An Easy Conversion of 2,3,4,5,6-Pentamethylbenzyl Derivatives to Hexamethylbenzene by Catalysis of Sulfuric Acid[1]

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In the acidic decomposition of 2,3,4,5,6-pentamethylbenzyl nitrate, an appreciable amount of hexamethylbenzene (HMB) was obtained as one of the main products.[2] Since the intermolecular migration of the methyl group can hardly be possible under those mild conditions, HMB must have been formed by some other ways. Perhaps the most satisfactory interpretation is that the nitrate underwent the complex ionization to yield pentamethylbenzyl cation (PMB^+),[3] which was then converted into HMB by the hydrogen atom abstraction.[4]

1) The Reaction of Polysubstituted Aromatics. Part X; Part IX: This Bulletin, **39**, 1201 (1966).

2) K. Maruyama, K. Nakamura and H. Suzuki, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*), **89**, 78 (1968).

3) L. P Kuhn, *J. Am. Chem. Soc.*, **69**, 1974 (1947).

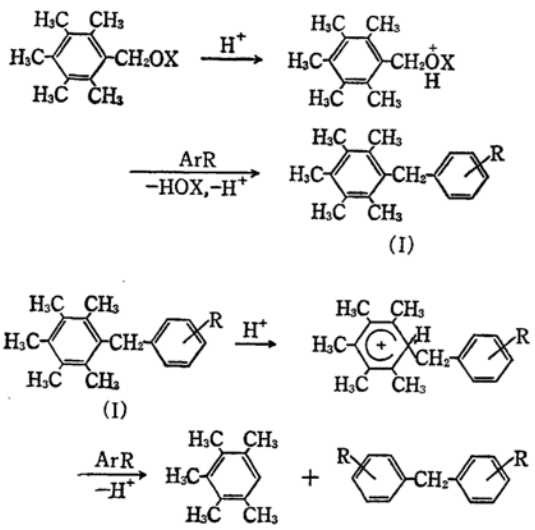
4) H. M. Buck, L. J. Oosterhoff, M. J. v. d. Sluys-v. d. Vlugt and K. G. Verhoeven, *Rec. Trav. Chim.*, **86**, 923 (1967).

Table 1. Yield of HMB

X in $C_6(CH_3)_5CH_2X$	(g)	H_2SO_4 (ml)	Conditions	Yield (g)	Yield (%)*
OH	2.0	10	30 min at 13°C	0.66	72
ONO_2	2.0	20	2 hr at 0—10°C	0.04	6[2]
$OCOCH_3$	2.0	10	30 min at 13°C	0.51	70
$OCOCH_3$	2.0	10	30 min at 13°C in methylcyclohexane (30 ml)	0.86	118
Cl	2.0	10	30 min at 13°C	0.53	64

* Calculated on the assumption that one mole of HMB was formed from two moles of the starting material.

With an intent to confirm this, some 2,3,4,5,6-pentamethylbenzyl derivatives were prepared and subjected to the action of sulfuric acid. All these compounds were found to be reduced with great ease to HMB, the yield of which could be increased considerably when the reaction was carried out in alkane medium. The characteristic color changes from purple-red into dark purple were observed during these transformations. Although the similar color change was observed by dissolving 2,3,4,5,6-pentamethylbenzyl alcohol in trifluoroacetic acid, the reduction was slow and incomplete at room temperature. However, PMR spectroscopy has revealed that the addition of small amounts of sulfuric acid to the solution can complete the reduction within a few minutes. Rather surprisingly, an attempted synthesis of bis(2,3,4,5,6-pentamethylbenzyl) ether by heating the alcohol with tosyl chloride in presence of pyridine also led to the formation of some HMB. The alcohol and its esters were especially subject to the easy reduction; even from the chloride HMB was slowly formed with continuous evolution of hydrogen chloride. The remarkable stability of PMB^+ has recently been established in strong acid system (SbF_5-SO_2),[5] but the present work has shown that PMB^+ is readily reduced to HMB under ordinary conditions. No pentamethylbenzene could be detected during these reactions.



In the medium of an aromatic hydrocarbon, the methylene group was transferred from PMB^+ to the solvent with the consequent formation of pentamethylbenzene and diphenylmethane derivatives. The process must be similar to those of the transcarbonylation,[6] the transbenzylation,[7] and the transsulfonation,[8] and may be explained in terms of steric crowdedness and strong electrophilic character of PMB^+.

Experimental

2,3,4,5,6-Pentamethylbenzyl derivatives were prepared as described in the literature: the alcohol (mp 160—161°C),[9] the nitrate (mp 95—97°C),[2] the acetate (mp 84.5—86.5°C),[9] and the chloride (mp 81—82°C).[10]

All these compounds dissolved readily in sulfuric acid to give a purple solution which was, after having stood for some time, diluted with excess of water. A solid precipitate was chromatographed on alumina using light petroleum to give HMB as an early eluate; it was spectroscopically identical with the authentic specimen, and showed no depression of the mixed melting point (mp 164—165°C).[11] A dark brown powder of no definite melting point (on heating, it turned to yellow with gradual decomposition) remained on the top of the column, and dissolevd readily in carbon tetrachloride to give a brown-red solution, the PMR spectrum of which showed a broad methyl absorption at around 7.8—8.0 τ. Thus it is a polymeric substance probably formed as a result of the hydrogen atom abstraction by PMB^+. Yields of HMB from various sources were recorded in Table 1.

2,3,4,5,6-Pentamethylbenzyl acetate (2.0 g) in methylcyclohexane (30 ml) was treated with sulfuric acid

5) J. M. Bollinger, M. B. Comisarow, C. A. Cupas and G. A. Olah, *J. Am. Chem. Soc.*, **89**, 5687 (1967).
6) R. C. Fuson, G. R. Bakker and B. Vittimberga, *ibid.*, **81**, 4858 (1959).
7) C. Serres and E. K. Fields, *ibid.*, **82**, 4685 (1960).
8) H. Drews, S. Meyerson and E. K. Fields, *ibid.*, **83**, 3871 (1961).
9) O. Jacobsen, *Ber.*, **22**, 1217 (1889).
10) F. Bennington, R. D. Morin and L. C. Clark, *J. Org. Chem.*, **23**, 2034 (1958).
11) L. I. Smith and F. H. MacDougall, *J. Am. Chem. Soc.*, **51**, 3001 (1929).

(10 m*l*) under vigorous agitation at 13°C for 30 min. The mixture immediately turned into dark purple and some heat was evolved. Quenching with water, extraction by ether, and removal of the solvent under reduced pressure left a light brown solid, the chromatography of which on alumina using light petroleum gave HMB (mp 164—165°C, 0.86 g) as an early eluate.

A deep purple solution of 2,3,4,5,6-pentamethylbenzyl alcohol (0.5 g) in a large excess of trifluoroacetic acid was stirred at room temperature for 40 hr. Ordinary working-up and the subsequent chromatography on alumina gave HMB (0.03 g, 14%*) from the light petroleum eluates. Most products (mainly trifluoroacetate) remained on the top of the column.

The transfer of the methylene group of PMB^+ to another aromatic nucleus was realized by stirring a mixture of a pentamethylbenzyl derivative (2.0 g) with an aromatic hydrocarbon (40 m*l*) and sulfuric acid (15 m*l*) at 10°C for 1.5—2 hr. Products were analyzed by gas chromatography and identified by comparison with the authentic specimens; pentamethylbenzene and diphenylmenthane were formed nearly in equal quantity. Small amounts of another diphenylmethane compound (probably *unsym*-polymethyldiphenylmethane of the type I) were not further investigated.