Isomerisations under Electron Impact.[1] The Imide–Isoimide Interconversion and its Dithione Analogue

By C. M. ANDERSON and R. N. WARRENER*

(*Department of Chemistry, School of General Studies, Australian National University, Canberra,* 2600)

and C. S. BARNES

(*C.S.R. Research Laboratories, Roseville, N.S.W.* 2069, *Australia*)

JOHNSTONE, MILLARD, and MILLINGTON,[2] and subsequently others,[3,4] have reported the loss of CO_2 from phthalimides upon electron impact, which it has been suggested arises by fragmentation of the isoimide, generated from the initial phthalimide upon electron impact. We have confirmed this by subjecting *N*-phenylisophthalimide[†] (II) to electron impact (70 ev) where we find the fragmentation pattern to be almost indistinguishable from that of the isomeric *N*-phenylphthalimide. Control experiments show that each isomer is thermally stable at temperatures considerably higher than those of the spectrometer's heated inlet system.[‡] This suggests that the rearrangement is induced by electron impact and is not due to thermal isomerisation prior to bombardment, as recently suggested[4] by Aplin and Jones. This imide to isoimide rearrangement can also explain[5] the formation of benzonitrile on pyrolysis (480°) of phthalimide, although the reverse reaction occurs when *N*-substituted isomaleimides are heated with sodium acetate or triethylamine acetate.[6] As phthalimide also shows this $(M - 44)$ peak in its mass spectrum, this may be another example of a parallel between thermal and electron impact fragmentations.

This isomerisation also occurs in the maleimide series, where the mass spectrum of *N*-phenylmaleimide is almost indistinguishable from that of *N*-phenylisomaleimide (see Figure). Again *NO*

[†] *N*-Phenylisophthalimide was prepared from *N*-phenylphthalamic acid by cyclisation in methylene chloride with dicyclohexylcarbodi-imide, and purified by chromatography on silica gel.

[‡] A Perkin-Elmer-Hitachi Model R.M.U.-6D mass spectrometer with an all glass inlet was used for all mass spectral measurements.

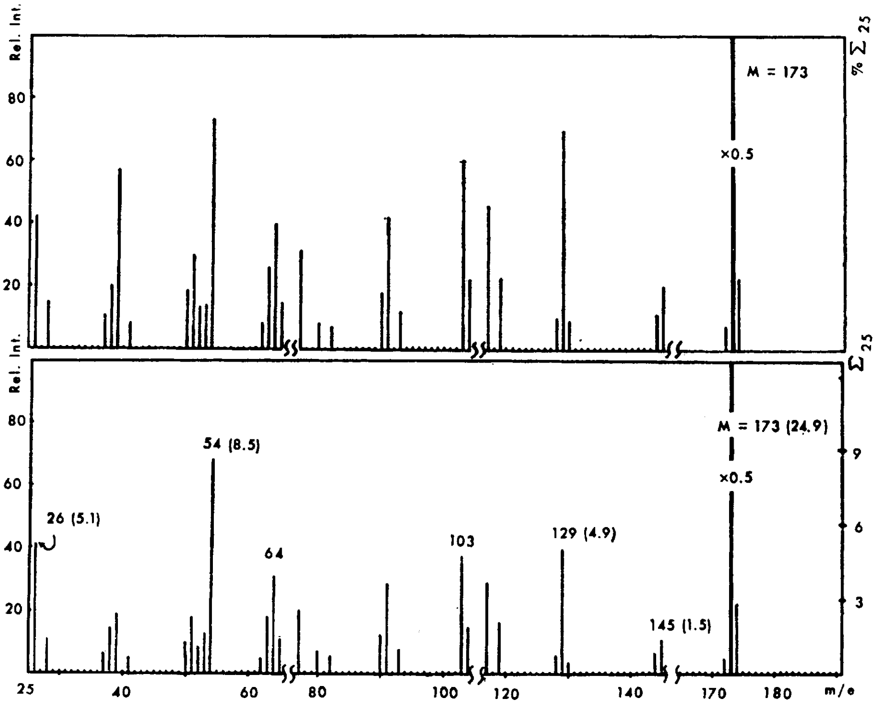
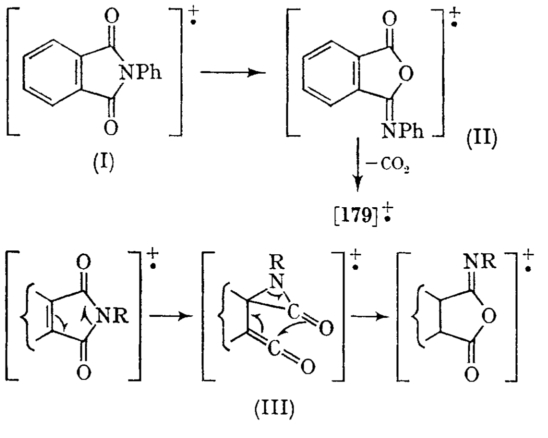


