

Addition of Alcohols to Mesityl Oxide Using an Acid Ion Exchange Resin Catalyst

N. B. LORETTE

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The preparation of diacetone alcohol ethers from mesityl oxide and alcohols with basic and acidic catalysts has been reported.¹⁻⁶ Hoffman¹ prepared these ethers with a sulfuric acid catalyst and a reaction time of 12 days while the same reaction

for the removal of the unreacted mesityl oxide (b.p. 42°) followed by 4-methoxy-4-methyl-2-pentanone, confirmed by infrared, b.p. 74°/40 mm., n_D^{25} 1.4159, d_{25} 0.900, (Lit.¹ d_{25} 0.901).

In Table I the results of four runs made at varying feed rates are given.

Preparation of 4-ethoxy-4-methyl-2-pentanone. The same resin that was used above was used for this experiment after it was washed with ethanol. A solution composed of 24.9 moles of anhydrous ethanol and 9.7 moles of mesityl oxide was passed over the resin at a rate of 0.552 ml. per min. The reaction solution was then distilled at 170 mm. until all of the ethanol (b.p. 45°) was removed and then at 40 mm. for the mesityl oxide removal followed by 20 mm. for the 4-ethoxy-4-methyl-2-pentanone, b.p. 67°/20 mm., n_D^{25} 1.4152,

TABLE I

Run No.	Feed Rate, Ml./Min.	Volume of Stock Soln., Ml.	High Boiling Residue, G.	Mesityl Oxide	
				% Conv.	% Yield ^a
1	0.377	1585	35	57.0	88.2
2	0.616	1800	28	56.6	93.7
3	1.29	1800	27	46.5	94.0
4	2.41	1800	28	40.9	94.0

^a Based on unrecovered mesityl oxide.

described by Halbig and Treibs⁴ required only 12 hr. Acid ion exchange resins have been used by a number of investigators for catalyzing various reactions,^{7,8} but the utilization of an acid resin for preparing ethers of diacetone alcohol is a new observation. Dowex 50, a sulfonic acid ion exchange resin, effectively catalyzed the formation of ethers of diacetone alcohol from mesityl oxide and alcohols. The advantages of this catalyst were the reaction time was greatly reduced, the yields were excellent, and the catalyst was easily separated from the reaction solution.

EXPERIMENTAL

The Dowex 50 was converted to the acid form with 3*N* hydrochloric acid, washed with water, and then methanol. Sufficient resin was put in a vertical Pyrex tube 90 cm. long, 19 mm. ID, so that there was a catalyst bed 71 cm. deep. The catalyst bed occupied a total volume of 200 ml. of which 155 ml. was resin beads and 45 ml. was void volume.

The temperature used for all experiments was 25°.

Preparation of 4-methoxy-4-methyl-2-pentanone. A stock solution of equal volumes of methanol and mesityl oxide (2.86 moles of methanol per mole of mesityl oxide) was used. In run 2 of Table 1, 1800 ml. (7.88 moles of mesityl oxide and 21.9 moles of methanol) of the stock solution was passed over the ion exchange resin at an average rate of 0.616 ml. per min. The effluent was first distilled using an efficient glass column at 200 mm. until all of the methanol (b.p. 35°) was removed. The pressure was then reduced to 40 mm.

(1) A. Hoffman, *J. Am. Chem. Soc.*, **49**, 530 (1927).

(2) A. Hoffman, U. S. Patent **1,729,255**.

(3) C. W. Simms, U. S. Patent **1,823,704**.

(4) P. Halbig and A. Treibs, U. S. Patent **2,217,167**.

(5) B. P. Geyer and S. A. Ballard, U. S. Patent **2,413,822**.

(6) J. B. Tindall, U. S. Patent **2,430,436**.

(7) F. Helfferich, *Angew. Chem.*, **66**, 241 (1954).

(8) F. C. Nachod and J. Schubert, editors, *Ion Exchange Technology*, Academic Press, Inc., New York, 1956, pp. 279-284.

d_{25} 0.884 (lit.¹ d_{25} 0.886). A 37 g. high boiling residue remained. A recovery of 7.04 moles of mesityl oxide and 2.19 moles of ether represented a conversion of 27% and a yield of 82% based on unrecovered mesityl oxide.

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Reaction of Alkyl and Aryl Silicon Isocyanates with Amines

ROY G. NEVILLE¹

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Silicon tetrakisocyanate and alkyl and aryl-silicon isocyanates have been extensively studied by Forbes and Anderson,^{2,3} and by Eaborn.⁴ Although it is known that silicon tetrakisocyanate reacts with water to form silica no study has been made of the reaction of silicon isocyanates with primary and secondary aliphatic and aromatic amines.⁵

(1) For reprints: 3267 57th Avenue S.W., Seattle 16, Wash.

(2) G. S. Forbes and H. H. Anderson, *J. Am. Chem. Soc.*, **62**, 761 (1940); *J. Am. Chem. Soc.*, **66**, 1703 (1944); *J. Am. Chem. Soc.*, **67**, 1911 (1945); *J. Am. Chem. Soc.*, **69**, 1241 (1947); *J. Am. Chem. Soc.*, **70**, 1043, 1222 (1948).

(3) H. H. Anderson, *J. Am. Chem. Soc.*, **66**, 934 (1944); *J. Am. Chem. Soc.*, **72**, 193, 196, 2761 (1950); *J. Am. Chem. Soc.*, **75**, 1576 (1953).

(4) C. Eaborn, *Nature*, **165**, 685 (1950).

(5) Incidentally to another study, Anderson reacted aniline with silicon tetrakisocyanate, *n*-butylsilicon triisocyanate, diphenylsilicon diisocyanate, *n*-propylsilicon triisothiocyanate, diethylsilicon diisothiocyanate, and triethylsilicon isothiocyanate, but did not characterize the products, where formed. See H. H. Anderson, *J. Am. Chem. Soc.*, **73**, 2351 (1951).