

A Reliable and Selective Reagent for Cyclic Azo Compounds

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CuCl in acetonitrile is a reliable and selective reagent for the detection of cyclic azoalkanes on thin-layer chromatograms.

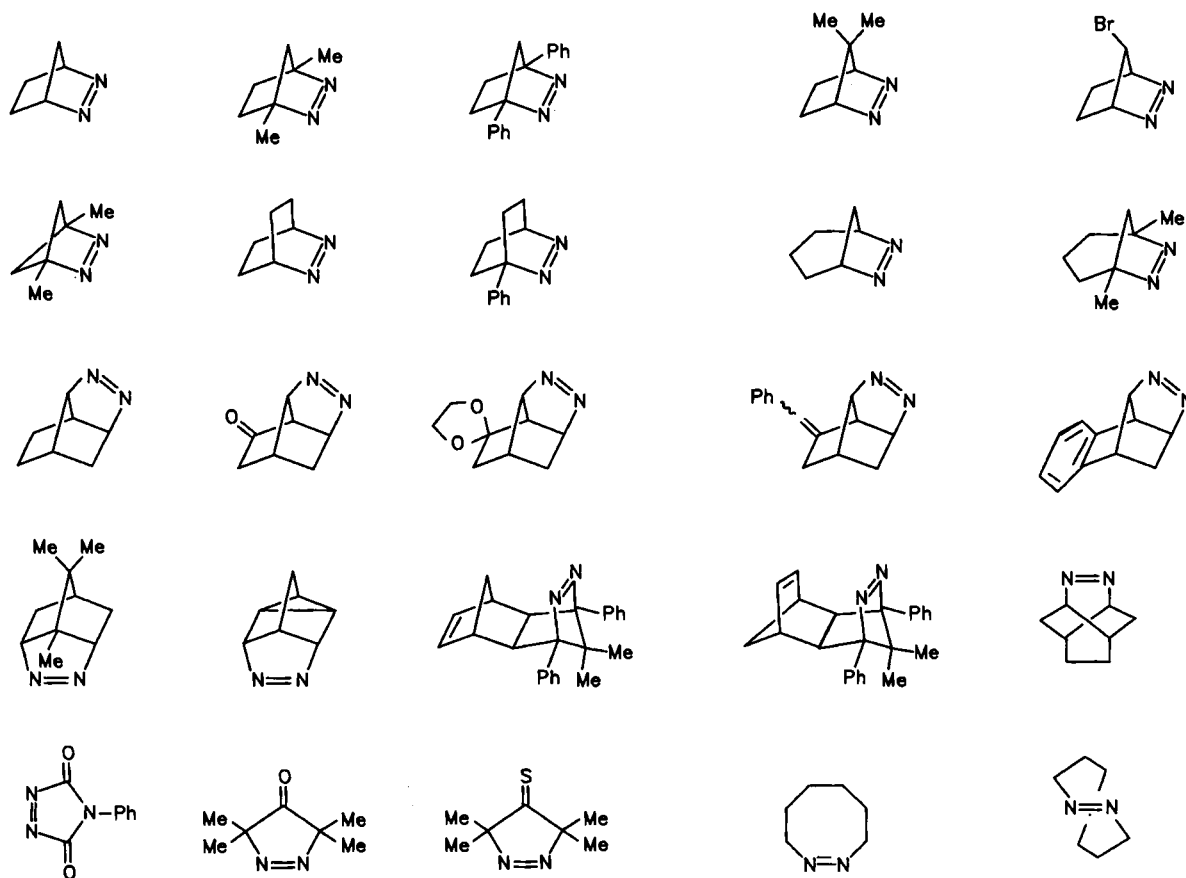
Although cyclic azoalkanes are extensively used in synthetic and mechanistic work¹⁾, to date no reliable and selective reagent exists for their detection in thin layer chromatography (TLC). In the conversion of azoalkanes into cyclic peroxides²⁾ we observed incidentally that the selective ferrous thiocyanate³⁾ peroxide spray also responded to azo compounds, resulting in characteristic rust-brown colored spots. Unfortunately, sterically encumbered cyclic azoalkanes went undetected with the ferrous thiocyanate spray.

In the preparation of azo compounds, usually by the hydrolysis-oxidation sequence of hydrazo compounds and urazoles¹⁾ as pre-

cursors, the azoalkane is precipitated in form of its brick red colored copper complex with cuprous salts⁴⁾. Indeed, freshly prepared cuprous chloride-saturated acetonitrile solutions (ca. 400 mg of CuCl in 10 ml of CH₃CN) proved to be a reliable and selective reagent for detecting cyclic azo compounds by their characteristic brick red color, although yellow and brown-red shades were observed as well.

Of the ca. forty cyclic azoalkanes investigated, a representative sampling of twenty-five is given in the Table. Even dilute solutions (ca. 10⁻⁵ M) of the azoalkane could be readily made visible on the TLC plate. Of the various cuprous salts tried, including Cu(Ph₃P)₂NO₃ in CH₂Cl₂ and [(CuOTf)₂C₆H₆] in C₆H₆, CuCl in CH₃CN stood out as the preferred in terms of sensitivity, reliability, and shelflife (ca. one day). Solubilizing the CuCl with NaCl or HCl in water gave less satisfactory results. Furthermore, acyclic azo compounds such as azobis(isobutyronitrile), *trans*-azo-1-adaman-

Table: Representative cyclic azo compounds that responded to the cuprous chloride (in acetonitrile) reagent^{a)} on TLC^{b)}



^{a)} Prepared by vigorously shaking ca. 400 mg of CuCl in 10 ml of CH₃CN; solution can be kept about one day. — ^{b)} Polygram[®] SIL G UV₂₅₄ plates from Macherey and Nagel Co. were used.

tane, *trans*-azo-1-bicyclo[2.2.2]octane, and *cis*- and *trans*-azo-1-norbornane⁵⁾ went undetected or at best gave only very faint coloration on the TLC plate.

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⁵⁾ We thank Prof. Ch. Rüchardt for the sample of *trans*-azo-1-norbornane. The *cis* isomer was obtained by irradiation of a solution of the *trans* isomer in toluene ($1.4 \cdot 10^{-2}$ M) at 350 nm according to M. Schmitt, A. Schulz, Ch. Rüchardt, E. Hädicke, *Chem. Ber.* **114** (1981) 3533.

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