Tetrahedron, 1957, Vol. 1, pp. 338–342. Pergamon Press Ltd., London

NOTES

Chemistry of the sydnones—III[*]

FURTHER experimental observations on the decomposition of 3-phenylsydnone in alkaline solutions are described. When a reducing agent is also present, a highly coloured product, believed to result from isomerisation of glyoxylic acid phenylhydrazone, is formed.

A characteristic reaction of 3-phenylsydnone, not shared by most of the other sydnones, is its decomposition in boiling, weakly alkaline solutions.[1] The explanation of this reaction offered by Baker, Ollis and Poole[2] supposed the initial conversion of the sydnone into N-nitrosoanilinoacetic acid and subsequent decomposition of this, in accordance with the observation of Fischer,[3] into carbon dioxide and N-nitrosomethylaniline. In actual fact, the decomposition of N-nitrosoanilinoacetic acid is a more complex reaction. Carbon dioxide is evolved and a small proportion of volatile N-nitroso-compound can be isolated, but the principal product is a red tar which dissolves in concentrated sulphuric acid with a crimson colour. In contrast with this, 3-phenylsydnone decomposes under the weakly alkaline conditions specified to give carbon dioxide and a dark brown resin which dissolves in sulphuric acid with a greenish-brown colour, no volatile nitroso-compound being formed. Further, the addition of a little phenol to the solution entirely prevents the decomposition of the sydnone. This observation suggests that the reaction under discussion is essentially one of polymerisation. Other substances found similarly to inhibit the reaction were choral hydrate, *o*-phenylenediamine, resorcinol and anilinoacetic acid.

Treatment of 3-phenylsydnone with sodium hydroxide solution and zinc dust produces an intense crimson colour, which disappears on prolonging the reaction, together with small amounts of ammonia and aniline. Other reducing agents giving the same colour were ferrous hydroxide and sodium hydroxide, and hydrogen in the presence of finely divided nickel and sodium hydroxide.

The coloured substance is present in such small amounts that it could not be isolated, but it has the following definite properties:

(a) It is converted by further reduction to a colourless substance which is re-oxidised by air.
(b) It becomes yellow with acetic acid and strongly pink with mineral acids.
(c) It is adsorbed from alkaline solution by magnesium oxide, forming a brilliant, pink-violet lake.

The same colour appears, and apparently exclusively, in alkaline solutions in which phenyl hydrazine and sodium glyoxylate may be presumed to be present. For example, each of the following solutions warmed with a solution of phenylhydrazine hydrochloride rapidly becomes intensely crimson and the coloured substance present has the properties described above:

(a) Dichloroacetic acid boiled with excess of 2 N sodium hydroxide and cooled;
(b) An aqueous solution of oxalic acid, shaken with zinc dust, filtered and made alkaline;
(c) Glycollic acid heated with equal volumes of concentrated nitric acid and water and then made alkaline.

The crimson-coloured by-product obtained by Chattaway[4] during the oxidation of phenylhydrazine in alcoholic alkaline solutions probably results from the formation of a small amount of glyoxylate by oxidation of the alcohol.

Glyoxylic acid phenylhydrazone is easily prepared by boiling dichloroacetic acid and phenylhydrazine in alkaline solution and subsequently precipitating with hydrochloric acid. Recrystallisation from aqueous alcohol yields a product melting at 139°, identical with that prepared directly from glyoxylic acid. The crude product always gives crimson alkaline solutions, but purification is effected, without great loss, by boiling the alkaline solution with zinc dust or magnesium oxide. In the former

[*] Part II—*Rec. Trav. Chim.* **75**, 1080 (1956).

[1] R. A. Eade and J. C. Earl *J. Chem. Soc.*, 2307 (1948).

[2] W. Baker, W. D. Ollis and V. D. Poole *J. Chem. Soc.*, 307 (1949).

[3] O. Fischer *Ber. Dtsch. Chem. Ges.* **32**, 249 (1899).

[4] F. D. Chattaway *J. Chem. Soc.* **91**, 1323 (1907).

case the impurity is removed by reduction, in the latter by adsorption. The purified hydrazone does not give a crimson colour on dissolving in alkali, but the solutions become pink on standing or warming.

The general character of the coloured substance suggests that it is an azo compound with an acid, salt-forming group. Many such compounds among the azo-dyes, a simple example being phenylazophenol, dissolve in both strong acids and strong alkalis giving pronounced colours, whereas in weakly acid or alkaline solutions less intense colours are produced. The isomerisation, under some conditions, of glyoxylic acid phenylhydrazone to phenylazoacetic acid, $C_6H_5{\cdot}N{=}N{\cdot}CH_2{\cdot}COOH$, is quite probable and this substance would be expected to form highly coloured salts in both alkaline and strongly acid solutions.

