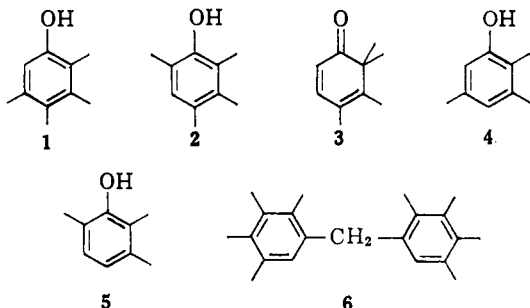


to phenols and quinones in low yield.⁴ We reasoned that coordination of a Lewis acid with an organic peracid might facilitate departure of ionic electrophilic hydroxyl from the latter and furnish a potent oxidant under mild conditions.

This communication reports preliminary results on the use of peroxytrifluoroacetic acid with boron fluoride as a source of positive hydroxyl. Mesitylene was converted directly and rapidly to mesitol in 88% yield, with efficient use of the peracid.⁵ Similarly, isodurene gave isodurenenol in 62% yield (one experiment).

Extension of the reaction to prehnitene gave, in addition to the expected 2,3,4,5-tetramethylphenol (1), a number of other products (2-6) which reveal the potency of the reactive intermediate formed by this



reagent.⁶⁻⁹ Attack of OH^+ at a vacant ring position furnishes 1 (9.0%). Similar attack at C-1, followed by a methyl shift, accounts for 2 (3.6%) and 3 (1.8%).¹⁰ The tarry residue (about 27%), which showed no aromatic protons in the n.m.r. and strong $\text{C}=\text{O}$ and $\text{C}=\text{C}$ absorption (bands at 1634, 1661, 1695, 1736 and 1750 cm^{-1}), probably contains dimer or polymer from 3 and analogous cyclohexadienones from attack of OH^+ at C-2.

The remaining products (which account for a major fraction of the prehnitene consumed) either lack (4 and 5) or have an extra (6) carbon atom. Complete absence of trimethylbenzenes and of isomeric trimethylphenols suggests that 4 and 5 arise from loss of the *para* methyl group of 1 and 2, respectively, according to the scheme shown (for 1).¹¹

(4) J. D. McClure and P. H. Williams, *J. Org. Chem.*, **27**, 24 (1962). It was, however, effective in the Baeyer-Villiger conversion of ketones to esters.

(5) Although the yield when boron fluoride is omitted is reasonably good,¹ the conversion is very poor.

(6) Identification of the products, which were isolated by a combination of distillation and chromatographic techniques, will be described in a full account. All are previously known except 3, whose structure is based on a satisfactory analysis of its 2,4-dinitrophenylhydrazone, m.p. 153-156°, and on its spectra. In carbon tetrachloride, 3 had bands at 1663 and 1630 cm^{-1} , and in ethanol it had λ_{max} 327 $\text{m}\mu$ ($\log \epsilon$ 3.48), which compare favorably with suitable models.⁹ Its n.m.r. spectrum in carbon tetrachloride showed singlets at 8.85 and 8.15 τ , corresponding to six protons each, and doublets at 4.19 and 3.15 τ ($J = 19$ c.p.s.) each corresponding to a single proton.

(7) When the reaction was repeated with boron fluoride, but without the peracid, prehnitene was recovered (94%) unchanged. Study of the reverse conditions (peracid but no boron fluoride) will be reported in a full account.

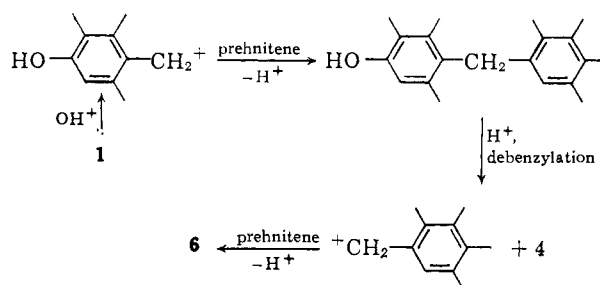
(8) For simplicity, this intermediate will be referred to as OH^+ .

(9) See L. Mandell, D. Caine and G. E. Kilpatrick, *J. Am. Chem. Soc.*, **83**, 4457 (1961), and leading earlier references therein.

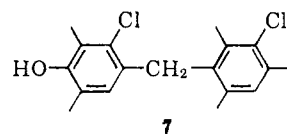
(10) The formation of a cyclohexadienone from 2,6-dimethylphenol and peroxytrifluoroacetic acid³ is not strictly analogous to the present reaction, since the potential ketonic oxygen was already present in the aromatic substrate. The hydrogen bonding invoked to rationalize the product in ref. 3 is not possible here.

(11) This mechanism requires that the sum of moles of 4 and 5 equal the yield of 6. In fact, from 0.0332 mole of prehnitene consumed, there was obtained 0.0048 mole of 4, 0.0017 mole of 5 and 0.0039 mole of 6. The sum of 4 and 5 is too large, but the yield of these products was determined from v.p.c. curves, whereas that of 6 is of isolated, purified crystalline product and is probably low.

