3-Hydroxy-3,5,5-trimethylpyrazoline, a Stable α-Azo-carbinol

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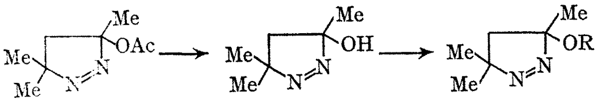
Summary A stable α-azo-carbinol, 3-hydroxy-3,5,5-trimethylpyrazoline, has been isolated, characterized spectroscopically, and converted into an ether and an ester.

α-AZO-CARBINOLS are extremely rare compounds, only two rather unusual examples having previously been reported.[1,2] Since these compounds may be viewed as adducts of alkyldi-imides and carbonyl compounds, it could be assumed that they would decompose readily, with loss of nitrogen, to a carbonyl compound and a hydrocarbon. A previous attempt to prepare the α-azocarbinol, 3-hydroxy-3,5,5-trimethylpyrazoline (I), had appeared to lead to this expected result when alkaline hydrolysis of 3-acetoxy-3,5,5-trimethylpyrazoline (II)[3] produced a mixture of isobutyl methyl ketone and pinacolone.[4]



(II) (I) (III) R=Me

(IV) R=$CO\cdot C_6H_4\cdot NO_2$-*p*

A more careful study of this hydrolysis revealed that decomposition of carbinol (I) occurred only very slowly and under vigorous conditions. Carbinol (I) may be isolated by conventional means from either the hydrolysis or hydrogenolysis ($NaBH_4$) of acetate (II). The remarkable stability of the conjugate base of (I) is shown by its isolation in the form of its sodium salt; the alcohol can be recovered to the extent of 70% after the salt is heated in ethanol for 2 hr.

The n.m.r. spectrum (neat) of (I) showed sharp singlets (H_3) at δ 1·32, 1·42, and 1·58 for the methyl groups, a broad signal (one proton) at δ 5·88 (OH) and a signal at δ 1·53 due to the inner members of the AB quartet of the ring methylene group [*cf.* the n.m.r. spectrum[3] of (II)]. Its i.r. spectrum showed the presence of an OH group, and a *cis*-azo-band at 1560 cm.$^{-1}$.

The chemistry of the carbinol as investigated so far is similar to that of ordinary alcohols but not that expected of a tertiary alcohol. Alkylation of the sodium salt of (I) with methyl iodide produced the methyl ether (III) [n.m.r. data: singlets (H_3) at δ 1·27, 1·35, 1·46, and 3·25, centre of AB multiplet at δ 1·40; i.r.: *cis*-azo-band, 1566 cm.$^{-1}$]. Treatment of (I) with *p*-nitrobenzoic acid, toluene-*p*-sulphonyl chloride, and pyridine[5] produced the *p*-nitrobenzoate (IV).

On the other hand, the carbinol fails to give a typical reaction with the Lucas reagent ($HCl–ZnCl_2$). It is partially decomposed by acids to produce isobutyl methyl ketone but other products, among them mesityl oxide, are also present. This sensitivity to acids, which appears to involve proton attack at C-5 rather than ionization at C-3, has complicated reactions such as attempted acylation with anhydrides.

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