Aromatic Sulphonation. Part 71.[1] Sulphonation and Protonation of 1,2-Diphenylcyclopropenone

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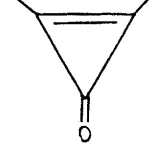
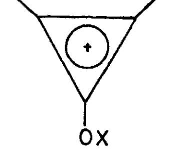
The oxygen protonation and the phenyl substitution of 1,2-diphenylcyclopropenone in sulphuric acid as well as the sulphur trioxide sulphonation in CCl_3F as solvent have been studied. 1,2-Diphenylcyclopropenone is half protonated at *ca.* 63 wt-% H_2SO_4. Sulphonation in 105 wt-% sulphuric acid yields the 1,2-diphenylcyclopropenone-3′,3″-disulphonic acid. The sulphonation with 5 equivalents of sulphur trioxide in CCl_3F led to a substrate conversion of 64% with formation of 45 ± 3% 3′-sulphonic acid and 19 + 3% 3′,3″-disulphonic acid. The entity undergoing substitution in fuming sulphuric acid is identified as it is for aprotic sulphonation.

IN relation to the sulphonation of biphenyl and its derivatives[2] and of a number of benzene derivatives containing a positive pole as substituent,[3] the sulphonation of 1,2-diphenylcyclopropenone (1) has been investigated. The sulphonation has been achieved both in 105 wt-% sulphuric acid and with sulphur trioxide in CCl_3F. In order to determine the nature of the species undergoing sulphonation in sulphuric acid [*viz.* (1) or (2)] and with sulphur trioxide [*viz.* (1) or (2b)], both the phenyl substitution pattern for the two sulphonating systems, and the substrate protonation in aqueous sulphuric acid have been determined.



(1)



(2) a ; X = H
b ; X = SO_3^-
c ; X = SO_3H

RESULTS

Protonation.—The protonation of 1,2-diphenylcyclopropenone has been studied in aqueous sulphuric acid ranging in the concentration range 55—99.7 wt-% H_2SO_4 by means of ^1H n.m.r. spectroscopy. The ^1H n.m.r. spectra of (1) dissolved in 58.0 and 93.1 wt-% sulphuric acid are shown in Figure 1. Spectrum B is ascribed to the species (2a). The assignments are shown in Figure 1. A plot of the difference in chemical shift of the *ortho*- and *meta*-hydrogens against the H_0^a acidity function,[4], † is shown in Figure 2.‡ The chemical shift difference above 75 wt-% H_2SO_4 was taken to represent that of (2a). Apparently there is a medium effect on the $\Delta\delta$ of that ion. The much steeper slope of the graph below 75 wt-% is ascribed to the deprotonation of (2a). The protonation of a Brønsted base will be effected in a range of 2.5—3.0 units of the appropriate acidity function. Accordingly, it may be concluded from Figure 2 that the half-protonation of (1) occurs at *ca.* 63 wt-% H_2SO_4.

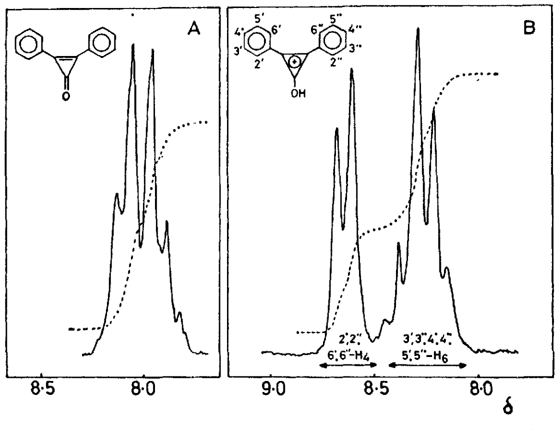


FIGURE 1 The ^1H n.m.r. spectra of 1,2-diphenylcyclopropenone in 58.0 (A) and 93.1 (B) wt-% H_2SO_4

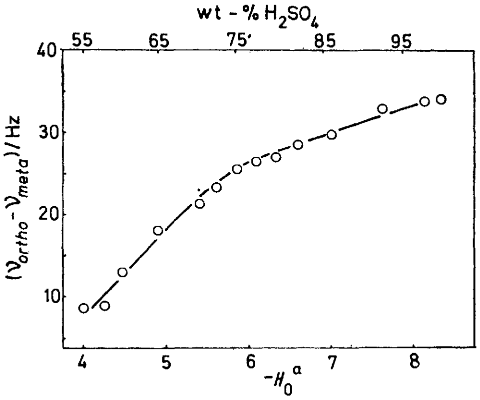


FIGURE 2 Protonation of 1,2-diphenylcyclopropenone in sulphuric acid

Sulphuric Acid Sulphonation.—1,2-Diphenylcyclopropenone has been sulphonated in 105 wt-% H_2SO_4 at 25 ± 3 °C. The ^1H n.m.r. spectrum of the reaction mixture, recorded after one week, consisted of a singlet at 9.29 (H_2-2′,2″), two doublets with $J = 8$ Hz at 9.14 and 8.99 (H_2-4′,4″ and H_2-6′,6″), and a triplet with $J = 8$ Hz at 8.61 p.p.m. (H_2-5′,5″) which was assigned to the presence of 1,2-diphenyl-3-hydroxycyclopropenium-3′,3″-disulphonic acid. The 3′,4″-disulphonic acid is not apparent beyond its limit of ^1H n.m.r. detection which is *ca.* 4%.

