Tetrahedron Letters No. 1, pp 75 - 78, 1976. Pergamon Press. Printed in Great Britain.

THERMOLYSIS OF BENZOYL PEROXIDE IN THE PRESENCE OF N-SULPHINYL-ANILINE

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(Received in UK 10 November 1975; accepted for publication 20 November 1975)

Recent work assumes the similarity of the electronic and structural characteristics of SO_2 and N-sulphinyl-aniline[1-2]. N-sulphinyl-anilines(Ar-N=S=O) are heterocumulenes which present a cis[3] structure as regards the central bond -N=S; the -N=S=O group is coplanar[4] and has a moderate resonance interaction with the benzene ring unless para groups showing conjugative effects and acting as weak π-electron acceptors are present[5-6]. The -N=S is the reactive bond[7], as confirmed in our recent research[8] on the addition of arylnitrenes to double bonds of heteroatoms.

Continuing the investigation concerning the nature of this similarity[9] and bearing in mind the fact that SO_2 has a characteristic behaviour if attacked by phenyl radicals[10], it was decided that it might be interesting to examine an analogous reaction with Ar-N=S=O.

We wish now to report the results obtained by thermal decomposition of benzoyl peroxide in the presence of N-sulphinyl-aniline[11].

The reaction of equimolecular amounts of benzoyl peroxide(I) and p-substituted N-sulphinyl-aniline(II) in boiling dry benzene[12] under nitrogen atmosphere for 70 hours, yields: biphenyl(III), diphenyl disulphide(IV), p-p'-di-R-azobenzene(V), diphenyl thiosulphone(VI) and benzensulphonic anhydride(VII)

$$\underset{(I)}{(C_6H_5CO_2)_2} + \underset{(II)}{\underline{p}\text{-R-}C_6H_4NSO} \xrightarrow[\text{boiling Bz.}]{\Delta t} \underset{(III)}{C_6H_5\text{-}C_6H_5(22\%)} + \underset{(IV)}{\underline{p}\text{-R-}C_6H_4\text{-N=N-}C_6H_4\text{-R-}\underline{p}(31\%)} +$$

$$\underset{(V)}{C_6H_5\text{-S-S-}C_6H_5(10\%)} + \underset{(VI)}{C_6H_5\text{-S-}SO_2\text{-}C_6H_5(20\%)} +$$

R = -Cl

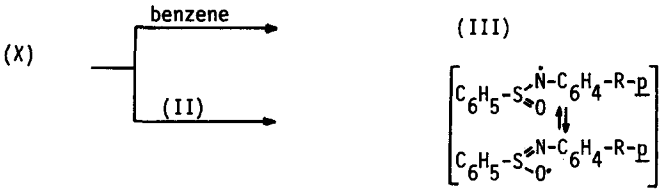
$$\underset{(VII)}{C_6H_5SO_2\text{-O-}SO_2C_6H_5(5\%)}$$

Diphenyl sulphide(VIII) and diphenyl sulphone(IX) were absent.

Reaction products were identified by G.L.C., after treatment of the reaction mixture with a solution of $NaHCO_3$ 5%, washing with H_2O and drying with Na_2SO_4, (Perkin-Elmer F11/column 5% FFAP on Chromosorb G AW-DMCS - lenght 2m.;a.a. 1/8 inch - progr.temp. 90 - 210°C). Separation was also achieved by column chromatography (SiO_2, elution petroleum ether - ether) and the products were identified by I.R. (Nujol or KBr), mass spectra and by mixed m.p. with an authentic sample when solid.

The formation of these products can be shown as follows:

$$(I)^{13} \xrightleftharpoons{\Delta t} 2C_6H_5\text{-}CO_2^{\cdot} \longrightarrow \underset{(X)}{2C_6H_5^{\cdot}} + 2CO_2\uparrow$$



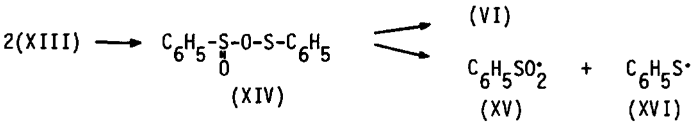
(XI)

$$(X) \begin{cases} \xrightarrow{\text{benzene}} (III) \\ \xrightarrow{(II)} \left[C_6H_5\text{-}S(\text{=}O)\text{-}\dot{N}\text{-}C_6H_4\text{-}R\text{-}\underline{p} \leftrightarrow C_6H_5\text{-}S(\text{-}O^{\cdot})\text{=}N\text{-}C_6H_4\text{-}R\text{-}\underline{p} \right] \end{cases}$$

