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THE REACTIONS OF ω-(PHENYLTHIO)ACETOPHENONE

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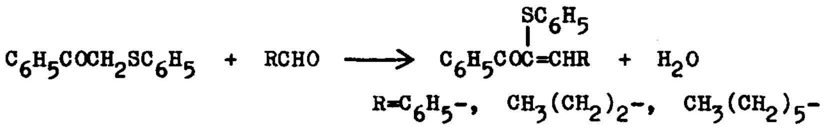
Since the hydrogen atoms attached to the carbon atom flanked by the carbonyl and mercapto groups would become acidic, ω-(phenylthio)acetophenone(I)[1)] is expected to be used either as an addend to activated double bonds or as a participate in nucleophilic substitutions to yield a new carbon-carbon bond. In the present study, the reactions of (I) with aldehydes, phenyl isocyanate, acrylonitrile, amide mercaptal and amino sulfide were tried.

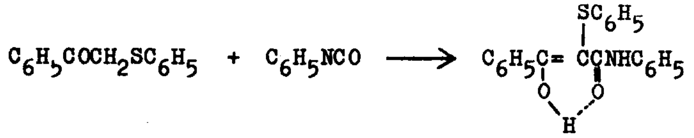
The treatment of (I) with aldehydes in the presence of a catalytic amount of piperidine afforded condensation products according to a mechanism analogous to that of the Knoevenagel condensation. When equimolar amounts of (I) and freshly distilled benzaldehyde were refluxed in benzene for 4 hours in the presence of a catalytic amount of piperidine, 1-benzoyl-1-phenylthio-2-phenylethylene, m.p.73.5°, calcd. for $C_{21}H_{16}OS$; C:79.72 H:5.10%. found; C:79.77 H:5.25%, was obtained in 78% yield. Aliphatic aldehydes such as n-butyraldehyde and n-heptylaldehyde also reacted with (I) under the same condition to give 1-benzoyl-1-phenylthio-pentene-1, b.p. 146-148°/0.13 mmHg, calcd. for $C_{18}H_{18}OS$; C:76.57 H:6.43%. found; C;76.17 H:6.35%, in 78% yield and 1-benzoyl-1-phenylthio-octene-1, b.p. 168-170°/0.13 mmHg, calcd. for $C_{21}H_{24}OS$; C:77.75 H:7.46%. found; C:77.39 H:7.46%, in 77% yield, respectively (eq.1). Recently, the Knoevenagel condensation of β-cyano and β-carbethoxy sulfides with aromatic aldehydes was reported by Dressler and Graham.[2)]



$$C_6H_5COCH_2SC_6H_5 \ + \ RCHO \longrightarrow C_6H_5CO\overset{SC_6H_5}{\overset{|}{C}}{=}CHR \ + \ H_2O \qquad (1)$$

$$R{=}C_6H_5-,\quad CH_3(CH_2)_2-,\quad CH_3(CH_2)_5-$$

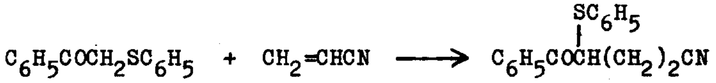
It was also found that the reaction of equimolar amounts of (I), phenyl isocyanate and sodium hydride in benzene at room temperature yielded a pale yellow crystal(II), m.p. 147°(eq.2). This compound was confirmed to be an 1:1 adduct (81%) of (I) and phenyl isocyanate by means of the elemental analysis, calcd. for $C_{21}H_{17}NO_2S$; C:72.61 H:4.92 N:4.03%. found; C:72.63 H:5.19 N:4.23%. Its infrared absorption spectrum showed characteristic bands attributable to secondary amine(3250 cm^{-1}s),to conjugated carbonyl group (1520 cm^{-1} vs),* to mono-substituted benzene ring (1600, 760 and 695 cm^{-1} s) and to hydroxy group (3500 cm^{-1} w).



II

(2)

When (I) was treated with acrylonitrile in the presence of such a basic catalyst as sodium hydride or Triton B in benzene, the mono-cyanoethylation product, 4-benzoyl-4-phenylthio-butyronitrile, b.p. 168-171°/0.14 mmHg, calcd. for $C_{17}H_{15}NOS$; C:72.58 H:5.37 N:5.00%. found; C:72.95 H:5.49 N:5.24%, was obtained in 83% yield (eq.3). The nitrile thus obtained did not further react with acrylonitrile even when they were refluxed in benzene in the presence of a basic catalyst.



$$C_6H_5COCH_2SC_6H_5 + CH_2{=}CHCN \longrightarrow C_6H_5CO\overset{SC_6H_5}{CH}(CH_2)_2CN \qquad (3)$$

Next, the reaction of (I) with N,N-dimethylformamide diethylmercaptal(III)[3] was tried with the expectation that the condensation product, 1-benzoyl-1-phenylthio-2-dimethylamino-ethylene(V), would be formed by eliminating 2 moles of ethyl

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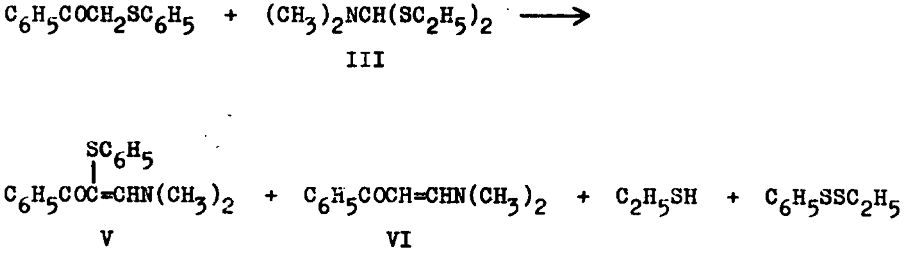
* αβ-Unsaturated β-hydroxy or amino ketone, L. J. Bellamy, "The Infrared Spectra of Complex Molecules", p.132 and 137, John Wiley and Sons, Inc., New York,(1958).

