

ON THE REACTIVITY OF DICYCLOPENTADIENE-1,8-DIONE

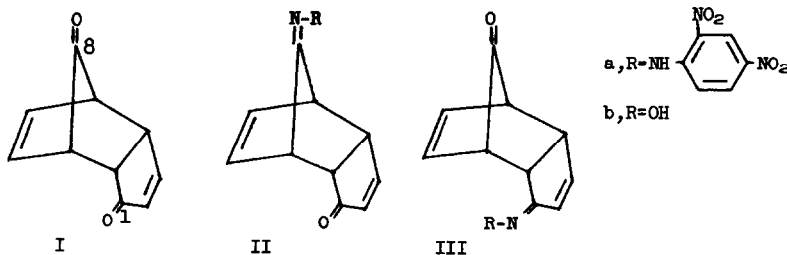
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In the course of our investigations on molecular rearrangements of dicyclopentadienes (1) we have secured results which bear directly on the apparently dichotomous reactivity of dicyclopentadiene-1,8-dione which has just been described (2).

Although the dione I reacts preferentially at C-8 with sodium borohydride (2) or ethylene glycol (3,2), it gave only the 1-monooxime when treated with hydroxylamine and pyridine in methanol, and appeared to condense preferentially at C-1 with one equivalent of 2,4-dinitrophenylhydrazine (2). The possibility that a Woodward-Katz rearrangement (e.g., from IIb to IIIb) may have occurred under the conditions of the reaction was noted (2).



We find that the reaction of dicyclopentadiene-1,8-dione (I) (4) with one equivalent of 2,4-dinitrophenylhydrazine in diglyme-95% ethanol and a

catalytic amount of hydrochloric acid gives, after a reaction time of 5 minutes, an 85% yield of the bright orange 8-2,4-dinitrophenylhydrazone derivative IIA (m.p. 196-198° (dec.), strong carbonyl band in the infrared at 1710 cm^{-1} ; Anal. Calcd. for $\text{C}_{18}\text{H}_{12}\text{N}_4\text{O}_5$: C, 56.47; H, 3.55; N, 16.47. Found: C, 55.84; H, 3.70; N, 16.67).

This derivative may be partially and smoothly rearranged to the red 1-2,4-dinitrophenylhydrazone IIIa (m.p. 200-201°, strong carbonyl at 1790 cm^{-1} ; Anal. Found: C, 56.35; H, 3.49; N, 16.55) by allowing it to remain in the acidic reaction mixture or by heating it in refluxing chloroform, nitromethane, or chlorobenzene.

Mixtures of the two 2,4-dinitrophenylhydrazones IIA and IIIa may be conveniently separated by thin-layer chromatography on alumina using benzene-chloroform (5:1, v/v) as the developer.

The reaction of dione I with hydroxylamine in methanol-pyridine gives, after a work-up which removes all of the unreacted starting material (2), a crude product which exhibits strong bands in the infrared of roughly equal intensities at 1790 and 1710 cm^{-1} . Recrystallization of this mixture of oximes, IIB and IIIB, from benzene gives the known 1-monooxime IIIB, m.p. 154-156°, $\nu_{\text{max}}^{\text{CHCl}_3}$ 1790 cm^{-1} (lit. (5) m.p. 158-159°, ν_{max} 1786 cm^{-1}).

It seems, then, that the reported (2) selectivity shown by the dione I in its reactions with 2,4-dinitrophenylhydrazine and hydroxylamine is only apparent.

Dicyclopentadiene-1,8-dione and 2,4-dinitrophenylhydrazine condense first at C-8 to form IIA which rearranges readily to IIIa. An analogous sequence is probably followed in the reaction of I with hydroxylamine. There is ample precedent for preferential nucleophilic attack on the dione I at C-8 (6) and for the molecular rearrangements between structures II and III (7).

REFERENCES

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