Polymerization of Terpenes

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Polymerization of terpene hydrocarbons by means of the metallic halide catalysts has been reported by a number of workers. Aluminum chloride has been used in the presence of aromatics by Thomas,[1] who states that there results a resinous reaction product with the alkylbenzene used. On the other hand,[2] numerous researches have failed to state that the solvent used enters into the reaction, and have described the resulting products as being polymers of the terpene used, indicating by analysis the exclusion of solvent as part of the resulting polymer. Since unsaturated hydrocarbons undergoing polymerization do so with great rapidity, it would be unusual if aromatic entry could be accomplished. The present workers are familiar with the experimental work above,[1] and believe that very definite conclusions were derived from inconclusive evidence. The direct line of attack on the problem was to repeat the reported work, and account for the material on a quantitative basis and note the distribution of the aromatics used in the reactions. Results were found by following the described technique and are conclusively tabulated for the first time.

Experimental

Materials.—Pinene was prepared by the repeated fractionation of a good grade of turpentine over metallic sodium. The final cut had a boiling point of 156–159°, and specific gravity of 0.862 at 15°. Toluene, benzene, xylene and hexane were commercial narrow range cuts termed 2, 2, 5, and 5° cuts, respectively. Baker C. P. aluminum chloride was used.

Method.—The pinene and aromatic used were weighed carefully into a 500-cc. round-bottomed flask fitted with agitator and thermometer. The mixture was cooled to 10° in an ice-bath, and the specified weight of catalyst added in small portions, keeping the temperature below 15°. One hour was required for the addition; nine hours more was allowed to complete the reaction. Neutralization was completed by the addition of 20 cc. of concentrated aqueous ammonia to the mixture with stirring. Re-weighing at this step usually showed a loss of less than 1 g. Without filtration, the mixture was carefully fractionated to a liquid temperature of 210°, and steam blown through the polymer residue to remove unchanged pinene, aromatic and high boiling oils. Deduction of catalyst weight from the weight of the residue in the flask gave the yield of hard resinous polymer.

The distillate was separated into two layers in a funnel, and the water discarded. Fractionation of this dry material gave the reported yields of unchanged terpene and recovered aromatic. The residue remaining after this step was reported as oily polymer. The aromatic chosen, the terpene used, and the grade of hexane had boiling points sufficiently different to allow of close separation.

TABLE I

EXPERIMENTAL RESULTS

One mole of terpene was used in all experiments, except that using cedarwood oil. One mole of toluene is 92 g.; xylene, 106 g.; benzene and hexane were used in such weights as to provide equal volumes of reaction mixture.

Aromatic, g.	Terpene, g.	$AlCl_3$, g.	Aromatic recovered, %	Hard polymer, g.	Oily polymer, g.	Unreacted terpene	Expt. no
Toluene 184	Pinene 136	10	98.5	81.3	19.0	33.4	4
Toluene 92	Pinene 136	10	97.3	80.3	19.2	34.2	5
Benzene 187	Pinene 136	10	98.8	80.0	19.4	34.0	6
Hexane 133	Pinene 136	10	99.0	60.0	39.0	35.3	7
Xylene 106	Pinene 136	10	99.6	91.2	8.4	34.3	8
Toluene 184	Pinene 136	10	98.1	83.0	16.4	34.8	9
Toluene 92	Dipentene 136	10	99.0	46.8	49.4	36.1	10
Toluene 92	Cedarwood 136	10	98.0	90.4	9.9	32.8	11

Summary of Results

1. The sum total of polymeric products and unreacted material does not exceed the weight of terpene undergoing polymerization.

2. Under the conditions of the experiments approximately three-fourths only is polymerized; the balance can be recovered as unreacted material.

3. The role of the aromatic is that of solvent only, and it can be recovered at the end of the reaction in essentially 100% yield.

4. Polymerization of terpenes in the presence of aromatics, with aluminum chloride as catalyst, takes place without interreaction of aromatic and terpene.

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(1) C. A. Thomas, U. S. Patent 1,939,932.

(2) Ellis, "The Chemistry of Synthetic Resins," 36 references.