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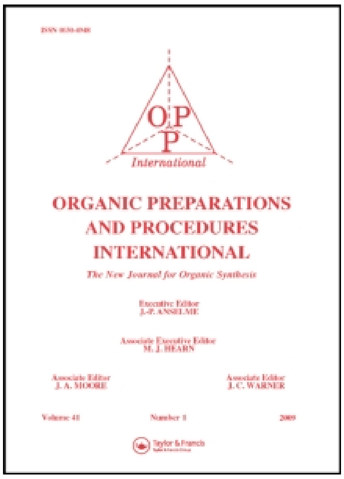

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AN IMPROVED SULFONIC ACID-RESIN CATALYZED CYCLIDEHYDRATION OF 2-METHYL-4-PHENYL-2-BUTANOL TO 1,1-DIMETHYLINDAN

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AN IMPROVED SULFONIC ACID-RESIN CATALYZED CYCLIDEHYDRATION OF 2-METHYL-4-PHENYL-2-BUTANOL TO 1,1-DIMETHYLINDAN

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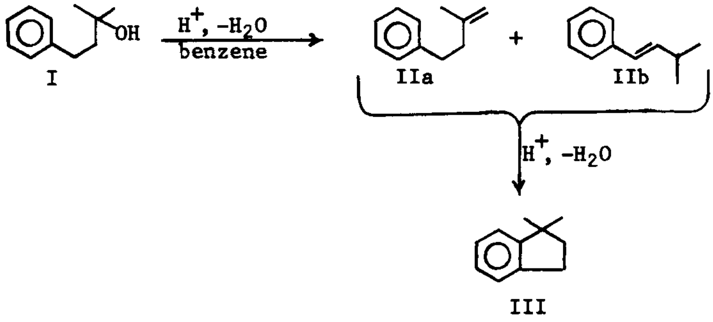
1,1-Dimethylindan (III) is of interest as an intermediate in the preparation of substituted indans and indanones. It may be considered to be the initial stable product of the sulfuric acid-catalyzed cyclialkylation reaction of isoprene and benzene.[2a-c,g] Since the cyclialkylation reaction is impractical for the preparation of III, we undertook a study of the cyclidehydration[2d-f] of 2-methyl-4-phenyl-2-butanol (I) to III as shown below. This study included the use of Bradsher's reagent[3a] (48% HBr and acetic acid), sulfuric acid,[2a-c,f,g] formic acid,[3b] and the sulfonic acid resin Amberlyst-15 (A-15).[3c]



Of the reagents studied, A-15 gave the best overall results and it was the most convenient to use.[3d] Our gas-liquid chromatography (glc) studies show that initially, the A-15 catalyst functions as a dehydrating agent since all of I rapidly disappears from the reaction mixture with concomitant formation of IIa and IIb. These olefins are then cyclized at

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the reflux temperature of benzene to III in 61-80% yield in 1-5 hr. The rates of disappearance of I, IIa, and IIb and the yield of III appear to be concentration-dependent (Table I).

TABLE I

A-15 CATALYZED CYCLIDEHYDRATION OF I IN REFLUXING BENZENE

Moles[a] I	Time[b]	% Yield III	Distillation Residue (g)[c]
0.1	1.0	80	3.3
0.2	1.3	75	5.6
0.3	2.0	67	10.6
0.5	2.8	65	15.4
1.0	5.0	61	41.7

a) In 1500 ml benzene containing 25 g A-15 resin. *b*) Hr required for all of I and olefins IIa and IIb to disappear as reactants as shown by glc of samples at 200° on a 12-ft x 0.25-in. column of Chromosorb G treated with DMCS and coated with 5% UC W-98 silicone rubber. *c*) This residue contains a mixture of five dimers as shown by glc at 260° and the mass spectrum of the mixture (70 eV), *m/e* 292.[3e]

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Solvent-temperature effects on cyclidehydration were investigated. The yield increased in the order toluene (67%), cyclohexane (70%), benzene (75%), and *p*-xylene (80%), each at the reflux temperature. The ease of separation of III from solvent led us to select benzene for its preparation. The optimum conditions with this solvent were determined through the concentration studies shown in Table I. As expected, dilution with solvent shows an increase in yield of III and a lessening of condensation products.

In comparison to the results obtained with A-15, Bradsher's reagent[3a] required 92 hr of reflux time and while the yield of crude product was higher (80-85%), the presence of unidentified impurities[4a] showed the latter reagent to be less suitable; sulfuric acid is also less suitable than A-15. As expected,[2a-c] sulfonation, condensation to higher-weight hydrocarbons and tar formation cause a lowering in yield[2e,f] of III to 60%. Formic acid-catalyzed cyclidehydration led to a variable mixture of unreacted I, ester,[4b] olefins IIa, IIb, and III, and consequently, the use of this reagent was not investigated further.

EXPERIMENTAL

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Dehydration of I to 2-Methyl-4-phenyl-1-butene (IIa) and 3-Methyl-1-phenyl-1-butene (IIb). To a 100-ml, two-neck flask equipped with heating mantle, Teflon-coated magnetic stirring bar, condenser, and thermometer were added 2 g of dried[5] A-15 catalyst, 5 g of I and 50 ml cyclohexane. The temperature was raised to 65° and held for 80 min. The catalyst was removed by filtration and the mixture was distilled. A fraction weighing 4.15 g (93%), bp 50-53° (0.4 mm), containing IIa:IIb (1:4) was collected. Preparative glc (UC W-98) provided pure samples of IIa and IIb. Comparison of the ir, nmr, and glc data of IIa and IIb with authentic materials established their structures.

Cyclidehydration of I to 1,1-Dimethylindan (III). To a 3-l., three-neck, round-bottom flask equipped with mechanical stirrer, Dean-Stark trap[6] and an addition funnel were added 1.5 l. of distilled benzene and 25 g of dried A-15 catalyst.[3c,5] The mixture was stirred and heated to the reflux temperature. A 32.8 g (0.2 mole) sample of I was added over 3 min and the mixture was heated under reflux for 2 hr, cooled and filtered. The filtrate was distilled through a 6-in. Vigreux column until the temperature rose above 80°. Distillation at 37-40° (0.7 mm) gave 22 g (75%) of III: bp 190-191° [lit.[2e] 189-191°].

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(b) Ibid., p. 202;
(c) We thank the Rohm and Haas Co., Philadelphia, Pa. for a sample of Amberlyst-15. Literature describing its use may be obtained from this source;
(d) This catalyst is a solid, readily weighed and easily filtered out of a hydrocarbon reaction mixture. It shows considerable promise as an insoluble acid catalyst;
(e) We thank M. C. Hamming, Continental Oil Company, for this information.

(4) (a) Assumed to be bromo derivatives to account for the greater than theoretical yield of crude products;
(b) Ir (neat) 1715 (C=O) cm^{-1}.

(5) Dried at 105° (0.5 mm).

(6) Ref. 3a, Vol. I, p. 617.

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