Primary, secondary and tertiary alcohols can be easily distinguished due to their reactivity towards tribromoisocyanuric acid (TBCA). The test is performed by adding TBCA to the alcohol in a test tube heated in a boiling water bath. Orange color develops in the tube containing the primary alcohol, light yellow is observed in the tube containing the secondary alcohol while the tertiary alcohol results in a colorless mixture.

Keywords: tribromoisocyanuric acid; alcohols; spot test.

INTRODUCTION

Although spectroscopic methods are capable of differentiating primary, secondary and tertiary alcohols, the use of chemical methods for this purpose is still of great value, as these techniques are cheaper and of easier access to organic chemists. Among the chemical tests used in the differentiation of alcohols, the Lucas,\(^1,2\) chromic acid,\(^1,2\) xanthate\(^3,4\) and vanadium oxinate\(^4\) tests are the most employed for this purpose. However, some disadvantages, such as the toxic compounds involved, e.g. Cr(VI) salts in the chromic acid test and carbon disulfide in the xanthate test, and the need for more than one test for the differentiation of the three classes of alcohols, as shown in Figure 1, prompts the search for new alternatives.

RESULTS AND DISCUSSION

The test to distinguish the alcohols was performed in 3 different test tubes containing about 8 drops of a primary (butanol), a secondary (sec-butanol) and a tertiary (tert-butanol) alcohol, respectively. Approximately 20 mg of TBCA was added to each tube containing the alcohols and after 2 min in a boiling water bath an orange color develops in the tube containing the primary alcohol, light yellow is observed in the tube containing the secondary alcohol while the tertiary alcohol results in a colorless mixture (Figure 3). It was found that the test requires the use of excess alcohol to perform the differentiation among the different colors.

In 1997, Hiegel and Chaharmohal developed a new method for the differentiation of primary and secondary alcohols based on the rate of oxidation of trichloroisocyanuric acid (TCCA, Figure 2) and formation of a precipitate of cyanuric acid.\(^5,6\) According to the authors, secondary alcohols react faster than primary alcohols with TCCA in acid solution of acetonitrile.

In this study, a spot test for distinguishing alcohols was developed based on the oxidation reaction of alcohols by tribromoisocyanuric acid (TBCA, Figure 2). This reagent is an easily handled white solid that can be safely prepared from isocyanuric acid.\(^7\)

**Figure 1.** Testing scheme for the differentiation of alcohols

**Figure 2.** Structures of trichloroisocyanuric (TCCA) and tribromoisocyanuric (TBCA) acids

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alcohols (Table 2 and Figure 1S, supplementary material) obtaining results consistent with the previous ones.

The utility of the test for solid alcohols was evaluated by solubilizing them in 1 mL of hexane. The solution was then poured into the test tube containing 20 mg of TBCA. In this case, the color development was found to be slow, requiring 20 min for completion. Furthermore, in the case of secondary alcohols, the test initially resulted in a yellow color in the same manner as the secondary liquid alcohols, but in the end the liquid became colorless. This phenomenon is probably due to long heating time.

Unsaturated alcohols (Figure 4) led to ambiguous results because there was no change in color of the liquid, which behaved similarly to tertiary alcohols. Thus, the TBCA cannot be employed for these cases. This result is possibly due to the reaction of TBCA with the unsaturated function groups (alkenes, alkynes, etc.) leading to bromine consumption.

Figure 4. Unsaturated alcohols tested

It was observed by following the reaction using 1H, 13C NMR and GC-MS that butanol, in the presence of TBCA, generates butyl butyrate as the major product. The analysis of the reaction by UV-Vis showed that the staining observed was due to the formation of Br2 in the reaction system. To confirm this, the reaction of butanol with TBCA in a water bath was repeated and, after 2 min, cyclohexene was added to the reaction medium and an immediate bleaching of the mixture was observed. Analysis by GC-MS revealed the presence of 1,2-dibromocyclohexane among the products, confirming the in situ formation of Br2.

A similar study using sec-butanol with TBCA showed the formation of 2-butanone as the main product. By monitoring the reaction by UV-Vis it was found that the coloration was again due to formation of Br2 and it was observed that bleaching occurs for the formation of a-bromo-butanone, as disclosed by GC-MS.

