Studies on the Sulphonation of Anthracene. Part 2.[1] Sulphonation in Acetic Acid and Related Solvents

By **John O. Morley**, Imperial Chemical Industries Limited, Organics Division, Grangemouth, Stirlingshire, Scotland

The sulphonation of anthracene with either sulphuric acid and acetyl chloride or chlorosulphuric acid and acetic acid gives anthracene-1- and -2-sulphonic acids, a mixture of anthracenedisulphonic acids, and smaller amounts of 9-chloroanthracene and its monosulphonic acids. The proportion of the 2-sulphonic acid and the disulphonic acids formed increases with increasing temperature. A related reaction with sulphuric acid and acetic anhydride gives the 1-, 2-, and 9-sulphonic acids along with a mixture of disulphonic acids. The nature of the sulphonating reagents involved in these reactions has been examined by ^1H n.m.r. spectroscopy.

ALTHOUGH the reaction of anthracene with either oleum or chlorosulphuric acid in acetic acid is known to produce a mixture of anthracene-1- and -2-sulphonic acids,[2,3] the ratio found at different temperatures, the proportion and isomer distribution of disulphonic acids present (if any), and the nature of the sulphonating species have not been resolved. Recently, it has been claimed that anthracene-1- and -9-sulphonic acids are formed from a related reaction at 0 °C with acetic anhydride and sulphuric acid.[4]

Products from the 4 h reactions of anthracene with chlorosulphuric acid and acetic acid (A), sulphuric acid and acetyl chloride (B), or sulphuric acid and acetic anhydride (C)

	Reaction A			Reaction B		Reaction C	
Product composition	30 °C	50 °C	100 °C (*)	30 °C	50 °C	30 °C	50 °C
Anthracene-1-sulphonic acid	23.0 g, 8.9%	118.8 g, 46.0%	78.5 g, 30.4%	18.3 g, 7.1%	112.9 g, 43.7%	65.5 g, 25.3%	83.2 g, 32.2%
Anthracene-2-sulphonic acid	7.6 g, 2.9%	36.4 g, 14.1%	53.0 g, 20.5%	4.91 g, 1.9%	39.1 g, 15.1%	22.8 g, 8.8%	26.1 g, 10.1%
Anthracene-9-sulphonic acid	Trace			Trace		21.3 g, 8.3%	Trace
Anthracene-1,5-disulphonic acid	4.1 g, 1.2%	18.2 g, 7.1%	23.7 g, 7.0%	1.42 g, 0.42%	19.3 g, 5.7%	24.9 g, 7.4%	41.4 g, 12.2%
Anthracene-1,8-disulphonic acid	5.4 g, 1.6%	21.0 g, 6.2%	24.7 g, 7.3%	1.39 g, 0.41%	20.0 g, 5.9%	29.9 g, 8.8%	52.4 g, 15.5%
Anthracene-1,6- and -1,7-disulphonic acids		10. 6g, 3.1%	19.6 g, 5.8%	0.78 g, 0.23%	13.2 g, 3.9%	19.9 g, 5.9%	27.6 g, 8.2%
Anthracene-2,6- and -2,7-disulphonic acids		Trace	6.8 g, 2.0%		Trace	Trace	5.1 g, 1.5%
9-Chloroanthracene	6.60 g, 3.2%	9.72 g, 4.6%		4.62 g, 2.2%	4.83 g, 2.3%		
Unchanged anthracene	137.6 g, 77.2%	8.28 g, 4.7%		149.4 g, 83.8%	18.2 g, 10.2%	38.4 g, 21.5%	
Ratio of 1-isomer to 2-isomer	3.1 : 1	3.3 : 1	1.5 : 1	3.7 : 1	2.9 : 1	2.9 : 1	3.2 : 1
Ratio of monosulphonic to disulphonic acids	4.2 : 1	3.6 : 1	2.3 : 1	8.5 : 1	4.0 : 1	1.9 : 1	1.1 : 1

* Approximately 6% of a mixture of 10-chloroanthracene-1- and -2-sulphonic acids was also detected by t.l.c. and n.m.r. analysis.

