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NUCLEOPHILIC SUBSTITUTIONS OF α-CHLOROKETONES. VI

1-CHLORO-3-PHENYLMERCAPTO-2-BUTANONE

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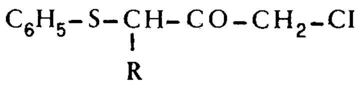
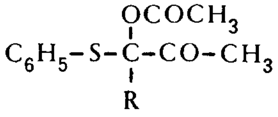
In a previous communication(1) it has been reported that the reaction of 1-chloro-3-phenylmercapto-propanone (Ia) with an alkali acetate in acetic acid solution gives essentially a mixture of 1-acetoxy-1-phenylmercapto-propanone and phenyl O.acetyl-thiol-α-lactate. The formation of the acetoxy-ketone (IIa) had been tentatively interpreted on the basis of a mechanism involving the attack of the nucleophile on the intermediate carbonium ion (IIIa):



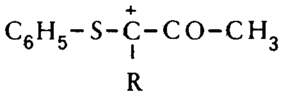
$C_6H_5-S-\underset{R}{CH}-CO-CH_2-Cl$

(Ia) : R = H
(Ib) : R = CH_3



$C_6H_5-S-\overset{OCOCH_3}{\underset{R}{C}}-CO-CH_3$

(IIa) : R = H
(IIb) : R = CH_3



$C_6H_5-S-\overset{+}{\underset{R}{C}}-CO-CH_3$

(IIIa) : R = H
(IIIb) : R = CH_3

The above reaction mechanism has now received an indirect confirmation from the results obtained in the acetolysis of the homologous chloroketone (Ib).

1-Chloro-3-phenylmercapto-2-butanone (Ib) was obtained as an oil (b.p. 115° at 0,09 mm Hg) in 75% yield by reacting 2-phenylmercapto-propionyl chloride with diazomethane in ether and treating the intermediate diazoketone with a slight excess of dry HCl in chloroform.

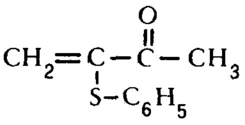
The NMR spectrum showed a singlet at 2,55 τ (5 H, aromatic), a singlet at

5,60 τ (2 H, CO-CH_2-Cl),a quadruplet centered at 5,95 τ (1 H, CH_3-C$\underline{H}$; J 6,90 cps) and a doublet centered at 8,55 τ (3 H, $C\underline{H}_3$-CH ; J 6,90 cps).

The reaction of (Ib) with three moles of sodium acetate in acetic acid solution,after three hours refluxing,gave a 50% yield of a crystalline,unsaturated ketone $C_{20}H_{20}O_2S_2$ (m.p. 78° from ethanol; IR ν_{CO} at 1724 cm^{-1}, $\nu_{C=C}$ at 1645 cm^{-1}). The NMR spectrum showed a multiplet centered at 2,6 τ (10 H, aromatic) and a complex signal (10 H) between 7,1 and 8,1 τ ,with two peaks emerging at 7,8 and 7,96 τ ;the latter signals could be attributed respectively to a methyl on a carbonyl group and a methyl on an olefinic carbon atom,while the remaining of the complex signal (4 H), on account of the chemical shifts, could be ascribed to two adiacent methylene groups attached to tertiary carbon atoms.

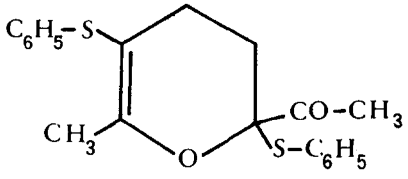
The mass spectrum showed the molecular peak M^+ at 356 and peaks at 313 (M^+ - CH_3CO),247 (M^+- C_6H_5S ; m* at 171,5),203 (247 - CH_3CHO ; attributed to 2-methyl-3-phenylmercapto-pyrylium ion),178 (attributable to the radical ion derived from (IV), 161 (203 - CH_2 = CO),135 (178 - CH_3CO ; m* at 102,5):other peaks were at 191,147 and 128.

