

## Identification of Dialkylsulfides as Dialkyl *p*-Bromophenacyl Sulfonium Picrates

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The preparation and the titratability of dialkyl *p*-bromophenacyl sulfonium picrates with perchloric acid in glacial acetic acid has been investigated.

Diarylsulfides and thioanisoles do not react with *p*-bromophenacyl bromide.

Dialkyl sulfides with mobile alkyls (allyl or benzyl), refluxed with *p*-bromophenacyl bromide, form bis-(*p*-bromophenacyl) sulfide instead of dialkyl *p*-bromophenacyl bromide.

Jureček, Večeřa and Gasparič<sup>1</sup>, referring to previous work of Bost and Schultze<sup>2</sup>, recommended the characterisation of dialkyl sulfides as dialkyl *p*-bromophenacyl sulfonium salts, preferring for the picrates or bromides the perchlorates, as these salts showed the widest range of melting points.

Recalling the very convenient method of estimating alkyl halides by converting them into alkyl thiuronium picrates which are then dissolved in glacial acetic acid and titrated with perchloric acid in the same solvent (Schotte and Veibel<sup>3</sup>), we investigated the preparation of a series of tertiary sulfonium picrates and their titratability with perchloric acid, examining at the same time the possible extension of the method to aromatic sulfides and mixed aromatic-aliphatic sulfides (thioanisoles).

We found that in the case of uncomplicated dialkyl sulfides the preparation of the dialkyl *p*-bromophenacyl sulfonium picrates presented no serious difficulties, although some of the picrates, as stated by Jureček *et al.*<sup>1</sup>, may first separate as oils. As expected, the picrates are easily titratable with perchloric acid.

As to the aromatic sulfides, however, no formation of a tertiary sulfonium salt took place, neither from the diaryl sulfides nor from the thioanisoles.

Using aliphatic sulfides where the carbon-sulfur bond may be expected to be weakened, due to the structure of the aliphatic radical (as in diallyl sulfide or dibenzyl sulfide) we were unable to isolate the dialkyl *p*-bromophenacyl sulfonium picrate. Instead of this we isolated a substance which was in both instances bis-(*p*-bromophenacyl) sulfide, formed by exchange of the radicals originally bound to the sulfur atom for *p*-bromophenacyl radicals. Evidently, the sulfide thus formed is unable to combine with *p*-bromophenacyl bromide to form tris-(*p*-bromophenacyl) sulfonium bromide.

In order to explain the formation of bis-(*p*-bromophenacyl) sulfide the mechanism proposed by Ray and Levene<sup>4</sup> is adopted:



just as we obtained the bis-(*p*-bromophenacyl) sulfide by reacting, *e.g.*, diallyl sulfide with *p*-bromophenacyl bromide.

### EXPERIMENTAL

The sulfonium bromides were prepared according to Jureček *et al.*<sup>1</sup> by refluxing equivalent amounts of *p*-bromophenacyl bromide and the sulfide under investigation (0.005 mole) in methanol (5 ml) during 10 minutes. After cooling the sulfonium bromide was precipitated by addition of 200 ml of ether, isolated, if possible, by filtration, washed with ether, dissolved in water and precipitated as picrate on addition to a saturated aqueous solution of picric acid. The picrates were recrystallised from ethanol.

0.001 mole was dissolved in 50 ml glacial acetic acid and titrated with 0.1 N perchloric acid in glacial acetic acid (indicator: crystal violet, end point: green). Some results are given in Table 1.

Table 1. Titration of some dialkyl *p*-bromophenacyl picrates with perchloric acid in glacial acetic acid.

Alkyl	M.p.		M calc.	M found
	Lit.	Found		
Di- <i>n</i> -propyl	119 <sup>o1</sup>	120°	544.4	545.3 546.6 544.5
Di- <i>n</i> -butyl	79 <sup>o1</sup>	80–81°	572.5	573.7 573.3 573.8
Methyl hydroxyethyl	—	140–41°	518.3	518.7 517.2 517.5
Methyl <i>n</i> -butyl	121–21.5 <sup>o1</sup>	119–20°	530.4	530.1
Diallyl		142°		*
Dibenzyl		142°		*

\* In these cases a substance (the same for both sulfides) precipitated during the refluxing. The substance was not able to form a picrate with aqueous picric acid, its m. p. (142°) and composition corresponded to that of bis-(*p*-bromophenacyl) sulfide. (Found: C 44.85; H 2.85; Br 37.52; S 7.56. Calc. for C<sub>16</sub>H<sub>12</sub>O<sub>4</sub>Br<sub>2</sub>S: C 44.88; H 2.83; Br 37.32; S 7.49.

*Reaction between n-butyl sulfide and phenacyl bromide.* The standard procedure yielded an oily picrate which crystallised after 24 h in the ice box. Purified by recrystallisation from ethanol it showed m.p. 99–100° and M 449.5, calculated for methyl butyl phenacyl sulfonium picrate (C<sub>19</sub>H<sub>21</sub>O<sub>5</sub>N<sub>3</sub>S) 451.5.

Financial support from *Rask-Ørsted Fondet* is gratefully acknowledged.

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Received July 28, 1956.

*Acta Chem. Scand.* 10 (1956) No. 9