JOURNAL
OF
THE CHEMICAL SOCIETY

Solutions in Sulphuric Acid. Part XIV. Cryoscopic Measurements on Some Unsaturated Aromatic Ketones and Aldehydes.*

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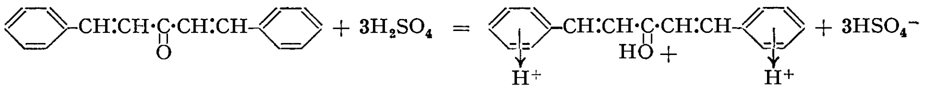
[Reprint Order No. 4371.]

The behaviour of fourteen unsaturated aromatic ketones and aldehydes in solution in sulphuric acid has been studied by the cryoscopic method. It is concluded that all these substances behave as bases, addition of a proton taking place on the carbonyl group, and that many of them also undergo aromatic sulphonation, in some cases exceedingly rapidly.

AROMATIC aldehydes and ketones generally behave as simple bases in sulphuric acid, but otherwise undergo no change (Part I, *J.*, 1950, 2473; Hantzsch, *Z. physikal. Chem.*, 1907, **61**, 257; 1908, **65**, 41; Oddo and Casalino, *Gazzetta*, 1917, **47**, II, 200). Investigations of certain unsaturated ketones appeared, however, to indicate a different behaviour. Thus Hantzsch (*Ber.*, 1922, **55**, 953) obtained an *i*-value of 4 for dibenzylideneacetone, which he suggested was due to the following ionisation: $(Ph\cdot CH{:}CH)_2CO + 3H_2SO_4 = (Ph\cdot CH{:}CH)_2\overset{+}{C}\cdot SO_3H + H_3O^+ + 2HSO_4^-$. Later, Hammett and Deyrup (*J. Amer. Chem. Soc.*, 1933, **55**, 1900) found that cinnamylideneacetophenone appeared to behave similarly, producing a 4-fold freezing-point depression, whereas benzylideneacetophenone was found to behave as a simple base having an *i* factor of 2. Both substances were stated to be recoverable on dilution. These authors did not comment on the nature of the ionisation which produced the 4-fold freezing-point depression, but Hammett (" Physical Organic Chemistry," McGraw-Hill, New York, 1940, p. 62) subsequently observed that " these substances ionise in a more complicated fashion." Another theory has been advanced more recently by Dewar (" Electronic Theory of Organic Chemistry," O.U.P., 1949, p. 170) to explain the 4-fold depression of the freezing point given by dibenzylideneacetone. He suggested that one proton is attached to the carbonyl oxygen atom and that two more are held by π-bonds to the benzene rings.



Compounds of this type have also attracted attention for many years for another reason: their sulphuric acid solutions are generally intensely coloured. Various coloured compounds with other acids, such as perchloric acid (Pfeiffer, *Annalen*, 1916, **412**, 253), and with stannic chloride (*idem, ibid.*, 1911, **383**, 92) have actually been isolated. In addition, the absorption spectra of a number of these compounds in sulphuric acid have also been studied (Hantzsch, *loc. cit.*; Claisen and Pondorf, *Annalen*, 1884, **223**, 142; Baeyer and Villiger, *Ber.*, 1902, **35**, 3013; Baker, *J.*, 1907, **91**, 1945; Baly, Collie, and Watson, *J.*, 1909, **95**, 144; Stobbe and Haertel, *Annalen*, 1909, **370**, 99; Kehrmann, *Ber.*, 1921, **54**, 417). The results of such investigations were ambiguous and conflicting, and different interpretations were put upon them: *e.g.*, Vorländer (*Ber.*, 1903, **36**, 1470, 3528) believed that the colours were due to the interaction of the double bonds with the acid, whereas

* Part XIII, *J.*, 1953, 964.

Hantzsch (*loc. cit.*) and Pfeiffer (*loc. cit.*) considered that only the carbonyl oxygen was involved, and Kehrmann (*loc. cit.*) considered both to be necessary in order to explain the results.

In the present work the freezing-point depression produced by a variety of unsaturated aromatic ketones and aldehydes has been investigated.

