Solutions in Sulphuric Acid. Part XV. The Sulphonation of Some Unsaturated Aromatic Ketones in Sulphuric Acid.*

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Sulphonates of dibenzylideneacetone, cinnamylideneacetophenone, and dicinnamylideneacetone have been isolated from solutions of the ketones in sulphuric acid. The sulphonation of unsaturated aromatic ketones in sulphuric acid is discussed.

IN Part XIV * it has been shown that the cryoscopic behaviour of a number of unsaturated aromatic ketones in sulphuric acid can be adequately accounted for if it is assumed that, in addition to protonation on the carbonyl group, many of them are sulphonated, in some cases very rapidly and more than once. We have found only one reference in the literature to a sulphonic acid of this type (Schroedter and Vorländer, *Ber.*, 1903, **36**, 1493). Moreover, it is found in general that substances which dissolve in sulphuric acid to form positive ions are very resistant to sulphonation. It appeared necessary, therefore, to confirm the conclusions drawn from the cryoscopic experiments by isolating sulphonic acids of some of the ketones from their sulphuric acid solutions. This paper describes the isolation and identification of sulphonates of dibenzylideneacetone, cinnamylideneacetophenone, and

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* Part XIV, preceding paper.

dicinnamylideneacetone and discusses certain aspects of the sulphonation of unsaturated aromatic ketones in solution in sulphuric acid.

EXPERIMENTAL

Isolation of the Dilution Products.—The general method for isolating the salts was to prepare solutions of the ketones of the order of ten times the concentration employed in the cryoscopic experiments and then to dilute and neutralise the solutions in a manner which varied with the particular ketone. The period of time between the preparation and the dilution of a solution was determined by reference to the cryoscopic results, an i-factor of 4 being taken to indicate the formation of a monosulphonic acid, and so on, as has already been explained in Part XIV (*loc. cit.*). It was necessary, however, to take into account the fact that higher concentrations were used than were employed for the cryoscopic measurements. When the solute concentration is high, the sulphuric acid becomes appreciably diluted during the course of the sulphonation, so the time for complete sulphonation may be considerably increased.

Dibenzylideneacetone.—100 g. of a 5% solution of dibenzylideneacetone in 100% sulphuric acid were set aside for a day. A little oleum was added to restore the acid to its original strength, and the solution kept for a further day. It was then poured on 100 g. of ice, and 100 c.c. of water were added. The acid was partly neutralised by addition of 50 g. of anhydrous sodium carbonate, and the resulting solid filtered off and extracted with ether to remove unchanged dibenzylideneacetone. The remaining solid was the sodium sulphonate. It was purified by recrystallisation first from sodium chloride solution and finally from very small quantities of distilled water. 5·5 G. of the crude sodium salt, and 0·8 g. of unchanged dibenzylideneacetone were obtained. The corresponding barium salt was prepared from the sodium salt by precipitation with barium chloride, and purified by recrystallisation first from barium chloride solution and finally from distilled water.

Cinnamylideneacetophenone.—The procedure in this case was essentially similar to the above; 6·5 g. of the sodium salt, and no unchanged cinnamylideneacetophenone, were obtained from 5·7 g. of cinnamylideneacetophenone, after a 5% solution in 100% sulphuric acid had been kept for 3 hours.

Dicinnamylideneacetone.—Difficulty was experienced in obtaining a sodium sulphonate in this case, as might be expected from the cryoscopic results, which show that a disulphonic acid is obtained on dissolution of dicinnamylideneacetone in 100% sulphuric acid. In addition to solubility difficulties, it was found that polymerisation occurred on dilution, leading to the formation of resinous products. Of a variety of procedures tried, the most satisfactory was the slow addition of the 100% sulphuric acid solution to aqueous sodium carbonate, with cooling and stirring. Sufficient sodium carbonate was used to neutralise all the acid. The salt was obtained as a finely-divided yellow solid, which was separated by centrifugation. It was recrystallised from sodium chloride solution, and finally precipitated from aqueous solution by addition of acetone.