Under alkaline conditions there is evidently a small amount of hydrolytic fission of 3-phenylsydnone at the 3:4 bond giving sodium glyoxylate as one product. When a reducing agent is present the other fragment from the fission is reduced to phenylhydrazine, which reacts with the sodium glyoxylate. Since 3-phenylsydnone is known to be reconverted in high yield into sodium N-nitrosoanilinoacetate by alkaline hydrolysis, the amount of fission at the 3:4 bond is undoubtedly small. The 4-halogenoderivatives, however, have been shown to undergo breakdown at the 3:4 link much more readily, although here the simultaneous production of aniline and sodium nitrite remains to be explained.[1]

The reactions of 3-phenylsydnone recorded above and in the earlier contributions of this series furnish examples of the fission of the sydnone ring, additional to those already well-known. It appears that acid hydrolysis, alkaline hydrolysis and reduction under a variety of experimental conditions are all effective in opening up the characteristic sydnone ring-structure. The different reagents attack different parts of the ring-system and some of the break-down reactions are almost quantitative. It can, therefore, be said that the sydnone ring is not a particularly stable structure, compared with the benzene or pyridine rings which are entirely unaffected by most hydrolytic reagents and do not readily undergo reductive fission. This being so, it is appropriate to comment on statements in the literature such as "... the sydnones are thus compounds exhibiting aromatic characteristics[2]". "The sydnones must be regarded as possessing a single hybrid structure of aromatic type[5]" and "... the known facts of sydnone chemistry indicate that the five-membered ring has aromatic properties and is planar; i.e. considerable delocalisation of the π electrons occurs[6]". It is clear that the authors of these statements do not regard "aromatic" as necessarily connoting a ring-structure stable against attack by chemical reagents.

EXPERIMENTAL

(a) *Resinification of* 3-*phenylsydnone by sodium acetate*

The sydnone (2 g) in water (150 ml) was boiled in a distilling flask while a 10 per cent solution of crystalline sodium acetate (10 ml) was added drop by drop during 15 min. The distillate contained a small amount of yellow oil which hardened on standing and did not give the Liebermann nitroso reaction. The principal product was a dark, non-volatile oil which solidified on cooling to a brittle resin soluble in concentrated sulphuric acid with a greenish-brown colour.

(b) *Resinification of* 3-*phenylsydnone with* 0·1 N *sodium borate*

The sydnone (0·186 g) was mixed with the sodium borate solution (25 ml) and heated to boiling. Rapid darkening and evolution of gas took place, with separation of a dark oil similar to that obtained with sodium acetate.

(c) *Effect of phenol on the resinification*

The sydnone (0·212 g), 0·1 N sodium borate (25 ml) and 1 per cent phenol solution (2 ml) were boiled under reflux for 30 min. The solution remained clear and pale yellow. On cooling and titrating with 0·1 N hydrochloric acid (methyl orange indicator), 24·95 ml were required, showing that no nitroso-acid had been formed. From the solution, on cooling, unchanged sydnone (0·11 g) crystallised out in almost white needles, m.p. 135°.

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[5] W. Baker, W. D. Ollis and V. D. Poole *J. Chem. Soc.*, 1542 (1950).
[6] W. J. Orville Thomas *Chem. and Ind.*, 533 (1955).

(d) *Decomposition of* N-*nitrosoanilinoacetic acid in boiling aqueous solution*

Water (50 ml) and the acid (1·0 g) were boiled under reflux for 10 min. The steam-volatile product was distilled off and found to give the Liebermann nitroso reaction. The red, sticky tar remaining in the distilling flask did not give the Liebermann reaction, but dissolved in concentrated sulphuric acid with a crimson colour.

(e) *Alkaline reduction of* 3-*phenylsydnone*

The sydnone (0·162 g) was mixed with 0·5 N sodium hydroxide (100 ml) and zinc dust (0·2 g) and heated to boiling for 23 min, the volatile products being continuously collected in 1 per cent boric acid (25 ml). During the heating the solution acquired a crimson colour which subsequently disappeared. Titration of the boric acid with 0·1 N hydrochloric acid required 0·9 ml, corresponding to 9 per cent of the calculated possible yield of ammonia. The residual colourless solution was filtered from excess of zinc dust and exposed to air when it became strongly pink. Acidification with dilute acetic acid changed the colour to yellow, but on making alkaline again the pink colour was restored. Addition of hydrochloric or nitric acid gave a pink colour, irreversibly discharged on warming. Addition of magnesium sulphate to the alkaline solution gave an intensely coloured precipitate which was filtered off, yielding a colourless filtrate. In other larger experiments unsuccessful attempts were made to isolate the substance responsible for the pink colour. The highly coloured magnesium lake was gelatinous; after repeated washing and drying in air it gave a dull brownish-red mass, one sample of which was found to yield 53·7 per cent of magnesium oxide on ignition.

