

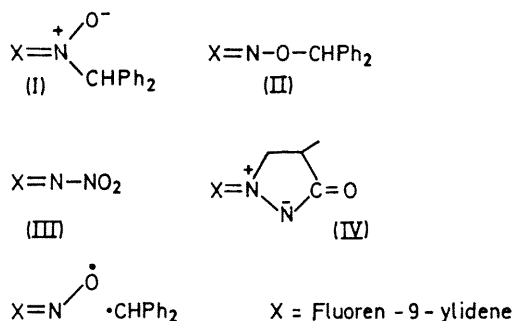
Nuclear Polarization in the Martynoff Rearrangement of Nitrones

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Summary A novel synthesis of nitron (I) is described; ^1H n.m.r. CIDNP emission in the formation of oxime ether (II) from thermolysis of (I) implicates caged radical pairs in the migration process.

ACTIVATION parameters and substituent effects show that the Martynoff rearrangement of benzophenone *N*-benzhydryl nitron to benzophenone *O*-benzhydryloxime¹ at $>160^\circ$ involves a first-order homolytic mechanism,² and e.s.r. measurements have indicated the presence of iminoxyl radicals, and also nitroxide radicals from a secondary reaction.³ Emission and enhanced absorption in the n.m.r. spectrum of diamagnetic products is also evidence for the involvement of caged radical pairs in homolytic processes.⁴



Nitrones amenable to the Martynoff rearrangement are laboriously obtainable through alkylation of ambient oximate anions or reaction of ketimines with substituted hydroxylamines.⁵ We have more conveniently synthesised fluorenone *N*-benzhydryl nitron (I), m.p. 180–182°, ν_{max} 1210 cm^{-1} (KBr), in 85% yield from fluorenone nitroimine⁶ (III) and *N*-benzhydrylhydroxylamine in equimolar amounts, either in refluxing ethanol or by fusion at *ca.* 90°. Nitrous oxide was evolved and after 2–3 min the crude nitron precipitated. Analogously the azomethine imine (IV), m.p. 207–208°, was synthesised from (III) and 3-methylpyrazolidone⁷ in ethanol solution. Nitrous oxide was characterised by high resolution mass spectroscopy; these reactions show the propensity of nitrous oxide as a leaving group.†

We have examined the Martynoff rearrangement of (I) in hexachlorobutadiene by n.m.r. spectroscopy at 100 MHz (hexamethylbenzene as lock signal). When a solution of

(I) was heated externally to momentary boiling (*ca.* 230°) and placed in a probe pre-set at 200° a significant emission signal became apparent after *ca.* 40 s at 435 Hz downfield from the hexamethylbenzene signal. The emission was of *ca.* 10 min duration and was ultimately replaced by the absorption of the oxime ether (II). T.l.c. indicated that the product contained 52% of (II) and 23% of fluorenone. Small amounts of other products were formed, including some from interaction with solvent, but control experiments indicated that these did not interfere with CIDNP observations on the methine proton of (II). Compound (II) independently synthesised gave no emission signal under the same conditions.

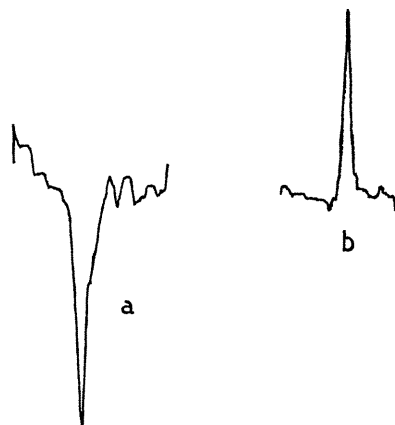


FIGURE. (a) CIDNP effect after 5 min for the methine proton of (II), 435 Hz downfield from hexamethylbenzene; (b) methine proton absorption of (II) after completion of rearrangement.

The emission in the product from thermolysis of (I) may be unambiguously assigned to (II), and this in turn implicates a paramagnetic precursor; in the Martynoff rearrangement this takes the form of a caged benzhydryl-iminoxyl radical pair (V). The present CIDNP observations thus provide direct evidence for the intermediacy of the benzhydryl radical which it was not possible to detect directly in earlier e.s.r. studies and indicate that the mechanism of the Martynoff rearrangement is similar to that of the Meisenheimer rearrangement of amine oxides.¹⁰

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† Nitrous oxide has been postulated or observed as a leaving group in various reactions. In particular nitrous oxide rather than nitrogen may be evolved in certain deamination reactions.^{8,9}

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