

## Photochemical and Thermal Inertness of a Bicyclo[2,2,2]octadienone Di-imine

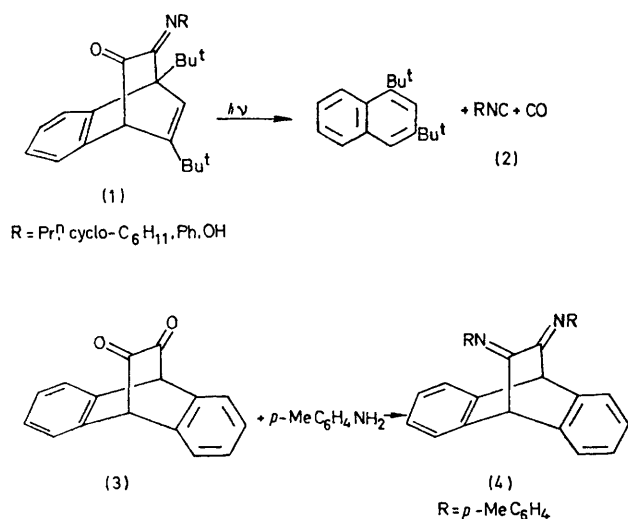
By HAROLD HART\* and ROBERT W. PEIFFER

(Chemistry Department, Michigan State University, East Lansing, Michigan 48824)

**Summary** The di-imine (4), readily prepared from the diketone (3) and *p*-toluidine, is remarkably inert to u.v. irradiation and to heat (575°). (2H, s, Ar), 7.29 (12H, br s, Ar);  $\lambda_{\max}$  (MeOH) 367 ( $\epsilon$ 3240), 284 sh (6430), 233 (27,400).

It was recently reported<sup>1</sup> that the monoimines of bicyclo[2,2,2]octadienones (1) readily cleave, on irradiation, to 1,3-di-*t*-butylnaphthalene and the isocyanides (2). These results are similar to those observed previously with analogous ketones,<sup>2</sup> 1,2-diketones,<sup>3</sup> and methyleneketones.<sup>4</sup> Attempts to synthesize di-imines corresponding to (1) were reported to be unsuccessful,<sup>1</sup> an unexpected result in view of the formation of bis-hydrazones from analogous compounds.<sup>5</sup>

We found that the di-imine (4) is readily prepared from the corresponding diketone (3).<sup>5</sup> Reflux of an anhydrous benzene solution of (3) and *p*-toluidine (1:2.25 mol ratio) in an apparatus which included a Dean-Stark trap packed with 4A molecular sieve afforded, after 65 h and subsequent work-up, a nearly quantitative yield of (4). The di-imine was purified by column chromatography (Celite 545, 1:19 ethyl acetate in heptane) to give yellow crystals, m.p. 203–204°; † i.r. (CHCl<sub>3</sub>)  $\nu$ 1663 cm<sup>-1</sup> (imine); <sup>1</sup>H n.m.r. (CDCl<sub>3</sub>)  $\delta$ 2.42 (6H, s, Me), 5.45 (2H, s, bridgehead), 6.77 and 6.92



† Initial preparations used 1:9 chloroform-hexane and consisted of a 1:1 complex of (4) with chloroform (elemental analysis, and chloroform peaks in the mass spectrum). The elemental analysis of the higher melting product agreed with theory for (4).

The structure of (4) was proved by quantitative hydrolysis (chloroform-10% aqueous hydrochloric acid, two-phase system, 1 h at ambient temperature) to (3) and *p*-toluidine.

The mass spectrum of (4) gave evidence for bridge cleavage, with a base peak at  $m/e$  178 for the anthracene cation [compared with  $m/e$  412 ( $M^+$ ) with a relative intensity of 5.6].<sup>†</sup> However, in sharp contrast with the monoimines (1), it was not possible to achieve this cleavage except in poor yield, either photochemically or thermally.

Irradiation of (4) through Pyrex (200 W, 20 h,  $1.96 \times 10^{-3}M$  in benzene) or Corex (200 W, 3 h,  $1.3-3.0 \times 10^{-3}M$  in methanol or ether) gave only recovered starting material. In the latter solvents, with a Vycor filter, some reaction occurred after 4-8 h but no anthracene was detected (t.l.c.), and most of the (4) could be recovered. It is possible that

the considerable energy absorbed by (4) is consumed in isomerizations at C=N.

Pyrolysis of a benzene solution of (4) ( $N_2$  atmosphere, 5-20 Torr) at 430° and 575° with a residence time of about 10 s gave >95% recovered (4), and only traces of anthracene. The di-imine appears to be more stable thermally than the diketone (3).

In view of the photochemical inertness of (4) relative to (1), it seems likely that the bridge elimination in (1) is initiated by Norrish Type I cleavage  $\alpha$  to the C=O, not the C=N bond.

We thank the National Institutes of Health and the National Science Foundation for financial support.

(Received, 5th November 1973; Com. 1520.)

<sup>†</sup> No significant peak corresponding to the other fragment ( $m/e$  234) was present, although a peak corresponding to the isocyanide cation ( $m/e$  117) was present (rel. intensity 3.4).

<sup>1</sup> J. H. Boyer and K. G. Srinivisan, *J.C.S. Chem. Comm.*, 1973, 699.

<sup>2</sup> R. K. Murray, jun., and H. Hart, *Tetrahedron Letters*, 1968, 4995; A. Oku, T. Kakihana, and H. Hart, *J. Amer. Chem. Soc.*, 1967, 89, 4554.

<sup>3</sup> J. Strating, B. Zwanenburg, A. Wagenaar, and A. C. Udding, *Tetrahedron Letters*, 1969, 125.

<sup>4</sup> H. Hart, D. L. Dean, and D. N. Buchanan, *J. Amer. Chem. Soc.*, 1973, 95, 6294.

<sup>5</sup> J. E. Baldwin, R. H. Holm, R. W. Harper, J. Huff, S. Koch, and T. J. Truex, *Inorg. Nuclear Chem. Letters*, 1972, 8, 393; J. E. Baldwin and J. Huff, *J. Amer. Chem. Soc.*, 1973, 95, 5757.