EXPERIMENTAL

Apparatus and Procedure.—The apparatus used for making the cryoscopic experiments was very similar to that described in Part I (*J.*, 1950, 2473), except that the platinum resistance thermometer was replaced by a mercury thermometer which in the early experiments was a Beckmann thermometer, but which for most of the work was an N.P.L.-calibrated " Hortvet " solid-stem mercury thermometer. This was graduated in 0·01° and covered the range 5—13°. It could be read to ± 0·001° with a cathetometer. A stem correction was applied which was usually close to −0·018°. Beckmann thermometers were found to be quite unsuitable for the present work as their setting changes slowly with time, owing to distillation of mercury from the reservoir to the column or *vice versa* (cf. Thompson and Ubbelohde, *Trans. Faraday Soc.*, 1950, **46**, 349), and it was necessary in many cases to follow changes in the freezing-point depression of a given solution over periods of hours or days.

The technique of making the freezing-point measurements was essentially the same as that described in Part I (*loc. cit.*). The really accurate measurement of the freezing-point depression was often not possible owing to its rapid variation with time. Moreover, it was not desired to measure the exact degree of ionisation of all the compounds studied, but rather to establish general modes of ionisation. It was therefore considered satisfactory to use as the solvent sulphuric acid containing a small amount of water or potassium sulphate to repress the autoprotolysis, and to express the results in terms of the van't Hoff *i*-factor, which is defined by the equation $i = \Delta\theta/\Delta m k_f$, where $\Delta\theta$ is the change in the freezing-point depression caused by a small change Δm in the molality of the solute, and k_f is the cryoscopic constant. The value of k_f was taken as 5·98 deg. mole^{-1} kg. (Part I, *loc. cit.*). This is justifiable because the *i*-factor approximates sufficiently closely to the more precise ν-value (Part I, *loc. cit.*) for our present purpose over the range of solute concentrations that we used.

In studying many of our compounds it was necessary to follow changes in the freezing point of their sulphuric acid solutions over long periods. In such cases the solutions were kept at a constant temperature, usually 25°, between measurements of the freezing point by keeping the cryoscope in a suitable thermostat. It was essential to do this in order to be able to decide when reactions had gone very nearly to completion, and in order to be able to distinguish simultaneous and consecutive reactions that often occurred with considerably different speeds.

Materials.—*Cinnamaldehyde.* The commercial product was washed with sodium carbonate solution, dried ($MgSO_4$), and distilled *in vacuo*; liquid boiling over a 1° range was collected and used immediately.

4-*Benzoyldiphenyl.* A sample kindly supplied by Dr. R. P. Alvarez-Ossorio was recrystallised twice from ethyl alcohol and once from light petroleum (b. p. 60—80°); it had m. p. 102°.

A number of unsaturated ketones were prepared by reactions of the aldol type. The methods used may be divided into two classes: the recent methods of " Organic Syntheses," which employ carefully controlled conditions and high alkali concentrations, and the older German methods in which long periods of reaction and low alkali concentrations are used. We found the latter type of method to be the more reliable and certain.

Benzylideneacetone was prepared by Drake and Allen's method (" Organic Syntheses," Coll. Vol. 1, 2nd Edn., p. 77) from benzaldehyde and acetone, sodium hydroxide being used as catalyst. The final purification was carried out by low-temperature recrystallisation from acetone, instead of by fractionation at reduced pressure. The dried solid (over P_2O_5) had m. p. 41—42°.

Benzylideneacetophenone was prepared by Kohler and Chadwell's method (*op. cit.*, p. 78) from benzaldehyde and acetophenone, with sodium hydroxide as catalyst. Repeated attempts to follow this method gave oils, and difficulty was experienced in obtaining crystals from the oils. Final purification was by recrystallisation from alcohol; the product had m. p. 55·5—56·5°.

Dibenzylideneacetone was prepared from benzaldehyde and acetone with sodium hydroxide as catalyst (*op. cit.*, Coll. Vol. 2, p. 167). The product, after three crystallisations from ethyl acetate, had m. p. 111—111·5°. Benzylidenecinnamylideneacetone was prepared following Scholtz's method (*Ber.*, 1896, **29**, 614), cinnamylideneacetone and benzaldehyde being used with sodium hydroxide as catalyst. It was recrystallised three times from alcohol, and then had m. p. 105·5—106°. Cinnamylideneacetone was prepared by Diehl and Einhorn's method (*Ber.*, 1885, **18**, 2321). The crude material, purified by low-temperature recrystallisation from acetone, had m. p. 66—67°. Cinnamylideneacetophenone was prepared similarly to benzylideneacetophenone and recrystallised three times from 80% alcohol (saturated at 30° and cooled in ice); it had m. p. 99—100°. Dicinnamylideneacetone was prepared by Diehl and Einhorn's method (*loc. cit.*) from cinnamaldehyde and acetone. Recrystallised from alcohol and from ethyl acetate, it had m. p. 138—139·5°.

