



compounds was studied. It was found that they were comparatively non-toxic as compared to sulfones of type I, which indicates the detoxifying effect caused by the introduction of the carbethoxy group. However, regardless of the mode of administration, oral, intravenous or intraperitoneal injection, none of these disulfones caused hypnosis in the experimental animals. Evidently the presence of the salt forming methylene groups caused too great a shift in the oil-water distribution ratio which is necessary for hypnotic action.

### Experimental

**Mercaptoacetic Acid.**—In order to prepare the thioketals in good yields it was necessary to have the pure anhydrous acid. Eastman Kodak Co. technical mercaptoacetic acid (thioglycolic acid) was mixed with an equal volume of toluene and the mixture subjected to distillation. After the water and toluene had distilled the residual oil was distilled under reduced pressure. The fraction boiling 87–90° at 4 mm. was collected and used.

**Dialkyl bis-(Carboxymethylmercapto)-methanes (III).**—A mixture of 50 g. of the anhydrous mercaptoacetic acid and 50 g. of each of the anhydrous ketones was saturated with dry hydrogen chloride. The flask was stoppered and chilled in an ice-salt mixture until crystallization was complete. The crystals were filtered, washed with petroleum ether, then with cold water and dried in a vacuum desiccator. Table I summarizes their properties.

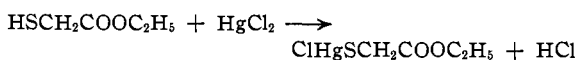
TABLE I  
R<sub>2</sub>C(—SCH<sub>2</sub>COOH)<sub>2</sub>

R	M. p., °C. (corr.)	Yield, %	Molecular formula	S Analyses, % Calcd.	Found
CH <sub>3</sub>	134–135	82	C <sub>7</sub> H <sub>12</sub> O <sub>4</sub> S <sub>2</sub>	28.57	28.57
C <sub>2</sub> H <sub>5</sub>	125–126	96	C <sub>9</sub> H <sub>16</sub> O <sub>4</sub> S <sub>2</sub>	25.39	25.11
n-C <sub>3</sub> H <sub>7</sub>	133–134	92	C <sub>11</sub> H <sub>20</sub> O <sub>4</sub> S <sub>2</sub>	22.85	22.56
n-C <sub>4</sub> H <sub>9</sub>	86–87	94	C <sub>13</sub> H <sub>24</sub> O <sub>4</sub> S <sub>2</sub>	20.80	21.01

**Dialkyl bis-(Carbethoxymethylmercapto)-methanes (IV).**—Fifty grams of each of the above acids was dissolved in 600 ml. of absolute ethanol in a two-liter, three-necked flask fitted with a mercury-sealed stirrer and protected by a calcium chloride tube. The flask was immersed in an ice-bath and 75 g. of anhydrous magnesium sulfate was added. Dry hydrogen chloride was passed over the vigorously stirred suspension for six hours. Six hundred milliliters of absolute ether was then added. The magnesium sulfate was removed by filtration and washed with a small amount of absolute ether. The combined filtrate and washings were poured into ice-cold, dilute sodium hydroxide and shaken thoroughly. The ether layer was separated and washed again with ice-cold sodium hydroxide and twice with ice water. An emulsion formed upon washing with ice water. It was broken by adding a few grams of sodium sulfate and shaking thoroughly. After drying over sodium sulfate the ether was distilled and the last traces removed by gentle heating (not over 60°) *in vacuo*. The properties of these esters are summarized in Table II.

Upon distillation *in vacuo* the diethyl, di-*n*-propyl and di-*n*-butyl-bis-(carbethoxymethylmercapto)-methanes were found to decompose. After distillation from a Claisen flask the combined fractions obtained from each compound were separated by distillation through a column packed with glass helices.<sup>3</sup>

The lowest boiling fraction from the three compounds was found to boil at 25° at 1.8 mm. and possessed  $d_{20}^{20}$  1.0980;  $n_D^{20}$  1.4578. The  $M_D$  calculated for ethyl mercaptoacetate was 30.02 and the found value, 29.85. The solid derivatives of this ester mentioned in the literature are the chloromercuri derivatives which Wislicenus<sup>4</sup> mentioned as melting somewhere under 100°, and a nickel complex<sup>5</sup> which melted at 101°. The ethyl chloromercuri-mercaptoacetate was prepared by adding an alcoholic solution of the ester to an excess of mercuric chloride dissolved in alcohol. The white amorphous reaction



product was removed by filtration and recrystallized from alcohol. Fine, colorless needles melting sharply at 105° were obtained.

