[Contribution from the Research Department, Standard Oil Company (Indiana)]

Addition of 1,3,4-Thiadiazole-2,5-dithiol to Olefinic Compounds

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Received October 31, 1955

1,3,4-Thiadiazole-2,5-dithiol adds to a variety of olefinic compounds to give mono- and di-thioethers. Twelve such adducts are described. Styrene gives the abnormal, peroxide-catalyzed type of adduct. 1-Octene gives only the normal adduct, even in the presence of peroxides.

The only known thioethers of 1,3,4-thiazole-2,5-dithiol (DMTD) are the dimethyl and dibenzyl thioethers. These were made by Busch[1] from the potassium salt of DMTD and the corresponding halides. In these laboratories it has been found that DMTD adds to a variety of olefinic compounds to give mono- and di-thioethers. Twelve such adducts are described in Table I.

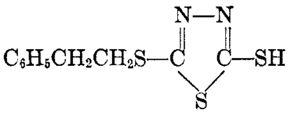
TABLE I

Adducts of DMTD With Olefinic Compounds

Olefin	Mol Ratio, DMTD: Olefin	Yield, %	Adducts M.p., °C.	n_D^{20}	Analyses C Calc'd	C Found	H Calc'd	H Found	N Calc'd	N Found	S Calc'd	S Found
Styrene	1:1	92	103	—	47.24	47.40	3.97	3.72	11.02	10.86	37.79	37.60[b]
	1:2	60	—	1.6742	60.34	60.55	5.03	5.21	7.82	7.73	26.80	26.80
α-Methyl-styrene	1:1	66	122	—	—	—	—	—	10.45	10.33	35.82	35.80
	1:2	88	—	1.6750	—	—	—	—	7.25	7.33	24.87	24.70
1-Octene	1:1	52	—	1.6223	45.78	45.60	6.88	6.66	10.69	10.75	36.64	36.40
1-Octadecene	1:1	52	72–74	—	—	—	—	—	6.97	6.94	23.90	23.70[c]
α-Pinene	1:2	67	—	1.5998	—	—	—	—	6.68	6.55	22.86	22.60
dl-Limonene	1:1	91	—	1.5991	—	—	—	—	9.80	9.59	33.55	33.70
Benzalacetone	1:1	95	117	—	—	—	—	—	9.46	9.33	32.41	32.20
	1:2	94	—	[a]	—	—	—	—	6.08	6.30	20.80	20.80
Acrylic acid	1:1	95	138	—	—	—	—	—	12.62	12.88	43.25	43.10
2-Ethylhexyl acrylate	1:2	100	—	1.5293	55.75	56.00	8.10	8.01	5.42	5.50	18.53	18.80

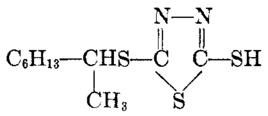
[a] Substance was a glass. [b] Molecular weight, 239. [c] Molecular weight, 409.

With one mole of styrene, DMTD rapidly reacts, presumably by a chain mechanism, to give



In the presence of an added strong antioxidant and in the dark, no reaction takes place; DMTD thus behaves like thioglycollic acid with styrene.[2]

With 1-octene, DMTD unexpectedly gives only the normal addition product



even in the presence of peroxides and light. The structure of this adduct was proved by the synthesis of the two 2-octylthia-5-mercapto-1,3,4-thiadiazoles from mono-potassium DMTD and 1- and 2-bromooctane. The 2-bromooctane gave a liquid with the same refractive index as the octene adduct, whereas the 1-bromooctane product was a solid, melting at 75°. Kharasch, May, and Mayo[3] found that this type of reaction is not always reliable as a proof of structure. However, the infrared absorption data showed that the 2-bromooctane derivative and the octene adduct were the same, and that both differed markedly from the 1-bromooctane derivative.

It is known that mercaptans add to olefins in the presence of strong acids to give the normal adduct.[4] DMTD was prepared under purified nitrogen and was reacted with peroxide-free 1-octene *in vacuo* to preclude the formation of acid at any point. The same product was obtained as from 2-bromooctane and DMTD. The identical product was again formed, though more rapidly, when 1% ethanesulfonic acid was added to the DMTD and 1-octene.

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(1) M. Busch, *Ber.*, **27**, 2518 (1894).

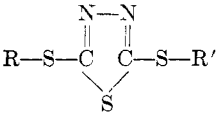
(2) M. S. Kharasch, A. T. Read, and F. R. Mayo, *Chemistry and Industry*, 752 (1938).