1 : 13-Diphenyltrideca-1 : 3 : 5 : 8 : 10 : 12-hexaen-7-one was prepared by Vorländer, Fischer, and Kunze's method (*Ber.*, 1925, **58**, 1288) from 5-phenylpentadienal, acetone, and sodium hydroxide. It was purified by three recrystallisatious from ethyl acetate and then had m. p. 188—189°. The necessary aldehyde was prepared from cinnamaldehyde and acetaldehyde, with piperidine as catalyst (Kuhn and Winterstein, *Helv. Chim. Acta*, 1928, **11**, 113); the yields were poor, and the aldehyde difficult to purify. It was used for the preparation of this and the following ketone immediately after distillation *in vacuo*.

1 : 11-*Diphenylundeca*-1 : 3 : 6 : 8 : 10-*pentaen*-5-*one* was prepared from cinnamylideneacetone and 5-phenylpentadienal, in a similar way to benzylidenecinnamylideneacetone. The compound was purified by two recrystallisations from ethyl acetate and one from alcohol and dried (P_2O_5); it had m. p. 143·5—144° (corr.) (Found: C, 87·8; H, 6·5. $C_{23}H_{20}O$ requires C, 88·4; H, 6·45%).

2 : 6-Dibenzylidene*cyclo*hexanone was prepared in a similar manner to dicinnamylideneacetone, and recrystallised from ethyl alcohol; it had m. p. 116—116·5°. Di-4-methylbenzylideneacetone was prepared in a similar manner to dicinnamylideneacetone and recrystallised from ethyl acetate–alcohol; it had m. p. 173·5—174·5°.

Di-4-*bromobenzylideneacetone* was prepared in a similar manner to dicinnamylideneacetone, and purified by five recrystallisations from ethyl acetate; the m. p. was 212—212·5° (corr.) (Found: C, 51·5; H, 3·0; Br, 39·8. $C_{17}H_{42}OBr_2$ requires C, 52·1; H, 3·1; Br, 40·8%).

RESULTS

The results of all the cryoscopic measurements are listed in Tables 1 (where m = molality) and 2. For the two compounds in Table 1, the *i*-factor was found to be independent of time, and so a number of successive additions of the solute could be made. For all the other solutes (Table 2) the *i*-factor increased with time and the results for these substances show the variation of *i* with time for a single addition of the solute. The time from the first determination of the freezing point, which was made as soon as possible after the dissolution of the solute was complete, is given in the first column. Col. 2 gives the freezing-point depression, and Col. 3 the *i*-factor.

TABLE 1.

Dicinnamylideneacetone,* (CHPh:CH·CH:CH)$_2$CO.

m	Δθ	i	m	Δθ	i
0·00279	0·097°	5·82	0·01655	0·594°	5·99
0·00642	0·231	6·01	0·01890	0·678	5·98
0·01227	0·435	5·92			

Di-4-bromobenzylideneacetone,† (Br·C$_6$H$_4$·CH:CH)$_2$CO.

m	Δθ	i	m	Δθ	i
0·01246	0·187°	2·10	0·0425	0·493°	1·95
0·0282	0·338	2·01			

* These measurements were carried out during 2 days. After a further day at room temperature, the final freezing-point depression had increased to 0·686°.

† These measurements were made during 27 hr. After a further 24 hr. at room temperatures, the final freezing-point depression had increased to 0·500°.

TABLE 2.

(Time is given throughout in hours unless denoted by d for days.)

Benzylideneacetophenone, CHPh:CH·COPh.

Molality of solute = 0·0252. Temp. 25° except where otherwise stated.

Time	Δθ	i	Time	Δθ	i	Time	Δθ	i	Time	Δθ	i
0·0	0·309°	2·04	4·5	0·409°	2·70	40·7	0·555°	3·67	135·1	0·555°	3·67
0·5	0·329	2·18	20·9	0·526	3·48	63·8	0·555	3·67	158·1 †	0·562	3·71
1·5	0·359	2·37	26·9	0·531	3·52	87·6	0·556	3·68	164·1 †	0·562	3·71
2·8	0·389	2·57	33·4	0·547	3·62						

† Temp. 35°.

