necessity limited to systems which give sufficiently stabilized carbocationic products.

Experimental Section

All hydrocarbon precursors used were either commercially available or synthesized by known procedures. Nitrosonium hexafluorophosphate (Cationics, Inc.) and trifluoromethanesulfonic acid (3M Company) were used without further purification.

The ^{1}H NMR spectra were recorded on a Varian Associates A56/60A spectrometer and the ^{13}C NMR spectra were obtained on a Varian Associates XL-100 spectrometer operating in a pulsed FT mode. Chemical shifts were measured from an external (capillary) Me_4Si signal. Gas chromatographic analyses of the quenched products were obtained on a Hewlett-Packard 5700A gas chromatograph with a 2 ft × $\frac{1}{8}$ in. SE-30 column eluted with helium at 250 °C.[18a] GC–MS were obtained on a DuPont 21-094 mass spectrometer coupled to a Varian Associates Aerograph 2700 gas chromatograph using a 10 ft × $\frac{1}{8}$ in. Porapak Q column eluted with helium.

Hydrogen Abstraction from Hydrocarbons with Nitrosonium Hexafluorophosphate. To a solution of $NO^+PF_6^-$ (1.40 g, 8 mmol) in ca. 5 mL of liquid sulfur dioxide at −78 °C was slowly added an appropriate hydrocarbon (4 mmol). The reaction vessel was sealed and kept at room temperature for 3 h. Thereafter the solution was cooled to −20 °C, the vessel was opened, and aliquots were analyzed, upon transfer to NMR tubes by spectral analysis and, after hydrolysis, by GLC by comparison with known amounts of standard pure alcohols.

Triphenylmethyl (mp ~146 °C dec)[18b] and cycloheptatrienyl hexafluorophosphate (mp 210–215 °C dec) were isolated in quantitative yield upon recrystallization of the residue, obtained from the evaporation of the volatile components of the reaction mixture, from CH_2Cl_2.

Hydrogen Abstraction from Hydrocarbons by Nascent Nitrosonium Ion. To ice-cooled trifluoromethanesulfonic acid (6.75 g, 45 mmol) was added sodium nitrite (1.05 g, 15 mmol), followed by the hydrocarbon precursor (5 mmol) while the mixture was stirred with a Fisher Vortex stirrer. After 10 min, an aliquot was taken to record the NMR spectra. Complete consumption of the starting material was observed and the spectra observed were those of the carbocationic species.

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Registry No.—Cycloheptatrienyl hexafluorophosphate, 29663-54-5; nitrosonium triflate, 51637-52-6.

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Carbon Monoxide–Hydrogen–Water: Reduction of Benzophenone, Diphenylcarbinol, and Diphenylmethane

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Introduction

A mixture of carbon monoxide and water is regarded to be superior to hydrogen as a reducing agent for the liquefaction of lignite.[1–5] How carbon monoxide functions in the lignite reduction is still largely a matter of speculation. Since a mixture of carbon monoxide and hydrogen can be made from lignite and its inherent water by the water gas reaction, the commercial utilization of carbon monoxide or a mixture of carbon monoxide and hydrogen as a reducing agent is promising. Sodium carbonate, ferrous sulfide, and the mineral matter in lignite are reported to be catalysts for liquefaction. Appell et al.[4] have proposed that sodium carbonate reacts with the water to form a basic medium, and the base interacts with carbon monoxide to give the formate ion. The formate ion is a reducing agent which augments the reducing power of the hydrogen present, particularly for carbonyl compounds. Appell et al.[4] has suggested that hydrogen more so than carbon monoxide favors the cracking of carbon chains.[4]

A study of the carbon monoxide reduction mechanism is of direct value for developing improved catalysts for the liquefaction process, as well as for reduction of other organic compounds. This study relates data on the reduction of model compounds which best represent critical chemical linkages in lignite. The three title compounds contain one-carbon linkages between aromatic rings. A comparison has been made with hydrogen, hydrogen–carbon monoxide–water, and carbon monoxide–water as reducing gases, sodium carbonate, sodium formate, sodium hydroxide, and iron oxide as possible catalysts, and tetralin as a hydrogen donor solvent.

Results and Discussion

The reduction products of benzophenone are diphenylcarbinol, diphenylmethane, benzene, and toluene. Diphenylcarbinol, under the same conditions, gives diphenylmethane, benzophenone, benzene, and toluene. Diphenylmethane is only converted in low yield, i.e., 1–3%, to benzene and toluene by even the most rigorous of conditions.

