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Cationic Polymerization of Various Isopropenyl Aromatic Monomers

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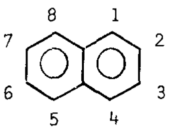
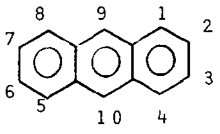
Summary

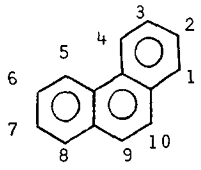
The preparations of 9-and 3-isopropenyl phenanthrene are reported. The cationic polymerization of various isopropenyl aromatic monomers is described. 2-isopropenyl naphthalene, 3-isopropenyl phenanthrene, 2-isopropenyl anthracene give low polymers ; 1-isopropenyl naphthalene, 9-isopropenyl phenanthrene, 1-isopropenyl anthracene give only dimers ; 9-isopropenyl anthracene does not polymerize. The results are discussed with respect to steric interferences.

Introduction

The numbering of the carbon atoms is given below :







Various studies relative to the cationic polymerization of vinyl naphthalenes, vinyl anthracenes and vinyl phenanthrenes have already been published by our group [BLIN et al., (1978)] , [BUNEL et al., (1975), (1978), in press] , [COUDANE et al., (1978) in press] .

The behaviour of the various monomers is as follows :

- 1-and 2-vinyl naphthalenes polymerize, 1-isopropenyl naphthalene only gives a dimer whose structure has been completely determined [BUNEL et al., in press] .
- 1-,2-and 9-vinyl anthracenes give low polymers [LAGUERRE (1974)].
- 9-isopropenyl anthracene does not polymerize cationically [COUDANE (1978)] and according to [STOLKA (1976)] neither do 1-and 2-isopropenyl anthracenes.
- 2-and 3-vinyl phenanthrenes give low polymers [BLIN et al., (1975)]

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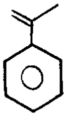
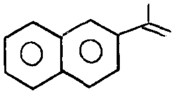
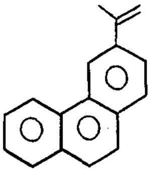
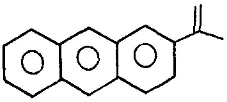
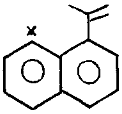
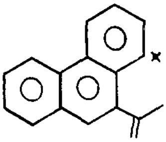
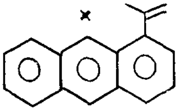
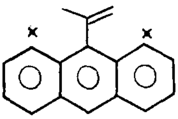
TABLE 1

	Isopropenyl benzene	High Polymer
	2-isopropenyl naphthalene	Low polymers or oligomers
	3-isopropenyl phenanthrene	
	2-isopropenyl anthracene	
	1-isopropenyl naphthalene	dimer (a) m.p. = 202°C
	9-isopropenyl phenanthrene	dimer (a) m.p. = 124°C
	1-isopropenyl anthracene	dimer (a) m.p. = 205°C
	9-isopropenyl anthracene	Monomer is unchanged

(a) the structure of the dimer which is cyclic in all cases is described in the two next articles (COUDANE, 1979).

In this work the behaviour of the following monomers in presence of $TiCl_4$ is examined : 2-isopropenyl naphthalene, 1,2- and 9-isopropenyl anthracenes, 3-and 9-isopropenyl phenanthrenes.

Experimental : Monomers

2-isopropenyl naphthalene was prepared by BUNEL's method (to be published), m.p. (°C) = 56.

1-and 2-isopropenyl anthracenes were prepared by STOLKA's method (1976) m.p. (°C) : 1(23) ; 2(153) and 9-isopropenyl anthracene according to COUDANE (1978) m.p. (°C) = 79.

3-isopropenyl phenanthrene was obtained by dehydratation of 3-phenanthryl propanol which was prepared by reaction of 3-bromophenanthryl magnesium bromide with propanone : m.p. (°C) 3-phenanthryl propanol = 95. Dehydratation of 3-phenanthryl propanol has been carried out by distillation catalysed by HSO_4K in vacuo (0.1 torr) (R = 60 %) m.p. (°C) : 3-isopropenyl phenanthrene = 30.

9-isopropenyl phenanthrene was obtained by dehydratation of 9-phenanthryl propanol which was prepared either by reacting 9-bromophenanthryl magnesium with propanone or 9-acetyl phenanthrene with iodomethyl magnesium. Dehydratation of 9-phenanthryl propanol has been carried out by distillation catalysed by HSO_4K in vacuo (0.1 torr) (R = 75 %) m.p. (°C) (9-isopropenyl phenanthrene) = 75.

Polymerizations

These were carried out under nitrogen in methylene chloride purified by NGUYEN ANK HUNG's technique (1970).

Results and Discussion

The results reported in table 1 have been obtained under the following conditions : $[M] = 0.1$ M, $[TiCl_4]$ in the range 0.01 to 0.2 M ; temperature - 72°C to 20°C ; contact time 2 hours.

Examination of table 1 shows that if there is at least one hydrogen in position "peri" of the vinyl group no polymerization takes place ; at the most a dimer is obtained (positions "peri" are starred in table 1). This is due to a steric interference between this hydrogen and the isopropenyl group. When there is only one hydrogen in position "peri" the isopropenyl group is no longer in the plane of the aromatic ring but the deconjugation is not complete. When there are two hydrogens interfering with the isopropenyl group, this group is almost perpendicular to the plane and the deconjugation is complete in that case, there is probably no cation formation. These assumptions are in agreement with the fact that 9 propenyl and 1 propenyl anthracenes which have no steric hindrance polymerize even though their reactivities (calculated by quantum chemistry) are below those of the monomers listed in table 1.

Moreover, all the vinyl monomers having the same structure as have the monomers listed in table 1 give polymers when they are reacted with $TiCl_4$.

Study of carbocations by ^{13}C NMR spectroscopy is now under way in our laboratory.

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