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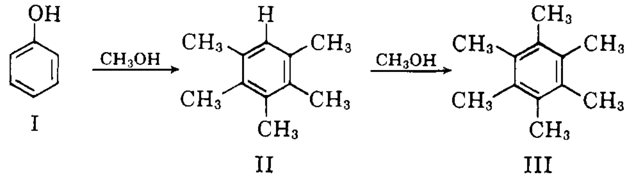
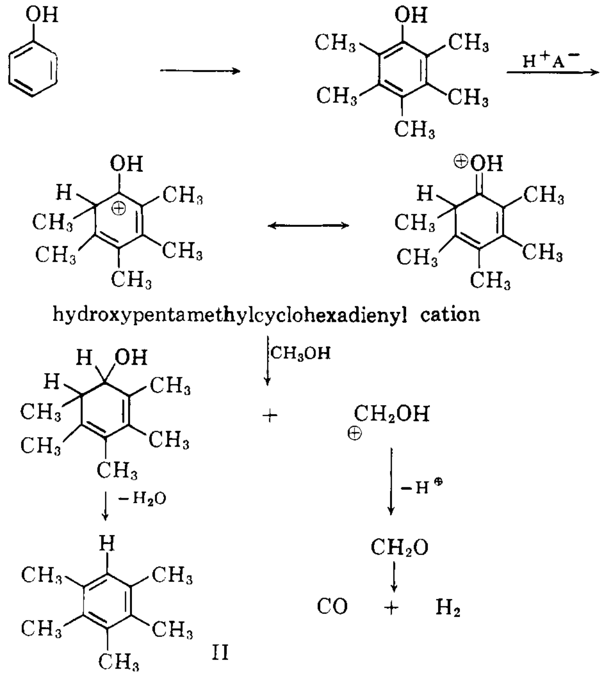
In the reaction of phenol with methanol at 400° over an acidic alumina catalyst to form hexamethylbenzene,[1-3] we have obtained evidence that the reaction proceeds through pentamethylbenzene as an intermediate.



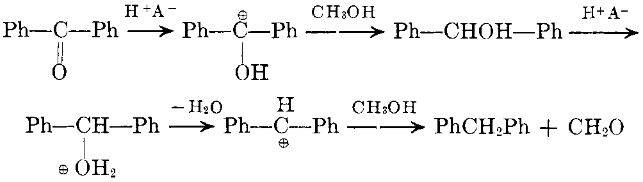
The amount of II in the crude reaction product increased with increasing space velocity (shorter contact time). Furthermore, II was readily converted exclusively to III under the reaction conditions.

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:



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

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

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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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 aliphatic or aromatic amines, carbon monoxide, and sulfur.[3-5]

$$2RNH_2 + CO + S \longrightarrow RNHCONHR + H_2S$$

In the course of those investigations, it was observed that in the preparation of ureas, a loss in yield occurred when methanol was used as a solvent, and the corresponding urethane could be isolated as a portion of the product. Therefore, the possibility was considered of establishing a preparative method for urethanes from mixtures of amines, alcohols, carbon monoxide, and sulfur by suitable modifications of the urea procedure.

Such a preparation is feasible, for example in the case of methyl N-phenylurethane, provided conditions exist that allow the equilibrium, $PhNHCONHPh + MeOH \rightleftharpoons PhNHCO_2Me + PhNH_2$, to favor urethane formation under experimental conditions. The preparation of methyl-N-phenylurethane in this manner was demonstrated when mixture of 0.1 mole of diphenylurea and 150 ml. of methanol were heated in an autoclave for five hours. The results are summarized in Table I.

TABLE I

REACTION OF METHANOL AND DIPHENYLUREA

Temp., °C.	Product composition Aniline (% yield)	Methyl-N-phenylurethane (% yield crude)	Diphenylurea (% recovered)
120	37.4	34.4[a]	45.8
160	79.8	70.8	None

[a] After recrystallization from petroleum ether (b.p. 60–90°), yield 26.2%, m.p. 45°.