Identification of the Dilution Products.—A preliminary qualitative investigation of the above sulphonic acid salts showed that each contained sulphur and sodium and each dissolved in sulphuric acid to form a solution whose colour was identical with that of the solution of the parent ketone. The solubility of the sodium sulphonate of dicinnamylideneacetone was much more sharply dependent on the sodium-ion concentration than were the solubilities of the other two sodium salts. This difference in behaviour is consistent with the assumption that the former is the normal salt of a dibasic acid while the other two are salts of monobasic acids.

Samples of each of these compounds when analysed quantitatively gave results which were not reproducible. The composition and structure of the dilution products were therefore confirmed in three ways: (i) by examining them cryoscopically in sulphuric acid; (ii) (in the cases of the dilution products from dicinnamylideneacetone and dibenzylideneacetone) by oxidation and identification of the oxidation products; and (iii) (in the case of the dilution product from cinnamylideneacetophenone) by conversion into the *S*-benzyl*iso*thiuronium derivative.

(i) *Cryoscopic evidence.* It follows from the definition of the i-factor that, for any solution,

$$M/i = (1000wk_f)/\Delta\theta W$$

where M is the molecular weight of the solute, $\Delta\theta$ is the freezing-point depression caused by addition of w g. of the solute to W g. of the solvent (sulphuric acid), and k_f is the cryoscopic constant (5·98 deg. mole^{-1} kg.). The results of some cryoscopic experiments, with slightly aqueous sulphuric acid as solvent, carried out to determine *M*/*i* for each of the salts of the dilution products are given in the following table.

Solute *	F. p.	$\Delta\theta$	*w*, g.	*M*/*i*		Solute *	F. p.	$\Delta\theta$	*w*, g.	*M*/*i*	
				expt.	theory					expt.	theory
I	10·039°	—	—	—	—	III	9·838°	—	—	—	—
	9·598	0·441°	0·7703	83·0	84		9·555	0·283°	0·4911	84·4	84
	8·827	1·212	2·069	81·2			9·345	0·493	0·8501	83·8	
II	9·616	—	—	—	—		8·611	1·227	2·043	81·0	
	9·356	0·260	0·5711	107	109	IV	9·548	—	—	—	—
							9·250	0·298	0·5039	80·7	82

* I, Sodium salt of dilution product of dibenzylideneacetone.
II, Barium ,, ,, ,,
III, Sodium ,, ,, cinnamylideneacetophenone.
IV, Sodium ,, ,, dicinnamylideneacetone.

The theoretical *M*/*i* values given in the last column of this table have been calculated by assuming that the solutes (I)—(III) are salts of the monosulphonic acids but that (IV) is the disodium salt of the disulphonic acid of dicinnamylideneacetone, and that they undergo complete solvolysis in solution in sulphuric acid, as has been demonstrated for other sodium sulphonates (Part VII, *J.*, 1950, 2537), according to the equations

$$\text{(I)}\quad \mathrm{C_6H_5{\cdot}CH{:}CH{\cdot}CO{\cdot}CH{:}CH{\cdot}C_6H_4{\cdot}SO_3^-\}Na^+ + 2H_2SO_4 =}$$
$$\mathrm{C_6H_5{\cdot}CH{:}CH{\cdot}\overset{+}{C}(OH){\cdot}CH{:}CH{\cdot}C_6H_4{\cdot}SO_3H + Na^+ + 2HSO_4^-}\quad (i = 4)$$
$$\text{(II)}\quad \mathrm{C_6H_5{\cdot}CH{:}CH{\cdot}CO{\cdot}CH{:}CH{\cdot}C_6H_4{\cdot}SO_3^-\}\tfrac{1}{2}Ba^{++} + 2H_2SO_4 =}$$
$$\mathrm{C_6H_5{\cdot}CH{:}CH{\cdot}\overset{+}{C}(OH){\cdot}CH{:}CH{\cdot}C_6H_4{\cdot}SO_3H + \tfrac{1}{2}Ba^{++} + 2HSO_4^-}\quad (i = 3{\cdot}5)$$
$$\text{(III)}\quad \mathrm{C_6H_5{\cdot}[CH{:}CH]_2{\cdot}CO{\cdot}C_6H_4{\cdot}SO_3^-\}Na^+ + 2H_2SO_4 =}$$
$$\mathrm{C_6H_5{\cdot}[CH{:}CH]_2{\cdot}\overset{+}{C}(OH){\cdot}C_6H_4{\cdot}SO_3H + Na^+ + 2HSO_4^-}\quad (i = 4)$$
$$\text{(IV)}\quad \mathrm{(Na^+\{^-O_3S{\cdot}C_6H_4{\cdot}[CH{:}CH]_2)_2CO + 3H_2SO_4 =}$$
$$\mathrm{(HO_3S{\cdot}C_6H_4{\cdot}[CH{:}CH]_2)_2\overset{+}{C}(OH) + 2Na^+ + 3HSO_4^-}\quad (i = 6)$$