(3) M. S. Kharasch, E. M. May, and F. R. Mayo, *J. Org. Chem.*, **3**, 175 (1938).

(4) B. H. Shoemaker and H. R. Batchelder, U. S. Patent 2,211,990, August 20, 1941; W. A. Schulze and W. W. Crouch, U. S. Patent 2,454,409, November 23, 1948.

TABLE II

COMPOUNDS SYNTHESIZED FOR PROOF OF STRUCTURE



Compound		Yield, %	M.p., °C.	Analyses C		H		N		S	
R	R′			Calc'd	Found	Calc'd	Found	Calc'd	Found	Calc'd	Found
2-Phenylethyl	H	80	103	—	—	—	—	11.02	11.00	37.79	37.70
1-*n*-Octyl	H	92	75	45.78	45.60	6.88	6.66	10.69	10.69	36.64	36.60
2-*n*-Octyl	H	94	[a]	45.78	45.65	6.88	7.09	10.69	10.46	36.64	36.40[b]
1-*n*-Octadecyl	H	85	97	59.65	59.50	9.46	9.37	6.97	6.74	23.90	23.80
1-*n*-Octadecyl	Carboxymethyl	90	96	—	—	—	—	6.08	6.06	20.85	21.00
2-*n*-Octadecyl	Carboxymethyl	92	76–78[c]	—	—	—	—	6.08	5.87	20.85	20.59

[a] n_{D}^{20} 1.6220. [b] Molecular weight, 270. [c] Sinters at 62°.

In another attempt to form the "abnormal" addition product, *tert*-butyl hydroperoxide and DMTD were added simultaneously in small portions to 1-octene. The product yielded no crystalline adduct, and its infrared absorption showed none of the differentiating bands of the thioether from 1-bromooctane and DMTD.

EXPERIMENTAL

2,5-Dimercapto-1,3,4-thiadiazole (DMTD) was prepared from hydrazine and carbon disulfide, and was recrystallized from alcohol under nitrogen to give colorless crystals, m.p. 168° (dec.). *Acrylic acid* and *2-ethylhexyl acrylate* were from Rohm and Haas; *1-octene* and *1-octadecene*, from Humphrey-Wilkinson; all other chemicals, from Eastman.

Preparation of adducts. To prepare the adducts, DMTD generally was stirred with each olefin at 110–130° until all solid disappeared. When 1 mole of olefin was used per mole DMTD, the mixture was stirred for one more hour; with 2 moles of olefin, for 10–24 hours. No solvent was needed except with 1-octadecene, in which case dioxane was used. All crystalline adducts were recrystallized from benzene:-petroleum ether.

The non-crystalline 1:1 adducts, which have an acidic SH group, were purified by dissolving in excess 10% sodium carbonate solution, separating the aqueous solution, and acidifying it with dilute hydrochloric acid. The liberated oils were separated, dried, and filtered. Traces of moisture were removed by heating under a vacuum at 80°.

The 1:2 adducts, all viscous oils or glasses, were purified by dissolving in ether, washing the ether solutions 4 times with 10% sodium carbonate solution, drying, and evaporating—finally at 0.1 mm. and 120° for 16 hours.

Proof of structure. The structures of three of the adducts were determined by independent synthesis, mixture melting point, and infrared absorption.

1:1 Styrene adduct. DMTD (30 g., 0.2 mole), in 200 ml. of 95% ethanol was converted to the mono-potassium salt with 11.2 g. (0.2 mole) of potassium hydroxide in 60 ml. of ethanol, and was refluxed for 5 hours with 37 g. (0.2 mole) of 2-bromoethylbenzene. The reaction mixture was poured into 1 liter of water and the solid was collected on a filter. It was washed thoroughly with water, sucked dry, and crystallized from benzene:petroleum ether to give 40.6 g. of 2-(β-phenethylthio)-5-mercapto-1,3,4-thiadiazole, m.p. 103°; mixture m.p. with the 1:1 styrene adduct, 103°.