TABLE 2. (*Continued.*)

Dibenzylideneacetone, $(\mathrm{CHPh{:}CH})_2\mathrm{CO}$.

Molality of solute = 0·0485. Temp. 25°.

Time	Δθ	*i*	Time	Δθ	*i*	Time	Δθ	*i*	Time	Δθ	*i*
0·0	0·771°	2·66	3·6	1·169°	4·02	60	1·466°	5·05	8·5 d	1·644°	5·66
0·33	0·982	3·38	19	1·303	4·49	3·5 d	1·530	5·27	17·5 d	1·683	5·80
1·0	1·098	3·78	27	1·345	4·63	5·5 d	1·587	5·46	23·5 d	1·695	5·83
2·0	1·143	3·94	44	1·424	4·90						

Benzylidenecinnamylideneacetone, $(\mathrm{CHPh{:}CH{\cdot}CH{:}CH})_2\mathrm{CO}$.

Molality of solute = 0·0402. Temp. 25°.

0·0	0·921°	3·83	1·1	1·147°	4·77	5·0	1·332°	5·50	26·2	1·407°	5·85
0·2	0·993	4·13	2·1	1·220	5·08	19·2	1·407	5·85	41·8	1·426	5·93
0·5	1·068	4·44	4·1	1·290	5·37						

1 : 11-Diphenylundeca-1 : 3 : 6 : 8 : 10-pentaen-5-one, $\mathrm{CHPh{:}CH{\cdot}[CH{:}CH]_2{\cdot}CO{\cdot}CH{:}CH{\cdot}CH{:}CHPh}$.

Molality of solute = 0·0155. Temp. 25°.

0·0	0·622°	6·71	1·0	0·712°	7·66	4·8	0·802°	8·63	24·8	0·906°	9·75
0·33	0·677	7·28	2·4	0·759	8·17	19·7	0·905	9·73			

1 : 13-Diphenyltrideca-1 : 3 : 5 : 8 : 10 : 12-hexaen-7-one, $\mathrm{CHPh{:}CH{\cdot}[CH{:}CH]_2{\cdot}CO{\cdot}[CH{:}CH]_2{\cdot}CH{:}CHPh}$.

Molality of solute = 0·00814. Temp. 25°.

0	0·316°	6·5	40·0	0·600°	12·3	3·5 d	0·653°	13·4	6·7 d	0·750°	14·5
1·0	0·413	8·3	62·5	0·625	12·8	4·5 d	0·670	13·8	11·4 d	0·745	15·3
16·5	0·534	11·0									

Cinnamylideneacetophenone, $\mathrm{CHPh{:}CH{\cdot}CH{:}CH{\cdot}COPh}$.

Molality of solute = 0·0228. Temp. 25°, except last entry (*) at 35°.

0 d	0·502°	3·68	1 d	0·523°	3·84	3 d	0·558°	4·09	5 d *	0·646°	4·73

Benzylideneacetone, $\mathrm{CHPh{:}CH{\cdot}COMe}$.

Molality of solute = 0·0292. Temp. <10°.

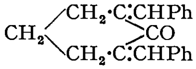
0 d	0·352°	2·02	2 d	0·556°	3·19	7 d	0·651°	3·74	9 d	0·683°	3·91
1 d	0·518	2·97	3 d	0·587	3·36	8 d	0·665	3·81			

Cinnamylideneacetone, $\mathrm{CHPh{:}CH{\cdot}CH{:}CH{\cdot}COMe}$.

Molality of solute = 0·00891. Temp. 25°.

0·0	0·175°	3·28	1·5	0·199°	3·74	3·75	0·219°	4·11	26·2	0·301°	5·65
0·5	0·187	3·51									

2 : 6-Dibenzylidene*cyclo*hexanone,



$$\mathrm{CH_2}\begin{array}{l}\diagup\,\mathrm{CH_2{\cdot}C{:}CHPh}\\ \qquad\qquad\quad >\mathrm{CO}\\ \diagdown\,\mathrm{CH_2{\cdot}C{:}CHPh}\end{array}$$

Molality of solute = 0·02004. Temp. 25°.

