of crystalline product was obtained and was characterized as isoandrosterone by infrared spectrometry. A portion, m.p. 175–176°, when admixed with an authentic sample of isoandrosterone, m.p. 175–178°, showed no depression of the m.p.

The aqueous alkaline layer from the saponification of the oxidation product was acidified and extracted with ether. The ether layer was washed free of acid with sodium chloride solution and dried. Evaporation of the solvent yielded 48 mg. of product, m.p. 157–167°, which proved to be identical with isoandrololactone (IIIa), m.p. 169–170°, by its infrared spectrum. Upon acetylation and recrystallization from ether–petroleum ether, isoandrololactone acetate (IIIb), m.p. 155–157°, was obtained which did not depress the m.p. of an authentic sample of isoandrololactone acetate[10] and exhibited an identical infrared spectrum with the authentic product.

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Quinoxaline-2-thiol and Derivatives

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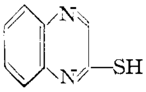
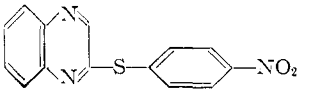
During a study of quinoxaline compounds of possible therapeutic value, the preparation of quinoxaline-2-thiol (I) and related compounds was undertaken. The parent thiol I was obtained readily by treating 2-chloroquinoxaline with thiourea followed by hydrolysis of the resulting S-2-quinoxalylisothiouronium chloride. 2-Quinoxalyl *p*-nitrophenyl sulfide (II) was prepared from 2-chloroquinoxaline and *p*-nitrothiophenol. In a similar manner, 2-chloro-6-(or 7)-nitroquinoxaline formed the expected sulfide when treated with *p*-nitrothiophenol. It is of interest that the sulfide II was not obtained from the thiol I and *p*-nitrochlorobenzene under the conditions studied. On the other hand, the thiol readily yielded di-2-quinoxalyl sulfide when heated with 2-chloroquinoxaline.



I



II

The sulfides were converted to the sulfones by oxidation with hydrogen peroxide.

Experimental

Quinoxaline-2-thiol.—A solution of 22 g. of 2-chloroquinoxaline[1] and 20 g. of thiourea in 150 ml. of methanol was refluxed for ten minutes. After cooling to 5°, the crystalline crude isothiouronium hydrochloride was separated. The crude product, 31.5 g., 97.7% yield, melted at 150–155°; a sample recrystallized from methanol melted at 159–160°.

A mixture of 15 g. of the crude isothiouronium hydrochloride and 100 ml. of 2.5 *N* sodium hydroxide was heated on a steam-bath for 45 minutes. The orange solution was cooled, acidified with acetic acid and the product was separated by filtration. On recrystallization from 200 ml. of methanol, a bright orange crystalline product, m.p. 204–205°, 7.3 g., 73% yield, was obtained.

Anal.[2] Calcd. for $C_8H_6N_2S$: C, 59.3; H, 3.7; N, 17.3. Found: C, 59.2; H, 3.9; N, 17.3.

2-Quinoxalyl *p*-Nitrophenyl Sulfide.—A solution of 55 g. of *p*,*p'*-dinitrodiphenyl disulfide,[3] 26 g. of sodium sulfide nonahydrate and 14 g. of sodium hydroxide in 1500 ml. of 60% ethanol–water was refluxed for 20 minutes. The hot solution was added to a warm solution of 61 g. of 2-chloroquinoxaline in 1250 ml. of ethanol. The resulting dark red solution was refluxed 30 minutes and then refrigerated 18 hours at 5°. The crude product, 50 g., was filtered and recrystallized from 2 l. of methanol. The product, 19.5 g., 19.3% yield, was obtained as pale yellow needles having a silky appearance, m.p. 151–152°.

Anal. Calcd. for $C_{14}H_9N_3O_2S$: C, 59.4; H, 3.2; N, 14.8. Found: C, 59.0; H, 3.3; N, 15.2.

