(b) A mixture of I (1 g.) and chloroacetyl chloride (3 ml.) was left at room temperature for 24 hr. The solution was poured into ice–water (20 ml.), the dark solid which separated, was filtered and crystallized several times from methanol to yield brown prisms (0.4 g.), m.p. 136–139°. It was purified by sublimation *in vacuo* followed by crystallization from ethyl acetate to afford white irregular prisms, m.p. 141°, undepressed on admixture with specimen obtained in (a).

Anal. Calcd. for $C_8H_7ClO_5$: C, 43.95; H, 3.22. Found: C, 43.72; H, 3.08.

Formation of Hexamethylbenzene from Phenol and Methanol

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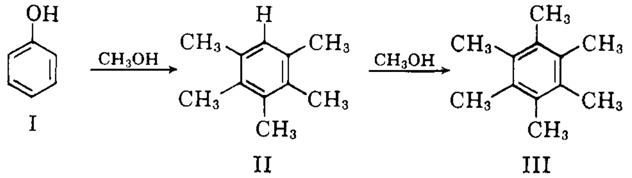
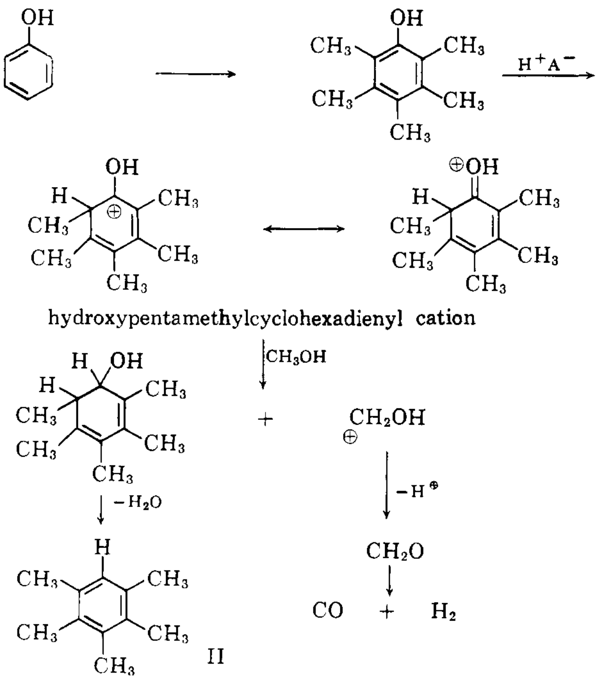
In the reaction of phenol with methanol at 400° over an acidic alumina catalyst to form hexamethylbenzene,[1-3] we have obtained evidence that the reaction proceeds through pentamethylbenzene as an intermediate.



I II III

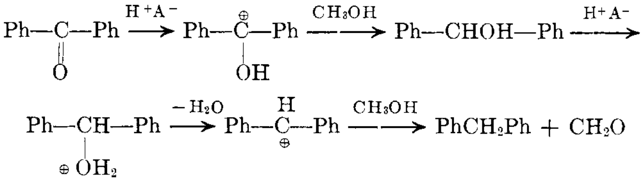
The amount of II in the crude reaction product increased with increasing space velocity (shorter contact time). Furthermore, II was readily converted exclusively to III under the reaction conditions.

A plausible reaction mechanism for the conversion of I to II is the following:



In agreement with this mechanism we have found substantial amounts of formaldehyde in addition to the previously reported carbon monoxide, hydrogen, and methane. Also, no di-, tri-, or tetramethylbenzene could be detected in the crude reaction products.

One important step in the above mechanism is a hydride ion transfer reaction between a relatively stable cyclohexadienyl carbonium ion and methanol. A similar mechanism can apply to the reaction of benzophenone with methanol over alumina at 450°, wherein diphenylmethane and formaldehyde were found as the only products:



$$\mathrm{Ph{-}\underset{\underset{O}{\|}}{C}{-}Ph} \xrightarrow{H^+A^-} \mathrm{Ph{-}\underset{\underset{OH}{|}}{\overset{\oplus}{C}}{-}Ph} \xrightarrow{CH_3OH} \mathrm{Ph{-}CHOH{-}Ph} \xrightarrow{H^+A^-}$$

$$\mathrm{Ph{-}\underset{\underset{\oplus OH_2}{|}}{CH}{-}Ph} \xrightarrow{-H_2O} \mathrm{Ph{-}\underset{\oplus}{\overset{H}{C}}{-}Ph} \xrightarrow{CH_3OH} \mathrm{PhCH_2Ph + CH_2O}$$

The intermediates here are again resonance-stabilized benzylic carbonium ions which undergo hydride ion transfer reactions. There are a number of analogies in the literature including the formation of cyclohexanol (among other products) from 1,4-cyclohexanediol and methanol over alumina[4] and the reaction of aryldiazonium salts with methanol to form aromatic hydrocarbons and formaldehyde.[5]

Experimental

Penta- and Hexamethylbenzene.—Ten grams of 8–15-mesh Alcoa F-10 alumina was placed in a $^3/_4 \times 12$ in. Vycor reactor heated by external heating wire. With the temperature at 400° a solution of 9.4 g. (0.1 mole) of phenol in 20 ml. of methanol was introduced through a syringe needle from a constant rate syringe drive pump (JKM Instrument Co., Durham, Pa.). Products were collected in a series of air-cooled and ice-cooled receivers. The products included a light yellow solid suspended in water and unchanged methanol. Filtration and thorough drying yielded 8 g. of crude solid, m.p. 130–155°. Vapor phase chromatography using silicone rubber packing, and high molecular weight mass spectrometry, easily established the presence of 9% pentamethylbenzene, 89% hexamethylbenzene, and 2% of a mixture of high molecular weight methylated polyaromatics. Recrystallization of the crude solid using cyclohexane yielded hexamethylbenzene, m.p. 164–165°. Pentamethylbenzene was subsequently separated from the crude mixture by preparative VPC and its identity confirmed by mixed m.p. (52–53°) and by infrared comparison.

Diphenylmethane.—Using the previously described technique, 9.1 g. of benzophenone in 100 g. of methanol was passed over 10 g. of F-10 alumina. There was obtained 7.1 g. of white solid m.p. 27°, established as diphenylmethane by analysis, infrared, and mixed m.p. comparison with an authentic sample.

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(1) E. Briner, W. Pluss, and H. Paillard, *Helv. Chim. Acta*, **7**, 1046 (1924).

(2) H. J. Backer, *Rec. trav. chim.*, **54**, 745 (1935).

(3) N. M. Cullinane and S. J. Chard, *J. Chem. Soc.*, 821 (1945).

(4) R. C. Olberg, H. Pines, and V. N. Ipatieff, *J. Am. Chem. Soc.*, **66**, 1096 (1941).

(5) D. F. Detar and T. Kosuge, *ibid.*, **80**, 6072 (1958).

A New Synthesis of Ureas. V. The Preparation of Methyl-N-phenylurethane from Carbon Monoxide, Sulfur, Aniline, and Methanol

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Earlier publications in this series describe a new method for the synthesis of substituted ureas from