*Anal.* Calcd. for C<sub>4</sub>H<sub>7</sub>O<sub>3</sub>SHgCl: S, 9.01; Hg, 56.49. Found: S, 9.12; Hg, 56.59.

For comparison purposes, mercaptoacetic acid was esterified and the properties of the synthetic ethyl ester found to check those recorded above. The chloromercuri derivative was also made and found to melt at 105° and its melting point was not depressed by addition of the above sample.

The second fraction obtained corresponded to the carbethoxymethylmercaptoalkenes (VI). Their properties and analyses are as follows:

**3-Carbethoxymethylmercaptopentene-2.**—B. p. 78.5° at 2 mm.,  $d_{20}^{20}$  1.0127,  $n_D^{20}$  1.4797;  $M_D$  calcd. 52.82; found,  $M_D$  52.73.

*Anal.* Calcd. for C<sub>6</sub>H<sub>10</sub>O<sub>2</sub>S: S, 17.02. Found: S, 17.16.

**4-Carbethoxymethylmercaptoheptene-3.**—B. p. 90° at 1.8 mm.,  $d_{20}^{20}$  0.9838;  $n_D^{20}$  1.4749;  $M_D$  calcd. 62.06; found,  $M_D$  61.87.

*Anal.* Calcd. for C<sub>11</sub>H<sub>20</sub>O<sub>2</sub>S: S, 14.81. Found: S, 15.00.

**5-Carbethoxymethylmercaptanonene-4.**—B. p. 108° at 1.8 mm.;  $d_{20}^{20}$  0.9588;  $n_D^{20}$  1.4750;  $M_D$  calcd. 72.29; found,  $M_D$  72.11.

*Anal.* Calcd. for C<sub>13</sub>H<sub>24</sub>O<sub>2</sub>S: S, 13.13. Found: S, 13.16.

**Dialkyl bis-(Carbethoxymethanesulfonyl)-methanes (II).**—A solution of 4 g. of each of the above esters in 35 cc. of carbon tetrachloride was added over a period of an hour to 300 cc. of 10% sulfuric acid solution to which was added powdered potassium permanganate at such a rate that the solution was always purple. From 10 to 17 g. of permanganate was required. The mixture was stirred for an additional hour and then sodium bisulfite added until the solution was clear. The carbon tetrachloride layer was

(3) Whitmore and Lux, *THIS JOURNAL*, **54**, 3448 (1932).

(4) Wislicenus, *Ann.*, **146**, 145 (1868).

(5) Drummond and Gibson, *J. Chem. Soc.*, 3073 (1926).

TABLE II  
 $R_2C(SCH_2COOC_2H_5)_2$ 

R	B. p., °C.	Press., mm.	Yield, %	$d_{20}^{20}$	$n_D^{20}$	$M_D$ Calcd.	$M_D$ Found	S Analyses, % Calcd.	% Found
CH <sub>3</sub>	152-153	1.8	69	1.1368	1.4970	72.26	72.18	22.81	22.92
C <sub>2</sub> H <sub>5</sub>	162-163	2	65	1.1140	1.4969	81.50	80.80	20.77	20.73
<i>n</i> -C <sub>3</sub> H <sub>7</sub>	178-179	3	89	1.0758	1.4909	90.74	90.49	19.04	19.06
<i>n</i> -C <sub>4</sub> H <sub>9</sub>	183-184	3	90	1.0269	1.4862	99.99	99.64	17.58	17.55

separated, washed with water and sodium bicarbonate solution and dried with sodium sulfate. The carbon tetrachloride was evaporated and the residual oil chilled in an ice-bath until it solidified. The sulfones were recrystallized from a mixture of ethanol and water. They were all

colorless crystals. Their properties are summarized in Table III.