The unstable intermediate (XI) can decompose to give aryl nitrene(XII) and phenylsulphinyl radical(XIII)

$$(XI) \longrightarrow \underset{(XII)}{\underline{p}\text{-}R\text{-}C_6H_4\text{-}\ddot{N}\cdot} + \underset{(XIII)}{C_6H_5\text{-}SO\cdot}$$

The two phenylsulphinyl radicals(XIII) by head to tail combination give[14] sulphenyl sulphinate(XIV) which then can either rearrange to (VI), or decompose to phenylsulphonyl-(XV) and thioaryl-radicals(XVI)



$$2(XIII) \longrightarrow \underset{(XIV)}{C_6H_5\text{-}\underset{O}{\underset{\Vert}{S}}\text{-}O\text{-}S\text{-}C_6H_5} \begin{cases} \longrightarrow (VI) \\ \longrightarrow \underset{(XV)}{C_6H_5SO_2^{\cdot}} + \underset{(XVI)}{C_6H_5S\cdot} \end{cases}$$

Two thioaryl radicals(XVI) then combine to give (V), the phenylsulphonyl radicals(XV) yield (VI) and (VII)[15]. The absence of (VIII) and (IX) from the mixture excludes the following probable combination:

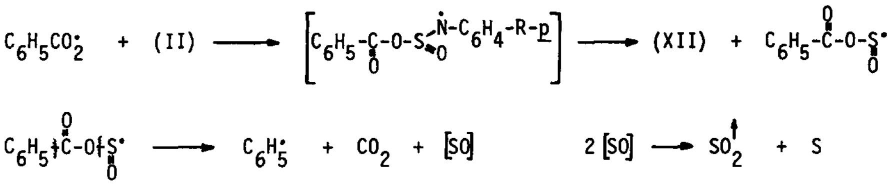
$$(XVI) + C_6H_5^{\cdot} \not\longrightarrow C_6H_5\text{-}S\text{-}C_6H_5$$

$$(XV) + C_6H_5^{\cdot} \not\longrightarrow C_6H_5\text{-}SO_2\text{-}C_6H_5$$

Azobenzene(IV) is formed by the known[16] combination of triplet arylnitrene(XII).

The presence of the arylnitrene intermediate is supported by the reaction of benzoyl peroxide with o-phenyl-N-sulphinylaniline in our typical conditions. The isolation of carbazole proved probably[17] the supposed decomposition of the unstable intermediate (XI).

The competitive intervention of the benzoyloxy radicals can be justified as follows:



$$C_6H_5CO_2^{\bullet} + (II) \longrightarrow \left[C_6H_5\text{-}\underset{O}{\overset{}{C}}\text{-}O\text{-}\overset{\dot{N}\text{-}C_6H_4\text{-}R\text{-}p}{\underset{O}{S}}\right] \longrightarrow (XII) + C_6H_5\text{-}\overset{O}{C}\text{-}O\text{-}\underset{O}{S}^{\bullet}$$

$$C_6H_5 \nmid \overset{O}{C}\text{-}O \nmid \underset{O}{S}^{\bullet} \longrightarrow C_6H_5^{\bullet} + CO_2 + [SO] \qquad 2[SO] \longrightarrow SO_2\uparrow + S$$

The development of SO_2 was observed:on passing nitrogen through a neutral permanganate solution manganese dioxide was produced. Sulphur was isolated by column chromatography.

The reaction obtained is particularly interesting for the following reasons:

a) it promotes an easy -N=S bond cleavage by means of radicals which otherwise would only occur at high temperatures (800°C)

b) it is an important example of the addition of phenyl radicals on a double bond between heteroatoms which confirms the properties of sulphur atoms as radical acceptors

c) there is induced generation of aryl nitrenes whose presence as intermediates is shown by the presence of azo-derivatives and carbazole

d) the similarity between SO_2 and Ar-N=S=O is further confirmed, as the supposed intermediates, e.g. $PhSO_2^{\bullet}$ and (XI), are analogous.

Kinetic and E.P.R. studies are being carried out to broaden the study of the mechanism of this reaction extended to a series of heterocumulenes.

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