Table I. Hydroxylation of Aromatics with 30% H_2O_2 in HF/BF_3 at −78 °C

starting aromatic	% yield[a]	isomeric alkylphenol distribution,[b] %
benzene	37	
toluene	52	70 (2), 9 (3), 21 (4)
ethylbenzene	58	65 (2), 11 (3), 24 (4)
cumene	43	48 (2), 12 (3), 40 (4)
tert-butylbenzene	36	30 (2), 14 (3), 56 (4)
p-xylene	50	65 (2, 5), 35 (2, 4)
o-xylene	53	7 (2, 6), 66 (2, 3), 27 (3, 4)
mesitylene	41	100 (2, 4, 6)

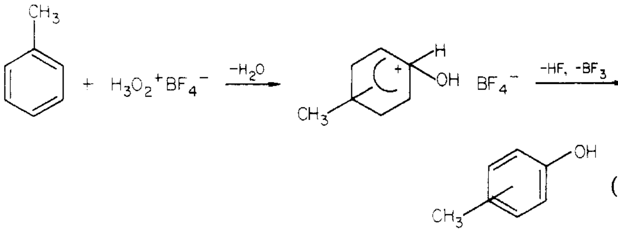
[a] Isolated yield based on aromatics. [b] Based on gas-liquid chromatographic analysis of trimethylsilylated phenolic products. Parentheses show the position of the substituents. The amount of dihydroxylated byproducts in all experiments was less than 1%, the limit of observation taking into account possible loss during silylation.

and acid recovery is feasible when needed. Data are summarized in Table I.

$$\mathrm{ArH} \xrightarrow[30\%\ \mathrm{H_2O_2}]{\mathrm{HF/BF_3}} \mathrm{ArOH} \qquad (1)$$

A probable mechanism of the reaction involves electrophilic hydroxylation of the aromatics by the hydroperoxonium ion (eq 2 and 3).

$$\mathrm{HOOH} + \mathrm{HF{-}BF_3} \rightarrow \mathrm{H_3O_2^+BF_4^-} \qquad (2)$$



(3)

For the monosubstituted alkylbenzenes, the ortho–para isomer ratio follows the predicted trend (from 3.33 for toluene to 0.54 for *tert*-butylbenzene) on consideration of the increasing steric hindrance to ortho substitution as a consequence of the increasing bulk of the alkyl group. The isomer ratios of hydroxyalkylbenzenes (shown in Table I) reflect the isomerizing ability of the superacidic $HF-BF_3$ system. *p*-Xylene also gives, besides the expected 2,5-dimethylphenol, the 2,4-product. Similarly, *o*-xylene also yields, besides the 3- and 4-hydroxylated products, some 2,6-dimethylphenol, indicative of methyl migration.

It is noteworthy to point out that polyhydroxylation is practically suppressed under the present reaction conditions because the phenols formed are protonated[8] by the superacid (HF/BF_3) and thus are deactivated against further electrophilic attack or secondary oxidation. As HF/BF_3 is readily handled, inexpensive, and recoverable, the method described represents a significant improvement in direct aromatic hydroxylation.

Experimental Section

To a vigorously stirred solution of the corresponding aromatic (0.1 mol) in HF (60 mL, saturated with BF_3) in a polyolefin or Teflon reaction flask is added dropwise a solution of 30% H_2O_2 (4.1 g, 0.125 mol; Mallinckrodt Co.) in HF/BF_3 (25 mL) by using a polyolefin or Teflon dropping funnel at −78 °C over a period of 20–25 min. The reaction mixture is then further saturated with BF_3 and stirred for an additional 30 min while the temperature is maintained at −60 °C by external cooling. Thereafter, the solution is carefully quenched with ice–water, extracted with ether, washed with 10% sodium bicarbonate solution to remove acid, and then extracted by 10% sodium hydroxide solution. No insoluble residue remained. Following acidification of the basic extract and extraction with ether, the organic layer is dried over mangesium sulfate and the solvent removed to yield crude phenolic product which is further puridied by distillation. Products were characterized by NMR and/or IR spectroscopy. The aliquots of the product were silylated by *N,O*-bis(trimethylsilyl)trifluoroacetamide (Pierce) and identified as the trimethylsilyl ethers by GLC. Gas chromatographic analyses were carried out by using a Varian Associates Model 3700 gas chromatograph equipped with an electronic intergator and using a 25 ft × 0.25 mm i.d. OV-101 glass capillary column coated with MBMA (*m*-diphenoxybenzene plus Apiezon L) and eluted with Helium. Gas chromatograph analysis was used to determine isomer ratios.

Acknowledgment. Support of our work by the National Science Foundation and the National Institute of Health is gratefully acknowledged.