FIGURE. *Mass spectra of* N-*phenylmaleimide* (*lower portion*) *and* N-*phenylisomaleimide* (*upper portion*) *at* 70 ev.

thermal isomerisation of the *N*-phenyl maleimide was observed,§ even after heating for 1 hr. at 200°. Some decomposition occurred on heating the isomaleimide, judging from the darkening of the sample, but only resonances due to the isoimide were observed in the ^{1}H n.m.r. spectrum.

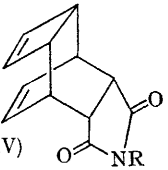


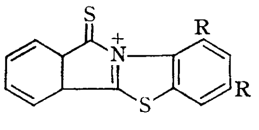
No examples of this (M − 44) loss has been observed[7] in the mass spectra of a large variety of imides which lack the $\alpha\beta$-unsaturated bond, even in cases where the imide is sterically confined and fused to a rigid alicyclic system such as compound (IV). To accommodate this dependence on the presence of an $\alpha\beta$-unsaturated double bond it is suggested that rearrangement occurs *via* an intermediate related to the spiro-lactam (III). Such an intermediate, contrary to that suggested by Johnstone and his co-workers,[2] would not be available to those imides which lack the double bond.

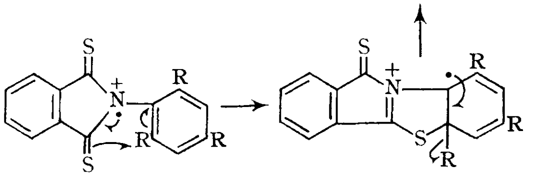
A similar isomerisation may operate with the related dithiophthalimides (V) which show a strong (M − 76) peak due to loss of CS$_2$. The behaviour of the 2′,4′,6′-trideuteriated derivative (Vb) confirms that the (M − 76) peak is not due

---

§ The thermal stability was conveniently monitored by ^{1}H n.m.r. spectrometry. The n.m.r. spectrum (60 Mc./sec. in CDCl$_3$) of *N*-phenylmaleimide showed the narrow symmetrical multiplet of the phenyl protons (5H, τ 2·48—2·70) and the *N*-phenylisomaleimide displayed a broad unsymmetrical multiplet in the phenyl proton region (6H, τ 2·45—2·85), coincident with the lower-field doublet of the vinylic protons (AB type) together with the higher-field vinylic proton (1H, doublet, τ 3·32, J = 5·5 c./sec.).


(IV)


(VI)


(a) R=H, (b) R=D

to the elimination of benzyne from the *N*-substituent. Metastables for the transition (*M*) to (*M* — 76) are not present, although the (*M*) and (*M* — 76) ions have suitable isotope peaks consistent with this assignment. The most prominent peak in the spectrum of (Va) is the (*M* — 1) peak (94%). This is assigned to the cyclic product (VI). The corresponding (*M* — 2) peak appears in the deuterio-derivative (Vb), together with a significant (*M* — 1) peak, suggesting that some scrampling of the label may have occurred prior to conversion to (V).

(*Received, October* 31*st*, 1967; *Com.* 1176.)

---

[1] Considered as part of the series "Excited State Reactions of Imides and Anhydrides." For previous part, see J. B. Bremner and R. N. Warrener, *Chem. Comm.*, 1967, 926.

[2] R. A. W. Johnstone, B. J. Millard, and D. S. Millington, *Chem. Comm.*, 1966, 600.

[3] J. L. Cotter and R. A. Dine-Hart, *Chem. Comm.*, 1966, 809; H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, San Francisco, 1967, p. 364; J. Sharvit and A. Mandelbaum, *Israel J. Chem.*, 1967, **5**, 33.

[4] R. T. Aplin and J. H. Jones, *Chem. Comm.*, 1967, 261.

[5] H. Meyer and A. Hofmann, *Monatsh.*, 1917, **38**, 343.

[6] R. J. Cotter, C. K. Sauer, and J. M. Whelan, *J. Org. Chem.*, 1961, **26**, 10.

[7] C. M. Anderson, C. S. Barnes, J. B. Bremner, and R. N. Warrener, unpublished results.