0·0	0·436°	3·64	2·2	0·557°	4·66	7·0	0·628°	5·24	26·0	0·660°	5·51
0·7	0·494	4·13	4·5	0·602	5·03	20·0	0·662	5·53	42·0	0·665	5·55

Di-4-methylbenzylideneacetone, $(\mathrm{C_6H_4Me{\cdot}CH{:}CH})_2\mathrm{CO}$.

Molality of solute = 0·02137. Temp. 25°, except last two entries (*) at 35°.

0·0	0·503°	3·94	2·0	0·685°	5·36	8·3	0·728°	5·70	41·0	0·733°	5·74
0·33	0·572	4·48	3·0	0·706	5·33	18·6	0·731	5·73	44·7 *	0·741	5·81
1·0	0·635	4·97	4·8	0·719	5·63	25·6	0·731	5·73	64·0 *	0·745	5·83

4-Benzoyldiphenyl, $\mathrm{Ph{\cdot}C_6H_4{\cdot}COPh}$.

Molality of solute = 0·01867. Temp. : room temp.

			0 d	0·410°	3·67	1 d	0·420°	3·76			

Cinnamaldehyde, $\mathrm{CHPh{:}CH{\cdot}CHO}$.

Molality of solute = 0·0524. Temp. : room temp. except entries (*) at 25°.

0 *	0·664°	2·12	3 d	1·406°	4·48	6 d	1·463°	4·67	10 d	1·495°	4·77
16 *	1·205	3·84	4 d	1·429	4·55						

DISCUSSION

Contrary to the observations of earlier workers, all the substances examined, except dicinnamylideneacetone and di-4-bromobenzylideneacetone, have been found to give freezing-point depressions in sulphuric acid which increase with time and in many cases only reach constant limiting values after a long period. The stable *i*-factor of 6 given by dicinnamylideneacetone shows at once that the theories of Hantzsch (*loc. cit.*) and Dewar (*loc. cit.*) are incorrect, as neither can account for an *i*-factor greater than 4. Moreover, neither of the theories can account for the relatively slow increase in the *i*-factor that occurs in most cases.

Protonation of alternate carbon atoms of the unsaturated chain, giving rise to a multiply charged carbonium ion :

$$Ph{\cdot}[CH{:}CH]_2{\cdot}CO{\cdot}[CH{:}CH]_2{\cdot}Ph + 5H_2SO_4 = 5HSO_4^- + Ph{\cdot}\overset{+}{C}H{\cdot}CH_2{\cdot}\overset{+}{C}H{\cdot}CH_2{\cdot}\overset{+}{C}(OH){\cdot}CH_2{\cdot}\overset{+}{C}H{\cdot}CH_2{\cdot}\overset{+}{C}HPh$$

would account for the *i*-factor of 6 given by dicinnamylideneacetone, but it is highly improbable that such a multiply charged carbonium ion would be stable, and in any case a similar explanation will not account for the very high *i*-factors given by $Ph{\cdot}[CH{:}CH]_3{\cdot}CO{\cdot}[CH{:}CH]_2{\cdot}Ph$ and $Ph{\cdot}[CH{:}CH]_3{\cdot}CO{\cdot}[CH{:}CH]_3{\cdot}Ph$. Some compounds such as mesitoic acid and triphenylmethanol undergo " complex " ionisation in sulphuric acid, giving rise to four or more particles, *e.g.*, $Me_3C_6H_2{\cdot}CO_2H + 2H_2SO_4 = Me_3C_6H_2{\cdot}\overset{+}{C}O + H_2\overset{+}{O} + 2HS\overset{-}{O}_4$ (Treffers and Hammett, *J. Amer. Chem. Soc.*, 1937, **59**, 1788), but it is extremely difficult to devise any reasonable type of complex ionisation (cf. Hantzsch, *loc. cit.*) that would account for the number of ions produced by all the compounds we have investigated.

It seems therefore that some reaction other than protonation or complex ionisation must be occurring. Addition of sulphuric acid to the double bonds might at first sight appear to be a possibility, but this would not produce ions, and would not, therefore, account for the high *i*-values. In addition, it would be expected to lead to the formation of colourless compounds, since this is known to occur with the halogen acids (Strauss, *Ber.*, 1904, **37**, 3277). Solutions kept for as long as 4 months in sealed tubes showed only a slight, if any, diminution in the intensity of their colour.

