

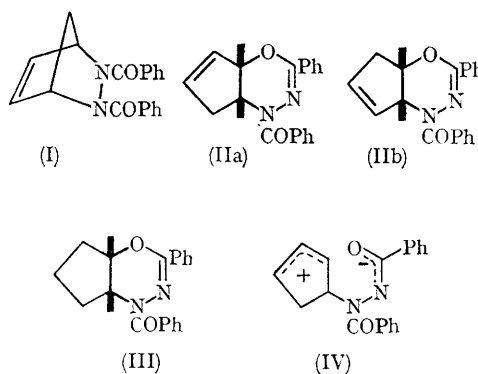
## The So-called Labile and Stable Adducts of Cyclopentadiene and Dibenzoyldi-imide

By LOUIS A. CARPINO and ERIC S. RUNDBERG, JUN.

(Department of Chemistry, University of Massachusetts, Amherst, Massachusetts, 01002)

WHEREAS earlier investigators<sup>1</sup> obtained only one isomer in the reaction of cyclopentadiene with dibenzoyldi-imide, Waters and his co-workers<sup>3</sup> showed that two different 1:1 adducts could be isolated depending on the reaction conditions. The "labile" adduct was obtained by reaction in an excess of cyclopentadiene, or in benzene solution, and was shown to undergo irreversible isomerization to the "stable" adduct at the melting point, in polar solvents, or in the presence of acid catalysts. On the basis of n.m.r. data, the labile adduct was assigned the Diels-Alder structure (I). The structure of the stable adduct was not confirmed but n.m.r. data suggested that the two phenyl groups were in different environments. Compound (I) has now been characterized by catalytic reduction in anhydrous tetrahydrofuran over palladium-carbon to the dihydro-derivative, m.p. 166.5—167.5°, which was shown to be identical with an authentic sample prepared by benzoylation of 2,3-diazabicyclo[2,2,1]heptane.<sup>3</sup> Of the five most reasonable<sup>4</sup> structures for the stable adduct three were eliminated on the basis of the published n.m.r. data and the intense u.v. absorption† at 290 m $\mu$  ( $\epsilon$  16,100). The u.v. data pointed to one of the double-bond isomers represented by structure (II). This supposition was confirmed by catalytic hydrogenation of the stable adduct to give a dihydro-derivative, m.p. 143.5—145°,  $\lambda_{\max}$  (95% EtOH): 290 m $\mu$  ( $\epsilon$  15,700). This was shown to have structure (III) by reductive degradation by means of Raney nickel in ethanol<sup>5</sup> under reflux to give *cis*-2-benzoylamino-cyclopentanol (78%), m.p. 130—131° (lit.,<sup>6</sup> m.p. 130—131°) which was identified by hydrolysis with

dilute hydrochloric acid to give *cis*-2-aminocyclopentanol hydrochloride.<sup>6†</sup> Presumably the initial Raney nickel-cleavage product undergoes loss of the iminobenzoyl group during neither the reaction or the work-up procedure.



The mechanism of the unusual isomerization of (I) has not been established although the fact that it takes place in polar solvents suggests that the dipolar intermediate (IV) may be involved. If so, the stable adduct can tentatively be assigned structure (IIa).

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† The analogous norbornene-azodibenzoyl adduct shows u.v. absorption at 292 m $\mu$ , ( $\epsilon$  15,400) (ref. b).

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<sup>2</sup> D. Mackay, U. F. Marx, and W. A. Waters, *J. Chem. Soc.*, 1964, 4793.

<sup>3</sup> O. Diels, J. H. Blom, and W. Koll, *Annalen*, 1925, **443**, 242; L. A. Carpino, P. H. Terry, and S. D. Thatte, *J. Org. Chem.*, 1966, **31**, 2867.

<sup>4</sup> For a review of reactions between azodicarbonyl compounds and olefins and dienes see (a) E. Fahr and H. Lind, *Angew. Chem.*, 1966, **78**, 376; (b) J. J. Tufariello, T. F. Mich, and P. S. Miller, *Tetrahedron Letters*, 1966, 2293.

<sup>5</sup> C. Ainsworth, *J. Amer. Chem. Soc.*, 1954, **76**, 5774.

<sup>6</sup> G. E. McCasland and D. A. Smith, *J. Amer. Chem. Soc.*, 1950, **72**, 2190.