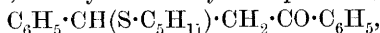


LVII.—*The Combination of Mercaptans with Unsaturated Ketonic Compounds.*

By SIEGFRIED RUHEMANN.

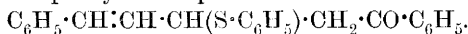
LATELY (Trans., 1905, **87**, 17) I have shown that, under the influence of sodium ethoxide or piperidine, olefinic ketonic compounds combine with mercaptans to yield additive products. The further study of this reaction seemed to be advisable, because Posner, on using as catalytic agent hydrogen chloride either alone or in conjunction with zinc chloride, frequently obtained mixtures, since the mercaptans, besides acting additively at the ethylenic linking, partly condensed also with the ketonic group of the olefinic ketones. Thus Posner (*Ber.*, 1902, **35**, 809) found that *isoamyl* mercaptan on treatment with benzylideneacetophenone yielded an oil which, from a sulphur determination, he concluded was a mixture, and which on oxidation with

potassium permanganate furnished a small quantity of the sulphone, $\text{C}_6\text{H}_5 \cdot \text{CH}(\text{SO}_2 \cdot \text{C}_5\text{H}_{11}) \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{C}_6\text{H}_5$. As shown in this paper, on employing piperidine as catalytic agent, there is thus formed the additive compound, *iso*amylthiolbenzylacetophenone,

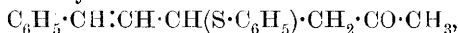


which melts at 49—50°. In my former communication (*loc. cit.*), the action of mercaptans on various mono-olefinic ketonic compounds containing the grouping $-\text{CH}:\text{CH} \cdot \text{CO}-$ has been described; I have since applied this reaction to several other members of this type of ketones, namely, benzylidenedeoxybenzoin and ethyl benzylidenebenzoylacetate. The behaviour, also, of piperidine towards a mixture of phenyl mercaptan and bromobenzylideneacetophenone, $\text{C}_6\text{H}_5 \cdot \text{CBr}:\text{CH} \cdot \text{CO} \cdot \text{C}_6\text{H}_5$, has been studied, with the unexpected result that phenylthiolbenzylacetophenone is formed, identical with the substance which is produced by the union of phenyl mercaptan with benzylideneacetophenone.

I have previously (*loc. cit.*) shown that cinnamylideneacetophenone, the di-olefinic ketone of the type $-\overset{\cdot}{\text{C}}:\overset{\cdot}{\text{C}}:\overset{\cdot}{\text{C}}:\overset{\cdot}{\text{C}}-\text{CO}-$, unites with one molecule only of a mercaptan, and that this result differs from Posner's statement (*Ber.*, 1904, **37**, 509), according to which this ketone forms additive products with two molecules of mercaptans. Prof. Posner has since, by letter, recognised the error and confirmed my result that the compound which is formed from cinnamylideneacetophenone and phenyl mercaptan has the formula



After having established the behaviour of mercaptans towards this di-olefinic ketone, it seemed probable that Posner's statement as to the action of mercaptans on cinnamylideneacetone was also not correct. In his paper (*loc. cit.*), he records the experimental results of one of his pupils who thus has obtained oils which he has been able to transform into disulphones, whilst he has failed in producing a sulphone on oxidising the additive compound of benzylideneacetophenone with phenyl mercaptan. I have found, indeed, that my view is correct, for cinnamylideneacetone unites with one molecule only of phenyl mercaptan to yield the substance



which is not an oil, but a solid melting at 53—54°.

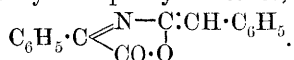
In the light of these results, it may be expected that cinnamylidenebenzylideneacetone, $\text{C}_6\text{H}_5 \cdot \text{CH}:\text{CH} \cdot \text{CH}:\text{CH} \cdot \text{CO} \cdot \text{CH}:\text{CH} \cdot \text{C}_6\text{H}_5$, will form additive products with two molecules of mercaptans only.

