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

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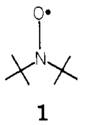
Received April 29, 1981

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]



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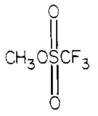

$CH_3O\overset{O}{\underset{O}{S}}CF_3$

2

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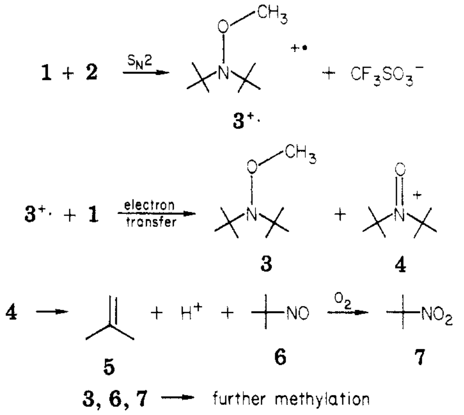
(1) (a) Malatesta, V.; Ingold, K. U. *J. Am. Chem. Soc.* **1973**, *95*, 6404. (b) Hoffman, B. M.; Eames, T. B. *Ibid.* **1969**, *91*, 2169. (c) Hoffman, B. M.; Eames, T. B. *Ibid.* **1969**, *91*, 8168.

(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

Scheme I



we report some of our results at this time.

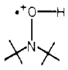
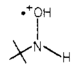
When **2** was mixed with **1**, either neat or in benzene solution, ESR studies on the brilliant blue solution(s) showed only the nitroxide **1** when **1** was in excess and no paramagnetic species when **2** was in excess. By UV–vis, GC/MS, and ^1H NMR spectroscopies, isobutene (**5**), 2-methyl-2-nitrosopropane (**6**), and 2-methyl-2-nitropropane (**7**) were identified as products of the reaction.[3] On the basis of these limited observations, the anticipated S_N2 character of the initial reaction between **1** and **2**, and the fact that anodic oxidation of **1** is known to yield **5** and **6** via the oxoammonium ion **4**,[4] one can write the plausible mechanism shown in Scheme I.

Clearly it would be difficult to prove the mechanism for a reaction so complex. If one could detect $3^{+\cdot}$ by ESR spectroscopy during the course of the reaction between **1** and **2**, however, this observation would at least constitute evidence for the viability of the above scheme. Because nonaqueous acids are known to stabilize radical cations,[5] we repeated the reaction of **1** and **2** in several nonaqueous acids in hopes of observing $3^{+\cdot}$. The results of these experiments are shown in Table I.

It is quite clear from the results shown in Table I that $3^{+\cdot}$ is not observed in any of the reactions. Either it is not produced in a given reaction or it has only a transitory existence. Nonetheless, quite interesting and unexpected results were observed in triflic acid (CF_3SO_3H). In the acid alone, a six-line ESR spectrum belonging to protonated **1** (**8**) (a_N = 22 G, a_H = 3.2 G) was observed; this is similar to the results of Malatesta and Ingold in other acid media.[1a] Addition of **2** to this solution had no apparent effect on the reaction; only **8** was observed here. On the other hand, when **1** was added to a mixture of **2** and triflic acid, the ESR spectrum of the resulting solution showed, in addition to the six lines belonging to **8**, 12 other lines of equal intensity.[6,7] Whatever is occurring, it is clear that a reaction involving **2** with **1** can compete with the protonation of **1**.

If the new paramagnetic species yields only these 12 lines in the ESR spectrum, this species is assigned structure **9** with a_N = 21.0 G, a_{NH} = 28.5 G, and a_{OH} = 3 G. If, on the other hand, there are six additional lines hidden under those belonging to **8**, a species with a_N = 21 G, a_N = 14 G, and a_H = 3 G will yield a spectrum which fits the experimental one satisfactorily. The following demonstrates that **9** is the new radical cation yielding the ESR spectrum. First, the a_N/a_{NH} ratio for neutral hydronitroxides is solvent dependent;[8] the value of 0.74 observed here is reasonable for structure **9** in triflic acid. Second, it is difficult to see how a paramagnetic species with two nonequivalent nitrogens can be generated in this reaction. Third, if one were to repeat the reaction in CF_3SO_3D, the ESR spectrum, be it due to **9** or some other species, will change in a predictable fashion. The results of the reaction in CF_3SO_3D were in complete accord with that expected for **9**[9] and not in accord with that for the other species.

Table I. Addition of 1 to Nonaqueous Acids with and without 2

	component(s) observed[a,c]			
addition of **2** to	**1**	**6**	 **8**	 **9**
CH_3COOH[b]	X			
CH_3COOH, then add **2**		X		
CF_3COOH[d]		X		
CF_3SO_3H			X	
CF_3SO_3H, then add **2**			X	
CF_3SO_3H/**2**[e]			X	X
FSO_3H/**2**[e]			X	
100% magic acid/**2**[e,f]			X	

[a] **1**, **8**, and **9** were identified by ESR, while **6** was characterized by UV–vis. [b] Results were identical with those reported in ref 1a. [c] X indicates the component(s) observed in a given case. [d] Neither here nor in ref 1a was **1** observed; we did detect **5**. [e] **1** is added to a mixture of **2** and the appropriate acid. [f] Magic acid is a 1:1 mixture of FSO_3H and SbF_5.