The good agreement between the theoretical and experimental values of *M*/*i* strongly suggests that the assumptions on which the theoretical values were calculated is correct.

(ii) *Oxidation evidence.* (*a*) 3·05 g. of the sodium salt of the dilution product of dicinnamylideneacetone were refluxed with a slight excess (11·8 g.) of potassium permanganate in alkaline solution for 2½ hr. After being filtered and acidified, a part of the solution was tested for sulphate ion. The negative result obtained showed that none of the sulphur in the original substance could be attached to the side chain. The main bulk of the solution was evaporated to 20 c.c. and cooled in ice, and the resulting precipitate separated by filtration. 1·87 g. of a colourless crystalline solid were obtained and shown to be a *p*-carboxybenzenesulphonate. No benzoic acid could be isolated. The *p*-carboxybenzenesulphonic acid was identified in three ways. A part was fused with potassium hydroxide, and *p*-hydroxybenzoic acid shown to be formed by a mixed m. p. determination. Another part was converted into the potassium salt and titrated. The equivalent weight was thus found to be 240·7 (Calc.: 240·3). A third part was converted by way of the silver salt into the acid; m. p. 255—258°. It was therefore concluded that the sole aromatic oxidation product was *p*-sulphobenzoic acid, and that the original substance was the disodium salt of di-4-sulphocinnamylideneacetone, $\mathrm{(Na^+\{^-O_3S{\cdot}C_6H_4{\cdot}[CH{:}CH]_2)_2CO \longrightarrow 2Na^+\{^-O_3S{\cdot}C_6H_4{\cdot}CO_2H}$.

(*b*) A solution of the sodium salt of the dilution product of dibenzylideneacetone was oxidised in a similar manner. In the early stages of the oxidation benzaldehyde was detected. Benzoic acid was extracted from the oxidised solution by means of ether, and *p*-sulphobenzoic acid was obtained as the acid salt by evaporation and cooling, and identified in the same manner as above. 0·99 G. of the original salt yielded 0·24 g. of benzoic acid and 0·52 g. of the acid potassium salt. It was concluded that the original substance was the sodium salt of 4-sulphodibenzylideneacetone, $\mathrm{Na^+\{^-O_3S{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}CO{\cdot}CH{:}CH{\cdot}C_6H_5 \longrightarrow Na^+\{^-O_3S{\cdot}C_6H_4{\cdot}CO_2H + C_6H_5{\cdot}CO_2H}$.

(iii) The sodium salt of the dilution product of cinnamylideneacetophenone was converted into the S-*benzyl*iso*thiuronium* derivative (Clarken and Watt, *J. Org. Chem.*, 1941, **6**, 376). This was recrystallised three times from ethanol and had m. p. 200—201° (Found: C, 62·7; H, 5·0; N, 5·9; S, 13·6. $\mathrm{C_{15}H_{24}O_4N_2S_2}$ requires C, 62·5; H, 5·0; N, 5·8; S, 13·4%). It was concluded therefore that the original substance was the sodium salt of 4-sulphocinnamylideneacetophenone.

DISCUSSION

It may reasonably be concluded from the above results and those in the preceding paper that (1) dibenzylideneacetone in dilute solution in sulphuric acid reacts completely in a few hours at 25° to give mainly 4-sulphodibenzylideneacetone, (2) cinnamylideneacetophenone in dilute solution in sulphuric acid reacts rapidly at 25° to give mainly 4-sulphocinnamylideneacetophenone, and (3) dicinnamylideneacetone reacts completely in a few minutes at 25° to give mainly di-4-sulphocinnamylideneacetone. The above results do not exclude the possibility that a certain amount of the *ortho-* and *meta-*sulphonic acids are formed in addition to the *para-*isomer in each case, although it seems that the last is formed in the greatest amount.