The order of conversion effectiveness of the reducing gases in the presence of sodium carbonate for the benzophenone reduction is hydrogen < carbon monoxide–water < carbon monoxide–water–hydrogen (Table I). For diphenylcarbinol, the order is hydrogen < carbon monoxide–water ≃ carbon monoxide–water–hydrogen (Table II). The hydrogen donor solvent tetralin has no influence on the conversion yields for the carbon monoxide–water–hydrogen reduction (runs 6 and 9, Table I), the carbon monoxide–water reduction (runs 2 and 8, Table I), and the hydrogen reduction (runs 5 and 10, Table I). However, tetralin did influence the product distribution by causing more diphenylmethane to be formed at the expense of diphenycarbinol (runs 2 vs. 8 and 5 vs. 10, Table I), though this is not consistent (run 6 vs. 9, Table I).

The reduction of diphenylcarbinol gives disproportionation in addition to reduction. Diphenylcarbinol, in the absence of reducing gases under the reaction conditions, gives a 1:1 molar ratio of benzophenone to diphenylmethane, cf. run 1, Table II. Sodium carbonate is not necessary for the disproportionation, cf. runs 1 and 2, Table II.

Table I. Reduction of Benzophenone[a]

Run	Temp, °C	Reducing agent[b]	Solvent[c]	Catalyst[d]	% $C_{10}H_{16}$	% $C_{10}H_{12}$	% Ph_2CHOH[e]	% Ph_2CH_2[e]	% PhH[e]	% $PhCH_3$[e]	% conversion[f]
1	400	CO, H_2O	None	Na_2CO_3			32.1	6.4	0.5		38.9
2	425	CO, H_2O	None	Na_2CO_3			22.4	19.2	0.7	0.03	42.3
3	450	CO, H_2O	None	Na_2CO_3			6.3	42.3	4.6	0.8	54.0
4	475	CO, H_2O	None	Na_2CO_3			3.9	45.0	19.3	1.8	60
5	425	H_2, H_2O	None	Na_2CO_3			25.4	6.2	1.2	0.03	32.8
6	425	CO, H_2, H_2O	None	Na_2CO_3			9.5	47.0	2.5	0.6	59.6
7	425	CO, H_2,[g] H_2O	None	Na_2CO_3			2.9	52.4	1.1	0.3	51.6
8	425	CO, H_2O	$C_{10}H_{16}$	Na_2CO_3	93.6	6.4	3.7	33.6	0.8	0.3	38.4
9	425	CO, H_2, H_2O	$C_{10}H_{16}$	Na_2CO_3	92.9	7.1	13.5	42.2	4.4	0.6	58.7
10	425	H_2, H_2O	$C_{10}H_{16}$	Na_2CO_3	95.2	4.8	21.1	11.8	1.7	Tr	35.0
11	425	CO, H_2O	None	None			0.0	6.8	0.2	0.3	7.2
12	425	CO, H_2O	None	NaOH			6.5	32.8	0.8	0.2	40.1
13	425	CO, H_2O	None	$NaCHO_2$			12.9	31.6	1.3	0.3	45.9
14	425	CO, H_2O	None	Fe_3O_4			Tr	31.9	0.9	0.3	33.0

[a] 0.15 mol, all results are duplicated. [b] Each gas at partial pressure of 750 psi and argon is added to bring the initial pressure to 1500 psi if necessary. [c] 0.015 mol of tetralin when used and 0.6 mol of water. [d] 0.015 mol. [e] Product mole percent yields normalized to converted benzophenone. [f] Based on recovered benzophenone. [g] 375 psi of CO and 375 psi of H_2.

Table II. Reduction of Diphenylcarbinol[a]

Run	Reducing agent[b]	Catalyst[c]	% Ph_2CO[d]	% Ph_2CH_2[d]	% PhH[d]	% $PhCH_3$[d]	% conversion[e]
1	H_2O	None	48.4	50.5	0.8	0.3	100.0
2	H_2O	Na_2CO_3	47.1	33.5	1.0	0.2	81.8
3	CO, H_2O	None	26.4	72.7	0.6	0.3	100.0
4	CO, H_2, H_2O	None	14.6	82.9	1.5	1.0	100.0
5	CO, H_2O	Na_2CO_3	12.8	83.1	1.9	1.3	99.1
6	H_2, H_2O	Na_2CO_3	11.6	76.0	1.3	0.4	89.3
7	CO, H_2, H_2O	Na_2CO_3	8.2	88.2	1.5	0.9	98.8
8	CO, H_2, H_2O	Fe_3O_4	0.0	94.4	2.7	2.8	100.0

[a] 0.15 mol, all results are duplicated and obtained at 425 °C. [b] The reducing gases used singly were at 750 psi initial pressure and when both were present each was at 375 psi. Argon is added to make the total initial pressure 1500 psi. [c] 0.015 mol. [d] Product mole percent yields normalized to converted diphenylcarbinol. [e] Based on recovered diphenylcarbinol.