A reinvestigation has shown that the isomer distribution in both reactions is far more complex than the literature indicates. The reaction of anthracene with 2 mol. equiv. of chlorosulphuric acid in 6 mol. equiv. of acetic acid (reaction A) during 4 h at 30, 50, or 100 °C gives a mixture of anthracene-1-sulphonic acid, the 2-isomer, anthracene-1,5-disulphonic acid, a mixture of the 1,6- and 1,7-isomers, the 1,8-isomer, the 2,6- and 2,7-isomers, and 9-chloroanthracene. The conversions and yields are shown in the Table. The rate of reaction increases with increasing temperature and conversions range from 22.8% at 30 °C to complete conversion at 100 °C. Both the ratio of the 1-sulphonic acid to the 2-isomer and the ratio of monosulphonic acids to disulphonic acids decrease with increasing temperature. The ratio of the 1-isomer to the 2-isomer observed, therefore, is temperature dependent, as in the related sulphonations with chlorosulphuric acid in dioxan,[1] although the picture is complicated by the presence of substantial quantities of disulphonic acids especially at higher temperature, which are absent in the dioxan system. Traces of anthracene-9-sulphonic acid can be detected by t.l.c. in the reaction carried out at 30 °C though none is present at higher temperatures. Furthermore, small amounts of 10-chloroanthracene-1- and -2-sulphonic acids are observed at 100 °C although sulphonation is accompanied by degradation.

A related reaction between anthracene and 2 mol. equiv. of 100% sulphuric acid, 2 mol. equiv. of acetyl chloride, and 4 mol. equiv. of acetic acid (reaction B) during 4 h at either 30 or 50 °C gives similar results to those obtained with reaction A at the same temperatures

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[1] Part I, J. O. Morley, *J.C.S. Perkin II*, preceding paper.

[2] M. Battegay and P. Brandt, *Bull. Soc. chim. France*, 1923, **33**, 1667.

[3] G.P. 215,695/1911; U.S.S.R. Pat. 187,805/1966.

[4] H. Cerfontain, A. Koeberg-Telder, C. Ris, and C. Shenk, *J.C.S. Perkin II*, 1975, 966.

(Table). Thus, the yields and conversions obtained, the ratio of the 1-isomer to the 2-isomer, and the ratio of monosulphonic acids to disulphonic acids are reasonably consistent within both series of experiments, which implies that a similar sulphonating species is involved in both cases.

In contrast, a reaction between anthracene and 2 mol. equiv. of 100% sulphuric acid and 2 mol. equiv. each of acetic anhydride and acetic acid (reaction C) during 4 h at either 30 or 50 °C shows different characteristics (Table). Despite the presence of 2 mol. equiv. of mineral acid in each of the three systems examined, only in the last system are significant quantities of anthracene-9-sulphonic acid formed. At 50 °C, however, only traces of the 9-isomer were detected and here the ratio of the 1-isomer to the 2-isomer resembled that observed in reactions A and B. Furthermore, the relative rates of reaction, as assessed by the proportion of substrate consumed during 4 h at 30 °C, are different. Whereas 78.5% of the substrate is consumed in reaction C, only 22.8 and 16.2% conversions are observed in reactions A and B, respectively. Moreover, the ratio of monosulphonic to disulphonic acids formed in reaction C decreases with increasing temperature as in the other cases with the exception that almost equal proportions of both are present at 50 °C, in contrast to reactions A and B where the former are present in considerable excess over the latter.

DISCUSSION

The u.v.–visible spectrum of anthracene in chlorosulphuric acid [Figure 1(A)] shows absorptions at 440 and 680 nm which arise from the proton complex and the cation radical.[1] However, the spectrum in acetic acid shows only the presence of anthracene with its characteristic absorptions at 320—400 nm [Figure 1(B)]. The corresponding spectrum of anthracene in acetic acid–chlorosulphuric acid (mol. ratio 4 : 1) is similar to that observed in acetic acid alone; there is no absorption in the visible region. The spectrum observed in equimolar quantities of the organic and mineral acids shows few changes except that a broad absorption of very weak intensity now appears between 450 and 750 nm. A further increase in the molar proportion of the mineral acid in the solvent to give an acetic acid–chlorosulphuric acid ratio of 1 : 2, results in a spectrum [Figure 1(C)] which resembles that obtained in chlorosulphuric acid alone [Figure 1(A)]. Therefore, whereas an excess of chlorosulphuric acid generates both the proton complex and cation radical, neither of these species is present in detectable concentration in the sulphonating systems described here, especially at 30—50 °C, because of the three-fold excess of the organic acid. Thus, sulphonation is the major reaction which occurs in the acetic acid–mineral acid systems. Reactions at 100 °C, however, proceed with evolution of some sulphur dioxide, and it is probable that the cation radical is present to some extent in these systems though the u.v.–visible spectra have not been examined.