(f) *Preparation and purification of glyoxylic acid phenylhydrazone*

Dichloroacetic acid (2·88 g), phenylhydrazine hydrochloride (3·2 g) and sodium hydroxide (3·2 g) were dissolved in water (20 ml) and boiled under reflux for 1 hr. On cooling and acidifying with hydrochloric acid an oil was precipitated which soon solidified. Recrystallisation from aqueous alcohol gave 1·42 g of the phenylhydrazone melting at 135–139° which dissolved in alkali to an intensely crimson solution.

The crude product (1·0 g) was dissolved in 2 N sodium hydroxide (5 ml) and water (10 ml), zinc dust (1·0 g) being added. After boiling for 10 min the solution was cooled, filtered and acidified with hydrochloric acid. The precipitated phenylhydrazone after washing and drying (0·6 g) melted at 137° and dissolved in N sodium hydroxide without immediate pink colour.

Another sample of crude phenylhydrazone (0·5 g) was dissolved in 2 N sodium hydroxide (10 ml) and water (30 ml) and finely powdered, "light" magnesium oxide (1·5 g) added. After boiling for 30 min, the solution was filtered and the phenylhydrazone precipitated by acid. The product (0·35 g) melted at 141° and did not give an immediate pink colour when dissolved in alkali.

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Reduction of ketenes with lithium aluminium hydride—I. Diphenylketene

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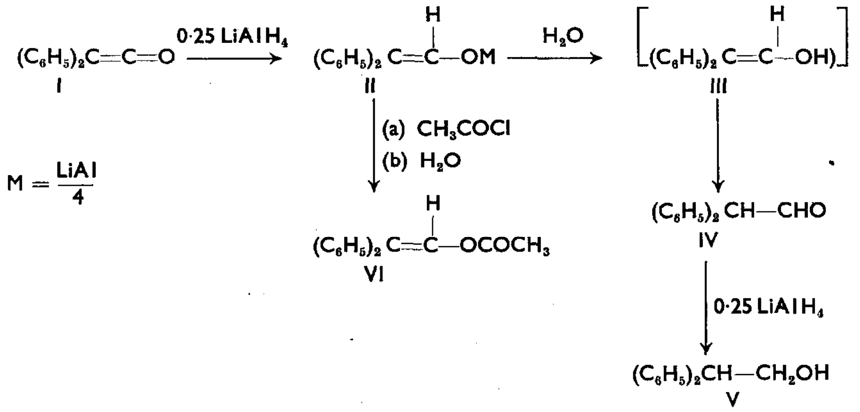
While alkyl ketene dimers have been reduced with lithium aluminium hydride to the corresponding β-ketocarbinols,[1,2] the reaction between free ketenes and the complex metal hydride, to our knowledge, has not hitherto been reported.

Lithium aluminium hydride attacks diphenylketene (I) by a 1:2-addition mechanism affording the complex II, which upon hydrolysis gives diphenylacetaldehyde (IV) in 93 per cent yield, probably via the intermediate enol III. Even in the presence of more than 0·25 mole of lithium aluminium hydride per mole of ketene (e.g. with a 200 per cent excess), the reduction of I stops at the aldehyde (enol) stage, and no difference in yield was observed. However, the isolated diphenylacetaldehyde (IV) is readily further reduced with the same agent to the corresponding alcohol, diphenylethanol (V).

The existence of the complex II has been demonstrated by converting it, upon addition of acetyl chloride, to the enol acetate of diphenylacetaldehyde (VI), in 95 per cent yield.



The reduction of other ketenes with lithium aluminium hydride is now being investigated as well as the possibility of obtaining α-substituted aldehydes or vinyl compounds by reaction of intermediate complexes of type II with various agents, such as halogens, alkyl halides, alcohols.