The direct reduction of diphenylcarbinol to diphenylmethane is occurring in addition to the indirect route via benzophenone, since the presence of reducing gases does enhance the conversion, cf. run 2 vs. 5, 6, and 7, Table II. Further evidence that diphenylcarbinol is the precursor of diphenylmethane is that as the reaction temperature is lowered, the percentage of diphenylmethane decreases, and the amount of diphenylcarbinol increases, cf. runs 1–4, Table I.

Sodium formate and sodium hydroxide are equal to sodium carbonate in effectiveness for the carbon monoxide-water conversion of benzophenone, cf. runs 12 and 13 with run 2, Table I. This is evidence for the mechanistic sequence postulated by Appell et al. A new feature which does not fit this mechanistic scheme is that iron oxide, which is not basic, also catalyzes the conversion of benzophenone; cf. run 14, Table I. This perhaps catalyzes the reference production of hydrogen via the shift reaction.

Though benzene and toluene are formed from the reduction of diphenylmethane, the benzophenone reduction must also directly yield benzene in order to account for the abnormally high benzene–toluene ratio among the products, i.e., 1–23. Diphenylmethane reduces to give equimolar amounts of benzene and toluene. Therefore a second benzene formation reaction and/or a toluene destruction reaction must be operating. Both ethylbenzene and diphenylmethane are very slowly converted under the reaction conditions, i.e., in 1–3% yields for both; hence, toluene could not be expected to be a significant source of benzene.

The two likely precursors of the excess benzene are benzophenone and diphenylcarbinol. If diphenylcarbinol were the precursor to the extra benzene produced in the benzophenone reduction, the diphenylcarbinol reduction should produce a benzene–toluene ratio equal to or greater than that from benzophenone. However, it gives an intermediate value with an average ratio of 2.3 (Table II) vs. that of benzophenone at 9.1 (Table I). Therefore, the source of the extra benzene must be benzophenone, and most probably the benzene originates via the reaction sequence 1 → 2 → 3.

$$Ph_2CO \xrightarrow{\Delta} PhCO\cdot + Ph\cdot \quad (1)$$

$$PhCO\cdot \rightarrow Ph\cdot + CO \quad (2)$$

$$Ph\cdot + \text{sh)solvent)} \rightarrow PhH + S\cdot \quad (3)$$

By way of analogy, aliphatic aldehydes are known to decarbonylate with di-*tert*-butyl peroxide or other peroxides.[7,8] Aromatic aldehydes can also be decarbonylated using catalysts such as palladium or chlorotris(triphenylphosphine)rhodium.[9–11] Therefore, the decarbonylation of the benzoyl radicals at the temperatures of these reductions is not unreasonable.

Experimental Section

Batch Autoclave Reductions. All the reductions were done until duplicated results were obtained in two 250-mL Hastelloy alloy "C" batch autoclaves (Autoclave Engineers, Inc.) with a heater designed to accommodate both autoclaves and the mixing of contents achieved by rocking of the autoclaves. This procedure allowed two runs to be done simultaneously. The conditions of each run were varied, but each autoclave contained, when specified, a catalyst, solvent, water, and reducing gases. The time of each run was 2 h, which does not include heat-up and cool-down times.

After the autoclaves were cooled and decompressed, the organic and water layers were separated. The organic layers were filtered through sintered glass funnels and analyzed by gas chromatography.

The gas chromatograph used in this study was a Varian Aerograph 90-P. The column used was $\frac{1}{4}$ in. × 8 ft 5% Carbowax 20M with Chromosorb G was column support and the column temperatures were 60–80 °C and 180–200 °C. The internal standard selected was 1-bromonaphthalene. In each run the results were normalized to the conversion percentage. Then the average of the duplicated results were entered into the tables. The precision in the yields is ±6%.

