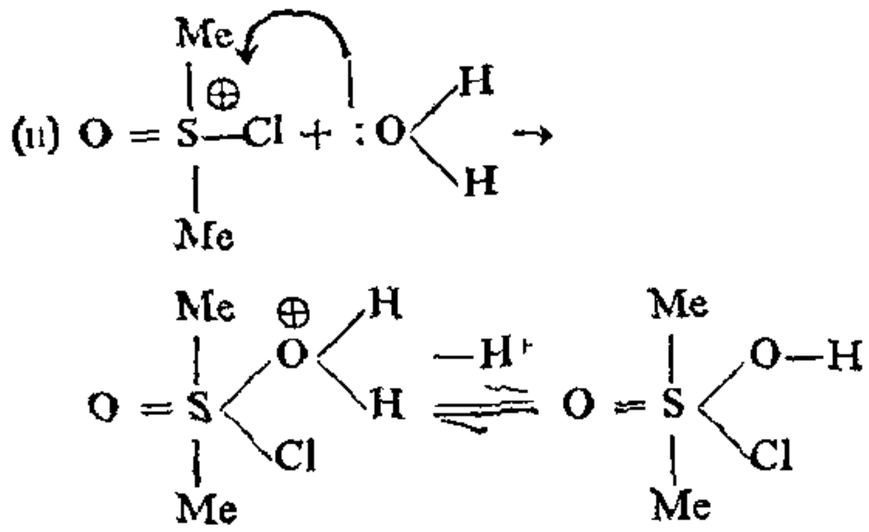
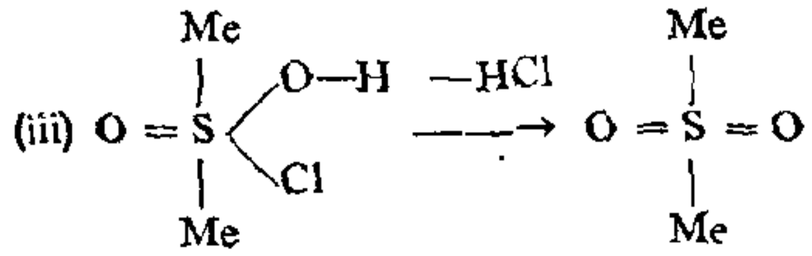


(ii) $O=S(Me)(Me)-Cl + :O(H)(H) \rightarrow$

$O=S(Me)(Cl)-O(H)(H) \rightleftharpoons O=S(Me)(Cl)-O-H + H^+$



(iii) $O=S(Me)(Cl)-O-H \xrightarrow{-HCl} O=S(Me)=O$

(iv) $RNH^- + H^+ \rightarrow RNH_2$.

Increase in the rate of reaction by the addition of chloride ion is similar to its effect observed in the Orton re-arrangement of N-haloamides[6]. The latter refers to the migration of chlorine from the side chain of an N-haloamide or a ring substituted derivative of chloroamide to the ring, in the presence of H^+ and Cl^- ions. The present results can be explained by the following scheme, where an electrophilic attack by Cl^- ion on RNHCl is assumed, accounting for the catalytic effect of chloride ions:

$$RNCl^- + H^+ \overset{K_1}{\rightleftharpoons} RNHCl \quad \text{.....(i) fast}$$

$$RNHCl + DMSO + Cl^- \overset{K_2}{\rightleftharpoons} X' \quad \text{..(ii) slow}$$

$$X' \xrightarrow{k_3} X'' \quad \text{.....(iii) slow and rate determining}$$

$$X'' \xrightarrow{k_4} \text{Products} \quad \text{.....(iv) fast.}$$

If $[CAB]_T = [RNCl^-] + [RNHCl] + X'$, then the rate law at constant $[H^+]$ would be

$$\text{Rate} = \frac{kK_2k_3[CAB]_T[DMSO][Cl^-]}{1 + k + kK_2[DMSO][Cl^-]} \qquad (2)$$

where $k = K_1[H^+]$.

When catalysis is effected simultaneously by H^+ and Cl^-, an order of 1·45 on the gross concentration of HCl is observed. This may be traced to a mixed order kinetics following the rate law:

$$-\frac{d[CAB]}{dt} = k'[CAB][H^+][DMSO]^{0.66} + k''[CAB][Cl^-]^{0.43}[DMSO]^{0.66}. \qquad (3)$$

In the composite rate law, the first term accounts for H^+ catalysis and the second for Cl^- catalysis.