Subsequently, however, it was found that the reaction of aniline, carbon monoxide, and sulfur in the presence of a large excess of methanol gave a yield no larger than 13.5%, even under the most favorable experimental conditions. The low yield in these experiments was somewhat surprising in view of the conversions of diphenylurea to methyl-N-phenylurethane shown in Table I and the high yields of diphenylurea that are possible from carbon monoxide, sulfur, and aniline.

It then seemed that if the conditions of the experiment could first be adjusted to produce diphenylurea, and subsequently readjusted to induce methanolysis of the urea, the yield of urethane could be increased. In an additional experiment, 0.2 mole of aniline, 0.4 mole of sulfur, 0.4 mole of carbon monoxide, 2 g. of triethylamine, and 150 ml. of methanol were heated in an autoclave under conditions known to be favorable to the formation of diphenylurea (4 hr. at 120°). At the conclusion of the initial heating period, the autoclave was immediately heated to 160° and maintained at that temperature for eight hours. Under these conditions, the yield of crude urethane was increased to 24.3%, a higher value than had been obtained for any other combination of experimental conditions.

It appears that temperatures favoring methyl-N-phenylurethane formation from diphenylurea are unfavorable for the formation of diphenylurea or diphenylurea precursors, which may form methyl-N-phenylurethane by interaction with methanol. The preferred synthesis route would then involve the preparation and isolation of diphenylurea in the manner described earlier.[5] The diphenylurea may then be converted to the urethane in good yield by methanolysis at higher temperatures.

Experimental

All experiments were carried out in a 2.1 Magnedash autoclave. The following is typical of a series of experiments in which methyl-N-phenylurethane was prepared directly from aniline, carbon monoxide, sulfur, and methanol.

The autoclave was charged with 18.6 g. (0.2 mole) of aniline, 6.7 g. (0.2 mole) of sulfur, 10.1 g. of triethylamine, 120 ml. of methanol, and carbon monoxide at 300 p.s.i.g. After a warm-up period of 1 hr., the autoclave was heated at 160° for 5 hr., cooled to 80°, and vented. The products were washed from the bomb, diluted with methanol to about 250 ml., and filtered. The methanol solution was evaporated to dryness, and the residue was treated with 100 ml. benzene to yield 0.37 g. benzene-insoluble diphenylurea, m.p. 230–232° (yield 1.8%). The benzene-soluble portion was extracted with three 25-ml. portions of 2.5 *N* hydrochloric acid, evaporated, and the residue was extracted with several portions of petroleum ether (b.p. 60–90°). Evaporation of the solvent extracts gave a residue which was recrystallized from petroleum ether to yield 4.07 g. (13.5% yield) of methyl-N-phenylurethane, melting 47–50°.

In variations of this procedure, the following conditions were employed: (a) Either an aniline–sulfur mole ratio of 1:1.05 or 1:1.5; (b) triethylamine or sodium methoxide as a catalyst; (c) either an aniline–catalyst mole ratio of 1:0.1 or 1:0.5; (d) 80 or 120 ml. of methanol; (e) an initial carbon monoxide pressure of 150 or 300 p.s.i.g.; (f) a temperature of 160 or 200°; and (g) a heating time of 3 or 5 hr.

Reactions of Isocyanic Acid with Acid Chlorides. Preparation of Acyl Isocyanates, Isocyanatosilanes, and Phosphor(diisocyanatidites)

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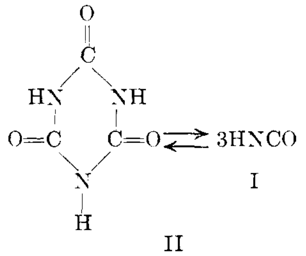
Isocyanic acid (I), which can be obtained readily by thermal decomposition of cyanuric acid (II), has been studied in this laboratory for the past three years. It has been found that isocyanic acid undergoes some interesting reactions, which may be of practical value.



II

(1)

In this paper we report the preparation of acyl isocyanates, isocyanatosilanes, and phosphor(isocyanatidites) from isocyanic acid and the corresponding acid chlorides.

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(2) Midwest Research Institute.

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