I have found that this tri-olefinic ketone readily takes up one molecule of either phenyl mercaptan or *iso*amyl mercaptan, and that, on using an excess of phenyl mercaptan, a mixture of compounds con-

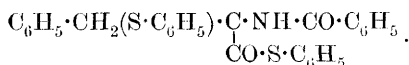
taining one and two molecules of the mercaptan is produced. Various attempts to separate this mixture have been unsuccessful.

Like the olefinic ketones, so do the ketones of the acetylene series form additive compounds with mercaptans. These are similar to the substances which are produced from phenylpropionic and acetylenedicarboxylic esters (see Ruhemann and Stapleton, *Trans.*, 1900, **77**, 1181). As yet I have studied in this connection methoxybenzoylphenylacetylene, $C_6H_5 \cdot C \equiv C \cdot CO \cdot C_6H_4 \cdot O \cdot CH_3$, which unites with one molecule of phenyl mercaptan. This additive compound differs from the substances which are formed by the union of mercaptans with olefinic ketones inasmuch as it is deep yellow, whilst the latter are almost all colourless.

Analogous to the action of mercaptans on olefinic ketones with the ketonic group in open chains is the behaviour of the mercaptans towards olefinic cyclic ketones. For example, I have used benzylidenephnylmethylpyrazolone, $C_6H_5 \cdot N \begin{smallmatrix} \nearrow N=C \cdot CH_3 \\ \searrow CO \cdot C \cdot CH \cdot C_6H_5 \end{smallmatrix}$, and the product of the condensation of benzaldehyde with hippuric acid. The latter substance has lately been recognised by Erlenmeyer (*Annalen*, 1904, **337**, 268) as benzylidenephnylazlactone,

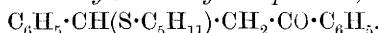


Both these compounds readily react with phenyl mercaptan, especially, however, the azlactone, which unites with the mercaptan even without the use of a catalytic agent. Whilst benzylidenephnylmethylpyrazolone takes up one molecule only of the mercaptan, the derivative of azlactone unites with two molecules of the mercaptan. This circumstance, together with the fact that the azlactone ring readily opens, leads to the view that the additive compound of phenyl mercaptan with benzylidenephnylazlactone is probably to be represented thus:



EXPERIMENTAL.

isoAmylthiolbenzylacetophenone,



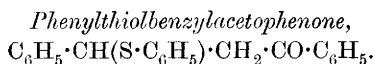
The union of benzylideneacetophenone with *isoamyl* mercaptan has been effected by mixing the ketone (2 grams), dissolved in a little benzene, with the mercaptan (1 gram), and adding 3—4 drops of piperidine. After standing overnight, light petroleum is added, when a white solid is precipitated; this is washed with dilute alcohol and crystallised from boiling alcohol, in which it is readily soluble. Thus

colourless prisms are obtained, which melt at 49—50° and dissolve in cold concentrated sulphuric acid, yielding a yellow solution.

0·2019 gave 0·5680 CO₂ and 0·1407 H₂O. C = 76·72; H = 7·74.

C₂₀H₂₄OS requires C = 76·92; H = 7·69 per cent.

Posner (*Ber.*, 1902, **35**, 809), on using hydrogen chloride as catalytic agent, obtained from the ketone and *isoamyl* mercaptan an oily product which he found to be a mixture.



Benzylideneacetophenone (2 grams), dissolved in cold benzene, interacts with phenyl mercaptan (1·2 grams) on adding a few drops of piperidine, and the reaction is accompanied by development of heat. After a short time, the whole sets to a semi-solid, which dissolves in boiling alcohol with difficulty, and, on cooling, crystallises in colourless needles. These melt at 120—121° and dissolve in cold concentrated sulphuric acid, forming a yellowish-red solution.

0·2010 gave 0·5825 CO₂ and 0·1025 H₂O. C = 79·03; H = 5·66.

