9.0$ Hz) at $\tau=4.89$.

Irradiation of Diethylthioparabanate (Id). The ester (Id) was treated by the similar manner to that employed in the case of dimethylthioparabanate (Ic). The NMR spectrum of the crude mercaptan (IId) showed a mercapto proton as a sharp doublet ($J=9.0$ Hz) at $\tau=2.93$ and a 2-methyne proton as a sharp doublet ($J=9.0$ Hz) at $\tau=4.89$. The crude reaction products was chromatographed on alumina in chloroform, and when the resultant pale yellow oil was allowed to stand for two weeks, colorless needles separated out, giving 2-(1-hydroxyethyl)-1,3-diethyl-2-mercapto-imidazolidine-4,5-dione (III), mp 134.0—135.0°C, by crystallization from cyclohexane. The NMR spectrum in d_6-DMSO showed a singlet (mercapto proton, 1H) at $\tau=3.02$, a doublet (hydroxy proton, 1H, $J=4.5$ Hz) at $\tau=4.87$, a complex absorption composed of a multiplet (methyne proton, 1H) centered at $\tau=6.35$ and a quartet (two methylene protons, 4H, $J=6.3$ Hz) at $\tau=6.38$, and a complex absorption composed of two triplets (methyl protons of two ethyl groups, 6H, $J=6.3$ Hz) at $\tau=8.75$ and 8.91 and a doublet (methyl protons of hydroxyethyl group, 3H, $J=6.3$ Hz) at $\tau=8.85$. These assignment were confirmed by spin-decoupling experiments.

Found: C, 46.39; H, 6.99; N, 12.25%. Cacld for $C_9H_{16}O_3N_2S$: C, 46.54; H, 6.94; N, 12.06%.

Irradiation of Thioparabanic Acid. A 0.05 mol/*l* solution of thioparabanic acid in ethanol was irradiated with a 200-W high-pressure mercury arc under a nitrogen atmosphere for 10 hr. During irradiation the evolution of carbon monooxide and hydrogen sulfide was observed. A trace of formaldehyde was also detected in the reaction mixture by Denigès' method. The evaporation of ethanol from the solution gave crude thiourea in the yield of 73%.

Irradiation of Some Monoesters of Thioparabanic Acid. The photochemical reduction reactions were attempted for phenylthioparabanate and benzylthioparabanate. In these cases the formation of acetaldehyde was recognized and no corresponding mercaptan (II) was obtained, only a tarry product.

Irradiation of Dimethylthioparabanate (Ic) with Amylene in Chloroform. A solution of dimethylthioparabanate (Ic) (5.0 g, 0.032 mol), and amylene (40.0 g, 0.57 mol) in chloroform (25 m*l*) was irradiated with a 200-W high-pressure mercury arc under a nitrogen atmosphere for 20 hr. After irradiation, the unreacted amylene and solvent were distilled off from the reaction mixture. Then an oily residue was dissolved in 20 m*l* of chloroform and chromatographed on alumina (150 g) in 1 : 1 chloroform and petroleum ether. This gave, successively, colorless needles (IV) (210 mg), colorless leaflects (V) (30 mg), and dimethylparabanate (200 mg) as a colorless leaflets which showed a mp of 152.0°C, after crystallization from cyclohexane (Biltz and Topp[8]) give mp 154.0°C). The recrystallization of IV from cyclohexane yielded the trimethylenesulfide (IVa), mp 136.0—137.0°C. The NMR spectrum in deuteriochloroform showed a complex absorption comprised of a quartet (a-methyne proton, 1H, $J=6.0$ Hz) at $\tau=6.54$, two singlets (c- and d-methyl protons, 6H) at $\tau=6.63$ and $\tau=6.78$, a doublet (b-methyl protons, 3H, $J=6.0$ Hz) at $\tau=8.71$, and two singlets (e- and f-methyl protons, 6H) at $\tau=8.70$ and $\tau=8.95$. These assignments were confirmed by spin-decoupling experiments. The infrared spectrum in chloroform showed $\nu_{C=O}$ at 1740 cm^{-1}. The mass spectrum exhibited fragment ions at *m*/*e* 103.058 ($^{12}C_5{}^1H_{11}{}^{32}S$ requires 103.0576) and *m*/*e* 169.098 ($^{12}C_8{}^1H_{13}{}^{14}N_2{}^{16}O_2$ requires 169.0982).

Found: C, 52.45; H, 6.92; N, 12.20%. Calcd for $C_{10}H_{16}O_2N_2S$: C, 52.55; H, 7.00; N, 12.25%.

The identification of V is not yet complete, but we presume, from its NMR and mass spectra, and from the results of elemental analysis, that V is a 2 : 2 adduct of dimethylthioparabanate (Ic) and amylene.

---

8) H. Biltz and E. Topp, *Ber.*, **47**, 1387 (1913).