Synthetic Reactions with Iminyl Radicals

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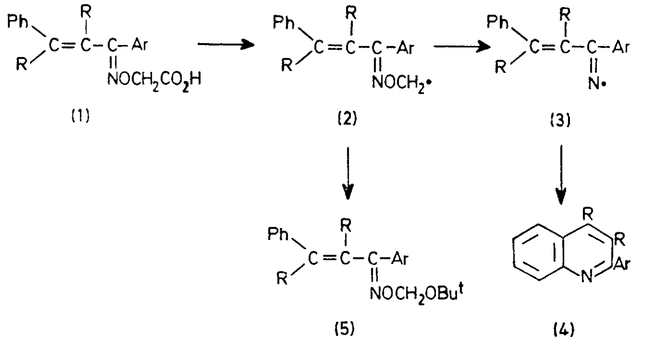
Summary Aryl(triarylvinyl)iminyls readily cyclise to quinolines while isopentyl-, butyl-, and propyl-(phenyl) iminyls yield tetralones by intramolecular hydrogen abstraction followed by cyclisation of the ensuing alkyl radicals.

We have shown[1] that iminyl radicals, conveniently generated from oximinoacetic acids by oxidation with persulphate, readily cyclise onto an adjacent aromatic ring or intramolecularly abstract benzylic γ-hydrogen atoms. We now illustrate the synthetic potential of these reactions.

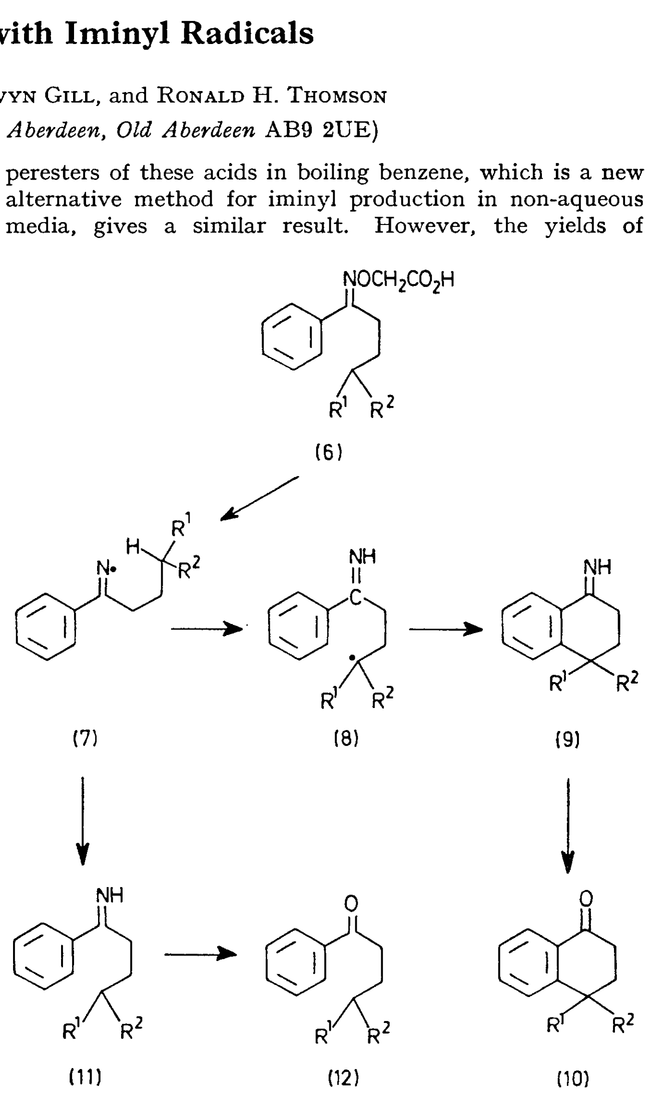


Oxidative decarboxylation of the oximinoacetic acids (**1**; R = Ar = Ph and R = Ph, Ar = o-MeC$_6$H$_4$) in boiling aqueous solution gives the corresponding quinolines (**4**) in 91 and 75% yield, respectively. Thermolysis of the t-butyl peresters of these acids in boiling benzene, which is a new alternative method for iminyl production in non-aqueous media, gives a similar result. However, the yields of quinoline (35%) are lower because recombination of the geminate t-butoxyl and oxalkyl radical (**2**) [yielding the acetal (**5**) (45%)] competes with fragmentation of the

Table

Yields (%) of products obtained by the persulphate oxidation of acids (**6**)

Acid (**6**)	Ketone (**10**)	Ketone (**12**)
R^1=R^2=Me	73	5
R^1=Me; R^2=H	57	9
R^1=R^2=H	32	42



latter. The intermediate iminyls in the perester decomposition are sufficiently long-lived to be detectable by e.s.r. spectroscopy[2] (a_N *ca.* 9·0 G) at 75—80 °C. Significantly, the iminyl (**1**; R = Ph, Ar = *o*-MeC_6H_4) prefers to cyclise rather than to abstract hydrogen from the *o*-methyl substituent. Arylvinyliminyls (a_N *ca.* 10·0 G) with only one β-aryl substituent, *e.g.* (**3**; Ar = Ph, R = H) do not give quinolines, presumably because of the unfavourable *trans*-arrangement of the β-aryl and iminyl groups. In such cases small amounts (3—10%) of 2,4,6-triarylpyrimidines and triarylpyridines are formed but these may arise *via* the imine (*cf.* ref. 3).

Intramolecular hydrogen abstraction by iminyls is not restricted to γ-benzylic hydrogens. Thus, the iminyl (**7**; $R^1 = R^2 =$ Me) (a_N *ca.* 10·1 G), generated from the acid (**6**; $R^1 = R^2 =$ Me) in the usual way, abstracts the tertiary γ-hydrogen of the isopentyl group forming a tertiary alkyl radical (**8**; $R^1 = R^2 =$ Me), cyclisation of which gives the imine (**9**; $R^1 = R^2 =$ Me) and hence the tetralone (**10**; $R^1 = R^2 =$ Me) by hydrolysis. This scheme is supported by the yields of cyclic (**10**) and acyclic (**12**) ketones formed on oxidation of the short series of acids listed in the Table. If it is assumed that the acyclic ketone (**12**) is the ultimate product (**7** → **11** → **12**) of all intermolecular hydrogen abstractions by the iminyl then clearly there is a strong preference for intramolecular hydrogen abstraction *via* a 6-membered transition state. These reactions provide the first examples of the iminyl equivalent of the Barton[4] (alkoxyl radicals), Yang[5] (triplet carbonyls), and Hofmann–Löffler–Freytag[6] (aminium radical-cations) reactions.

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