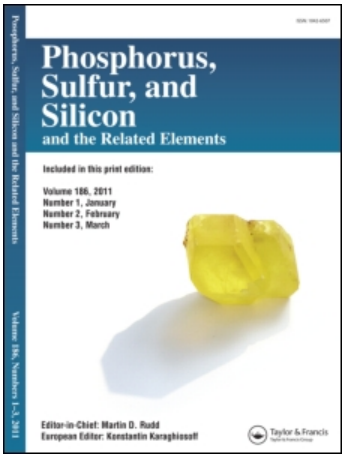

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SULFONATION OF 9-ALKYLANTHRACENES

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SULFONATION OF 9-ALKYLANTHRACENES

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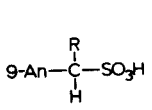
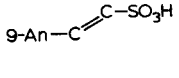
The reaction of anthracene, 9-phenylanthracene and some 9-alkylanthracenes with dioxan-SO_3 has been studied. Anthracene yields the 1-, 2- and 9-sulfonic acid in a ratio of 24 : 6 : 70. 9-Phenyl- and 9-neopentyl-anthracene both yield a mixture of the 4- and 10-sulfonic acids in a ratio of 33 : 67 and 15 : 85 respectively. Unexpectedly, 9-methylanthracene yields, in a more rapid reaction, exclusively 9-anthrylmethanesulfonic acid (1, R=H) 9-Alkylanthracenes of which the alkyl group contains at least one α-H yield as main product(s) the α-sulfonic acids 1 and/or (depending on the further structure of the alkyl group) the sulfonic acids 2-4.



1 R=H,Me,Et Pr,Bu,iBu



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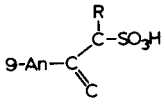
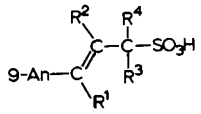


3 R=H,Me



4 $R^1=R^2=R^3=R^4=H$
$R^1=R^2=R^3=H$; $R^4=Me$
$R^1=R^2=R^3=H$; $R^4=Et$
$R^1=R^2=H$; $R^3=R^4=Me$
$R^1=R^3=R^4=H$; $R^2=Me$
$R^2=R^4=H$; $R^1+R^3=(CH_2)_3$

A mechanism for the formation of the sulfonic acids will be proposed. The formation of the unsaturated sulfonic acids proceeds via the corresponding 9-alkenylanthracenes which are formed from the 9-alkylanthracene and SO_3 in a redox reaction. Supporting evidence in favour of the mechanisms to be proposed comes from the sulfonation of behaviour of the 9-alkenyl-anthracenes proper, and of their benzene analogues.