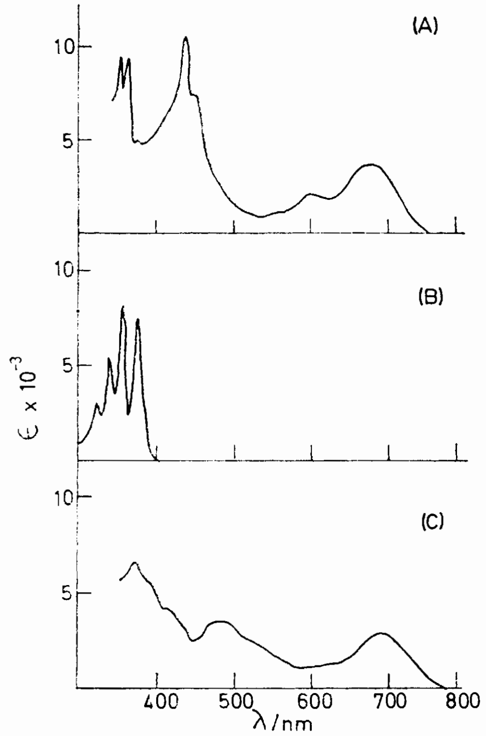

FIGURE 1 U.v.–visible spectra of anthracene: (A) in chlorosulphuric acid; (B) in acetic acid; (C) in acetic acid–chlorosulphuric acid (mol. ratio 1 : 2)

There seems little doubt that the reactions of either sulphuric acid with acetic anhydride or sulphur trioxide (or oleum) with acetic acid result in acetic sulphuric anhydride formation.[5-9] Indeed, recent Raman studies have shown that the equilibria (1)—(6) are established.[7]

$$n(\mathrm{MeCO})_2\mathrm{O} + \mathrm{H_2SO_4} \rightleftharpoons \mathrm{MeCO_2SO_3^-} + \mathrm{MeCO_2H_2^+} + n - 1(\mathrm{MeCO})_2\mathrm{O} \quad (1)$$

$$\mathrm{MeCO_2SO_3^-} + 2\mathrm{MeCO_2H_2^+} + \mathrm{H_2SO_4} \rightleftharpoons 3\mathrm{MeCO_2H_2^+} + \mathrm{S_2O_7^{2-}} \quad (2)$$

$$\mathrm{MeCO_2SO_3^-} + \mathrm{H_2SO_4} \rightleftharpoons \mathrm{MeCO_2H_2^+} + \mathrm{S_2O_7^{2-}} \quad (3)$$

$$\mathrm{S_2O_7^{2-}} + \mathrm{H_2SO_4} \rightleftharpoons \mathrm{HS_2O_7^-} + \mathrm{HSO_4^-} \quad (4)$$

$$2\mathrm{MeCO_2H} + \mathrm{SO_3} \rightleftharpoons \mathrm{MeCO_2SO_3^-} + \mathrm{MeCO_2H_2^+} \quad (5)$$

$$\mathrm{MeCO_2SO_3^-} + \mathrm{H_2S_2O_7} \rightleftharpoons \mathrm{MeCO_2S_2O_6^-} + \mathrm{H_2SO_4} \rightleftharpoons \mathrm{MeCO^+} + \mathrm{HS_2O_7^-} + \mathrm{HSO_4^-} \quad (6)$$

However, under the conditions of sulphonation described here where equimolar ratios of acetic anhydride and

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[5] A. J. Van Peski, *Rec. Trav. chim.*, 1921, **50**, 103; L. J. Tanghe and R. J. Brewer, *Analyt. Chem.*, 1968, **40**(2), 350.

[6] J. Russell and A. E. Camerson, *J. Amer. Chem. Soc.*, 1938, **60**, 1345; S. J. Benkovic and R. C. Hevey, *ibid.*, 1970, **92**, 4971.

[7] A. Casadevall, A. Commeyras, P. Paillons, and H. Collet, *Bull. Soc. chim. France*, 1970, **5**(2), 719.

[8] A. Casadevall and A. Commeyras, *Bull. Soc. chim. France*, 1970, **5**(2), 1850.