The material balance accounted for 85% of the prehnitene consumed; it is unlikely that any significant products with low molecular weights (under 200) were missed.



Consistent with this scheme is the isolation of 7 as the major product from the reaction of our reagent with



chloromesitylene.¹² The chlorine apparently does not prevent the hydride abstraction, but does inhibit the debenzylation. Nitromesitylene gave a product similar to 7.

Typical of the experimental procedure is the following preparation of mesitol. To a solution of 56.1 g. (0.468 mole) of mesitylene¹³ in 100 ml. of methylene chloride was added peroxytrifluoroacetic acid prepared from 35 g. (0.167 mole) of trifluoroacetic anhydride, 50 ml. of methylene chloride and 4 ml. (0.148 mole) of 90% hydrogen peroxide.¹⁴ Boron fluoride was bubbled through the reaction mixture during the addition, which required 2.5 hr. The reaction was strongly exothermic, and the temperature was kept below 7° by external cooling.¹⁵ After addition was complete, water was added and the organic layer was washed with bisulfite and bicarbonate, dried and distilled. There was obtained 32.0 g. of unchanged mesitylene and 17.7 g. (88%) of mesitol, m.p. 69-70°.

Acknowledgment.—We are grateful to the Petroleum Research Fund of the American Chemical Society for financial support (G-488C).

(12) The structure of 7, m.p. 142.5-143.5°, is based on a satisfactory analysis, hydroxyl at 3535 cm^{-1} , n.m.r. and mass spectra consistent with the structure, and reduction to products with one or both chlorines removed. We are indebted to Mr. S. Meyerson, American Oil Company, Whiting, Indiana, for mass spectral data and interpretation for 6 and 7.

(13) Excess hydrocarbon reduces further oxidation of the primary product.

(14) The peracid was prepared by mixing the reagents at 0°, then allowing them to warm to room temperature.

(15) If boron fluoride was omitted, the reaction was much less exothermic and gave mesitol in 47% yield based on peracid; this is, nevertheless, an appreciable improvement over the earlier¹ procedure.

(16) National Science Foundation Cooperative Fellow, 1962-1963.

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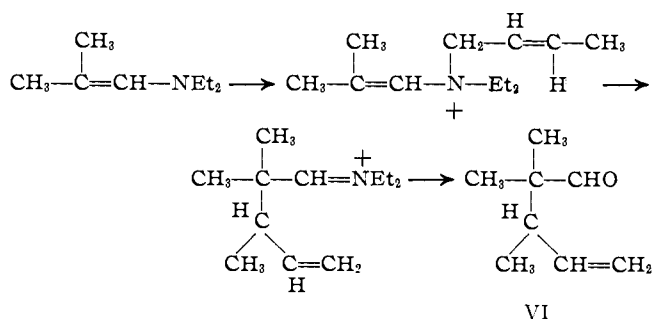
RECEIVED MAY 16, 1963

A New Method for the Alkylation of Ketones and Aldehydes: the C-Alkylation of the Magnesium Salts of N-Substituted Imines

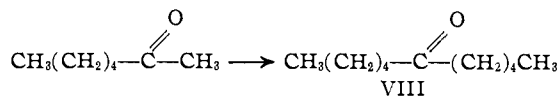
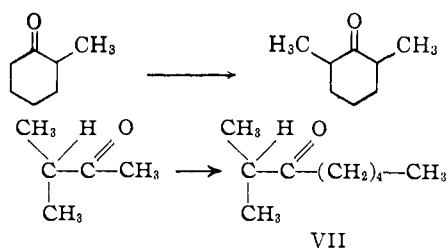
Sir:

The difficulties involved in monoalkylating ketones and aldehydes are well known. As we have pointed out in a previous communication,¹ the enamine alkylation procedure which was devised to circumvent some of these difficulties is general only with electrophilic olefins (conjugated ketones, esters, nitriles, etc.). With alkyl halides, however, it has turned out that although

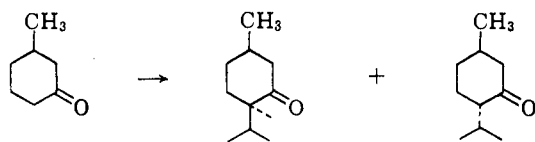
(1) G. Stork, A. Brizzolarra, H. Landesman, J. Szmuszko and R. Terrell, *J. Am. Chem. Soc.*, **85**, 207 (1963).



(5) The reaction normally introduces the new alkyl group on the less alkylated side of an unsymmetrical ketone.¹⁰ The magnesium salt of the cyclohexylimine of 2-methylcyclohexanone reacted with methyl iodide to give an 83% yield of 2,6-dimethylcyclohexanone. Alkylation on the less substituted side applies even to *methyl* alkyl ketones. Methyl isopropyl ketone gave, by the imine-magnesium salt method, with butyl iodide, 70% of 2-methyl-3-octanone (VII). Again, the major product from 2-heptanone was 6-undecanone (VIII).



