

## A Thermally Degenerate [1,9] Sigmatropic Shift

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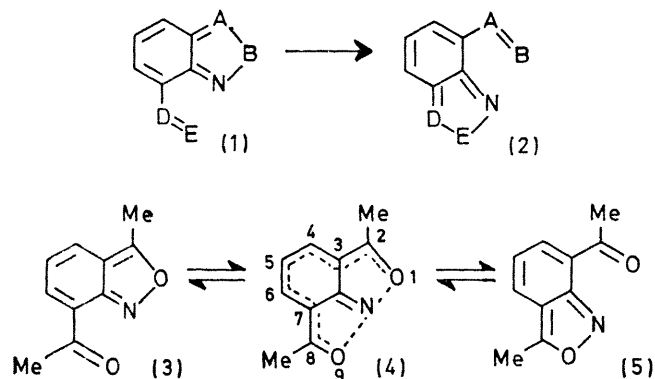
**Summary** When 7-acetyl-3-methylanthranil (**3**) is heated to 160–180° the n.m.r. signals of the two methyl groups coalesce as a result of valence tautomerism for which a novel type of [1,9] sigmatropic mechanism is suggested.

BOULTON, KATRITZKY, and their co-workers have described several irreversible rearrangements of the general type (1) → (2), mostly based on the ready opening of a benzofuroxan ring to give an aromatic nitro-compound.<sup>1</sup> We now describe the first reversible rearrangement of this class, the structurally degenerate valence tautomerism (3) ⇌ (5) which occurs when 7-acetyl-3-methylanthranil is heated.

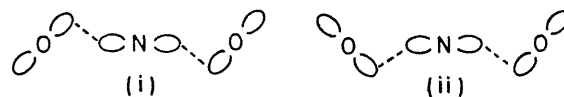
Treatment of the diacid chloride of 2-nitroisophthalic acid<sup>2</sup> with excess of the sodium salt of diethyl malonate, followed by hydrolysis with hydrochloric acid in acetic acid, gave 1,3-diacetyl-2-nitrobenzene, m.p. 160°, which on reduction with stannous chloride gave 7-acetyl-3-methylanthranil (**3**), m.p. 103°.

From the coalescence temperature and the frequency separation of the methyl signals the free energy of activation,  $\Delta G^\ddagger$ , was calculated to be 23.0 kcal mole<sup>-1</sup> in dimethyl sulphoxide and 23.5 kcal mole<sup>-1</sup> in trichlorobenzene. These  $\Delta G^\ddagger$  values, and particularly the small difference between them for the two solvents of very different polarity are in accord with a concerted, cyclic mechanism for the exchange process. Further, this process was not subject to any significant nucleophilic catalysis, by potassium cyanide, or electrophilic catalysis, by mercuric chloride.

The rearrangement, (3) ⇌ (5), is a sigmatropic shift of a type not generally recognised, where the migrating atom is *sp*<sup>2</sup> rather than *sp*<sup>3</sup> hybridised. It also provides, we believe, the first example of a sigmatropic shift of order [1,9]. In the transition state (4) the central nitrogen atom must interact through a *p*-type orbital, lying in the plane of the molecule, with orbitals on the two oxygen atoms [(i) or (ii)]. For this



The two methyl groups of (**3**) appeared as sharp, clearly separated singlets in the 60 MHz spectra at  $\delta$  2.78 and 2.92 p.p.m. in hexadeuteriodimethyl sulphoxide and at  $\delta$  2.73 and 2.90 p.p.m. in 1,2,4-trichlorobenzene. On heating to 165° in dimethyl sulphoxide and to 180° in trichlorobenzene these signals coalesced into singlets; the original spectra were reproduced on cooling.



10-electron reaction to be thermally allowed as a concerted process it must involve either suprafacial migration with retention of configuration in the migrating atom or antarafacial migration with inversion. The former is sterically impossible in this case, and the reaction must proceed antarafacially through a transition state, (i), having a two-fold axis of symmetry, rather than a plane of symmetry, (ii).

The product in this particular system does not differentiate between the allowed antarafacial and the disallowed suprafacial modes, though replacement of the oxygens by suitably substituted *sp*<sup>2</sup> carbon could make such a distinction possible.

This reaction can also be considered, with the same results, as an allowed [ $\pi 8_s + \sigma 2_s$ ] or [ $\pi 8_a + \sigma 2_a$ ] process.

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<sup>1</sup> A. J. Boulton, I. J. Fletcher, and A. R. Katritzky, *J. Chem. Soc. (C)*, 1971, 1193, and references therein.

<sup>2</sup> R. W. Isensee and B. E. Christensen, *J. Amer. Chem. Soc.*, 1948, **70**, 4061.