To the best of our knowledge the ESR spectrum of **9** has never been reported before. It is doubtful, in fact, if one could have prepared this species for ESR study by a rational method.[10] These results demonstrate again that the chemical behavior of nitroxides can be complex. The nucleophilic character of nitroxides still remains to be proven.

Experimental Section

General Comments. ^1H NMR spectra were recorded on Varian T60A and HA-100 spectrometers. ESR spectra were recorded on a Varian 112 spectrometer on thoroughly degassed

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[3] ^1H NMR and GC/MS indicated the presence of other components.

[4] Sayo, H.; Shigeko, O.; Masui, M. *Chem. Pharm. Bull.* **1973**, *21*, 1988.

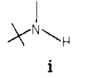
[5] Band, A. J.; Ledwith, A.; Shine, H. J. *Adv. Phys. Org. Chem.* **1970**, *13*, 155.

[6] Compound **8** is present in approximately twice the concentration of the new species.

[7] The spectrum of **8** in CF_3SO_3H is sharper than it is in $CF_3SO_3H/2$.

[8] Wajer, T. A. J. W.; Mackor, A.; deBoer, T. J. *Tetrahedron* **1969**, *25*, 175. (b) Stout, G.; Engherts, J. B. F. N. *J. Org. Chem.* **1974**, *39*, 3800.

[9] Structure i would also be in accord with the ESR spectrum if only one of the three methyl hydrogens couples to the odd electron. This is quite unreasonable here.



i

[10] (a) *tert*-Butyl nitroxide, the obvious precursor to **9**, has been prepared in several nonacidic solvents by oxidation of *tert*-butylhydroxylamine[8b,11a] and reduction of 2-nitroso-2-methylpropane.[8a,11b] Because of the lability of the nitroxide[11] it is doubtful if one could remove the solvent and transfer the nitroxide to acid. Furthermore, it is unlikely that one could generate **9** directly in the acid from *tert*-butylhydroxylamine or 2-nitroso-2-methylpropane. These latter compounds likely would not survive in acid. (b) The mechanism by which **9** is generated in this reaction is unclear. One can write several.

[11] (a) Bowman, D. F.; Brokenshire, J. L.; Gillan, T.; Ingold, K. U.; *J. Am. Chem. Soc.* **1971**, *93*, 6551. (b) Perkins, M. J.; Ward, P.; Horsfield, A. *J. Chem. Soc. B* **1970**, 395.

samples. UV–visible spectra were recorded on a Cary 17 spectrometer. Gas chromatography/mass spectrometry was performed on a Hewlett-Packard 5980A instrument using an OVM-1 column. Some difficulty was encountered in the GC/MS experiments because **1** decomposes in the instrument. Best results were obtained with the injector at 100 °C and temperature programming from 40 to 130 °C at 8 °C/min. Mass spectra were recorded on both the reaction of **1** and **2** as well as for **1** alone. The reaction mixture gave four peaks in addition to those observed for **1** alone. Two of these components are isobutene (**5**) and unreacted methyl trifluoromethanesulfonate (**2**); the other two components are unidentified but gave their largest mass peaks at *m/e* 72 and 89, respectively.

Compounds. Di-*tert*-butyl nitroxide (**1**) and methyl trifluoromethanesulfonate (**2**) were commercial compounds and used as received. 2-Methyl-2-nitrosopropane (**6**) and CF_3SO_3D were synthesized as shown below.

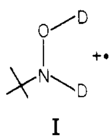
2-Methyl-2-nitrosopropane (6). Compound **6** was prepared by a modification of the method of Stowell.[12] A solution of *tert*-butylamine (1 mol) and sodium tungstate ($Na_2WO_4 \cdot 2H_2O$, 8 g) in 100 mL of water was cooled in an ice/brine bath. Hydrogen peroxide solution (206 mL of 30% H_2O_2 plus 100 mL of H_2O) was added dropwise with stirring at a rate that maintained the temperature below 25 °C. A blue-green layer was seen to form on top of the aqueous layer. After the addition of all the peroxide, the literature procedure was modified slightly. Attempts to work up the reaction by Stowell's method led to large mechanical losses as the blue monomer dimerized, coating the apparatus with a white solid. To avoid this, we extracted the reaction mixture with several portions of 100–115 °C ligroine. Distillation of the combined extracts gave a brilliant blue liquid (bp 50 °C) which turned to white needles upon cooling. Care must be taken that the dimerization product (the needles) does not clog the distillation apparatus. The modified procedure gave a slightly better yield (26%) than reported by Stowell.

The compound gave a UV-vis value for λ_{max} of 677 nm. This band was used to characterize **6** which is produced in the reaction of **1** and **2**.

