SOME MERCAPTOLES OF 1,2-ETHANEDITHIOL[1]

E. EMMET REID AND ARTHUR JELINEK

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Two dithiolanes from 1,2-ethanedithiol and simple ketones, acetone and benzophenone, are recorded (1). It seemed worth while to enlarge this group. Dithiolanes described herein have been prepared from several aliphatic ketones, from acyl benzenes—acetophenone to caprylophenone, from cyclopentanone,

TABLE I

PROPERTIES AND ANALYSES OF 1,3-DITHIOLANES WITH 2,2-SUBSTITUENTS

NO.	KETONE	B.P.		n_D^{25}	d_4^{25}	ANALYSES					
						C		H		S	
		°C.	MM.			Calc'd	Found	Calc'd	Found	Calc'd	Found
1	Methyl ethyl	55	3	1.5350	1.0680	48.60	48.83	8.16	8.33	43.24	43.45
2	Methyl isopropyl	61	3	1.5302	1.0511	51.80	51.87	8.69	8.86	39.51	39.71
3	Dipropyl	86	2	1.5200	1.0158	56.79	57.01	9.53	9.69	33.68	33.52
4	Ethyl butyl	102	5	1.5191	1.0126	56.79	57.01	9.53	9.69	33.68	33.52
5	Diisopropyl[a]	94	4	—	—	56.79	56.80	9.53	9.67	33.68	33.62
6	Methyl hexyl	120	6	1.5110	0.9926	58.77	58.87	9.86	10.13	31.37	31.72
7	Diisobutyl	115	6	1.5115	0.9892	60.49	60.43	10.16	10.43	29.36	29.64
8	Acetophenone	131	3	1.6162	1.1819	61.18	61.57	6.16	6.41	32.66	32.83
9	Propiophenone	135	3	1.6050	1.1542	62.80	63.12	6.71	6.93	30.49	30.62
10	Butyrophenone	145	4	1.5915	1.1287	64.24	64.44	7.19	7.48	28.57	28.32
11	Valerophenone	154	4	1.5830	1.1035	65.49	65.75	7.61	7.86	26.90	26.82
12	Caprylophenone	169	4	1.5755	1.0838	66.61	66.98	7.99	8.30	25.40	25.39
13	Cyclopentanone	89	5	1.5679	1.1464	52.45	53.14	7.55	7.67	40.00	39.89
14	Cyclohexanone	107	5	1.5650	1.1288	55.12	55.44	8.10	8.34	36.79	37.20
15	4-Methylcyclohexanone	126	13	1.5478	1.0907	57.40	57.97	8.57	8.77	34.05	33.89
16	Camphor	131	4	1.5606	1.0839	63.10	63.75	8.83	9.06	28.07	28.39
17	Fluorenone[b]	—	—	—	—	70.26	70.50	4.72	4.83	25.01	25.05
18	2-Acetylthiophene	123	1.4	1.6300	1.2756	—	—	—	—	47.52	47.64
19	2-Benzoylthiophene[c]	—	—	—	—	—	—	—	—	36.36	36.14

[a] M.p. 40°. [b] M.p. 125°. [c] M.p. 53.5°.

cyclohexanone, 4-methylcyclohexanone, camphor, and fluorenone. Those from the last five are *spiro* compounds. In addition there are two from thiophene derivatives, 2-acetylthiophene and 2-benzoylthiophene.[2] Properties and analyses are given in Table I.

[1] The compounds were prepared in Personal Laboratory at Johns Hopkins University. Determinations of properties and analyses were done at Du Pont Experimental Station, Wilmington, Delaware.

[2] Determination of properties and analyses by H. O. Hartough and S. L. Meisel of Socony-Vacuum Laboratories.

EXPERIMENTAL

All of the dithiolanes were prepared in practically the same way, saturating a mixture of the ketone and 1,2-ethanedithiol with hydrogen chloride. The two solid ketones were brought into solution by the addition of benzene. With the two active ketones, cyclopentanone and cyclohexanone, aqueous hydrochloric acid was used instead of the gas. In some cases the reactants were in stoichiometric proportions and in others the ketone was in slight excess while in one, No. 9, 84% excess of the dithiol was put in by mistake. Variations in the proportions appear to make no difference in the products. The aliphatic ketones reacted at once, with evolution of heat; so did cyclopentanone and cyclohexanone and its 4-methyl derivative, while the acyl benzenes reacted appreciably slower. To facilitate the collection of the separated water, calcium chloride was added to some and zinc chloride to others. The zinc salt is better. After a reaction mixture had stood overnight the organic layer was decanted and resaturated with hydrogen chloride. Ether was added, the ether solution separated, washed with water and dilute alkali, and dried over potassium carbonate. After removal of the ether the residue was distilled through an 8-inch Vigreux column. There were no appreciable distillation residues. The dithiolane from diisopropyl ketone was further purified by recrystallization from methanol. Those from fluorenone and benzoylthiophene were not distilled but were recrystallized from ethanol.

SUMMARY

The preparation and properties of 19 new 2,2-substituted-1,3-dithiolanes, 7 from aliphatic, 5 from aralkyl, 5 from cyclic, and 2 from thiophene ketones, are described.

BALTIMORE 18, MD.

REFERENCE

(1) FASBENDER, *Ber.*, **20**, 460 (1887); FASBENDER, *Ber.*, **21**, 1473 (1888).