Registry No. Benzene, 71-43-2; toluene, 108-88-3; 2-methylphenol, 95-48-7; 3-methylphenol, 108-39-4; 4-methylphenol, 106-44-5; ethylbenzene, 100-41-4; 2-ethylphenol, 90-00-6; 3-ethylphenol, 620-17-7; 4-ethylphenol, 123-07-9; cumene, 98-82-8; 2-(1-methylethyl)phenol, 88-69-7; 3-(1-methylethyl)phenol, 618-45-1; 4-(1-methylethyl)phenol, 99-89-8; *tert*-butylbenzene, 98-06-6; 2-(*tert*-butyl)phenol, 88-18-6; 3-(*tert*-butyl)phenol, 585-34-2; 4-(*tert*-butyl)phenol, 98-54-4; *p*-xylene, 106-42-3; 2,5-dimethylphenol, 95-87-4; 2,4-dimethylphenol, 105-67-9; *o*-xylene, 95-47-6; 2,6-dimethylphenol, 576-26-1; 2,3-dimethylphenol, 526-75-0; 3,4-dimethylphenol, 95-65-8; mesitylene, 108-67-8; 2,4,6-trimethylphenol, 527-60-6; phenol, 108-95-2; H_2O_2, 7722-84-1.

Direct Conversion of Alcohols to Alkanes

William W. Paudler* and Thomas E. Walton

Department of Chemistry, The University of Alabama, University, Alabama 35486

Received May 12, 1981

We have recently described the reaction of microcrystalline cellulose (ROH) with hydrogen and iodine and with hydrogen and hydrogen iodide.[1] These reactions afforded a number of alkanes and alkenes and represent an interesting conversion sequence for the generation of hydrocarbons from wood and other cellulosic materials.

In order to examine the general utility of these reactions, we elected to study them on monofunctional model compounds. Since the major reactivity of the microcrystalline cellulose must be associated with the presence of hydroxyl groups, and since the conversion of alcohols to alkyl iodides by HI are well-known, we studied these reactions on primary (*n*-butyl alcohol), secondary (cyclohexanol), and tertiary alcohols (*tert*-butyl alcohol).

It is well-known that hydrogen and iodine react to form HI in a thermally reversible manner (K_{eq} = 70 at 300 °C).[2] Thus, a priori, it is established that these conversions can involve any or all of the following inorganic species: H_2, I_2, HI.

When *n*-butyl alcohol was treated with molecular iodine in an atmosphere of hydrogen, at 1000 lb/in.^{2} and at 300 °C, a high yield of hydrocarbons was obtained. Gas chromatographic analyses in conjunction with mass spectroscopy and comparison with authentic samples established that the volatile products are composed of *n*-butane and isobutane, along with some propane (see Table I). A similar distribution of hydrocarbons is obtained

---

(1) (a) T. E. Walton and W. W. Paudler, *Fuel*, 1981, in press; (b) J. J. Th. M. Geerards, D. W. van Krevelen and H. I. Waterman, *Brennst.-Chem*,. 11 (*1958*).

(2) W. J. Moore, "Physical Chemistry", Prentice-Hall, Englewood, Cliffs, NJ, 1972, p 341.

J. Org. Chem. **1981**, *46*, 4307–4309

Table I. Formation of Alkanes from Alcohols and Alkyl Iodides

alkyl compd	% yield of alkanes	alkanes formed (% of total)
n-C_4H_9OH	60	*n*-C_4H_{10} (54), $(CH_3)_3CH$ (20), C_3H_8 (15)
n-C_4H_9I	60	*n*-C_4H_{10} (80), $(CH_3)_3CH$ (20)
cyclohexanol	40	cyclohexane (33), methylcyclopentane (66), dicyclohexane (1)
cyclohexyl iodide	66	cycohexane (50), methylcyclopentane (49), dicyclohexane (1)
tert-butyl alcohol	66	*n*-C_4H_{10} (54), $(CH_3)_3CH$ (20), 2,2,3,3-tetramethylbutane (2)

[a] Hydrogen pressure: 1000 lb/in.^{2} (7 MPa) at room temperature. Iodine to alcohol or alkyl iodide ratio, 5:1. Reaction temperature, 300 °C/2 h. The same products and distributions are obtained when glass-lined bombs are employed.

when *n*-butyl iodide is reacted with hydrogen gas only, under the above described reaction conditions. Thus, the primary step in the alcohol conversion is the formation of the alkyl iodide by this well-known reaction. The second step involves reduction of the alkyl iodide by means of molecular hydrogen concurrent with some carbon skeletal rearrangement. It is noteworthy that this reduction does *not* require the presence of any noble metal catalysts!

The reaction of cyclohexanol with molecular iodine and hydrogen at 1000 lb/in.^{2} (7 MPa) and at 300 °C affords cyclohexane and methylcyclopentane in excellent yield (see Table I). A similar mixture of these two hydrocarbons is obtained when iodocyclohexane is treated with hydrogen under the same experimental conditions.

The reaction of *tert*-butyl alcohol with I_2 and hydrogen under these conditions affords 2-methylpropane as the major product, along with some *n*-butane.