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SYNTHESIS WITH DIAZOALKANES AND *o*-BENZOYL BENZOYL CHLORIDE

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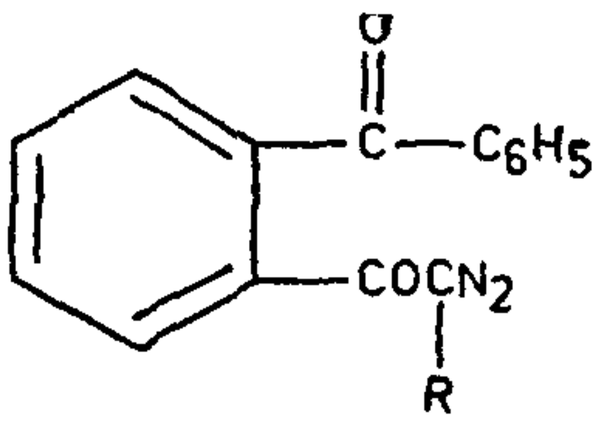
o-Benzoyl benzoyl chioride contains two sites of reactivity, the carbonyl group and an acid chloride group, both of which are susceptible towards diazoalkanes. By using different amounts of diazoalkanes it is possible to attack either one or both the sites present. The action of 2 moles of diazoalkanes on one mole of the acid chloride attacked only the acid chloride group while the carbonyl group, the other site, was also affected when 3 moles of diazoalkanes were used, resulting the *a*-diazoketones.

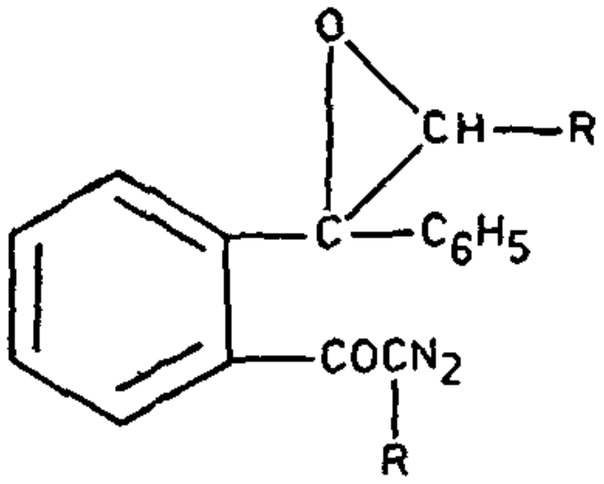
ω-diazo-*ω*-alkyl-*o*-benzoyl acetophenone (I) and *ω*-diazo-*ω*-alkyl-*o*-1-alkyl-2-phenyl-1,2-epoxy-ethyl acetophenone(II) were synthesised by the action of 2 and 3 moles of diazoalkanes on *o*-benzoyl benzoyl chloride (1 mol).

By adopting the method of Arndt, Eistert and Partale[2,7] the action of 2 moles of diazomethane, diazoethane, diazopropane, diazo-*n*-butane and phenyl diazomethane on *o*-benzoyl benzoyl chloride in ether at 0° C was studied and diazoketone I (R = –H, $-CH_3$, $-C_2H_5$, $-n-C_3H_7$ and $-C_6H_5$) was obtained. When 3 moles of diazoalkanes were used the carbonyl group[1] was also attacked, resulting in the formation of II (R = –H, $-CH_3$, $-C_2H_5$, $-n-C_3H_7$ and $-C_6H_5$).

All these diazoketones were found to be orange or brown liquids, which could not be purified by distilla-

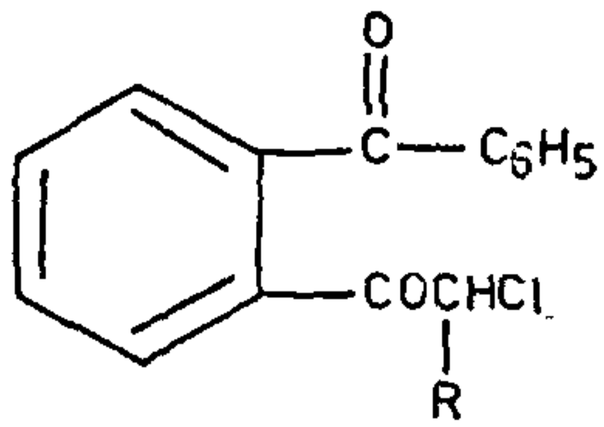


(I)