[9] E. A. Jeffrey and D. P. N. Satchell, *J. Chem. Soc.*, 1962, **1887**, 1913.

sulphuric acid have been employed only sequence (1) occurs; at higher sulphuric acid to acetic anhydride ratios the equilibria shown in equations (2)—(4) operate and result in the gradual removal of acetic sulphuric anhydride and the appearance of the hydrogen sulphate and disulphate anions. Solutions of sulphur trioxide or oleum in acetic acid also generate acetic sulphuric anhydride by the sequence shown in equation (5), but an excess of the inorganic reagents leads to the acylium ion shown in equation (6).[7,10]

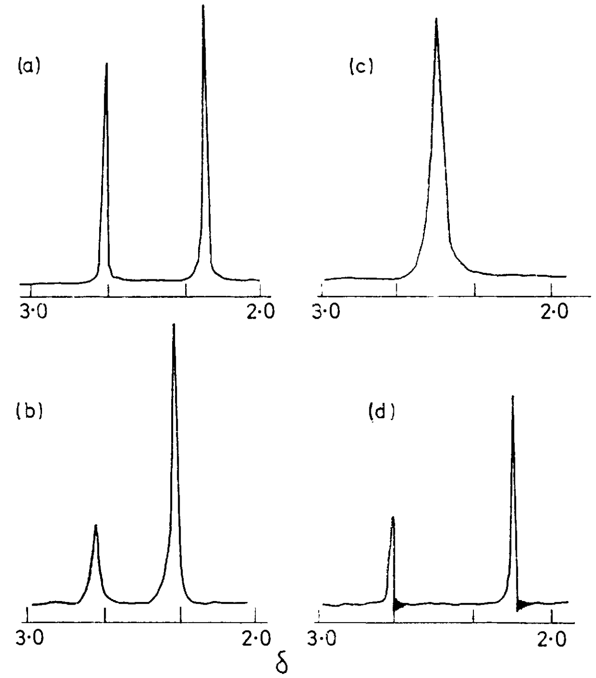

FIGURE 2 ^{1}H N.m.r. spectra of an equimolar mixture of acetyl chloride and acetic acid with added sulphuric acid: (a) 20%; (b) 40%; (c) 100%; (d) 100% sulphuric acid with a large excess of dioxan

The related reactions of acetyl chloride with sulphuric acid and acetic acid with chlorosulphuric acid have received less attention, though it has been claimed that 1 : 1 addition compounds are formed between the reagents, mainly on the basis of the Raman spectrum of the related benzoyl chloride–sulphuric acid system.[11] N.m.r. studies have shown, however, that chlorosulphuric acid initially reacts with acetic acid to generate acetyl chloride [equation (7)]. Furthermore, an examination

$$\mathrm{ClSO_3H + MeCO_2H \rightleftharpoons MeCOCl + H_2SO_4} \quad (7)$$

of mixtures of acetyl chloride with 100% sulphuric acid in acetic acid has demonstrated that part of the acetyl chloride reacts irreversibly with the mineral acid at 20 °C. For example, the slow addition of 1 mol. equiv. of 100% sulphuric acid to equimolar amounts of both acetyl chloride and acetic acid results in gradual disappearance of the acetyl chloride resonance at δ 2.65 and the appearance of a broad absorption at δ 2.45 [Figure 2 (a—d)]. The addition of a large excess of dioxan to the ' titrated ' acetyl chloride solution [Figure 2(c)], results in the re-appearance of only *ca.* 66% of the original intensity of the acetyl chloride resonance [Figure 2(d)]. A related reaction with 100% sulphuric acid and equimolar amounts of acetyl chloride and dioxan shows a number of interesting features [Figure 3(a—c)]. The acetyl chloride resonance is gradually reduced on addition of acid to the system as before with concomitant formation of a new species, δ 2.45 [Figure 3(b and c)], similar to that observed in acetic acid [Figure 2(c)]. Addition of a large excess of dioxan results in the regeneration of *ca.* 66% of the acetyl chloride consumed as before and leaves a single resonance at δ 2.1 attributable to acetic sulphuric anhydride since no acetic acid is present in this system [Figure 2(d)]. These observations suggest that acetyl chloride is a stronger base than dioxan and accepts most of the available protons when equimolar quantities of both are present, but loses them in the presence of a large excess of dioxan.

