

sorption of the enol lactone obtained above. The acidic fraction (VI), 91 mg., was crystallized from ethanol, m.p. 154–156°, undepressed with the keto acid above.

**Oxidation of Methyl Dehydroabietate (VIII).**—The methyl ester, m.p. 62–63°, 3.14 g., was oxidized at 70° in 300 ml. of acetic acid with 7.8 g. of chromium trioxide in 4 ml. of water and 100 ml. of acetic acid as already described in previous oxidations. The neutral oxidation product was recrystallized from ethanol in the form of prisms, m.p. 143–144°. This substance has been shown by ultraviolet and infrared spectral comparisons and by mixed m.p. to be 1,2-dimethyl-1-carbomethoxy-7-acetyl-1,2,3,4,9,10,11,12-octahydro-9-phenanthrene (IX).<sup>6</sup> Yields ranging from 17–20% of IX were obtained from a series of duplicate oxidations.

## Some Esters of 2-Thenoic Acid

BY BORIS WEINSTEIN

RECEIVED SEPTEMBER 6, 1955

Several 2-thenoic acid esters were prepared by refluxing 10 g. (0.07 mole) of the acid in an excess (125 ml.) of the required alcohol containing 5 ml. of concd. sulfuric acid. After heating for four hours, the crude ester was worked-up in the usual manner and vacuum distilled. The ethyl<sup>1</sup> and phenyl<sup>2</sup> esters have been reported previously.

TABLE I  
ESTERS OF 2-THENOIC ACID

Ester	Yield, %	B.p. uncor.		$n_D^{20}$	$d_4^{20}$	Carbon		Hydrogen		Sulfur		MR <sub>D</sub>	
		°C.	Mm.			Calcd.	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.	Calcd. <sup>a</sup>	Obsd.
Methyl	71	40	0.50	1.5420	1.2290	50.71	50.80	4.26	4.20	22.52	22.49	36.38	36.35
Ethyl	78	45	.40	1.5248	1.1620	53.84	53.88	5.16	5.00	20.50	20.60	41.03	41.18
<i>n</i> -Propyl	75	57	.45	1.5170	1.1123	56.46	56.48	5.92	6.10	18.81	18.56	45.70	46.28
Isopropyl	31	36	.05	1.5120	1.1026	56.46	56.52	5.92	5.88	18.81	18.73	45.71	46.33
<i>n</i> -Butyl	80	58	.15	1.5122	1.0859	58.69	58.64	6.57	6.56	17.38	17.31	50.32	50.93
Isobutyl	60	43	.06	1.5083	1.0751	58.69	58.54	6.57	6.67	17.38	17.38	50.35	51.12
<i>sec</i> -Butyl	32	46	.18	1.5075	1.0862	58.69	58.62	6.57	6.88	17.38	17.36	50.15	50.52
<i>n</i> -Amyl	67	63	.13	1.5071	1.0573	60.59	60.84	7.12	7.16	16.15	15.96	54.98	55.82
Tri-isoamyl	59	76	.07	1.5068	1.0593	60.59	60.91	7.12	6.93	16.15	16.26	54.93	55.60
<i>n</i> -Decyl	83	130	.13	1.4947	0.9995	67.13	67.19	9.02	8.92	11.93	11.97	78.05	78.28
Benzyl	22	98	.03	1.5720	1.1672	64.70	64.63	3.95	3.91	15.68	15.65	60.63	61.54

<sup>a</sup> Contains the sulfide value derived from dialkyl sulfides. constant based on alkylphenyl sulfides.

Individual sums are increased by 0.56 unit using the sulfide

A total of 220 mg. of crude acidic product was isolated which melted at 120° and evolved carbon dioxide at 160°. Consequently 177 mg. of this material was heated between 120–160° until gas evolution ceased, giving a weight loss of 16 mg. A portion of this product (130 mg.) was separated into neutral and acidic fractions in the usual way. The acidic fraction (99 mg.) was crystallized, after seeding, from methanol as prisms of the keto acid VI, m.p. 154–156°, undepressed with VI from the deamination reactions above. The neutral fraction could not be crystallized but gave the infrared absorption attributed to the enol lactone VII above.

**Interconversion of Enol Lactone VII and Keto Acid VI.**—The neutral product, VII, (10 mg.) from the deamination of IV and V and from the oxidation of methyl dehydroabietate was refluxed for 5 minutes in 10 ml. of 5% aqueous alcoholic sodium hydroxide. After dilution of the clear solution with 50 ml. of water, the solution was acidified and extracted with ether. Crystallization of the residue from the ether solution gave prisms of the keto acid VI, m.p. 154–156°, mixed m.p. undepressed.

The keto acid (20 mg.) was refluxed in 5 ml. of acetic anhydride for 12 hours. This was diluted with 20 ml. of water and warmed for a short time, after which it was further diluted and extracted with ether. After washing and elimination of the ether, a resinous substance remained which resisted crystallization but gave infrared absorption identical to that of the enol lactone VII obtained above.

CONTRIBUTION NO. 1250 FROM  
STERLING CHEMISTRY LABORATORY  
YALE UNIVERSITY  
NEW HAVEN, CONNECTICUT

(6) We wish to thank the Hercules Powder Company for supplying us with a sample of this diketo ester from their Experimental Station for these comparisons.

The molar refractivities of the esters are slightly higher than the calculated values.<sup>3</sup> A similar exaltation is shown by 2-acetylthiophene<sup>4</sup> although thiophene gives an optical depression.<sup>5</sup> It should be noted that Vogel's quotation for the sulfide refraction value was based upon a dialkyl sulfide series. However, phenyl alkyl sulfides exhibit a consistently higher value for the sulfide constant.<sup>6</sup> The "high" molar refraction values of the esters would be eliminated by using the modified sulfide constant. The esters' infrared spectra (2–35 $\mu$ ) will be discussed elsewhere.

**Acknowledgment.**—The author wishes to thank Mr. W. R. Powell, Mrs. N. E. Srp, Lt. G. D. Oshesky and Lt. E. F. Wolfarth for technical assistance and Mr. F. F. Bentley for suggesting the problem.

MATERIALS LABORATORY  
WRIGHT-PATTERSON AFB, OHIO

(1) H. D. Hartough, "Thiophene and Its Derivatives," Interscience Publishers, Inc., New York, N. Y., 1952, p. 376.

(2) H. W. Rhodelhamel, Jr., and E. F. Degering, *J. Am. Pharm. Assoc.*, **31**, 281 (1942).

(3) A. I. Vogel, *J. Chem. Soc.*, 1842 (1948).

(4) G. C. Johnson, *THIS JOURNAL*, **69**, 150 (1947).

(5) R. Nasini and G. Carrara, *Z. physik. Chem.*, **17**, 539 (1895).

(6) A. I. Vogel, *J. Chem. Soc.*, 1820 (1948).