Having now definitely established that the variation of the *i*-factor with time of the unsaturated aromatic ketones considered in Part XIV (*loc. cit.*) is due to their sulphonation, we may discuss certain aspects of the sulphonation of this type of compound. Although the *i*-factor of most of the ketones was studied as a function of time at 25°, no quantitative conclusions can be drawn from the data because the concentration of the acid was changed throughout any given experiment by the water formed in the sulphonation process, and the rate of sulphonation is markedly dependent on the concentration of the sulphuric acid solvent. Certain qualitative rules, however, emerge. Study of the cryoscopic results at once shows the overwhelming dependence of the rate of sulphonation of a given phenyl group on the length of the conjugated chain separating the phenyl group from the carbonyl group. Closer study shows that the rate of sulphonation also depends, though to a much smaller extent, on the total conjugation of the molecule: thus the length of the conjugated chain on the remote side of the carbonyl group also has an effect on the rate of aromatic sulphonation. At 25° sulphonation of these compounds in dilute solution in sulphuric acid appears to be governed by the following rules:

(1) The group Ph·CO· is stable in sulphuric acid. This rule is illustrated by the behaviour of benzaldehyde, acetophenone, and benzophenone.

(2) The group Ph·CH:CH·CO is slowly sulphonated, largely in the *para*-position. The behaviour of benzylideneacetone, benzylideneacetophenone, dibenzylideneacetone, 2 : 6-dibenzylidene*cyclo*hexanone, and cinnamaldehyde is in accordance with this rule. In the case of the third and the fourth compound the effect of the conjugation of the molecule as a whole is noticeable, for, whereas the other three compounds give initially two-fold freezing-point depressions, dibenzylideneacetone gives an initial *i*-value of about 3. The deactivating effect of the first sulphonic acid group is also noticed in the case of dibenzylideneacetone: the second group enters much more slowly than the first. The compound di-4-methylbenzylideneacetone follows a similar rule, although in this case the sulphonic acid groups enter positions other than the *para*-position.

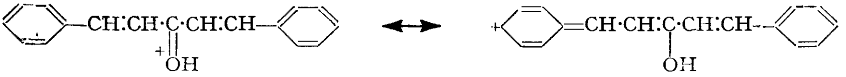
(3) The group Ph·[CH:CH]$_2$·CO· is monosulphonated, mainly in the *para*-position, very rapidly. This is exemplified by the behaviour of cinnamylideneacetophenone and dicinnamylideneacetone. Following this rule and the previous one, benzylidenecinnamylideneacetone is disulphonated, the first group entering rapidly and the second slowly.

(4) The group Ph·[CH:CH]$_3$·CO· is sulphonated in the *para*-position very rapidly, and in both *ortho*-positions slowly. This rule is suggested by the cryoscopic results obtained with 1 : 13-diphenyltrideca-1 : 3 : 5 : 8 : 10 : 12-hexaen-7-one. The orientation of the sulphonic acid groups is an assumption, but it seems unreasonable to expect the most reactive of the compounds to form *meta*-derivatives when no such derivatives have been detected in the case of the less reactive ketones. The behaviour of 1 : 11-diphenylundeca-1 : 3 : 6 : 8 : 10-pentaen-5-one is in line with this rule and the preceding one.

Preparative sulphonation procedures generally employ drastic conditions: long periods of heating at high temperatures with sulphuric acid containing excess of sulphur trioxide. In addition, in the only previous preparative work on compounds of this type, Schroedter and Vorländer (*loc. cit.*) obtained 4-sulphodibenzylideneacetone by storing a solution of dibenzylideneacetone in 100% sulphuric acid for *one month*, a fact which doubtless explains why previous workers have not interpreted the cryoscopic results in terms of sulphonation. For these reasons, the ready sulphonation that we have observed in the case of certain unsaturated aromatic ketones deserves comment. One of the reasons for the extreme conditions employed in preparative sulphonations is simply that it is undesirable to use a large excess of acid, as in the cryoscopic experiments, because of the greater difficulty of isolating the products. The water formed in the course of the reaction consequently dilutes the acid appreciably and the reaction rate falls correspondingly. Thus in order to ensure that the reaction goes to completion, long reaction times, high temperatures, and sulphonating mixtures of high sulphur trioxide content are used. The one month's reaction time used by Schroedter and Vorländer (*loc. cit.*), even for such a reactive compound as dibenzylideneacetone, is understandable in view of the relatively concentrated solution that they employed.