The results suggest that the primary alcohol is oxidized to its respective aldehyde and ester with concomitant Br2 formation, which produces orange staining in the reaction medium (Scheme 1).

Table 1. Spot test of differentiation of alcohols diluted in different solvents (1 mL)

<table>
<thead>
<tr>
<th>Solvent</th>
<th>t (min)</th>
<th>(-\text{OH})</th>
<th>(-\text{OH})</th>
<th>(-\text{OH})</th>
</tr>
</thead>
<tbody>
<tr>
<td>hexane</td>
<td>5</td>
<td>orange</td>
<td>light yellow</td>
<td>colorless</td>
</tr>
<tr>
<td>ethyl acetate</td>
<td>15</td>
<td>dark yellow</td>
<td>light yellow</td>
<td>colorless</td>
</tr>
<tr>
<td>acetonitrile</td>
<td>10</td>
<td>dark yellow</td>
<td>light yellow</td>
<td>colorless</td>
</tr>
<tr>
<td>methylene dichloride</td>
<td>10</td>
<td>orange</td>
<td>light yellow</td>
<td>colorless</td>
</tr>
<tr>
<td>butylamine</td>
<td>10</td>
<td>cloudy</td>
<td>cloudy</td>
<td>cloudy</td>
</tr>
<tr>
<td>butylamine *</td>
<td>10</td>
<td>cloudy</td>
<td>cloudy</td>
<td>cloudy</td>
</tr>
<tr>
<td>ethyl ether</td>
<td>10</td>
<td>orange</td>
<td>light yellow</td>
<td>light yellow</td>
</tr>
<tr>
<td>ethyl ether *</td>
<td>10</td>
<td>dark yellow</td>
<td>light yellow</td>
<td>colorless</td>
</tr>
<tr>
<td>acetone</td>
<td>2</td>
<td>colorless</td>
<td>colorless</td>
<td>colorless</td>
</tr>
<tr>
<td>acetone*</td>
<td>5</td>
<td>dark yellow</td>
<td>light yellow</td>
<td>colorless</td>
</tr>
</tbody>
</table>

*8 drops
Crespo et al. (2005) demonstrated that the α-bromo-ketone, the reaction leading to a light yellow or colorless mixture (depending on whether consumption of Br₂ was partial or total) (Scheme 2).

**CONCLUSION**

The use TBCA in the differentiation of primary, secondary and tertiary alcohols proved to be a straightforward and practical test for laboratory use. The different colors are due to the different reactivities of the alcohols with TBCA. TBCA in the presence of a primary alcohol is oxidized to an ester whilst Br₂ is formed as a co-product turning the reaction mixture orange. Secondary alcohols are oxidized to their corresponding ketones, again generating bromine as a co-product. However, the generated ketone further reacts with Br₂ affording α-bromoketones, leading to the bleaching reaction medium. By contrast, tertiary alcohols cannot be oxidized by TBCA, therefore no color change is observed with these compounds.

**EXPERIMENTAL**

In a test tube containing about 20 mg of tribromoisocyanuric acid (TBCA), 8 drops of the alcohol were added (solid alcohols were dissolved in hexane). The test tube was left in a boiling water bath for 2 min. The tubes containing the primary alcohol turned orange, those containing secondary alcohols exhibited a light yellow color whereas no change in color was observed in the tubes containing tertiary alcohols.

**SUPPLEMENTARY MATERIAL**

Photos of the color test for distinguishing primary, secondary and tertiary alcohols are available at http://quimicanova.sbq.org.br, in pdf file with free access.

**ACKNOWLEDGMENTS**

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The use of Tribromoisocyanuric Acid to Distinguish Among Primary, Secondary and Tertiary Alcohols

Lívia T. C. Crespo*
Departamento de Química Orgânica, Instituto de Química, Universidade Federal do Rio de Janeiro, CP 68545, 21945-970 Rio de Janeiro – RJ, Brasil

Marcio C. S. de Mattos e Pierre M. Esteves
Departamento de Química Orgânica, Instituto de Química, Universidade Federal do Rio de Janeiro, CP 68545, 21945-970 Rio de Janeiro – RJ, Brasil

Figure 1S. Spot test of TBCA with (A) primary alcohols; (B) secondary alcohols; (C) tertiary alcohols

*e-mail: livia.vilela@ifrj.edu.br