

There might also be a possibility that some of the *cis*-isomer of 1,2-diiodoethene were formed during the reaction. This is an oily liquid and has a melting point of 13.8° C below zero<sup>5</sup>. Attempts were made to isolate this compound by a fractional crystallization of the mother liquor when the *trans*-isomer had crystallized. It was, however, impossible to prove the presence of a *cis*-isomer, apparently it is not formed by this method. The reason may be that the *cis*-isomer decomposes slowly in the dark and faster in the light and that it is transferred to the *trans*-isomer in the presence of iodine.

After concluding this work the author came across a paper written by Keiser<sup>7</sup>, in which he briefly mentions that acetylene-diiodide may be obtained by passing acetylene through a solution of iodine in potassium iodide. Keiser gives no reference and no details of the process and the method is not mentioned in Beilstein's *Handbuch der Organischen Chemie*.

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## Methylpyrazolonethiocarbamide and Aromatic Halogene Ketones

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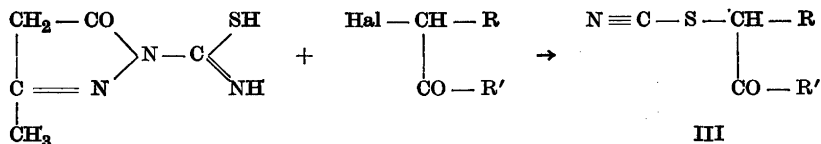
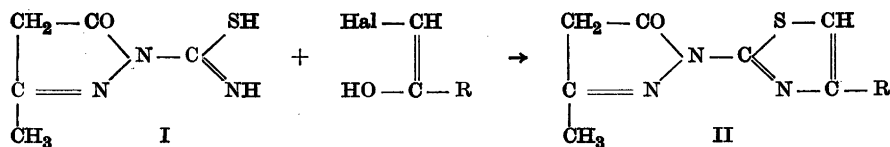
In attempts to prepare thiazole substituted pyrazolones we have used 3-methylpyrazolone(5)-1-thiocarbamide (I)<sup>1</sup>. It seemed probable that this compound in a normal way should react with halogene ketones to form thiazole derivatives. However, an unexpected reaction took place with some aromatic halogene ketones. *m*-Nitrophenacyl bromide reacted in the expected way with formation of II, R = *m*-NO<sub>2</sub> · C<sub>6</sub>H<sub>4</sub>.

If the thiocarbamide was treated with phenacyl chloride no thiazole compound was obtained but phenacyl rhodanide (III, R = H; R' = C<sub>6</sub>H<sub>5</sub>) in a yield of more than 70 %. Desyl chloride reacted in the same way, furnishing the corresponding rhodanide in a yield of nearly 90 % (III, R = R' = C<sub>6</sub>H<sub>5</sub>).

In these cases the thiocarbamide obviously was splitted. Probably the pyrazolone nucleus was desintegrated too, because it was impossible to isolate the simple methylpyrazolone from the mother liquor.

*Methylpyrazolonethioamide and m-nitrophenacyl bromide.* Finely ground thioamide (5 g) and *m*-nitrophenacyl bromide (8 g) were suspended in ethanol (100 ml) and heated on a water bath for 30 minutes with reflux. After cooling to 0° over night the precipitate (8 g) was sucked off. Recrystallised from ethanol (500 ml), m. p. 235—236°. The analytical data agree with those of compound II, R = *m*-NO<sub>2</sub> · C<sub>6</sub>H<sub>4</sub>

C<sub>13</sub>H<sub>10</sub>O<sub>3</sub>N<sub>4</sub>S (302.3)  
Calc. N 18.5 S 10.6  
Found » 18.4 » 10.5



*Methylpyrazolonthioamide and phenacyl chloride.* The thioamide (5 g) and phenacyl chloride (5 g) were suspended in ethanol (100 ml) and heated on water bath. After 4 hours a clear solution was obtained. It was evaporated to a volume of 40 ml and cooled in ice water. The crystals (5 g) were sucked off and recrystallised from petrol ether. M. p. 72—73°.

$\text{C}_9\text{H}_7\text{ONS}$  (177.2)

Calc. C 61.0 H 3.96 N 7.92 S 18.0  
Found » 60.9 » 3.99 » 8.05 » 17.9

Phenacyl rhodanide was prepared according to the method of Arapides<sup>2</sup>. M. p. 73—74°, mixed m. p. with the substance above 72.5—73.5°.

*Methylpyrazolonthioamide and desyl chloride.* Desyl rhodanide was prepared in the

same way from thioamide (5 g), desyl chloride (7.5 g) and ethanol (80 ml). Yield 5.7 g. After three recrystallisations from ethanol-water 3 : 1 m. p. 110—110°.

$\text{C}_{15}\text{H}_{11}\text{ONS}$  (253.3)

Calc. C 71.2 H 4.35 N 5.53 S 12.6  
Found » 71.0 » 4.33 » 5.62 » 12.3

Desyl rhodanide, prepared according to the method of Wheeler and Johnson<sup>3</sup>, m. p. 108—109°. Mixed m. p. with the substance above 108—110°.

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