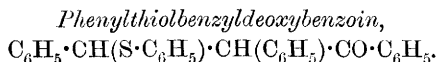
C₂₁H₁₈OS requires C = 79·24; H = 5·66 per cent.

This substance is identical with that which Posner (*loc. cit.*) prepared by the action of hydrogen chloride on a mixture of benzylideneacetophenone and phenyl mercaptan. It is formed, also, by the action of phenyl mercaptan on bromobenzylideneacetophenone.

On adding piperidine (3 grams) to the mixture of phenyl mercaptan (2 grams) and bromobenzylideneacetophenone (5 grams), dissolved in alcohol, heat is developed and a solid is formed which crystallises from alcohol in colourless needles. The identity of this compound with phenylthiolbenzylacetophenone has been ascertained by the melting point (121°) and the following analysis:

0·2015 gave 0·5845 CO₂ and 0·1040 H₂O. C = 79·11; H = 5·73.

C₂₁H₁₈OS requires C = 79·24; H = 5·66 per cent.



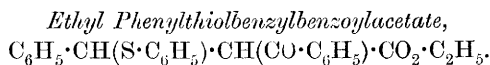
Posner (*Ber.*, 1904, **37**, 505) previously studied the action of mercaptans on benzylidenedeoxybenzoin, and found that additive products only were formed when the mixture of the ketone and the mercaptan was dissolved in glacial acetic acid and the solutions saturated with hydrogen chloride, the reaction taking place either in the cold or at 40—50°. I find that the union of mercaptans with the olefinic ketone is readily effected by using piperidine as catalytic

agent, and I have examined, especially, the additive product with phenyl mercaptan. This is formed by adding a few drops of piperidine to a mixture of the ketone (2.5 grams), dissolved in warm benzene, and the mercaptan (1 gram). The solution, when cold, deposits a solid which is almost insoluble in alcohol, but dissolves in boiling glacial acetic acid, and, on cooling, crystallises in colourless needles which melt at 204—205°.

0.2000 gave 0.6022 CO₂ and 0.1005 H₂O. C = 82.12 ; H = 5.58.

C₂₇H₂₂OS requires C = 82.23 ; H = 5.58 per cent.

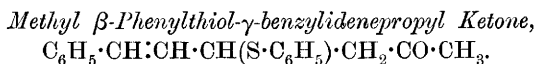
The solution of this substance in concentrated sulphuric acid is yellowish-red.



Heat is developed on adding 3—4 drops of piperidine to a mixture of ethyl benzoylacetate (2.5 grams), dissolved in benzene, and phenyl mercaptan (1 gram). The solution, which remains clear after being left overnight, is treated with light petroleum, when a white solid is precipitated. This crystallises from alcohol in bunches of colourless needles, which melt at 100—101° and dissolve in cold concentrated sulphuric acid, forming a yellowish-red solution.

0.2013 gave 0.5439 CO₂ and 0.1020 H₂O. C = 73.68 ; H = 5.65.

C₂₄H₂₂O₃S requires C = 73.84 ; H = 5.64 per cent.



Posner (*Ber.*, 1904, **37**, 509), in recording the experiments of his pupil, S. Werner, stated that under the influence of hydrogen chloride mercaptans reacted with cinnamylideneacetone to form oils, which, on oxidation, yielded disulphones. I have not studied the action of potassium permanganate on the substances which are produced by the union of mercaptans with this di-olefinic ketone, because Professor Posner proposes to re-examine the results at which his pupil arrived. I have only ascertained that the behaviour of phenyl mercaptan towards cinnamylideneacetone is analogous to the reaction of mercaptans with cinnamylideneacetophenone, and under the influence of piperidine takes up 1 molecule only of the mercaptan. The ketone (3 grams) dissolves in phenyl mercaptan (2 grams) on slightly warming ; the solution, when treated with a few drops of piperidine, turns red and solidifies after a short time. The solid dissolves in hot light petroleum, and, on cooling, gradually crystallises in colourless prisms, which are readily soluble in alcohol and melt at 53—54°.