As we have already shown in the case of cellulose, the same reactions occur whether H_2 and I_2 and HI are employed in these reactions. This is, of course, in agreement with the presence of the $H_2 + I_2 = 2HI$ equilibrium, where $K_{eq} = 900$ at room temperature and $K_{eq} = 70$ at 300 °C. The individual reactions that must be involved in these transformations are the following:

$$H_2 + I_2 = 2HI$$

$$ROH + HI = RI$$

$$RI + H_2 = RH + HI$$

The net reaction, a summation of these three, is

$$ROH + H_2 = RH + H_2O$$

Consequently, iodine, whether in its molecular form or present as HI, becomes simply a catalyst in these reactions. This is confirmed experimentally by the fact that in all of these reactions, the molar ratio of alcohol or alkyl iodide to molecular iodine is, *at least*, 5:1.

While there is no question regarding the ionic nature of the initial reaction (formation of the alkyl iodines), the reduction of the alkyl iodides, which is accompanied by some carbon-skeletal rearrangements, will require detailed mechanistic studies.

Initially, we have established that products resulting from free radical dimerizations, dicyclohexane and 2,2,3,3-tetramethylbutane in the cyclohexanol and *tert*-butyl alcohol conversions, respectively, are also formed in these reactions.

These initial studies have established that *alcohols can be converted to hydrocarbons in an overall one-step process, employing inexpensive and recoverable reagents.*

Experimental Section

The reactant and iodine (in the case of alcohols only) were placed in a 500-mL parr bomb (Type 316 stainless steel, Model 4001). The bomb was sealed and flushed 3 times with hydrogen. The bomb was then pressurized to approximately 1000 at 25 °C and placed into a preheated furnace and allowed to attain the desired temperature. It was kept at this temperature for 2 h. With the bomb at the reaction temperature, it was vented through a bubbler containing water (to trap any hydrogen iodide), and the more volatile products were condensed in a preweighed vessel cooled to liquid nitrogen temperature (the weight of the volatiles was thus determined). The bomb was then removed from the furnace, cooled to room temperature, and washed sequentially with water, thiosulfate solution, and acetone or methylene chloride. The organic fraction was filtered and dried over anhydrous sodium sulfate, and the solvent was evaporated, leaving the less volatile products.

Both fractions were analyzed by a HP 5985 A gas chromatography/mss spectrometry (GC/MS) system, using a glass capillary 80-m, SE54 column: inlet split, 21/1; carrier gas, helium; flow rate, 31 cm/s; injector and interface temperature, 260 °C; ion source temperature, 200 °C; and GC program, injected at 50 °C, 20 °C/min to 90 °C and then 2 °C/min to 250 °C. The availability of a computerized mass spectral data search system facilitated the identification of compounds. The more common compounds were verified by comparative GC/MS analysis. Table I lists the various analytical data thus obtained. The maximum pressures attained at the elevated experimental temperatures were 2000 lb/in.^{2} (14 MPa).

Acknowledgment. We thank the University of Alabama School of Mines and Energy Development for initial support of this work.

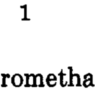
Reaction of Di-*tert*-butyl Nitroxide with Methyl Trifluoromethanesulfonate. Unexpected Formation of *N*-*tert*-Butylhydroxylamine Radical Cation in Trifluoromethanesulfonic Acid

Robert J. Smith and Richard M. Pagni*

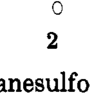
Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37916

Received April 29, 1981

It is well-known that nitroxides (RR′N–O·) can function as weak bases.[1] Can they also function as nucleophiles in S_N2 reactions? In pursuit of this goal, we studied the reaction of di-*tert*-butyl nitroxide (1) with the highly reactive methyl trifluoromethanesulfonate (2). Because of the recent interest in the chemical behavior of nitroxides,[2]



1



$CH_3OS(=O)_2CF_3$

2

---

[1] (a) Malatesta, V.; Ingold, K. U. *J. Am. Chem. Soc.* **1973**, *95*, 6404. (b) Hoffman, B. M.; Eames, T. B. *Ibid.* **1969**, *91*, 2169. (c) Hoffman, B. M.; Eames, T. B. *Ibid.* **1969**, *91*, 8168.

[2] (a) Aurich, H. G.; Weiss, W. *Top. Curr. Chem.* **1975**, *59*, 65. (b) Scott, A. C.; Tedder, J. M. *J. Chem. Soc., Perkin Trans, 2* **1980**, 260. (c) Singh, H.; Tedder, J. M. *ibid.* **1980**, 1259. (d) Singh, H.; Tedder, J. M. *J. Chem. Soc., Chem. Commun.* **1980**, 1095. (e) Singh, H.; Tedder, J. M.; *Ibid.* 1981, 70. (f) Moad, G.; Rizzardo, E.; Solomon, D. H. *Tetrahedron Let.* 1981, 1165.

0022-3263/81/1946-4307$01.25/0