Photodecarbonylation of 1,3-Diphenylinden-2-one Adducts; 1,5-Sigmatropic Shifts in Sterically Stabilised *o*-Quinodimethanes

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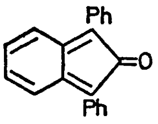
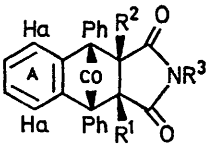
Summary Photodecarbonylation of the 1,3-diphenylinden-2-one–substituted maleimide adducts (II) and (VI) gave the sterically stabilised *o*-quinodimethanes (V; $R^1 = R^2 = R^3 =$ Me) and (V; R^1, $R^2 = [CH_2]_4$, $R^3 =$ Me) in which 1,5-sigmatropic shift of the imido-group is preferred to alkyl migration.

THE remarkable stability of naphtho[2,3-*a*]-*o*-carborane[1] prompted the preparation of related *o*-quinodimethanes stabilised by steric shielding but lacking the possibility of aromatic stabilisation.

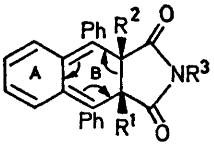
1,3-Diphenylinden-2-one (I) generated reversibly by dissociation of its dimer,[2] reacted smoothly with trimethylmaleimide to give the *endo*-adduct (II; $R^1 = R^2 = R^3 =$ Me) in which the methylimino-group is located above ring A and appears at high field (τ 7·46) as in the *N*-methylmaleimide adducts of both compound (I) and benzo[*c*]furan.[3]† Photodecarbonylation of the adduct (II) gave the crystalline *o*-quinodimethane (V; $R^1 = R^2 = R^3 =$ Me) (80%), m.p. 176—179°. Decarbonylation of the adduct (VI) gave the similar *o*-quinodimethane (V; R^1, $R^2 = [CH_2]_4$, $R^3 =$ Me). Both the compounds (V) are stable, supporting the view[1] that naphthocarborane has little aromatic character but is stabilised by steric hindrance. Steric shielding of the usually reactive ring B diene system is reflected by the failure of compound (V; R^1, $R^2 = [CH_2]_4$, $R^3 =$ Me) to react with dimethyl acetylenedicarboxylate and by reaction of compound (V; $R^1 = R^2 = R^3 =$ Me) with 2,3-diaza-



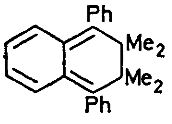
(I)



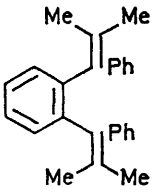
(II) $R^1 = R^2 = R^3 =$ Me
(III) $R^1 = R^2 =$ H, $R^3 =$ Ph
(IV) $R^1 = R^2 =$ H, $R^3 = [2,4,6\text{-}^2H_3]$ Ph
(VI) R^1, $R^2 = [CH_2]_4$, $R^3 =$ Me



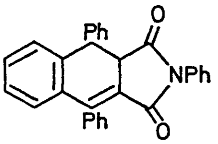
(V)



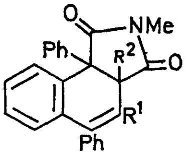
(VII)



(VIII)



(IX)



(X)

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† Unlike the n.m.r. spectra of these *N*-methylmaleimide adducts the spectra of compound (III) and related *N*-phenylmaleimide adducts show two high-field aromatic protons. These were thought (M. P. Cava and N. M. Pollock, *J. Amer. Chem. Soc.*, 1966, **88**, 4112) to be the protons H_a which lie over the carbonyl groups but are in fact the protons *ortho* to the nitrogen atom as the shielded protons in the spectrum of compound (III) disappear in the deuteriated analogue (IV). For a probably erroneous configurational assignment based on the original misconception see N. J. Mruck and H. Tieckelman, *Tetrahedron Letters*, 1970, 1209.

1,4-naphthoquinone which affords a mixture of two adducts derived by addition to the two faces of ring A.

The compounds (V) are presumably constrained from electrocyclic ring opening by the fused imido-ring. An attempt to prepare compound (VII) by photodecarbonylation of the 1,3-diphenylinden-2-one–tetramethylethylene adduct gave the valence isomer (VIII).

The stability of the compounds (V) is also influenced by the slow 1,5-sigmatropic shift of alkyl (and acyl) groups compared to hydrogen. Photodecarbonylation of the adduct (III) gave instead of compound (V; $R^1 = R^2 = H$, $R^3 = Ph$), the product of a 1,5-hydrogen shift (IX).[4,5]‡ Compound (V; $R^1 = R^2 = R^3 = Me$) was cleanly converted (70%) in boiling toluene into (X; $R^1 = R^2 = Me$) the product of a 1,5-shift of the imido-group; the product of the alternative methyl shift was not observed. Similarly on heating in boiling xylene compound (V; R^1, $R^2 = [CH_2]_4$, $R^3 = Me$) gave compound (X; R^1, $R^2 = [CH_2]_4$) and did not give the product from a 1,5-alkyl shift. These results indicate the order of tendency to migration is hydrogen > imido > alkyl and complement earlier observations on the 1,5-sigmatropic shift.[6] Experiments now in hand are aimed at determining the tendency to migration of other groups, and elucidating the possible role of homoconjugation in determining the order of alkyl and imido-group migration.

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‡ The 1,5-shift is suprafacial, since the properties of (IX) agree with those reported for the *cis*-isomer (ref. 4).

[1] D. S. Matteson and R. A. Davis, *Chem. Comm.*, 1970, 669.
[2] J. M. Holland and D. W. Jones, *J. Chem. Soc.* (*C*), 1971, 608.
[3] R. N. Warrener, *J. Amer. Chem. Soc.*, 1971, **93**, 2346.
[4] G. Quinkert, K. Opitz, W. W. Weisdorff, and M. Finke, *Annalen*, 1966, **693**, 44.
[5] *Cf.* the reaction of *N*-phenylmaleimide with 1,3-diphenylbenzo[*c*]thiophen 2,2-dioxide, M. P. Cava and J. McGrady, *Chem. Comm.*, 1968, 1648.
[6] L. L. Miller, R. Greisinger, and R. F. Boyer *J. Amer. Chem. Soc.*, 1969, **91**, 1578.