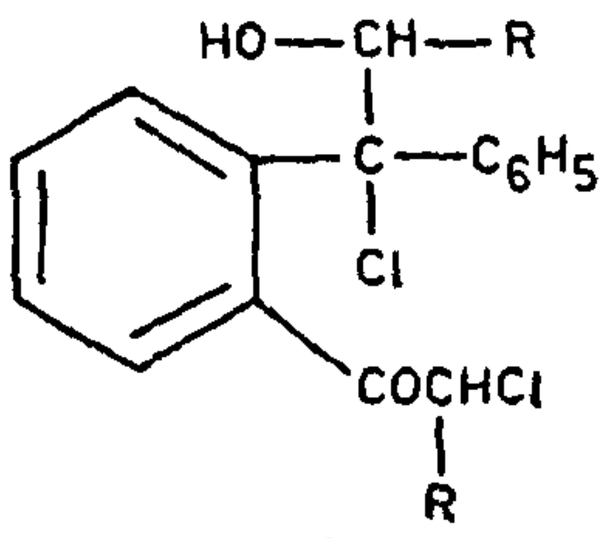


(II)

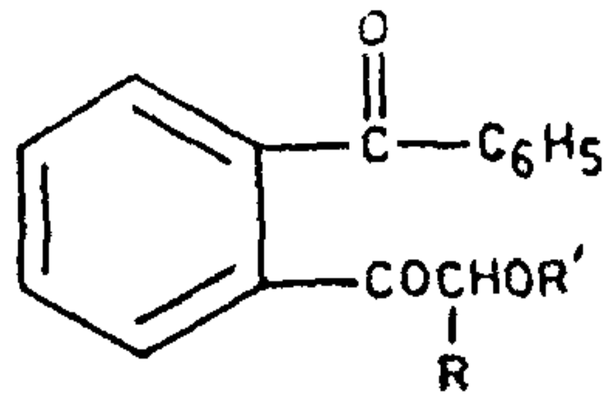
(I and II, R = –H, $–CH_3$, $–C_2H_5$, $–n–C_3H_7$ and $–C_6H_5$)



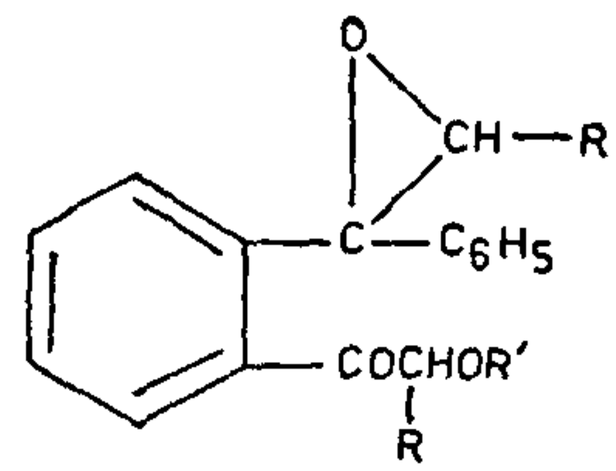
(III)



(IV)



(V)



(VI)

tion even under reduced pressure due to their decomposition. All the diazoketones (except II, R = $–n–C_3H_7$) on treatment with aqueous alcoholic sulphuric acid solution of 2,4-dinitrophenylhydrazine[3,8] afforded the corresponding, 2,4-dinitrophenylosazone derivatives.

These diazoketones (I and II) on treatment with dry HCl gas[5] in benzene evolved nitrogen and produced *ω*-chloro-*ω*-alkyl-*o*-benzoyl acetophenone(III) and *ω*-chloro-*ω*-alkyl-*o*-hydroxy-alkyl-chlorobenzyl acetophenone(IV).

All these diazoketones (I and II) on heating with molten phenol[5] and benzoic acid[5] separately and working out the reaction mixture afforded *ω*-phenoxy-*ω*-alkyl-*o*-benzoyl acetophenone (V, R′ = C_6H_5), *ω*-phenoxy-*ω*-alkyl-*o*-1-alkyl-2-phenyl-1,2-epoxy-ethyl acetophenone (VI, R′ = C_6H_5), *ω*-benzoyloxy-*ω*-alkyl-*o*-benzoyl acetophenone (V, R′ = COC_6H_5) and *ω*-benzoyloxy-*ω*-alkyl-*o*-1-alkyl-2-phenyl-1,2-epoxy-ethyl acetophenone (VI, R′ = COC_6H_5) respectively.

All the above compounds (except IV, VI, R = $–n–C_3H_7$) afforded their 2,4-dinitrophenylhydrazones, characterised by IR spectroscopy[4,6] and elemental analysis.

