New Chemistry of Iminyl Radicals

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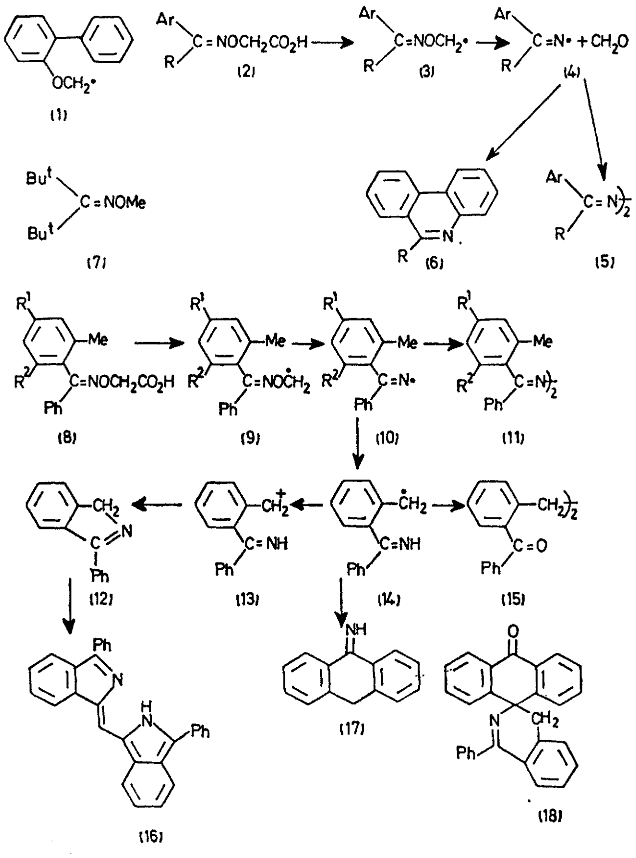
Summary Aryliminyls, produced by oxidation of oximino-acetic or -propanoic acids with persulphate, may either dimerise, cyclise on to an adjacent phenyl group to give a phenanthridine, or abstract hydrogen from an *o*-methyl group to give a benzyl radical.

Iminyls are among the least studied of nitrogen radicals. Recent interest has been centred mainly on their e.s.r. spectra and electronic structure[1] and so far dimerisation to azines, fragmentation to nitriles and alkyl radicals,[2,3] and reduction to imines[3] are their only known reactions. We now describe a new route to iminyls which promises to be more useful for chemical studies than existing methods for spectroscopic work. This is demonstrated by two new intramolecular reactions.

Oxidative decarboxylation of *o*-phenylphenoxyacetic acid with persulphate gives aryloxymethyl radicals (**1**) which cyclise on to the adjacent phenyl group to give a dibenzopyran.[4] However, the oximinoacetic acid† (**2**; Ar = R = Ph) with persulphate gave the azine (**5**; Ar = R = Ph) (97%) and formaldehyde. The most likely route to the azine (**5**; Ar = R = Ph) is *via* the iminyl (**4**; Ar = R = Ph) formed by loss of formaldehyde from the initial oximinomethyl radical (**3**; Ar = R = Ph). Using suitable acids it is possible to trap the intermediate iminyls by intramolecular cyclisation on to an adjacent phenyl group. The acids (**2**; Ar = o-PhC_6H_4; R = H, Me, and Ph) gave the phenanthridines (**6**; R = H, Me, and Ph) in yields of 71, 60, and 66%, respectively. Similar results were obtained with the corresponding series of oximino-propanoic acids (**2**; CMe_2 in place of CH_2) when the phenanthridines (**6**; R = H, Me and Ph) were obtained in 78, 71, and 75% yield, respectively. In these examples the iminyls (**4**) are formed by loss of acetone from (**3**; Me_2C in place of CH_2).



Our proposals are supported by the observations that the oximinomethyl radical (**3**; Ar = o-PhC_6H_4, R = Ph), generated by hydrogen abstraction from the corresponding methyl ether with di-t-butyl peroxalate in benzene, also yielded 9-phenylphenanthridine (22%), and the e.s.r. spectrum of di-t-butyliminyl[2] (a_N 10·2, a_H 1·0 G) was observed when the methyl ether (**7**) was irradiated in di-t-butyl peroxide in the cavity of a spectrometer.

o-Tolylphenyliminyl (**10**; $R^1 = R^2 =$ H) unlike diphenyliminyl gives little of the corresponding azine. The principal products are anthraquinone (23%) and the parent ketone (22%) with smaller amounts of the bibenzyl (**15**) (5%), the known[5,6] deep blue isoindole derivative (**16**) (1·5%), and a colourless compound (4%), $C_{28}H_{19}NO$ (ν_{max} 1670 cm^{-1}; δ 3·18, s, CH_2), thought to be the spiroanthrone (**18**). We consider that the above products stem from the benzyl radical (**14**) formed from the iminyl (**10**; $R^1 = R^2 =$ H) by intramolecular hydrogen abstraction (*cf.* ref. 7). This radical (**14**) may dimerise to the bibenzyl (**15**) (after hydrolysis), intramolecularly cyclise to give (**17**), and hence anthraquinone and the spiroanthrone (**18**), and be oxidised to the isoindolenine (**12**), *via* the carbonium ion (**13**), from which the blue compound (**16**) arises by reaction with formaldehyde.[5] Significantly, the ketone and the oxime from which the acid (**8**; $R^1 = R^2 =$ H) was derived were little affected by treatment with persulphate thus obviating the possibility that the above products arose by direct oxidation of the methyl substituent by the persulphate.

Oxidation of the oximino-acid (**8**; R^1 = Me, R^2 = H) gave a similar mixture of products but not the more hindered homologue (**8**; $R^1 = R^2$ = Me) which gave only the azine (**11**; $R^1 = R^2$ = Me) (22%) and starting acid. Steric interaction between one of the *ortho*-methyl groups and the adjacent phenyl ring in the iminyl (**10**; $R^1 = R^2$ = Me) must prevent the attainment of the near planar 6-membered transition state apparently necessary for the intramolecular hydrogen transfer (**10**) → (**14**) to proceed. With the oximino-propanoic acids (**8**; $R^1 = R^2$ = H and R^1 = Me, R^2 = H; CMe_2 in place of CH_2), iminyls are formed by loss of acetone from the oximino-methyl radicals; the product mixtures are similar except for the absence of blue compounds.

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† Satisfactory elemental analyses and spectroscopic data were obtained for all new compounds.

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