These considerations partly explain the very rapid sulphonation, under cryoscopic conditions, of the unsaturated aromatic ketones we have investigated. Nevertheless, it is evident that these compounds are very reactive towards aromatic sulphonation and probably towards aromatic electrophilic substitution generally. The carbonyl group, which becomes protonated in 100% sulphuric acid, deactivates the aromatic nucleus by its negative inductive and mesomeric effects. Thus, benzophenone, for example, is stable in 100% sulphuric acid at 25°, and when sulphonation does occur, it does so at high temperature and in the *meta*-position (Lapworth, *J.*, 1898, **73**, 408). The deactivating effect of the carbonyl group would be expected to be much reduced in the group ·CH:CH·CO·, partly because of the intervention of the carbon chain but mainly because the ethylenic group exerts a positive electromeric effect. Accordingly, compounds which include the group C_6H_5·CH:CH·CO· are readily sulphonated at 25° mainly in the *para*-position. Of related interest are the results of Bordwell and Rhode (*J. Amer. Chem. Soc.*, 1948, **70**, 1191) who showed that cinnamic acid is nitrated mainly in the *ortho*- and *para*-positions at approximately the same rate as chlorobenzene, of Baker and Wilson (*J.*, 1927, 842) who found that only 2% of the *meta*-isomer was formed in the nitration of ω-nitrostyrene, and of Baker and Eccles (*J.*, 1927, 2125) who found only 3% of the *meta*-isomer in the nitration of methyl benzylidenemalonate, C_6H_5·CH:C$(CO_2Me)_2$. The introduction of further double bonds between the carbonyl group and the aromatic nucleus would be expected to obscure completely the deactivating effect of the carbonyl group and lead to an overall activating effect for the groups ·$[CH:CH]_2$·CO· and ·$[CH:CH]_3$·CO·. Accordingly, compounds containing the group C_6H_5·$[CH:CH]_2$·CO· are monosulphonated very rapidly, mainly in the *para*-position, and those containing the group C_6H_5·$[CH:CH]_3$·CO· are polysulphonated very rapidly in both the *ortho*- and *para*-positions. The only related compound that appears to have been studied previously from the point of view of aromatic substitution is methyl cinnamylidenemalonate, the nitration of which was shown by Baker and Eccles (*loc. cit.*) to yield less than 1% of the *meta*-isomer.

It was mentioned in Part XIV (*loc. cit.*) that one of the reasons for the early interest taken in the compounds we have been studying was their halochromism in sulphuric acid and other acids. This halochromism has been further studied recently by means of ultraviolet absorption spectra measurements by the present authors in collaboration with Dr. V. Gold and Dr. B. W. V. Hawes, and the results of this work will be reported later. The present work shows that the colour of these compounds in sulphuric acid cannot be attributed to any type of " complex " ionisation such as the ionisation of triphenylmethanol as a secondary base to give the coloured triphenylcarbonium ion : $CPh_3{\cdot}OH + 2H_2SO_4 = CPh_3^+ + H_3O^+ + 2HSO_4^-$, but is due simply to the protonation of the carbonyl group giving rise to an ion which is intensely coloured because of the possibility of resonance of a positive charge along a conjugated chain, *e.g.*,



In agreement with theory (cf. Maccoll, *Quart. Reviews*, 1947, **1**, 16) the colour of the sulphuric acid solutions of these substances changes from yellow to deep red, *i.e.*, the wave-length of the absorption maximum shifts to longer wave-lengths, as the length of the conjugated chain is increased, *e.g.*, in the series Ph·COMe, Ph·CH:CH·COMe,

$Ph{\cdot}[CH{:}CH]_2{\cdot}COMe$. Finally, it may be concluded that the conflicting spectroscopic results obtained by the many early workers on the halochromism of these compounds were due largely to their failure to recognise the occurrence in many cases of rapid sulphonation in sulphuric acid solution.

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