Alkyl groups further removed from the carbonyl than the α -carbon atoms would not be expected to exert as profound a directing influence, but an experiment is worthy of note in this respect. Alkylation of the cyclohexylimine from 3-methylcyclohexanone with isopropyl iodide, by the usual procedure, followed by acid hydrolysis of the alkylated imine, gave 61% of the equilibrium mixture of *dl*-menthone and isomenthone.



(10) The reason for the direction of alkylation as well as for the monoalkylation of the imine salts is of the same type as we have discussed in the case of enamines, *cf.* ref. 1.

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SUSAN R. DOWD

RECEIVED MAY 31, 1963

Selective Catalytic Dehydration of 2-Alcohols; a New Synthesis of 1-Olefins

Sir:

Vapor phase dehydrations of 2-butanol and 2-pentanol catalyzed by alumina yield mixtures of olefins rich in the 2-olefin.¹ Numerous other metal oxide catalyzed dehydrations have been reported to give similar product distributions.² Mechanisms proposed

for dehydrations catalyzed by alumina and similar catalysts involve oxonium ion and carbonium ion intermediates or transition states.^{1,2}

We have observed that thoria and other oxides of group IIIB elements catalyze the dehydration of secondary 2-alcohols to yield 1-olefins as the major products. Representative examples are listed in Table I.

TABLE I
THORIA-CATALYZED DEHYDRATION OF 2-ALCOHOLS

Alcohol	Products % ^a	
	1-Olefin	2-Olefin
2-Butanol	93	7
2-Octanol	95-97	3-5
4-Methyl-2-pentanol	96-98	2-4
1-Cyclohexyl-1-ethanol	96-98	2-4

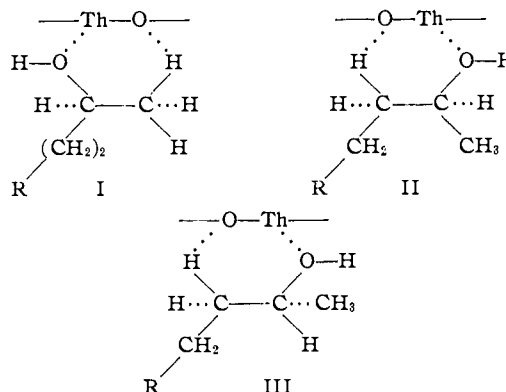
^a A small but erratic yield of ketone (1-6%) arising from competing dehydrogenation is not included in these calculations. Yields are based on consumed alcohol (excluding ketone). Conversions of 20-90% were obtained.

These experiments were conducted in a flow system at 350-450° with contact times of 0.1 to 0.5 sec. Products were separated by distillation and analyzed by gas chromatography,³ infrared and n.m.r. spectroscopy.

The most active and selective thoria catalysts we have obtained were prepared by calcining thorium oxalate at 350-450° for a few hours.⁴ However, thoria catalysts with equal selectivity, although with somewhat less activity, have been prepared from the acetate and carbonate. Sixteen other oxides of group IIIB elements were tested briefly as selective dehydration catalysts. In most examples studied the 1-olefin comprised 90% and often over 95% of the olefins produced. Little significance is attached to these differences at present since impurities or methods of catalyst preparation could be of major importance.⁵ The oxides of W, Mo, Ti, Zr and Al were found not to be selective dehydration catalysts, in agreement with published results.²

While the efficiency of rare earth oxides as dehydration catalysts has long been known, the general and remarkably specific nature of this dehydration has not been recognized previously. Thoria has been used to prepare butadiene by the dehydration of 2,3-butane-1,2-diol.⁴ Alumina-catalyzed dehydration of 2,3-butane-1,2-diol yielded chiefly methyl ethyl ketone.

We suggest that the mechanism of selective dehydration involves concerted elimination of the elements of water. This requires the alcohol to be chemisorbed on the catalyst surface in the conformations I-III. Complexes or transition states II and III are expected



(3) Silver nitrate-tetraethylene glycol, Carbowax or tricresyl phosphate on inert supports were used in g.l.c. analysis.

(4) M. E. Winfield, *J. Council Sci. Ind. Res. Australia*, **18**, 412 (1945).

(1) H. Pines and W. O. Haag, *J. Am. Chem. Soc.*, **83**, 2847 (1961).

(2) M. E. Winfield, "Catalytic Dehydration and Hydration," in "Catalysis," Vol. IV, P. H. Emmett, Ed., Reinhold Publ. Corp., New York, N. Y. 1960, pp. 93-182.

(5) Passage of a pure 1-olefin over the best catalysts under dehydration conditions resulted in 1-2% isomerization to the 2-isomer.