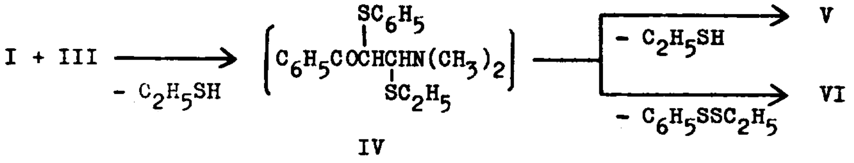
mercaptan. When a solution of (I) and (III) in benzene was heated at about 60°C for 4 hours, (V), m.p.110°, calcd. for $C_{17}H_{17}NOS$; C:72.06 H:6.05 N:4.94%. found; C:71.74 H:5.83 N:4.98%, was obtained in 76% yield along with 1-benzoyl-2-dimethylamino-ethylene (VI)(21% yield) and ethyl phenyl disulfide (10% yield) (eq.4). The formation of these two enamines, (V) and (VI), might be explained



$$\underset{}{C_6H_5COCH_2SC_6H_5} + \underset{\text{III}}{(CH_3)_2NCH(SC_2H_5)_2} \longrightarrow$$

$$\underset{\text{V}}{C_6H_5CO\overset{SC_6H_5}{\overset{|}{C}}{=}CHN(CH_3)_2} + \underset{\text{VI}}{C_6H_5COCH{=}CHN(CH_3)_2} + C_2H_5SH + C_6H_5SSC_2H_5 \qquad (4)$$

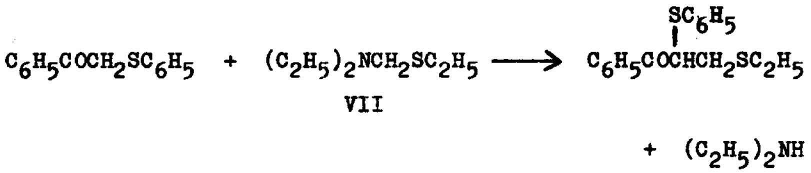
by assuming the intermediate(IV), which has two alternative pathways of decomposition forming (V) and (VI) by the loss of another ethyl mercaptan and ethyl phenyl disulfide, respectively, as shown in the following scheme (5).



$$\text{I} + \text{III} \xrightarrow[- C_2H_5SH]{} \underset{\text{IV}}{\left[C_6H_5CO\overset{SC_6H_5}{\overset{|}{C}}H\underset{SC_2H_5}{\underset{|}{C}}HN(CH_3)_2\right]} \begin{cases} \xrightarrow{- C_2H_5SH} \text{V} \\ \xrightarrow[- C_6H_5SSC_2H_5]{} \text{VI} \end{cases} \qquad (5)$$

In a similar way, the reactions of ω-phenyl-ω-(phenylthio)acetophenone[1] and ω,ω-bis(phenylthio)acetophenone[4] with (III) gave the corresponding enamines. These results are listed in Table.

When diethylaminomethyl ethyl sulfide(VII)[5] was used instead of amide mercaptal(III) in the above reactions, 1-benzoyl-1-phenylthio-2-ethylthio-ethane, b.p. 157°/0.06 mmHg, calcd. for $C_{17}H_{18}OS_2$; C:67.54 H:6.00%. found; C:68.00 H:6.16%, was obtained in 79% yield by eliminating diethylamine(eq.6).



$$C_6H_5COCH_2SC_6H_5 + \underset{\text{VII}}{(C_2H_5)_2NCH_2SC_2H_5} \longrightarrow C_6H_5CO\overset{SC_6H_5}{\overset{|}{C}}HCH_2SC_2H_5 + (C_2H_5)_2NH \qquad (6)$$

TABLE

Reaction of sulfides and mercaptal with amide mercaptal(III)

	product	properties		yield
$C_6H_5COCH_2SC_6H_5$	$C_6H_5CO\overset{SC_6H_5}{\overset{\vert}{C}}=CHN(CH_3)_2$	m.p.110°	yellow	76%
	$C_6H_5COCH=CHN(CH_3)_2$	m.p.89-91°	yellow	21%
$C_6H_5CO\overset{C_6H_5}{\overset{\vert}{C}}HSC_6H_5$	$C_6H_5CO\overset{C_6H_5}{\overset{\vert}{C}}=CHN(CH_3)_2$	m.p.129-130°	yellow	61%
$C_6H_5COCH(SC_6H_5)_2$	$C_6H_5CO\overset{SC_6H_5}{\overset{\vert}{C}}=CHN(CH_3)_2$	m.p.110°	yellow	93%

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