The remaining possibility appears to be sulphonation of the aromatic nuclei or the conjugated side-chains. The fact that di-4-bromobenzylideneacetone gives a stable two-fold depression of the freezing point and an orange-coloured solution supports the view that sulphonation in the other compounds occurs in the aromatic nucleus and that the colour produced is due simply to protonation on the carbonyl oxygen atom. We shall now show that the assumptions that protonation of the carbonyl group occurs in all cases, and that in many cases the aromatic nuclei are sulphonated, can be used to explain all the cryoscopic results.

It is first necessary to assess the effect on the *i*-factor of the sulphonation process, which can be represented as follows :

$$\overset{+}{X}\text{–}H + H_2SO_4 = \overset{+}{X}\text{–}SO_3H + H_2O$$

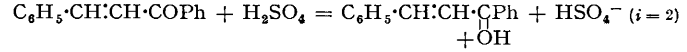
followed by

$$H_2O + H_2SO_4 = H_3\overset{+}{O} + HS\overset{-}{O}_4$$

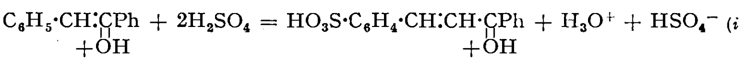
$$\overset{+}{X}\text{–}SO_3H + H_2SO_4 = \overset{+}{X}\text{–}SO_3\overset{+}{H}_2 + HS\overset{-}{O}_4$$

where $\overset{+}{X}\text{–}H$ is the conjugate acid of a carbonyl compound, H being a nuclear hydrogen atom. It may be seen that for each sulphonation process a molecule of water is produced. This will increase the number of particles per molecule of solute by a little less than 2 (Part II, *J.*, 1950, 2493), the exact value depending on the concentration of water and of hydrogen sulphate ion in the solution. In addition, sulphonic acids are in general slightly ionised (Part VII, *J.*, 1950, 2537), and this small basic ionisation may reasonably be considered to balance the incomplete ionisation of the water formed, so that each sulphonation process will produce approximately an extra 2 particles per solute molecule, and hence the *i*-factor of the solute will be increased by approximately 2.

Benzylideneacetophenone.—The variation of the *i*-factor with time at 25° is shown in Fig. 1 : the *i*-factor is initially 2 but slowly approaches a limiting value of 4. These results show that benzylideneacetophenone dissolves with simple protonation, but at 25° a monosulphonic acid is slowly formed, which is almost certainly, for reasons given in the following paper (Part XV), 4-sulphobenzylideneacetophenone :



$$C_6H_5\cdot CH{:}CH\cdot COPh + H_2SO_4 = C_6H_5\cdot CH{:}CH\cdot \underset{\underset{+OH}{\|}}{C}Ph + HSO_4^- \quad (i = 2)$$



$$C_6H_5\cdot CH{:}\underset{\underset{+OH}{\|}}{C}Ph + 2H_2SO_4 = HO_3S\cdot C_6H_4\cdot CH{:}CH\cdot \underset{\underset{+OH}{\|}}{C}Ph + H_3O^+ + HSO_4^- \quad (i = 4)$$

Dibenzylideneacetone.—The variation of i with time at 25° is shown in Fig. 2. Curve A shows that a limiting i factor close to 6 is slowly reached. For curve B the time scale has been expanded to show that the reaction is in two stages, the first fast and the second relatively slow. Evidently a monosulphonic acid is formed quickly and this reacts slowly to form a disulphonic acid. The first product has been shown (Part XV, following paper) to be 4-sulphodibenzylideneacetone, and the final product is almost certainly di-4-sulphobenzylideneacetone.

Benzylidenecinnamylideneacetone.—The variation of i with time at 25° is shown in Fig. 3. It seems clear that this ketone is monosulphonated very quickly, that is in the time taken to dissolve it at a temperature of 10°, which was approximately 30 min., and that the subsequent variation of i with time corresponds to the entry of a second sulphonic acid group. The first product is considered to be benzylidene-4-sulphocinnamylideneacetone, and the second, 4-sulphobenzylidene-4-sulphocinnamylideneacetone.