When an equimolar mixture of acetyl chloride and sulphuric acid alone is heated at 85 °C during 5 h, *ca.* 85% of the theoretical quantity of chlorine present in the system is evolved as hydrogen chloride and an n.m.r. analysis of the mixture in deuterium oxide shows

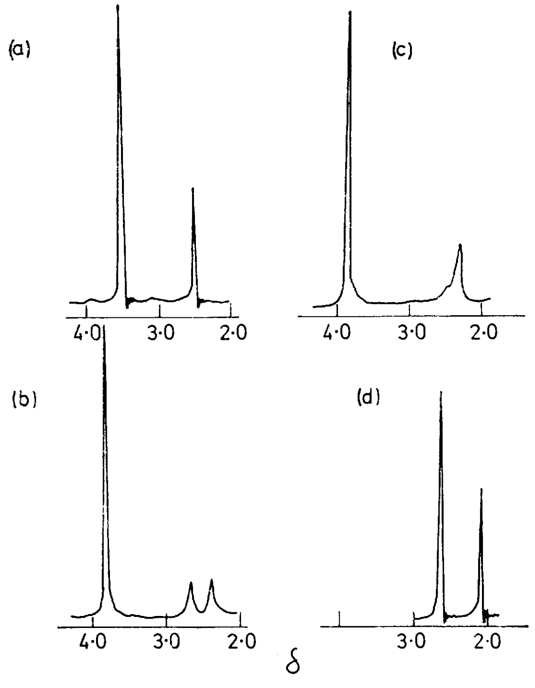

FIGURE 3 ^{1}H N.m.r. spectra of an equimolar mixture of acetyl chloride and dioxan with added sulphuric acid: (a) none; (b) 50%; (c) 100%; (d) 100% sulphuric acid with a large excess of dioxan

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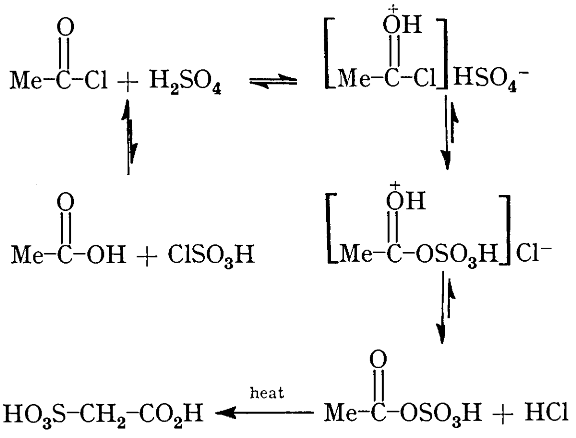
[10] A. Commeyras and G. A. Olah, *J. Amer. Chem. Soc.*, 1969, **91**, 2929; N. C. Deno, C. H. Pittman, and M. J. Wisotsky, *ibid.*, 1964, **86**, 4370.

[11] F. Carré and R. Corriu, *Bull. Soc. chim. France*, 1967, 2898; F. Carré, R. Corriu, and G. Dabosi, *ibid.*, p. 2905.

a resonance due to acetic sulphuric anhydride at δ 4.1 (60% yield based on the original amount of acetyl chloride present). The results from the thermal reaction, therefore, confirm those described previously.[5,11]

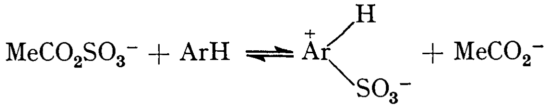
As a result of these studies it is probable that the sequences shown in the Scheme occur during the reaction of acetyl chloride with sulphuric acid or of acetic acid with chlorosulphuric acid. The downfield shift of the resonance of the methyl protons of acetic acid (Figure 2) and the methylene protons of dioxan (Figure 3) during the addition of sulphuric acid to acetyl chloride is probably due to protonation of each solvent either by the acetic sulphuric anhydride formed [in a similar way to that shown in equations (1) and (5)] or by the hydrogen chloride liberated. The addition of a large excess of dioxan to each system results in deprotonation of the acetyl chloride–sulphuric acid complex and the regeneration of all the original species except that proportion which has already formed acetic sulphuric anhydride and hydrogen chloride.



SCHEME

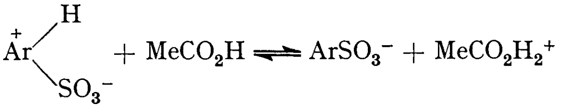
The effective sulphonating agent in all the systems described here is probably acetic sulphuric anhydride. The proportions present initially in reaction mixtures A, B, and C, however, are different. In reaction C, acetic sulphuric anhydride formation is virtually complete on mixing the reagents [see equation (1)], and thus, the sulphonation of anthracene at 30 °C is rapid with a high conversion into products and a low ratio of mono- to di-sulphonic acids due to the excess of sulphonating agent in the system. In reactions A and B, acetic sulphuric anhydride is gradually formed as the reaction proceeds and sulphonation is relatively slow. Both reactions result, therefore, in low anthracene conversions and a higher ratio of mono- to di-sulphonic acids than that observed in reaction C.