0.2009 gave 0.5637 CO₂ and 0.1153 H₂O. C = 76.52; H = 6.40.

0.2015 „ 0.5646 CO₂ „ 0.1162 H₂O. C = 76.41; H = 6.40.

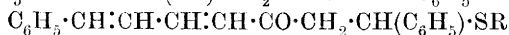
C₁₈H₁₈OS requires C = 76.60; H = 6.38 per cent.,

whilst the additive compound with 2 mols. of the mercaptan, C₂₄H₂₄OS₂, requires C = 73.46; H = 6.12 per cent.

The compound dissolves in concentrated sulphuric acid, yielding a deep red solution, as do the additive products of cinnamylideneacetophenone with mercaptans.

The Union of Mercaptans with Cinnamylidenebenzylideneacetone.

The tri-olefinic ketone, C₆H₅·CH:CH·CH:CH·CO·CH:CH·C₆H₅, prepared after Scholtz's directions (*Ber.*, 1896, 29, 614), readily unites with 1 mol. of phenyl mercaptan, as well as *iso*amyl mercaptan, to form additive products, which may be represented either by the formula C₆H₅·CH:CH·CH(SR)·CH₂·CO·CH:CH·C₆H₅ or



(R denoting C₆H₅ or C₅H₁₁).

The additive compound with *iso*amyl mercaptan is best obtained by adding a few drops of an alcoholic solution of sodium ethoxide to the mixture of the tri-olefinic ketone (2.5 grams) dissolved in alcohol and the mercaptan (1 gram). The solid which separates after a short time is very soluble in benzene or chloroform, less so in alcohol, and crystallises from light petroleum in faintly yellow needles which melt at 69—70°.

0.1654 gave 0.4808 CO₂ and 0.1151 H₂O. C = 79.22; H = 7.73.

C₂₄H₂₈OS requires C = 79.12; H = 7.69 per cent.

The solution of this substance in cold concentrated sulphuric acid is magenta-coloured.

The union of phenyl mercaptan with cinnamylidenebenzylideneacetone has been effected by mixing the ketone (2.3 grams), dissolved in benzene, with the mercaptan (1 gram) and adding 4—5 drops of diethylamine. After a few minutes, a solid separates, and in the course of 2 hours the whole mixture sets to a semi-solid. The additive compound is very soluble in chloroform, with difficulty, however, in cold alcohol or benzene, and crystallises from the latter solvent in nearly colourless needles which melt at 133—134°.

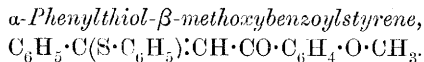
0.2030 gave 0.6020 CO₂ and 0.1088 H₂O. C = 80.88; H = 5.95.

C₂₅H₂₂OS requires C = 81.08; H = 5.94 per cent.

The solution of this compound in concentrated sulphuric acid is deep purple.

On using an excess of phenyl mercaptan, I have obtained a product

which melts indefinitely at 127° , and which is a mixture of the ketone with 1 and 2 molecules of the mercaptan. I have tried in vain to separate it by fractional crystallisation, different fractions yielding, on analysis, numbers intermediate between those required for the additive substances with 1 and 2 mols. of the mercaptan.

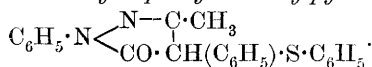


Methoxybenzoylphenylacetylene, $\text{C}_6\text{H}_5\cdot\text{C}:\text{C}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CH}_3$, which Stockhausen and Gattermann (*Ber.*, 1892, **25**, 3538) prepared by the action of aluminium chloride on a mixture of phenylpropiolyl chloride and anisole, has since been studied by E. R. Watson (*Trans.*, 1904, **85**, 1324), who showed that it formed additive compounds with various organic bases. Mercaptans also readily unite with the acetylenic ketone, but as yet I have examined only the additive product with phenyl mercaptan. This is formed by mixing the ketone (2 grams), dissolved in benzene, with the mercaptan (1 gram) and adding a few drops of piperidine. Heat is developed, and the yellow solution, which remains almost clear on mixing with light petroleum, yields a solid, which crystallises from alcohol in yellow plates. These melt at $121\text{--}122^{\circ}$ and dissolve in concentrated sulphuric acid, forming a deep red solution.