FIG. 1. *Benzylideneacetophenone.*

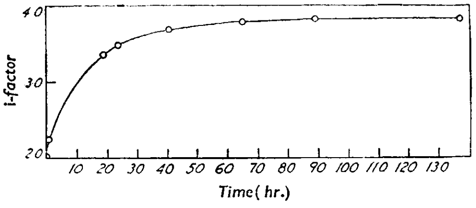


FIG. 2. *Dibenzylideneacetone.*

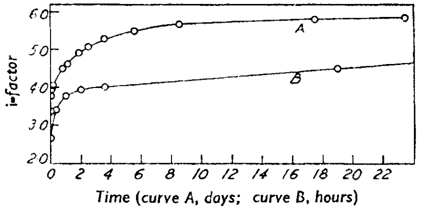
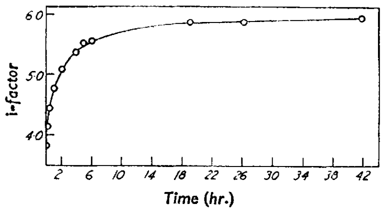


FIG. 3. *Benzylidenecinnamylideneacetone.*



Dicinnamylideneacetone.—This substance has a constant i factor of 6. A disulphonated product is produced in the time taken to dissolve the compound at room temperature. This has been shown to be di-4-sulphocinnamylideneacetone (Part XV, following paper).

1 : 11-*Diphenylundeca*-1 : 3 : 6 : 8 : 10-*pentaen*-5-*one* *and* 1 : 13-*Diphenyltrideca*-1 : 3 : 5 : 8 : 10 : 12-*hexaen*-7-*one.*—The initial behaviour of these substances is similar to that of the previous compound in that a disulphonic acid is formed immediately on dissolution. However, their i-values continue to increase and limiting values are somewhat more difficult to fix definitely than with the other compounds we have considered. It appears that reactions other than sulphonation, such as oxidation, are faster with these compounds than with the simpler ketones. Nevertheless, limits of approximately 10 and 14 respectively may be discerned. The i-factor of 10 corresponds to a tetrasulphonic acid which may plausibly be assigned the structure 1-(4-sulphophenyl)-11-(2 : 4 : 6-trisulphophenyl)undeca-1 : 3 : 6 : 8 : 10-pentaen-5-one. The i-factor of 14 corresponds to a hexasulphonic acid, which may be 1 : 13-di-(2 : 4 : 6-sulphophenyl)-trideca-1 : 3 : 5 : 8 : 10 : 12-hexaen-7-one.

Cinnamylideneacetophenone.—The results show that a monosulphonic acid is formed rapidly at 25°. This compound has been shown to be 4-sulphocinnamylideneacetophenone (Part XV, following paper). On continued storage at 35° the *i*-factor continues to increase, which may indicate further sulphonation.

Benzylideneacetone.—This substance gives initially a two-fold depression of the freezing-point. Because the solution was not kept at a constant temperature the assignment of an accurate limiting value of *i* is not possible. Nevertheless, the value of 3·9 attained after 8 days at a temperature of less than 10° is probably close to a limit. The compound 4-sulphobenzylideneacetone is probably formed.

Cinnamylideneacetone.—It seems likely that this compound forms a monosulphonic acid rapidly. The continued relatively rapid increase of the value of the *i*-factor above 4 is, however, rather surprising in view of the fact that the *i*-factor of cinnamylideneacetophenone only reaches a value appreciably greater than 4 during a long period at 35°.

2 : 6-*Dibenzylidene*cyclo*hexanone.*—The interpretation of the results for this compound is similar to that of dibenzylideneacetone, except that both sulphonations are faster than the corresponding processes in dibenzylideneacetone. The final limiting *i* value of 5·5 is, however, rather low and no explanation for this can be offered.

Di-4-*methylbenzylideneacetone.*—The behaviour of this substance is again similar to that of dibenzylideneacetone, but again the sulphonation rate is greater. In this case the sulphonic acid groups cannot enter the 4-positions, since these are already occupied. There is no evidence whether they enter the 2- or the 3-position.

Di-4-*bromobenzylideneacetone.*—The constant *i*-factor of 2 obtained for this compound indicates that it is protonated but not sulphonated.

4-*Benzoyldiphenyl.*—It is interesting that this compound behaves similarly to cinnamylideneacetophenone, a stable monosulphonic acid being formed rapidly. The activating effect of the phenylene group is apparently very similar to that of the butadiene group for aromatic sulphonation.

Cinnamaldehyde.—The results suggest the slow formation of a monosulphonic acid.

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[*Received, June 9th*, 1953.]