6-(or 7)-Nitro-2-quinoxalyl *p*-Nitrophenyl Sulfide.—The reaction was carried out as above with 10 g. of 6-(or 7)-nitro-2-chloroquinoxaline,[4] m.p. 184–186°. The crude product was recrystallized from glacial acetic acid yielding a pale orange micro-crystalline solid, m.p. 196°, 10.3 g., 65.5% yield.

Anal. Calcd. for $C_{14}H_8N_4O_4S$: C, 51.2; H, 2.4; N, 17.1. Found: C, 51.3; H, 2.5; N, 17.4.

Di-2-quinoxalyl Sulfide.—A solution of 16 g. of 2-chloroquinoxaline, 16 g. of quinoxaline-2-thiol and 5.35 g. of sodium methylate in 270 ml. of methanol was refluxed 16 hours. The mixture, containing some precipitated product, was cooled and filtered. The crude product was recrystallized from 1500 ml. of methanol, whereupon material, 16 g. melting at 159°, was obtained. A second crop (3 g., total yield 67.1%), m.p. 158–159°, was obtained by concentrating the recrystallization liquors.

Anal. Calcd. for $C_{16}H_{10}N_4S$: N, 19.4. Found: N, 19.4.

2-Quinoxalyl *p*-Nitrophenyl Sulfone.—A mixture of 11 g. of 2-quinoxyl *p*-nitrophenyl sulfide, 400 ml. of glacial acetic acid and 30 ml. of 30% hydrogen peroxide was shaken for four hours and the resultant solution allowed to stand four days at 30°. The crude product, precipitated by pouring the mixture into 1500 ml. of water, was recrystallized from 100 ml. of glacial acetic acid. The product, 5.6 g., 45% yield, was obtained as silky needles having a yellowish cast, m.p. 197–199°. A sample recrystallized for analysis from ethanol melted at 202–203°.

Anal. Calcd. for $C_{14}H_9N_3O_4S$: C, 53.4; H, 2.9; N, 13.3. Found: C, 53.3; H, 3.0; N, 13.5.

Di-2-quinoxalyl Sulfone.—The same method of preparation was used, the product, m.p. over 360°, was obtained as white needles in 32% yield.

Anal. Calcd. for $C_{16}H_{10}N_4O_2S$: C, 59.7; H, 3.1; N, 17.4. Found: C, 59.4; H, 3.5; N, 17.5.

6-(or 7)-Nitro-2-quinoxalyl *p*-Nitrophenyl Sulfone.—The same method of preparation was used, the product, m.p. over 240°, was obtained as white needles having a tan cast in 20% yield.

Anal. Calcd. for $C_{14}H_8N_4O_6S$: C, 46.8; H, 2.2; N, 15.5. Found: C, 46.8; H, 2.3; N, 15.4.

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[2] Microanalyses were kindly performed by Messrs. R. Boos, E. Thornton, J. MacGregor, A. Rosalsky and Mrs. C. Miess.

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[4] F. J. Wolf, K. Pfister, R. H. Beutel, R. M. Wilson, C. A. Robinson and J. R. Stevens, THIS JOURNAL, **71**, 6 (1949).

The Reaction of the Alkoxides of Titanium, Zirconium and Hafnium with Esters

BY R. C. MEHROTRA

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The reaction of aluminum isopropoxide with organic esters has been studied by Baker.[1] The preparation and properties of the alkoxides of titanium, zirconium and hafnium have been described in a number of recent communications[2] and it has been shown that in contrast with the tetraalkoxy silanes, the alkoxides of titanium, zirconium and hafnium readily exchange their alkoxy groups with other alcohols. In this communication, it has been

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[1] R. H. Baker, THIS JOURNAL, **60**, 2673 (1938).

[2] D. C. Bradley, R. C. Mehrotra and W. Wardlaw, *J. Chem. Soc.*, 2027, 4204, 5020 (1952); 1634 (1953).