On the basis of the spectroscopic data,the structure of 2-acetyl-6-methyl-2,5-diphenylmercapto-2,3-dihydropyran (V) was assigned to the compound $C_{20}H_{20}O_2S_2$.



$CH_2{=}\underset{\displaystyle S-C_6H_5}{C}-\overset{\displaystyle O}{\overset{\|}{C}}-CH_3$

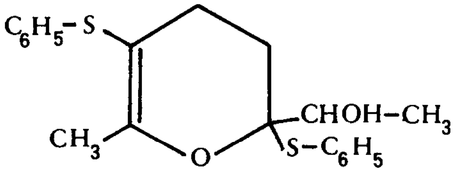
(IV)



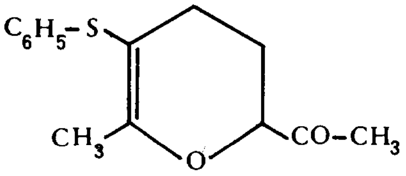
(V)

The assignment of structûre (V) is also supported by the sodium borohydride reduction of ketone $C_{20}H_{20}O_2S_2$,which gave an unsaturated carbinol $C_{20}H_{22}O_2S_2$ (m.p. 83-4°,from hexane; IR ν_{OH}3333 cm^{-1}, $\nu_{C=C}$ 1640 cm^{-1}), formulated as (VI) on the basis of spectroscopic evidences.Its NMR spectrum showed à multiplet centered at

2,5 τ (10 H, aromatic), a quartet centered at 6,04 τ (1 H,CH_3-$C\underline{H}$; J 6,90 cps), a doublet centered at 8,62 τ (3 H,$C\underline{H}_3$-CHOH ; J 6,90 cps) and a complex signal between 7 and 8,5 τ (8 H), from which emerged a peak at 7,85 τ ($C\underline{H}_2$- C = C).



(VI)



(VII)

Also,the hydrogenolysis of compound $C_{20}H_{20}O_2S_2$ in the presence of an excess of palladium charcoal gave an oily unsaturated ketone $C_{14}H_{16}O_2S$ (b.p.115°/ /0,05 mm Hg ; IR ν_{CO} at 1718 cm^{-1}, $\nu_{C=C}$ at 1634 cm^{-1}). The NMR spectrum of this ketone showed a multiplet centered at 2,62 τ (5 H, aromatic), a multiplet centered at 5,5 τ (1 H, O-$C\underline{H}$-$COCH_3$),a complex signal betwenn 7,5 and 8,4 τ (10 H) from which emerged a singlet at 7,64 τ (CH_3-CO) and singlet at 7,75 τ (CH_3- C=C).

The mass spectrum showed the molecular peak M^+ at 248 and peaks at 205 (M^+ - CH_3CO),178 (attributable to the radical ion derived from (IV),161 (205 - - CH_2=CH-OH),135 (178 - CH_3CO); 110 (C_6H_5-SH); other peaks were at 188, 147 and 123.

The formation of the dihydropyran (V) from the acetolysis of α-chloroketone (Ib) can be easily interpreted on the basis of a reaction mechanism involving the intermediate carbonium ion (IIIb); the latter could give (IV) by simply loosing a proton,the driving force of the process being the formation of a conjugated system.

The subsequent **cycloaddition** of (IV) to (V) is a reaction quite analogous to the thermal dimerization of acrolein and of methyl vinyl ketone to the corresponding 2,3-dihydro-pyrans.At the present,the acetoxyketone (IIb) has not yet been detected in the reaction products.

The formation of (V) represents a convincing evidence that the acetolysis of α'-arylmercapto-α-chloroketones proceeds *via* an intermediate carbonium ion of type (III), the electron deficiency of which can be stabilized by the adiacent sulfur atom.

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REFERENCES

1) V.Rosnati, G.Pagani and F.Sannicolò, Tetrahedron Letters, 46, 4545 (1967).
2) V.Alder and E.Ruden, Ber, 74, 920 (1941).