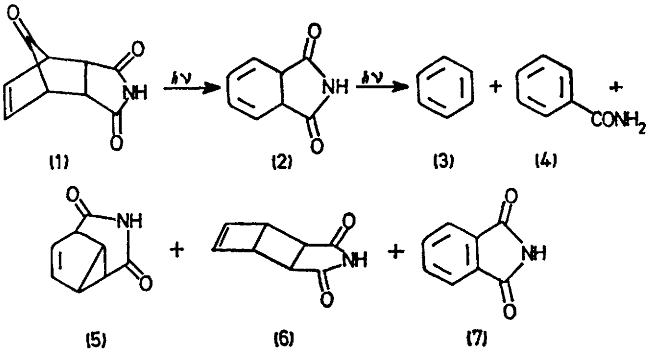
Photochemistry of 1,2-Dihydrophthalimide

By GAD SCHARF and BENZION FUCHS*
(*Department of Chemistry, Tel-Aviv University, Tel-Aviv, Israel*)

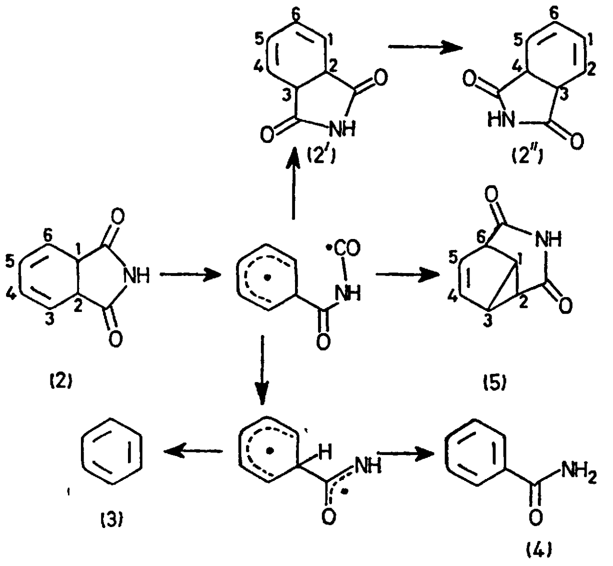
Summary The title compound undergoes irradiation-induced transformations, the most interesting being fragmentations to benzene and benzamide, and rearrangements including degenerate 1,5-acyl shifts and 1,2-acyl shifts with cyclopropane ring closure; a mechanism is proposed, following product isolation and deuterium labelling studies.

We have recently described the photochemical behaviour of 1,2-dihydrophthalic anhydride[1] and have now investigated the photochemistry of the related 1,2-dihydrophthalimide (**2**). The latter was obtained by photo-decarbonylation of 7-oxonorborn-5-ene-2,3-dicarboximide (**1**). We were particularly interested to see whether similar fragmentation processes obtain and what additional reaction paths are available.



Scheme 1

Irradiation of the imide (**2**) at 257 nm in MeCN gave benzene (**3**) (16%), benzamide (**4**) (25%), bicyclo[3,1,0]-hex-3-ene-2,6-dicarboximide (**5**) (18%), *anti*-bicyclo[2,2,0]-hex-5-ene-2,3-dicarboximide (**6**) (3%) and phthalimide (**7**) (2%) (Scheme 1).†



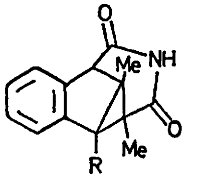
Scheme 2

Sensitization and quenching attempts have failed, suggesting that a singlet excited state operates. Various *N*-substituted derivatives of (**2**) were also studied and variable wavelength studies were performed. No basic differences in behaviour were found except for explainable variations in the yields of the corresponding products. These results will be reported in detail in the full report.

From the product composition we propose a mechanism involving an α-cleavage of the β,γ-unsaturated carbonyl compound (**2**) to a diradical intermediate (Scheme 2), followed by, either fragmentation to benzene (**3**) or benzamide (**4**) or recombination processes. The latter include degenerate 1,5-shifts to (**2′**), etc., and 1,2-shifts to (**5**). However, a concerted mechanism for these rearrangement processes cannot be definitely excluded, at the present stage of the investigation.

Benzene is formed in lower chemical yield as well as lower quantum yield (ϕ = 0·01) than in the fragmentation of 1,2-dihydrophthalic anhydride.[1] This is understandable in terms of the relative thermodynamic stabilities of the small molecular species formed in the two fragmentation processes. Benzamide (**4**) formation can be understood as the result of hydrogen abstraction from the tertiary centre, most reasonably envisaged as a 1,3-carbon to nitrogen, hydrogen shift.

The 1,2-shift to (**5**) is the most interesting new feature of this study. Two recent analogous cases are available, (**8**)[2] and (**9**),[3] but without mention of the mechanistic aspects of the problem. There is also the possibility of substitutional bias in the outcome of these rearrangements; however, an earlier short communication on a related case[4] makes no mention of such rearrangement processes.



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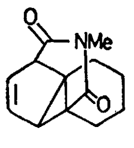

(9)

The rearrangement of (**2**) to (**5**) involves a 1,2-acyl shift with two possible modes of cyclopropane ring closure; C(1)—C(5) (as in the original oxa-di-π-methane rearrangements)[5] or C(1)—C(3). Our symmetrical starting compound (**2**) does not differentiate between the two modes but a deuterium labelling experiment using 1,2-[$^2H_2$]-(**2**) pointed unequivocally to the second mode, i.e. the whole diene grouping participates in the rearrangement. This result is in accord with those of the substituted derivatives (**8**)[2] and (**9**)[3] and lends additional plausibility to the diradical mechanism suggested above. In the oxa-di-π-methane rearrangement this mechanism is rejected[5,6] mainly on the

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† All new compounds gave satisfactory elemental analyses and spectroscopic data.

strength of the cyclopropyl radical being thermodynamically unstable with respect to an initial allyl radical,[6] but our case deals with the conversion of a 2,4-pentadienyl radical to a 2-cyclopentenyl one which appears to be thermodynamically favoured.[7] The deuterium labelling experiment enabled us also to see the degenerate 1,5-shift in (**2**)‡ and will be described in detail elsewhere.

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‡ Although a double 1,3-shift cannot be excluded.

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