Preparation of Iron Oxide.[12] Ferrous sulfate (115 g) was dissolved in 1 L of water by heating and adding a small amount of concentrated sulfuric acid (~10 mL). Aqueous ammonium sulfide (22.3%, J. T. Baker, Phillipsburg, N.J.) was added until the precipitation was complete and then an additional 5 mL was added. Ammonium hydroxide was added until the acidity was gone, and the mixture was filtered and washed with water until a negative sulfate ion test was achieved ($BaCl_2$). The solid was air-dried and calcined at 500 °C for 3 h to a dark red solid powder which does not produce hydrogen sulfide on exposure to dilute sulfuric acid. Because the product is magnetic, it is probably Fe_3O_4.

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Registry No.—Benzophenone, 119-61-9; diphenylcarbinol, 91-01-0; diphenylmethane, 101-81-5; carbon monoxide, 630-08-0; hydrogen, 1333-74-0; water, 7732-18-5.

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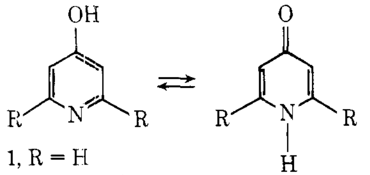
Communications

Self-Association and the Protomeric Equilibria of 4-Hydroxypyridine–4-Pyridone and Related Compounds

Summary: Extensive self-association of 4-pyridone is reported and suggested to shift the apparent position of the protomeric equilibrium between 4-pyridone and 4-hydroxypyridine in favor of the former in chloroform and cyclohexane. Self-association of 4-pyridones is shown to be suppressed by 2,6-substitution of the ring.

Sir: We have estimated the protomeric equilibrium constant for 4-hydroxypyridine (**1**)–4-pyridone (**2**) to be ca. 10^{-5} (K_T = [NH]/[OH] = 2/1) in the gas phase.[1,2] While it might be expected that **1** would also be the only detectable protomer in nonpolar weakly hydrogen bonding solvents,[3] a K_T of $10^{0.11}$ has been reported recently for this system in chloroform and a K_T of 10^{-1} may be estimated for cyclohexane.[4] Because of a continuing interest in this area we have reinvestigated that work. We wish to report that the apparent equilibrium between **1** and **2** in chloroform and cyclohexane, in fact, is dominated by the extensive oligomerization of **2** and that this self-association can be suppressed in derivatives of 4-pyridones by appropriate substitution of the 4-pyridone ring.



1, R = H
3, R = $C(CH_3)_3$

2, R = H
4, R = $C(CH_3)_3$

Multiwavelength analysis of the ultraviolet spectrum of **1**–**2** in cyclohexane and chloroform at 10^{-7} and 10^{-5} M, respectively, shows an absorption attributable to the chromophore of **2** to be the only detectable species. If that result is expressed in terms of K_T for **1**–**2** a value >10 in favor of **2** is obtained. Such an equilibrium would be even further from the expected predominance of **1** than suggested by the recent work from East Anglia.[3,4]

Vapor-pressure osmometry of solutions of 4-pyridone in chloroform establishes that **2** is very strongly associated by hydrogen bonding. We find, for example, the modal association number of 4-pyridone at 0.049 M in chloroform to be 9. In fact, some years ago Coburn and Dudek suggested that 4-pyridone was a hydrogen-bonded trimer at ca. 10^{-3} M in chloroform.[5,6] If the association of 4-pyridone is analyzed as a statistical distribution of oligomers, an association free energy of −6.1 kcal/mol, an association constant of 30 000 ± 700, and the distribution of oligomers shown in Figure 1 may be derived from studies of molecular weight as a function of dilution. For this model <30% of the material would be monomeric under the conditions of the ultraviolet determination. Direct determination of the association in cyclohexane was precluded by limited solubility.

The 6.1 kcal/mol self-association energy of **2** in chloroform is clearly more than sufficient to dominate the position of protomeric equilibrium for **1**–**2** under the conditions reported. In fact this energy of hydrogen bonding is 1.5 kcal/mol stronger than for the dimerization of 2-pyridone in chloroform. The apparent position of protomeric equilibrium between 2-pyridone and 2-hydroxypyridine also has been shown to be determined by self-association in chloroform and cyclohexane under most conditions of measurement.[5–9] It is noteworthy that the association of 2-pyridone in cyclohexane is several kilocalories per mole stronger than in chloroform, a result which is taken to suggest that the apparent equilibrium for **1**–**2** is also dominated by association in cyclohexane.

These results again show the importance of correctly assessing the effect of molecular environment and association effects on molecular energies of protomeric systems.[1,2,7] Interpretation of equilibria determined on associated material

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