EXPERIMENTAL*

Reagents. Diphenylketene (I) was prepared in 73 per cent yield from diphenylchloroacetyl chloride by means of zinc, according to the method of Staudinger.[3]† Stock solutions of lithium aluminium hydride in anhydrous diethyl ether were prepared[4] and the hydride content determined iodometrically.[5]

Reduction procedure. All reductions were carried out in the usual way, by adding dropwise a solution of the substance to be reduced in anhydrous diethyl ether to an ethereal solution of lithium aluminium hydride, at such a rate as to maintain gentle boiling of the solvent. After the addition had been completed, stirring was continued until the reaction mixture had cooled to room temperature. The reduction complexes were then carefully hydrolysed with water (ice cooling) and the inorganic precipitate dissolved in 10 per cent sulphuric acid. The reduction products were extracted with ether, the ethereal layer washed with 4 per cent aqueous sodium carbonate solution and with water, and the residue, after drying and evaporation of the solvent, was either distilled under reduced pressure or recrystallised.

Reduction of diphenylketene (I). Diphenylketene (11·2 g, 0·058 mole) in 50 cm^3 of ether and 78 cm^3 of lithium aluminium hydride solution (containing 0·0145 mole + 10 per cent excess of hydride) gave 10·6 g (93·1 per cent) of *diphenylacetaldehyde* (IV), b.p. 178–180°/12·5 mm.[6] Semicarbazone, m.p. 158–160°;[7] oxime, m.p. 111°;[8] 2:4-dinitrophenylhydrazone, m.p. 144–145°.[9]

The same reduction with a 200 per cent excess of hydride afforded diphenylacetaldehyde in 92·5 per cent yield.

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* All melting points are uncorrected.

† This procedure, in our hands, appeared to be superior to the one described in *Org. Syntheses* Coll. Vol. 3, p. 356 (1955).

[1] R. L. Wear *J. Amer. Chem. Soc.* **73**, 2390 (1951).

[2] A. S. Spriggs, C. M. Hill and G. W. Senter *J. Amer. Chem. Soc.* **74**, 1555 (1952).

[3] H. Staudinger *Ber. Dtsch. Chem. Ges.* **38**, 1735 (1905).

[4] W. G. Brown *Org. React.* **6**, 470 (1951).

[5] H. Felkin *Bull. Soc. Chim. France* 347 (1951).

[6] A. Béhal and M. Sommelet *C. R. Acad. Sci., Paris* **138**, 91 (1904).

[7] E. P. Kohler and N. L. Drake *J. Amer. Chem. Soc.* **45**, 1281 (1923).

[8] P. Lipp *Liebigs Ann.* **449**, 26 (1926).

[9] T. A. Favorskaya and L. A. Remizova *J. Gen. Chem.* (*U.S.S.R.*) **23**, 817 (1953).

Reduction of diphenylketene (I) *with addition of acetyl chloride*, Diphenylketene (8·0 g, 0·041 mole) in 50 cm^3 of ether was added to 54 cm^3 of an ethereal solution of lithium aluminium hydride (containing 0·01 mole + 10 per cent excess of hydride), and the resulting complex was treated dropwise with 3·6 g (0·041 mole + 10 per cent excess) of acetyl chloride in 10 cm^3 of anhydrous ether. The reaction mixture turned yellow and a granular precipitate separated. After heating 30 min to boiling, the reaction product was hydrolysed and worked up as described above to yield 9·25 g (94·7 per cent) of the *enol acetate of diphenylacetaldehyde* (VI), m.p. 58° [10]* (from dilute ethanol) (Found : C, 80·60; H, 5·98. $C_{16}H_{14}O_2$ requires C, 80·65; H, 5·92 per cent).

The same enol acetate (m.p. 58°) was obtained in 78·2 per cent yield (9·5 g) by heating 11·8 g (0·051 mole) of diphenylacetaldehyde with 8 cm^3 (0·081 mole) of acetic anhydride and 1·4 g (0·017 mole) of anhydrous sodium acetate for 1 hr at 160–165°, pouring the cooled mixture into water and extracting the oily layer with ether.[10]* A mixture of both enol acetates gave no depression in melting point.

Reduction of diphenylacetaldehyde (IV). Diphenylacetaldehyde (6·0 g, 0·031 mole) in 50 cm^{3}of ether was reduced with 45 cm^3 of lithium aluminium hydride solution-(containing 0·008 mole + 10 per cent excess of hydride) to produce 5·95 g (97·5 per cent) of *diphenylethanol* (V), b.p. 178–180°/13 mm, m.p. 59–61°[11,12] (from petroleum ether). Benzoate, m.p. 90°[11].

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* This author gives a m.p. of 59° for the enol acetate. However, the experimental procedure for its preparation and analysis are not reported.

[10] M. Tiffeneau *C. R. Acad. Sci., Paris* **150,** 1181 (1910).

[11] P. Ramart and P. Amagat *Ann. Chim.* [10] **8,** 263 (1927).

[12] E. Bergmann *J. Chem. Soc.* 412 (1936).