### Summary

A series of dialkyl *bis*-(carbethoxymethanesulfonyl)-methanes has been prepared by oxidizing dialkyl *bis*-(carbethoxymethylmercapto)-methanes. The latter were obtained by esterification of the corresponding acids which were produced by the reaction between mercaptoacetic acid and the simple ketones. These disulfones possessed no hypnotic activity.

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TABLE III

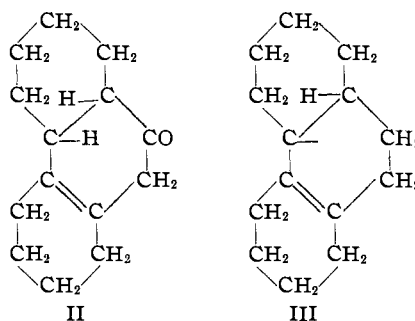
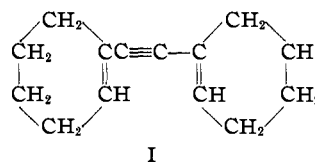
R	$R_2C(-SO_2CH_2COOC_2H_5)_2$		Mol. formula	S Analyses, %	
	M. p., °C. (corr.)	Yield, %		Calcd.	Found
CH <sub>3</sub>	84-85	32	C <sub>11</sub> H <sub>20</sub> O <sub>8</sub> S <sub>2</sub>	18.61	18.79
C <sub>2</sub> H <sub>5</sub>	73-74	41	C <sub>13</sub> H <sub>24</sub> O <sub>8</sub> S <sub>2</sub>	17.20	17.08
<i>n</i> -C <sub>3</sub> H <sub>7</sub>	90-91	37	C <sub>15</sub> H <sub>28</sub> O <sub>8</sub> S <sub>2</sub>	16.00	15.82
<i>n</i> -C <sub>4</sub> H <sub>9</sub>	74-75	42	C <sub>17</sub> H <sub>32</sub> O <sub>8</sub> S <sub>2</sub>	14.95	15.07

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

## Cyclization of Dienynes. VII.<sup>1</sup> Dehydrogenation of *trans*-Dodecahydrophenanthrene and a Further Study of *trans*-3,4-Dialkylcatalones

BY C. S. MARVEL, RALPH MOZINGO<sup>2</sup> AND E. C. KIRKPATRICK<sup>3</sup>

In an attempt to prepare phenanthrene derivatives<sup>4</sup> it was found that the cyclization of di- $\Delta^1$ -cyclohexenylacetylene (I) gave a ketone described as  $\Delta^{11}$ -dodecahydro-9-phenanthrone (II), which on Clemmensen reduction yielded a hydrocarbon considered to be  $\Delta^{11}$ -dodecahydrophenanthrene (III). Attempts to dehydrogenate these compounds with selenium did not give phenanthrene or a phenanthrol. The hydrocarbon (III) was converted by this treatment to a compound which appeared to be identical with the *trans-as*-octahydrophenanthrene (IV) reported by van de Kamp and Mosettig.<sup>5</sup> Moreover, reduction of the hydrocarbon (III) gave a product with physical properties which checked closely those of tetradecahydrophenanthrene obtained by the hydrogenation of phenanthrene.<sup>4</sup> These facts seemed to establish the phenanthrene



structure and pointed to the conclusion that selenium does not dehydrogenate fused *trans* ring systems.

Recently, however, Cook, Hewett and Robinson<sup>6</sup> have shown that van de Kamp and Mosettig's *trans-as*-octahydrophenanthrene contains also the *cis*-isomer (V) and the spiran (VI).

(1) For the sixth communication in this series see Pinkney and Marvel, *THIS JOURNAL*, **59**, 2669 (1937).

(2) Röhm and Haas Special Research Assistant in Chemistry, 1937-1939.

(3) Solvay Company Fellow in Organic Chemistry, 1937-1938.

(4) (a) Pinkney, Nesty, Wiley and Marvel, *THIS JOURNAL*, **58**, 972 (1936); (b) Pinkney, Nesty, Pearson and Marvel, *ibid.*, **59**, 2666 (1937).

(5) Van de Kamp and Mosettig, *ibid.*, **58**, 1062 (1936).

(6) Cook, Hewett and Robinson, *J. Chem. Soc.*, 168 (1939).