Sulphur Trioxide Sulphonation.—The aprotic sulphon-

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† Protonation on oxygen is not governed by H_0,[5] but by H_0^a (benzophenone,[4] and alkane- and arene-sulphonates [6]).

‡ The graph of the chemical shifts of the *ortho*-hydrogens proper (*i.e.* relative to the external reference tetramethylsilane) against H_0^a is similar in shape to that of Figure 2.[7]

ation of 1,2-diphenylcyclopropenone has been effected in CCl_3F with *ca.* 5 equivalents of sulphur trioxide at 0 °C. After work-up of the heterogeneous reaction mixture 36% of the substrate (1) was recovered. The ^1H n.m.r. spectra of the solutions of the sulphonate in D_2O and in 98 wt-% H_2SO_4 showed the presence of $70 \pm 4\%$ 1,2-diphenylcyclopropenone-3′-sulphonate and $30 \pm 4\%$ 1,2-diphenylcyclopropenone-3′,3″-disulphonate. The ^1H n.m.r. chemical shifts for the sulphonate mixture in 98 wt-% H_2SO_4 were for the 3′-sulphonic acid: 9.25 (s, H-2′), 9.10 (d, H-4′), 8.95 (d, H-6′), 8.75 (d, $J = 8$ Hz, H_2-2″,6″), 8.60 (t, H-5′), and 8.35 (m, H_3-3″,4″,5″), and for the 3′,3″-disulphonic acid: 9.25 (s, H_2-2′,2″), 9.10 (d, H_2-4′,4″), 8.95 (d, H_2-6′,6″), and 8.60 p.p.m. (t, H_2-5′,5″).

DISCUSSION

1,2-Diphenylcyclopropenone in aqueous sulphuric acid is protonated on the carbonyl oxygen. The three-membered ring of the resulting species containing only two π-electrons and will thus be aromatic according to Hückel's rule.[8] The half-protonation occurs at *ca.* 63 wt-% H_2SO_4. This is at lower sulphuric acid concentration than with aliphatic ketones for which the half-protonation occurs at *ca.* 80 wt-% sulphuric acid.[9] The higher basicity of 1,2-diphenylcyclopropenone can be explained in terms of the (enhanced) aromatic character of the cyclopropenone moiety upon oxygen protonation.

The sulphonation of 1,2-diphenylcyclopropenone in strongly fuming sulphuric acid leads to the 3′,3″-disulphonic acid. The very predominant formation of this disulphonic acid is easily explained in terms of (2a), (2b), or (2c) as the substrate species undergoing substitution.* For it would be expected that (1) in view of its stilbene structure would undergo *para*-phenyl and/or double-bond sulphonation.[12] The sulphur trioxide sulphonation of (1) leads only to *meta*-substitution, illustrating that the substrate species undergoing substitution in this system is not (1) (which would yield *para*-phenyl substitution and double-bond sulphonation, see earlier), but apparently (2b). As to the relative low substrate conversion, in comparison to the amount of SO_3 employed, it has to be realized that 1 equivalent of SO_3 is consumed for the oxygen sulphation, and that 2 equivalents are required for one phenyl sulphodeprotonation.[13]

Similar high degrees of *meta*-substitution were recently reported for the bromination,[14] nitration,[15] and sulphonation [3] of benzene derivatives containing a positive pole (N^+H_3 and N^+Me_3) as substituent. Also the nitration of 1,2-diphenylcyclopropenone with $NaNO_3$ in sulphuric acid yields only the mono *meta*-nitro-derivative.[16]

EXPERIMENTAL

Materials and Spectrometers.—Diphenylcyclopropenone was synthesized from diphenylethyne.[17] The other reagents were described.[2] The ^1H n.m.r. spectra were 100 MHz spectra recorded on a Varian HA 100 spectrometer, using neat tetramethylsilane (sealed capillary) as an external reference.

Procedures.—For the protonation studies 50 mg of 1,2-diphenylcyclopropenone was dissolved in 1.0 ml of aqueous sulphuric acid of the desired strength and the ^1H n.m.r. spectrum recorded.

For the sulphuric acid sulphonation 100 mg of 1,2-diphenylcyclopropenone was dissolved in 1.0 ml of 105 wt-% sulphuric acid. The reaction mixture was left for one week in a thermostatically controlled room kept at 25 ± 3 °C, and the ^1H n.m.r. spectrum of the solution recorded both before and after dilution to 98 wt-% H_2SO_4.

For the sulphonation with sulphur trioxide 310 mg of 1,2-diphenylcyclopropenone was dispersed in CCl_3F (10 ml), and 600 mg SO_3 dissolved in CCl_3F (10 ml) was added dropwise at 0 °C with stirring during 20 min. The reaction mixture was further stirred first for 30 min at 0 °C and then for 30 min at room temperature. After being cooled to −5 °C, the reaction mixture was neutralized with K_2CO_3 and dissolved in 8 ml D_2O. The undissolved material was taken up in CCl_4 and shown by ^1H n.m.r. spectroscopy to be (1). The CCl_3F was evaporated from the CCl_3F–D_2O mixture, and an ^1H n.m.r. spectrum recorded from the resulting D_2O solution. Then the D_2O was removed by rotary evaporation, the residue taken up in 98 wt-% H_2SO_4, and once again an ^1H n.m.r. spectrum was recorded.

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* In fuming sulphuric acid in addition to protonation sulphur trioxide complexation of (1) with SO_3 or SO_3H^+ may also be considered,[6,10] since the a_{SO_3}/h_0 ratio increases with increasing sulphuric acid concentration and is, therefore, very much greater in fuming than in concentrated aqueous sulphuric acid.[11]

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