0.2005 gave 0.5600 CO_2 and 0.0944 H_2O . $\text{C} = 76.17$; $\text{H} = 5.23$.

$\text{C}_{22}\text{H}_{18}\text{O}_2\text{S}$ requires $\text{C} = 76.30$; $\text{H} = 5.20$ per cent.

4-Phenylthiolbenzyl-1-phenyl-3-methylpyrazol-5-one,



Benzylidenephénylmethylpyrazolone (2.2 grams), when dissolved in benzene, readily reacts with phenyl mercaptan (1 gram) even without the use of a catalytic agent (see Knorr, *Annalen*, 1887, **238**, 179). The deep red colour of the solution rapidly fades, and in the course of a day deposits a white solid; this increases in quantity on adding light petroleum, but at the same time an oil is precipitated which converts the solid into a pasty product. Its solution in hot dilute alcohol, on cooling, yields colourless needles which melt at 140° to a red liquid.

0.2019 gave 0.5490 CO_2 and 0.0993 H_2O . $\text{C} = 74.15$; $\text{H} = 5.46$.

0.2168 „ 14.3 c.c. moist nitrogen at 19° and 764 mm. $\text{N} = 7.62$.

$\text{C}_{23}\text{H}_{20}\text{ON}_2\text{S}$ requires $\text{C} = 74.15$; $\text{H} = 5.46$; $\text{N} = 7.52$ per cent.

The solution of this substance in boiling alcohol is red, but on cooling it becomes light yellow; cold concentrated sulphuric acid dissolves the compound, yielding a deep red solution.

Action of Phenyl Mercaptan on Benzylidenepherylazlactone.

The condensation of aldehydes with hippuric acid has been carefully studied by E. Erlenmeyer, jun. For the preparation of the compound which is formed from benzaldehyde and hippuric acid, I have followed his directions (*Annalen*, 1893, **275**, 3), and in examining its behaviour towards phenyl mercaptan I have ascertained that it forms an additive product with 2 mols. of the mercaptan. As has been stated in the introduction to this paper, the compound is probably to be represented thus: $\text{C}_6\text{H}_5 \cdot \text{CH}_2(\text{S} \cdot \text{C}_6\text{H}_5) \cdot \text{C}(\text{CO} \cdot \text{S} \cdot \text{C}_6\text{H}_5) \cdot \text{NH} \cdot \text{CO} \cdot \text{C}_6\text{H}_5$. This substance is obtained by adding a few drops of diethylamine to the mixture of equal weights of benzylidenepherylazlactone and phenyl mercaptan, dissolved in benzene, when after about half an hour the whole sets to a semi-solid mass of crystals. These are sparingly soluble in boiling alcohol, more readily in hot benzene, and on cooling crystallise from the latter solvent in colourless needles which melt at 156—157°.

0.2012 gave 0.5292 CO_2 and 0.0908 H_2O . $\text{C} = 71.73$; $\text{H} = 5.01$.

0.1965 „ 5.2 c.c. moist nitrogen at 15° and 774 mm. $\text{N} = 3.15$.

$\text{C}_{28}\text{H}_{23}\text{O}_2\text{NS}_2$ requires $\text{C} = 71.64$; $\text{H} = 4.90$; $\text{N} = 2.99$ per cent.

The additive compound dissolves in cold concentrated sulphuric acid, yielding a yellow solution which gradually darkens and finally becomes deep red.

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