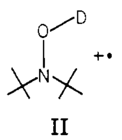
Trifluoromethanesulfonic Acid-*d*. (a) Trifluoromethanesulfonic anhydride (triflic anhydride) was prepared by dehydration of triflic acid. A 100-mL flask was charged with fresh, anhydrous P_2O_5 (25 g) and triflic acid (20 mL) and stirred for 1 h. The flask was then equipped for distillation over a short Vigreux column, and 11–12 mL (ca. 19 g) of anhydride was distilled; bp 82–83.5 °C [lit. bp 81–83 °C (745 mm)]. The anhydride was sealed in glass ampules under Ar until needed.

(b) CF_3SO_3D was produced by reaction of triflic anhydride with D_2O. Triflic anhydride (11 mL, 0.03 mol) and D_2O (0.59 g, 0.03 mol) were placed in a heavy-walled Pyrex tube which was cooled and sealed. The tube was placed in a 100 °C oil bath overnight, or until two phases were no longer visible. The tube was cooled and opened, and the contents were distilled; bp 164–164.7 °C. Mass spectrometry showed the product to be free of D_2O, H_2O, and the protic acid.

Reaction of 1 with CF_3SO_3D/2. ESR Study. If **9** is the correct structure for the new paramagnetic species produced in the reaction of **1** with CF_3SO_3D, the ESR spectrum of the corresponding species (I) produced in CF_3SO_3D will lie under the spectrum of II.[13] If, on the other hand, the paramagnetic species had $a_N = 21$ G, $a_N = 14$ G, and $a_H = 3$ G, many of the lines for the corresponding deuterated species would not lie under those for II. Although not well resolved, only three broad signals were observed. Lines attributable to the latter paramagnetic species, resolved or not, would have been easily detected outside the domain of the three broad signals; these lines were not observed.[14] Thus, **9** is consistent with the ESR spectrum and the other species is not.



I



II

Acknowledgment. R.J.S. thanks the Gulf Oil Co. for fellowship support.

Registry No. 1, 2406-25-9; **2**, 333-27-7; **6**, 917-95-3; **8**, 78698-38-1; **9**, 78698-39-2.

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[12] Stowell, J. C. *J. Org. Chem.* **1971**, *36*, 3055.

[13] For a discussion of how one can calculate the ESR spectrum of a deuterated species if the ESR spectrum of the protio species is known, see: Wertz, J. E.; Bolton, J. R. "Electron Spin Resonance"; McGraw-Hill: New York, 1972.

[14] For a detailed discussion and analysis of these points see: Smith, R. J.; Ph.D. Dissertation, University of Tennessee, 1980.

On Some Guaiol Oxidation Products[1]

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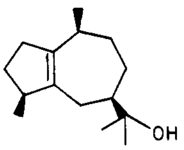
Oxidation of the sesquiterpene alcohol guaiol (I) with potassium permanganate was first described by Semmler and Mayer in 1912.[4] Nearly 30 years later, Ruzicka and Haagen-Smit reinvestigated this reaction[5] and determined the correct composition of the high-melting (220 °C) reaction product. Furthermore, they demonstrated that it was also formed on ozonolysis of guaiol.[5] Its structure, as the ketol II, was finally deduced by Plattner and Magyar inter alia by conversion to cadalene.[6] These workers suggested that diketone III was an intermediate in the formation of II, and thus oxidative degradation of guaiol became an important part in the proof its structure. More recently, Takeda and Minato obtained triol IV from I and oxidatively transformed it to II.[7] Also, Nadgouda et al. have reported[8] the conversion of diketone III to ketol II under basic conditions. Thus the reaction sequence I → IV → III → II apears justified.



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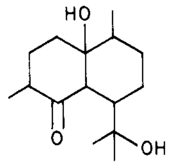

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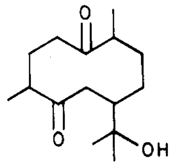
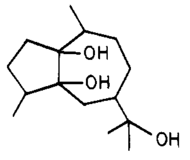


III



IV

Our interest in these reactions had two initial objectives: (i) to develop a preparative method for obtaining ketol II and if possible diketone III and (ii) to determine the stereochemistry of the guaiol oxidation products. In this

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[1] Portions of this work were presented at the 15th Midwest Regional Meeting of the American Chemical Society, St. Louis, MO, Oct 1979.

[2] Taken in part from the dissertation submitted by R.J.Z. in partial fulfillment of requirements for the MS (Chem) degree, University of Missouri—St. Louis, Dec 1978.

[3] NSF Undergraduate Research Participant, Summer 1979.

[4] Semmler, F. W.; Mayer, E. W. *Chem. Ber.* **1912**, *45*, 1391–97.

[5] Ruzicka, L.; Haagen-Smit, A. J. *Helv. Chim. Acta* **1931**, *14*, 1122–32.

[6] Plattner, P. A.; Magyar, G. *Helv. Chim. Acta* **1941**, *24*, 191–7.

[7] Takeda, K.; Minato, H. *Chem.* Pharm. *Bull* **1961**, *9*, 619–25.

[8] Nadgouda, S. A.; Trivedi, G. K.; Bhattacharyya, S. C. *Indian J. Chem., Sect. B.* **1978**, *16B*, 205–6.

0022-3263/81/1946-4309$01.25/0