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Preferential Polysubstitution in Organic Soid State Reactions

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Preferential Polysubstitution in Organic Solid State Reactions

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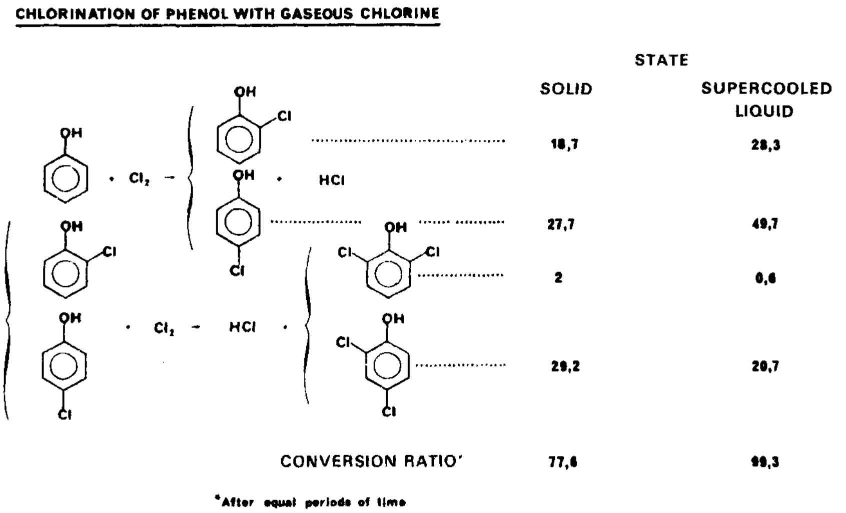
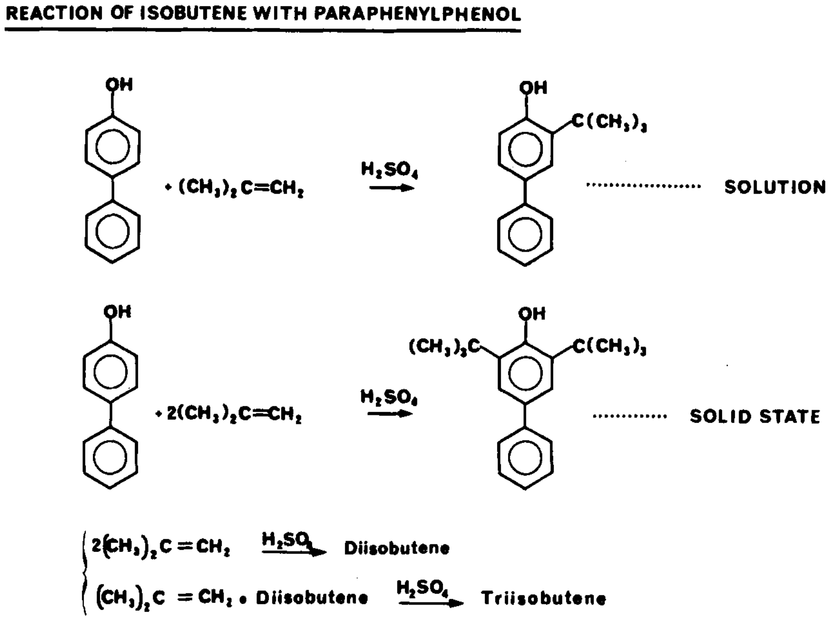
We have studied a number of reactions of chlorination and alkylation of phenols in a fluid phase and in the solid state. We show the predominance of the polysubstitution when phenols react in the solid state.

The first example examined is the chlorination of phenol (m.p. 41°C) with gaseous chlorine (Scheme 1).

For the solid state reactions, the temperature was 20°C. For the fluid state, the temperature was also 20°C, the phenol was supercooled.



Scheme 1



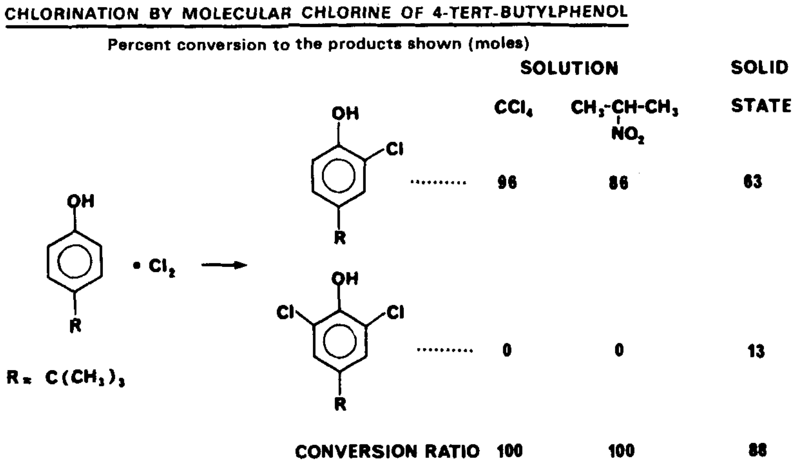
Scheme 2

In the solid state, the ratio of the number of moles of dichlorophenols found to the number of moles of monochlorophenols was 0.67. For the liquid state, the ratio was only 0.27. The total conversion was greater than in the solid state.

The second example is concerned with the reaction of isobutene with solid paraphenylphenol[1] (m.p. 165°C). Reactions are as follows (Scheme 2).

We have shown that, when two moles of isobutene are added to the phenol to give 2.6-di-tert-butyl-4-phenylphenol, two further moles of isobutene are simultaneously converted into diisobutene and triisobutene. It is worth remarking that, for a concentration of sulfuric acid of 1.1% by weight, one phenol only is formed: 2.6-di-tert-butyl-4-phenylphenol. There is no 2-tert-butyl-4-phenylphenol in this mixture, whereas this substance is obtained from the reaction of paraphenylphenol dissolved in 3.5-dimethylphenol.[2]

The last example investigated refers to chlorination by molecular chlorine of 4-tert-butylphenol (m.p. 100°C) in an apolar solvent, in a polar solvent, and in the solid state (Scheme 3). For the same temperature, after the reaction of one mole of chlorine with one mole of 4-tert-butylphenol in the solid state 2.6-dichloro-4-phenylphenol is obtained. There is practically no formation of 2.6-dichloro-4-tert-butylphenol in carbon tetrachloride and 2-nitro-



Scheme 3

propane. For an equivalent conversion, polychlorinated products are preferably formed in the solid state.

Can this greater polysubstitution for reagents in the solid state be explained? It is observed in the first place, that this phenomenon cannot be attributed to fact that the phenol is diluted or to the influence of solvents. In fact, the phenol is in a condensed state in both cases investigated. Moreover, no solvent was used. We believe that, in the case of solid state reactions, the predominance of polysubstitution can be accounted for by the fact that this state is ordered. Under these circumstances, the reaction products formed first do not diffuse in the medium and they remain in an activated state or stay in a more easily accessible site. In the liquid state, or with solvents, the products formed first can diffuse away and are deactivated.†

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2. R. W. G. Preston, *Brit. pat.*, 933022, 1960.

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† Diffusion alone may not be a sufficient explanation. If no diffusion occurs the percentage of the polysubstituted reaction products, can increase only when the reaction products formed first are in an activated state that is to say in an energy state higher than the ground state. If diffusion occurs the reaction products are deactivated by collisions with the other molecules. We can also say that in the solid state the reaction products formed first are in direct contact with gas whereas in solution the reaction products are surrounded by a great number of reagent and solvent molecules.