The presence of significant amounts of anthracene-9-sulphonic acid in the products from reaction C at 30 °C as compared with the traces formed in reactions A and B show that there are important differences amongst the reactions. Since acetic sulphuric anhydride formation is complete in reaction C it is suggested that sulphonation proceeds by the reaction of anthracene with the *O*-acetylsulphate anion and results in the displacement of the acetate anion to generate a σ-complex similar to that proposed for the dioxan–chlorosulphuric acid system,[1] *i.e.* equations (7)—(9). The formation of the 9-sulphonic acid by proton transfer from the σ-complex may be the rate controlling step, as in the related aprotic sulphonation.[4,12] It follows, therefore, that the rate of desulphonation will be expected to be related to, and increase with, the acidity of the solvent. Both the acetyl chloride–sulphuric acid and the acetic acid–chlorosulphuric acid system generate up to 1 mol. equiv. each of acetic sulphuric anhydride and hydrogen chloride. The acidity of these systems is likely to be greater than that of the acetic anhydride–sulphuric acid system since a maximum of 1 mol. equiv. of acetic sulphuric anhydride is generated here. As a result, the proportion of 9-sulphonic acid present in reactions A and B would be expected to be small because of the increased rate of the desulphonation reaction. The isomerisation of the 9-sulphonic acid into the 1- and 2-isomers probably occurs *via* desulphonation and resulphonation in a similar way to that described previously.[1] It is apparent, however, that the rate of isomerisation increases considerably with temperature since little or no 9-sulphonic acid was detected in any of the reactions at 50 °C after 4 h.



$$\mathrm{MeCO_2SO_3^-} + \mathrm{ArH} \rightleftharpoons \overset{+}{\mathrm{Ar}}{<}^{\mathrm{H}}_{\mathrm{SO_3^-}} + \mathrm{MeCO_2^-} \qquad (7)$$

$$\mathrm{MeCO_2^-} + \mathrm{MeCO_2H_2^+} \rightleftharpoons 2\mathrm{MeCO_2H} \qquad (8)$$



$$\overset{+}{\mathrm{Ar}}{<}^{\mathrm{H}}_{\mathrm{SO_3^-}} + \mathrm{MeCO_2H} \rightleftharpoons \mathrm{ArSO_3^-} + \mathrm{MeCO_2H_2^+} \qquad (9)$$

EXPERIMENTAL

General purpose reagents were used throughout. I.r. spectra (potassium bromide discs) and u.v. spectra were recorded with Perkin-Elmer 457 and 124 spectrophotometers, respectively. N.m.r. spectra were recorded with a Perkin-Elmer R32 instrument operating at 90 MHz and mass spectra with an A.E.I. MS9 instrument. Authentic samples of anthracene mono- and di-sulphonic acids, 9-chloroanthracene, and its monosulphonic acids were provided by I.C.I. Ltd. Products were analysed by t.l.c. and n.m.r. spectroscopy as described previously.[1]

Reactions of Anthracene.—(a) *With chlorosulphuric acid in acetic acid.* Chlorosulphuric acid (233 g, 2 mol) was slowly added to glacial acetic acid (360 g, 6 mol) maintained below 25 °C during the addition (ice-bath). The solution was heated to the appropriate temperature, and anthracene (178 g, 1 mol) was added. After 4 h the mixture was added to an equal volume of warm water, and the resulting suspension was heated to boiling. The precipitate was filtered off and washed thoroughly with hot water until the filtrates were free from acid, then dried, and the filtrates

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[12] A. Koeberg-Telder and H. Cerfontain, *Rec. Trav. chim.* 1972, **91**, 22.

and washings were combined; both were analysed by standard procedures.[1] The results are shown in the Table.

(b) *With sulphuric acid and acetyl chloride in acetic acid.* 100% Sulphuric acid (196 g, 2 mol) was slowly added to a mixture of acetyl chloride (157 g, 2 mol) and glacial acetic acid (240 g, 4 mol) maintained below 25 °C during the addition (ice-bath). The solution was heated to the appropriate temperature, anthracene (178 g, 1 mol) was added, and the mixture was treated as in method (a).

(c) *With sulphuric acid and acetic anhydride in acetic acid.* 100% Sulphuric acid (196 g, 2 mol) was slowly added to a mixture of acetic anhydride (204 g, 2 mol) and glacial acetic acid (120 g, 2 mol) maintained below 25 °C during the addition (ice-bath). The solution was heated to the appropriate temperature, anthracene (178 g, 1 mol) was added, and the mixture was treated as in method (a).

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