Experimental

Distilled *o*-benzoyl benzoyl chloride[9] was dissolved in ether and added to the pre-estimated ethereal solution of diazoalkanes (2 and 3 moles) respectively at 0° and kept overnight. Next day the solvent was stripped off and *α*-diazoketones (I and II) were obtained as orange to brown liquids which could not be purified even under vacuum due to their decomposition.

The alcoholic solution of all these diazoketones, on treatment with aqueous alcoholic sulphuric acid solution of 2,4-dinitrophenyl hydrazine, gave the corresponding 2,4-dinitrophenylosazones (except II, R = $–n\ C_3H_7$) which failed to give derivative.

The diazoketones I and II were dissolved in dry benzene and the solution was cooled in a freezing mixture. In this solution dry hydrogen chloride gas was bubbled for about half an hour and the reaction mixture was kept as such overnight. Next day, the solvent was distilled off and the chloroketones III

TABLE I

Final products I and II, their % yield and state	m.p. of 2,4-DNP of I and II	m.p. of 2,4-DNP of III and IV	m.p. of 2,4-DNP of V and VI ($R' = -C_6H_5$)	m.p. of 2,4-DNP of V and VI ($R' = -COC_6H_5$)
I ($R = -H$), 96·39 orange viscous liquid	180°	(III, $R = -H$), 210°	(V, $R = -H$), 75°	(V, $R = -H$), 102°
II ($R = -H$), 96 orange viscous liquid	207°	(IV, $R = -H$), 118°	(VI, $R = -H$), 90°	(VI, $R = -H$), 90°
I ($R = -CH_3$), 96 orange viscous liquid	144°	(III, $R = -CH_3$), 95°	(V, $R = -CH_3$), 134°	(V, $R = -CH_3$), 112°
II ($R = -CH_3$), 95·5 orange viscous liquid	230°	(IV, $R = -CH_3$), 114°	(VI, $R = -CH_3$), 85°	(VI, $R = -CH_3$), 125°
I ($R = -C_2H_5$), 100 orange viscous liquid	110°	(III, $R = -C_2H_5$), 180°	(V, $R = -C_2H_5$) not melted upto 305°	(V, $R = -C_2H_5$) 107°
II ($R = -C_2H_5$), 92·52 orange viscous liquid	125°	(IV, $R = -C_2H_5$), 169°	(VI, $R = -C_2H_5$), 140°	(VI, $R = -C_2H_5$), 162°
I ($R = -C_3H_7$), 90 orange viscous liquid	245°	(III, $R = -n-C_3H_7$) does not form 2,4-DNP	(V, $R = -n-C_3H_7$) does not form 2,4-DNP	(V, $R = -n-C_3H_7$) does not form 2,4-DNP
II ($R = -C_3H_7$), 96·7 orange viscous liquid	..	(IV, $R = -n-C_3H_7$) does not form 2,4-DNP	(VI, $R = -n-C_3H_7$) does not form 2,4-DNP	(VI, $R = -n-C_3H_7$) does not form 2,4-DNP
I ($R = -C_6H_5$), 93·75 brown mobile liquid	238°	(III, $R = -C_6H_5$), 245°	(V, $R = -C_6H_5$), 215°	(V, $R = -C_6H_5$), 220°
II ($R = -C_6H_5$), 96·38 orange mobile liquid	217°	(IV, $R = -C_6H_5$), 179°	(VI, $R = -C_6H_5$), 234°	(VI, $R = -C_6H_5$), 239°

Elemental analysis and IR data agreed with the literature values within the limit of experimental errors and also supported the structures.

and IV were obtained as red brown viscous liquids which were free from nitrogen and contained chlorine.

The diazoketones I and II were also treated with phenol and benzoic acid in two separate boiling tubes. For this purpose molten phenol and benzoic acid were taken in two separate boiling tubes and diazoketone I was gradually added to them. The mixture was heated on a low flame until the evolution of nitrogen was ceased. It was kept as such overnight. Next day it was dissolved in ether and washed with mild alkali solutions. The ethereal layer was washed with water and dried. After removal of ether the phenoxy and benzoyloxy ketones were obtained as red-brown viscous liquids. These could not be distilled due to their low yields.

The same procedure was repeated with the diazoketone II. The phenoxy and benzoyloxy ketones were obtained as red-brown viscous liquids.

All the above compounds (except IV, $R = -n-C_3H_7$) afforded their 2,4-dinitrophenylhydrazones, characterised by IR spectroscopy[4,6] and element analysis.

The results are summarised in Table I.

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