

## SYNTHESIS OF DIMERCAPTHIOPYRONE DERIVATIVES

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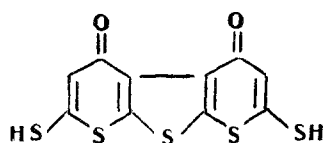
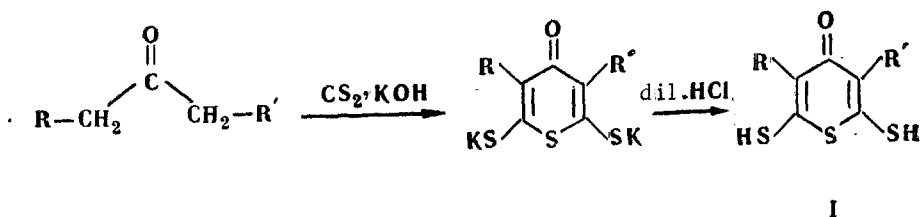
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Dimercapthiopyrone derivatives are synthesized. These compounds, which have not been described in the literature, can be used as new analytical reagents.

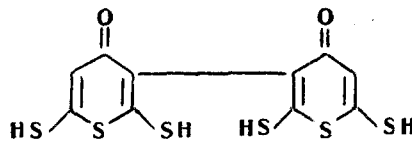
As an extension of previous work [1, 2], a number of new dimercapthiopyrone derivatives I, not previously described in the literature, have been synthesized, with a view to discovering sensitive and selective reagents for individual cations [3].

Preliminary experiments show that derivatives DF, DE, DP, and DB (see Table) are especially sensitive to bismuth ions. Derivatives DP and P are more suitable for copper.

The synthesis of dimercapthiopyrones is based on reaction of carbon disulfide and potassium hydroxide with ketones. The products are obtained from the reaction mixture by acidifying, and are purified in the usual way. The equation is:



II



III

EXPERIMENTAL

Synthesis of dimercapthiopyrones. A mixture of appropriate ketone, carbon disulfide, and powdered potassium hydroxide (the last two in slight excess over the stoichiometric amounts) is placed in a flask fitted with a reflux condenser, and refluxed gently for two hours, then left for 24 hr at room temperature. The contents of the flask are periodically mixed; they gradually turn brown and solidify. When reaction is finished, excess carbon disulfide and unreacted carbon disulfide are poured off, and the solid mass dissolved in water.

Residual carbon disulfide and ketone are extracted with ether. Then, with good cooling, the dimercapthiopyrone is carefully precipitated by acetic acid, and then by dilute hydrochloric acid. Carbon disulfide and carbon dioxide are copiously evolved. The crude product forms a brownish-organic precipitate. It is purified by precipitation from 4M alkali or sodium acetate, followed by acidification with dilute hydrochloric acid. After 3-5 reprecipitations the pure reaction product is dried for 5-6 hr at 70-80°.

The starting compounds for preparing dimercapthiopyrones MP, G, B [1], P, DB, DP and Bis 3-3 [1] were, respectively, butyl ethyl ketone, methyl heptyl ketone, benzyl acetone, methyl butyl ketone, diamyl ketone, dibutyl ketone, and acetylacetone.

Two types of compounds II and III could conceivably be formed by reaction of acetylacetone with carbon disulfide and potassium hydroxide.

Elementary analysis of the product and its molecular weight indicate that what is actually formed is a compound of type II. Found: S 57.3%, M 365, calculated for II: S 50.6%, M 316; for III: S 57.8%, M 374.

The dimercapthiopyrone derivatives prepared (yields 5-25%) are crystalline substances which form yellow, red, orange, or yellowish-brown needles. They are very soluble in alkalis, sodium acetate, alcohol, dioxane, xylene and acetic acid, insoluble in hexane and petrol ether. The recrystallized substances are dried at 60°/17 mm. The molecular

weights were determined by the Rast method in freshly distilled phenol. The table gives the analytical results.

Derivatives of dimercaptothiopyrone I

Com- pounds	R	R'	Crystalliza- tion solvent	Mp, °C	Mol. formula	S, %		M	
						found	calc.	found	calc.
MP	CH <sub>3</sub>	C <sub>3</sub> H <sub>7</sub>	sodium acetate or alkali	89—91	C <sub>9</sub> H <sub>12</sub> OS <sub>3</sub>	41.3	41.4	252	232
G	H	C <sub>6</sub> H <sub>13</sub>	sodium acetate	118—119	C <sub>11</sub> H <sub>16</sub> OS <sub>3</sub>	36.2	36.8	258	260
B [1]	H	H <sub>2</sub> CC <sub>6</sub> H <sub>5</sub>	toluene + petrol ether	152—154	C <sub>12</sub> H <sub>10</sub> OS <sub>3</sub>	36.1	36.2	262	266
P	H	C <sub>3</sub> H <sub>7</sub>	chloroform + petrol ether	126—129	C <sub>8</sub> H <sub>10</sub> OS <sub>3</sub>	44.4	44.1	229	218
DB	C <sub>4</sub> H <sub>9</sub>	C <sub>4</sub> H <sub>9</sub>	chloroform + petrol ether	131—132	C <sub>13</sub> H <sub>20</sub> OS <sub>3</sub>	32.7	32.3	256	288
DP	C <sub>3</sub> H <sub>7</sub>	C <sub>3</sub> H <sub>7</sub>	sodium acetate	92—94	C <sub>11</sub> H <sub>16</sub> OS <sub>3</sub>	35.9	36.8	261	260
Bis 3-3 [1]	H	H	chloroform + petrol ether	193—194	C <sub>10</sub> H <sub>6</sub> O <sub>2</sub> S <sub>6</sub>	57.3	57.8	365	374

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1. H. Apitzsch, Ber., 38, 2888, 1905.
2. Yu. I. Usatenko and A. M. Arishkevich, Author's Certificate 144843, 1962; Byul. izobret., no. 4, 1962.
3. Yu. I. Usatenko and M. A. Arishkevich, DAN URSR, 4, 504, 1962.

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