1:1 Octene adduct. Mono-potassium DMTD was reacted with 1- and 2-bromooctane in the same way as with bromoethylbenzene. 1-Bromooctane gave 2-(1-*n*-octylthio)-5-mercapto-1,3,4-thiadiazole, m.p. 75°. 2-Bromooctane gave a viscous yellow oil with a refractive index almost identical to that of the octene adduct. The infrared absorption spectra of the thioether from 2-bromooctane and the octene adduct were identical; both had a strong methyl band at 1375 cm.$^{-1}$. The thioether from 1-bromooctane has a similar spectrum, but it has some different bands and only a very weak band at 1375 cm.$^{-1}$

The literature contains no infrared absorption data for DMTD. When examined in a potassium bromide pellet, it showed strong bands at 3060, 2850, 2462, 1504, 1452, 1265, 1123, 1060, 1050, and 716 cm.$^{-1}$

1:1 Octadecene adduct. Mono-potassium DMTD with 1-bromooctadecane gave 2-(1-*n*-octadecylthio)-5-mercapto-1,3,4-thiadiazole, m.p. 97°. This compound was reacted with a four-fold excess of chloroacetic acid in excess 5% sodium carbonate solution at 80° for 3 hours with stirring; the solution was acidified and the solid was collected on a filter, washed, dried, and crystallized from petroleum ether. The 2-(1-*n*-octadecylthio)-1,3,4-thiadiazole-5-mercaptoacetic acid melted at 96°. The same reaction with the octadecene adduct gave an acid sintering at 62° and melting at 76–78°.

Oxidant and antioxidant reactions. A solution of 0.1 mole of DMTD and 0.1 mole of styrene containing 0.01% *tert*-butylcatechol in peroxide-free dioxane in the dark at 25° showed no change in titratable acidity after 144 hours. The same solution was treated with 1 mol-% *tert*-butyl hydroperoxide and exposed to room light at 25°; it showed 44% reaction after 144 hours.

A solution of 0.1 mole of octene, 0.1 mole of DMTD, and 0.001 mole of *tert*-butyl hydroperoxide in 100 ml. of dioxane was heated at 100° for 4 hours. Every hour an additional 0.001 mole of *tert*-butyl hydroperoxide was added. The dioxane and unreacted octene were distilled *in vacuo* and the cooled residue was filtered. The filtrate, 5.2 g., was a yellow oil, n_{D}^{20} 1.6224. The yellow solid on the filter melted over a wide range and was probably a mixture of unreacted DMTD and DMTD polysulfides.

Peroxide-free 1-octene (0.1 mole) was distilled over sodium *in vacuo* into a tube containing 0.1 mole of DMTD which had been prepared under purified nitrogen. The tube was sealed off and heated at 100° for 26 hours. The cooled contents were diluted with 50 ml. of benzene:petroleum ether; the solid (4.7 g., unreacted DMTD) was filtered off, and the filtrate was evaporated *in vacuo*, giving 8.2 g. (31%) of an oily adduct, n_{D}^{20} 1.6224.

A mixture of 15.56 ml. (0.1 mole) of 1-octene, 7.5 g. (0.05 mole) of DMTD, and 0.2 g. of ethanesulfonic acid was stirred under nitrogen at 100°. After 8 hours all the solid had gone into solution. The mixture was diluted with 50 ml. of benzene, washed thoroughly with water to remove the sulfonic acid, dried, filtered, and evaporated under a vacuum. The residue was stirred with 250 ml. of *n*-heptane, and the lower insoluble layer was separated and freed from heptane under a vacuum. The product, 8.1 g. (60%), n_D^{20} 1.6218, had the same infrared absorption as the thioether from 2-bromooctane and DMTD.

To 31.12 ml. (0.2 mole) of 1-octene at 100° was added simultaneously 2 ml. of *tert*-butyl hydroperoxide and a solution of 3 g. (0.02 mole) of DMTD in 30 ml. of dioxane with stirring over a 2-hour period. The mixture was taken up in 50 ml. of benzene, washed thoroughly with water, dried, filtered, and evaporated to a 20-ml. volume under a vacuum. This liquid was diluted with 150 ml. of *n*-heptane, and the lower layer was separated and washed twice with 50 ml. of *n*-heptane, and finally was evaporated at 100° and 0.1 mm. The product was a dark reddish-brown oil which could not be induced to crystallize, and which gave the same infrared absorption bands as the thioether from 2-bromooctane and DMTD.

No reaction was observed between 2,2′-dimercapto-5,5′-bis-1,3,4-thiadiazole disulfide[5] and octene-1, octadecene-1, or 2-ethylhexyl acrylate after 10–12 hours at 120°, with or without *tert*-butyl hydroperoxide.

Acknowledgment. The author is indebted to R. R. Hopkins for the infrared absorption data, and to Professor M. S. Kharasch of the University of Chicago for his constructive suggestions in his role as referee.

WHITING, INDIANA

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[5] M. Busche and E. Ziegele, *J. prakt. Chem.*, [2] **60**, 40(1899).